

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1935.

General, Physical, and Inorganic Chemistry.

Isotope effect in the Lyman series of hydrogen. S. S. BALLARD and H. E. WHITE (Physical Rev., 1933, [ii], 43, 941).—Using H_2O containing a high $[\text{H}^2]$, six members of the Lyman series of H have been observed as close doublets. In agreement with the theory of broadening of lines due to the Doppler effect, the H^1 component is broader than the H^2 .

L. S. T.

Spin of hydrogen isotope. G. N. LEWIS and M. F. ASHLEY (Physical Rev., 1933, [ii], 43, 837).—The emission spectrum of mol. H_2 , containing approx. 25% H_2 , 50% H^1H^2 , and 25% H_2^2 shows that the spin of H^2 is neither 0, $1/2$, nor $3/2$; it is, in all probability, $2/2$.

L. S. T.

Band spectrum of the H^1H^2 molecule. M. F. ASHLEY (Physical Rev., 1933, [ii], 43, 770).—An electronic isotopic shift of approx. 2.4 wave-nos. has been observed.

L. S. T.

He fluorescence and collisions of the second kind of excited He atoms. W. MAURER and R. WOLF (Z. Physik, 1934, 92, 100—115).

A. B. D. C.

Partial resolution of the Be I line 4572.69 Å. and probable spin of the Be^9 nucleus. A. E. PARKER (Physical Rev., 1933, [ii], 43, 1035—1036).—There is a separation of $0.033 \pm 0.005 \text{ cm}^{-1}$ between the two components of the Be I line 4572.69 Å. The weaker component, a 2^1P_1 — 3^1D_2 transition, contains $36 \pm 4\%$ of the total intensity, which indicates a nuclear spin of $1/2$ for Be^9 .

L. S. T.

Metastable 2D level of the nitrogen atom. H. STUCKLEN and E. P. CARR (Physical Rev., 1933, [ii], 43, 944—945).

L. S. T.

Intensity measurements in the first positive bands of nitrogen. A. ELLIOTT and W. H. B. CAMERON (Proc. Physical Soc., 1934, 46, 801—804).—Integrated intensities measured by photographic photometry, using as sources the high-frequency discharge, the d.c. discharge, and the afterglow of active N, show that the probability of transition between two vibrational levels is independent of excitation conditions.

N. M. B.

Wave-lengths and terms of the fluorine spectrum, F IV. B. EDLÉN (Z. Physik, 1934, 91, 19—26).

A. B. D. C.

Moving striations in neon. (FRL.) B. VAN MANEN (Physica, 1934, 1, 967—978).—In the positive column with moving striations for Ne at 0.2 mm. pressure, the difference between the max. and min. potentials of a striation falls with increasing

column current for a W cathode. For an oxide cathode the p.d. depends on the no. of striations, but the results are not reproducible.

M. S. B.

Transition probabilities in the sharp and diffuse series of the alkalis. L. S. ORNSTEIN and J. KEY (Physica, 1934, 1, 945—952).—The transition probability for p - d and s - p lines in Na and K has been determined using the a.c. arc. It has also been calc. for Rb and Cs from previous data.

M. S. B.

Starting potential of the glow discharge in neon-argon mixtures between large parallel plates. I. Results. F. M. PENNING and C. C. J. ADDINK. II. Ionisation and excitation by electrons and metastable atoms. F. M. PENNING (Physica, 1934, 1, 1007—1027, 1028—1044).—I. Measurements previously made with pure Ne have been extended to pure A and mixtures of A and Ne.

II. Calculations have been made of: the relation between V_c , the starting potential of the corona discharge between infinite parallel plates, and η_2 , the ionisation coeff. for A (A in mixture $< 0.01\%$); the ionisation coeff. η_{2e} due to direct ionisation of A atoms by electrons; the relation between η_2 and the ionisation by metastable Ne atoms; the influence of the energy loss of the electrons in elastic collisions; the relation of V_c to the proportion of A and the gas d .

M. S. B.

Effect of mercury vapour on the high [spectral] terms of the alkali [metals]. B. PONTECORVO (Atti R. Accad. Lincei, 1934, [vi], 20, 105—109).—Hg vapour has a very weak effect in displacing the limits of the series of Na and K.

O. J. W.

Paschen-Back effect and the polarisation of resonance radiation. Sodium ($5^2P_{1/2,3/2}$ — $3^2S_{1/2}$). N. P. HEYDENBURG (Physical Rev., 1933, [ii], 43, 1045).—Preliminary data are given.

L. S. T.

Zeeman effect and the magnetic quenching of the fluorescence of S_2 and Te_2 . I. I. AGARBICEANU (Compt. rend., 1934, 199, 1036—1038; cf. A., 1933, 1095; 1934, 1, 353).—The decrease in the fluorescence of S_2 and Te_2 vapours under a magnetic field is explained by the Zeeman and Paschen-Back effects.

J. W. S.

Additional bands in the band system of sulphur. R. K. ASUNDI (Current Sci., 1934, 3, 154; cf. A., 1931, 996).

L. S. T.

Spectra of potassium, K IV and K V, and of calcium, Ca V and Ca VI. I. S. BOWEN (Physical Rev., 1934, [ii], 46, 791—792).—Data and classifications

for 19 new lines of K IV, 26 of K V, 36 of Ca V, and 31 of Ca VI, including singlet and intercombination lines, below 650 Å., are tabulated. The presence in nebulae of lines due to the forbidden $^3P-^1D$ transitions in Si I, Cl II, A III, K IV, and Ca V is discussed.

N. M. B.

Highly ionised potassium and calcium spectra. A. E. WHITFORD (Physical Rev., 1934, [ii], 46, 793).—Classifications of 75 lines of K VI, K VII, K VIII, K IX, Ca VII, and Ca VIII, and term vals. are tabulated.

N. M. B.

Nuclear moment of scandium (Sc^{45}). H. SCHULER and T. SCHMIDT (Naturwiss., 1934, 22, 758–759).—The hyperfine structure of the Sc spectrum between 4700 and 6500 Å. was investigated. The nuclear moment is $7/2$.

A. J. M.

Nuclear moment of scandium. H. KOPFERMANN and E. RASMUSSEN (Z. Physik, 1934, 92, 82–86).—The moment is $7/2$.

A. B. D. C.

Hyperfine structure and nuclear moment of cobalt. N. S. GRACE (Physical Rev., 1933, [ii], 43, 762).—Examination of the hyperfine structure of the spectrum of Co I indicates that the nuclear moment of Co is $5/2$ and $\approx 9/2$.

L. S. T.

Absorption measurements in the band spectra of zinc and cadmium vapours. S. MROZOWSKI (Z. Physik, 1934, 91, 600–608).

A. B. D. C.

Intensity measurements in a fine structure multiplet of As II. S. TOLANSKY and J. F. HEARD (Proc. Roy. Soc., 1934, A, 146, 818–824).—The mean vals. of the intensity ratios in the fine structure triplet of As II $\lambda 5231$ ($5s^3P_1-5p^3P_0$) are 0.98:2:2.99, in agreement with the theoretical vals. 1:2:3. The quantum wts. of the fine structure levels in the $5s^3P_1$ term thus $\propto 2F+1$.

L. L. B.

I. Complexity of the resonance spectrum of selenium. II. Influence of nitrogen on the fluorescence spectrum of selenium. S. GAWRONSKI (J. Phys. Radium, 1934, [vii], 5, 533–534, 535–537).—I. The complexity of the fluorescence spectrum of Se, excited by the Hg 4359 and 4047 Å. lines, using a low-pressure cooled Hg lamp, showed no difference if excited by broad or narrow Hg lines, and was uninfluenced by the temp. of the Se vapour or the mol. kinetic energy. The complexity is attributed to the existence of a large no. of isotopes.

II. Addition of N_2 extinguished the multiplets and slightly weakened the characteristic rotation doublets. With increasing pressure of N_2 the multiplets disappeared, giving place to band fluorescence, which in turn disappeared, passing to the continuous glow with only the rotation doublets visible.

N. M. B.

Lack of observed hyperfine structure in strontium. A. N. BENSON and R. A. SAWYER (Physical Rev., 1933, [ii], 43, 766–767).—Forty lines of Sr I and Sr II in the region 5600–4000 Å. gave no evidence of hyperfine structure. Sr has no nuclear spin or isotope shift $> 0.050 \text{ cm}^{-1}$.

L. S. T.

Nuclear moments of niobium from hyperfine structure. S. S. BALLARD (Physical Rev., 1934, [ii], 46, 806–811).—The observed hyperfine structure in the arc spectrum can be accounted for by attribut-

ing mechanical and magnetic moments to the nucleus. The nuclear spin is $9/2$. The approx. nuclear g -factor is 0.83, giving a magnetic moment of 3.7 nuclear magnetons.

N. M. B.

Excitation of atomic lines in the molecular absorption in Cd vapour. E. KALINOWSKA (Acta phys. polon., 1933, 2, 111–117; Chem. Zentr., 1934, ii, 19).—From the dependence of the intensity of the fluorescence on that of the exciting light it is shown that excitation of Cd atom to the 2^3S_1 state at approx. 600° requires two absorption processes by the Cd mol. At approx. 900° only one is needed.

H. J. E.

Polarisation of the fluorescence of Cd vapour. L. SOSNOWSKI (Acta phys. polon., 1932, 1, 327–332; Chem. Zentr., 1934, ii, 19).—Data are recorded.

H. J. E.

Fluorescence of mixtures of Cd and Zn vapours. F. SPIEWANKIEWICZ (Acta phys. polon., 1932, 1, 345–350; Chem. Zentr., 1934, ii, 19–20).—Light between 2300 and 2150 Å. excites a band at 4850–6400 Å. in the mixed vapours at 780°.

H. J. E.

Extension of the platinum I-like isoelectric sequence to tellurium IV, lead V, and bismuth VI. G. K. SCHOEFFLE (Physical Rev., 1933, [ii], 43, 374).

L. S. T.

Fluorescence and absorption spectrum of I_2 vapour. I. I. AGARBICEANU (Ann. Physique, 1934, [xi], 2, 347–447).—Six anti-Stokes lines of the fluorescence spectrum of I_2 , excited by the $\lambda\lambda 5460$, 5770, and 5790 Hg lines, have been observed for the first time, the excitation being independent of the width of the exciting line. An interpretation is proposed. New absorption bands are reported. Addition of O_2 or N_2 causes a broadening of the absorption lines, more marked in the case of O_2 , and increasing with pressure. From the broadening the active radius of the I_2 mol. is calc. A connexion between this broadening and the depolarisation of resonance lines is found. From photographs of fluorescence lines excited by Hg $\lambda 5461$ it is shown that, for a normal and excited level, the resonance line is more affected by a perturbing factor than the corresponding absorption line under the same conditions, analogous to the effect of a magnetic field.

N. M. B.

Molecular spectrum emitted from atomic iodine vapour. O. OLDENBERG (Physical Rev., 1933, [ii], 43, 501).—The intensity of the continuous spectrum shown by I vapour at high temp. decreases with a decrease in pressure; it is emitted from a mol. just formed by a pair of atoms, one of which is excited (cf. A., 1924, ii, 579).

L. S. T.

Light absorption of adsorbed caesium. J. H. DE BOER, J. F. H. CUSTERS, and C. J. DIEFFEL (Physica, 1934, 1, 935–944).—The absorption spectrum of Cs adsorbed by CaF_2 has been measured for different degrees of occupation of the adsorbed layer. For low occupation the spectra are due to Cs atoms adsorbed on active spots by electrostatic polarisation, and strong light absorption beyond 440 mμ is no longer observed. Polyat. layers, in which the atoms are bound by van der Waals

forces, give a spectrum almost the same as that of a thin film of Cs metal. The high photo-electric yield at a low degree of occupation, and the shift of the threshold towards longer wave-lengths, are correlated with the absorption spectra. M. S. B.

Nuclear magnetic moment of caesium from the polarisation of resonance radiation. N. P. HEYDENBURG (Physical Rev., 1934, [ii], 46, 802—805; cf. A., 1934, 1279).—For a nuclear spin of $7/2$ the hyperfine separation consts. for the $7^2P_{3/2}$ and $7^2P_{1/2}$ levels of Cs I are 1.42×10^{-3} and 4.86×10^{-4} cm.⁻¹, respectively. The calc. nuclear magnetic moments are 2.40/1840 and 2.41/1840 Bohr magnetons, respectively, in agreement with the val. 2.52/1840 obtained from the splitting of the lower $6^2S_{1/2}$ level. N. M. B.

Isotopes of samarium. H. SCHULER and T. SCHMIDT (Z. Physik, 1934, 92, 148—152).—Optical isotope separation for Sm 150 and 152 is twice that for Sm 152 and 154, indicating a definite nuclear structure change in passing from 150 to 152. A. B. D. C.

Hyperfine structure and isotopic constitution of tungsten. N. S. GRACE and H. E. WHITE (Physical Rev., 1933, [ii], 43, 1039; cf. A., 1934, 339).—The arc spectrum of W shows patterns corresponding with only three components which are attributed to the isotopes of even no. A fourth isotope, possessing a magnetic and a mechanical nuclear moment, is indicated. L. S. T.

Application of the mechanical interval recorder to the analysis of the spectrum of osmium I. W. ALBERTSON (Physical Rev., 1933, [ii], 43, 501; cf. A., 1934, 468).—Some energy levels of Os I have been found by means of the mechanical interval recorder. L. S. T.

Band systems of mercury. T. S. SUBBARAYA (Proc. Indian Acad. Sci., 1934, 1, A, 166—177).—A theoretical survey of the band systems and an analysis of five of them. N. M. B.

Explosion spectrum of mercury compared with arc spectra under ordinary pressure and in a vacuum. H. NAGAOKA and T. FUTAGAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 111—126).—The spectrum (I) produced by exploding a thin stream of Hg by an electric discharge has been compared with spectra from Hg-vapour lamps working at approx. atm. pressure (II) and in a vac. Owing to the violence of the explosion no bands appear in (I), and there are many lines due to ionised Hg. In (II) structureless bands are conspicuous. R. S. B.

Intensity distribution in the fluorescence bands of mercury vapour. I. MROZOWSKA (Acta phys. polon., 1933, 2, 81—89; Chem. Zentr., 1934, ii, 18—19).—The effect of temp. and pressure on the intensity distribution in bands excited by the Zn line 2558 Å. was studied. H. J. E.

Zeeman effect of the hyperfine structure of the Hg line 2536. A. ŽVIRONAS (Helv. phys. Acta, 1933, 6, 273—276; Chem. Zentr., 1934, ii, 18).—Data are recorded, agreeing with theory. H. J. E.

Anomalous Zeeman effect of single hyperfine structure components of the mercury resonance line 2537 Å. I. The π components. A. ŽVIRONAS (Helv. phys. Acta, 1934, 7, 224—256; Chem. Zentr., 1934, i, 3026).—Data are recorded and discussed. H. J. E.

Emitter of the bands near 2482.07 Å. in the mercury spectrum. L. JOB (Acta. phys. polon., 1933, 2, 31—37; Chem. Zentr., 1934, ii, 398).—Fine structure measurements are recorded. The origin of the bands is discussed. H. J. E.

Resonance series of lead vapour. M. DOMANIEWSKA-KRUGER (Acta phys. polon., 1932, 1, 357—362; Chem. Zentr., 1934, ii, 18).—Two resonance series excited at 900° by 4358.3 and 5461 Å. Hg lines are described. H. J. E.

Emission spectrum of the night sky. I. Ultra-violet. J. DUFAY. II. Ultra-violet extremity. J. GAUZIT (J. Phys. Radium, 1934, [vii], 5, 523—526, 527—532; cf. A., 1934, 232).—I. Data for 78 bands or lines in the region 4815—3000 Å. are tabulated. The spectrum differs from that of the polar aurora by the weak intensity of the negative N₂ bands and of the bands of the second positive group, and by the presence of numerous lines of unknown or doubtful origin. Data on relationships with the spectra of A, He, and those of comet nuclei are extended to the ultra-violet.

II. Data for about 110 emission lines are given, with possible identifications, and comparisons with the results of other investigators. Absorption by atm. O₃ was not found; the spectral intensity of the night sky decreased only slowly towards 3000 Å. N. M. B.

Auroral spectrum and its interpretation. L. VEGARD (Trans. Amer. Geophys. Union, 1933, 68—69).—A review. CH. ABS. (e)

Electric furnace ionisation effect. A. S. KING (Physical Rev., 1933, [ii], 43, 214).—When a substance of moderate ionisation potential is vaporised in a C-tube furnace a temp. is found at which practically the whole neutral spectrum and the stronger lines of the ionised atom are given. When the furnace is subsequently run at the same temp. and total pressure with but little of the substance present, a spectrum in which the enhanced lines are relatively strong is obtained. This effect is marked for Ca, Ba, Sr, and Nd. L. S. T.

Anode temperature and emission of X-rays. F. HALLA and H. NOWOTNY (Z. Physik, 1934, 92, 76—81).—Rise in temp. increases emission with const. anode current. A. B. D. C.

Natural X-ray line widths: correction for finite resolving power. L. G. PARRATT (Physical Rev., 1934, [ii], 46, 749—754).—The resolving power of the X-ray double-crystal spectrometer is increased 2—4 times by employing etched quartz crystals. The shapes of the $K\alpha$ lines of Mo, Cu, and Ti were observed in anti-parallel positions. Correction for finite resolving power was negligible. N. M. B.

Weak X-ray lines of niobium and antimony. P. A. ROSS and P. KIRKPATRICK (Physical Rev.,

1933, [ii], 43, 1036).—Data for new weak emission lines of the *K* series of these elements are recorded.

L. S. T.

Absolute X-ray wave-lengths by refraction in quartz. J. A. BEARDEN and C. H. SHAW (Physical Rev., 1934, [ii], 46, 759—763).—High-precision measurements, with X-rays incident both internally and externally, gave $1-\mu=(8.553\pm0.005)\times10^{-6}$. Abs. wave-lengths calc. from quantum theory and from revised data for photographic results confirmed the vals. found by the ruled grating.

N. M. B.

K α X-ray lines of carbon and carbon compounds. H. BROILL, R. GLOCKER, and H. KIESSIG (Z. Physik, 1934, 91, 27—41).

A. B. D. C.

Self-ionisation of sodium and caesium at glow-in-tungsten and rhenium surfaces. H. ALBERTHUM, K. KREBS, and R. ROMPE (Z. Physik, 1934, 92, 1—18).—Na and Cs are 20 and 50% ionised at Rh, and 8.5 and 54% at W, the temp. variation of Na (but not Cs) efficiencies obeying Langmuir's first formula.

A. B. D. C.

Ionisation potentials and probabilities for the formation of multiply-charged ions in the alkali vapours and in krypton and xenon. J. T. TATE and P. T. SMITH (Physical Rev., 1934, [ii], 46, 773—776; cf. A., 1931, 665).—Probability curves and ionisation potential data, obtained by mass-spectrograph analysis, are given for ions formed by electron impact in Na, K, Rb, and Cs vapours, and in Kr and Xe. Evidence of additional mechanisms of formation appear for K⁺ at 15.5 and 150, for Rb⁺ at 12.5, for Cs at 10, 17.5, and 60, and for Cs²⁺ at 80 volts.

N. M. B.

Electrical point action with spherical conductors of atomic and sub-atomic dimensions. A. UPMARK (Z. Physik, 1934, 91, 737—741).—Theoretical.

A. B. D. C.

Electrical clean-up of gases at low pressures. II. W. VON MEYEREN (Z. Physik, 1934, 91, 727—736; cf. A., 1933, 992).—Clean-up has been studied in He, A, and N₂ between 5×10^{-4} and 1×10^{-7} mm.

A. B. D. C.

Disappearance of hydrogen in presence of potassium and lithium ion sources. C. H. KUNSMAN and R. A. NELSON (J. Chem. Physics, 1934, 2, 752—755; cf. A., 1932, 892).—The disappearance of H₂ in a discharge tube containing an anode coated with either synthetic spodumene or an Fe-Al-K catalyst is shown to be completely accounted for by reaction with the anode material. No evidence of reaction in the gaseous phase was observed.

F. L. U.

Ionic shell effect in gas discharges. A. GUNTHER-SCHULZE (Z. Physik, 1934, 91, 724—726).—Decrease of electron velocity increases negative ions in a mol. gas; this forms a space charge in wide tubes maintaining the discharge within a narrow space.

A. B. D. C.

Photo-electric effect of caesium vapour. J. KUNZ (Physical Rev., 1933, [ii], 43, 1052).—The min. in the ionisation efficiency curve has again been established even in vapour at room temp.

L. S. T.

Photo-electric effect. I. External photo-electric effect of elements in the periodic table. R. SCHULZE (Z. Physik, 1934, 92, 212—227).—The long-wave limit, defined as the wave-length at which the electron current falls below 10^{-15} amp. for an incident light energy of 10 ergs per sec., follows the ionisation potential derived from series limits of the free atoms. The quantum efficiency is of the same order for atoms in one group of the periodic table.

A. B. D. C.

Energy distribution of photo-electrons as a function of the thickness of a potassium film. J. J. BRADY (Physical Rev., 1934, [ii], 46, 768—772; cf. A., 1932, 1184).—Current-voltage curves for 0.8, 2, 3, and 30 mol. layers, using 3650 and 4350 Å., and analysis curves by the theory of Du Bridge (cf. A., 1933, 657) are given. Max. retarding potentials at 0° abs. were found by three methods. The photo-current decreased after the formation of films < 3 mol. layers, but remained nearly const. for thicker layers, indicating that the K "dissolves" in the Ag more readily before than after the formation of a continuous film.

N. M. B.

Radiation quantum and photographic threshold. H. BROILL, R. GLOCKER, and H. LANGENDORFF (Z. Elektrochem., 1934, 40, 784—789).—A quant. relation is established.

E. S. H.

Chemical registration of the diffraction of electric waves. W. ARKADIEV (Compt. rend., 1934, 199, 848—849).—Detectors of the Branly coherer type, with electrodes of different metals, are arranged with the electrodes in contact with paper impregnated with an indicator. When irradiated with Herzian waves, colour changes occur where the rays have passed. The method can be applied to the detection of diffraction images of the source.

J. W. S.

Born's theory of the electron. J. FRENKEL (Proc. Roy. Soc., 1934, A, 146, 930—935).—Mathematical.

L. L. B.

Dependence of the magnetic susceptibility of an electron gas on temperature. K. F. NIESSEN (Physica, 1934, 1, 979—988).—Theoretical. A formula has been deduced showing that the magnetic susceptibility of an electron gas increases with rise of temp.

M. S. B.

Electron diffusion. M. J. DRUYVESTYEN (Physica, 1934, 1, 1003—1006).—An error in a previous communication on the positive column with moving striations (A., 1934, 468) is corr. The distribution of final velocities of the electrons in a homogeneous field has been calc. for the case when the electrons make elastic collisions only with the atoms of gas.

M. S. B.

Secondary electron emission from tantalum. C. L. UTTERBACK and E. A. WILLIAMS (Physical Rev., 1933, [ii], 43, 212).—The electron emission from Ta bombarded by Li⁺ has been measured.

L. S. T.

Diffraction of electrons as a search for polarisation. F. E. MYERS, J. F. BYRNE, and R. T. COX (Physical Rev., 1934, [ii], 46, 777—785).—Electrons accelerated by voltages 80—225 kv. passed through a thin homogeneous foil of polycryst. Au and formed

a diffraction pattern on a fluorescent screen, through a hole in which various rays of the diffracted beam fell on a second diffracting foil. The second diffraction pattern, obtained on a photographic plate, showed, on examination for asymmetry, no evidence ($<10\%$, if any) of polarisation of the electron beam.

N. M. B.

Effect of spin interaction in the diffraction and polarisation of electrons. J. H. HOWEY (Physical Rev., 1933, [ii], 43, 499).

L. S. T.

Electron transfer from metals to dielectrics. N. KALABUCHOV (Z. Physik, 1934, 92, 143—147).—The work of transfer of electrons from Ag to mica is 0.5, to rock-salt 1.8, volts $<$ that for transfer to vac.

A. B. D. C.

Collisions of slow electrons with atoms. IV. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1934, A, 146, 880—900).—The theory of electron exchange developed previously (cf. A., 1933, 613) is applied to a study of the angular distribution of electrons scattered inelastically by A and Na atoms, and good agreement is obtained with experiment. The effect of the disturbance of the at. field by the incident electron waves on the elastic scattering is discussed. The theory is applied to the scattering by H_2 and He. Comparison with experiment shows that the excess of scattering at small angles above that given by Born's approximation is due to this polarisation effect.

L. L. B.

Electron capture cross-sections. L. A. YOUNG and N. E. BRADBURY (Physical Rev., 1933, [ii], 43, 1054).—Vals. calc. on certain assumptions are of the same order of magnitude as experimental vals. for electronegative gases such as O_2 and CO_2 .

L. S. T.

Probability function for the production of He^{++} by single electron impact. W. BLEAKNEY (Physical Rev., 1933, [ii], 43, 378).—It is concluded that about 1% of the He ions produced by 330-volt electrons are originally doubly charged.

L. S. T.

Collision of K^+ ions with inorganic and organic gas particles. I. Elastic and inelastic collision. II. Mechanism of the collision process. O. SCHMIDT (Ann. Physik, 1934, [v], 21, 241—267, 268—273; cf. A., 1934, 863, 937).—I. The nature of the collision of K^+ ions with gas particles is indicated by the symmetry of the distribution curve. For the completely symmetrical curves, which are given by Hg, Kr, Xe, MeCl, CO_2 , and N_2 , there is pure scattering at 200 volts. The energy losses are small, and the collisions are elastic. All other gases give unsymmetrical curves, indicating energy losses on impact. Two groups may be recognised: (a) in which the asymmetry (I) decreases with increasing mass in a homologous series (inert gases), (b) in which (I) increases with decreasing mass (paraffins and olefines).

II. The occurrence of elastic and inelastic collisions between K^+ ions and gas particles (II) is due to difference in time of impact, which in turn depends on the deformability of (II).

A. J. M.

Speed of positive ions in nitrogen. J. H. MITCHELL and K. E. W. RIDLER (Proc. Roy. Soc.,

1934, A, 146, 911—921).—The mobility of the positive ions formed by a glow discharge in pure N_2 at 4—9 mm. pressure is 2.67 cm./sec./volt/cm. Evidence is adduced to prove that these ions are N_2^+ , and that their mobility is $7.5\% <$ that appropriate to their mass owing to the phenomenon of electron exchange. Vals. of the mobilities of NH_3^+ , Kr^+ , Xe^+ , and Hg^+ in N_2 all lie on a smooth curve connecting the mobility of an ion with its mass. Evidence for electron capture is obtained indirectly from the study of the breakdown of Langevin's law (mobility \times pressure = const.), when the velocity is increased above a certain val.

L. L. B.

Ions in oxygen and hydrogen. C. D. BOCK (Physical Rev., 1933, [ii], 43, 1053—1054).—The results of a study of aged ions in O_2 using a magnetic spectrometer with high-order focussing are recorded.

L. S. T.

High-velocity mercury ions. W. M. COATES and D. H. SLOAN (Physical Rev., 1933, [ii], 43, 212—213).—The method of successive acceleration of Hg ions has been developed to produce particles of 2.85×10^6 e.v. energy. Each ion striking a Mo target produces seven to ten secondary electrons.

L. S. T.

Mass spectrum analysis of the products of ionisation by electron impact in nitrogen and acetylene. J. T. TATE, P. T. SMITH, and A. L. VAUGHAN (Physical Rev., 1933, [ii], 43, 1054).—A comparison of the ionisation potentials (I) of N_2 and A gave for the former the val. 15.65 ± 0.02 e.v. Mass spectrum analysis of the products of ionisation by electron impact in C_2H_2 at low pressure showed the formation of $C_2H_2^+$ (11.2), C_2H^+ (17.8), C_2^+ (23.8), CH^+ (22.2), C^+ (24.5), and H^+ (21.7 and 25.6). (I) in e.v. are given in parentheses. The efficiency of formation of the H^+ ion increased sharply at 25.6 ± 1.0 e.v. C^{13} , forming an ion of mass 27, was found, but no negative ions.

L. S. T.

Mass of Be^9 and the at. wt. of beryllium. K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 367—368).—The vals. obtained by measurements of spectra for the mass of Be^9 are 9.0155 ± 0.0006 on the $O^{16}=16$ scale and 9.0154 ± 0.0008 ($Ne^{20}=19.9967$). It is improbable that the nucleus of Be^9 consists of two α -particles and one neutron, or of two α -particles, one proton, and one electron. The at. wt. of Be from the above is 9.0130 ± 0.0007 on the chemical scale and is $<$ Hönigschmid and Birckenbach's val. of 9.0179 ± 0.0009 . The packing fraction of Be^9 is $+17.2$. The mechanism of disintegration and γ -ray production from Be^9 is discussed.

L. S. T.

At. wt. of protoactinium. A. V. GROSSE (J. Amer. Chem. Soc., 1934, 56, 2501).—The mean val. 230.6 has been determined.

E. S. H.

Measurement of the masses of He and H^1 , Ne^{20} , Ne^{22} , B^{11} , Cl^{35} , and Cl^{37} with a mass spectrograph. K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 378; cf. A., 1933, 203).—Referred to $H^1=1.00778$, $He=4.00218 \pm 0.00004$. Referred to O^{16} , $Cl^{35}=34.9796 \pm 0.0012$, and $Cl^{37}=36.9777 \pm 0.0019$. For other vals. see A., 1933, 442.

L. S. T.

Relative abundance of the neon isotopes. W. BLEAKNEY (Physical Rev., 1933, [ii], 43, 1056).—

Intensities observed are $^{20}\text{Ne}^+ : ^{22}\text{Ne}^+ : ^{21}\text{Ne}^+ = 100 : 8.2 : 0.28$ and $^{20}\text{Ne}^{++} : ^{22}\text{Ne}^{++} : ^{21}\text{Ne}^{++} = 100 : 9.2 : 0.30$. The existence of $^{21}\text{Ne}^{++}$ thus appears to be established. No trace of ion of mass 23 could be detected (cf. A., 1933, 333). L. S. T.

Mass spectra of neon fractionated by G. Hertz and the non-existence of Ne^{23} . K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 1060).—No line corresponding with Ne^{23+} was observed in fractionated Ne containing Ne^{22} in the same abundance as Ne^{20} . Ne^{21} and Ne^{22} were enriched three and nine times their abundance in atm. Ne, and Ne^{23} , if present, would have been enriched 27 times in this fraction. Bloakney's result (cf. preceding abstract) is confirmed. L. S. T.

Isotopic constitutions of krypton, mercury, selenium, cadmium, and germanium. K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 43, 1056).—Results for Kr, Se, and Cd confirm Aston's work. There is no evidence for 9% of Se^{81} . Cd^{108} and Cd^{113} , found in band spectra, have not yet been observed, probably owing to technical difficulties and to their relatively small abundance. Lines attributed by Aston to Ge^{71} , Ge^{75} , and Ge^{77} are mainly, if not entirely, due to hydrides of Ge^{70} , Ge^{74} , and Ge^{76} . L. S. T.

Application of radioactive methods in chemistry. O. HAHN (Ber., 1934, 67, [A], 150—163).—A lecture. H. W.

New kind of radioactivity. R. M. LANGER and R. W. RAITT (Physical Rev., 1933, [ii], 43, 585).—General considerations and quantum theory lead to the conclusion that Be^9 should decompose spontaneously, giving off α -particles and possibly a neutron. Ra-free Be has an α -particle activity of 1 cm. range in air, and half-life period of 10^{14} years in accord with the He content of certain beryls. He^5 may be a product of the disintegration. This abnormal He content should not be explained in terms of the radioactivity of Be^8 , the life-period of which is too short for this isotope to have played any part in the chemistry of Be. L. S. T.

Attempt to observe a helium isotope. J. T. TATE and P. T. SMITH (Physical Rev., 1933, [ii], 43, 672).—A mass-spectrographic analysis of the gas obtained by heating a crushed crystal of beryl after passage through a C-liquid air trap showed the presence of He^4 . He^5 , if present, was < 1 in 4×10^4 relative to He^4 (cf. preceding abstract). L. S. T.

Radioactivity of beryllium. R. M. LANGER and R. W. RAITT (Physical Rev., 1933, [ii], 43, 1055).—The decomp. products of Be disintegration have a range about 1 cm. in air. The decay const. of Be is $10^{-21} \text{ sec.}^{-1}$. Strutt's data for the Acworth beryls lead to a const. of the same order of magnitude. The failure of the Condon-Gurney-Gamow theory in this case again indicates that the light nuclei, at least, are not composed of α -particles. L. S. T.

Formation of branched tracks (due to α -particle collisions) on photographic plates covered with a heavy layer of emulsion. A. P. ZHDANOV (Trav. inst. etat radium, U.S.S.R., 1933, 2, 249—

265).— α -Particles from Po in air were studied by photographing their tracks on thickly-coated plates. Of 3000 tracks, 35 showed breaks and 11 showed branchings. CH. ABS. (e)

Errors in α -particle measurements. I. E. STARIK and O. S. MELIKOVA (Trans. inst. etat radium, U.S.S.R., 1933, 2, 117—126). A discussion. Most of the variations and errors are due to the type of vessel used for holding the sample. CH. ABS. (e)

Continuous β -ray spectrum. A. BRAMLEY (Physical Rev., 1933, [ii], 43, 767; cf. A., 1933, 1100).—A discussion of the equivalence of mass and energy in β -particle disintegration processes. L. S. T.

β -Rays of radium-D. H. O. W. RICHARDSON and A. LEIGH-SMITH (Nature, 1934, 134, 772).—Expansion chamber β tracks from Ra-D tetramethyl show that the typical disintegration of Ra-D consists of a 47,200-volt γ -transition accompanied by the emission of a nuclear electron of 0—3 mm. range in air. The high energy limit of the nuclear spectrum is probably near 10—12 kv. β -Rays between 10 and 30 kv. found in previous experiments are absent. They are identified as secondary electrons which had lost energy in the solid material on which the radioelement had previously been mounted. L. S. T.

Molecular changes accompanying the radioactive transformation of radium-D. R. A. MORTENSEN and P. A. LEIGHTON (J. Amer. Chem. Soc., 1934, 56, 2397—2398).—Evidence is adduced to show that Ra-D tetramethyl is not broken down completely by the radioactive transformation into Ra-E and Ra-F, but adjusts itself to the new valency conditions by losing Me and completing an electron pair by acquiring an electron from the surroundings. E. S. H.

Diffusion of γ -rays. E. STAHEL and H. KETELAAR (J. Phys. Radium, 1934, [vii], 5, 512—522).—Work previously reported (cf. A., 1933, 1224) is extended with improved technique. Investigation by diffusion by thick screens shows that Pb, Au, and W emit radiation of which the hardest component is the same for each, and has an absorption coeff. 3.3×10^{-25} , against 1.9×10^{-25} for that of the hardest components of the incident radiation. N. M. B.

Supplementary radiations in the recoil from Th active deposit. (MISS) C. CHAMIE (Compt. rend., 1934, 199, 943—945).—The anomalies previously reported (cf. A., 1934, 5) in the decay curves of Th-C' from Th-C disappear when the quantity of Th-C' increases with time of exposure, and increase when the activation time diminishes. Steeper curves were obtained for activation times of fractions of a sec. The phenomenon was not observed for a brass collector not at a negative potential. It is suggested that the curves can be explained by the existence of unknown sources in the Th-C, or by a transmutation induced in the source by its own radiation. N. M. B.

Photographic determination of the half-period of thorium-B. T. R. WILKINS and S. D. BURDICK (Physical Rev., 1933, [ii], 43, 1059).—The val. determined by a photographic method is approx.

10.2 hr. as compared with the accepted val. of 10.6 hr., based on ionisation measurements. L. S. T.

Radioactivity and nuclear synthesis. H. J. WALKER (Phil. Mag., 1934, [vii], 18, 795—822).—Assuming a primary distribution of a gravitating gas “neutron” of zero at. no., and a const. no. of neutrons in the universe, a mechanism whereby the elements are formed by radioactive synthesis due to β -ray emission from missing isotopes is indicated.

F. L. U.

Artificial activation of lead by γ -rays. H. R. VON TRAUBENBERG and H. BARTELS (Naturwiss., 1934, 22, 758).—An artificial activation was induced in Pb by the action of γ -rays from Th emanation.

A. J. M.

Atomic disintegration of light elements by H and He. R. DOPEL (Z. Physik, 1934, 91, 796—809). Data are given for disintegration of Li, Be, and B.

A. B. D. C.

Separation of the isotopes of lithium and some nuclear transformations observed with them. M. L. OLIPHANT, E. S. SHIRE, and B. M. CROWTHER (Proc. Roy. Soc., 1934, A, 146, 922—929).—A method for preparing pure specimens of the separated isotopes of Li in quantities of the order of 10^{-6} g. is described. Targets of Li^6 and Li^7 were bombarded successively with protons and with deuterons at about 160 kv. energy. Li^6 with protons gives α -particles of 11.5 mm. range; with deuterons, α -particles of 13.2 cm. range and protons of 30 cm. range. Li^7 with protons gives α -particles of 8.4 cm. range; with deuterons, α -particles up to 8 cm. range, and neutrons.

L. L. B.

Disintegration of lithium by protons. J. R. OPPENHEIMER (Physical Rev., 1933, [ii], 43, 380; cf. A., 1933, 205).—Theoretical. The Gamow model is applicable to the case of Li.

L. S. T.

Disintegration experiments on elements of medium atomic number. M. A. TUVE, L. R. HAFSTAD, and O. DAHL (Physical Rev., 1933, [ii], 43, 942).—There is no evidence that disintegration protons or α -particles of range > 16 mm. are produced by bombardment of Al, Ni, and Ag by 600-kv. protons. Small effects observed are explained by the presence of 1/9000—1/100,000 of B impurities in the targets.

L. S. T.

Disintegration of aluminium by swiftly-moving protons. M. S. LIVINGSTON and E. O. LAWRENCE (Physical Rev., 1933, [ii], 43, 369).—The bombardment of Al by high-velocity protons produces radiations (I), presumed to be α -particles, which penetrate approx. 8 cm. of air. The distribution of the ranges of (I) is continuous. The effective nuclear cross-section for disintegration becomes const. at proton energies $> 8 \times 10^5$ volts.

L. S. T.

Neutron of high velocity, and energy relations for nuclear disintegration by non-capture. W. D. HARKINS, D. M. GANS, and H. W. NEWSON (Physical Rev., 1933, [ii], 43, 584—585; cf. A., 1934, 827).—The energy of a neutron from Be used in N^{14} disintegration experiments has been calc. as 16×10^6 e.v. and the velocity 5.6×10^9 cm. per sec. Disintegration by non-capture of the neutron in these experiments is discussed.

L. S. T.

Secondary emission from elements bombarded with neutrons. Z. OLLANO (Nature, 1934, 134, 735).—Measurements of the absorption of the radiations from Po+Be in different elements indicate that the abnormally low absorptions found for Sn and Sb are to be ascribed to more absorbable secondary radiations produced by the passage of the primary rays through these elements. These softer radiations are probably of the nature of γ -rays and arise from excitation of nuclear levels of elements near Sn in the periodic table.

L. S. T.

Secondary emission from elements bombarded with neutrons. M. L. OLIPHANT (Nature, 1934, 134, 735—736).—Strong ionising radiations are produced when Ag is placed in a beam of neutrons (I) formed by the bombardment of elements by accelerated H^2 ions. The effects observed (cf. preceding abstract) are probably due to the (I) in the radiation from Po+Be.

L. S. T.

Effective neutron collision radius. I. I. RABI (Physical Rev., 1933, [ii], 43, 838).—Neutron collision radii calc. for ten elements from C to Pb vary from 1.08 to 1.54, average val., 1.31×10^{-13} cm.

L. S. T.

Nitrogen disintegration by a very fast neutron. F. N. D. KURIE (Physical Rev., 1933, [ii], 43, 771).—Be bombarded by α -particles from Po gave an unusually fast neutron of 17×10^6 volts energy (see above). The recoiling nucleus, B^{11} , and the disintegration particle (He^4) when N_2 is bombarded by this neutron are of ordinary energies and the “loss” of 13.6×10^6 volts may be accounted for by the formation of a B^{11} slightly heavier than that measured in the mass-spectrograph.

L. S. T.

Transmutation of elements by neutrons. L. MEITNER (Naturwiss., 1934, 22, 759).—In extension of the work of Szilard and Chalmers (A., 1934, 77) it is shown that the neutrons emitted by the action of Ra γ -rays on Be will cause transmutation of I, Ag, and Au, but not of Na, Al, or Si. It is supposed that these neutrons have less energy than those emitted from Be by α -rays, and consequently can only effect certain nuclear changes.

A. J. M.

High-speed electrons liberated from fluorine after bombardment by neutrons. I. KURTSCHATOV, G. SCHTSCHEPKIN, and A. VIBE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 572—575).—Neutrons bombarding LiF liberated electrons of energy $4\text{--}5 \times 10^6$ e.v., confirming predictions based on Fermi's work.

H. J. E.

Fermi's element 93. A. V. GROSSE and M. S. AGRUSS (Nature, 1934, 134, 773; cf. A., 1934, 826, 1284).—Repetition of Fermi's experiments with Pa shows that the 13-min. product from U is chemically identical with element 91. In the Re sulphide reaction with Pa as indicator the element 91 is pptd. to the extent of 40—60% with Re sulphide from 15% HCl. It is concluded that the products with the 13 and 90—100 min. periods are isotopes of eka-Ta, changing by β -emission into isotopes of U. Fermi's proof of the non-identity of his products with element 91 is inconclusive.

L. S. T.

Periodic property of atomic nuclei. G. MONOD-HERZEN (Compt. rend., 1934, **199**, 859—860).—A curve relating the at. no. (Z) with the no. of nuclear types known between Z and $Z+4$ shows a periodicity with marked minima at $Z=26$ (Fe), 56 (Ba), and 86 (Rn), as well as sub-minima. The first group contains most of the common elements and shows only a relatively small no. of isotopes, agreeing with the view that the abundance of an element depends on its stability. J. W. S.

Classification of atomic nuclei. V. V. TSCHERDINTSEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 576—583).—Theoretical. Nuclear structures are discussed. H. J. E.

Equilibrium theory of the abundance of the elements. T. E. STERNE (Physical Rev., 1933, [ii], **43**, 585—586, 768).—If all nuclei are ultimately composed of electrons and protons, the most abundant element when equilibrium is established must usually be that of even mass no. and smallest packing fraction. L. S. T.

Hemi-alpha groups in atomic nuclei as related to the energy of binding. W. D. HARKINS (Physical Rev., 1933, [ii], **43**, 1059). L. S. T.

Low states of the heaviest elements. T. Y. WU and S. GOUDSMIT (Physical Rev., 1933, [ii], **43**, 496).—The energies of the $5f$, $6d$, $7s$, and $7p$ states of the atoms and ions built on the radon core have been calc. They depend chiefly on the degree of ionisation and change little with a change of nuclear charge from 92 to 89. L. S. T.

Positrons from γ -rays. C. D. ANDERSON and S. H. NEDDERMEYER (Physical Rev., 1933, [ii], **43**, 1034; cf. A., 1933, 658).—In addition to the positrons (I) ejected from Pb by hard γ -rays (II), there is an occasional simultaneous appearance of paired tracks of one positive and one negative particle with a common point of origin. The energy distribution of these pairs and of positively-charged particles is discussed. The (I) observed by other workers using neutrons with accompanying (II) may be due only to the latter and not to neutrons. L. S. T.

Annihilation of fast positrons by electrons in the K -shell. H. J. BHABHA and H. R. HULME (Proc. Roy. Soc., 1934, A, **146**, 723—736).—Mathematical. The probability of a stimulated transition of an electron from the K shell to a state of negative energy is calc. for the condition where all the states of negative energy are unoccupied. From this is calc. the probability of the corresponding spontaneous transition when only certain of the negative energy states are unoccupied. The probability of annihilation is always very small compared with that by free electrons, where 2 quanta are emitted. L. L. B.

New "annihilation" process of positive electrons. J. BRUNINGS (Physica, 1934, **1**, 996—1002).—The probability that a positron, combining with a K electron, should be annihilated, whilst the energy set free is taken up by the other K electron, has been calc. M. S. B.

Exchange of energy between a platinum surface and gas molecules. W. B. MANN (Proc. Roy.

Soc., 1934, A, **146**, 776—791).—The following vals. have been obtained for the accommodation coeffs. of different gases impinging on a clean Pt wire: He, 0.03 at room temp. and 0.04 at 80° abs. for mean filament temp. (T) 100—1000°; A, 0.55—0.35 at room temp., T 100—1000°; Hg vapour, about 1.0 at room temp., T 100° and 200°; H₂, 0.11—0.08 at room temp., T 100—1000°; O₂, 0.42—0.55 at room temp., T 100—1000°. The results indicate that the process of contamination is one of adsorption, and that it is chiefly dependent on the nature of the filament surface. A process analogous to etching causes marked changes in the adsorbing properties of the surface in He. With H₂, the accommodation is increased at higher temp. by absorption. L. L. B.

Variation of the K resonating strength with atomic number. J. A. WHEELER and J. A. BEARDEN (Physical Rev., 1934, [ii], **46**, 755—758).—The effective no. of K electrons, calc. on an approx. theory using Hartree wave functions, agrees, for at. no. < 40, with results obtained by anomalous dispersion, and by absorption data and theory. N. M. B.

Distribution of energy in the ultra-violet solar spectrum as inferred from the photochemical theory of the ozone equilibrium in the earth's atmosphere. D. EROPKIN (Phil. Mag., 1934, [vii], **18**, 838—841).—A preliminary calculation indicates that the sun's ultra-violet spectrum corresponds with Planck's curve if the O. mean height is 20 km. F. L. U.

Positively-charged component of cosmic rays. L. ALVAREZ and A. H. COMPTON (Physical Rev., 1933, [ii], **43**, 835—836).—Evidence for the existence of such a component, probably positrons, is given. L. S. T.

Nature of the primary cosmic radiation. W. F. G. SWANN (Physical Rev., 1933, [iii], **43**, 945—946). L. S. T.

Composition of cosmic rays. A. H. COMPTON and H. A. BETHE (Nature, 1934, **134**, 734—735).—A discussion. L. S. T.

Electric deflexion of cosmic ultra-radiation. E. LENZ (Nature, 1934, **134**, 809). L. S. T.

Rock-salt absorption of cosmic rays. S. ZIEMECKI (Nature, 1934, **134**, 773).—Measurements of the absorption of cosmic rays (I) by powdered rock-salt indicate that it is the most transparent substance for (I) so far examined. L. S. T.

Velocity of light. R. T. BIRGE (Nature, 1934, **134**, 771—772).—The val. $299,776 \pm 4$ km. per sec. is suggested as a final weighted average val. for c . L. S. T.

Value of e/m . R. T. BIRGE (Physical Rev., 1933, [ii], **43**, 211; cf. A., 1933, 1226; 1934, 580). L. S. T.

Electromagnetic fields in the quantum theory. I. L. GOLDSTEIN (J. Phys. Radium, 1934, [vii], **5**, 545—552).—Mathematical. Static fields of H-type atoms, neglecting electron spin, are considered non-relativistically. N. M. B.

Diffusion theory of the normal zero gradient of inert gases. G. ZIMMERMANN (Z. Physik, 1934, **91**, 767—774; **92**, 282).—This zero gradient observed between concentric electrodes with A and Ne is due to diffusion of electrons. A. B. D. C.

Transport phenomena in an ionised gas. R. C. MAJUMDAR (Z. Physik, 1934, **91**, 706—716).—Quantum-mechanical methods developed for metal-physics are applied to this problem. A. B. D. C.

Photon spin. L. DE BROGLIE and J. WINTER (Compt. rend., 1934, **199**, 813—816).—Mathematical. J. W. S.

Waves, spin, and constants. E. SEVIN (Compt. rend., 1934, **199**, 937—939).—Mathematical. N. M. B.

Atomic wave functions. F. W. BROWN and C. G. DUNN (Physical Rev., 1933, [ii], **43**, 1047). L. S. T.

Continuous current amplifier for microphotometric registration. M. MEUNIER and J. ANDRIOT (J. Phys. Radium, 1934, [vii], **5**, 538—540).

Photo-electric measurement of relative and absolute extinction. G. KORTUM and H. VON HALBAN (Z. physikal. Chem., 1934, **170**, 212—230).—The sources of error, and particularly the effect of using spectrally impure light, in the photo-electric method are examined. An improved form of the two-cell arrangement (A., 1922, ii, 332) is described, which, using either a rotating sector or polarisation prisms, permits the abs. determination of extinction coeffs. with a precision of 1—2% and the comparison of two extinctions with a precision of 0.01%. The possibilities of the apparatus are demonstrated by data for the absorption curve of the 2:4-dinitrophenoxide ion and its change with temp. R. C.

Absorption due to added substances in alkali halide crystals. M. BLAU (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 401—405; Chem. Zentr., 1934, i, 3034).—Passage of electrons into NaCl or KCl crystals containing Ag, Cu, Tl, or Pb produces new absorption spectra of unknown origin. H. J. E.

Photochemistry of alkali halide crystals. R. HILSCH and R. W. POHL (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 406—419; Chem. Zentr., 1934, i, 3034—3035).—The mechanism of photo-dissociation and the origin of the crystal coloration are discussed. H. J. E.

Spectrum of the afterglow of sulphur dioxide. A. G. GAYDON (Proc. Roy. Soc., 1934, **A**, **146**, 901—910).—The conditions of the production of the afterglow of SO₂ and the effects of change of pressure and electrical excitation on the spectrum have been studied. The spectrum consists of a continuum from 2400 to 4500 Å., and a band system from 3828 to 4699 Å. The vals. of the wave-no. intervals indicate that the afterglow bands are produced by mols. of SO₂. An examination of the spectrum of the exciting discharge leads to the conclusion that the afterglow is caused by the recombination of SO and O₂ in the form of a flame which gives the observed spectrum. L. L. B.

Perturbations due to spin-orbit forces in carbon monoxide and other band spectra. J. H. VAN VLECK (Physical Rev., 1933, [ii], **43**, 1047—1048). L. S. T.

Internal resonance in the carbon monoxide molecule. G. H. DIEKE (Physical Rev., 1933, [ii], **43**, 780; cf. A., 1933, 207). L. S. T.

Vibrational analysis of the GeO emission band spectrum. R. W. SHAW (Physical Rev., 1933, [ii], **43**, 1043).—Fifteen band heads in the region 2990—2500 Å., given by an arc with electrodes of graphite rods cored with fused GeO₃, have been measured. L. S. T.

Band spectrum of arsenic oxide (AsO). F. C. CONNELLY (Proc. Physical Soc., 1934, **46**, 790—800).—Data and vibrational analysis are tabulated for 35 lines of a system in the range $\lambda\lambda$ 3450—2950, degraded towards the red, and 66 lines of a system in the range $\lambda\lambda$ 2800—2350, degraded away from the red. Both are doublet systems, arising from transitions between two excited ² Σ levels and a ² Π ground level having a separation of 1026 cm.⁻¹ between the Π components. N. M. B.

Ultra-violet absorption spectrum of osmium tetroxide. A. LANGSETH and B. QVILLER (Z. physikal. Chem., 1934, **B**, **27**, 79—99; cf. A., 1930, 1089).—The absorption spectrum of OsO₄ vapour in the near ultra-violet between room temp. and 400° may be accounted for in terms of three electron transitions, each of which is probably in the Os atom. There is probably a fourth system of bands in the short-wave region, and a continuous absorption is superimposed on the whole spectrum. There are Raman frequencies of 568, 688, 917, and 1187 cm.⁻¹, corresponding with a regular tetrahedral mol., a structure also supported by other evidence. The absorption spectra of solutions of OsO₄ in H₂O, C₆H₁₄, and CCl₄ have been examined. The above observations confirm the rule that in the electron transition not all the characteristic frequencies appear in the initial and final states. R. C.

Absorption spectra of aqueous solutions of hydrochloric acid and of various chlorides in the ultra-violet. R. TREHIN (Compt. rend., 1934, **199**, 1047—1049).—Measurements are given for aq. solutions of HCl, LiCl, NaCl, KCl, CaCl₂, MgCl₂, SrCl₂, and BaCl₂, between 2110 and 2500 Å., and at 20—90°. HCl solutions are the more transparent in the nearer ultra-violet, but less so at shorter λ . The density of absorption increases with the at. no. of the cation. J. W. S.

Absorption spectra of bromine trifluoride, iodine pentafluoride, and cyanogen fluoride. C. F. WHITE and C. F. GOODEVE (Trans. Faraday Soc., 1934, **30**, 1149—1051).—The absorption by BrF₃ and IF₅ vapours is continuous and commences at approx. 2800 and 2400 Å., respectively. A band at 3000—3600 Å. (max. 3250) is attributed to BrF. CNF does not absorb at > 1840 Å. J. G. A. G.

Band systems of calcium chloride. R. K. ASUNDI (Current Sci., 1934, **3**, 153—154).—The bands consist of (i) a red system due to the transition ² $\Pi \rightarrow ^2\Sigma$ and (ii) an orange system involving a $\Sigma \rightarrow \Sigma$

transition. The heats of dissociation for the ${}^2\Pi$ and ${}^2\Sigma$ states are 4.60 and 3.46 volts, respectively, whilst those for the upper and lower states of (ii) are 1.53 and 1.52 volts, respectively. L. S. T.

Absorption spectra, in aqueous solution, of co-ordination compounds of chromium and cobalt. A. MEAD (Trans. Faraday Soc., 1934, **30**, 1052—1058).—The absorption has been determined between 3000 and 7000 Å. of 10^{-2} — $10^{-3}M$ -chlorides, -sulphates, and -K salts of $[M(C_2O_4)_3]^{3-}$, $[Cr en(C_2O_4)_2]'$, $[M en_2(C_2O_4)]'$, and $[M en_3]^{3+}$, where M is Cr^{III} and Co^{III} . Each ion has strong continuous absorption at < 3000 Å., and in the visible and near ultra-violet two broad bands of which the heads are in approx. const. relationship and probably represent two excitation states of the co-ordination electrons. The absorption max. of the Cr^{III} compounds are shifted regularly and the Co compounds less regularly towards the ultra-violet by progressive replacement of C_2O_4 by en. The absorption bands are symmetrical on a scale of wave-lengths and are reproduced by the formula of Lowry and Hudson (A., 1933, 889). J. G. A. G.

Absorption spectra of nitrates and nitrites in relation to their photo-dissociation. K. S. KRISHNAN and A. C. GUHA (Proc. Indian Acad. Sci., 1934, **1**, A, 242—249).—The absorption bands of inorg. nitrates with long wave-length limits at 3500 and 2300 Å. are attributed to dissociation into the nitrite and an O atom in the normal (3P) and excited (1D_2) states, respectively. From these wave-length limits the heat of dissociation of O_2 into two normal atoms is 114 kg.-cal. per mol., and the energy of excitation of O from the 3P to the 1D_2 level is 43 kg.-cal. per mol., in agreement with previous spectroscopic data. The dichroism of these absorption bands is attributed to the variation in quantum efficiency of the photo-dissociations with change in the direction of polarisation of the exciting light. The absorption bands of nitrites at 4000 and 3600 Å. are also attributed to dissociation with liberation of O in the normal and excited state, respectively. J. W. S.

Photochemical studies. XIX. Ultra-violet absorption spectrum of acetone vapour. W. A. NOYES, jun., A. B. F. DUNCAN, and W. M. MANNING (J. Chem. Physics, 1934, **2**, 717—725).—Bands in the neighbourhood of λ 3000 Å. and between 2000 and 1800 Å. have been measured and analysed. A third group between 1700 and 1300 Å. has been photographed. F. L. U.

The carbonyl group of aldehydes and ketones compared with carbon monoxide. V. HENRI (Compt. rend., 1934, **199**, 849—851).—From the ultra-violet and infra-red absorption spectra of aldehydes and ketones it is concluded that the CO group in these compounds is in the ${}^3\Pi$ electronic state, corresponding with the first state of activation of the CO mol. When such mols. are activated, the CO group passes into the ${}^3\Sigma$ state, and on thermal or photochemical decomp. involving liberation of the CO group, the latter passes into the ${}^1\Sigma$ state, and a CO mol. is formed in the normal state. It is suggested that the difference in electronic state accounts for the fact that aldehydes and ketones have high electric moments and CO a low moment, as

theoretically the ${}^3\Pi$ state of CO should have a high moment, and the normal ${}^1\Sigma$ state none. J. W. S.

Optical absorption of porphyrins. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1934, **170**, 337—350).—Absorption curves of solutions have been determined between 480 and 650 m μ . Solutions in dioxan (I) have four well-marked bands and a smaller band, the positions of which are not greatly altered by the most diverse substitutions, indicating the presence of a common porphin framework; introduction of a CO_2Me group into the latter, however, changes the whole form of the absorption curve. The curves indicate that ψ -verdoporphyrin Me_2 ester and rhodoporphyrin Me_2 ester are not isomeric. The spectra of solutions in 3*N*-HCl consist of two bands. With some isomeric porphyrins the absorption curves are indistinguishable in (I), but exhibit perceptible differences in HCl. Others exhibit detectable differences in (I). R. C.

Absorption spectra of alkaloids of calumba root and of some derivatives of berberine.—See this vol., 99.

New method for calculating molecular vibration frequencies. D. H. ANDREWS, V. DEITZ, and S. GOLDHEIM (Physical Rev., 1933, [ii], **43**, 373).—Theoretical. L. S. T.

Infra-red rotation vibration spectrum of hydrogen sulphide. A. D. SPRAGUE and H. H. NIELSEN (Physical Rev., 1933, [ii], **43**, 375; cf. A., 1933, 208).—The band at 1.9 μ has two max. at 1.93 μ , and 1.97 μ . A second max. of the 3.73 μ band occurs about 3.88 μ . L. S. T.

Vibrational isotope effects in polyatomic molecules. II. E. O. SALANT and J. E. ROSENTHAL (Physical Rev., 1933, [ii], **43**, 581—582; cf. A., 1933, 204).—Mathematical. L. S. T.

Infra-red spectra of silica. D. G. DRUMMOND (Nature, 1934, **134**, 739).—Absorption coeffs. and wave-lengths have been measured for various thicknesses of fused SiO_2 (I) and cryst. quartz (II). New bands have been found in (II), but that at 2.72 μ (A., 1929, 236) is absent, as are several bands in (I) between 2 and 4 μ (A., 1929, 974). A band near 2.73 μ is probably due not to SiO_2 but to dissolved CO_2 . L. S. T.

Rotation-vibration spectra in the photographic infra-red of molecules with the hydrogen isotope of mass 2. I. The $C_2H^1H^2$ spectrum and the C—C and C—H separation in acetylene. G. HERZBERG, F. PATAT, and J. W. T. SPINKS (Z. Physik, 1934, **92**, 87—99).—Bands were photographed at 0.784, 1.03, 1.09, and 1.19 μ . The moment of inertia is 27.753×10^{-40} when vibrationless, and 27.899×10^{-40} g.-cm.² in the ground state. The C—H distance is 1.058, and C—C 1.199 Å. The fundamentals of $C_2H^1H^2$ are 1840, 2570, and 3330 cm.⁻¹ A. B. D. C.

Vibration spectra and force constants of "heavy" acetylene. G. B. B. M. SUTHERLAND (Nature, 1934, **134**, 775—776).—Interpretations of recent observations on the infra-red and Raman spectra of $CH^1_2CH^2$ and C_2H_2 are discussed. L. S. T.

Rotation-vibration band of hydrogen cyanide near 10,381 Å. W. SCHEIB and K. HEDFELD (Z.

Physik, 1934, **91**, 792—795).—The moment of inertia of the lower state is 20×10^{-40} , and of the higher 19.44×10^{-40} g.-cm.²; the C-N separation is 1.1 Å.

A. B. D. C.

Near infra-red absorption of calciferol. E. SHELOW (Bull. Basic Sci. Res., 1933, **5**, 1—4).—Absorption bands of calciferol (I) occur at 1.55 and 2.05 μ and characterise the alcohol group. Transmission curves resemble that of ergosterol, with which (I) is probably isomeric.

CH. ABS. (p)

Influence of dissolved electrolytes on the constitution of water. C. S. RAO (Current Sci., 1934, **3**, 154—155; cf. A., 1931, 408).—The Raman band for H₂O in solutions of electrolytes (I) is always sharper than for pure H₂O, the max. of the band being nearly in the same position as that attributed to the (H₂O)₂ mols. With aq. solutions of HNO₃, H₂SO₄, NaNO₃, LiNO₃, and LiCl the band becomes sharper with an increase in concn. of (I) and shifts towards a greater frequency. With HCl, however, the band is sharper at 8N than at 11.7N, and the shift of the max. is in the opposite direction. These results indicate the extreme stability of the (H₂O)₂ mols. and the comparative instability of the H₂O and (H₂O)₃ mols. in solutions of (I).

L. S. T.

Raman effect and complexity of mercurous and thalious ions. L. A. WOODWARD (Phil. Mag., 1934, [vii], **18**, 823—827).—A strong Raman line 169 cm.⁻¹ observed in a sat. solution of Hg (ous) nitrate is ascribed to (Hg-Hg)⁺⁺. There is no similar evidence for (Tl-Tl)⁺⁺ in TlNO₃ solution. The amount of Tl₂⁺⁺, if it exists, is <10% of the total Tl present.

F. L. U.

Raman effect in selenic acid and some selenates. A. S. GANESAN (Proc. Indian Acad. Sci., 1934, **1**, A, 156—162).—Data are given for aq. H₂SeO₄ and the selenates of K, NH₄, Mg in solution, and of Tl (cryst.). Results for the acid differ considerably from those of the salts, for which the four lines are: 835 (strong), 875 (faint), 345, and 415 cm.⁻¹ A tetrahedral structure for SeO₄ is indicated. Heats of dissociation of Se-O and S-O are calc.

N. M. B.

Raman effect of triatomic molecules. V. Constitution of N₃' and NCS' ions. A. LANGSETH, J. R. NIELSEN, and J. U. SØRENSEN (Z. physikal. Chem., 1934, **B**, **27**, 100—110; cf. A., 1934, 942).—The Raman spectra of the above ions have been examined and the state of polarisation of the stronger Raman lines has been measured. Using the principle of isosterism in conjunction with the Raman data it is deduced that N₃' is linear and centro-symmetrical and NCS' linear, with the negative charge on the S atom, N-C-S'. R. C.

Raman spectrum of trichlorobromomethane. J. WOUTERS (Bull. Acad. roy. Belg., 1934, [v], **20**, 782—788).—The principal lines are at 195, 247, 295, 425, 715, and 774 cm.⁻¹, frequencies intermediate between those of CBr₄ and CCl₄. The Raman spectrum is compared with those of other compounds of similar structure.

H. F. G.

Raman spectra of five higher alcohols. P. L. BAYLEY (Physical Rev., 1933, [ii], **43**, 373—

374).—The Raman spectra of *n*-amyl to *n*-nonyl alcohol have been obtained. In heptyl, octyl, and nonyl alcohol only lines corresponding with the spectrum of EtOH were found. Comparison of the spectra of *n*- and *iso*-alcohols shows that the no. and relative positions of lines are determined almost entirely by the no. of C atoms in the chain. The broad line at $\Delta\nu$ 1450 is double in *iso*amyl and hexyl alcohols. The latter has a line beyond 1450, at 1657 Å.

L. S. T.

Raman effect in some organic substances. G. B. BONINO and M. ANSIDEI (Mem. R. Accad. Sci. Ist. Bologna, 1934, **12**, 3—7, 27—31).—Frequencies and intensities of Raman lines are recorded for 95 org. substances, including aromatic esters and aldehydes, phorone, alkyl sulphides, and derivatives of Ph₂, C₅H₅N, picoline, quinoline, pyrrole, pyrazole, indole, indene, and thionaphthene.

O. J. W.

Raman spectra of deca- and tetra-hydro-naphthalene. S. K. MUKERJI (Nature, 1934, **134**, 811—812).—The results of Bonino and Cella (A., 1932, 7) are confirmed, in the main, and additional frequencies are recorded.

L. S. T.

Intensity determinations with Raman lines. K. HABERL (Ann. Physik, 1934, [v], **21**, 285—300).—The variation of the intensity of the Raman lines of cyclohexane with the frequency of the exciting light was determined. Frequencies at 2835, 2920, and 2953 cm.⁻¹ were excited by the light of λ 3132, 3022, 2967, and 2652 Å., the intensities being given by Placzek's formula $I=c(\nu-\Delta\nu)^4/(\nu_0^2-\nu^2)^2$ assuming ultra-violet absorption $\nu_0=53,000$ cm.⁻¹ A. J. M.

Fluorescence of cyclohexane. K. HABERL (Ann. Physik, 1934, [v], **21**, 301—302).—Fluorescence of cyclohexane has been observed. The intensities of the max. vary with temp., but their positions do not.

A. J. M.

Photo-electric photometry of light scattering in fluids. R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1934, **1**, A, 201—211).—Data for C₆H₆, CS₂, PhCl, AcOH, Et₂O, MeOH, and EtOH, obtained by use of a photo-electric cell, are in agreement with previous measurements obtained visually.

J. W. S.

Optical evidence for molecular clustering in fluids. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1934, **1**, A, 211—216).—A method for detection of mol. clusters of magnitude comparable with the wave-length of light is developed, based on the anomalous depolarisation of light scattered by a fluid. Pure AcOH, MeOH, COMe₂, PhCl, *n*-C₇H₁₆, and CH₃·CH·CH₂·OH show no large mol. aggregates, but a mixture of CS₂ and MeOH shows such clusters between the crit. solution temp. (40.5°) and 61.5°.

J. W. S.

Scattering of light by particles suspended in a medium of higher refractive index. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1934, **1**, A, 147—155).—Mathematical. Calculations are made for three sizes of particles such as air bubbles suspended in a medium, and for three different vals. of *n*.

N. M. B.

Fluorescent radiation from nitrous oxide. P. K. SEN-GUPTA (Proc. Roy. Soc., 1934, A, **146**, 824—828).—The β -bands of NO were obtained in fluorescence when N_2O was illuminated by light of suitable wave-length. This indicates that NO, one of the products of photochemical dissociation of N_2O , is excited during the process. L. L. B.

Influence of KI on polarisation of fluorescence of dyes present in solutions. S. M. MITRA (Z. Physik, 1934, **91**, 61—63).—KI steadily increases polarisation of fluorescent light due to fluorescein and rhodamine-B in H_2O , and in H_2O -glycerol and glycerol increases it to a max. A. B. D. C.

Action of sera on the fluorescence of uranine solutions. C. ACHARD, A. BOUTARIC, and J. BOUTCHARD (Compt. rend., 1934, **199**, 903—906).—The addition of various therapeutic and human sera, when fresh, to a dil. solution of uranine in NaCl had no effect on the fluorescence; in the case of sera kept for > 5 days a progressive diminution of fluorescence was found, similar to that caused by catalysts which have a negative effect on oxidation processes. N. M. B.

Fluorescence of some substances containing vitamin-A. J. W. WOODROW and A. R. SCHMIDT (Physical Rev., 1933, [ii], **43**, 379).—Cod-liver oil (I) has a narrow fluorescent band from 530 to 570 m μ and a wider band (II) from approx. 410 to 510 m μ . The intensity of (II) is much reduced for (I) which has lost most of its vitamin-A (III) potency. The same bands, although less intense, are obtained with butter fat. (II) is also obtained with spinach and tomato juice. The fluorescence appears to be connected with either the (III) or the carotene present. L. S. T.

Fluorescence of solutions of chlorophyll-a. H. V. KNORR and V. M. ALBERS (Physical Rev., 1933, [ii], **43**, 379).—The fluorescence of solutions of chlorophyll-a in Et_2O (I), C_6H_6 (II), $COMe_2$ (III), and MeOH at 6°, excited by radiation from Hg arcs, consists of a main band with max. at 6718, 6767, 6720, and 6745 Å. for the respective solvents, and a second band with max. at 6330 Å. for (I), 6358 Å. for (II), and 6392 Å. for (III). L. S. T.

Luminescence from solidified gases and its interpretation. L. VEGARD (Physical Rev., 1933, [ii], **43**, 1060). L. S. T.

Electrostriction of gases. J. JAUMANN and V. STIPA (Z. Physik, 1934, **91**, 685—705).—A compensated microphone is used to measure pressure changes, and to determine electrostriction of O_2 , N_2 , CO_2 , SO_2 , H_2 , He, and A between 1 and 10 atm. The electrostriction of the first four gases increases with increasing pressure more rapidly than the dielectric const. A. B. D. C.

Effect of a small admixture of a foreign gas on the conductivity of a rare gas irradiated by its own resonance radiation. O. S. DUFFENDACK and R. SMITH (Physical Rev., 1933, [ii], **43**, 374).

The effect of impurities on the conductivity (I) produced in Ne and in He at pressures from 1 to 10 mm. by irradiation with their own resonance

radiation (II) has been investigated. Addition of 0.001% of A or Kr increases (I), whilst that of Ne to He decreases it. Metastable atoms which are probably formed indirectly through absorption of (II) may suffer either ionising collisions, increased (I), or dissipative collisions, decreased (I), depending on the ionisation potential of the added foreign gas. L. S. T.

Rectification phenomenon in a pyrolusite crystal. S. R. KHASTGIR and A. K. D. GUPTA (Current Sci., 1934, **3**, 153).—When a pyrolusite crystal (I) is dipped in Hg, a.c. is rectified to a large extent. Current-voltage curves are given. (I) had a large area of contact, so that the effect cannot be attributed to ordinary crystal-and-point rectification. Galena, Fe pyrites, bornite, magnetite, and molybdenite show no such effect. L. S. T.

Ionisation potentials and energies of formation of halogen molecules. J. SAVARD (Compt. rend., 1934, **199**, 939—941).—Ionisation potentials calc. from a relation previously proposed (cf. A., 1934, 11) are in satisfactory agreement, for BrCl, ICl, IBr, F_2 , and HF , with those given by Mulliken (cf. *ibid.*, 1288). N. M. B.

Temperature variation of the photo-effect of pure and impure metal surfaces at low temperatures. R. SUHRMANN and A. SCHALLAMACH (Z. Physik, 1934, **91**, 775—791).—Photo-effect was investigated for Be, Bi, and Ag, and for Ag with K as impurity at room, liquid air, and liquid H_2 temp. The emission potential remains const., and the intensity of emission decreases with fall of temp. in agreement with quantum theory. A. B. D. C.

Effect of gases on photo-electric effect of platinum. E. SCHAAFF (Z. physikal. Chem., 1934, B, **26**, 413—427).—With continued heating, the red limiting wave-length shifts to longer wave-lengths and back again. The effect of heating in H_2 and then in O_2 suggests that H creates the active Pt atoms required for adsorption of O. The effects of other gases have also been examined. R. C.

Effect of temperature on the electrical conductivity of a thin film of CuS. H. DEVAUX and J. CAYREL (Compt. rend., 1934, **199**, 912—914).—When thin films of CuS, obtained by the action of H_2S on the surface of Cu^{II} solutions, are heated to approx. 90° the conductivity increases rapidly to a max. and remains at this val. on cooling. The effect appears to be due to the elimination of gas or H_2O vapour occluded in the film. N. M. B.

Weiss law for Rochelle salt. H. MÜLLER (Physical Rev., 1933, [ii], **43**, 500; cf. A., 1933, 342).— ϵ for the salt has been measured between 23° and 50°; between 34° and 50°, Weiss' law is satisfied. The Curie const. is 128.5 and the dielectric Curie point 24.9°. The calc. Lorenz-Lorentz factor is 2.315. Assuming that the dielectric effect is due to freely rotating mols. of the H_2O of crystallisation this factor must be 2.314. The max. val. of ϵ , viz., 1540, is reached at the ferromagnetic Curie point 23.75°. L. S. T.

Dipole moment and Raman effect of molecules with groups capable of free rotation. S. MIZU-

SHIMA, Y. MORINO, and K. HIGASI (Physikal. Z., 1934, **35**, 905—911).—The limited rotation of the CH_2Cl groups in $\text{C}_2\text{H}_4\text{Cl}_2$ has been investigated quantitatively. An expression for the mean moment at different temp., assuming the Maxwell-Boltzmann distribution, gives vals. in agreement with observation. The val. of the const. β in the expression for the mutual potential energy of the two groups, $U = \beta(1 - \cos \phi)$, where ϕ is the angle of rotation, depends on the solvent. The dipole moments of $\text{C}_2\text{H}_4\text{Br}_2$, $m\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2$, $\text{C}_2\text{H}_4\text{ClBr}$, and $\text{C}_2\text{H}_4\text{I}_2$ in C_6H_{14} , CCl_4 , C_6H_6 , and CS_2 were determined. The mol. polarisation of these substances is the same in each solvent with the exception of C_6H_6 , where it is much smaller, showing that in C_6H_6 solution the probability of deviation from the *trans*-position is unexpectedly great. The intensity of the Raman lines of $\text{C}_2\text{H}_4\text{Cl}_2$ in C_6H_{14} , C_6H_6 , Et_2O , EtOH , and MeOH was also investigated. The smaller is the dielectric const. of the solvent, the greater is the intensity ratio (I) of the two Raman lines 752 and 653 cm^{-1} . The C_6H_6 solution is again an exception. (I) increases with increasing no. of mols. in the *trans*-position. A. J. M.

Vector analysis of dipole moments. F. R. Goss (J.C.S., 1934, 1467).—The validity of the vector analysis has been examined by calculating the moments of CHCl_3 and CH_2Cl_2 from the valency angles on the assumption that the moment due to the C-Cl linking is const.; the vals. obtained are identical with those calc. from polarisation data. H. F. G.

Determination of dipole moments in solution. F. FAIRBROTHER (J.C.S., 1934, 1846—1849; cf. A., 1934, 1156).—Calculation of the equations to the graphs of P_2 against $(\epsilon - 1)/(\epsilon - 2)$ by the method of least squares gives an average val. for μ of PhNO_2 in decane and *p*-xylene of 4.24×10^{-18} e.s.u. The slopes of the curves very nearly $\propto 1/\text{abs. temp.}$ A. J. M.

Dipole moment of chloromethyl ether. M. A. G. RAU and N. NARAYANASWAMY (Proc. Indian Acad. Sci., 1934, **1**, A, 217—223).—The electric moment of $(\text{CH}_2\text{Cl})_2\text{O}$ is 1.88 and 1.82— 1.85×10^{-18} e.s.u. in CCl_4 and C_6H_6 solutions, respectively. This indicates that either the CH_2Cl group possesses free rotation, or there is an equilibrium between the *cis*- and *trans*-forms of the mol. J. W. S.

A. Association of nitrobenzene in solutions and its dipole moment. B. Dielectric constant of nitrobenzene and its moisture. A. PIEKARA. C. Temperature dependence of the dielectric constant of nitrobenzene. A. PIEKARA and J. MAZUR (Acta phys. polon., 1932, **1**, 393—399, 405—409, 401—404; Chem. Zentr., 1934, ii, 401).—A. The Debye equation is valid for the temp. variation of the polarisation of PhNO_2 in C_6H_{14} solution. The electric moment is 4.0×10^{-18} . The measurements disagree with the assumption of two-fold association.

B. Vals. for wet and dry PhNO_2 are recorded. No anomaly was found at 9.6°.

C. Vals. between 8° and 11° show no discontinuity at 9.6°. H. J. E.

Dipole moment of *s*-trinitrobenzene. G. BRIEGLER and J. KAMBEITZ (Z. physikal. Chem., 1934, **B**, **27**, 11—14).—New determinations and a review of previous determinations indicate that the moment is very small, but fail to decide whether it is finite or not. R. C.

Influence of a magnetic field on the dielectric constant of liquids. A. PIEKARA and M. SCHÉRER (Compt. rend., 1934, **199**, 840—843).—At $\lambda = 600$ m., ϵ for C_6H_{14} , cyclohexane, PhMe , C_6H_6 , CCl_4 , CS_2 , quinoline, and PhNO_2 is increased by a magnetic field of 51,000 gauss parallel to the electric field, the effect being greatest for PhNO_2 and least for C_6H_{14} ($\Delta\epsilon = 250$ and 1.4, each $\times 10^{-3}$, respectively). The effect decreases rapidly with decreasing intensity of the magnetic field; it is undetectable below 25,000 gauss. As the effect is about 1000 times that predicted by theory for gases, it is suggested that under an intense magnetic field the frequency of oscillation of the mols. may approach that of the electric field. J. W. S.

Dielectric behaviour of germanium tetrachloride. J. G. MILLER (J. Amer. Chem. Soc., 1934, **56**, 2360—2362).—Measurements with pure GeCl_4 and with solutions in CCl_4 show a zero moment, suggesting a symmetrical tetragonal structure for the mol. E. S. H.

Determination of dielectric constants of aqueous solutions of electrolytes at high frequency. M. ROVER (Ann. Physik, 1934, [v], **21**, 320—344).—The results of the determination of the dielectric consts. of dil. aq. solutions of CuSO_4 and MgSO_4 at high frequency agree with the theory of Debye and Falkenhagen over the range for which this may be expected to hold. A. J. M.

Electrolytic solutions. XIV. Dielectric constant of solutions of electrolytes in benzene. G. S. HOOPER and C. A. KRAUS (J. Amer. Chem. Soc., 1934, **56**, 2265—2268; A., 1934, 1176).—Results are recorded for solutions of tetra- and tri-isoamylammonium picrate, tetraisoamylammonium bromide, and AgClO_4 , chiefly between 10^{-4} and $10^{-3}N$. The limiting mol. polarisation of these compounds is about 10 times that of ordinary polar mols., 2400—2700 c.c. The mol. polarisation decreases rapidly with increasing concn. for salts with two electrically symmetrical ions and slowly for salts with unsymmetrical ions. E. S. H.

Refraction and dispersion of gases and vapours. VIII. Molecular refraction of argon, krypton, and xenon. G. DAMKÖHLER (Z. physikal. Chem., 1934, **B**, **27**, 130—144; cf. A., 1934, 348).—The mol. refraction for 5461 and 6563 Å. has been determined with a precision of 0.07%, the results for A alone agreeing well with those of Cuthbertson (A., 1910, ii, 561). The max. error attributable to impurities in the gases was $\pm 0.02\%$. The metal double chamber of the Haber-Loewe interferometer sorbs and desorbs appreciable quantities of gas. R. C.

Refractive index and dispersion of normal and heavy water. L. W. TILTON and J. K. TAYLOR (J. Res. Nat. Bur. Stand., 1934, **13**, 207—209).—

Vals. of n at 25° for H_2O of d 1.001376, at 10 wavelengths, are recorded and compared with those of other observers. The additive law appears to be applicable to mixtures of H_2O and H_2O . H. F. G.

Index of refraction of carbon dioxide as a function of the density. F. L. BROWN (Physical Rev., 1933, [ii], 43, 373).—When plotted against d the inverse of the Lorenz-Lorentz function $(\mu_2 - 1)/[(\mu_2^2 + 2)p]$ shows a marked increase at the higher vals. of d . Data for $d > 0.8$ g. per c.c. and $\mu > 1.19$ have been obtained. L. S. T.

Optical activity of camphor in alcoholic solutions. C. F. POE and E. M. PLEIN (J. Physical Chem., 1934, 38, 883—887).—Sp. rotations of camphor (I) in aq. EtOH have been determined. Curves showing the relation between $[(I)]$, $[\text{EtOH}]$, and $[\alpha]$ are given. F. L. U.

Rotatory power of quartz for rays perpendicular to the axis and its dispersion in the ultra-violet. G. BRUHAT and P. GRIVET (Compt. rend., 1934, 199, 1034—1036).—It is confirmed that the ellipticity of the privileged vibrations in a sheet of α -quartz cut parallel to the optical axis varies from $14/2'$ for 5893 Å. to $38/2'$ for 2537 Å. (cf. A., 1934, 1160). J. W. S.

Rotations of the nitrophenyl esters of disubstituted acetic and propionic acids and of the corresponding free acids. P. A. LEVENE, A. ROTHEN, and G. M. MEYER (J. Biol. Chem., 1934, 107, 555—565).—The rotatory dispersion curves, in the homogeneous state (I) and in heptane solution (II), of the *p*-nitrophenyl esters of α -methyl-*n*-butyric, b.p. $137^\circ/0.1$ mm., -valeric, b.p. $130^\circ/0.01$ mm., -hexoic, b.p. $138^\circ/0.01$ mm., and of β -methyl-valeric, -hexoic, b.p. 138 — $140^\circ/0.02$ mm., -heptic, b.p. $152^\circ/0.01$ mm., and -octoic acid, b.p. $160^\circ/0.1$ mm., are tabulated and analysed to determine the partial rotation of the $\text{C}_6\text{H}_4\text{NO}_2$. In the series $\text{CHRMc}\cdot\text{CO}_2\text{H}$, and in $\text{CHRMc}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III) in (I), esterification causes a shift in rotation to the left. In (II) the considerable shift to the left observed with the first member of (III) diminishes successively to zero in the third member, and then changes direction in the fourth and all higher members of the series, and an explanation based on the relative predominance of the first and second partial rotations is elaborated. Hence in two configuratively related substances the two partial rotations of which are of opposite sign, identical substitution may effect shifts of rotation in different directions. J. W. B.

Walden inversion. XVIII. Analysis of rotatory dispersion curves of α -substituted *n*-carboxylic acids. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1934, 107, 533—553).—The ultra-violet absorption curves and the rotatory dispersions of *d*-CHMeI $\cdot\text{CO}_2\text{H}$ (I), *d*-CHMeBr $\cdot\text{CO}_2\text{H}$ (II), *d*- α -bromo-*n*-hexoic (III), *d*-lactic (IV), and *l*- α -methoxypropionic acid (V), and of their Na salts, and the Et esters of (IV) and (V), are recorded. In (I), (II), and (III), and the Na salt of (I), the first contribution is the dextrorotation of the halogen, (I) being configuratively related to (IV) and to *l*-

α -azidopropionic acid. All the acids show normal dispersion, represented by a two-term Drude equation in which the dispersion const. λ_0 of the first term corresponds with the head of the absorption band. J. W. B.

Magnetic birefringence and the critical dissolution point. A. PIEKARA (J. Phys. Radium, 1934, [vii], 5, 541—544).—The temp. coeff. of magnetic birefringence of solutions of PhNO_2 in hexane and in CCl_4 increases with concn. to an abnormal val. in the neighbourhood of the dissolution point. N. M. B.

Magnetochemical properties of samarium. P. W. SELWOOD (J. Amer. Chem. Soc., 1934, 56, 2392—2394).—The following sp. magnetic susceptibilities have been determined: Sm_2O_3 5.60×10^{-6} , SmBr_3 2.49×10^{-6} , $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 2.34×10^{-6} . Sm^{++} has a definite existence and its susceptibility and electronic configuration are identical with those of Eu^{++} . E. S. H.

Magnetic susceptibilities of the anhydrous and hydrated sulphates and double sulphates of the magnetic metals: increased susceptibility produced by heating cobalt salts. E. F. HERROUN (Proc. Physical Soc., 1934, 46, 872—881).—When K_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ is substituted for H_2O of constitution in the sulphates of Fe, Co, and Ni, susceptibility of the active constituent and of the mol. increase and so persist in the fully hydrated double salts. A similar but smaller effect is found for the sulphates of Mn and Cr, but for CuSO_4 a decrease is observed. CoCl_2 , CoSO_4 , $\text{Co}_3(\text{PO}_4)_2$, and $\text{Co}_2\text{P}_2\text{O}_7$ show increased susceptibility after heating. N. M. B.

Magnetic properties of organic vapours. S. R. RAO and P. S. VARADACHARI (Nature, 1934, 134, 812).—A discussion. L. S. T.

Diamagnetic susceptibilities and polarisabilities of ions. G. W. BRINDLEY (Physical Rev., 1933, [ii], 43, 1030—1031).—Agreement between calc. and experimental vals. for the g.-at. susceptibility indicates that the Kirkwood-Vinti equation connecting diamagnetic susceptibilities and ionic refractivities is valid. Calc. vals. for the polarisability of the inert gases and of certain ions are also compared with experimental vals. L. S. T.

Paramagnetic properties of cerous salts in solution. C. HAENNY and G. DUPOUY (Compt. rend., 1934, 199, 843—845).—Aq. solutions of $\text{Ce}(\text{NO}_3)_3$, CeCl_3 , and $\text{Ce}(\text{OAc})_3$, and EtOH solutions of $\text{Ce}(\text{NO}_3)_3$ obey the Curie-Weiss law. The magnetic moment of the Ce^{+++} ion, calc. from the magnetic susceptibilities of these solutions, is 2.49 Bohr magnetons, in agreement with theory. J. W. S.

Properties of Rochelle salt. H. MULLER (Physical Rev., 1933, [ii], 44, 854—855).—The dielectric, optical, electro-optical, and pyroelectric properties of Na K tartrate from -50° to 50° , which are summarised, can be explained by a generalisation of Weiss' theory of ferromagnetism. L. S. T.

Molecular structure of ozone. W. S. BENEDICT (Physical Rev., 1933, [ii], 43, 580—581).—A discussion. Further confirmation of the obtuse-angled

structure is given. Approx. mol. dimensions are apex half-angle 61° and O-O distance 1.29 \AA .

L. S. T.

Even and odd co-ordination numbers. R. C. MENZIES (J.C.S., 1934, 1755—1758).—The stability of compounds of Os, Pt, Au, and Pb with effective at. nos. (I) in the neighbourhood of 86 was investigated with reference to their co-ordination nos. (II). Stability depends not only on the attainment of 86 for (I), but also on the occurrence of an even (II). Pb diacetylacetone, having (I)=88 and (II)=4, has been prepared, but is readily hydrolysed. Pb Et₃ acetylacetone, having (I)=88 and (II)=5, could not be obtained.

A. J. M.

Electroaffinity scale, with data on valency states and on valency ionisation potentials and electron affinities. R. S. MULLIKEN (J. Chem. Physics, 1934, 2, 782—793).—Theoretical. A new "abs." scale is put forward, in which electroaffinity = average of ionisation potential and electron affinity, calc. for suitable valency states of the positive and negative ion. Tables of these quantities are given.

F. L. U.

Comparative chemistry. VI. Oxides. I. N. LONGINESCU (Bul. Chim. Soc. Romane, 1933, 36, 25—31).—Theoretical. More oxides of types MO, M₂O₃, and MO₂ exist than can be forecast from the periodic system, whilst M₂O₅ and MO₃ types are about as numerous as can be forecast.

T. W. P.

Transfer of vibrational energy between molecules. H. O. KNESER (Physical Rev., 1933, [ii], 43, 1051).

L. S. T.

Brownian movement of an ellipsoid. I. Dielectric dispersion for ellipsoidal molecules. F. PERIN (J. Phys. Radium, 1934, [vii], 5, 497—511).—Mathematical.

N. M. B.

Wave-mechanical treatment of the Li₂ molecule. H. M. JAMES (J. Chem. Physics, 1934, 2, 794—810).—Mathematical.

F. L. U.

Chemical forces in the light of quantum mechanics. H. HELLMANN and W. JOST (Z. Elektrochem., 1934, 40, 806—814).—Theoretical.

E. S. H.

Rotation of diatomic molecules. H. CASIMIR (Physica, 1934, 1, 1073—1076).—The moments of inertia of a diat. mol. are calc. by adding the masses of the closed electron shells to the masses of the corresponding nuclei.

M. S. B.

Potential energy of diatomic molecules. N. ROSEN (Physical Rev., 1933, [ii], 43, 671; cf. A., 1933, 206).

L. S. T.

Mathematical analysis of the single and double six-ring. P. C. HENRIQUEZ (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 532—547).—Mathematical. A method, based on a const. angle between the directions of the valencies of each C atom, and the absence of "strain," gives the configuration of the "fixed" (chair) form of the C₆ ring and the characterising magnitudes of the infinite no. of positions of the "mobile" form. The possible "strainless" configurations of the C₁₀H₈ ring system are deduced.

J. G. A. G.

Normal vibrations of molecules having octahedral symmetry. N. S. N. NATH (Proc. Indian Acad. Sci., 1934, 1, A, 250—259).—The theory developed is in agreement with experimental data for SF₆.

J. W. S.

Intramolecular rotation in organic compounds. M. A. G. RAU (Current Sci., 1934, 3, 145—150).—A review.

Probability of multiple processes of very high energies. W. HEITLER and L. NORDHEIM (Physica, 1934, 1, 1059—1072).—Theoretical.

M. S. B.

Approximations involved in calculations of atomic interaction and activation energies. A. S. COOLIDGE and H. M. JAMES (J. Chem. Physics, 1934, 2, 811—817).—Mathematical. Any modification of the complete Heitler-London treatment may lead to errors comparable in magnitude with the quantity to be computed.

F. L. U.

Interaction of electronic and nuclear motion for linear triatomic molecules. R. RENNER (Z. Physik, 1934, 92, 172—193).—Theoretical.

A. B. D. C.

Influence of inner shells on atomic interactions. H. M. JAMES (Physical Rev., 1933, [ii], 43, 589; cf. A., 1932, 1).—The inner shells of Li₂ appear to be responsible for a repulsion between the atoms which is of importance in comparison with the total energy of binding. The effect of neglecting these inner shells in computations on the alkali mols. is discussed.

L. S. T.

Surface tensions of ethyl alcohol and carbon disulphide at low temperatures. T. TONOMURA and (Miss) K. ISHIHARA (Bull. Chem. Soc. Japan, 1934, 9, 439—441).—Employing the method of capillary rise EtOH has been examined from -93° to 30° and CS₂ from -42.4° to 20° . For EtOH $\sigma(M/D)^{2/3} = 703.09 - 1.3901T + 0.0004318T^2$ and for CS₂ it is $2.0007(\tau - 9.28)$, where τ is temp. measured from crit. temp.

W. R. A.

Parachors of polycyclic compounds. D. N. KURSANOV (J. Gen. Chem. Russ., 1934, 4, 598—602).—Mumford and Phillips' view that a simple relationship exists between intramol. strain (I) and parachor variations (A., 1929, 1219) is not sustained by the vals. found for the parachors (P) of fenchane, cyclofenchene, carane, *d*-pinene, *cis*- and *trans*-decahydronaphthalene, and dicyclopentyl; in spite of considerable variations in (I) in this group, the experimentally determined P agree within 1% with the vals. calc. on the basis of Mumford's constns.

R. T.

Density and molecular structure of a pure normal liquid. R. LAUTIE (Compt. rend., 1934, 199, 932—934).—Mathematical. Calculations are derived from the MacLeod-Sugden and Eötvös-Ramsay-Shields formulæ.

N. M. B.

Application of Valouch's method of measuring the constants of crystal lattices to the precision method of Kunzl and Koppel. F. BOUCHAL and V. DOLEJSEK (Compt. rend., 1934, 199, 1054—1056; cf. A., 1933, 450).—The lattice const. of quartz, determined by measurement of the difference between the

angles of reflexion of the same order for two different X-ray lines, is in good agreement with previous vals.

J. W. S.

Theory of linear crystallisation velocity. R. KAISCHEV and I. N. STRANSKI (Z. physikal. Chem., 1934, **170**, 295—299).—Proceeding on the same lines as before (A., 1934, 946) an expression for the rate of linear crystallisation has been derived which differs from that of Volmer and Marder (A., 1931, 672) only in containing a factor $1/\Delta T^2$, where ΔT is the supercooling. It is compared with existing experimental data.

R. C.

Potassium models. Spatial representation of the saturation relations of potassium salts. E. JANECKE (Z. Elektrochem., 1934, **40**, 735—743).—A lecture.

E. S. H.

Inner equilibrium in solid phases. II. A. SMITS (Physikal. Z., 1934, **35**, 914—918).—The conclusion of Clusius and Perlick (A., 1934, 354) that the phase change in solid CH_4 at -252.8° is one of the second kind, as defined by Ehrenfest (A., 1933, 569), is probably incorrect. For accurate results it is necessary to use very pure substances. Comparison is made with the NH_4Cl system (*ibid.*, 1119).

A. J. M.

Inner equilibrium in solid phases. K. CLUSIUS and A. PERLICK (Physikal. Z., 1934, **35**, 918—919).—A reply to Smits (cf. preceding abstract). The effect noted was not due to impurities, and cannot be regarded as a phase change of the first order.

A. J. M.

[**Inner equilibrium in solid phases.**] A. SMITS (Physikal. Z., 1934, **35**, 919).—A reply to Clusius and Perlick (cf. preceding abstract).

A. J. M.

Intensities of X-ray spectra and the imperfections of crystals. R. W. JAMES (Z. Krist., 1934, **89**, 295—309).—A review of experimental facts about the angular range of reflexion of X-rays by existing crystals, and of ways of calculating the extinction which applies to the observed intensities.

B. W. R.

Intensities of X-ray reflexions from powders. G. W. BRINDLEY and F. W. SPIERS (Proc. Physical Soc., 1934, **46**, 841—852).—An improved and accurate method of photographic determination, by measuring the intensities of X-ray reflexions from a plane stationary layer of powder, is described. It is illustrated by comparison of reflexions of widely different intensity of $\text{Cu } K\alpha$ radiation from Cu powder, by comparison of intensities for $\text{Cu } K\alpha$ from $\text{KCl (420)} + \text{KCl (422)} + \text{Cu (220)}$, and by the accuracy for large-angle reflexions from Al powder.

N. M. B.

Atom scattering factor of beryllium. W. EHRENBERG (Z. Krist., 1934, **89**, 185—189).—The abs. intensities of X-ray reflexion are measured for Be powder and compared with Hartree curves for Be and Be^{++} . Better agreement is obtained with the former.

B. W. R.

Effect of temperature on the reflexion of X-rays from bismuth crystals. A. GOETZ and R. B. JACOBS (Physical Rev., 1933, [ii], **43**, 213).—The Debye-Waller relation for the temp. effect does not hold.

L. S. T.

Change in the width of X-ray interference lines of palladium when charged with hydrogen elec-

trolytically. E. NAHRING (Ann. Physik, 1934, [v], **21**, 303—319).—There is a widening of the X-ray interference lines of Pd with the absorption of H_2 , the Pd being made an electrode in an electrolysis apparatus. The cubic symmetry of the Pd lattice changes as the H_2 is absorbed.

A. J. M.

Broadening of X-ray lines of cold-worked aluminium. L. THOMASSEN and J. E. WILSON (Physical Rev., 1933, [ii], **43**, 763).—Broadening with Al cold-worked at -75° , but not at room temp., is indicated (cf. A., 1928, 693).

L. S. T.

Inner absorption in crystals of salts. D. BALAREV (Z. Krist., 1934, **89**, 268—281).—A summary chiefly of the author's work (cf. A., 1933, 364, 563), showing that impurities in a crystal are in general closely related to its mosaic structure. Real crystals are pictured as a "growth-conglomerate" and it is argued that thermodynamic equilibrium in the crystal state implies a macro-structure.

B. W. R.

Lineage structure of crystals. M. J. BUEGER (Z. Krist., 1934, **89**, 195—220).—"Lineages" indicate the filled-in dendritic structures which are supposed to occupy the interior of most crystals. These are exhibited optically with many examples, chosen from both single and poly-crystals. On the basis of the lineage structure the "mosaic" ideas of other authors (e.g., Adams, Coker, Straumanis) are developed, and X-ray extinction, electrical conductivity, gas absorption, plasticity, gliding, and Goetz' m.-p. phenomena are discussed.

B. W. R.

Mosaic structures of crystals. H. E. BUCKLEY (Z. Krist., 1934, **89**, 221—241).—A detailed summary of existing theories of the internal macrostructure of crystals. The theories of Smekal and Zwicky are reviewed, with the conclusion that the ideas of neither have a trustworthy experimental basis. The facts of X-ray extinction and reflexion width are undisputed, and indicate a mosaic of the Darwin type. Serious difficulties against such a mosaic are summarised as follows: passage of H_2O through crystals, existence of extremely thin crystals, etch figures, difficulty of understanding the formation of the mosaic interior, and the high surface perfection and optical homogeneity of existing crystals.

B. W. R.

Non-existence of a regular secondary structure in crystals. M. J. BUEGER (Z. Krist., 1934, **89**, 242—267).—A criticism of the ideas of Zwicky and his co-workers. In particular the work of Goetz is examined; the markings seen by him on a Bi surface are ascribed to gliding striae. His evidence for "block phase" in liquids near the m.p. is otherwise explained, and the alleged difference between the optical and X-ray expansion coeffs. of Bi is attributed to impurities. The various weaknesses of crystals are not accounted for by a secondary structure, and the experimental facts have been misinterpreted. Zwicky's argument based on the tendency of individual crystal planes to contract is shown to be fallacious.

B. W. R.

Transformations in homogeneous substances. G. TAMMANN (Z. physikal. Chem., 1934, **170**, 380—390).—Transformations in cryst. solids are of two

main types, according as the properties vary normally with the temp., T , above and below the transition temp., τ , and at τ change discontinuously owing to appearance of a second cryst. species, or as no recrystallisation occurs and the properties vary abnormally, but continuously, over a certain T range. Which type occurs depends on whether or not the changes occurring in the atom or mol. so alter the fields of force of the mols. that the original lattice ceases to be stable. Ehrenfest's views on phase change (A., 1933, 569) are criticised. R. C.

Universal significance of cubic face-centred lattice structure for the causal comprehension of hitherto unknown relations. R. REINICKE (Z. physikal. Chem., 1934, B, 27, 28—36).—The fitting together of equal cubes, edge to edge, necessarily leads to a face-centred arrangement of their centres of gravity, which are to be identified with the at. positions. If the NaCl lattice is regarded, not as a manifestation of a certain grouping of masses, but as the most symmetrical distribution of opposite charges, then, since many metals, as well as most of the inert gases, have a cubic face-centred lattice, it may be assumed that the metal atoms release their valency electrons and the latter occupy the positions occupied in the NaCl lattice by Cl'. The consequences of this conception are examined. R. C.

Review of new structure determinations of compounds of the type AB_3 . W. NOWACKI (Z. Krist., 1934, 89, 85—88).—A condensed account of further data since the author's previous review (cf. A., 1932, 796). B. W. R.

X-Ray study of the effect of heat on the structure of sputtered films of gold. S. R. SWAMY (Proc. Physical Soc., 1934, 46, 739—744).—Debye-Scherrer photographs of sputtered Au films of various thicknesses heated at stages in the range 200—900° showed that, on heating, the crystals grew, and oriented with their (111) planes parallel to the surface of deposition. Degree of orientation and crystal size depended on both film thickness and temp. N. M. B.

X-Ray investigation of the disperse structure of different kinds of graphite. V. S. VESSELOVSKI and K. V. VASSILIEV (Z. Krist., 1934, 89, 156—174).—A systematic treatment of disperse structures is suggested, a disperse structure being regarded as the sum of a large no. of separate elementary bodies. It is illustrated by a survey of different forms of C from single-crystal graphite to soots and anthracites. Particular attention is given to the size and orientation of particles. B. W. R.

Unit cell of uranium calculated from X-ray powder method data. T. A. WILSON (Physical Rev., 1933, [ii], 43, 781—782).—The unit cell has equal face perpendiculars of 2.535 Å. arranged in space at angles of 64°, 67° 45', 67° 45', respectively. The vol. is 20.26 Å.³, giving U an X-ray d of 19.32 compared with a previous val. of 18.68. L. S. T.

Lattice structure of beryllium carbide, Be_2C . J. VON STACKELBERG and F. QUATRAM (Z. physikal. Chem., 1934, B, 27, 50—52).— Be_2C has an antiferroite

lattice, with a 4.33 Å., d 2.44. The distance Be—C is 1.87 and the distance C—C 3.06 Å. R. C.

Crystal structure of aluminium carbide, Al_4C_3 . M. VON STACKELBERG and E. SCHNORRENBERG (Z. physikal. Chem., 1934, B, 27, 37—49).— Al_4C_3 has the space-group D_{3d}^2 and a layer-lattice, each layer consisting of four Al atom planes with three interposed C atom planes. R. C.

Structure of aluminium carbide, Al_4C_3 . M. VON STACKELBERG (Fortschr. Min., 1933, 18, 35—36; Chem. Zentr., 1934, i, 2713—2714).— Al_4C_3 has two modifications. The β -form (probably hexagonal-holohedral; a 3.27, c 21.6 Å.; 2.5 mols. in unit cell) is formed from the elements at approx. 1600°. The α -form (rhombohedral; a 3.32, c 24.9 Å.; 1 mol. in unit cell; space-group D_{3h}^2) is produced at $> 1600^\circ$. H. J. E.

Powder diagram of a new iron carbide. G. HAGG (Z. Krist., 1934, 89, 92—94).—Prolonged treatment of Fe or Fe_2O_3 by CO at low temp. (225°) seems to produce a new carbide Fe_2C . The prep. gives powder lines hitherto unknown, which are listed but not analysed. B. W. R.

Structural principles of carbides, silicides, nitrides, and phosphides of electropositive metals. M. VON STACKELBERG (Z. physikal. Chem., 1934, B, 27, 53—57).—The lattices of these compounds are ionic and the anions form a lattice of closest-packed spheres in the tetrahedral or octahedral interstices of which are the cations. Such a lattice is possible only if the no. or size of the cations is not such as to break up the anion lattice. R. C.

Redetermination of parameter for hauerite, MnS_2 . F. OFFNER (Z. Krist., 1934, 89, 182—184).—The unexpectedly large Mn—S distance in this compound (cf. A., 1934, 350) was confirmed by an accurate X-ray measurement. B. W. R.

Crystal structure of tetradymite, Bi_2Te_2S . D. HARKER (Z. Krist., 1934, 89, 175—181).—The cell is rhombohedral, a_0 10.31 Å., α 24° 10'. From intensity calculations the structure is found to be essentially metallic, adjacent layers containing one kind of atom only in the order S Bi Te Te Bi S Bi etc., forming a cubic close-packed lattice if the identity of the atoms be disregarded. B. W. R.

Orientation of crystallites in the ignition products of $Mg(OH)_2$ and $Ca(OH)_2$. C. D. WEST (Amer. Mineral., 1934, 19, 281—283).—From X-ray measurements, the CaO crystallites are oriented only along a 3-fold axis, whilst MgO crystallites are oriented on both 2- and 3-fold axes. An ignited Fe-brucite fibre contains magnesioferite with an orientation similar to that of MgO . CH. ABS. (e)

Crystal structure of tetramethylammonium silicofluoride. R. B. COREY (Z. Krist., 1934, 89, 10—17).— $(NMe_4)_2SiF_6$ has a tetragonal cell containing 2 mols., a_0 7.88, c_0 11.19 Å., space-group C_{4h}^2 . At. parameters were determined from intensity measurements on artificially shaped crystals. B. W. R.

Crystal structure of sodium uranyl acetate. I. FANKUCHEN (Physical Rev., 1933, [ii], 43, 1048).—Powder photographs show that Na U acetate is cubic,

a 10.69 Å., 4 mols. in unit cell. Rotation and oscillation photographs confirm the space-group T^1 (cf. A., 1930, 1351). The structure is similar to that of NaClO_3 with the UO_2 corresponding with Cl and the OAc with the O. L. S. T.

Crystallographic investigation of carhamide phosphate. C. MATIGNON and M. DODE (Bull. Soc. franç. Mineral., 1934, 56, 351—357; Chem. Zentr., 1934, ii, 426).—The crystals are orthorhombic ($a:b:c=0.831:1:0.981$). From solutions rich in $\text{CO}(\text{NH}_2)_2$ tables separate, whilst with excess of H_3PO_4 small orthorhombic octahedra form. The neutral salt could not be isolated. Solubility data are recorded. H. J. E.

X-Ray study of the crystal structure of Rochelle salt and the effect of temperature. B. E. WARREN and H. M. KRUTTER (Physical Rev., 1933, [ii], 43, 500).—Oscillation and rotation patterns give an orthorhombic unit cell containing 4 mols. of $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ with a 11.85, b 14.25, c 6.21 Å.; space-group V^3 . ϵ is unusually large between 20° and -20° . Integrated intensities measured at -50° and 25° showed for -50° only the normal increase to be expected from the usual Debye temp. factor. L. S. T.

Electron diffraction investigation of non-metallic halides. P. O. BROCKWAY and F. T. WALL (J. Amer. Chem. Soc., 1934, 56, 2373—2379).—The mol. structures of CCl_4 , SiCl_4 , SnCl_4 , CF_4 , SiF_4 , PCl_3 , AsCl_3 , PF_3 , and AsF_3 have been investigated. Deviations from additivity of the covalent radii are discussed in relation to ionic character of the linkings and the formation of double electron pair linkings. E. S. H.

X-Ray patterns of crystalline urease and pepsin. I. FANKUCHEN (J. Amer. Chem. Soc., 1934, 56, 2398).—The results show that probably neither compound contains straight chains of NH_2 -acid residues. E. S. H.

X-Ray diffraction patterns of cellulose particles and interpretation of cellulose diffraction data. W. K. FARR and W. A. SISSON (Contr. Boyce Thompson Inst., 1934, 6, 315—321).—Diffraction phenomena hitherto explained by the supposed existence of a micellar structure may be accounted for by the visible particles of cellulose occurring as units in young fibres and subsequently united by non-cellulose cementing substances to form fibrils. In the latter the individual particles cannot be observed. A. G. P.

X-Ray diffraction of liquid films. K. LARK-HOROVITZ and E. P. MILLER (Physical Rev., 1933, [ii], 43, 1060).—Diffraction patterns of very thin films of glycerol, paraffin oil fractions, and commercial mineral oil obtained at different temp. are described. Even at liquid air temp. the structure of the glycerol film remains quasi-liquid and shows no sign of orientation or crystal formation. L. S. T.

Conditions and limits of correct electron projection of images. Electron paths in the cylindrical electrical field of a coarse crystalline glowing wire. H. SEEMANN (Z. Physik, 1934, 92, 253—273). A. B. D. C.

Electron photographs of graphite. G. AMINOFF and B. BROOME (Z. Krist., 1934, 89, 80—85).—Two types of photograph may be obtained, the one analogous to the usual X-ray rotation photograph, the other showing straight bands (Kikuchi lines). Interpretation on the basis of the reciprocal lattice agrees with accepted X-ray data for graphite. B. W. R.

Diffraction of electrons by single molecules. L. R. MAXWELL, M. E. JEFFERSON, and V. M. MOSLEY (Physical Rev., 1933, [ii], 43, 777; cf. A., 1934, 17).—Diffraction rings for CCl_4 vapour give vals. corresponding with 2.98 Å. for the Cl-Cl distance. L. S. T.

Diffraction of electrons by oxide films on molten metals. J. A. DARBYSHIRE and E. R. COOPER (Trans. Faraday Soc., 1934, 30, 1038—1048).—Oxide films removed from the surface of Cd, Mg, Al, Bi, and 1% Mg-99% Sb (I) have been investigated. The data are consistent with the configurations deduced from X-ray studies, but discrepancies between the calc. and observed intensity ratios and anomalies indicate the inadequacy of the present optical theory of electron diffraction. The Al_2O_3 was in the face-centred cubic γ -form with a 7.78 Å., which is < earlier vals. Bi_2O_3 was, in general, in a body-centred tetragonal form with a 10.85 and c 11.28 Å. (I) afforded films of oriented MgO, whilst in the other films examined orientation was generally small. J. G. A. G.

New electron diffraction rings in zinc oxide and their interpretation. K. LARK-HOROVITZ and H. J. YEARIAN (Physical Rev., 1933, [ii], 43, 376—377).—The diffraction of ZnO powder deposited from an electric arc between Zn electrodes has been investigated with 6- to 20-kv. electrons. Besides the ordinary rings, rings of smaller intensity, interpreted by an inner potential of 4 volts for ZnO, occur. L. S. T.

X-Ray investigation of the mode of vibration of piezo-electric quartz plates. S. NISHIKAWA, Y. SAKISAKA, and I. SUMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 20—30). R. S. B.

Change of resistance of cobalt in longitudinal magnetic fields. M. S. ALAM (Current Sci., 1934, 3, 155—156).—Contrary to McCorkle (Physical Rev., 1923, [ii], 22, 271) the resistance of Co increases to a saturation val. at 1200—1300 gauss in longitudinal fields. Hysteresis also occurs. L. S. T.

Magnetic study of the metallic state and the Fermi-Dirac statistics. S. FREED and H. G. THODE (Nature, 1934, 134, 774—775).—Preliminary measurements of the at. susceptibility of Na in liquid NH_3 are recorded. L. S. T.

Longitudinal and transverse magneto-resistance and magnetic structure of ferromagnetic materials. G. ALOCCO (Atti R. Ist. Veneto Sci., 1932—1933, 92, 1353—1371; Chem. Zentr., 1934, i, 3446).—Polycryst. sheet Ni resembles single Ni crystals in its magneto-resistance. The elementary moments are oriented. H. J. E.

Magnetisation function for ferromagnetic substances applicable to all temperatures. H. LUDLOFF (Z. Physik, 1934, 91, 742—764).—Theoretical.

A. B. D. C.

Ferromagnetism of the iron-nickel alloys under hydrostatic pressure. R. L. STEINBERGER (Physical Rev., 1933, [ii], 43, 502).—The application of pressure causes a relatively large change, usually diminution, in flux density, and an incomplete recovery when pressure is released. In pure Fe, 20 and 80% Ni, the change is negative and linear. Pure Ni and 40, 50, and 90% Ni alloys show varying amounts of pressure hysteresis. In the 30 and 60% Ni alloys the rate of change of flux decreases with increasing pressure, and in the former the alloy becomes non-magnetic under pressure.

L. S. T.

Paramagnetism of metallic rhenium. N. PERAKIS, L. KAPATOS, and P. KYRIAKIDIS (Praktika, 1933, 8, 163—168; Chem. Zentr., 1934, ii, 404).—From measurement between -79° and 20° a val. of $\chi = 68.7 \times 10^{-6}$ was found.

H. J. E.

Magnetism of tin. S. R. RAO (Proc. Indian Acad. Sci., 1934, 1, A, 123—142; cf. A., 1934, 1061).—The susceptibility of white Sn *en masse* is 0.360 and is const. up to 220° ; at the m.p. (233°) it decreases rapidly to -0.0455 , and regains the val. 0.360 on cooling to 30° . Pure colloidal white Sn, after settling in ProH and centrifuging, becomes diamagnetic, this diamagnetism increasing at smaller particle sizes. On melting and recrystallising, paramagnetism is regained. The at. susceptibility of grey Sn is approx. -41.54×10^{-6} .

N. M. B.

Vectorial properties of ferromagnetic substances and the magnetic structure of polycrystalline materials. A. DRIGO (Atti R. Ist. Veneto Sci., 1932—1933, 92, 1373—1386; Chem. Zentr., 1934, i, 3446—3447).

H. J. E.

Permeability of iron at ultra-radio frequencies. W. ARKADIEV (Physical Rev., 1933, [ii], 43, 671—672).—The vals. obtained by other investigators (A., 1933, 117) are compared with those of the author.

L. S. T.

Theory of magnetostriction. T. HAYASI (Z. Physik, 1934, 91, 818—819).—A correction (cf. A., 1931, 1360).

A. B. D. C.

Magnetostriction in bismuth single crystals. A. WOLF and A. GOETZ (Physical Rev., 1933, [ii], 43, 213).—The magnetostriction of Bi single crystals has been measured in a longitudinal field of approx. 20,000 gauss in two different directions to the principal axis. The effect of impurities has been determined.

L. S. T.

Dispersion of the sodium-potassium feldspars. E. LEISEN (Z. Krist., 1934, 89, 49—79).—Optical data are obtained for different members of the plagioclase series, and are related to the crystallographic properties. Different types of dispersion are analysed relative to the anorthite content, and are illustrated by stereographic projection.

B. W. R.

"Banded spectrum" method for measurement of dispersion of birefringence of a crystal plate. H. BRASSEUR and J. PIERARD (Z. Krist., 1934, 89, 24—31).—A modified calculation is de-

scribed and applied to the measurement of birefringence of an (001) flake of $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$.

B. W. R.

Examination of anisotropic substances between crossed nicols [in reflected light]. M. BEREK (Z. Krist., 1934, 89, 125—143).—Previous descriptions (cf. A., 1931, 587, 703) of behaviour of anisotropic substances when viewed by reflected light through a nicol prism are extended to the use of two prisms. The following topics are discussed: use of monochromatic and of white light; significance of slight departures from the extinction positions; polarisation defects in the incident light; practical construction of opaque illuminators; and influence of the absorption in the substance examined.

B. W. R.

Theory of examination of anisotropic substances between crossed nicols [in reflected light]. M. BEREK (Z. Krist., 1934, 89, 144—155).—A parallel commentary, in mathematical language, to the preceding paper (cf. preceding abstract).

B. W. R.

Stability of ionic lattices. G. STEENSHOLT (Z. Physik, 1934, 91, 765—766).—The NaCl type lattice is shown to be most stable for RbBr.

A. B. D. C.

Photochemical properties of synthetic rock-salt crystals. Red displacement of colouring absorption bands by plastic deformation. K. HELBIG (Z. Physik, 1934, 91, 573—592).—Plastic deformation disturbs the photochemical photo-electric equilibrium, increases rate of bleaching, and displaces the colouring absorption band towards the red.

A. B. D. C.

Colour centres and plastic deformation of synthetic rock-salt crystals containing foreign atoms. E. POSER (Z. Physik, 1934, 91, 593—599).—The photochemical elastic limit of synthetic rock-salt and the red displacement of its colouring bands are independent of the presence of foreign mols. (SrCl_2) even though these vary with the mechanical strength.

A. B. D. C.

Fundamentals of the theory of practical strength. A. V. STEPANOV (Z. Physik, 1934, 91, 42—60).—Mechanical breakdown is brought about by changes due to plastic flow causing local strains within the crystal.

A. B. D. C.

Plasticity of crystals. F. ZWICKY (Physical Rev., 1933, [ii], 43, 765—766).—Polemical (cf. A., 1934, 559, 768, 1005).

L. S. T.

Previous deformations of crystals. W. F. BERG (Z. Krist., 1934, 89, 286—294).—By reflecting X-rays diverging from a suitable line focus from a crystal face, a photograph can be obtained which displays the past deformations of the lattice. The interpretation and use of such photographs are discussed.

B. W. R.

Investigations with pure α -, β -, and γ -manganese. F. BRUNKE (Ann. Physik, 1934, [v], 21, 139—168).—The three Mn phases were prepared in a state of purity as follows: α -Mn by vaporisation of pure Mn in vac.; β -Mn by quenching Mn melts from 1100° ; γ -Mn by electrolysis of an aq. solution of MnCl_2 and NH_4Cl . Determination of the temp. coeff.

of electrical conductivity of each phase, and other electrical and magnetic properties indicate that γ -Mn is the pure metal, whilst α - and β -Mn are mixed crystals of the γ -phase, and partake of the nature of alloys.

A. J. M.

Dimorphism of certain aliphatic compounds.
V. *n*-Primary alcohols and their acetates. J. W. C. PHILLIPS and S. A. MUMFORD (J.C.S., 1934, 1657—1665).—The f.p. and polymorphism of the *n*-alcohols and acetates from dodecyl to nonadecyl (with the exception of tridecyl) have been investigated. In alcohols, the m.p. of the α -forms lie on a smooth curve, whilst the m.-p. curve of the β -forms shows alternations. The two curves intersect at about C_{13} . The acetates of the even alcohols show monotropic dimorphism. The α -form of the acetates of the odd alcohols changes first into an opaque β -form monotropically, and this, on cooling, changes into a β_2 -form of higher m.p. The α -f.p. of all the acetates lie on a smooth curve, which intersects the β -curve of the odd members between C_{15} and C_{17} , and the β_2 -curve of the odd members, and the almost coincident β -curve of the even members somewhere above C_{20} . The alternation of properties in homologous series of aliphatic compounds is discussed.

A. J. M.

Swarm theory of liquid crystals. L. S. ORNSTEIN (Kolloid-Z., 1934, 69, 137—155).—A theoretical exposition (cf. A., 1934, 949) of the macroscopic properties, turbidity, X-ray diagrams, and influence of magnetic and electric fields.

E. S. H.

Superconductivity. A. J. RUTGERS (Physica, 1934, 1, 1055—1058).—An equation is deduced connecting the jump in sp. heat of a superconductive metal at the transition point with the derivative of the magnetic threshold val. with respect to temp.

M. S. B.

Superconductors. T. C. KEELEY, K. MENDELSOHN, and J. R. MOORE (Nature, 1934, 134, 773—774).—Further experiments with Hg, Sn, and Pb are recorded (cf. A., 1934, 492).

L. S. T.

Superconductivity of tin at radio-frequencies. F. B. SILSBEE, R. B. SCOTT, F. G. BRICKWEDDE, and J. W. COOK (Physical Rev., 1933, [ii], 43, 1050—1051).—The effective resistance of extruded Sn wire carrying radio-frequency currents at temp. slightly < the transition temp. (3.7° abs.) is < 1% of that at temp. slightly above.

L. S. T.

Temperature coefficient of electrical conductivity in thin metal films. R. DEAGLIO (Z. Physik, 1934, 91, 657—659).—Conductivity and temp. coeff. of thin anomalously conducting metal films are in agreement with Biltz' conclusions (A., 1924, ii, 515).

A. B. D. C.

Conductivity of thin metal films and the surface conductivity of metals. E. PERUCCA (Z. Physik, 1934, 91, 660—669).—Arguments are given supporting the hypothesis that metals normally have a surface layer of conductivity small compared with the bulk conductivity.

A. B. D. C.

Electrical resistivities of single and optically mosaic zinc crystals. W. J. PORPY (Physical Rev., 1934, [ii], 46, 815—821).—The Voigt-Thomson symmetry relation is confirmed for strain-free Zn

single crystals, and principal electrical resistivities are given. Effects of strain and complex effects of annealing are shown graphically. Optically mosaic specimens have abnormal resistivities, and are highly strain-sensitive.

N. M. B.

Peltier and Thomson effects and entropy. A. LIENARD (Compt. rend., 1934, 199, 838—840).—Mathematical.

J. W. S.

Thermal resistance of bismuth single crystals at low temperatures. W. J. DE HAAS and W. H. CAPEL (Physica, 1934, 1, 929—934).—The heat conductivity of single crystals of Bi has been determined at 81.5° and $20-16.5^\circ$ abs. along the directions parallel to a binary axis and to a bisectrix between two binary axes, both perpendicular to the direction of the trigonal principal axis for which λ has been previously determined (A., 1934, 983). For the two perpendicular directions the thermal resistance-temp. curve has a min. The prep. of the crystals is described.

M. S. B.

Velocity of sound in anisotropic media, particularly in quartz measured by piezo-electric excitation. R. BECHMANN (Z. Physik, 1934, 91, 670—678).

A. B. D. C.

Dispersion of ultrasonic waves in a liquid. B. G. SCHPAKOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 588—594).—Data are recorded for H_2O , EtOH, benzine, $PhNO_2$, ethylene chloride, amylacetate, EtOAc, and $COMe_2$. Up to frequencies of 10^6 cycles per sec. the velocity of sound in these liquids at $20-24^\circ$ was const.

H. J. E.

Ultrasonic absorption and reflexion coefficients in air and in carbon dioxide. R. W. CURTIS (Physical Rev., 1934, [ii], 46, 811—815).—Measurements were made using Hubbard's method (cf. *ibid.*, 1931, [ii], 38, 1011). In the frequency range 88—1000 kc. per sec. absorption in air increased with λ^2 , but in CO_2 gave a sharp max. at 98 kc. per sec. The reflexion coeff., for a brass reflector, decreased for both gases, to the order of 20% at higher frequencies, with increasing frequency.

N. M. B.

Effect of dissolved air on the specific heat of water. R. JESSEL (Proc. Physical Soc., 1934, 46, 747—763).—Data are tabulated and plotted for the temp. range $12-80^\circ$, as obtained by the continuous-flow electric method, for saturated and air-free distilled H_2O . In the latter case the vals. are lower. An explanation is proposed.

N. M. B.

Preliminary calculation of the molecular heat c_v of sodium chloride and metals at high temperatures. A. EUCKEN and W. DANNOHL (Z. Elektrochem., 1934, 40, 789—792).—Theoretical.

E. S. H.

Effect of temperature on the true specific heat of nickel. E. AHRENS (Ann. Physik, 1934, [v], 21, 169—181).—A new differential method for the determination of true sp. heats is described. It has been used to determine the true sp. heat of Pt and Ni between 20° and 460° . The sp. heat of Ni attains a max. at $349.5 \pm 0.5^\circ$. There is a max. in the curve of temp. coeff. of resistance and temp. within 1.5° of the above val.

A. J. M.

Specific heats of metals at high temperature. XVII. Calorimetric retardation phenomena of cerium and chromium. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 489—497; cf. A., 1934, 481).—The vals. of the sp. heat, C_p , of Ce in the range 296—551° depend on the preliminary thermal treatment. C_p is raised by keeping the sample at $>360^\circ$, and subsequent cooling at room temp. diminishes the acquired high C_p . The results are attributed to the complexity of the metal. A transition temp. at 360—370° is inferred. Vals. of the C_p of Cr between 400° and 1066° are reproducible, but the rate of evolution of heat is related to the preliminary thermal treatment of the sample. J. G. A. G.

Empirical heat capacity equations for simple gases. H. M. SPENCER and J. L. JUSTICE (J. Amer. Chem. Soc., 1934, **56**, 2311—2312).—The heat capacities of equilibrium Cl_2 , equilibrium HCl , and CO_2 between 300° and 1500° abs. have been calc. from published data. Empirical equations of the form $C_p = a + bT + cT^2$ fit the theoretical vals. for Cl_2 , HCl , CO_2 , H_2 , O_2 , N_2 , CO , Br , HBr , and H_2O vapour with average deviations 0.18—0.76%. E. S. H.

Specific heat, entropy, and free energy of gaseous nitric oxide computed from spectroscopic data. E. E. WITMER (J. Amer. Chem. Soc., 1934, **56**, 2229—2233).—The vals. have been calc. for the range 1—500° abs., and are compared with those published elsewhere. E. S. H.

Heats of crystallisation of the ethyl esters of the monobasic aliphatic acids. A. M. KING and W. E. GARNER (J.C.S., 1934, 1449—1456).—Data are recorded for the esters of the acids from $n=14$ to $n=30$. The form stable at the m.p. has a vertical chain when $n > 20$ and a tilted chain when $n < 20$. The heat of crystallisation of the vertical chain types is a linear function of n , but with tilted chains the curve changes slope at $n=20$ owing probably to a change of orientation of the ester group. The vertical forms have a higher sp. heat than the tilted, and a lower heat of crystallisation, on account of the greater amplitude of oscillation of the chain. The higher m.p. of the vertical forms is attributed to the increased probability of attachment of the chains to the surface of the solid. H. F. G.

Heat of vaporisation of acetone, and its saturated vapour pressure. N. A. DE KOLOSOVSKI and A. ALIMOV (J. Gen. Chem. Russ., 1934, **4**, 710—712).—Empirical formulæ for the latent heat of vaporisation and v.p. of COMe_2 at 0—80° are given. R. T.

Effect of high electrostatic fields on the vaporisation of molybdenum. G. B. ESTABROOK (Physical Rev., 1933, [ii], **43**, 383). L. S. T.

Effect of high electrostatic fields on the vaporisation of metals. A. G. WORTHING (Physical Rev., 1933, [ii], **43**, 383).—Theoretical. L. S. T.

F.p. of platinum. F. H. SCHOFIELD (Proc. Roy. Soc., 1934, A, **146**, 792—817).—The f.p. of Pt on the International temp. scale has been determined by measuring the ratio of brightness, for a certain wavelength, of black-body radiators held at the f.p. of Pt

and Au. The mean val. $1773.3 \pm 1^\circ$ is in good agreement with the only previous val. obtained by the same method (A., 1931, 1004). L. L. B.

Surface energy of molecules and their physico-chemical properties. IV. Surface energy and b.p. in certain organic and inorganic homologous series. V. Surface energy and dissociation temperature of complex compounds. S. G. MOKRUSCHIN (J. Gen. Chem. Russ., 1934, **4**, 577—579, 580—586).—IV [with E. I. KRILOV]. The formulæ $T = an + b$, and $T = cn + dn^2 + g$, where T is the b.p. of a member of a homologous series containing n homologous groups, and a, b, c, d , and g are consts., are verified for a no. of series.

V. The formula $T = k/(A/d)^{2/3}$, where T is the dissociation temp., A the at. wt. of the central atom, and d its density, is verified for compounds of the types $[\text{M}(\text{NH}_3)_6]\text{X}_2$, $[\text{M}(\text{NH}_3)_6]\text{SO}_4$, and $[\text{M}(\text{NH}_3)_4]\text{SO}_4$, where $\text{M} = \text{Ni}, \text{Fe}, \text{Cu}, \text{Mn}, \text{Zn}, \text{Cd}$, and Mg , and $\text{X} = \text{Cl}, \text{Br}$, and I . R. T.

Density of small crystals. J. D. BERNAL and D. CROWFOOT (Nature, 1934, **134**, 809—810).—The d of small amounts (> 0.05 mg.) of minute crystals has been determined by finding a liquid of known d in which no movement of the crystals occurs on centrifuging for 1—2 min. at 2000—4000 r.p.m. Vals. found are vitamin- B_1 hydrochloride 1.403 ± 0.003 , $\text{C}_{22}\text{H}_{16}$ 1.244 ± 0.002 , $\text{C}_{25}\text{H}_{24}$ 1.195 ± 0.003 , $\text{C}_{26}\text{H}_{26}$ 1.158 ± 0.003 , and $\text{C}_{27}\text{H}_{28}$ 1.135 ± 0.002 (four hydrocarbons obtained respectively by Se-dehydrogenation of cholic acid, cholesterol, ergosterol, and phytosterols). L. S. T.

Thermal expansion of bismuth single crystals. T. L. HO and A. GOERTZ (Physical Rev., 1933, [ii], **43**, 213).—The thermal expansion of Bi crystals with known admixtures of electro-positive and -negative impurities in low concn. has been determined between room temp. and the m.p. The decrease in the coeff. before the m.p. has been verified. Admixtures bring about definite changes at temp. characteristic for the impurity present. L. S. T.

Thermal expansion of alkali halides and metals at high temperatures. A. EUCKEN and W. DANNÖHL (Z. Elektrochem., 1934, **40**, 814—821).—The expansion coeffs. of Pb, Ag, Cu, Ni, NaCl, KCl, KBr, and KI have been measured over different ranges of temp. E. S. H.

X-Ray measurements of the thermal expansion of sodium nitrate. H. SAINI and A. MERCIER (Helv. phys. Acta, 1934, **7**, 267—272; Chem. Zentr., 1934, i, 3833).—Data are recorded between 18° and 200°, and the expansion coeffs. deduced. H. J. E.

Thermal expansion of calcite. J. WEIGLE and H. SAINI (Helv. phys. Acta, 1934, **7**, 257—266; Chem. Zentr., 1934, i, 3833).—Lattice const. measurements by the X-ray method are recorded for 18°, 100°, 200°, and 300°, and the expansion coeffs. deduced. H. J. E.

Thermal expansion of Jena thermometer glass 2954^{III}. W. H. KEESOM and D. W. DOBORZYŃSKÓ (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 480—481).—The equation $l = l_0[1 + 10^{-6}(545.89\tau + 19.55\tau^2 + 17.16\tau^3 + 27.99\tau^4 + 5.24\tau^5)]$, where $\tau = t/100$, is

valid between 100° and -273°. The coeff. of thermal expansion of fused SiO₂ is zero near -273°.

J. G. A. G.

Vapour density of sulphur dioxide. W. W. STEWART and O. MAASS (Canad. J. Res., 1934, 11, 530—538).—The sensitivity of the apparatus previously employed (cf. A., 1931, 1117) for v.d. determinations has been increased by the addition of a 50-litre container. It is shown that the apparent mol. wt.-pressure isothermal for SO₂ is not a straight line. This is in agreement with the equation of state for gases at low pressures. The experimental data give mol. wt. of 64.075 for SO₂.

M. S. B.

Vapour pressure of homologues of benzene. New method of determining vapour pressure. B. B. KUDRJAVTSEV (J. Gen. Chem. Russ., 1934, 4, 563—566).—The v.p. of PhMe, *m*-xylene, and cumene are determined by an ebullioscopic method at const. pressure (1—760 mm.). A manostat is described.

R. T.

Phase equilibria in hydrocarbon systems. V. Pressure-volume-temperature relations and thermal properties of propane. B. H. SAGE, J. G. SCHAAFSMA, and W. N. LACEY (Ind. Eng. Chem., 1934, 26, 1218—1224).—Measurements have been made at 21—104° and from atm. pressure to 3000 lb. per sq. in. in a steel vessel the vol. of which could be varied by pumping in Hg. Vals. of sp. vol., fugacity, heat content, and entropy are tabulated at various temp. and pressures. The crit. data are 643.3 lb. per sq. in., 100.1°, and 0.06896 cu. ft. per lb.

A. G.

Vapour pressure of anabasine and nicotine. S. V. GORBATSCHEV (J. Appl. Chem. Russ., 1934, 7, 388—391).—The v.p. *P* of anabasine is given by $\log P = \log T - 2586.6/T + 1.9143$, and of nicotine by $\log P = \log T - 2408.4/T + 1.9135$.

R. T.

Vapour pressure of calcium between 500° and 625°. E. RUDBERG (Physical Rev., 1934, [ii], 46, 763—767).—Using the method of mol. effusion, v.-p. data were obtained as a function of temp. for solid Ca. The calc. chemical const. is 4.53×10^4 g.-cal. per mol.

N. M. B.

Physical constants of methyl ethyl ketone and an investigation of its additive compound with sodium iodide dihydrate. W. A. FELSING, L. SHOFNER, and N. B. GARLOCK (J. Amer. Chem. Soc., 1934, 56, 2252—2254).—The following data are recorded: v.p. (-30° to 80°) $\log_{10} p$ (mm.) = $-2644.996/T - 313.0342 \times 10^{-2} \log_{10} T - 403.78573 \times 10^{-6} T + 19.778594$; b.p. 79.56°; *d* (-30° to 85°) $1.10717 - 103.125 \times 10^{-5} T$; (15—35°) $1.37799 - 0.000483(t - 20)$. The heat and mol. entropy of vaporisation have been calc.

E. S. H.

Joule-Thomson effect in argon. J. R. ROEBUCK and H. OSTERBERG (Physical Rev., 1934, [ii], 46, 785—790).—Investigations previously reported for He (cf. A., 1934, 481) are extended to Ar. Data for the isenthalpic curves are tabulated and plotted. Vals. of the Joule-Thomson coeff. for the pressure range 1—200 atm. and temp. -150° to 300° are calc., and plotted as a function of temp. and pressure. Results resemble those for air and N₂.

N. M. B.

Properties of real gases according to the thermodynamic equation of state. II. Joule-Thomson effect for helium. V. JACYNA (Z. Physik, 1934, 92, 204—211; cf. A., 1934, 1300).—*c_p* data are used to determine the Joule effect and change in internal isothermal energy.

A. B. D. C.

Viscosity. J. M. BURGERS (Chem. Weekblad, 1934, 31, 582—584).—Viscosity is discussed in relation to plasticity, elasticity, and the behaviour of systems containing elastic and plastic components. Reference is made to the mechanism of laminar flow and the relation between temp. and viscosity, especially in the light of Andrade's work.

H. F. G.

Viscosity and density of fused yellow phosphorus over the range 45—90°. N. D. LITVINOV and I. E. FURMER (J. Appl. Chem. Russ., 1934, 7, 321—327).—For yellow P fused under H₂O $\eta = 0.03314 - 0.965 \times 10^{-3} T + 0.1279 \times 10^{-4} T^2 - 0.576 \times 10^{-7} T^3$, and $d = 1.782 - 0.0009 T$, where *T* is temp.

R. T.

Determination of viscosity of water vapour. W. SCHILLER (Forsch. Ingenieurw., 1934, A, 5, 71—74; Chem. Zentr., 1934, ii, 393).—Measurements are recorded at 100—300° and 1—30 atm.

H. J. E.

Connexion between rotatory and translatory viscosity. J. L. SNOEK (Physikal. Z., 1934, 35, 911—914).—The ratio, *K*, of the viscosity of the solution to that of the solvent for solutions of dipole substances (PhNO₂, *o*-C₆H₄Cl₂, C₅H₁₁·NO₂, C₅H₁₁·OAc, 1-C₁₀H₇Br, C₅H₅N) in non-polar solvents (CCl₄ and C₆H₆) was determined. *K*-1 in C₆H₆ is > in CCl₄, due to the solvation of the solute by C₆H₆. Experiments with non-polar solutes which would be expected to have the same val. of *K*-1 in the two solvents give no such definite result.

A. J. M.

Changes in the viscosity of liquids with temperature, pressure, and composition.—See B., 1934, 992.

Purity of zinc for which thermal diffusivity was recently reported. R. H. FRAZIER (Physical Rev., 1933, [ii], 43, 762; cf. A., 1933, 217).

L. S. T.

Solidification diagram for sodium-cæsium alloys. E. RINCK (Compt. rend., 1934, 199, 1217—1219; cf. A., 1933, 771).—The equilibrium diagram has a eutectic at -30° (75% Cs) and a transition temp. at -8°; the compound Na₂Cs is formed. K, Rb, and Cs dissolved in Na at its m.p. are present to the extent of 18, 22, and 64%, respectively, as diat. mols.

H. J. E.

Phase diagram of the system copper-gallium. F. WEIBKE (Z. anorg. Chem., 1934, 220, 293—311).—A close similarity is shown to exist between Cu-Al and Cu-Ga alloys. The compounds Cu₂Ga and Cu₃Ga₄ are formed.

M. S. B.

Phase diagram of the system copper-indium. F. WEIBKE and H. EGGERS (Z. anorg. Chem., 1934, 220, 273—292).—71 different alloys of Cu and In have been prepared and analysed by thermal, microscopical, and X-ray methods. The results are

combined in a phase diagram. Mixed crystals and solid solutions are formed and possible compounds are Cu_4In and Cu_2In . M. S. B.

System copper-lead. W. CLAUS (Metallwirts., 1934, 13, 226—227; Chem. Zentr., 1934, ii, 319).—Phase relations are discussed. H. J. E.

System praseodymium-gold. A. ROSSI (Gazzetta, 1934, 64, 748—757).—The f.-p. diagram shows the formation with marked heat evolution of 4 compounds between Au and Pr (99.5%, m.p. 950°), viz., AuPr_2 (transition point 710°), AuPr (m.p. 1350°), Au_2Pr (m.p. 1210°), and Au_4Pr (m.p. 1200°). The mutual solubility in the solid phase is very small. Continued heating at 600° of the alloys rich in Pr gives rise to a new cubic face-centred phase which is supposed to be a solid solution of β -Pr in small amounts of Au or in the impurities present (Si and C). The sp. heat of Pr in the range 20—100° is 0.0486 ± 0.0007 (at. heat = 6.85). O. J. W.

Intermetallic compounds formed in mercury. V. Compounds in the Zn-Mn, Zn-Co, Zn-Ni, Al-Fe, Sn-Mn, and Sn-Co systems. A. S. RUSSELL, T. R. KENNEDY, and R. P. LAWRENCE (J.C.S., 1934, 1750—1754).—Metallic systems which form binary compounds in Hg without inclusion of Hg itself have been investigated. These have been analysed chemically without removal from Hg (cf. A., 1932, 456). The empirical formulæ are in satisfactory agreement with those determined for the same systems by thermal and X-ray methods. The following compounds have been detected: Zn-Mn, Zn_4Mn , Zn_3Mn , Zn_{12}Co , Zn_3Co , ZnCo_4 , Zn_{12}Ni , Zn_3Ni , ZnNi , AlFe , Al_4Fe_3 , AlFe_3 , Sn_3Mn , Sn_2Mn , SnMn , SnMn_2 , Sn_2Co , and SnCo_2 . M. S. B.

A manganese-silicon solution of A2 type. F. LAVES (Z. Krist., 1934, 89, 189—191).—Confirming previous work, Mn_2Si has been found by X-rays to have the A2 structure (cubic space-centred lattice); it is regarded as a mixed crystal, not as a compound. B. W. R.

Transformation processes in β -aluminium bronze. G. WASSERMANN (Metallwirts., 1934, 13, 133—137; Chem. Zentr., 1934, i, 3914).—The β phase is stable above 570° (cubic body-centred structure). It passes on slow cooling into the stable $\delta + \alpha$ phase. Rapid cooling yields the β' phase, which is stable at < 300° but at > 300° forms the β_1 phase, which passes at higher temp. into $\delta + \alpha$. H. J. E.

Further X-ray studies in the diffusion of the nickel-copper system. C. MATANO (Mem. Coll. Sci. Kyoto, 1933, A, 16, 249—259).—The interdiffusion of Ni and Cu was investigated by the X-ray method with (a) a thin layer of Cu on Ni, (b) a thin layer of Ni on Cu, and (c) alternate layers of Ni and Cu, heated, in each case, at 500°, 650°, and 900°. The coeff. of diffusion is not const. as demanded by Fick's law, but varies with concn. It is given by $D = Ae^{-\beta/T}$, where A is a const. independent of T , but varying with concn., and β is a const. which differs for the two metals. A. J. M.

Electrical conductivity and equilibrium diagram of binary alloys. XV. System lithium-lead. G. GRUBE and H. KLAIBER. XVI. System

lithium-tin. G. GRUBE and E. MEYER (Z. Elektrochem., 1934, 40, 745—754, 771—777; cf. A., 1934, 1065).—XV. The compounds LiPb (m.p. 482°), Li_5Pb_2 , Li_3Pb , Li_7Pb_2 (m.p. 726°), and Li_4Pb have been recognised.

XVI. The existence of the compounds LiSn_2 , LiSn (m.p. 485°), Li_2Sn , Li_3Sn_2 , Li_7Sn_2 (m.p. 783°), and Li_4Sn (m.p. 765°) has been established. Li does not enter appreciably into solid solution in pure Sn. E. S. H.

System iron-nickel-molybdenum. W. KOSTER (Arch. Eisenhüttenw., 1934—1935, 8, 169—171).—The system has been investigated by dilatometric, magnetometric, hardness, and micrographic methods from the Fe corner to the line joining FeMo_2 and MoNi , which form a continuous series of solid solutions (δ). The eutectic equilibria of the three component binary systems merge at 1350° into a 4-phase equilibrium in the ternary system: liquid + $\alpha = \gamma + \delta$, from which the 3-phase field $\alpha + \gamma + \delta$ extends to room temp. The boundaries of the various fields in the solid state have been determined by observations on the occurrence of pptn.-hardening on tempering. The magnetic transformation (M) of α -alloys with 4% Ni occurs at 760—720° according to the Mo content, that of the irreversible Fe-Ni alloys falls with increasing Mo, and that of Ni-Mo alloys reaches room temp. at 9% Mo. M points for numerous other alloys have been determined in the heterogeneous and homogeneous states; they are generally lower in the latter than in the former. A. R. P.

Influence of nickel on solubility and separation processes in the system silver-copper. H. PRISTER and P. WIEST (Metallwirts., 1934, 13, 317—320; Chem. Zentr., 1934, ii, 503).—The solubility of Ag in Cu is reduced somewhat by 1% Ni. The influence on the separation processes has been studied by X-rays and by changes in the hardness. H. J. E.

Carbon solubility of iron-chromium-silicon alloys. O. LUCAS and H. WENTRUPP (Z. anorg. Chem., 1934, 220, 329—333).—Mixtures of Fe, Cr, and Si have been fused together under C at different temp. and the resulting alloys analysed. They contained approx. 40—80% Cr, 0—40% Si, 1—10% C. For the same alloy the C content falls by about 0.3% per 100° rise of temp. It increases with Cr content, but is strongly diminished by Si. M. S. B.

Mechanism of eutectic crystallisation. A. A. BOTSCHVAR (Z. anorg. Chem., 1934, 220, 334—336).—The progress of crystallisation at the eutectic has been followed microscopically using two differently coloured substances, azobenzene and piperonal (I). After supercooling, inoculation takes place only if both kinds of crystals are present. (I), however, actually begins to crystallise first. The character of the eutectic mixture varies with the degree of supercooling. M. S. B.

Heterogeneity of a solid solution and its mechanical and chemical properties. P. CHEVENARD (Compt. rend., 1934, 199, 861—863).—The mechanical properties and resistance to corrosion of samples of the austenitic Fe-Ni-Cr-C alloy, quenched

from 1200° in H₂O and subsequently annealed, show analogous variation with the period of annealing.

J. W. S.

Intermetallic solid solutions. E. R. JETTE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Pub. 560, 1934, 16 pp.).—A discussion of the parallel between Raoult's law for solutions and the Vegard additive law for solid solutions. CH. ABS. (e)

Diffusion of elements in the solid state. B. N. SEN (Compt. rend., 1934, **199**, 1189—1190).—Diffusion phenomena (e.g., for Cu-Pt or Fe-C) are correlated with data for the min. distance of approach of the atoms. H. J. E.

Theory of supercooled solid solutions. S. KONOBEJEVSKI (Z. physikal. Chem., 1934, **171**, 25—35).—From consideration of the variation of solubility with particle size it is deduced that if in the separation of a second solid phase from a supersaturated solid solution a large no. of small nuclei are formed, the system will attain a comparatively stable state when supersaturation is still present. The primary process in separation is probably the concn. distribution of the components in the lattice of the solid solution, and by applying the theory of fluctuations to determine this distribution it becomes possible to calculate the conditions under which separation may occur, the results agreeing with experimental data. In the formation within a solid phase of a new cryst. species, the latter assumes such orientations as result in its surface energy being a min.; the formation of Widmanstätten structures is accounted for in this way. R. C.

Viscosity of mixtures of liquids at high pressures. R. B. DOW (Physical Rev., 1933, [ii], **43**, 502).—The effect of pressures up to 12,000 kg. per sq. cm. on the η of six mixtures has been investigated over the whole range of composition at 30° and at 75°. The isobaric η -composition graphs are linear for n -C₆H₁₄- n -C₁₀H₂₂ and n -C₉H₁₈-CS₂, whilst those for n -C₆H₁₄-PhCl, n -C₆H₁₄-Et₂O, and eugenol-CS₂ are complex; irregularities appear in certain regions of composition. The n -C₆H₁₂-C₆H₆ isobaric curves show unusual sags which are functions of temp. Interlocking between mols. of different sizes and shapes is probably the cause of the large increase in η with an increase in pressure. L. S. T.

Viscosity of the binary systems Na₂B₄O₇-B₂O₃ and NaBO₂-NaPO₃ in the fused state. M. P. VOLAROVICH and D. M. TOLSTOI (J. Soc. Glass Tech., 1934, **18**, 209—221t).—The system Na₂B₄O₇-B₂O₃ has been previously described (A., 1931, 676). For NaPO₃ η can be measured down to 450° and for NaBO₂ down to 844° only, but, in spite of supercooling, η remains comparatively low for both salts (cf. following abstract). The η isotherm at 650° for the binary system has a point of inflexion corresponding with the max. of the m.-p. curve at a composition which suggests the presence of an equimol. compound. The mixture containing 60% NaBO₂ has the anomalous η common to colloidal solutions and suspensions, the apparent η being a function of the velocity gradient and decreasing with increase of velocity. A two-phase system is apparently formed, owing to the

separation of cryst. particles. On coming to rest the mixture becomes plastic. η has been determined for K₂SiO₃ at 875° and 906°. M. S. B.

Viscosity of the binary system Na₂B₄O₇-NaH₂PO₄ in the fused state. M. P. VOLAROVICH (J. Soc. Glass Tech., 1934, **18**, 201—208t).— η has been determined by the rotating-cylinder method in the temp. range 527—920°. Na₂B₄O₇ alone readily supercools and the results confirm previous observations on the rapid rise in η for supercooled liquids as the temp. falls. At 590° (151° below the m.p.) η for Na₂B₄O₇ is 1000 times the val. at 741°. The η -composition isotherms for the binary system give no indication of the formation of complex compounds. M. S. B.

Refractivity of liquid mixtures. G. NARASIMHAIAH (Proc. Indian Acad. Sci., 1934, **A**, **1**, 34—38).—Mathematical. The Raman-Krishnan theory is extended to binary liquid mixtures. The formula obtained is verified for COMe₂-H₂O and MeOH-H₂O mixtures. N. M. B.

Molecular polarisation and association. K. L. WOLF and W. HEROLD (Z. physikal. Chem., 1934, **B**, **27**, 58—70).—The form of the polarisation-composition curves for solutions of aliphatic alcohols in non-polar difficultly polarisable solvents may be accounted for by supposing the solutions to contain some double and triple alcohol mols., with dipole moments respectively < and > that of the single mol. The double mols. will have all forms between the two extremes in which the arrangement of the constituent mols. is parallel and anti-parallel. With increasing chain length and branching near the OH groups association occurs to a diminishing extent. In polarisable solvents the energy relations involved in association are considerably influenced by the polarisability of the solvent. R. C.

Thermodynamics of binary liquid mixtures: formic acid and water. A. N. CAMPBELL and A. J. R. CAMPBELL (Trans. Faraday Soc., 1934, **30**, 1109—1114).—The heat of mixing (H_m) and of evaporation (H_e), the v.p. and composition of the vapour of mixtures of H₂O and HCO₂H have been determined at 30° and 50°. The const.-boiling mixtures contain 63.5 and 66.0% HCO₂H at 30° and 50°, respectively. H_e calc. from H_m and H_e for the pure components agrees approx. with the observed vals. The partial pressures of H₂O and HCO₂H at 50° have been calc. from the vals. at 30° by means of the Clausius-Clapeyron equation, and agree approx. with observed vals. for H₂O, but for HCO₂H large deviations occur owing to association in the vapour. R. S. B.

Measurement of vapour pressure of solutions by the dew-point method. B. B. KUDRJAVTSEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 601—602).—Data are recorded for aq. H₂SO₄, the method depending on condensation of the vapour on a metallic junction cooled by the Peltier effect. H. J. E.

Thermal dissociation and vapour pressure of boric acid and its volatility in water vapour. A. THIEL and H. SIEBENECK (Z. anorg. Chem., 1934, **220**, 236—246).—The dissociation pressure of H₃BO₃

at 100° is 113 ± 1 mm. and of HBO_2 4–5 mm. Pure HBO_2 can therefore be prepared from H_3BO_3 by drying at 100–111° in a current of gas in which the partial pressure of H_2O vapour is between 5 and 113 mm. If it is < 4 mm. pure $\text{H}_2\text{B}_2\text{O}_7$ may be obtained. The volatility of H_3BO_3 in H_2O vapour depends on the partial pressure of H_2O vapour (p_W) in the transporting gas, since p_B (v.p. of H_3BO_3 at 100°) = $2.5 \times 10^{-6} \cdot p_W$. For HBO_2 at 105° $p_B = 2.3 \times 10^{-3} \cdot p_W$. The volatility of undecomposed H_3BO_3 in boiling H_2O increases with distillation velocity. The dependence of the volatility of H_3BO_3 on the formation of complexes with H_2O is discussed.

M. S. B.

Droplet formation in vapours. M. VOLMER and H. FLOOD (Z. physikal. Chem., 1934, 170, 273–285).—The relation between the crit. supersaturation, S , of H_2O vapour and the temp. of cooling by adiabatic expansion agrees with Volmer and Farkas' theory of nucleus formation (A., 1926, 676; 1927, 524). For seven org. liquids the vals. of S agree with the theory, except for MeOH.

R. C.

Formation of droplets in supersaturated mixtures of ethyl alcohol and water vapour. H. FLOOD (Z. physikal. Chem., 1934, 170, 286–294; cf. preceding abstract).—Measurements of the min. adiabatic expansion required to cause formation of droplets in absence of air ions lead to a val. of the crit. saturation represented by $S' = (p/p_0)^N (p'/p_0')^{N'}$, where N and N' are mol. fractions in the nuclei, p and p' supersaturation pressures, and p_0 and p_0' partial v.p. of EtOH and H_2O over liquid of the composition of the nuclei. The vals. so obtained are throughout <, but run parallel with, the vals. obtained from the Volmer–Farkas equation $\log S' - k(\gamma/T)^{2/3} V'$, where γ is the interfacial tension between droplet and vapour and V' the mol. vol. of the liquid of the droplet.

R. C.

Anomalous diffusion. D. KRUGER and H. GRUNSKY (Z. physikal. Chem., 1934, 170, 161–171; cf. A., 1930, 1358).—The possible reasons why the diffusion coeff., D , determined by Oehlm's method, or methods fundamentally similar, varies in certain cases with the position in the diffusing system are critically reviewed. Solvation may cause an abnormally high rate of transport in those parts of the system which are remote from the stratum in which the diffusion started. In general, it may be anticipated that the presence together of several diffusible substances will cause deviations from Fick's law. The reason why the mol. wts. of cellulose derivatives cannot be deduced from data for diffusion in org. solvents is that such data do not permit the calculation of D (cf. A., 1934, 357).

R. C.

Diffusion of heavy into light water. W. J. C. ORR and D. W. THOMSON (Nature, 1934, 134, 776).—The preliminary val. obtained for the diffusion coeff. of H_2O (0.5–3.0 mol.-%) in aq. solutions is approx. 9×10^{-4} cm.² per sec. at 15°. This unexpectedly high val. indicates than an at. interchange is involved.

L. S. T.

Diffusion of gases through metals. C. J. SMITHELLS and C. E. RANSLEY (Nature, 1934, 134, 814).—The rate of diffusion of H_2 through Cu, Ni, Fe,

and Mo, and of N_2 through Mo, has been measured. The results can be satisfactorily explained, when the influence of adsorption on diffusion is taken into account, by $D = K[abP/(1+aP)]P^{\frac{1}{2}}$, where $abP/(1+aP)$ is the Langmuir isotherm representing the fraction of the surface covered by adsorbed moles. L. S. T.

Solubility of hydrogen in liquid ammonia at 25°, 50°, 75°, and 100° and at pressures to 1000 atmospheres. R. WIEBE and T. H. TREMEARNE (J. Amer. Chem. Soc., 1934, 56, 2347–2360).—The data recorded show that the solubility increases with rising temp. and increasing pressure. E. S. H.

Solubility of sulphur dioxide at low partial pressures. Ionisation constant and heat of ionisation of sulphurous acid. H. F. JOHNSTONE and P. W. LEPLA (J. Amer. Chem. Soc., 1934, 56, 2233–2238).—The solubility of SO_2 in H_2O has been measured between 0.2 and 10.3 mm. at 25°, 35°, and 50°. The ionisation const. (0.0130 at 25°) has been calc. from published conductance data. The free energy and heats of solution and ionisation (in g.-cal.) are: (1) for $\text{SO}_2(\text{gas})$ $\text{SO}_2(\text{aq.})$ $\Delta H = -6260$, $\Delta F_{298} = -123$, (2) for H_2SO_3 $\text{H}^+ + \text{HSO}_3^-$ $\Delta H = -3860$, $\Delta F_{298} = 2725$. The total heat of absorption of SO_2 in infinite dilution is $-10,120$ g.-cal.

E. S. H.

Solubility of krypton and xenon in liquid oxygen. M. VON STACKELBERG [with M. HEINRICH and W. SCHULTE] (Z. physikal. Chem., 1934, 170, 262–272).—The solubility at 70–90° abs. has been measured, saturation temp. being determined by v.-p. measurements. The solubilities are < the vals. calc. from the heats of fusion of the solutes assuming ideality of the systems, indicating that heat must be absorbed on mixing the liquid components. The O partial pressures are > those indicated by Raoult's law. Heats of mixing and, for the system O–Kr, the complete crystallisation curve have been calc.

R. C.

Heterogeneous binary systems. I. System aniline-cyclohexane. (MLLE.) H. SCHLEGEL (J. Chim. phys., 1934, 31, 517–529).—Previous work on partly miscible liquids is reviewed. The mutual solubility of NH_2Ph and cyclohexane has been determined. Cryoscopic measurements indicate that neither substance is associated when dissolved in the other.

F. L. U.

Solubility of magnesium sulphate heptahydrate. H. H. TING and W. L. McCABE (Ind. Eng. Chem., 1934, 26, 1207–1208).—The results obtained suggest that previous vals. are too high. A. G.

Solubility of sodium thiocyanate in ethyl alcohol. J. R. PARTINGTON and R. J. WINTERTON (Trans. Faraday Soc., 1934, 30, 1104–1105).—The method of Hughes and Mead (A., 1929, 1375) is criticised; the solubility at 25° is 20.66 g. NaCNS per 100 g. of EtOH (cf. A., 1927, 1020). J. G. A. G.

Solubility of ammonium thiocyanate in water, methyl alcohol, and ethyl alcohol. L. SHNIDMAN (J. Physical Chem., 1934, 38, 901–906; cf. A., 1933, 897).—Vals. are given for the temp. interval 13–72° (H_2O) and 20–70° (MeOH and EtOH). F. L. U.

Solubility of chlorides and nitrates of alkali metals in ammonia-water mixtures. A. GUYER, A. BIELER, and E. SCHMID (Helv. Chim. Acta, 1934, 17, 1530—1537).—The solubility of NaCl in mixtures of NH_3 and H_2O containing 0–100% of H_2O has been determined between -40° and 25° . A diagram showing the region of stability of $\text{NaCl}\cdot 5\text{NH}_3$ is given. Solubility curves of KCl at -15° and 25° , and of NaNO_3 and KNO_3 at 0° , are also given. The three last-named form no ammoniate. F. L. U.

Solubility isotherms for complex metal thiocyanates. IV. The system $\text{Ca}(\text{SCN})_2\text{--Co}(\text{SCN})_2\text{--H}_2\text{O}$. A. DE SWEEMER (Natuurwetensch. Tijds., 1934, 16, 242—244).—The stable solid phases at 25° are $\text{Co}(\text{SCN})_2\cdot 3\text{H}_2\text{O}$, $\text{CaCo}(\text{SCN})_4\cdot 8\text{H}_2\text{O}$, and $\text{Ca}(\text{SCN})_2\cdot 4\text{H}_2\text{O}$. D. R. D.

Effect of one salt on the solubility of another. VI. Solutions of cobaltammines in aqueous lanthanum thiocyanates. L. O'NEILL and J. R. PARTINGTON (Trans. Faraday Soc., 1934, 30, 1134—1144).—The solubilities of the isothiocyanato-salts $[\text{Co}(\text{NH}_3)_5\text{CNS}](\text{NO}_3)_2$ (I) and $[\text{Co}(\text{NH}_3)_5\text{CNS}]\text{I}_2$ (II) in solutions of $\text{La}(\text{CNS})_3$ (III), determined at 25° , do not agree with the simple Debye-Hückel theory, and the modified theory which allows for finite mean ionic diameter (a) gives only the correct trend. The theory of La Mer *et al.* gives an adequate explanation up to an ionic strength 0.1. For (I) the assumption $a_0\text{--}3.72\text{ \AA}$. ($a_0=a$ in pure solvent) gives an almost const. val. of $a=4.02\text{ \AA}$. (mean) for a range of concns. of (III); for (II) the constancy is not so good, the best agreement holding with $a_0\text{--}5\text{ \AA}$. when $a=5.60\text{ \AA}$. (mean). R. S. B.

Physical chemistry of amino-acids, peptides, and related substances. II. Solubility of α -amino-acids in water and in alcohol-water mixtures. E. J. COHN, T. L. MCMEEKIN, J. T. EDSALL, and J. H. WEARE (J. Amer. Chem. Soc., 1934, 56, 2270—2282; cf. A., 1934, 595).—The solubilities of $\alpha\text{-NH}_2$ -acids in EtOH are very small and of the same order; the solubilities in H_2O are much greater, and increase as the hydrocarbon chain decreases. These properties are related to the high d in the solid state, which is characteristic of the close packing of charged mols. In dil. aq. EtOH the logarithm of the solubility of all $\alpha\text{-NH}_2$ -acids appears to diminish inversely as the dielectric const. The difference between the logarithm of the solubility in H_2O and in abs. EtOH decreases by the same amount for each CH_2 group, rendering it possible to analyse the activity coeffs. in terms of electrical and non-electrical forces due to NH_3^+ and CO_2^- groups.

E. S. H.
Solubility of cellobiose octa-acetate in binary organic liquids. M. TANIGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1934, 37, 682—685B).—For binary mixtures of two non-polar liquids, or of a non-polar liquid with a feebly associated polar liquid, the solubility-composition curves are approx. linear. When one (or both) is highly polar the curves may be markedly non-linear, the shape depending on the degree of association and on the tendency to complex formation. A. G.

Dispersion relations in aqueous solutions of monocalcium aluminate. H. KUHL, F. THILO, and A. C. YU (Zement, 1934, 23, 249—256; Chem. Zentr., 1934, ii, 112).—On shaking $\text{CaO}\cdot\text{Al}_2\text{O}_3$ with aq. $\text{Ca}(\text{OH})_2$ the solution became supersaturated with respect to Al_2O_3 . This is attributed to colloidal dispersion. H. J. E.

Supersaturation and crystal formation in seeded solutions. H. H. TING and W. L. MCCABE (Ing. Eng. Chem., 1934, 26, 1201—1207).—Seeded and stirred supersaturated solutions of $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ were cooled at a const. rate, and the degrees of supercooling corresponding with the first formation of new nuclei (I) and with the formation of a cloud of new crystals and a pronounced heat effect (II) were observed. (II) is $>$ (I), but both are similarly affected by changing variables. They are diminished nearly linearly by increasing wt. of seed crystals, rise to a max. with seed crystals passing 28 mesh per in., increase with increasing rate of cooling, decrease with increasing concn., and decrease to a min. with increasing rate of stirring. A. G.

Formation and properties of precipitates. Theory of co-precipitation. IV—VI. I. M. KOLTHOFF (Chem. Weekblad, 1934, 31, 526—533, 550—558, 598—603; cf. A., 1934, 840).—IV—V. It is not certain that mixed crystal formation occurs in the adsorption of alkali perchlorates and permanganates by BaSO_4 . The geochemical reactions described by O. Hahn and his school may be regarded as involving abnormal mixed crystal formation. The ageing of micro-cryst. ppts. is discussed; it may be due to recrystallisation, with consequent growth of the larger particles; to isolation of the internal active centres by adsorption at the surface, an effect which may be reversed by heating; or to complete change of structure as the result of transition to a more stable form. Heating a ppt. causes internal changes which in the case of amorphous and finely-divided materials may reduce the active surface and adsorptive power, whereas with cryst. materials the tendency is to the production of a more porous ppt.

VI. The hygroscopic properties of Ca oxalate are discussed; the decrease which occurs on ageing of the ppt. before filtration is due to recrystallisation and the growth of perfect crystals, which reduce the active surface. For analytical purposes the Ca solution, should be about 0.1N and have a p_H of 4—6, and should be treated with oxalate at room temp.; if the ppt. is digested at 90° for 20 hr. it contains, when air-dried, only 0.1—0.3% of H_2O . Co-pptn. of Na is $>$ that of K or NH_4^+ . Co-pptn. of alkalis is the greater when the $\text{C}_2\text{O}_4^{2-}$ is in excess, but diminishes with rise of temp.; it varies exponentially with the concn. of the alkali salts. Pptn. by Willard's method, i.e., in such a manner that large crystals are formed, results in greatly reduced co-pptn. Co-pptn. of one ion does not hinder that of a second. Excess of Ca^{++} favours co-pptn. of anions. From neutral solution $\text{Ca}(\text{OH})_2$ is co-pptd., especially at 100° . It is shown that these results are in full accord with the author's theory of co-pptn. H. F. G.

Mechanism of the Liesegang phenomenon. E. C. BAUGHAN (*Nature*, 1934, 134, 778).—The migration of Ag^+ ions under a fixed p.d. into gelatin gels containing NaCl (approx. $0.01N$) gave sets of rings approx. equidistant along the direction of the current. The results support the theory that the phenomenon is due to the de Broglie wave-length of the diffusing mol. species. L. S. T.

Liesegang phenomenon in silicic acid gel. A. T. LINCOLN and J. C. HILLYER (*J. Physical Chem.*, 1934, 38, 907—917).—The formation of banded ppts. of CuCrO_4 , HgI_2 , Hg , PbCrO_4 , PbI_2 , PbSO_4 , and basic Bi dichromate in SiO_2 gel has been studied by keeping the concn. of one of the reacting salts const. in the gel and in the superposed solution in alternate series of experiments, that of the other being varied. In the former case the no. of bands and the depth to which they extend increase with the concn. of salt in the solution. In general, the banding is best and deepest when the ratio of the concn. of salt in the solution to that in the gel is greatest. No bands were obtained with PbBr_2 , $(\text{HCO}_2)_2\text{Pb}$, Bi oxalate, citrate, or iodide. The results indicate the rate of diffusion as the controlling factor in the distribution of the ppt. F. L. U.

Supersaturation theory of the intervals in space and time between Liesegang precipitates. H. BAUER (*Z. physikal. Chem.*, 1934, B, 27, 145—160).—The theory previously developed (A., 1933, 898) has been reconstructed and improved. It now agrees excellently with Morse and Pierce's experimental data (A., 1904, ii, 14). R. C.

Distribution of radioactive substances between crystalline and liquid phases. IX. Distribution of U-X_1 between crystals and solution of $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 100° . A. E. POLESITZKI (*Trans. inst. état radium (U.S.S.R.)*, 1933, 2, 82—86; cf. A., 1932, 1198).—The distribution follows the simple law.

CH. ABS. (e)

Adsorption. Silica gel and its applications. A. TRAVERS (*Bull. Soc. chim.*, 1934, [v], 1, 1281—1304).—A lecture.

Absorption and adsorption of hydrogen by nickel. J. SMITTENBERG (*Rec. trav. chim.*, 1934, 53, 1065—1083; cf. A., 1934, 839).—The absorption (α) of H_2 by Ni wire of diameter 0.022 mm. , evacuated at 900° , has been measured isothermally at 300° and at 600° , at pressures (p) $<$ approx. $1.5 \times 10^{-2}\text{ cm.}$, and isobarically from 20° to 600° at 10^{-2} cm. For the isotherms $\alpha \propto p$ and at const. p increases with rise of temp. in agreement with the results of Sieverts (cf. A., 1911, ii, 895). Equilibrium is established within 3 min. The heat of absorption is calc. from the isobar to be 2.62 kg.-cal. At 90° and 193° abs. a small adsorption occurs, the val. of which depends on the previous heat-treatment of the Ni. The amount of H_2 adsorbed at successively smaller vals. of p is $>$ that adsorbed at the same pressure at successively greater vals. of p (hysteresis), and the same result is obtained with A. The max. adsorption of H_2 corresponds with only 4% of a monat. surface layer. It is inferred that the surface of the Ni is contaminated with impurities. R. S. B.

Adsorption of light and heavy hydrogen on nickel. R. KLAR (*Naturwiss.*, 1934, 22, 822; cf. Pace and Taylor, A., 1934, 1181).—There are considerable differences in the variation of the adsorption velocity (I) of D_2 and H_2 on Ni powder with temp. between 0° and 100° . There is equality in (I) only over a narrow temp. range. A. J. M.

Adsorption of hydrogen and of carbon monoxide on a surface of zinc and molybdenum oxides. H. S. TAYLOR and G. OGDEN (*Trans. Faraday Soc.*, 1934, 30, 1178—1190).—Adsorption isotherms and velocities have been determined for the low-temp. van der Waals and high-temp. activated adsorption of H_2 and CO on a $\text{ZnO-Mo}_2\text{O}_5$ catalyst prepared from Zn NH_4 paramolybdate. The heats of activation and adsorption have been determined. The adsorption of H_2 is $<$ that of CO at low temp., but the reverse is true in the region of activated adsorption. The surface is stable, being only slightly affected by heat-treatment with CO . The addition of Mo_2O_5 to ZnO lowers the catalytic efficiency because the amount of H_2 adsorbed at high temp. is considerably reduced and the activation energy is increased. R. S. B.

Chemistry of solid surfaces. II. Rate of adsorption of hydrogen and deuterium on chromic oxide. H. W. KOHLSCHUTTER (*Z. physikal. Chem.*, 1934, 170, 300—308; cf. A., 1934, 1168, 1181).— H and H^2 are adsorbed at $184^\circ/1\text{ atm.}$ by hydrated Cr_2O_3 acting as a hydrogenation catalyst at equal rates, and this is still the case if the adsorbent has previously taken up larger amounts of H or H^2 . The H^2 reversibly displaces H in the H_2O contained in the adsorbent. R. C.

Clean-up of various gases by magnesium, calcium, and barium. A. L. REIMANN (*Phil. Mag.*, 1934, [vii], 18, 1117—1132).—Pressure variation-time curves for the absorption or clean-up effect of dispersed Mg , Ca , and Ba on O_2 , N_2 , H_2 , CO , and CO_2 in vac. vessels are given. Speed, capacity, temp. effect, mechanism, the re-liberation of gas, and the electric discharge-assisted clean-up of CO by Mg are discussed. N. M. B.

Adsorption of alkali metals on metal surfaces. II. Dipole moment of adsorbed Cs ions; adsorption isotherm. III. Adsorption energy of the ions. J. H. DE BOER and C. F. VEENEMANS (*Physica*, 1934, 1, 953—959, 960—965).—II. The lowering of the work function by Cs^+ adsorbed on W (cf. A., 1934, 1066) has been calc. and the results are compared with Langmuir's theory (*Physical Rev.*, 1933, [ii], 44, 423). The energy of evaporation of Cs atoms, the adsorption isotherm, and the relation between the electron emission of a W filament covered by Cs and the v.p. of Cs have been deduced.

III. After the formation of a double layer on the surface of W by Cs^+ , additional Cs^+ will be attached more strongly on account of the electrical field formed. This increase in adsorption energy has been calc. and the expression for electron emission has been modified to conform with this increase. M. S. B.

Chemisorption on charcoal. IV. Influence of activation on the sorption of water vapour.

A. KING and C. G. LAWSON (Trans. Faraday Soc., 1934, 30, 1094—1103).—The increase in wt. in air of 31–85% R.H. of purified sugar C, outgassed at 1000° and activated at temp. between 17° and 900° in a stream of O₂, has been determined. At low humidities the total adsorption by C activated at 385° is > that by C activated at 880°, but this relation is reversed at high humidities. Higher rates of flow of O₂ during activation and exposure of the C to air (I) increase the rate and amount of adsorption. The effect of (I) is attributed to chemisorption of O₂ and the formation of a low-temp. oxide. As the temp. of activation, T_a , is raised, the rate of adsorption rises to a max. which probably corresponds with the highest temp. at which the acidic oxide of C oxidised at 200–500° is stable. The adsorption of I, AcOH, and NH₃ increases with rise of T_a , but that of NH₃ is almost const. with T_a > 450°, showing that there is less adsorption per unit area at the higher temp. The initial rate of adsorption of AcOH and NH₃ is max. with T_a approx. 450°. The data are interpreted in terms of the acidic surface oxide formed at T_a 200–600°, and another oxide existing at higher temp. J. G. A. G.

Adsorption of oxygen by platinum, ferric oxide, and chromium oxide. B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1934, 40, 754–764).—Adsorption is normal with Fe₂O₃ and Cr₂O₃ so long as chemical reaction does not occur; with Cr₂O₃ reaction begins at 65°. With Pt, dissolution of at. O occurs in addition to adsorption. Measurements between 20° and 400° at different pressures are in fair agreement with Langmuir's equation. On the basis of these results and those for the adsorption of SO₂ (cf. following abstract) a mechanism for the catalytic combination of SO₂ and O₂ is proposed. E. S. H.

Adsorption of sulphurous acid by vanadium pentoxide. B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1934, 40, 764–765).—The form of the adsorption isotherms indicates that the reaction $V_2O_5 + SO_2 = V_2O_4 + SO_3$ occurs. E. S. H.

Activated adsorption of hydrocarbons. J. TURKEVICH and H. S. TAYLOR (J. Amer. Chem. Soc., 1934, 56, 2254–2259).—The changes which occur in the adsorption of C₂H₄, C₂H₆, CH₄, and C₃H₈ on MnO–Cr₂O₃ and of C₂H₄ on active Cu have been examined at –78.5° to 444°. The results are interpreted in terms of activated adsorption and C₂H₄ decomp. The adsorption measurements define the conditions for exchange reactions between H₂ and C₂H₄ or C₂H₆. E. S. H.

Adsorption from solution. II. Adsorption of styphnic acid by activated sugar charcoal. L. T'SAI and H. YU (J. Chinese Chem. Soc., 1934, 2, 193–197).—The adsorption isotherm consists of five sections, each of which satisfies the Langmuir equation. A. G.

Adsorption by precipitated barium sulphate. E. G. R. ARDAGH, R. E. RICHARDSON, L. A. RICHARDSON, and C. M. HUMBER (Chem. and Ind., 1934, 1035–1041). The influence of temp., acidity, and presence of NH₄Cl on the shape of pptd. BaSO₄ crystals has been investigated. Conditions for the production of perfect, orthorhombic crystals have been worked out;

such crystals remain colourless when formed in presence of a dye, whilst irregular crystals are always stained uniformly throughout. Adsorption probably occurs during brief periods in which a change in the manner of crystal growth occurs. The error in the gravimetric determination of Ba⁺⁺ and SO₄⁼⁼ is probably reduced under conditions such that the bulk of the ppt. consists of orthorhombic crystals. E. S. H.

Adsorbing power of manganese for ionium. A. N. PULKOV (Trans. inst. métrol. stand. U.R.S.S., 1934, No. 6, 13–20).—MnO₂ is pptd. from the solution by treating with H₂SO₄ (*d* 1.84) and then with (NH₄)₂S₂O₈. The MnO₂ carries down with it the Io and its isotope U-X₁. MnO₂ is superior to Ce(C₂O₄)₃ as an adsorbent. CH. ABS. (e)

Sorption of vapours by ferric oxide gel. I. Aliphatic alcohols. A. G. FOSTER (Proc. Roy. Soc., 1934, A, 147, 128–140).—Isothermals of MeOH, EtOH, PrⁿOH, PrⁱOH, and BuⁿOH on Fe₂O₃ gel have been determined at 25°. All show a large hysteresis loop extending over nearly half the entire range. The relative pressures at which hysteresis occurs decrease from MeOH to BuOH, but the capillary radius remains const. at about 22 Å. The amounts of the different alcohols adsorbed at corresponding pressures below about 0.01 of the saturation val. or their mol. wts. The evidence suggests that the surface is covered by an adsorbed unimol. layer. With BuOH this process is followed immediately by capillary condensation, but with the lower alcohols there is a tendency to form a second layer. L. L. B.

Adsorption of water by silica gel and an examination of Patrick's adsorption formula. R. C. RAY and P. B. GANGULY (Trans. Faraday Soc., 1934, 30, 997–1007).—The adsorption isotherms for H₂O vapour on SiO₂ gel in an air-free system at 32° and 40° conform to the Freundlich equation except at pressures approaching saturation. The utility of Patrick's formula is limited, since the consts. vary with factors other than the structure of the gel. The heat of wetting, *W*, decreases linearly with increasing H₂O content of the gel. Since *W* is almost identical with the heat of adsorption and is zero at the saturation point, which corresponds with the composition 2H₂O : SiO₂, the formation of an unstable adsorption compound is inferred. J. G. A. G.

Adsorption of gases by chromium oxide gel. J. HOWARD and H. S. TAYLOR (J. Amer. Chem. Soc., 1934, 56, 2259–2264).—Isotherms have been obtained for van der Waals adsorption of N₂ and C₂H₆ over a wide temp. range, for H₂ and He at 85° and 194.5° abs., and for C₂H₄ at 194.5° abs. on Cr₂O₃ gel. The corresponding heats of adsorption have been calc. The rates of activated adsorption of H₂ (373–457° abs.) and C₂H₄ (353° and 388° abs.) by Cr₂O₃ gel have been measured and the activation energies calc. The decomp. of C₂H₄ associated with activated adsorption at high temp. has been studied analytically. On surfaces similar in area, as deduced from van der Waals adsorption, there is a variable proportionality factor between velocity of activated adsorption and the activation energy term in the kinetic expression for velocity of adsorption. The rate of

activated adsorption is the rate-determining stage in the hydrogenation of ethylene; variations in this rate account for differences in the observed activities of various oxides. E. S. H.

Adsorption of methylamine on silica gel, alumina gel, and charcoal. Heats of adsorption of ammonia and the methylamines on silica gel. W. A. FELSING and C. T. ASHBY (J. Amer. Chem. Soc., 1934, 56, 2226—2229).—Adsorption isotherms have been determined at 0°, 30°, and 40°. The heats of adsorption by SiO₂ gel at 25° are: NH₃ 14.8, NH₄Me 18.7, NMe₃ 19.0, NHMe₂ 20.1 kg.-cal. E. S. H.

Reaction metal hydroxide solution-cellulose fibre; comparison of X-ray results with equilibrium measurements of the metal hydroxide distribution in the system fibre-solution. W. SCHRAMMEK [with H. VELTEN, C. SCHUBERT, H. NEUMANN, and O. VIERTTEL] (Kolloid-Beih., 1934, 40, 87—157).—The adsorption of NaOH in aq. solution at different concns. by cellulose (I) has been measured under various conditions, and the X-ray diagram of the product investigated. In < 8% NaOH native (I) and (I) hydrate behave in accordance with Langmuir's adsorption isotherm; raw (I) adsorbs NaOH more strongly than does the pure material; in this region of concn. none of the forms of (I) gives a changed X-ray pattern. In > 8% NaOH, pure and raw native (I), (I) hydrate, and ramie show a change in the X-ray diagram, which is traced to the formation of Na-(I). The various equilibria and reactions involved are discussed. E. S. H.

Swelling of charcoal. III. Experiments with lower alcohols. D. H. BANGHAM, N. FAKHOURY, and A. F. MOHAMED. IV. Stoichiometric relations for the films of the alcohols. D. H. BANGHAM (Proc. Roy. Soc., 1934, A, 147, 152—175, 175—188; cf. A., 1932, 1199).—III. Adsorption-expansion measurements carried out with MeOH, EtOH, PrOH, BuOH, and pinewood charcoal, using the apparatus and technique previously described (*loc. cit.*), confirm the view that the expansion \propto the surface pressure of the adsorbed phase. The Gibbs equation holds for EtOH and MeOH, except at low pressures. The straight-chain alcohols form two types of film, "primary" and "annealed"; transition from the former to the latter occurs more rapidly at high temp. than at low. A comparison of the expansion data with those for the lowering of the surface tension of Hg by the vapours of the same alcohols reveals so much resemblance as to indicate a similarity of mechanism in the two cases. The branched-chain alcohols give rise to larger expansions than their straight-chain isomerides and have also a much slower rate of adsorption.

IV. A study of the "annealed" films of MeOH, EtOH, PrOH, and BuOH on charcoal shows that the amounts of each alcohol causing equal expansions of the charcoal are equal. Comparison of the expansion data with the data of Cassel and Salditt (A., 1931, 1120) for the films on Hg indicates that on Hg also there occurs, with rise of concn., a transition from the primary to the annealed type of film. The primary films are probably unimol., whilst the thick-

ness of the annealed films \approx about 2 C chains. Coeffs. of thermal dilatation and compressibility are calc. for the annealed films of the *n*-alcohols. L. L. B.

Influence of surface tension on the rate of rise of aqueous solutions in porous bodies. P. BERTHIER (Compt. rend., 1934, 199, 1221—1223).—Data are recorded for the wetting of filter-paper by aq. camphor, isoamyl alcohol, menthol, and saponin. Comparison with vals. for H₂O shows that the rate is independent of the surface tension of the solution and is the same as for H₂O. H. J. E.

Surface tension and tangential pressure in the capillary film in connexion with the osmotic pressure in the film theory of Pockels, Langmuir, and Adam. G. BAKKER (Z. physikal. Chem., 1934, 171, 49—69).—It is shown from purely mechanical considerations that in the surface film of a liquid there is a tangential pressure, p_T , connected with the normal pressure, p_N , surface tension, γ , and thickness of the film, ζ , by $\gamma = (p_N - p_T)\zeta$. $p_T < p_N$ and for low temp. is negative and may be numerically very large. For a pure liquid in equilibrium with its vapour p_N is the v.p. and p_T can be calc. from the equation of state. It is calc. that at low temp. $\zeta \sim 2-3$, and at a reduced temp. of 0.9 $\sim 4-5$ mol. diameters. The thermodynamic potential is the same in the surface film and in the two extended phases. In Langmuir's trough apparatus for studying insol. films on H₂O the force experienced by the movable barrier is equal to the difference between the vals. of $p_T\zeta$ for the two sides. For a gaseous film this leads to Adam and Jessop's osmotic pressure formula. R. C.

Applications of a method of capillary analysis. R. DUBRISAY (Compt. rend., 1934, 199, 1304—1305; cf. A., 1934, 728).—Data are recorded for changes in the interfacial tension between a C₆H₆ solution of sapamine and H₂O due to the solubility of MgO in H₂O, to the acids formed in the photo-oxidation of alcohols, and to the solubility of glass in H₂O. H. J. E.

Why does water wet glass? M. HOLDERER (Compt. rend., 1934, 199, 1046).—The wetting of glass by H₂O is attributed to the affinity between O atoms combined in the glass and the O atoms of unassociated H₂O mols. Similar affinity explains why Hg adheres at certain points to glass in presence of a trace of HgO. J. W. S.

Structure of monolayers of myristic acid. Erratum. N. W. H. ADDINK (J. Chem. Physics, 1934, 2, 822; cf. A., 1934, 1169). F. L. U.

Quantitative correlation of interfacial free surface energies. F. E. BARTELL and L. S. BARTELL (J. Amer. Chem. Soc., 1934, 56, 2205—2210).—Theoretical. A linear relation between the cosine of the interfacial angle and the adhesion tension of any given liquid for a series of solids has been established. Equations are developed by which the adhesion tension of a solid for any liquid can be calc. from a single measurement of adhesion tension or of contact angle for the solid and a given liquid. E. S. H.

Properties of albumin in unimolecular layers. E. GORTER [with G. M. PHILIPPI] (Chem. Weekblad,

1934, 31, 586—589).—When albumin solution (5 mg. per c.c.) is allowed to flow on to the surface of 0.1*N*-HCl, a film about 7.5 Å. thick is formed. With casein the max. spreading is obtained at the isoelectric p_H and below p_H 2, and the min. at p_H 3.6, whilst with pepsin the min. is at p_H 6. The influence of electrolytes on the spreading shows that at the max. the $\cdot\text{CO}\cdot\text{NH}\cdot$ groups lie on the surface, and that at the min. ionisation occurs. These views are confirmed by measurements with a long-chain tripeptide (from α -amino-octioic acid), which spreads to the extent of 1.2 m.² per mg.; the area is increased in acid solution by cations, and at p_H 8 by anions.

H. F. G.

Validity of Antonov's rule. E. G. CARTER and D. C. JONES (Trans. Faraday Soc., 1934, 30, 1027—1038).—With very carefully purified materials and with special precautions for keeping the liquid phases saturated, it is found that Antonov's rule is followed by the systems of H₂O with C₆H₆, PhNO₂, COEt₂, and *o*-C₆H₄Me·OMe. Systems which do not conform involve either (1) org. substances which have a negative initial spreading coeff., *S*, on H₂O, e.g., CH₂I₂, CS₂, or (2) org. substances which have high initial *S* on H₂O and for which the final *S* is not zero but negative, e.g., C₇H₁₅·OH, isoamyl alcohol, Bu^oOH, and *m*-cresol. The non-conformity with the "rule" is attributed to an oriented adsorption film on the saturated aq. phase.

J. G. A. G.

Streaming potentials using paraffin capillaries. H. R. KRUYT and R. RUYSSSEN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 498—505).—The electrokinetic ζ -potentials are calc. from the p.d. between the ends of a paraffin wax capillary through which 0—1*M*-KCl, -BaCl₂, -AlCl₃, and -Th(NO₃)₄ is forced under pressure. With KCl, ζ has a max. at 0.1*M*; BaCl₂ affords a sharp max. at 0.005*M* and a min. at 0.2*M*. Paraffin wax is charged positively by AlCl₃ and Th(NO₃)₄ except at very low concn. The differences observed in earlier work (A., 1928, 1091) are attributed to the chemical properties of glass.

J. G. A. G.

Electric potential and charge of dissolved and adsorbed proteins. H. A. ABRAMSON (Cold Spring Harbor Symposium Quant. Biol., 1933, 1, 39—50).—A study of the electric potential of ovalbumin, serum-albumin, caseinogen, and insulin, and of the effects thereon of various ions and alcohols.

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Dielectric potentials of physiologically-active substances. B. KAMIENSKI (Nature, 1934, 134, 776).—The potential (I) at the interface solution-air is large at low concns. compared with that for other substances. Vals. for quinine, cinchonine, cinchonidine, and morphine are given. (I) changes with [H⁺]. The *d*- and *l*-isomerides of the same substance have different vals.

L. S. T.

Electrical potential of amorphous and crystalline amphoteric surfaces in liquids. O. WINTERSTEINER and H. A. ABRAMSON (Physical Rev., 1933, [ii], 43, 372—373).—The electric mobility of crystals of insulin (I) has been compared with that of amorphous (I), adsorbed or in particle form.

L. S. T.

Influence of the dielectric constant of the medium on the potential and charge of a protein surface in a liquid. H. A. ABRAMSON and J. DANIEL (Physical Rev., 1933, [ii], 43, 773).—Correlation of the surface potential and surface charge calc. from the observed electric mobilities of microscopic quartz particles covered with a film of adsorbed protein in different concns. of EtOH, with the charge obtained by the thermodynamic method indicates that the characterisation by the two parameters η and ϵ of the solvent in the Helmholtz-Debye theory is correct. The data are considered in relation to their biological importance, particularly in connexion with cell permeability.

L. S. T.

Cataphoresis of gliadin. I. Adsorption of gliadin on quartz. II. Effect of strong electrolytes on the mobility. I. KEMP and E. K. RIDEAL (Proc. Roy. Soc., 1934, A, 147, 1—10, 11—24).—I. The velocity of adsorption of gliadin mols. at the surface of suspended quartz particles is unimol. Preferential adsorption of gliadin occurs at the gliadin-liquid interface. The electrical work function at the quartz-liquid interface is of the order of the measured electrokinetic potential.

II. The acid and basic dissociation consts. of gliadin are calc. from mobility- p_H curves and titration data. The isoelectric point is dependent on the ionic strength of the medium, and the no. of OAc' adsorbed per mol. of gliadin are computed from the shifts of the isoelectric point. The Debye-Huckel expression for cataphoretic velocity is applicable to the systems investigated over a limited range of concns. The application of a correction for ionic adsorption gives good agreement with theory for conc. solutions, but with more dil. solutions the decrease of the effective surface charge on the protein owing to the existence of a Donnan ionic equilibrium between ions inside and outside the double layer must be considered.

L. L. B.

Electro-osmosis. V. S. IMAI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1351—1362).—The electrokinetic potentials of liquid org. compounds have been determined by measuring the electro-osmotic velocity through sintered SiO₂ diaphragms, and are < the vals. obtained using a diaphragm of hard glass powder.

R. S. B.

F.p. of aqueous solutions. VIII. Mixtures of sodium chloride with glycine and ethyl alcohol. IX. Mixtures of the reciprocal salt pair potassium nitrate-lithium chloride. G. SCATCHARD and S. S. PRENTISS (J. Amer. Chem. Soc., 1934, 56, 2314—2319, 2320—2326; cf. A., 1934, 963).—VIII. The analytical expression of the thermodynamic functions of dil. solutions has been extended to solutions containing ions. Measurements of f.p. depressions of mixed aq. solutions of NaCl with glycine and EtOH are treated by this method and the results compared with other properties of the solutions.

IX. F.p. measurements have been made for aq. solutions of all the possible mixtures of the reciprocal salt pair KNO₃-KCl. The derivation of the coeffs. for the sp. interaction of ions is extended to the coeffs. of the higher powers of the concn. The parameters necessary to determine the thermodynamic functions

of any mixture of this reciprocal salt pair agree with the extended theory of Brönsted. E. S. H.

Apparent volume of salts in solution and their compressibilities. A. F. SCOTT and R. W. WILSON (J. Physical Chem., 1934, 38, 951—977).—Masson's empirical equation (A., 1930, 31) connecting apparent mol. vol. of a solute with its concn. is shown to be valid for solutions under high pressures. A relationship between apparent mol. compressibility (B) and concn. derived from this equation is employed to determine B of a solute at infinite dilution, using experimental data for alkali metal halides (cf. following abstract). The results are discussed from the point of view of contraction of the solvent caused by the solute.

F. L. U.

Compressibility coefficients of solutions of alkali halides. A. F. SCOTT, V. M. OBERHAUS, and R. W. WILSON (J. Physical Chem., 1934, 38, 931—940; cf. A., 1933, 556).—Compressibility coeffs. (B) of aq. solutions of LiCl, LiBr, NaCl, NaBr, NaI, KCl, KBr, and KI have been determined at different concns. The B -concn. curves of the Li salts show discontinuities.

F. L. U.

Viscosity and fluidity of lithium chloride in acetone solution. G. R. HOOD and L. P. HOHLFELDER (J. Physical Chem., 1934, 38, 979—986).—Measurements have been made over the range 0.004—0.274*M* at 18° and 0.008—0.271*M* at 25°. The results are discussed from the point of view of interionic forces and of solvation.

F. L. U.

Effect of magnetic field on Brownian movement. J. METADIER (Compt. rend., 1934, 199, 1196—1198).—With fields $> 20,000$ gauss no effect on the Brownian movement was observed for emulsions of Prussian-blue, Fe(OH)₃, chrome-yellow, or gamboge.

H. J. E.

Derivation of distribution functions in problems of Brownian motion. L. S. ORNSTEIN and W. R. VAN WIJK (Physica, 1934, 1, 966).—Corrections (cf. A., 1934, 486).

M. S. B.

Dynamic investigations of colloidal systems. I. Basis and method of investigation of mechanical properties of solutions of organic compounds of high mol. wt. II. Determination of the dynamic viscosity of Cellite solutions and derivation of a dispersion formula. W. PHILIPPOFF (Physikal. Z., 1934, 35, 884—900, 900—905).—I. From streaming and relaxation experiments, and the dependence of the dynamic viscosity (η) and of the deformation resistance on frequency, a complete picture of the mechanical behaviour of a system may be obtained. A method for the determination of the abs. viscosity of viscous liquids (10—1000 c.g.s.) under the influence of a high-frequency field is described. (I) of honey, gum-arabic (44% solution in H₂O), glycerol (II), and aq. solutions of (II) is independent of frequency and agrees with the static viscosity. (I) of an 8% solution of Cellite in dioxan, however, decreases considerably with frequency.

II. The variation of (η) with frequency, of solutions of Cellite in dioxan is given by $\eta = \eta_0[1 + (\omega\tau)^2]^{-1}$, where ω is frequency and τ the relaxation time. The Maxwell relationship, $\tau = \eta_{\text{stat}}/\gamma$, where γ is the modulus

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of elasticity, holds. γ calc. from this formula agrees with the vals. obtained by Rabinovitsch (A., 1933, 1115) by a capillary method.

A. J. M.

Measurement of the viscosity of hydrophilic sols. H. G. B. DE JONG (Chem. Weekblad, 1934, 31, 584—586).—Limitations of the simple Einstein expression, the influence on viscosity of solvation and desolvation, and the electroviscous effect are discussed.

H. F. G.

Lowering the viscosity of cellulose nitrate. I. Action of strong and weak bases. S. N. DANILOV and L. I. MIRLAS (J. Gen. Chem. Russ., 1934, 4, 817—829).—For COMe₂ solutions of cellulose nitrate (I) is lowered to a greater degree by weak (aq. NH₃, C₂H₅N) than by equiv. concns. of strong bases (NaOH). The action of bases consists in partial denitration, with oxidation of cellulose by NO₃' with production of NO₂'. At the same time, the micellar structure of unchanged (I) is loosened, owing to formation of labile complexes of (I) with weak bases. 90% of (I) becomes EtOH-sol. after treatment with 0.2% aq. NH₃, the product being a heterogeneous mixture of (I) of different N contents and degrees of dispersion.

R. T.

Theory of lyosorption phenomena. E. LANDT (Z. physikal. Chem., 1934, 171, 119—120).—Comments are made on recent papers (cf. A., 1934, 960), and the part played by attractive forces between the particles in determining the settled vol. of a powder suspended in a liquid is emphasised.

R. C.

Physico-chemical transformation of gum-arabic sols on heating. A. BOUTARIC and (MILLER) M. ROY (Compt. rend., 1934, 199, 1219—1221).—Vals. are recorded for the change in viscosity, optical d , and surface tension after varied periods of boiling. The sols should be classed as micelles (I) and not as mol. colloids. Boiling causes hydrolysis and a growth of (I).

H. J. E.

Physico-chemical studies on gum-arabic solutions. D. R. BRIGGS (J. Physical Chem., 1934, 38, 867—881).—The equiv. conductivity of electro-dialysed arabic acid (I) solutions shows a max. at very high dilution, whilst the Li, Na, K, and Ca salts show min. at about 0.0025 equiv. per litre. This behaviour, which bears a superficial resemblance to that of soaps, is explained by the varying mobility of the cations as the solution is diluted, since the current is carried chiefly by these, and with the strychnine salt no min. is observed. The ionisation "const." of (I) decreases with dilution from 10^{-3} to 2×10^{-7} . The titration curve shows only one buffer range. (I) does not, however, act as a monobasic acid, but as one having several acid groups of rather uniformly graded strengths.

Soya lecithin. IV. Emulsifying action for oil-water mixtures. V. Properties of lecithin soap solutions. T. INABA, K. KITAGAWA, and M. SATO (J. Soc. Chem. Ind. Japan, 1934, 37, 595B).—With increasing concn., η of lecithin (I) solution increases and drop vol. against soya-bean oil (II) falls. (II) also falls with rising temp. (I) added to Na soap solution increases surface tension, foam no., stability, and Au no.; it lowers the turbidity and clearing temp.

by 3—5°. The drop no. against kerosene passes through a max. at 0.25% (I). G. H. C.

Variation in the capacity for [ionic] exchange of colloidal clay. A. L. S. BAR and H. J. C. TENDELOO (Rec. trav. chim., 1934, 53, 1128—1132).—Theoretical. The theory of Verwy and Kruyt (cf. A., 1934, 143) affords a quant. explanation of the increase in the capacity for ionic exchange (E) of colloidal clay after treatment with alkali in terms of changes in the electrical double layer; increase in $E \propto$ increase in the concn. of the potential-determining electrolyte on the clay surface. R. S. B.

Surface studies on ferric oxide by the emanation method. O. HAHN and V. SENFTNER (Z. physikal. Chem., 1934, 170, 191—211).—The changes in structure and surface of Fe_2O_3 gels when the temp., T , is progressively raised have been followed. With rise in T the surface, S , gradually decreases due to shrinkage caused by loss of adsorbed H_2O , but at about 400°, corresponding with the "glow temp." of Fe_2O_3 , there is a sudden rapid fall in S . There is then a slower decrease up to about 850°, when there is a further abrupt fall in S due to expulsion from the lattice of the last traces of H_2O followed by rapid recrystallisation to the pure hæmatite lattice. The amount of H_2O eliminated at this point is very small and varies with the history of the specimen; with an alcogel there is none, or very little compared with a gel aged under H_2O . Above about 1000° the increasing vigour of mol. motions causes a loosening of the lattice. The behaviour of co-pptd. mixtures of Fe_2O_3 and Al_2O_3 is similar to that of Fe_2O_3 if the proportion of Al_2O_3 is $>$ the solubility in Fe_2O_3 ; an excess of Al_2O_3 acts as a foreign substance. Artificial admixture of Al_2O_3 with Fe_2O_3 markedly hinders recrystallisation of the latter. ThO_2 gel behaves on heating like Fe_2O_3 gel, whilst $\text{Th}(\text{C}_2\text{O}_4)_2$ behaves quite differently. R. C.

Lyophilic colloids. XXIII. Heats of wetting and gelation of gelatin. L. W. J. HOLLEMAN, H. G. B. DE JONG, and R. S. T. MODDERMAN (Kolloid-Beih., 1934, 40, 211—240; cf. A., 1934, 842).—Determinations of heat changes in the system gelatin- H_2O as a function of H_2O content and temp. show that two effects can be distinguished. By progressively adding H_2O to gelatin, heat is evolved independently of temp.; this is regarded as heat of hydration. At const. H_2O content ($>$ a crit. val.) lowering of temp. causes evolution of heat over a certain temp. range. This quantity is traced to a transformation in the system and is regarded as heat of gelation. E. S. H.

Diffusion of electrolytes in silica gel. F. H. MACDOUGALL (J. Physical Chem., 1934, 38, 945—949).—A discussion of a paper by Patrick and Allan (A., 1934, 842), whose experiments on diffusion in SiO_2 gel are shown to be in quant. agreement with Nernst's theory. F. L. U.

Properties and structure of solutions of gum gels. L. AMY (Ann. Chim., 1934, [xi], 2, 287—414).—The sol. gum arabic and the insol. cherry-tree gum have been examined and compared. By electro-dialysing gum arabic the mineral constituents are removed and there remains a gel which readily breaks

up into a sol. portion, arabin, and an insol. gel. Arabin is very unstable and is readily hydrolysed, especially when heated, forming a reducing solution; it is a true acid and may be called arabic acid (I). It has not, however, a definite composition, since variations in equiv. wt., rotatory power, viscosity (η), conductivity (Λ), etc., with variation in origin, are observed, or even exist between different samples of the same origin. E.m.f. measurements give a dissociation const. of 2×10^{-4} at 19°, but $[\text{H}^+]$ in partly neutralised solutions of (I) varies much more rapidly on dilution than is accounted for by the ordinary dissociation theory. This effect is inhibited by neutral salts. η increases as neutralisation proceeds and is a linear function of the no. of real or apparent positive ions in the solution. Addition of excess of base or of neutral salts diminishes η . Λ in a partly neutralised solution is of the same order as in solutions of dialysable salts. It also varies with time. The diffusion of aq. Na arabate conforms to Fick's law at concn. below 1%. There is a sudden change above this concn. and a surface of separation is formed. Dehydration of (I) forms an acid gel, metagummic acid, of the same degree of acidity. Addition of alkali causes swelling, the slightest excess resulting in peptisation and re-formation of the arabate. The gel extracted from the natural gum behaves similarly. The insol. org. part of cherry-tree gum forms a gel with acid properties, cerasic acid (II), behaving towards bases in the same way as (I). It has two dissociation consts., 3.0×10^{-4} and 10^{-5} — 10^{-6} , at 25°, determined by e.m.f. measurements with and without the addition of an auxiliary salt. The second dissociation const. may be due to an impurity, since there is no simple relation between the amounts of base necessary for neutralisation of the separate stages. The gel swells as neutralisation proceeds. Addition of a neutral electrolyte produces contraction. By fine grinding, a suspension of (II), with properties very similar to those of (I), may be obtained. The resemblance is especially remarkable in the variation of Λ with dilution, and of η on the addition of an electrolyte. The colorimetric determination of $[\text{H}^+]$ by indicators, in a suspension of (II), results in considerable differences, according as the whole suspension or the intergranular liquid is taken into account. The similarity of the behaviour of (II) and (I) may be interpreted by assuming that arabates exist in solution, to a large extent, in the form of microscopic particles of swollen gel, filling the whole vol. available when the concn. is above 1%.

M. S. B.

Pectin. III. General theory of pectin jelly formation. A. G. OLSEN (J. Physical Chem., 1934, 38, 919—930; cf. B., 1933, 650).—The influence of sugar concn. (S), p_{H} , length of interval between mixing and pouring, and temp. on the strength of apple pectin jellies has been determined. As with citrus pectin, the effect of low acidity can be compensated by increasing S . Adopting Kruyt's theory of stability factors, the sugar is regarded as a dehydrating agent, and the acid as a discharging electrolyte. With low S , low temp., or short interval between mixing and pouring, an optimum p_{H} is no longer observed. The greater strength of jellies rapidly prepared at 55°, compared with that obtained by the boiling method, is not due

to hydrolysis of pectin at the higher temp., but to structural differences in the pectin network.

F. L. U.

Colloidal behaviour of sericin. VI. Colloidal behaviour of sericin-*A* and -*B*. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 461—474; cf. A., 1934, 1306).—When pptd. sericins are added to acid or alkaline solutions they combine stoichiometrically with the acid or alkali. The solubility is least at 4.5, which corresponds with the isoelectric point of natural sericin. The electric cataphoresis and the effect of salts on the cataphoretic velocity of the sericins have been studied. Sericin-*A* has greater protective action than sericin-*B*, and is more sensitive to heat, being converted gradually into sericin-*B* by heating. Apparent sp. gr. at 15°, colour reactions, biuret reaction, fluorescence in ultra-violet light, and swelling phenomena with changes of medium and temp. are discussed.

W. R. A.

Physical chemistry of starch and bread making. XXII. Comparative study of retrogression of starch pastes from various native starches by means of X-ray diagrams. J. R. KATZ [with T. B. VAN ITALLIE]. XXIII. Effect of alcohol concentration on X-ray diagram retrogression of starch pastes containing alcohol. (Preparation of starch for X-ray examination by dehydration with alcohol.) J. R. KATZ [with T. B. VAN ITALLIE and A. WEIDINGER] (Z. physikal. Chem., 1934, 170, 421—429, 430—439; cf. A., 1930, 1126; 1934, 1069).—XXII. Starch paste from the most diverse native starches retrogresses at room temp. to a state with a *B* diagram, observed with preps. dehydrated by means of EtOH, but the rate of appearance of the *B* diagram varies considerably with the variety of starch. Wheat starch paste, and *Gramineæ* starch pastes generally, retrogress much more slowly than paste of native starches with a *B* or *C* diagram.

XXIII. Addition of ~15 vol.-% EtOH markedly accelerates retrogression, as revealed by the X-ray diagram, whilst with >50% EtOH retrogression is delayed or suppressed. This is to be correlated with the observation that with increase in the amount of H₂O in starch paste free from EtOH the rate of retrogression passes through a max.; the action of the EtOH depends primarily on dehydration, but EtOH is also adsorbed. The technique of EtOH dehydration of starch pastes is described.

R. C.

Equilibrium constant of $\text{HH}^2\text{O} + \text{H}_2 = \text{H}_2\text{O} + \text{HH}^2$. T. FORSTER (Z. physikal. Chem., 1934, B, 27, 1—5).—The equilibrium const. has been calc. from spectroscopic data (cf. A., 1934, 1070). The calc. and observed vals. agree better if the zero point energy of HH²O is derived from the fundamental frequencies of H₂O, allowing for the difference in mass, than if it is deduced from the observed frequencies for HH²O.

R. C.

"Isotopic equilibria" in the hydrogen-hydrogen oxide system. R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1934, 2, 735—738; cf. A., 1934, 1070).—The distribution of H₂ between H₂ and H₂O has been determined at the temp. of boiling S and in presence of Pt. The amounts found agree with those

given by the equilibrium const. which have been calc. for the reactions involved.

F. L. U.

Equilibrium $\text{H}_2\text{O} + \text{HH}^2 = \text{HH}^2\text{O} + \text{H}_2$. L. FARKAS and A. FARKAS (Trans. Faraday Soc., 1934, 30, 1071—1079).—The establishment of the equilibrium of H₂ with heavy H₂O and heavy steam of known H² content has been investigated in the presence of Pt catalysts. The vapour-phase equilibrium const., $K = [\text{HH}^2\text{O}][\text{H}_2]/[\text{H}_2\text{O}][\text{H}^2]$ in the range 3—450° is given by $\log_{10} K = -0.1335 + 750/2.3RT$. The difference between the zero point energies of H₂O and HH²O is 1567 g.-cal., compared with the val. 1704 derived from spectroscopic data.

J. G. A. G.

Esterification constant in the gas phase co-existing with the liquid phase. W. SWIENIOWSKI and J. SALCEWICZ (Compt. rend., 1934, 199, 1308—1310).—Vals. of the const. for EtOAc (70—300°) are recorded.

H. J. E.

Theory of strong electrolyte solutions. J. G. KIRKWOOD (J. Chem. Physics, 1934, 2, 767—781).—Mathematical. A detailed investigation of the quant. importance of the approximations involved in the derivation of the Debye-Hückel equations confirms the validity of the theory within the limitations originally imposed.

F. L. U.

Two theorems concerning electrolytes. R. M. FUOSS (J. Chem. Physics, 1934, 2, 818—821).—(1) Fluctuations in the total electrostatic energy of the free ions of an electrolytic solution as calc. by the theory of Debye and Hückel are negligibly small at concns. at which the thermodynamic properties of the solution are measurably different from those of the solvent. (2) A new proof of the theorem that the free energy = 2/3 of the average electrostatic energy is given.

F. L. U.

Strength of acids. E. DARMOIS and Y. K. HENG (Compt. rend., 1934, 199, 1123—1125).—A method of measuring the strength of acids in terms of the lowering (I) of the rotatory power of NH₄ tetramolybdomalate is developed. (I) ∝ the strength of the acid. Data for HCl, HClO₄, and PhSO₃H are recorded.

H. J. E.

Thermodynamic primary dissociation constants of some normal dibasic acids at 25°. A. I. VOGEL and G. H. JEFFERY (Chem. and Ind., 1934, 964).—A preliminary note on the primary dissociation const., K_1 , of the dibasic acids (CH₂)_{*n*}(CO₂H)₂ for *n* = 1—6. The vals. of $K_1 \times 10^5$ are: 139.7, 6.626, 4.535, 3.715, 3.097, and 2.994, respectively.

O. J. W.

Dissociation constants of dicarboxylic acids. Strain relations in dicyclic systems. H. BODE (Z. physikal. Chem., 1934, 170, 231—252).—The first and second dissociation const. of various dicyclic dicarboxylic acids have been determined and used to calculate the effect of the CO₂H groups on each other through the mol., and thus the amount of strain. The results indicate that strain present in the mol. is operative only in the direction of the plane containing the C atoms which cause the strain. In cyclopoly-methylenedicarboxylic acids the interaction of the CO₂H groups increases with increasing strain for the

cis-acids, and falls for the *trans*-acids, and is apparently transmitted wholly through the solvent.

R. C.

Ionisation constants of the tartaric acids and the nature of borotartaric acids. I. JONES and F. G. SOPER (J.C.S., 1934, 1836—1842).—The first and second ionisation consts. of *d*- and meso-tartaric acids have been determined for ionic strengths 0.016—0.0016, and at temp. 25°, 50°, and 74°, electrometrically. The use of the liquid-liquid junction has been avoided by employing, as reference electrode, Ag-AgCl immersed in the acid mixture containing const. $[Cl^-]$. K_1 and K_2 for the *d*-acid are $>$ for the meso-acid, but the ratio of the two consts. for the meso- is $>$ for *d*-acid. With rise of temp. K_2 decreases and K_1 increases to a max. and then decreases, for both acids. The difference in K_1 for the two acids indicates the absence of free rotation, and may be explained on the basis of a difference of internal co-ordination as a result of the spatial configuration. Electrometric titrations of the two acids have also been carried out in the presence of different amounts of H_3BO_3 . The secondary ionisation of both acids is increased. The configuration of the complex borotartaric acids is discussed.

M. S. B.

Dissociation constants of weak and moderately strong electrolytes. I. Dissociation constant of 2:4-dinitrophenol, and range of validity of Debye-Hückel limiting formula. H. VON HALBAN and G. KORTUM (Z. physikal. Chem., 1934, 170, 351—379).—The methods of determining dissociation consts. are critically reviewed. The optical methods, as distinguished from electrometric and conductometric methods, are practically independent of hypotheses, *e.g.*, concerning the behaviour and mutual interaction of ions and mols., and optical absorption is const., independent of electrostatic forces, at far higher concns. than is, say, the conductivity. The classical dissociation const., K_c , of 2:4-dinitrophenol has been determined at 25° with a precision of 0.1% in pure aq. solution and in solutions of $KClO_4$, KCl , $NaCl$, and HCl at ionic concns. of 5×10^{-5} to 2.28M by photo-electric determination of the concn. of the absorbing anion. The results permit very precise extrapolation to zero concn. to obtain the thermodynamic dissociation const., $8.13 \pm 0.01 \times 10^{-5}$. Using this val., the Debye-Hückel limiting formula agrees excellently with the experimental data up to an ionic concn. of $\sim 3 \times 10^{-3}M$; at higher concns. systematic deviations appear. In presence of uni-univalent neutral salts K_c increases uniformly up to an ionic concn. of $\sim 0.01M$ and passes through a max. at $\sim 0.5M$.

R. C.

Erroneous conception with regard to carbonate solutions. Y. KAUKO (Maataloustiet. Aikakausk., 1934, 6, No. 2; Suomen Kem., 1934, 7, 96B).—Free CO_2 is practically non-existent in these solutions, and the usual conception of the relation between free and bound CO_2 is false. H carbonate solutions are not buffer solutions. It is shown that Henry's law does not hold for dil. H carbonate solutions, but that the solubility of CO_2 obeys the same laws as the surface adsorption of the vapour.

J. W. S.

Graphical representation of the equilibrium relations in the system base-carbon dioxide-water in dilute solutions from the viewpoint of the classical dissociation theory. Y. KAUKO (Ann. Acad. Scient. Fenn., 1934, A, 39, 1; Suomen Kem., 1934, 7, 96B; cf. A., 1934, 732).—The graphical representation of the mathematical relations developed previously has been applied to the hardness of H_2O . The usual methods of determining the free and combined CO_2 can lead to misleading results. The method recommended is the determination of basicity and $[H^+]$.

J. W. S.

Activities of ethylene and ethyl alcohol in sulphuric acid. M. GALLAGHER and D. B. KEYES (J. Amer. Chem. Soc., 1934, 56, 2221—2224).—The activities have been calc. from measurements of the partial pressures of C_2H_4 (from dil. solutions to mol. fraction 0.3122) in conc. H_2SO_4 , and of EtOH (from dil. solutions to mol. fraction 0.2400) in dil. H_2SO_4 .

E. S. H.

Activity coefficient of sulphuric acid at temperatures from 0° to 50°. J. SHRAWDER, jun., and I. A. COWPERTHWAIT (J. Amer. Chem. Soc., 1934, 56, 2340—2345).—The data have been calc. from e.m.f. measurements of the cells $Pb-Hg$ (2-phase), $PbSO_4(s), H_2SO_4(m), H_2$ at different concns.

E. S. H.

Apparent and real activity coefficients in solutions of electrolytes. II. L. BRULL (Gazzetta, 1934, 64, 734—742; cf. A., 1934, 1307).—The activities of $CdCl_2$ in aq. solutions of alkali and alkaline-earth chlorides have been calc. from e.m.f. measurements of the cell $CdHg|CdCl_2-MCl_n|Hg_2Cl_2|Hg$, where MCl_n represents the chlorides of Li, Na, K, Ca, Sr, and Ba, respectively.

O. J. W.

Activity of the hydrogen ions in Veibel's solution at different temperatures. Y. KAUKO (Maataloustiet. Aikakausk., 1933, 5, 149; Suomen Kem., 1934, 7, 96B).—The activity of H^+ has been determined from the conductivity and of these solutions.

J. W. S.

Raman spectrum, structure, and hydrolysis of solutions of stannic chloride. J. GUÉRON (Compt. rend., 1934, 199, 945—948).—Previous results (cf. A., 1934, 254, 960) are discussed in detail.

N. M. B.

Substitution equilibrium between different halogens in α -halogeno-fatty acids. E. HANNERZ (Svensk Kem. Tidskr., 1934, 46, 233—250).—Equilibrium consts. in the reaction $R \cdot CHX \cdot CO_2H + KX' \rightarrow R \cdot CHX' \cdot CO_2H + KX$ ($R=H$ or Me) have been determined in aq. solution at 50°. The equilibria were approached from both sides.

F. L. U.

Influence of p_H on the dissociation of hexamethylenetetramine and the hydriodide of hexamethylenetetramine-ethanol. G. TOUSSAINT, J. DETRIE, and M. VÉRAIN (Compt. rend. Soc. Biol., 1934, 171, 191—193).—The dissociation of the hydriodide of hexamethylenetetramine-ethanol to give CH_2O is $>$ that of $(CH_2)_6N_4$ (I) at 1—9. (I) is dissociated only below 5.

A. L.

Physico-chemical studies of complex acids. XIII. Constitution of quinquevalent and quadri-

valent vanadium solutions with a note on their respective reduction and oxidation. H. T. S. BRITTON (J.C.S., 1934, 1842—1846).—Electrometric titrations of aq. alkali vanadate with H_2SO_4 , and of V_2O_5 solutions in H_2SO_4 with NaOH , have been made, using the glass electrode. At 85° well-defined inflexions are observed in the titration curves, indicating the formation of metavanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$. At lower temp. the inflexions are indefinite and depend on time and temp. Glass electrode electrometric titration with NaOH of the blue solution obtained by reducing V_2O_5 in H_2SO_4 with SO_2 , confirms the view that VOSO_4 is formed, and shows also that V_2O_4 cannot react with any greater amount of H_2SO_4 . Contrary to the usual view, V_2O_4 is not amphoteric. The re-dissolution observed in alkaline solutions is caused by the oxidation in air to vanadic acid. Electrometric titrations of VOSO_4 solutions have been made, at 22° , 50° , and 75° , with $0.1N\text{-KMnO}_4$, using a bright Pt electrode, and 45° was selected as a suitable temp. at which to investigate the oxidation of V^{IV} . Back titrations have also been made with $0.1N\text{-FeSO}_4$. M. S. B.

Complex formation due to polarisation. J. H. HILDEBRAND and S. E. WOOD (J. Chem. Physics, 1934, 2, 822—823).—The conclusions of Glockler and co-workers (A., 1934, 21) on compound formation between Kr and HCl are criticised. F. L. U.

Complex formation due to polarisation. Definition of a molecule. G. GLOCKLER (J. Chem. Physics, 1934, 2, 823—824; cf. preceding abstract).—Reply to Hildebrand and Wood. A mol. is defined as any configuration of atoms, simple mols., or radicals which shows a potential min. F. L. U.

Amphoteric behaviour of metal hydroxides. VIII. Chromites. R. SCHOLDER and R. PATSCH (Z. anorg. Chem., 1934, 220, 411—424).—The dependence of the solubility of Cr_2O_3 in aq. NaOH on temp. varies with the concn. of the latter. The behaviour is due both to colloidal solutions and to the formation of complexes. A study of the system $\text{Cr}_2\text{O}_3\text{-Na}_2\text{O-H}_2\text{O}$ indicates the existence of the following *hydroxo-salts*: $[\text{Cr}(\text{OH})_6]\text{Na}_3$, $[\text{Cr}(\text{OH})_5(\text{H}_2\text{O})]\text{Na}_4 \cdot 2\text{-}3\text{H}_2\text{O}$ (I), and $[\text{Cr}(\text{OH})_8]\text{Na}_6 \cdot 4\text{H}_2\text{O}$ (II). (I) and (II) also form mixed crystals. By pptn. of aq. Na chromite with $\text{Ba}(\text{OH})_2$ or $\text{Sr}(\text{OH})_2$ the compounds $[\text{Cr}(\text{OH})_6]_2\text{M}_3$ (M=Ba or Sr) are obtained. Aq. Na chromite deposits $\text{Cr}(\text{OH})_3$ on long keeping, but Ba and Sr chromite are more stable. It is probable that Na_1 chromite exists, and possibly the Na_2 compound also. The constitution of chromites is discussed. M. S. B.

Equilibrium in the system vanadium tetroxide-carbon monoxide-vanadium trioxide-carbon dioxide. H. M. SPENCER and J. C. JUSTICE (J. Amer. Chem. Soc., 1934, 56, 2306—2311).—The equilibrium const. has been determined at temp. between 750° and 896° . Free energies and heats of formation have been calc. E. S. H.

Vapour pressures of saturated solutions. Lithium chloride and lithium sulphate. M. P. APPLEBY, F. H. CRAWFORD, and K. GORDON (J.C.S., 1934, 1665—1671).—Solubilities of LiCl and Li_2SO_4 have been determined, and also d and v.p. of the

saturated solutions, at temp. up to and including the b.p. at atm. pressure. The transition temp. for $\text{LiCl} \cdot 2\text{H}_2\text{O}$ to $\text{LiCl} \cdot \text{H}_2\text{O}$ is $19.1 \pm 0.25^\circ$ and for $\text{LiCl} \cdot \text{H}_2\text{O}$ to LiCl $93.5 \pm 0.5^\circ$. Osmotic pressures have been calc. by the Porter equation and compared with the data for other alkali salts. Li^+ has a very high osmotic activity. M. S. B.

Position of the separation quadruple point in the system ether-water. F. DE BOER (Z. physikal. Chem., 1934, 170, 253—255).—The equilibrium pressures corresponding with the two conjugate solutions + vapour and solution + ice + vapour have been determined at -19° to 34° . The quadruple point lies in the p - T diagram above the v.-p. curve of pure Et_2O . R. C.

System mercuric chloride-mercuric bromide. A. J. VAN PELT, jun., and F. DE BOER (Z. physikal. Chem., 1934, 170, 256—261).—From solubility measurements in the system $\text{EtOH-HgCl}_2\text{-HgBr}_2$ at 25° and measurements of heat of dissolution in COMe_2 it is probable that HgCl_2 and HgBr_2 form mixed crystals. R. C.

M.-p. diagram of the system p -cresol-benzoic acid. D. J. DA SILVA (Rec. trav. chim., 1934, 53, 1097—1100).—The system has a eutectic at 27.5° and 10.8 mol.-% BzOH . The BzOH curve is very nearly the same as for the system PhOH-BzOH (cf. A., 1933, 906), and $(1/T + \text{const.}) \propto \log \text{mol.-% BzOH}$. Extrapolation gives 5.59 kg.-cal. for the heat of fusion of BzOH . It is inferred that the dipole moment of non-associated BzOH is $1.64\text{—}1.7 \times 10^{-18}$ e.s.u. R. S. B.

Behaviour of the hydronitrogens and their derivatives in liquid ammonia. IX. Equilibria in the system ammonium trinitride-ammonia. D. H. HOWARD, jun., F. FRIEDRICH, and A. W. BROWNE. X. Equilibria in the system hydrazine trinitride-ammonia. D. H. HOWARD, jun., and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 2332—2340, 2348—2357).—IX. The system has been examined over the ranges $0\text{—}4000 \text{ mm.}$, -90° to 30° , and $0\text{—}100\%$ NH_3 . Two cryst. compounds, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$ and $\text{NH}_4\text{N}_3 \cdot 5\text{NH}_3$, have been obtained. The eutectic is at -87° and 76% NH_3 .

X. The system has been investigated over the ranges $0\text{—}3200 \text{ mm.}$, -15° to 80° , and $0\text{—}100\%$ NH_3 . A deliquescent, stable, white, cryst. solvate, $2\text{N}_2\text{H}_5\text{N}_3 \cdot \text{NH}_3$, with an inversion point at about 50° , has been obtained. Ammonolysis occurs in liquid NH_3 , depending on the temp. and concn. E. S. H.

Phases formed by the reduction of mixtures of iron oxide with other oxides. E. JENCKEL (Z. anorg. Chem., 1934, 220, 377—388).—From the experimental data of Schenck *et al.* (A., 1930, 43; 1932, 811) phase diagrams have been constructed for the ternary systems above 800° consisting of Fe and Fe_2O_3 with one of the following oxides: BeO , SiO_2 , MnO , MgO , Al_2O_3 , Cr_2O_3 , P_2O_5 , ZnO . M. S. B.

Slag systems. R. HAY, D. D. HOWAT, and J. WHITE (J. West Scot. Iron Steel Inst., 1934, 41, 97—105).—Diagrams are given for the systems FeO-MnO , MnO-SiO_2 , FeO-SiO_2 . FeO has not a definite m.p. At 1370° it undergoes a peritectic reaction giving a small amount of saturated solution of O in Fe (m.p.

1480°). At 1430° 37% of MnO is sol. in FeO and 44% FeO in MnO. CH. ABS. (e)

System sulphuric acid-ammonium sulphate-water. P. LOOUTY and P. LAFFITTE (Compt. rend., 1934, 199, 950—952; cf. A., 1933, 570).—Investigations previously reported are extended to 10° and 90°. The salts which separate at 10° are: $(\text{NH}_4)_2\text{SO}_4$, $\text{H}_2\text{SO}_4 \cdot 3(\text{NH}_4)_2\text{SO}_4$, $\text{H}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, and $3\text{H}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$; at 90° the last-named is absent, but a small zone of mixed crystals appears. A three-dimensional diagram indicates the most favourable conditions for the deposition of a given salt.

N. M. B.

Ternary systems cerous sulphate-alkali sulphate-water. I. Cerous sulphate-potassium sulphate-water. W. SCHRODER and H. SCHACKMANN (Z. anorg. Chem., 1934, 220, 389—410).—Data and diagrams are given for the system $\text{Ce}_2(\text{SO}_4)_3$ - K_2SO_4 - H_2O at 0°, 25°, 50°, and 75°. The presence of the following compounds is indicated: $\text{Ce}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $2\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4$.

M. S. B.

System bismuth iodide-potassium iodide-water. (MLE.) M. L. DELWAULE (Compt. rend., 1934, 199, 948—950).—At 15°, 35°, and 55°, the compounds $\text{BiI}_3 \cdot \text{KI} \cdot \text{H}_2\text{O}$ and $\text{BiI}_3 \cdot 2\text{KI} \cdot \text{H}_2\text{O}$ are formed. By slow evaporation these were obtained in the form of bright red monoclinic prisms and deep red pyramids, respectively.

N. M. B.

System cadmium sulphate-acetic acid-water at 25°. W. C. CAGLE, G. TARBUTTON, and W. C. VOSBURGH (J. Amer. Chem. Soc., 1934, 56, 2331—2332).—The solubility of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ decreases rapidly as AcOH is added and is very small in aq. solutions containing > 55% AcOH . $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ is the stable phase when $[\text{AcOH}]$ is < 85%. The composition of $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ has been confirmed.

E. S. H.

Ternary system potassium perchlorate-potassium borofluoride-water at 25°. R. C. RAY and H. C. MITRA (Trans. Faraday Soc., 1934, 30, 1161—1163).— $\text{KClO}_4 \cdot 2\text{KBF}_4$ and $\text{KClO}_4 \cdot 8\text{KBF}_4$ are formed, but cannot be isolated, as they are decomposed by H_2O with separation of solid KBF_4 , and are stable only in solutions containing more KClO_4 in proportion to KBF_4 than the salts themselves.

R. S. B.

Equilibrium diagrams of salts for salt baths. I. System $\text{Na}_2\text{B}_4\text{O}_7$ - NaCl - KCl . T. SATO and J. SUNAMI. II. System Na_2CO_3 - NaCl - KCl . T. SATO (Tech. Rep. Tôhoku, 1934, 31, 383—402, 403—416).—Numerical data and diagrams are given for the binary and ternary systems concerned. F. L. U.

Technique of thermal analysis in systems of three organic components, and summary of systems examined. K. HRYNAKOWSKI (Z. physikal. Chem., 1934, 171, 99—118).—A method of thermal analysis is described, and the results obtained for 22 ternary systems with components only partly miscible in the molten state are recorded. A scheme of classification of ternary systems is outlined.

R. C.

Dilatometer study of ternary silica-soda-alumina glasses. E. RENCKER (Compt. rend., 1934, 199, 1114—1116).—The transformation temp. and linear expansion of glasses of varying composition are represented in diagrams. Replacement of Na_2O or SiO_2 by Al_2O_3 lowers the expansion coeff. except in a limited region at > 20% Al_2O_3 .

H. J. E.

Heats of formation and dissolution of hydrogen sulphide. H. ZEUMER and W. A. ROTH (Z. Elektrochem., 1934, 40, 777—783).—The heat of formation, determined by combustion in O_2 , is $+4.80 \pm 0.15$ kg.-cal. per mol. The heat of dissolution is 4.52 ± 0.03 kg.-cal. per mol. The calc. heat of ionisation ($\text{H}^+ + \text{SH}^-$) is 3.8 kg.-cal.

E. S. H.

Thermal decomposition and heat of formation of sodium carbamate. S. ABÉ and R. HARA (J. Soc. Chem. Ind. Japan, 1934, 37, 699—700B).—When heated, $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na}$ decomposes as follows: $3\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na} \rightarrow \text{Na}_2\text{CO}_3 + \text{NaCNO} + \text{CO}_2 + 2\text{NH}_3$, NaHCO_3 being an intermediate product. In O_2 : $2\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na} + 3\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2$. From the heat of this reaction (bomb calorimeter) the following data for const. vol. and const. pressure at 18° are calc.: heat of combustion 74.11, 73.97, heat of decomp. 15.04, 15.62, heat of formation 175.45, 176.89 kg.-cal. (all ± 0.036).

A. G.

Thermochemistry of compounds occurring in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. V. Heats of formation of tricalcium silicate and dicalcium silicate. O. K. JOHANNSON and T. THORVALDSON (J. Amer. Chem. Soc., 1934, 56, 2327—2330; cf. A., 1930, 1524).—The prep. of β - $2\text{CaO} \cdot \text{SiO}_2$ is described. The isothermal heats of decomp. of β - and γ - $2\text{CaO} \cdot \text{SiO}_2$ and of $3\text{CaO} \cdot \text{SiO}_2$ in dil. HCl have been determined, and the following quantities calc.: (a) the isothermal heats of formation at 20° of β - $2\text{CaO} \cdot \text{SiO}_2$, γ - $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{SiO}_2$ from CaO and SiO_2 gel, (b) the isothermal heats of formation at 20° of $3\text{CaO} \cdot \text{SiO}_2$ from CaO and the above two forms of $2\text{CaO} \cdot \text{SiO}_2$, (c) the heat of transition at 20° of β - into γ - $2\text{CaO} \cdot \text{SiO}_2$. At 20°, β - $2\text{CaO} \cdot \text{SiO}_2$ is metastable with respect to γ - $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{SiO}_2$ is metastable with respect to CaO and β - and γ - $2\text{CaO} \cdot \text{SiO}_2$.

E. S. H.

Keten. III. Heat of formation and heat of reaction with alcohols. F. O. RICE and J. GREENBERG (J. Amer. Chem. Soc., 1934, 56, 2268—2270; cf. A., 1934, 1091).—From measurements of the heat of reaction of CH_3CO with dil. aq. NaOH the calc. heat of formation of gaseous CH_3CO from graphite and gaseous H_2 and O_2 is $+14.78$ kg.-cal. The following heats of reaction of CH_3CO with aliphatic alcohols have been determined: MeOH 36.93, EtOH 36.44, Pr^nOH 35.32, Bu^nOH 35.11, Bu^sOH 34.37, Pr^iOH 35.91, sec-BuOH 34.53, Bu^tOH 23.49 kg.-cal. per mol.

E. S. H.

Heats of dilution of strong electrolytes. A. L. ROBINSON and H. S. FRANK (J. Amer. Chem. Soc., 1934, 56, 2312—2313).—Examination of published data suggests that Åkerlöf's rule (A., 1934, 1173) is not equally valid at all temp.

E. S. H.

Partial molal heat of dilution of sulphuric acid from electromotive force measurements. I. A. COWPERTHWAIT and J. SHRAWDER, jun. (J.

Amer. Chem. Soc., 1934, 56, 2345—2347).—The data are derived from e.m.f. measurements of the cells Pb-Hg, PbSO₄(s), H₂SO₄(m), H₂ at intervals of 12.5° between 0° and 50° and at different concns.

E. S. H.

Water as a weak electrolyte in the heats of dilution of strong electrolytes. E. DOEHLEMAN and E. LANGE (Z. physikal. Chem., 1934, 170, 391—406).—The observed heat of dilution, V_m , of aq. solutions of salts and acids includes heat effects, Q , due to changes in the ionisation of the H₂O: (1) with neutral salts, Q is due to shift in the equilibrium $H^+ + OH^- \rightleftharpoons H_2O$ owing to change in activity coeff. of H₂O with salt concn.; (2) with acids, Q is due to repression of ionisation of H₂O by H⁺ of acid; (3) with hydrolysing salts, Q is due to variation of hydrolysis with concn. Examples of the calculation of these vals. are reproduced, and the correction required for deviation of the H₂O used for dilution from p_H 7 is calc. After application of these corrections to the V_m curve of NH₄Cl it fits in with the curves of the other Me-substituted NH₄ salts. V_m also probably includes a Q due to variation with concn. of the degree of association of the H₂O.

R. C.

Heats of dissolution and reaction in liquid ammonia. III. C. A. KRAUS and F. C. SCHMIDT (J. Amer. Chem. Soc., 1934, 56, 2297—2300; cf. A., 1934, 256).—Modifications in apparatus and technique are described. Data are recorded for heats of dissolution of Na, K, NH₂Ac, Li, NaBr, ice, phthalimide, Na in presence of KBr, and K in presence of NaBr, and for the heat of reduction of SnMe₃Br to SnMe₃Na.

E. S. H.

Thermochemical study of *d*-gluconic acid and its modifications. R. H. LE ROY and B. C. HENDRICKS (J. Amer. Chem. Soc., 1934, 56, 2243—2245).—The heats of dissolution to a dilution of 0.0003 mol. of solute per mol. of H₂O at 25° for *d*-glucono acid (I), *d*-glucono- δ -lactone (II), *d*-glucono- γ -lactone (III), and Na *d*-gluconate have been determined, as well as the heats of neutralisation of (I), (II), and (III) with 0.0102*N*-NaOH. The transformation of (II) into (III) is an endothermic change.

E. S. H.

Thermometric study of the precipitation of insoluble ferrocyanides. R. PARIS (Compt. rend., 1934, 199, 863—865; cf. A., 1934, 491).—The curves obtained by plotting the temp. rise against the amount of K₄Fe(CN)₆ added to solutions of Pb(OAc)₂, AgNO₃, ZnSO₄, and FeCl₃ show sharp breaks corresponding with the complete pptn. of Pb₂Fe(CN)₆, Ag₃KFe(CN)₆, K₂Zn₃[Fe(CN)₆]₂, and Fe₄[Fe(CN)₆]₃. With Ni, Cu^{II}, Co, and Cd salts the breaks do not correspond with simple formulæ, and differ according as the K₄Fe(CN)₆ is added to the salt or *vice versa*.

J. W. S.

Effect of ammonia and pyridine on mobility of cupric ion. J. WILLE (Z. physikal. Chem., 1934, 171, 93—98).—From the effect of the addition of NH₃ and C₅H₅N on the transport no. of Cu^{II} in aq. CuSO₄ it is concluded that NH₃ forms [Cu₄NH₃]^{II} and [Cu₅NH₃]^{II}, that 2—4 C₅H₅N mols. may be added to Cu^{II}, and that in pure Cu salt solutions there is equilibrium between Cu^{II} and [Cu _{x} H₂O]^{II}, where $x=1-5$.

R. C.

Electrical conductivity of strong electrolytes and its variation with temperature. C. J. B. CLEWS (Proc. Physical Soc., 1934, 46, 764—771).—Precision data are given for K₂SO₄, KNO₃, and Na₂SO₄ in the temp. range 18—85°, using a bridge method with a.c. supplied by a vac.-tube oscillatory circuit and amplified detector; temp. control was accurate to 0.02°.

N. M. B.

High-frequency conductivity of the solution of magnesium sulphate in a mixture of glycerol and water. M. HARADA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1340—1350).—Data for MgSO₄ solutions at 25° and —20° are recorded. At 25° the results agree qualitatively with the theory of Debye and Falkenhagen, but at —20° inexplicable deviations occur.

R. S. B.

Wien effect of a long-chain salt in aqueous solution, and an appropriate modification of the method of measurement for brief current pulses. J. MALSCH and G. S. HARTLEY (Z. physikal. Chem., 1934, 170, 321—336).—The Wien effect with aq. solutions of cetylpyridinium chloride at concns. < 0.001*N* is very small and of the same order as for normal electrolytes, but at higher concns. increases and at about 0.002*N* becomes very large, the conductivity for high field strength being > the conductivity at infinite dilution. The explanation is that with increasing concn. large multivalent ions are formed and part of the counter-ions contained in them are released, so that there are present more ions of high mobility and the charge of the large ions is increased. Examination of the effect of varying the duration of the current pulses gives no indication that strong fields break up the multivalent ion aggregates. A source of error in the Malsch-Wien apparatus has been eliminated (Ann. Physik, 1927, [iv], 83, 305).

R. C.

Revision of normal electrode potentials. J. SHRAWDER, jun., I. A. COWPERTHWAIT, and V. K. LA MER (J. Amer. Chem. Soc., 1934, 56, 2348).—The following data for E_{298}^0 are recorded: Pb-Hg(2-phase), PbSO₄(s), SO₄^{II} + 0.3505; Hg₂Hg₂SO₄(s), SO₄^{II} — 0.6141; Zn-Hg(2-phase), Zn^{II} + 0.7614; Zn, Zn^{II} — 0.7620; Cd-Hg(2-phase), Cd^{II} + 0.3519; Cd, Cd^{II} + 0.4024.

E. S. H.

Polarographic studies with the dropping mercury electrode. I. Anodic polarisation and the influence of anions. J. REVENDA (Coll. Czech. Chem. Comm., 1934, 6, 453—467).—Anions at concns. < 10^{−3}*M* give rise to characteristic limiting currents \propto the concn. on the current-voltage curves of the dropping Hg anode. The magnitudes of these currents are of the same order as those obtained with cations at the dropping Hg cathode, and have not been previously observed owing to the large concns. of anion used. The depolarising effect of large concns. of Cl[−], Br[−], I[−], OH[−], and S^{II} is due to ppts. formed with Hg⁰, whilst that of CN[−], CNS[−], SO₃^{II}, and S₂O₃^{II} is due to complex formation. The technique is detailed, and with traces of S^{II} or CN[−] the range of anodic polarisation extends from −0.7 to +0.3 volt with respect to the *N*-Hg₂Cl₂ electrode.

J. G. A. G.

Application of the glass electrode to a study of chromic acid. J. D. NEUSS and W. RIEMAN (J. Amer. Chem. Soc., 1934, 56, 2238—2243).—Measurements of H^+ activity of H_2CrO_4 and its salts at 25° by the glass electrode give 3.20×10^{-7} (error $\pm 3\%$) as the second ionisation const. The first ionisation is not quite complete; at an ionic strength 0.16, the const. is 0.18 ± 0.04 . The equilibrium const. of the reaction $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$ is 0.023 ($\pm 9\%$).

E. S. H.

Benzaldehyde electrode. T. C. HERNDON and H. A. WEBB (J. Amer. Chem. Soc., 1934, 56, 2500—2501).—Reproducible determinations between p_H 7 and 13.64 have been made, substituting $PhCHO$ for quinhydrone. The $PhCHO$ system is irreversible.

E. S. H.

Comparison of activity of alcohols and carboxylic acids under various conditions. B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1934, 4, 783—789).—The activity (I) of the H atom of CO_2H and OH groups, as measured by the e.m.f. of a Na electrode, diminishes with increase in the no. of C atoms in the chain. In C_5H_5N certain concns. exist at which max. (I) is found; these correspond with formation of 1:2 compounds of C_5H_5N and acid. The (I) of acids and of $PhOH$ in C_5H_5N is considerably $>$ in the absence of solvent.

R. T.

Potential series of acids and bases. (Acidity potential as a quantitative measure of acidity and basicity.) E. WIBERG (Z. physikal. Chem., 1934, 171, 1—24).—Accepting Bronsted's definition of acids and bases, the relation between an acid and the corresponding base is comparable with that between an oxidation-reduction pair. For an acid-base pair, there thus exists a "normal acidity potential," analogous to normal oxidation-reduction potential, and a potential series of acids and bases may be drawn up. Illustrations of the application of these principles are discussed.

R. C.

Oxidation-reduction potentials in non-aqueous solutions. I. Systems cuprous-cupric chlorides and ferrous-ferric chlorides in pyridine. J. R. PARTINGTON and J. W. SKEEN (Trans. Faraday Soc., 1934, 30, 1062—1071).—The e.m.f. of the cells $Cu|0.00228M-CuCl_2|0.0049-0.02M-CuCl_2 + 0.0038-0.032M-CuCl|Pt$, $Ag|0.0265M-AgCl|0.001-0.02M-CuCl_2 + 0.001-0.026M-CuCl|Pt$ and $Ag|0.027M-AgCl|0.001-0.02M-FeCl_2 + 0.001-0.028M-FeCl_3|Pt$ at 25° is recorded for anhyd. C_5H_5N solutions. The development of potential is explained on the basis of electron transfer between ions of different valency without the intervention of the solvent.

J. G. A. G.

Changes in the oxidation-reduction potential of a glucose solution under the influence of light and a photosensitiser. P. DUBOULOZ (Compt. rend. Soc. Biol., 1934, 116, 435—437).—The potential (I) is reduced on illuminating an O-free solution of glucose (0.05 mol.) in a phosphate buffer (p_H 7.7) containing eosin (1:5,000). For reductions with (I) < 350 mv. the phenomenon is reversible. A connexion with biological photosensitisation is suggested.

CH. ABS. (e)

Buffer mechanism of sea-water. E. G. MÖBERG, D. M. GREENBERG, R. REVELLE, and E. C. ALLEN (Bull. Scripps Inst. Oceanog. Univ. Calif. Tech. Ser., 1934, 3, 231—278).—The buffering of sea- H_2O (I) is discussed in terms of p_H , titratable base, and total CO_2 . The difference between the solubility product of $CaCO_3$ in (I) and in pure H_2O is due in part to the low activity coeff. of CO_3^{2-} in (I).

CH. ABS. (e)

Indicators. XXIV. Protein error of indicators. A THIEL and G. SCHULZ (Z. anorg. Chem., 1934, 220, 225—235).—Measurements of the protein error of Me-orange give results in accordance with Hartley's observations (A., 1934, 618). The distribution of the indicator between disperse phase and homogeneous solution has been determined and shows that the degree of dispersion of the protein changes with dilution. For small protein concn. the systems of isobaths for Me-orange are normal, but optical anomalies appear at higher concns. and indicate a qual. change in the character of the colour.

M. S. B.

Effect of pressure on overvoltage of electrolysis of water. H. M. CASSEL and E. KRUMBEIN (Z. physikal. Chem., 1934, 171, 70—82).—Examination of the effect of pressure, p , on the overvoltage, E , of H in $N-H_2SO_4$ and $N-KNO_3$ at Pt, Ni, and Ag electrodes has given results similar to those previously reported (A., 1933, 677). With increase in p the E of O on Pt and PbO_2 in $N-H_2SO_4$ and on Cr-Ni steel in $N-Cd(NO_3)_2$ falls, the effect being smallest with PbO_2 . The variation of E with p agrees, in direction, with Butler's theory (cf. A., 1924, ii, 598), but is the theoretical val. The fall in conductivity of aq. solutions of H and O with increasing gas pressure has been determined.

R. C.

Optical investigation of passivity of metals. II. Natural oxide film on polished iron surfaces. L. TRONSTAD and T. HOVERSTAD (Z. physikal. Chem., 1934, 170, 172—190).—The film can be removed, apparently completely, by anodically polarising in $N-Na_2SO_4$ and at the same time making contact with a Zn rod and brushing, or by intermittently polarising cathodically in a solution containing 0.2 g.-equiv. $Na_2C_2O_4$ and 0.02 g.-equiv. $H_2C_2O_4$ per litre. The resulting optical change in the surface corresponds with the removal of a film of average thickness 15—30 Å. and average $n \sim 3.5$. Even assuming that, due to roughness, the actual surface area is twice the measured val., this film cannot be regarded as a unimol. O film; it is rather a three-dimensional system of partly hydrated oxide. The passivity film produced by anodic passivation in $N-Na_2SO_4$ has an average thickness of 50—70 Å. and mean $n \sim 3.5$. The discrepancy between Muller and Machu's observations on initial c.d. and time of passivation and the results of the optical method of detecting thin films (A., 1932, 993) is explained.

R. C.

Electric penetration of thin layers of aluminium oxide in an electrolyte. W. C. VAN GEEL (Physica, 1934, 1, 989—995).—Penetration voltages for a thin layer of Al_2O_3 on Al in saturated aq. H_3BO_3 , containing varying concns. of $Na_2B_4O_7$, have been

determined at different temp. $V=A+BT \log C/N-DT^2$, where A , B , C , and D are consts. and N is the no. of ions per c.c. The penetration of the oxide layer is brought about by cold electron emission (A., 1934, 240). Two penetration voltages are found, the difference between them depending on the concn. of the electrolyte. This is explained by von Hippel's theory (A., 1933, 999) according to which penetration may take place in the different directions of the cryst. lattice. M. S. B.

Anodic passivation of gold in chloride solutions. G. ARMSTRONG and J. A. V. BUTLER (Trans. Faraday Soc., 1934, 30, 1173—1177).—The time of passivation of Au immersed in unstirred solutions containing Cl^- is given by $(i-i_0)t-\alpha$ (i =current, t =time, i_0 and α are consts.), and is unaffected when HCl is replaced by KCl , in agreement with the results of Shutt and Walton for stirred solutions (cf. A., 1934, 1178). A diffusion mechanism is suggested, α representing the amount of electrolysis required to form a uniform diffusion layer, and i_0 the const. rate of diffusion in the steady state. The thickness of the diffusion layer is calc. to be 4×10^{-4} cm. (Shutt and Walton's data), and $3-4 \times 10^{-2}$ cm. and 1.5×10^{-2} cm. from the authors' vals. of i_0 and α , respectively. R. S. B.

Electrolysis of copper into rock-salt. S. A. ARZIBISCHEV and U. A. PARFANOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 25—30).—The mobility of Cu ions through rock-salt varies exponentially with temp., and has 1/50 the val. of that for electrons. A. B. D. C.

Unstable intermediate products and the classical chemical mechanics. A. SKRABAL (Monatsh., 1934, 64, 289—332).—Mathematical. A complete reaction scheme, including a determination of unstable intermediate reaction products, has been developed for systems of simultaneous reactions which lead to one final reaction by a single reaction path. The scheme is illustrated by reference to the combination of H_2 with Br. M. S. B.

Rôle of charged particles in the propagation of flames. Propagation of flames in transverse electric fields. A. SOKOLIK and B. SLATOV (Physikal. Z. Sovietunion, 1934, 5, 676—686).—A 25% CO mixture was extinguished by 14 kv. Positively-charged diaphragms prevented passage of flames. A photographic method was used. CH. ABS. (e)

Thermal decomposition of ozone. M. RITCHIE (Proc. Roy. Soc., 1934, A, 146, 848—866).—The thermal decomp. of O_3 has been studied between 80° and 100° for pressures between 10 and 100 mm. The first stage is $\text{O}_3=\text{O}_2+\text{O}$, followed by $\text{O}+\text{O}_3=2\text{O}_2$. The addition of inert gases, in the absence of appreciable amounts of O_2 , increases the rate by preventing the diffusion of O to the wall. In the presence of O_2 the rate is retarded by the triple collision effect $\text{O}+\text{O}_2+\text{M}=\text{O}_3+\text{M}$, where M is a mol. of O_2 or of other added gas. At the higher pressures of O_3 the first reaction is predominantly unimol.; k_1 is approx. 4×10^{-4} sec. $^{-1}$ at 90° , agreeing with the val. of k_1 obtained for the decomp. of O_3 in CCl_4 solution. At the lower pressures the reaction becomes increasingly

bimol. The heat of activation of the first reaction is 19,000 g.-cal. (18 mm. pressure of O_3), that of the second is 14,000 g.-cal., and that of the triple collision $\text{O}+\text{O}_2+\text{O}_2=\text{O}_3+\text{O}_2$ is 5000 g.-cal. L. L. B.

Decomposition of ozone. A. W. EWELL (Physikal. Rev., 1933, [ii], 43, 779).—The decomp. of O_3 has been investigated under the various conditions of its use in purifying air. The reaction is unimol., $\text{O}_3=\text{O}_2+\text{O}$, following $dc/dt=-kc$, where k varies from 0.01 to 0.1 corresponding with half-disappearance in from 69 to 6.9 min. The equations $c=C(1-e^{-kt})$ and $c=Ce^{-kt'}$, where C is the final equilibrium concn., t the time after the supply $m-kC$ per min. starts, and t' the time after the supply of O_3 is cut off, are confirmed. L. S. T.

Kinetics of the thermal hydrogen-chlorine reaction. R. N. PEASE (J. Amer. Chem. Soc., 1934, 56, 2388—2391).—The thermal reaction is inhibited strongly by O_2 . A packing of broken Pyrex does not affect the rate in absence of O_2 , but accelerates the reaction in presence of O_2 . In absence of O_2 the reaction is approx. of the second order. HCl is not an inhibitor. No appreciable amount of O_2 is consumed in the inhibition process. E. S. H.

Reaction of heavy hydrogen with bromine vapour. F. BACH, K. F. BONHOEFFER, and E. A. MOELWYN-HUGHES (Z. physikal. Chem., 1934, B, 27, 71—78).—Results for the reaction with ordinary H_2 confirm those of Bodenstein and Lind (A., 1907, ii, 76) and supplement them at higher temp. The reaction with H^2 is materially slower, $\text{Br}+\text{H}_2=\text{HBr}+\text{H}$ and $\text{Br}+\text{H}_2=\text{H}^2\text{Br}+\text{H}^2$ having heats of activation, q , of 17.2 ± 0.5 and 19.33 ± 0.5 kg.-cal., respectively. This difference in q may be explained by the difference in zero point energies of H_2 and H^2 . R. C.

Reaction between oxygen and the heavier isotope of hydrogen. C. N. HINSHELWOOD, A. T. WILLIAMSON, and J. H. WOLFENDEN (Proc. Roy. Soc., 1934, A, 147, 48—57; cf. A., 1934, 736).—For the chain reaction in the gas at $550-560^\circ$, the ratio of the rates with H_2 and with H^2 is 0.6 in the early stages, but decreases to 0.4 as steam is formed. The smaller diffusion coeff. of the chain carriers in H^2 partly compensates for the lower reactivity in the early stages of the reaction, but as the latter proceeds the steam minimises the compensation, and the difference in reactivity appears. L. L. B.

Recombination of hydrogen atoms, and their reaction with oxygen and carbon monoxide. L. FARKAS and H. SACHSSE (Z. physikal. Chem., 1934, B, 27, 111—129).—By means of the reaction $\text{H}+p\text{-H}_2=o\text{-H}_2+\text{H}$ the stationary concn. of H atoms, produced by collisions of the second kind with photochemically excited Hg atoms, has been determined in H_2 and mixtures of this with N_2 , A, O_2 , and CO. The results indicate that the velocity coeff. of $\text{H}+\text{H}+\text{M}=\text{H}_2+\text{M}$ is of the same order whether M is H_2 , A, or N_2 . $\text{H}+\text{O}_2=\text{HO}_2$ occurs by a triple collision process and the ratio $k_{\text{H}+\text{O}_2}:k_{\text{H}+\text{H}}$ is $\sim 1:500$. In presence of CO a decomp. reaction of HCO (1) occurs at the same time as the addition $\text{CO}+\text{H}$ (2), the ratio of the velocity of (2) to that of (1) being $\sim 1:370$. R. C.

Thermal and electrical theories of spark ignition. J. D. MORGAN (Phil. Mag., 1934, [vii], 18, 827—832; cf. B., 1933, 134).—Combustion of a mixture of 5% of coal gas with air brought about by an electrically heated Pt wire occurs with a slightly smaller heating current when a point discharge at 4 kv. takes place near the wire, provided that the point is electrified in a discontinuous or fluctuating manner. The effect is due to radiation and not to the simple movement of ionised mols. in the field near the point. F. L. U.

Reaction between sulphur trioxide and water vapours and a new periodic phenomenon. C. F. GOODEVE, A. S. EASTMAN, and A. DOOLEY (Trans. Faraday Soc., 1934, 30, 1127—1133).—The reaction between H_2O and SO_3 vapours has been studied at room temp. by allowing air streams carrying the vapours to interdiffuse. At low partial pressures of the reactants a ring of liquid H_2SO_4 is formed on the wall; at higher concns. a flame-shaped mist is produced. The latter could not be used for determining the velocity, but from measurements on the ring it is inferred that, within a factor of approx. 10, 1 collision in 100 between reactants produces H_2SO_4 . Probably ternary collisions involving the carrier gas are necessary for reaction. Under certain conditions a periodic pptn. of mist occurs, which is explained by a modification of Ostwald's theory for Liesegang rings. R. S. B.

Kinetics of the reaction between hydrogen and nitrous oxide. II. III. Effect of oxygen. H. W. MELVILLE (Proc. Roy. Soc., 1934, A, 146, 737—759, 760—775).—II. The kinetics of the H_2 – N_2O reaction have been studied at 500–750°/1–30 mm. The reaction rate $\propto [\text{N}_2\text{O}]^2$, is nearly independent of $[\text{H}_2]$, is retarded by packing the reaction vessel, and is not affected by N_2 or A. The energy of activation is 49 kg.-cal. The kinetics differ from those of the high-pressure reaction, but complete correlation is obtained by assuming that the chains now end by the combination of H atoms on the walls. Chains may be initiated by H atoms produced by optically excited Hg atoms. At low pressures the photo-reaction rate $\propto [\text{N}_2\text{O}]$, and the intensity of the light (I), but is independent of $[\text{H}_2]$, $[\text{N}_2]$, and $[\text{A}]$. The activation energy is 17 kg.-cal. At high pressures the rate varies as \sqrt{I} .

III. The effect of the addition of O_2 on the H_2 – N_2O reaction has been investigated. The thermal and Hg-photosensitised reactions have been studied between 1 and 300 mm. At high pressures the kinetics change entirely; small quantities of O_2 increase the velocity, and the energy of activation decreases. Photochemical methods show that O_2 participates in the initiation and propagation of the chains. Packing experiments show that the initiation is homogeneous. At low pressures in the thermal reaction a transition point is observed, above which the reaction is rapid and below which it is slow, if wide bulbs are used. This point depends on the O_2 content and the temp., and is displaced to higher temp. on packing the reaction bulb. Photo-experiments confirm these measurements; as the temp.

raises the val. of n in rate = const. $\times I^n$ decreases from 1 to nearly 0. L. L. B.

Oxidation of ethane. W. A. BONE (Chem. and Ind., 1934, 962—963).—A criticism of the work of Steacie and Plewes (A., 1934, 1311), whose chain-reaction mechanism for the oxidation of C_2H_6 is considered to be unproven, mainly because their experimental procedure was not suitable for the identification of the primary reaction or the nature of the initial oxidation product. O. J. W.

Oxidation of ethane. H. H. GRAY (Chem. and Ind., 1934, 1007).—A reply to criticism (cf. preceding abstract). E. S. H.

Mechanism of the formation of methane and condensation products by the pyrolysis of ethane, ethylene, etc. M. W. TRAVERS and T. J. P. PEARCE (J.S.C.I., 1934, 53, 321—336r).—The pyrolysis of equilibrium mixtures of C_2H_6 , C_2H_4 , and H_2 was investigated between 550° and 620°, and at pressures up to 6 atm., by heating measured quantities of the mixtures in sealed SiO_2 tubes, and analysing the contents after definite periods. CH_4 and condensate (aromatic compounds) are formed by processes which are quite distinct, although in both cases the rate of reaction depends on $[\text{C}_2\text{H}_4]$. The rate of formation of condensate $\propto [\text{C}_2\text{H}_4]^2$, the parent reaction resulting in the formation of a four-C complex which has a very short life. The rate of formation of $\text{CH}_4 \propto [\text{C}_2\text{H}_4] \times ([\text{H}_2] + [\text{C}_2\text{H}_6] + [\text{CH}_4])$. The mechanism of the process is discussed. The pyrolysis of pure C_2H_6 results first in the primary decomp. into H_2 and C_2H_4 , with secondary formation of condensate and CH_4 at rates which are more rapid than in the case of the equilibrium mixtures. It is suggested that there is here an energy chain mechanism superimposed on the mechanism by which these products are formed from equilibrium mixtures. The rate of the processes taking place in the equilibrium mixtures appears to be independent of the surface, but dependent on the surface to a marked extent in the case of pure C_2H_6 .

Thermal decomposition of methyl alcohol. C. J. M. FLETCHER (Proc. Roy. Soc., 1934, A, 147, 119—128).—The influence of surface and initial pressure on this reaction has been investigated at 669°, and the temp. coeff. determined for initial pressures of 200 mm. over the temp. range 626—730°. The results can be expressed by $\log_e 1/t^{1/2} = 30.8 - 68,000/RT$. The reaction takes place in two stages, $\text{MeOH} \rightarrow \text{H}_2 + \text{CH}_2\text{O} \rightarrow 2\text{H}_2 + \text{CO}$, and is largely homogeneous. The first stage is mainly unimol. over the pressure range 10—400 mm., and determines the rate of reaction. The min. no. of energy terms which must be involved to account for the rate of reaction is 12. L. L. B.

Thermal decomposition of methyl alcohol. W. A. BONE (Chem. and Ind., 1934, 1006—1007).—A criticism (cf. preceding abstract). E. S. H.

Thermal decomposition and oxidation of nickel carbonyl. A. P. GARRATT and H. W. THOMPSON (J.C.S., 1934, 1822—1825).—The initial rate of decomp. of 16—65 mm. of $\text{Ni}(\text{CO})_4$ at 60—100° $\propto [\text{Ni}(\text{CO})_4]$. CO retards the reaction, which has an activation energy of approx. 12,000 g.-cal. A mechanism similar to that of the photodecomp. is proposed

(A., 1934, 582). There exists for $\text{Ni}(\text{CO})_4\text{-O}_2$ mixtures a crit. pressure limit, P , below which there is no pressure change and above which explosions occurs. P decreases markedly with rise of temp. from 40° to 60° . The data indicate a chain mechanism and deactivation at the walls. J. G. A. G.

Auto-ignition temperatures of aromatic *ortho*-compounds. O. KRUBER and W. SCHADE (Brennstoff-Chem., 1934, 15, 404; cf. A., 1932, 1093).—The ignition temp. (T) of aromatic compounds having substituents in the *o*-position are considerably $<$ those of the corresponding *m*- and *p*-compounds; cf., e.g., *o*-xylene 550° , *m*- or *p*-xylene 640° ; *o*-cresol 540° , *m*- or *p*-cresol 620° ; 1:2- $\text{C}_{10}\text{H}_6\text{Me}_2$ 510° , 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ 525° , 1:4-, 1:6-, 2:6-, or 2:7- $\text{C}_{10}\text{H}_6\text{Me}_2$ 600° . T vals. were determined in Jentzsch's apparatus. A. B. M.

Third-order ionic reaction without appreciable salt effect. H. A. LIEBHAFSKY and A. MOHAMMAD (J. Physical Chem., 1934, 38, 857—866; cf. A., 1933, 1250).—Of two rate-determining steps in the reduction of H_2O_2 by I^- in acid solution, one exhibits a normal salt effect, whilst another, $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+ = \text{H}_2\text{O} + \text{HOI}$, is without any appreciable salt effect. The salts used were NaClO_4 and $\text{Ba}(\text{ClO}_4)_2$, and the ionic strength was varied between 0.05 and 3.7. F. L. U.

Mechanism of the oxidation of hydrazo-compounds by iodine. M. GONZE (Bull. Acad. roy. Belg., 1934, [v], 20, 789—808).—The reaction between *mm*-trifluorohydrazotoluene and I in 65 vol.-% EtOH is unimol. with respect to both the reactants and is practically independent of between 2 and 5. Salts of strong acids do not influence the velocity of the reaction, but citrates and, more especially, acetates produce considerable acceleration. The mechanism involves a reaction between free I and I_3^- . The equilibrium const. of the system $\text{KI-KI}_3\text{-I}_2$ is of the order of 10^{-4} . It is not known whether the "free" I is at. or mol. H. F. G.

Esterification of the four isomeric 3-benzoyl-2-phenylcyclopropane-1-carboxylic acids in methyl, ethyl, and isopropyl alcohol in presence of hydrochloric acid. Effect of structure on rate of esterification. F. SCHENCK (Z. physikal. Chem., 1934, 170, 309—316).—A relation has been observed between the velocity coeffs., k , for a given alcohol, indicating that if the configuration of one of the acids is changed by rotating two of the substituents from one side of the plane of the ring to the other the net result on k is the product of the results produced by either rotation singly. For each isomeride (k in MeOH)/(k in Pr^nOH) = $[(k$ in $\text{MeOH})/(k$ in $\text{EtOH})]^{2.9}$. R. C.

Molecular structure and rate of reaction. W. HUICKEL (Ber., 1934, 67, [A], 129—138).—A lecture. H. W.

Rate of absorption of carbon dioxide. Effect of concentration and viscosity of caustic solutions. L. B. HITCHCOCK (Ind. Eng. Chem., 1934, 26, 1158—1167).—On the two-film theory of absorption of a gas by a liquid the initial rate of absorption $(dV/d\theta) = k'(C_i + C_s)/f(z)$, where C_i and C_s are concns. at the interface and in the main body of the liquid and

$f(z)$ is some function of the viscosity, in a given apparatus with given liquid velocity. C_i may be taken as approx. const. Steady initial rates of absorption of CO_2 into solutions of NaOH and KOH at 30° were determined and viscosities (up to 7N for NaOH and to 14N for KOH) measured by an Ostwald viscosimeter. Good agreement with the above equation was obtained by writing $f(z)$ as e^{az} , where $a = 0.4164$ for NaOH and 0.3846 for KOH . These consts. apply only to the apparatus used. If absorption is continued the rate falls more rapidly than can be accounted for by decrease in $[\text{NaOH}]$, perhaps owing to rising viscosity. C. I.

Velocity of absorption of gases by liquids.

IV. [Determination of] absorption of carbon dioxide by potassium carbonate solutions by a bubbling method. S. HATTA and A. BABA (Tech. Rep. Tôhoku, 1934, 11, 99—116).—See A., 1933, 233. F. L. U.

Rate of decomposition of strontium peroxide. M. BLUMENTHAL (J. Chim. phys., 1934, 31, 489—497; cf. A., 1933, 351).—Curves representing the rate of decomp. of SrO_2 at 1 atm. and at 1 mm. are similar, and above 232° and 205° , respectively, present a sharp max. This effect is due to an exothermic change, probably the formation of a second modification of SrO_2 stable at the higher temp. The curves for specimens containing $> 90\%$ of SrO_2 , and for pure SrO_2 below the temp. named, do not exhibit a max. A formula is given to represent the velocity of decomp. under the last-named conditions. F. L. U.

Optical observations on the effect of ozone and air on metals. L. TRONSTAD and T. HOVERSTAD (Trans. Faraday Soc., 1934, 30, 1114—1127).—The phase retardation and ratio of absorption coeffs. have been measured, and the thickness has been calc., for films formed on Ag, Cu, Zn, Fe, eutectoid steel, and austenitic stainless steel, in moist and dry 1.2% ozonised O_2 , mainly at $18\text{--}20^\circ$. The rate of oxidation in moist is much $>$ in dry O_2 , and in the former no protective films are formed. With Ag, Fe, and the steels in dry O_2 a film of limiting thickness is formed, but with Cu and Zn the film allows diffusion of O_2 , and no stationary state is reached. On heating Ag mirrors in air a sharp change in optical properties occurs at 180° , above which the decomp. of the oxide is more rapid than the oxidation, and at 280° a stationary state is reached (complete decomp.); on cooling, the film returns to the val. at room temp. by a different path. With Zn in dry and moist O_2 , and in pure air, the film thickness increases linearly with the time; in pure air at the slow rate of $5\text{--}6 \text{ \AA.}$ in 500 hr. It is suggested that the layer of protective pseudomorphic ZnO in contact with the metal is of const. thickness, and that the overlying layer of natural ZnO offers practically no resistance to diffusion. Cu and Fe in I vapour rapidly form thick films which are porous and cracked. R. S. B.

Corrosion phenomena. XVIII. Localisation of inhibiting action of surface-active substances in dissolution of metals in acids. A. THIEL and C. KAYSER (Z. physikal. Chem., 1934, 170, 407—420; cf. A., 1931, 46).—Experiments on the reaction with acids of Cd and Zn electrodes connected to a Pt or Cu

electrode in the same solution have shown that, contrary to Schunkert's findings (A., 1934, 37), the retarding action of adsorbed foreign substances on the dissolution in acids of metals reacting spontaneously with acids is due primarily to their hindering the evolution of gas by blocking the necessary local-element cathodes, and only in a minor degree to retardation of dissolution of the metal itself. R. C.

Kinetics of acetylation of cellulose fibres. IV. Acetylation of ramie swollen with acetic acid and the X-ray diagram of cellulose triacetate. I. SAKURADA and M. SHOJINO (J. Soc. Chem. Ind. Japan, 1934, 37, 599—603B).—The following vals. were found for the consts. k and m in the equation $x=kt^m$ (x =mols. AcOH per 100 mols. $C_6H_{10}O_5$) for the acetylation of ramie after various pretreatments: untreated 0.0576, 0.780; dried at 105°, 0.0129, 0.810; stored 12 days at room temp. in closed vessel with 30% H_2O (I), 8.318, 0.495; boiled with AcOH for 2 hr. (II), 12.59, 0.400; boiled with AcOH for 8 hr., 14.12, 0.391; boiled with C_6H_6 for 8 hr., 0.1122, 0.693. The X-ray diagrams of the cellulose acetates (I) and (II) are nearly identical. A. G.

Kinetics of penetration. IX. Models of mature cells. S. E. KAMERLING and W. J. V. OSTERHOUT (J. Gen. Physiol., 1934, 18, 229—234; cf. A., 1934, 486).—A model consists of two aq. solutions A and C separated by a mixture of guaiacol and p -cresol shaken with KOH. C contains $KHCO_3$ and CO_2 is bubbled in. The $[K']$ and vol. of C increase to const. vals. On decreasing the CO_2 supply by 0.75 the $[K']$ and vol. of C fell and rose subsequently. Replacing CO_2 by air causes an abrupt fall in $[K']$ and increased vol. The increase in vol. of C was prevented by addition of sucrose to A . By this means the vol. remained const. for > 2 weeks with a $[K']$ in C of 3.6 times that in A . H. D.

Influence of lead tetraethyl on the combination of hydrogen and oxygen. H. G. TANNER (J. Amer. Chem. Soc., 1934, 56, 2250—2252).—Addition of $PbEt_4$ increases the yield of H_2O_2 . A reaction mechanism which is consistent with the anti-knock effect is proposed. E. S. H.

Oxidation of sulphurous acid. III. Catalysis by manganous sulphate. IV. Catalysis by a glass powder containing manganese and iron. R. C. HOATHER and C. F. GOODEVE (Trans. Faraday Soc., 1934, 30, 1149—1156, 1156—1161; cf. A., 1934, 1157).—III. 0.001—0.01N aq. SO_2 is oxidised by aq. O_2 in presence of 0.3×10^{-5} to $8 \times 10^{-5}N$ - $MnSO_4$ at a const. rate until near completion of the reaction, which is of order 0 with respect to reactants, but of order 1.7 with respect to catalyst in spherical 150-c.c. vessels; temp. for most observations was 35°. In cylindrical vessels the order changes, owing probably to the influence of surface/vol. ratio on reaction chains. The reaction is mainly homogeneous, and is retarded by H_2SO_4 (0—0.004N), the influence of which is correlated with $[SO_3'']$, but the H_2SO_4 produced in the reaction does not appear to exert a retarding influence. The dependence on $[SO_3'']$ was confirmed by the addition of NaOH. The heat of activation is 27,300 g.-cal. $\pm 4\%$. $FeSO_4$ is 12 times as effective as

$MnSO_4$, but $10^{-4}M$ - $CuSO_4$ does not change the uncatalysed rate.

IV. Glass powder containing approx. 3% Fe and 5% Mn catalyses the oxidation in 150-c.c. spherical vessels with an approx. const. velocity, of order 0, cc the amount of glass, whereas glass free from Fe and Mn has no influence. In cylindrical vessels the order is 1 with respect to O_2 . On addition of H_2SO_4 and NaOH results similar to those in III are obtained. The heat of activation is < for $MnSO_4$ catalysis. The reaction does not proceed by dissolution of Mn and Fe from the glass, except that for Fe glass dissolved Fe may have an effect towards the end of the reaction, and does not proceed at the surface of the glass, as the rate is independent of stirring, and continues the same if the solution is transferred to another vessel, leaving the glass. It is suggested that a rapid reaction between H_2SO_3 and O_2 occurs on the glass, producing a compound which acts as a homogeneous catalyst by a chain mechanism.

R. S. B.

Kinetics and catalysis of the decomposition of calcium hydrogen carbonate in aqueous solution. R. STUMPER (Chim. et Ind., 1934, 32, 1023—1037).—The effects of temp., pressure, and concn. of $Ca(HCO_3)_2$ and CO_2 on the equilibria involved are considered. The rate-controlling step in the decomp. of $Ca(HCO_3)_2$ is $2HCO_3' \rightleftharpoons CO_3'' + H_2CO_3$, and by the decomp. of 0.005—0.02N- $Ca(HCO_3)_2$ with a current of air at 20°, the induction period, T , before pptn. commences is given by $T[Ca(HCO_3)_2]^2 = \text{const.}$, from which the reaction is of third order. T decreases with rise of temp. and is zero at 90°; the temp. coeff. of the velocity coeff., k , is < 2 between 30° and 80° and a change of mechanism at > 80° is inferred. T is eliminated by the initial addition of sufficiently fine $CaCO_3$, and k is increased by increasing the wt. of added $CaCO_3$. Similar but less marked effects are produced by C and shavings of Fe, Cu, and Al, but Zn and Zn^{++} diminish k and increase T . J. G. A. G.

Effect of hydrogen-ion concentration on the decomposition of hypohalites. R. M. CHAPIN (J. Amer. Chem. Soc., 1934, 56, 2211—2215).— OCl' is most stable at p_H 13.1 (except in strongly acid solutions) and least at p_H 6.7; OBr' is most stable at p_H 13.4 and least at p_H 7.3. The stability of OI' increases with increasing $[OH']$ between p_H 12.5 and 5N-KOH.

E. S. H.

Catalytic decomposition of hydrogen peroxide by the iodine-iodide couple. IV. Approach to the steady state. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1934, 56, 2369—2372; cf. A., 1932, 818, 1212).—The mechanism postulated by Abel (A., 1928, 1194) is capable of explaining the results obtained.

E. S. H.

Effect of electrolytes in ionic reactions. M. KILPATRICK (J. Amer. Chem. Soc., 1934, 56, 2326—2327).—The disagreement of the measurements of La Mer and Greenspan (A., 1934, 971) with the Brönsted theory is due to the fact that the results are not in the range of concn. to which this theory applies.

E. S. H.

Catalysis of an interface reaction by adsorbed molecules. B. TOPLEY and M. L. SMITH (J.C.S.,

1934, 1754—1755; cf. A., 1932, 26).—The rate (I) of the reaction $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$ is increased by the presence in the reaction interface of adsorbed HCl. Small partial pressures of NH_3 and MeOH diminished (I), but SO_2 had no effect.

J. G. A. G.

Heats of activation of the acetone-iodine reaction. G. F. SMITH (J.C.S., 1934, 1744—1750).—From velocity measurements at 0° and 25°, the energy of activation of the COMe_2 -I reaction has been evaluated with respect to the following catalysts: H^+ 20,680, AcOH 20,010, EtCO_2H 19,370, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ and $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ 19,230, AcO^+ 22,800, and EtCO_2^+ 22,910 g.-cal. Vals. of the probability factor, P , in the bimol. velocity equation $k = Pze^{-E/RT}$ (cf. A., 1934, 971) range from 0.15 for H^+ to 4×10^{-5} for EtCO_2H , and for acid catalysts (dissociation const. K_a), $P \sim K_a^{0.5}$ approx. This result is interpreted on the view that in a collision involving mols. of catalyst and reactant, in which the necessary energy conditions are satisfied, an essential condition for reaction is the simultaneous ionisation of the catalyst mol.

J. G. A. G.

Enzymic sucrose inversion in heavy water. E. W. R. STEACIE (Z. physikal. Chem., 1934, B, 27, 6—10; cf. A., 1934, 607).—The rate of inversion by β -*h*-fructosidase is a little < in ordinary H_2O .

R. C.

Kinetics of esterification. Reaction between acetic acid and methyl alcohol catalysed by hydrions. A. T. WILLIAMSON and C. N. HINSHELWOOD (Trans. Faraday Soc., 1934, 30, 1145—1149).—The reaction between MeOH and AcOH in presence of HCl has been studied at 0—45°, with results in agreement with Goldschmidt (cf. A., 1912, ii, 1154). The heat of activation is 10,200 g.-cal. Assuming binary collisions between AcOH and MeOH_2^+ the efficiency of activating collisions is 1.17×10^{-5} , but if ternary collisions involving in addition the solvent MeOH mols. are necessary for reaction the efficiency is calc. to be 0.78×10^{-3} , allowing for the temp. coeff. of η_{MeOH} . The latter result may be contrasted with the efficiency 1.5×10^{-7} for catalysis by undissociated AcOH.

R. S. B.

Application of quantum mechanics to certain cases of homogeneous catalysis. I. A. E. STEARN (J. Gen. Physiol., 1934, 18, 171—191).—The configurative energies of the groups in the reaction $:\text{C}:\text{N}: + \text{HOH} \rightarrow :\text{C}:\text{OH} + :\text{NH}$ are plotted for different configurations corresponding with degrees of reaction and the energies of activation deduced for catalysis with OH^+ and H^+ on the assumption that these ions alter the proportions of coulombic to vibrational energy; the vals. obtained are 14.5 and 18.6 kg.-cal. This would correspond with relative speeds of hydrolysis of 700:1; correcting this val. for the greater effective $[\text{H}^+]$ than indicated by p_{H} a val. of 13:1 is deduced.

H. D.

Vegetable lecithin as an antioxidant. E. W. KOCHENDERFER and H. G. SMITH (Proc. Iowa Acad. Sci., 1932, 39, 169—170).—Two samples of soya-bean lecithin acted as weak antioxidants. CH. ABS. (e)

Catalysis by palladium of the union of hydrogen and oxygen. New phenomenon of contact

catalysis. D. L. CHAPMAN and G. GREGORY (Proc. Roy. Soc., 1934, A, 147, 68—75).—Adsorbed H_2 does not react with O_2 at room temp., and can thus render the surface inoperative as a catalyst for the reaction. Kinetic measurements show that H_2 is an inhibitor and O_2 an accelerator of the reaction, in agreement with the above conclusion. The mechanism of the catalysis by Pd is mainly one of alternate oxidation of metal and reduction of the oxide.

L. L. B.

Activation of gases by metals. L. KAHLENBERG, N. J. JOHNSON, and A. W. DOWNES (J. Amer. Chem. Soc., 1934, 56, 2218—2221).—A disagreeable odour observed when most metals are heated in H_2 , N_2 , He, A, CO_2 , or O, has been traced to impurities acquired by contamination of the metal surfaces. The apparent ability of H_2 , after having passed over heated metals, to unite with S at room temp. and to reduce Fe^{+++} , KMnO_4 , etc. is due to the formation of H_2S by reaction with S compounds adsorbed by the metals from the air. These reactions are not obtained after the H_2 has passed for some time, but momentary exposure of the metal to the air at once produced the apparent "activation." A small fraction of the H_2 released from cathodically hydrogenated Pd, Ni, Si, or C reduced S above 65°.

E. S. H.

Catalysts for the production of nitric acid by the oxidation of ammonia. L. MARMIER (Compt. rend., 1934, 199, 868—869).—By passing a mixture of NH_3 and air over platinised porcelain at suitable temp., yields of 3.2—7 kg. of HNO_3 can be obtained per g. of Pt present per 24 hr. Other metals catalyse the reaction in the following order of activity: $\text{Fe} < \text{Sr} < \text{U} < \text{Mn} < \text{Ce} < \text{Mo} < \text{W} < \text{Cr}$. Cr is almost as active as Pt. Ozonisation of the air leads to increased yields, but these do not warrant the energy consumption in the ozoniser.

J. W. S.

Effect of ferrous iron in solutions of citric acid of different hydrogen-ion concentration on the corrosion of iron in presence of a limited supply of air. J. M. BRYAN (Trans. Faraday Soc., 1934, 30, 1059—1062; cf. A., 1933, 1251).—At $p_{\text{H}} < 5$, added Fe^{II} facilitates the corrosion of steel in the presence of a limited supply of air. The vol. of H_2 evolved is parallel with the corrosion, and Fe^{II} increases the vol. of O_2 absorbed, particularly at 4—6, and of H_2 depolarised.

J. G. A. G.

Catalytic oxidation of organic compounds in the vapour state. G. CHARLOT (Ann. Chim., 1934, [xi], 2, 415—490; cf. A., 1933, 680, 1019).—Each catalyst may have two sp. activities, one for complete oxidation to CO_2 and one for partial oxidation to aldehydes, acids, etc. The influence of surface area, amount, concn., and method of prep. of the catalyst has been studied for the particular case of the oxidation of PhMe. 35 oxide catalysts have been examined, and also metallic Pd, several reduced metals, and mixed catalysts in the form of salts, such as Sn vanadate or tungstate, both of which are often particularly active, or of simple mixtures of oxides of which the activity obeys approx. the mixture rule. Partial oxidation is obtained with the oxide catalysts only, not with metallic catalysts. The activity of a catalyst varies with time, three

periods being noticeable. For 10–20 min. there is a high activity, then a long period from a few hr. to 4 or 5 days of a const. lower activity, and finally a period during which there is a gradual diminution to zero activity. The catalytic oxidation of CO, SO₂, NH₃, and H₂ has been studied and compared with that of org. vapours, but there is no simple relation between them. An apparatus for the separation of the products of partial oxidation is described.

M. S. B.

Exchange reactions of hydrogen on metallic catalysts. I. HORIUTI and M. POLANYI (Trans. Faraday Soc., 1934, 30, 1164–1172).—H¹ in C₂H₄ and C₆H₆ is not replaced by H² from H₂O containing 2.7% H₂O in presence of Pt-black or Ni catalysts at room temp., but exchange reactions are observable at 80°, the rate for C₆H₆ being < that for C₂H₄. Exchange of H² between C₂H₄ and C₆H₆ containing H² is slower than exchange between H₂O and C₆H₆, and the latter is 10⁵ slower than the exchange between H₂ and C₆H₆ on Ni; a similar ratio is probable for C₂H₄. It is inferred that exchange does not proceed by the mechanism C₆H₆ ↔ Ph + HK, where K is the catalyst, and that hydrogenation or exchange proceeds by the chemisorption of H₂ and ethylenoid compound producing adsorbed H atoms and an opening of the double linking, the two halves of which unite with the catalyst, followed by union of adsorbed H and C. This gives replacement by elimination of H, or hydrogenation by the subsequent union of another adsorbed H with a second C. Hydrogenation is then bimol., whereas replacement is unimol., with respect to H, and hence the latter predominates at low pressures.

R. S. B.

Reaction of carbon monoxide on molybdenum oxides. H. M. SPENCER and J. L. JUSTICE (J. Amer. Chem. Soc., 1934, 56, 2301–2306).—MoO₃ is reduced very slowly by CO at 400°, probably to MoO₂. At 560° the reduction of Mo by CO yields Mo₂C, which catalyses the decomp. of CO. At 810° MoO₂ reacts with CO to form Mo₂C according to the reversible equation 2MoO₂ + 6CO ⇌ Mo₂C + 5CO₂. The equilibrium const. of this reaction is 1.46.

E. S. H.

Hydrogenation of benzene with nickel oxide [catalyst].—See B., 1934, 1049.

Catalytic action of soda in the reduction of carbon dioxide with charcoal. H. EDENHOLM and T. WIDELL (IVA, 1934, 26–39; Chem. Zentr., 1934, ii, 1257).—0.7% of Na₂CO₃ had no appreciable effect, whilst 2–3% lowered the reaction temp. by 150–200°. The dependence of the rate of CO₂ + C = 2CO on the CO₂ pressure and extent of C surface has been studied. The Na₂CO₃ has no effect on diffusion processes.

H. J. E.

Catalytic action of Japanese acid earth. VI. Action on cyclohexylamine and its derivatives. VII. Relation between the constituents of the earth and its catalytic action. H. INOUE and K. ISHIMURA (Bull. Chem. Soc. Japan, 1934, 9, 423–430, 431–439).—VI. On heating cyclohexylamine (I) and its Me derivatives with Japanese acid earth at 350° and atm. pressure NH₃ is first eliminated and then cyclohexene (II) or the appropriate Me deriv-

ative. (II) undergoes isomeric change yielding methylcyclopentane (III). The earth promotes dehydrogenation; methylcyclohexylamine yields NH₂Ph and carbazole, whilst Me derivatives of (II) give PhMe. 15–20% of the reaction products are polymerisation or condensation products. The yields of (III) and of polymerides are greatest from (I).

VII. When C₁₀H₈ is heated with powdered Japanese earth in a sealed tube at 300° a quantity of a resinous substance, mainly ββ'-dinaphthyl (IV), is produced. The yield of (IV) was studied with earth which had been pretreated before use as the catalyst, and with essential constituents of the earth separately or in groups. Other similar catalysts were used and results are discussed. (IV) is produced when SiO₂ and Al₂O₃ coexist in the catalyst, the yield being uninfluenced by Fe(OH)₃ and Mg(OH)₂, but considerably diminished by hydroxides of alkali or alkaline-earth metals.

W. R. A.

Active oxides. LXXX. Characterisation of active states of system magnesium oxide-ferrous oxide by their activity in catalysing the decomposition of nitrous oxide. G. F. HUTTON, W. NOVAK-SCHREIBER, and H. KITTEL (Z. physikal. Chem., 1934, 171, 83–92).—The magnetic susceptibility and catalytic activity, *A*, of equimol. mixtures of MgO and Fe₂O₃ which have been heated at various temp., *T*, have been measured. With rise in *T*, *A* passes through a max. The high *A* of forms intermediate between the mixture MgO + Fe₂O₃ and cryst. MgFe₂O₄ depends on the presence in great no. of only a single species of active mol., the heat of activation of which for the N₂O decomp. is 37,960 g.-cal. Variation in *A* is caused by variations, not in the quality, but in the no. of active points. The corners and edges of the cryst. phases have a higher *A* than the "active" amorphous intermediate stages.

R. C.

Oxidising action of colloids. III. Oxidising action of colloidal metals. Y. SHIBATA and K. YAMASAKI (J. Chem. Soc. Japan, 1934, 55, 693–698).—The oxidation rate of pyrogallol is accelerated by colloidal Pt, but not by colloidal Au or Ag.

CH. ABS. (e)

Concentration of heavy water. A. I. BRODSKI, V. A. ALEXANDROVITSCH, M. M. SLUTSKAJA, and M. K. SCHELUDEKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 615–619).—A process of electrolysis using Fe electrodes with 3–4% KOH or Pb or Pt electrodes with 2–4% H₂SO₄ gave approx. a 5–6-fold concn. of H₂O for a 10-fold vol. reduction.

H. J. E.

Concentration of deuterium in some industrial waters. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1934, 9, 457–459).—Samples of H₂O from a commercial electrolytic cell (I) (1 year), Cr-plating bath (II) (4 years), Pb accumulators (III) (9 years), and Edison batteries (IV) (6–9 months) were purified and their *d* determined by the buoyancy balance method. The increases in *d*, due to H² enrichment occurring throughout the period given in parentheses, are (p.p.m.) (I), 28; (II), 7; (III), 0–3; (IV), 27–28. It is uncertain whether the increase for (IV) arises from increased H² content or from impurities retained in H₂O.

W. R. A.

Potentiometric and conductometric studies.

I. Potentiometric. J. PIERER (Z. Elektrochem., 1934, 40, 793—805).—A study of the Sb electrode in acid-alkali, oxidation-reduction, and pptn. titrations has been made. The val. of Sb deposited on Pt depends on the conditions of prep.; such electrodes are not easily reproducible, but a correction may be applied. The use of the triodometer for potentiometric titrations has been studied; the influence of temp. and other variables is considered. E. S. H.

Electrometallurgy of aluminium. W. D. TREADWELL and L. TEREBESI (Z. Elektrochem., 1934, 40, 744).—A reply to criticism (cf. A., 1934, 1078). E. S. H.

Cathodic behaviour of organic copper salts.

Study of the electrolysis as a function of time. G. KRAVTSOFF (Compt. rend., 1934, 199, 1029—1031; cf. A., 1933, 913).—From the change in p_H and the Cu deposited during the electrolysis of $(HCO_2)_2Cu$, $Cu(OAc)_2$, and $CuSO_4$ for periods of 15 min. to 24 hr. and at c.d. of 10—500 milliamp. per sq. dm., it is shown that the Cu_2O content is the greater the shorter is the period of electrolysis, and the longer the electrolysis the lower is the Cu_2O content. It is suggested that Cu^{++} is initially reduced to Cu_2^{+} , but that the latter hydrolyses to Cu_2O , which deposits at the cathode, and the acid, the increase in acidity favouring the discharge of Cu^{++} . J. W. S.

Evolution of CO_2 in the a.-c. electrolysis of sodium carbonate and hydrogen carbonate solutions and the discharge potentials of carbonate and hydrogen carbonate ions. J. W. SHIPLEY (Canad. J. Res., 1934, 11, 539—546).—No CO_2 is evolved in the a.-c. electrolysis of aq. Na_2CO_3 at voltages up to 110, even when arcing occurs. With aq. $NaHCO_3$ and Pt electrodes H_2 , O_2 , and CO_2 are evolved freely until Na_2CO_3 only is left, when evolution of CO_2 ceases. In the a.-c. electrolysis of aq. $NaHCO_3$ and aq. Na salts of aliphatic acids, finely-divided Pt is deposited on the electrodes and inhibits the evolution of gases, probably due to recombination, but does not affect current flow. The decomp. potential of aq. $NaHCO_3$ for evolution of CO_2 on smooth Pt with d.c. is 2.2 volts, and of aq. Na_2CO_3 3.5 volts. The anodic discharge potential of HCO_3^- is -1.45 to -1.50 volt and of CO_3^{--} -1.90 to -1.95 volt. Evolution of CO_2 does not cause polarisation. M. S. B.

Electro-deposition of zinc-cadmium alloys from alkaline cyanide solutions.—See B., 1934, 1107.

Effect of oxidising agents on nickel solutions.

I. Hydrogen peroxide and nickel nitrate. A. W. HOTHERSALL and R. A. F. HAMMOND (Trans. Faraday Soc., 1934, 30, 1079—1094).—With solutions buffered with H_3BO_3 or $(NH_4)_2SO_4$, the cathode efficiency decreased linearly with increasing concn. of added $Ni(NO_3)_2$ and H_2O_2 ; the effect increased slightly as the H_2O_2 was raised from 2.7 to 5.9. The primary process is depolarisation of H; NO_3^- is reduced to NH_3 , and the effects produced are dependent on the oxidising powers of NO_3^- and H_2O_2 . With increasing $[NO_3^-]$ and $[H_2O_2]$, the quantity of gaseous H_2 evolved at the cathode gradually fell to

zero and no gas was discharged over a concn. range. At still higher $[NO_3^-]$ and $[H_2O_2]$, coincident with a sharp rise of cathode potential, evolution of gas recommenced, except with $(NH_4)_2SO_4$ solutions containing NO_3^- . Addition of NO_3^- and H_2O_2 increased the hardness, stress, and brightness of the Ni deposits, which tended to crack and become exfoliated. This is attributed to increased pptn. of colloidal basic matter with rising rate of H^+ discharge, i.e., diminishing cathode efficiency. The prevention of pitting by H_2O_2 and NO_3^- is parallel with their effects in inhibiting H_2 evolution from pure solutions; H_2O_2 also prevents pitting in solutions containing impurities (II) responsible for pitting by oxidising and pptng. Fe compounds on which (II) are adsorbed.

J. G. A. G.

Influence of temperature on the products of electrolysis of acetate solutions. J. ROBERTSON (Trans. Faraday Soc., 1934, 30, 1007—1017).—In the electrolysis of KOAc in anhyd. AcOH, the ratio $C_2H_6 : H_2$ is approx. 0.95 : 1 and is little affected by electrode material or change of temp., but small quantities of H_2O decrease the yield of C_2H_6 and increase the oxidation, whilst the products are affected by the anode material. Electrolysis of aq. KOAc leads to C_2H_6 formation (I), O_2 formation (II), and complete oxidation (III). (I) predominates at low temp., but diminishes with rise of temp. as (III) increases to a max., after which (II) increases as (III) decreases and (I) tends to zero. (I) with a Au anode is < with bright Pt, but in all cases (I) increases with rise of c.d. and increasing [KOAc]. The results are consistent with the discharge theory of the reaction.

J. G. A. G.

Mechanism of Kolbe's reaction. I. Electrolysis of free acetic acid. M. MATSUI and K. KIZAKI (Mem. Coll. Sci. Kyoto, 1933, A, 16, 297—307).—The reaction has been investigated with 5—60% aq. AcOH at 15—45°. At 15° and c.d. 0.071 amp. per sq. cm. the proportion of C_2H_6 in the evolved gas is max. with 30% AcOH and the $C_2H_6 : H_2$ vol. ratio is 0.75 : 1, but the proportion of C_2H_6 decreases with rise of temp. and increases with rise of c.d. Evolution of C_2H_6 is greatly diminished by small quantities of H_2SO_4 , H_3PO_4 , $H_2C_2O_4$, and HCO_2H , but is not affected by $LiBO_3$, which does not change the dissociation of AcOH. Strong electrolytes also diminish C_2H_6 evolution owing to decreased concn. of discharged AcO^- . The results discriminate against the "simple oxidation theory" in favour of the "discharge theory." J. G. A. G.

Mechanism of the electrochemical chlorination of benzene. W. JEUNEHOMME (Compt. rend., 1934, 199, 1027—1029).—On electrolysis of a MeOH solution of HCl, containing C_6H_6 , the latter is chlorinated by two simultaneous processes, a surface reaction with Cl atoms at the electrode, and a homogeneous reaction with Cl_2 in solution. The efficiency of the current in producing PhCl can reach 85%. Traces of $C_6H_4Cl_2$, C_6H_5Cl , and chlorinated phenols are also produced. J. W. S.

Chemical action in the glow discharge. XIII. Chain reactions in the oxidation of hydrogen in the positive column. A. K. BREWER and P. D.

KUBCK (J. Physical Chem., 1934, **38**, 889—900; cf. A., 1930, 1533).—The rate of oxidation of H_2 in the positive column increases with both current and voltage, with rise of temp., and linearly with the addition of A up to 50%, whilst the proximity of glass surfaces retards it. The results are explained by the presence in the positive column of reaction chains of the cluster type. F. L. U.

Electrolytic oxidation. V. Formation of hydrogen peroxide by electrolysis with a glow-discharge anode. S. GLASSTONE and A. HICKLING (J.C.S., 1934, 1772—1773).—With 0.05—0.1N acid and salt solutions, and a glow-discharge anode, yields of H_2O_2 50—100% of those calc. from Faraday's laws were obtained. H_2O_2 persists in the solution only if formed out of contact with the solid electrode. With a glow-discharge cathode, H_2O_2 was not detected. The results accord with the view that H_2O_2 is formed by the union of discharged OH ions (cf. A., 1934, 258). J. G. A. G.

Decomposition of sulphur dioxide by electric discharge. S. S. JOSHI and K. K. SHARMA (J. Chim. phys., 1934, **31**, 511—516).—The decomp. of SO_2 by a silent electric discharge has been followed by measuring the change of pressure occurring. The reaction becomes slower with time and tends towards an equilibrium. Under the conditions used (a.c. 6000—12,000 volts, 50 cycles) no decomp. is observed at pressures > 200 mm. The final mixture contains SO_3 , O_2 , about 10% of SO_2 , and two solid products not identified. F. L. U.

Dissociation products of carbon monoxide formed by primary electron impact. W. W. LOZIER (Physical Rev., 1933, [ii], **43**, 776; cf. A., 1934, 1159).— O^- and C^+ ions both appear as primary products of electron impact. O^- ions first appear at 9.5 ± 0.1 volts electron energy, and again at 20.9 ± 0.1 volts electron energy accompanied by an equal no. of C^+ ions. At 22.8 ± 0.1 volts electron energy the production of C^+ ions markedly increases. L. S. T.

Chemical change of carbon disulphide under electrodeless discharge. M. EMI (Bull. Chem. Soc. Japan, 1934, **9**, 442—446).—Experimental details are given. When CS_2 at 0.08 mm. was subjected to electrodeless discharge the pressure fell to 0.075 mm. and dark solid deposits sol. in CS_2 were formed on the condenser. These are polymerised forms of CS and C_3S_2 . W. R. A.

Heterogeneous chemical reactions under the silent electric discharge. X. Preparation of colloidal solutions by silent electric discharge. S. MIYAMOTO (J. Chem. Soc. Japan, 1934, **55**, 611—617; cf. A., 1934, 739).—The prep. of Au sols from aq. $HAuCl_4$ and aq. Au hydroxide suspensions, Ag sols from aq. $AgNO_3$, or aq. suspensions of Ag_2O , $AgCO_3$, or $AgCN$, Pt sols from H_2PtCl_6 , and Pd sols from $PdCl_2$ dissolved in dil. HCl is described. Ag sols in Bu^iOH or amyl alcohol are prepared similarly. CH. ABS. (e)

Dissociation of nitrous oxide in the high-frequency glow discharge. E. A. STEWARDSON (Trans. Faraday Soc., 1934, **30**, 1018—1027).—By means of the diaphragm gauge described, the rate of

decomp. at const. vol. of < 3 mm. of N_2O is shown to be unimol. with respect to N_2O in sufficiently intense fields, but in weak fields the initial rate is approx. independent of the initial pressure (cf. A., 1926, 619), although the decomp. as a whole approximates to a first-order law of which the coeff. depends on the initial pressure. J. G. A. G.

Photolysis of water and the action of light in electrodes. R. AUDUBERT (J. Phys. Radium, 1934, [vii], **5**, 567).—Errata (see A., 1934, 1315).

Inability of X-rays to decompose water. H. FRICKE and E. R. BROWNSCOMBE (Physical Rev., 1933, [ii], **44**, 240).—Irradiation with dosages up to 150 kiloroentgen showed that pure air-free H_2O is not decomposed by X-rays. L. S. T.

Photochemical reaction of oxygen with hydrogen in the Schumann region. H. NEUMANN and B. POPOV (Z. physikal. Chem., 1934, **B**, **27**, 15—27).—The reaction with H_2 of O_2 optically dissociated by light of λ 1350—1750 Å. into O atoms in the normal state and a metastable state (1D) has been examined. The reaction is homogeneous and the quantum yield ~0.1, and the metastable O atoms are much more reactive than the normal O atoms. Probably the processes involved are $O' + H_2 \rightarrow OH + H$, $OH + H_2 \rightarrow H_2O + H$, and $OH + OH + M \rightarrow H_2O_2 + M$ ($M = \text{wall}$). Preliminary measurements have been made on the reaction of O atoms with CO. R. C.

Comparison of the photosensitised reaction of hydrogen and oxygen, and deuterium and oxygen. M. G. EVANS (J. Chem. Physics, 1934, **2**, 726—732).—There is very little difference between the rates of reaction of H_2 and of D_2 with O_2 when illuminated by ultra-violet light in presence of Hg vapour. The temp. coeffs. between 30° and 50° are also equal within the experimental error. Possible mechanisms are discussed. F. L. U.

Induction period of the photochemical reaction between hydrogen and chlorine. J. G. A. GRIFFITHS and R. G. W. NORRISH (Proc. Roy. Soc., 1934, **A**, **147**, 140—151).—In the induction period of the photochemical H_2 - Cl_2 reaction, due to NCl_3 produced by interaction of dry NH_3 and Cl_2 , NCl_3 is decomposed photosensitively by the Cl_2 in a zero-order reaction. If H_2O is absent, NH_4Cl does not cause an induction period, as it does not react with Cl_2 . The quantum efficiency of the decomp. is given by $\gamma = 2.5 + 1/(0.0038P_{Cl_2} + 0.0009P_{H_2})$. Hence H_2 behaves like an inert gas in shortening the chain length of the photosensitised decomp. of NCl_3 . In the inhibition period, which lasts until all the NCl_3 is decomposed, the yield of HCl is < 0.2 mol. per quantum absorbed. L. L. B.

Inert gas effects in the photosynthesis of hydrogen bromide. M. RITCHIE (Proc. Roy. Soc., 1934, **A**, **146**, 828—848).—The rate of photochemical formation of HBr at 200° in presence of various foreign gases has been investigated from two points of view: (a) the removal of Br atoms from the gas phase by diffusion to the wall of the reaction vessel, and (b) the removal of Br atoms by a recombination process involving a third atom as stabiliser. In (a) the addition of foreign gas increases the rate of reaction in the order

$\text{CCl}_4 > \text{CO}_2 > \text{N}_2 > \text{A} > \text{H}_2$ and He. In (b) the rate of reaction is decreased by facilitating the recombination of Br atoms. The series is given by $\text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{A} > \text{He} > \text{H}_2$.
L. L. B.

Photolysis of dry ozone at λ 208, 254, and 280 m μ . I. Quantum yields. L. J. HEIDT and G. S. FORBES (J. Amer. Chem. Soc., 1934, 56, 2365—2368).—The quantum yield, ϕ , is as high as 6.7, indicating an energy chain mechanism. The temp. coeff. of ϕ is 1.2 per 10°. No direct dependence of ϕ on wave-length was observed.
E. S. H.

Photochemistry of mixtures of chlorine and ozone. A. C. BYRNS and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 2245—2250; cf. A., 1934, 369).—When mixtures of Cl_2 and O_3 are illuminated with blue light, ClO_2 and Cl_2O_7 are formed in appreciable quantities. The Cl_2O_7 is relatively inert, but the ClO_2 undergoes a thermal decomp., a Cl_2 -sensitised photo-decomp., and a reaction with O_3 . One product of the last reaction is Cl_2O_7 . One of the primary products of the thermal decomp. is ClO_2 .
E. S. H.

Kinetic expression for rate of the photosensitised decomposition of ammonia and deutero-ammonia. M. G. EVANS and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 732—734; cf. A., 1934, 1078).—The cause of the deviation of the experimental data from the kinetic expression used by Melville (A., 1933, 35) is considered to be due partly to the assumption, made in deriving the expression, that every quenching collision leads to decomp. Further, in addition to a difference between NH_3 and ND_3 in quenching excited Hg, there is a difference in the probabilities of decomp. of the NH_3 and ND_3 mols. which have received energy from the Hg. An empirical expression in harmony with the data is given.
F. L. U.

Photochemical oxidation of phosphine above the upper explosion limit. H. W. MELVILLE (J. Chem. Physics, 1934, 2, 739—752; cf. A., 1933, 678).—Speeds of the direct and of the Hg-sensitised photo-reaction have been measured. The former is given by $-d[\text{PH}_3]/dt = k_1[\text{PH}_3]^2/[\text{O}_2]^2$, and the latter by $-d[\text{PH}_3]/dt = k_2[\text{PH}_3]/[\text{O}_2]^2I$. The reactions are of the chain type, and the results are consistent only with the destruction of the chain-carrier in a ternary collision either with 2O_2 or with $\text{O}_2 + \text{N}_2$ (or A). The carrier is probably an O atom. The observed displacement of the upper limit to higher pressures by illumination is not predicted by theory. F. L. U.

Combined action of radiation and a catalyst. I. Influence of ultra-violet light on the activity of the catalyst in the catalysis of hydrogen peroxide in aqueous solution. L. V. PISAR-SHEVSKI, R. K. KORABELNIK, and E. S. RINSKAJA (Bull. Acad. Sci. U.R.S.S., 1934, 7, 931—951).—The activity (I) of PbO_2 and Pt is increased by previous exposure to ultra-violet light. Irradiation during the H_2O_2 catalysis increases the (I) of graphite, charcoal, PbO_2 , and Pt, but may produce a decrease in the latter case. The results are in agreement with the theory that electrons are transferred from H_2O_2 mols. adsorbed on inactive regions to those at the active centres.
R. S.

Spectra and photochemical decomposition of metallic carbonyls. II. Photochemical data. A. P. GARRATT and H. W. THOMPSON (J.C.S., 1934, 1817—1822).—The absence of both pressure change and deposition of Ni when $\text{Ni}(\text{CO})_4$ vapour is irradiated with λ 366—301 m μ is attributed to the rapid recombination $\text{CO} + \text{Ni}(\text{CO})_3 \rightarrow \text{Ni}(\text{CO})_4$ (cf. A., 1934, 582) and the inferred relation between the energy levels of $\text{Ni}(\text{CO})_4$. Consistent with the absorption spectrum, photo-decomp. occurs in solution only with $\lambda < 400$ m μ . In CCl_4 , the quantum efficiency, γ , is 2.2 and increases as λ decreases. Smaller vals. of γ are found in C_6H_{14} and cyclohexane. The deviation of γ from the val. 4 required by the mechanism previously advanced (*ibid.*) is discussed. J. G. A. G.

Optimum composition of uranyl oxalate solutions for actinometry. G. S. FORBES and L. J. HEIDT (J. Amer. Chem. Soc., 1934, 56, 2363—2365).—When a solution containing 0.01M- UO_2SO_4 and 0.05M- $\text{H}_2\text{C}_2\text{O}_4$ is diluted 10-fold, the quantum yields, ϕ , at λ 313, 280, 254, and 208 m μ are unchanged (within 3%). Advantages of the more dil. solution at the shorter wave-lengths are indicated. By substituting $\text{UO}_2\text{C}_2\text{O}_4$ for UO_2SO_4 purification is simplified and ϕ remains unchanged. ϕ also remains unchanged (except at 208 m μ) in a solution containing 0.005M- $\text{UO}_2\text{C}_2\text{O}_4$ and 0.0025M- $\text{H}_2\text{C}_2\text{O}_4$.
E. S. H.

Higher order reversals in the solarisation region. L. T. DEVORE and W. J. SAYLOR (J. Opt. Soc. Amer., 1934, 24, 303—304).—Experiments have been made to determine the characteristics of higher order reversals in a photographic emulsion on prolonged exposure. The H. and D. curves show a second max. and the commencement of a second downward slope. The slopes of the original and second upward straight-line portions are identical, but the second max. is much < the first. Colour changes are also observed in the images.
J. L.

Action of various elements and compounds on photographic plate. A. AOYAMA, T. FUKUROI, and I. TAKAHASHI (Sci. Rep. Tôhoku, 1934, 23, 384—404).—The effect of metals and other substances on photographic plates in the dark is attributed to the formation of activated gases in the vicinity of the specimen, due to desorption or to reflexion from active centres, and the action of these activated mols. on the plate.
J. W. S.

Ultra-short-time effect and its interpretation. A. NARATH (Z. wiss. Phot., 1934, 33, 145—150, 153—166).—The failure of the reciprocity law with ultra-short exposures is explained as a surface effect, dependent on the predominant colour-sensitivity of the surface layers of an emulsion. Using known double-layer emulsions, one having a yellow- and the other a blue-sensitive top layer, the results are in agreement with theoretical expectations. For the usual homogeneous emulsions the effect is found to be dependent on development time; the dispersion effects of development are examined by means of the Kerr electro-optical effect. Four different emulsions show the different types of effect obtainable. (Cf. Kuster and Schmidt, Wiss. Veröff. Agfa, 2, 94.)

Photo-bromination of acetylene. J. E. BOOHER and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 2288—2294).—The reaction, forming $C_2H_2Br_2$, has been studied kinetically at 150° . Measurements of the quantum yield indicate a chain reaction with a chain length of approx. 500 at 15° , increasing to about 3000 at 20° , independently of wave-length. Equations representing the rate laws at high and low concns. of C_2H_2 have been derived and are supported by a mechanism involving Br , Br_3 , $C_2H_2Br_3$, and C_2H_2Br as intermediates. The influence of temp. is very small. The calc. heat of activation is about -1500 g.-cal.

E. S. H.

Chemical action of light on di-iodo-derivatives of hydrocarbons: di-iodoethanes, di-iodomethane. G. EMSCHWILLER (Compt. rend., 1934, 199, 854—856).—In its mode of photochemical decomp., $CHMeI_2$ resembles CH_2I_2 in the affinity shown between the H and I atoms, instead of between the I atoms, as in $(CH_2I)_2$. CHI_3 is only very slowly decomposed in solution in the absence of O_2 , and this with liberation of HI, again showing affinity between the H and I atoms.

J. W. S.

Reactions involving free alkyl groups. I. Photo-reaction of methane, chlorine, and oxygen. II. Photo-oxidation of gaseous ethyl iodide. L. T. JONES and J. R. BATES (J. Amer. Chem. Soc., 1934, 56, 2282—2284, 2285—2287).—I. The photochemical reaction between CH_4 and Cl_2 accords with Thon's equation for the inhibiting effect of O_2 and takes place through a Nernst chain mechanism. The chain carrier is probably the Me group.

II. After illumination for a long period, EtI decomposes to an uncondensable gas, probably C_2H_4 and C_2H_6 . Oxidation is rapid, giving $MeCHO$ and $EtOH$, at a rate which increases to a max. with increasing O_2 content and then falls asymptotically. A mechanism involving the intermediate formation of Et_2O_2 is proposed.

E. S. H.

Quantum yield in the photo-decomposition of liquid ethyl iodide at 3130, 2654, and 2537 Å. B. M. NORTON (J. Amer. Chem. Soc., 1934, 56, 2294—2297).—Using a modified technique the quantum yield at 20° is 0.315 at 3130 Å., 0.38 at 2654 Å., and 0.41 at 2537 Å.

E. S. H.

Free radicals and atoms in primary photochemical processes. Photo-dissociation of aliphatic ketones and aldehydes. T. G. PEARSON (J.C.S., 1934, 1718—1722).—Free alkyl radicals have been detected, by the action on Sb, Te, and Pb mirrors, in the primary products of the photolysis of the vapours of $COMe_2$, $COMeEt$, and $COEt_2$, but not in the case of $COMeBu$, $MeCHO$, and $EtCHO$. These results are in complete accord with the mechanism proposed by Norrish, Kirkbride, and Appleyard (A., 1931, 1138; 1934, 852) for the photolysis of aliphatic aldehydes and ketones. Under the conditions described, the half-life period of the Me radicals from $COMe_2$ was 5.3×10^{-3} sec., whilst the radicals from $COEt_2$ had a shorter period.

J. G. A. G.

Transformation of formic acid by irradiation of its aqueous solution with X-rays. H. FRICKE and E. J. HART (J. Chem. Physics, 1934, 2, 824; cf.

A., 1933, 793).—The mode of decomp. of aq. HCO_2H by X-rays depends on the concn. and on the pH . Results so far obtained indicate that the neutral mol. gives $H_2 + CO_2$, and the ionised form $H_2 + H_2C_2O_4$.

F. L. U.

Photo-isomerisation of o-nitrobenzaldehydes. I. Photochemical results. II. Mathematical treatment. P. A. LEIGHTON and F. A. LUCY (J. Chem. Physics, 1934, 2, 756—759, 760—766).—I. The quantum yield in the photochemical conversion of $o\text{-NO}_2 \cdot C_6H_4 \cdot CHO$ and of $2:4\text{-C}_6H_3(NO_2)_2 \cdot CHO$ into the corresponding NO-acids either in the solid state or dissolved in $COMe_2$ or ligroin is 0.5. For the $2:4:6$ -trinitroaldehyde it is higher on account of the effects of a NO_2 -group on both sides of the aldehyde.

II. The probable course of the reaction is discussed mathematically.

F. L. U.

Possibility of separating D_2O from H_2O by fractional freezing. G. BRUNI (Atti R. Accad. Lincei, 1934, [vi], 20, 73—75).—After 9 fractionations, in which 4000 litres of ordinary purified H_2O were reduced to 280 c.c., no separation of H_2O from H_2O was obtained.

O. J. W.

Content of deuterium in water of crystallisation. K. OKABE, M. HARADA, and T. TITANI (Bull. Chem. Soc. Japan, 1934, 9, 460—461).—20 litres of tap- H_2O were saturated with anhyd. Na_2SO_4 and the solution was quickly cooled. $Na_2SO_4 \cdot 10H_2O$ crystallised and was separated from the mother-liquor (R_1), and converted by heating into Na_2SO_4 and the remaining clear solution (C_1) was filtered off. The process was repeated with R_1 and C_1 eight times, each time retaining only the fractions corresponding with R_1 and C_1 . The final fractions R_8 and C_8 were purified and their densities compared with normal H_2O were 2 p.p.m. greater. Similar work has been done on Na_2CO_3 . With such salts at low $[H^2]$ no isotopic fractionation occurs.

W. R. A.

Production of large single crystals of ice. J. M. ADAMS and W. LEWIS (Rev. Sci. Instr., 1934, [ii], 5, 400—402).—One face of a columnar fragment of commercial ice is frozen to the bottom of a metal can kept at -10° , and the opposite face allowed to dip into previously boiled distilled H_2O .

C. W. G.

Additive compounds of alkali halides and organic bases. M. RAGNO and S. FRASTI (Gazzetta, 1934, 64, 746—748).—By mixing saturated solutions of $(CH_2)_6N_4$ and alkali halide the compounds $MX \cdot 4H_2O \cdot (CH_2)_6N_4$ have been obtained, where $MX = LiBr$, NaI , and $NaBr$, respectively. No compounds were obtained with $NaCl$, $LiCl$, KBr , KCl , and KI .

O. J. W.

Decomposition of sodium carbonate. E. PRESTON and W. E. S. TURNER (J. Soc. Glass Tech., 1934, 18, 182—193r).—On heating in air Na_2CO_3 shows appreciable decomp. with formation of $NaOH$ at 800° , which is lower than the temp., viz., 980° , at which a dissociation pressure can be observed in vac. (A., 1931, 800). A slight decomp. may even be detected on heating for 1 day in air at 400° . The reaction appears to be due to atm. H_2O and, by heating in a current of N_2 containing H_2O vapour, it has been shown to

depend on the partial pressure of the latter. In the prep. of pure Na_2CO_3 for analytical purposes it is not advisable to heat above 400° . M. S. B.

Reactivity of sodium amide. A. PERRET and R. PERROT (Compt. rend., 1934, 199, 955–957).—The following reactions were observed: $3\text{NaNH}_2 + \text{NaN}(\text{CN})_2 \rightarrow 2\text{Na}_2\text{CN}_2 + 2\text{NH}_3$, above 150 – 160° ; $\text{COCl}_2 + 3\text{NaNH}_2 \rightarrow \text{NaNCO} + 2\text{NaCl} + 2\text{NH}_3$, in the cold; $\text{COCl}_2 + 5\text{NaNH}_2 \rightarrow \text{Na}_2\text{CN}_2 + 2\text{NaCl} + \text{NaOH} + 3\text{NH}_3$, at approx. 250° ; S_2Cl_2 in PhMe, after about 60 hr. gives N_4S_4 ; at 120° in absence of air the reaction is $3\text{S}_2\text{Cl}_2 + 12\text{NaNH}_2 \rightarrow 3\text{Na}_2\text{S}_2 + 8\text{NH}_3 + 6\text{NaCl} + 2\text{N}_2$. N. M. B.

Potassium oxides. C. A. KRAUS and E. F. PARNENTER (J. Amer. Chem. Soc., 1934, 56, 2384–2388).—The prep. of K_2O_2 and K_2O_4 by oxidation of K in liquid NH_3 is described. The existence of K_2O_3 , $\text{K}_2\text{O}_2 \cdot \text{H}_2\text{O}$, $\text{K}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, and $\text{K}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been established and their properties and reactions are described. E. S. H.

Basic copper carbonate and green patina. W. H. J. VERNON (J.C.S., 1934, 1853–1859).—Cu immersed in aq. CO_2 affords green basic Cu carbonate (I), the rate of conversion of arsenical Cu being $>$ of pure Cu. In air containing CO_2 and H_2O , (I) is formed only in the presence of another reactant, e.g., traces of carboxylic acid vapours (II); chlorides and traces of SO_2 behave similarly but less effectively. Probably a normal Cu salt is formed initially and (I) is formed when this is hydrolysed in presence of CO_2 . Thus, in an atm. containing $\text{CO}_2 \gg \text{SO}_2$, the green deposit contained 31.5% SO_4^{2-} and 0.76% CO_3^{2-} . Fourcroy's statement (1786) that open-air patina consists of (I) is incorrect, since the (I) in patina formed near the sea is secondary to basic chloride and inland is secondary to basic sulphate, but in certain urban districts the proportion of (I) rises to 25% probably owing to the action of (II).

J. G. A. G.

So-called diaquobisethylenediaminocupric ion. Reinvestigation of its simple salts and alleged optical isomerism. C. H. JOHNSON and S. A. BRYANT (J.C.S., 1934, 1783–1786).—The ion hitherto believed to be $[\text{Cu}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2(\text{H}_2\text{O})_2]^{2+}$ affords a nitrate which, however it is prepared, is completely anhyd., a chloride and bromide having only $1\text{H}_2\text{O}$ per mol., an efflorescent iodide with $2\text{H}_2\text{O}$ per mol., efflorescent sulphates with 4.5 and $2\text{H}_2\text{O}$ per mol., and a tartrate (I). In all cases, H_2O is quickly and completely removed over P_2O_5 in vac. (I) could not be resolved (cf. A., 1928, 395, 1077), and from electrode potential determinations the complex ion is unstable. The ion is $[\text{Cu}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]$, the Cu²⁺ having a co-ordination valency of 4, and therefore optical isomerism is excluded.

J. G. A. G.

Addition of hydrogen phosphide to cuprous and silver halides. R. SCHOLDER and K. PATTOCK (Z. anorg. Chem., 1934, 220, 250–256).—By the action of PH_3 on EtOH solutions of Cu^+ and Ag halides, containing the corresponding acids, the following compounds have been obtained: $\text{CuCl} \cdot \text{PH}_3$ (I), $\text{CuBr} \cdot \text{PH}_3$ (II), $\text{CuI} \cdot 2\text{PH}_3$ (III), $2\text{AgI} \cdot \text{PH}_3$. The stability of the Cu^+ compounds decreases in the order

(I) $>$ (II) $>$ (III). No PH_3 additive compounds could be obtained with AgCl and AgBr . The results indicate that an ionic lattice, and not a mol. lattice only (cf. Holtje, A., 1933, 127), can take up PH_3 .

M. S. B.

Preparation and properties of aurothiosulphates of ammonium, calcium, and quinine. PRON (Compt. rend., 1934, 199, 952–954).—From aq. quinine hydrochloride, quinine aurothiosulphate can be obtained by double decomp. and crystallisation; by the action of excess of NH_3 and evaporation in vac. the NH_4 salt is obtained. The Ca salt is prepared by the action of $\text{Ca}(\text{S}_2\text{O}_3)_2$ on AuCl_3 neutralised by CaCO_3 in presence of excess of $\text{Ca}(\text{OH})_2$, and isolated by the elimination of CaCl_2 with EtOH. The three salts are sol., and in most reactions the Au is eliminated as a higher sulphide, or as Au_2S in neutral solution. Reducing agents give Au. Evidence points to the structure $\text{O}_3\text{S}(\text{ONa})\text{SAu} \cdot \text{Na}_2\text{S}_2\text{O}_3$.

N. M. B.

Hydrothermal synthesis of some carbonates. W. BILTZ and A. LEMKE (Z. anorg. Chem., 1934, 220, 312–316).—By heating the corresponding chlorides in HCl solution with $\text{CO}(\text{NH}_2)_2$ in a bomb for 18–24 hr. at 200° , carbonates of Cd, Sr, Ba, Mn, Fe^{II} , Co, and Pb have been synthesised. $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ has also been obtained. Analytical and density data are given.

M. S. B.

Additive compounds of halides of bivalent metals with organic bases. VIII. G. SCAGLIARINI and G. C. CESARI (Gazzetta, 1934, 64, 742–745; cf. A., 1930, 328).—By mixing cold conc. solutions of $(\text{CH}_2)_6\text{N}_4$ (X) and the metallic halide in the solvents given in parentheses the following compounds have been obtained: $(\text{H}_2\text{O}) \text{ZnCl}_2 \cdot 4\text{H}_2\text{O} \cdot \text{X}$; $2\text{ZnBr}_2 \cdot 8\text{H}_2\text{O} \cdot 3\text{X}$; $2\text{ZnI}_2 \cdot 8\text{H}_2\text{O} \cdot 3\text{X}$; $\text{ZnI}_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{X}$; (95% EtOH) $3\text{ZnCl}_2 \cdot 2\text{X}$; $\text{ZnBr}_2 \cdot \text{X}$; $2\text{ZnI}_2 \cdot 3\text{X}$; $(\text{COMe}_2) \text{ZnCl}_2 \cdot \text{X}$.

O. J. W.

Hydrates of dicalcium aluminate. R. SALMONI (Gazzetta, 1934, 64, 719–734).—The hydrates $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, where $n=1, 3, 6, 10$, and 11, have been prepared. Heats of dissolution and X-ray structures of the hydrates with $n=1, 3, 5, 7$, and 9 are given. The higher hydrates all have the same lattice structure as the pentahydrate; this differs from that of the monohydrate.

O. J. W.

Effects of fluorides on thermal synthesis of calcium aluminates. I. S. NAGAI and T. YOSHURA (J. Soc. Chem. Ind. Japan, 1934, 37, 693–695B).—The interaction of a mixture of CaCO_3 and Al_2O_3 (3:1) at 900 – 1400° for 1 hr. is accelerated by the presence of 1% of CaF_2 and the product at the lower temp. is richer in CaO. The amount of CaF_2 volatilised increases with the temp. and the amount originally present.

J. A. S.

Effect of fluorides on thermal synthesis of calcium silicates. III. S. NAGAI and M. MIYASAKA (J. Soc. Chem. Ind. Japan, 1934, 37, 549–552B).—In presence of CaF_2 , $3\text{CaO} \cdot \text{SiO}_2$ is formed when CaCO_3 is heated with SiO_2 at $< 1300^\circ$; in its absence $2\text{CaO} \cdot \text{SiO}_2$ is formed up to 1400° . More CaF_2 remains in the product when heated dry than when the heating gas contains H_2O .

A. G.

Hydrothermal synthesis of calcium hydrosilicates. V. A. VIGFUSSON, G. N. BATES, and T. THORVALDSON (Canad. J. Res., 1934, 11, 520—529).—A *Ca hydrosilicate*, $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, identical with a cryst. substance observed in steam-cured Portland cement mortar (B., 1930, 146), can be prepared by hydrothermal synthesis from mixtures of iO_2 sand with $\text{Ca}(\text{OH})_2$, Ca_2 with Ca_3 silicate, or SiO_2 gel with $\text{Ca}(\text{OH})_2$, after preliminary steam treatment and ignition, or, finally, by the action of saturated aq. $\text{Ca}(\text{OH})_2$ on quartz crystals or fused SiO_2 plates. The compound is slowly decomposed by aq. MgSO_4 and alkali carbonates and rapidly by dil. acids and NH_4 salts. Aq. Na_2SO_4 , CaSO_4 , or alkali hydroxides have no action. The crystals are thin prisms showing parallel extinction, positive elongation, and moderate birefringence. A second cryst. *Ca hydrosilicate* was obtained, as very small needles, by hydrothermal synthesis from excess $\text{Ca}(\text{OH})_2$ and SiO_2 gel. $\text{CaO} : \text{SiO}_2$ is 2 : 1 with an uncertain amount of H_2O of at least 1 mol. The birefringence is very low. Optical and X-ray data for both compounds are given; they differ from the data for hillebrandite, which has the same composition. M. S. B.

Preparation of boron hydride. II. Action of phosphoric acid on magnesium and beryllium boride. E. WIBERG and K. SCHUSTER (Ber., 1934, 67, [B], 1805—1808; cf. A., 1930, 720).—The yield of B hydrides (essentially B_4H_{10}) from Mg_3B_2 is increased from 4.6% to 11.4% if 4*N*-HCl is replaced by 8*N*- H_3PO_4 . Increase of $[\text{H}_3\text{PO}_4]$ depresses the yield. Similar replacement in the case of Be_3B_2 doubles the yield. H. W.

Composition and constitution of the alkali aluminates. (Are the aluminates hydroxo-compounds?) P. JUCATIS (Z. anorg. Chem., 1934, 220, 257—267).—The composition of the aluminates, $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$ (I), $\text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 2.5\text{H}_2\text{O}$ (II), and $\text{Al}_2\text{O}_3 \cdot 3\text{Na}_2\text{O} \cdot 6\text{H}_2\text{O}$ (III), has been determined by Schreinemaker's residue method and confirmed by drying experiments. By dehydration at different temp. in a current of air it is shown that (I) and (II) are true salts. (I) becomes anhyd. at 370° and (II) at 100°. (III) is probably an oxo-hydroxo-aluminate, $\text{Na}[\text{OAl}(\text{OH})_4]\text{Na}_2 \cdot \text{H}_2\text{O}$. M. S. B.

Substitution and decomposition of alkalis in blue ultramarine. K. LESCHEWSKI, H. MÖLLER, and E. PONSCHUS (Z. anorg. Chem., 1934, 220, 317—328).—By fusing Na ultramarine (I) with alkali nitrates at temp. below 500° an alkali exchange takes place. The extent depends on the ionic vol. of the metal. A yellowish-brown Ag Na ultramarine may be similarly formed. By treating (I) with boiling aq. NH_4Cl a Na NH_4 ultramarine (II) is obtained and is specially suitable for the prep. of other ultramarines by decomp. with aq. metallic nitrites, when NH_4NO_2 is completely removed. By heating (II) with aq. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ a blue N_2H_5 Na ultramarine containing 6.8% N_2H_5 is obtained. By heating an incompletely dehydrated blue ultramarine in a current of Cl_2 at 400°, the colour gradually disappears, giving a yellow product from which three different substances have been obtained: a white, alkali-free, cryst. Cl-compound, a white, alkali-free, amorphous

compound similar to that obtained by treating ultramarine with $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{OH}$ (A., 1932, 351), and a greenish-yellow amorphous compound with full alkali content. All the compounds contain S. For the appearance of the blue colour it seems necessary for S'' and Na^+ to form part of the recognised ultramarine crystal lattice. M. S. B.

[Primary processes in the oxidation of graphite.] V. SIHVONEN (Z. Elektrochem., 1934, 40, 743—744; cf. A., 1934, 1082).—A reply to criticism. E. S. H.

Volatility of silica. E. PRESTON and W. E. S. TURNER (J. Soc. Glass Tech., 1934, 18, 222—224*tr*).— SiO_2 discs do not change in wt. when heated in air for 20 hr. at 1400°, but if subjected to the action of H_2O vapour under the same conditions of time and temp., or for 4 hr. at 1500°, there is a small but definite loss in wt. The surface becomes slightly pitted and glossy, suggesting that the loss is due to chemical action rather than true volatility. At 1300° the loss in wt. after 20 hr. is negligible. M. S. B.

Stannic and stannous thiocyanates. I. V. KROTOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 603—608).—The compounds $\text{Sn}(\text{CNS})_2 \cdot 2\text{EtOH}$ and $\text{Sn}(\text{CNS})_4 \cdot 9\text{EtOH}$ were prepared by the interaction of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SnCl_4 , respectively, with KCNS in EtOH solution. H. J. E.

Lead acetato-chloride. E. GRILLOT (Compt. rend., 1934, 199, 1049—1051).—The solubility of PbCl_2 is increased in presence of $\text{Pb}(\text{OAc})_2$. When a warm 70% $\text{Pb}(\text{OAc})_2$ solution, saturated with PbCl_2 , is cooled, crystals of the lead acetato-chloride, $\text{Pb}_2(\text{OAc})_3\text{Cl} \cdot 1.5\text{H}_2\text{O}$ (I), are deposited. In H_2O (I) is hydrolysed giving $\text{Pb}(\text{OH})\text{Cl}$, showing it to be a complex and not a double salt. (I) is also formed by interaction of $[\text{Pb}_2(\text{OAc})_3]\text{ClO}_4$ and KCl, and of $\text{Pb}_2(\text{OAc})\text{OH}$ and HCl. J. W. S.

Preparation of standard solutions of thorium chloride and its disintegration products. A. N. PULKOV (Trans. inst. metrol. stand. U.R.S.S., 1934, No. 6, 3—12).—Allanite $[(\text{SiO}_4)_6\text{Ca}_6\text{Ca}_4(\text{OH})_2]$ (I) contains no U, and is therefore suitable for preparing standard ThCl_4 solutions. 100 g. of (I) are treated with 250 c.c. of aqua regia, SiO_2 , Fe, Ca, Mg, and the rare earths are removed, and the ThCl_4 solutions standardised by the emanation method. CH. ABS. (e)

Spontaneous decomposition of ammonium nitrate melts. H. TRAMM and H. VELDE (Angew. Chem., 1934, 47, 782—783).— NH_4NO_3 is stable at 175° when pure or in presence of chloride or acid, but when both these are present an accelerating decomp. occurs at 145° with evolution of gas (30% N_2O , 70% N_2) and rise of temp. The decomp. can be stopped by neutralisation with NH_3 . A. G.

Preparation of ammonium azide from dry mixtures of sodium azide and an ammonium salt. W. J. FRIERSON and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 2384).—Equimol. mixtures of NaN_3 and $(\text{NH}_4)_2\text{SO}_4$ are heated in a sealed tube in vac. or in a sublimation apparatus through which a current of dry air is passed. The yield of NH_4N_3 is 87%. E. S. H.

Nitrogen compounds of germanium. V. Germanous nitride. W. C. JOHNSON and G. H. RIDGELY (J. Amer. Chem. Soc., 1934, 56, 2395—2397; cf. A., 1933, 38, 683).— Ge_3N_2 has been prepared by thermal decomp. of GeNH_3 . Its properties have been determined. At $> 500^\circ$ Ge_3N_2 decomposes into Ge and N_2 . E. S. H.

Action of potassium and sodium hydroxides on germanoformic acid. A. TCHAKIRIAN (Compt. rend., 1934, 199, 866—868; cf. A., 1932, 901).—Treatment of $\text{Ge}(\text{OH})_2$ with 50% NaOH or KOH yields Na_2GeO_3 or K_2GeO_3 with liberation of H_2 , and small quantities of GeH_4 and Ge. The mechanism of the reaction is discussed. J. W. S.

Oxygen preparation from sodium peroxide: a dangerous experiment. J. N. FRIEND and S. MARKS (Nature, 1934, 134, 778).—Owing probably to the presence of unoxidised Na, the gas obtained by the action of H_2O on Na_2O_2 exploded violently on ignition. L. S. T.

Sulphur monoxide. IV. Oxidation of sulphur. P. W. SCHENK (Z. anorg. Chem., 1934, 220, 268—272).—An apparatus for the prep. of SO by burning S in O_2 at reduced pressure is described. The yield improves as the pressure is diminished down to 5 mm. and for each pressure there is an optimum temp. M. S. B.

Processes in the reaction between hydrogen sulphide and sulphurous acid in aqueous and alkaline solutions and their efficiency for purposes of preparation. O. VON DEINES and H. GRASSMANN (Z. anorg. Chem., 1934, 220, 337—369).—Mixtures of H_2S and SO_2 in proportions varying from 2:1 to 1:2 have been passed slowly, at different temp., through H_2O and aq. NaOH and the solutions obtained have been analysed. At 20—40° $\text{H}_2\text{S}_5\text{O}_6$ alone is formed in pure H_2O . At higher temp. a little $\text{H}_2\text{S}_4\text{O}_6$ appears. In aq. NaOH $\text{Na}_2\text{S}_2\text{O}_3$ is obtained, and the yield is quant. and unaccompanied by the separation of S if $\text{H}_2\text{S}:\text{SO}_2=2:1$ and the passage of gas is interrupted at the neutral point. On passing excess of gas $\text{Na}_2\text{S}_2\text{O}_3$ disappears and $\text{S}_5\text{O}_6^{2-}$ is formed and partly decomposed to $\text{S}_4\text{O}_6^{2-}$. A large excess of SO_2 favours the production of polythionates. The following salts have been prepared: $\text{CaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, white, stable; a mixture of Fe^{II} pentathionate and dipentathionate, white; ZnS_5O_6 containing 7% of the acid salt. By stabilisation with CH_2O the existence of a labile intermediate product in the reaction is demonstrated. It is probably thiosulphurous acid, $\text{H}_2\text{S}_2\text{O}_2$. The most favourable ratio of $\text{H}_2\text{S}:\text{SO}_2$ for its production is 1:1. The mechanism of the reactions in Wackenroder's liquid is discussed. M. S. B.

Active chromic oxide. H. W. KOHLSCHUTTER (Z. anorg. Chem., 1934, 220, 370—376).— Cr_2O_3 prepared by pptg. gelatinous $\text{Cr}(\text{OH})_3$ from dil. aq. Cr and drying, readily adsorbs H_2 above 100°. Its behaviour varies according to whether pptn. takes place slowly and in stages (I) or rapidly and continuously (II). (II) takes up H_2 at a higher temp. than (I), but constituents adversely affecting adsorption, such as residual H_2O , are more difficult to remove from (II) than from (I). M. S. B.

Fluorine. II. Reactions of oxygen fluoride with water and solutions of sodium hydroxide. F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA (Sci. Rep. Tōhoku, 1934, 23, 431—448; cf. A., 1934, 1187).—Dissolution of OF_2 in H_2O obeys Henry's law. The velocity of reaction between gaseous OF_2 and $\text{H}_2\text{O} \propto [\text{OF}_2]$. The temp. coeff. is 2.7 per 10°. OF_2 reacts instantaneously with very dil. alkali solution, dissolution occurring slowly relative to the velocity of reaction in the liquid phase. The velocity of decomp. of OF_2 in contact with undisturbed aq. NaOH \propto the concn. of gaseous OF_2 , but the temp. coeff. is 1.5 per 10°. J. W. S.

Iodine monochloride. J. CORNOG, R. A. KARGES, and H. W. HORRABIN (Proc. Iowa Acad. Sci., 1932, 39, 159).—ICl is prepared from I and liquid Cl at -78° . NH_4Cl or KCl dissolved in liquid ICl yields conducting solutions. V.-p. measurements (30—60°) indicate that ICl is polar. CH. ABS. (e)

Periodic acid and periodates. IV. Reactions of disodium paraperiodate with soluble salts of zinc and metals of the alkaline earths. J. R. PARTINGTON and R. K. BAHL (J.C.S., 1934, 1771—1772).—The substances pptd. by boiling $\text{Na}_2\text{H}_3\text{IO}_6$ with conc. solutions of Zn, Ca, and Ba salts have the following const. compositions when dried at 85°: $4\text{ZnO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, $2\text{CaO} \cdot \text{I}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$, and $2.3\text{BaO} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$. The existence of salts described in the lit. was not confirmed. The composition of the ppt. from Sr salts is variable. J. G. A. G.

Physico-chemical investigation of a new basic ferric ammonium sulphate. R. JIRKOVSKÝ (Coll. Czech. Chem. Comm., 1934, 6, 445—452).—The salt $(\text{NH}_4)_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ crystallises slowly from Mohr's salt solution in a closed bottle exposed to diffuse light. $2\text{H}_2\text{O}$ are evolved at 220—280°, $1\text{H}_2\text{O}$ and all the NH_3 at 280—320°, and $4\text{H}_2\text{O}$ at 320—325°. The dehydration and thermal decomp. of the analogous Fe^{III} Na salt, natrojarosite, follows a similar course. It is inferred that the salt crystallising from a Fe^{III} sulphate solution is always more basic than corresponds with the composition of the original solution. J. G. A. G.

Mechanism of the oxidation of iron. Reactions and equilibria involving iron in wines. J. RIBERAU-GAYON (Bull. Soc. chim., 1934, [v], 1, 1269—1280; cf. A., 1931, 575).—The data for oxygenated liquids are consistent with the existence of an equilibrium (I) between the Fe^{II} and Fe^{III} ions, respectively, in equilibrium with undissociated Fe^{II} and Fe^{III} compounds. In the solutions considered, Fe^{III} was present chiefly as complex ions and (I) was shifted by salts which formed Fe^{III} so that the total Fe^{III} was rapidly increased by oxidation, whilst $[\text{Fe}^{\text{II}}]$ and $[\text{Fe}^{\text{III}}]$ were diminished. As the p_{H} val. of a white wine was raised, the concn. of Fe^{III} complexes increased parallel with an increased rate of oxidation of Fe^{II} , and the pptn. of FeSO_4 diminished at $> \text{a sp. } p_{\text{H}}$ val. The reaction of $\text{K}_4\text{Fe}(\text{CN})_6$ with the Fe in wines is discussed. J. G. A. G.

Configuration of bisdimethylglyoxime diamine cobaltic salts. Y. NAKATSUKA and H. IINUMA

(J. Chem. Soc. Japan, 1934, 55, 630—643).—Compounds of the type $[\text{Co}(\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2(\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NO})_2]\text{X}$ are obtained in which the $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ acts as a mono-base. In $[\text{Co}(\text{NH}_2\text{Ph})_2(\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NO})_2]\text{X}$, 2 dimethylglyoximes are in a plane in a very firm combination and the 2 NH_2Ph groups are always *trans*. New compounds are derived by replacing NH_2Ph by other bases and with $\text{X}=\text{Cl}$, Br , I , CNS , or $0\cdot5\text{SO}_4$.
CH. ABS. (e)

Action of magnesium on solutions of nickel sulphate and cobalt sulphate. G. GIRE (Bull. Soc. chim., 1934, [v], 1, 1241—1247).—Mg powder added to excess of aq. NiSO_4 evolves H_2 and ppts. a salt which effloresces to $\text{NiSO}_4\cdot4\text{NiO}\cdot17\text{H}_2\text{O}$ at room temp. and affords $\text{NiSO}_4\cdot4\text{NiO}\cdot10\text{H}_2\text{O}$ at 100° . The salt dissolves in warm aq. acids only. From aq. CoSO_4 Mg evolves H_2 and deposits a mixture of $\text{CoSO}_4\cdot5\text{CoO}$ and Co .
J. G. A. G.

Platinum-black. G. VON HEVESY and T. SOMIYA (Z. physikal. Chem., 1934, 171, 41—48).—Pt-black (I) obtained by electrolysis of aq. H_2PtCl_6 containing $\text{Pb}(\text{OAc})_2$ (II) contains an appreciable amount of Pb, which increases rapidly with $[\text{Pb}(\text{OAc})_2]$, and most of it is apparently not present in solid solution. The best (I), judged by its resistance to cathodic polarisation, is given by an electrolyte made up according to Lummer and Kurlbaum's formula, and has the largest particles. Pure Pt solutions do not give (I), but Au, Tl, or Cd may be used instead of Pb.
R. C.

Complex platinum compounds with ter- and quinque-valent platinum. VII. P. C. RAY and N. N. GHOSH (Z. anorg. Chem., 1934, 220, 247—249; cf. A., 1934, 44).—By the action of $\text{C}_5\text{H}_5\text{N}$ on $\text{PtClEt}_2\text{S}_2$ under different conditions the compounds $\text{Pt}_2\text{Cl}_2(\text{Et}_2\text{S}_2)_2\cdot2\text{C}_5\text{H}_5\text{N}$ (I), m.p. 190° , $\text{Pt}_2\text{Cl}_2(\text{Et}_2\text{S}_2)_2\cdot2\text{C}_5\text{H}_5\text{N}$ (II), $\text{Pt}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$, m.p. 288° , and $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$, m.p. 285° , are obtained. (I) is insol. in ordinary org. solvents. Determinations of the electrical conductivity of (II) is COMe_2 have been made. By the action of $\text{C}_5\text{H}_5\text{N}$ on $\text{PtBrEt}_2\text{S}_2$ the compound $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Br}_2$, m.p. 297° , is obtained.
M. S. B.

Spectrographic analysis. II. Spectrum analysis of solutions. Y. UZUMASA and H. OKUNO (J. Chem. Soc. Japan, 1934, 55, 622—626).—The min. concn. for the spectrographic detection of the characteristic lines of 16 common elements has been determined. The lines are weakened by the presence of HCl .
CH. ABS. (e)

Extraction and analysis of gases in rocks and minerals. A. A. CHEREPENNIKOV (Trav. inst. état radium (U.S.S.R.), 1933, 2, 136—139).—The specimen is either dissolved in HCl or HNO_3 or heated at 380° .
CH. ABS. (e)

Potentiometric titration in non-aqueous solutions. II. Source of error in acidimetry. I. E. WOOTEN and A. E. RUEHLE (Ind. Eng. Chem. [Anal.], 1934, 6, 449—451; cf. B., 1931, 849).—In titrating a moderately strong acid in Bu°OH with alkali a weak acid may be introduced as the alkali salt, due to oxidation of the alcohol. A quant. test

for the presence of such impurities may be made by titrating portions of standard picric acid solution.

E. S. H.

Electrometric determination of total acidity of intensely coloured solutions by the Bucharov-Evstigneev method. B. A. MINAEV (Zavod. Lab., 1934, 3, 863—864).—A potentiometric procedure is described.
R. T.

New indicators for acidimetry. E. S. VASSERMAN (Zavod. Lab., 1934, 3, 868—869).—Wenker's nitrazine-yellow, and its 8-Cl-, -Br-, and -I-derivatives, give sharp transition points, from yellow to blue or grey at p_H 6·5—6·8. Directions for preparing the indicators are given.
R. T.

Determination of p_H of natural waters. J. I. USATENKO (Zavod. Lab., 1934, 3, 946—948).—For natural H_2O $p_H=7\cdot719+\log k/a$, where k is the temporary hardness in $^\circ$ German, and a the CO_3 content in mg. per litre.
R. T.

Micro-determination of base by electrodiagnosis. G. S. ADAIR and A. B. KEYS (J. Physiol., 1934, 81, 162—166).—Stoddard's method is modified for samples containing 0·2 mg.-equiv. of base.
CH. ABS. (p)

Drop reaction for hydrogen peroxide. E. PLANK (Z. anal. Chem., 1934, 99, 105—106).—Fresh aq. K Ce^{III} carbonate [i.e., $\text{Ce}_2(\text{SO}_4)_3$ +excess K_2CO_3] gives a yellow coloration with $< 10^{-7}$ g. of H_2O_2 .
J. S. A.

Determination of active chlorine by a combined reagent. A. V. JAKOVLEV (Zavod. Lab., 1934, 3, 900—903).—The solution, containing OCl^- or MnO_4^- , is added to 3—10 ml. of reagent (0·5 g. of starch in 20 ml. of H_2O are added to 100 ml. of 20% aq. NaCl at 100° , the solution is filtered, 2·5 g. of KI are added 2·5 hr. later, followed by 40 ml. of 7% KOH , 20 ml. of 40% AcOH , and 10 ml. of 0·1N- $\text{Na}_2\text{S}_2\text{O}_3$; the reagent has p_H 4·4, and is stable for < 6 months) to the appearance of a blue coloration. The method is rapid (4—6 min.) but not very accurate.
R. T.

Electrometric determination of chlorides in the ash and sap of plants and in ground waters. J. R. NELLER (Ind. Eng. Chem. [Anal.], 1934, 6, 426—428).—Comparison of the electrometric and volumetric titrations gives good agreement, but the electrometric method is preferred. Cl^- can be titrated directly in some plant saps, but the ashing step must be included in juices containing appreciable amounts of the salts of weak acids (e.g., citrus fruits). The electrometric method gives a more sensitive end-point than the volumetric method in determining Cl^- in ground H_2O containing SO_4^{--} and S^{--} .
E. S. H.

Volatilisation of iodine from dilute iodine-potassium iodide solutions. W. A. HOUGH and J. B. FICKLEN (Ind. Eng. Chem. [Anal.], 1934, 6, 460).—No significant loss of I occurs at room temp. by the passage of air under the usual conditions of sampling gas or vapour. The loss is minimised by reducing the temp., rate of air flow, and $[\text{I}]$.
E. S. H.

Detection of traces of iodides in the presence of chlorates, bromates, and iodates. A. VASSILOV (Praktika, 1933, 8, 324—326).—10 c.c. of the

neutralised test solution are shaken with 2 c.c. of a 0.05% solution of I in CHCl_3 . After addition of 3 drops of 1% starch solution the mixture is again shaken. A blue coloration in the aq. layer indicates I' . Other salts, notably BrO_3' , may yield a violet coloration. A. G. P.

Rapid detection and determination of iodates in presence of bromates and chlorates. A. VASSILIOU (Praktika, 1933, 8, 252—254; Chem. Zentr., 1934, ii, 287).—To 10 c.c. of a (5%) solution of the salt mixture are added 2 c.c. of CHCl_3 , 1 c.c. of $\text{N-H}_2\text{SO}_4$, and 1 c.c. of 0.001N- $\text{Na}_2\text{S}_2\text{O}_3$. After 1 min. the mixture is well shaken. With solutions containing 1 in 100,000 of IO_3' the CHCl_3 is coloured reddish-violet. On a quant. scale the I in CHCl_3 solution may be determined colorimetrically or by titration. A. G. P.

Greeff's method for the determination of small quantities of fluorine. M. GIORDANI (Annali Chim. Appl., 1934, 24, 496—503).—Visintin's procedure (A., 1934, 980) leads to inaccurate results. T. H. P.

Determination of fluorine in fluorspar.—See B., 1934, 1098.

Determination of sulphide-sulphur in alkaline solutions containing other sulphur compounds. E. L. BALDESCHWIELER (Ind. Eng. Chem. [Anal.], 1934, 6, 402—403).— S'' can be determined in alkaline solutions containing SO_4'' , SO_3'' , $\text{S}_2\text{O}_3''$, mercaptide, and sulphonate by making use of the solubility of Pb salts of the above in aq. NH_4OAc . With the procedure described an accuracy of $\pm 0.3\%$ is claimed. E. S. H.

Use of ultra-violet light for detection of traces of sulphides. J. GRANT and H. PROCTER-SMITH (Analyst, 1934, 59, 749).—The method of detection of SO_3'' (A., 1932, 1009) is modified for the detection of S'' by the use of aq. quinine (Q) in place of the solid. The max. sensitiveness is 0.1 mg. of S'' . A method is described by means of which the fluorescence of 1 part of Q in 0.5×10^8 of H_2O may be detected. E. C. S.

Determination of sulphuric acid in aerosols by electro-filtration methods. N. S. ARTAMONOV (Zavod. Lab., 1934, 3, 818—820).—The mist is passed through a high-tension electric field, and the condensed H_2SO_4 is determined by the ordinary methods. R. T.

Volumetric determination of sulphates. D. POLUSHIN (Iskuss. Volokno, 1934, 5, No. 2, 33—34).—The determination of sulphates by pptn. with $\text{Pb}(\text{NO}_3)_2$ and back-titration of excess $\text{Pb}(\text{NO}_3)_2$ with Na_2CO_3 gives low vals. in presence of $(\text{NH}_4)_2\text{SO}_4$ owing to decomp. of NH_4NO_3 by Na_2CO_3 . Accurate results are obtained by first converting the $(\text{NH}_4)_2\text{SO}_4$ into $(\text{CH}_2)_6\text{N}_4$. CH. ABS. (e)

Titration of adsorption indicators. IV. *o*-Cresolphthalein as an indicator in the argentometric titration of thiocyanates and halides. Y. UZUMASA and Y. MIYAKE (J. Chem. Soc. Japan, 1934, 55, 627—629).—A 1% solution of *o*-cresolphthalein in an $\text{EtOH-H}_2\text{O}$ mixture is suitable. CH. ABS. (e)

Conductometric titration of selenocyanates with silver nitrate. R. RIPAN-TILICH (Z. anal. Chem., 1934, 99, 110—112).— SeCN' may be rapidly and accurately titrated conductometrically with AgNO_3 . J. S. A.

Determination of tellurium in [copper anode] sludges.—See B., 1934, 1064.

Rapid determination of nitrogen by a Kjeldahl-Nessler process. W. H. KITTO (Analyst, 1934, 59, 733—735).—The material is digested with Chiles' mixture (A., 1928, 312) containing in addition 1.15 g. of NaSeO_4 per 100 ml. The solution after digestion is suitable for Nesslerisation. E. C. S.

Stability of aqueous solutions of boric acid used in the Kjeldahl method. A. EISNER and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1934, 6, 473).—The solutions are stable when pure H_2O is used (cf. A., 1934, 46). E. S. H.

Determination of ammonia in aqueous hydrogen cyanide solutions. R. CUTHILL and J. JACKSON (J.S.C.I., 1934, 53, 354—356r).—Various methods of determination have been examined, the most satisfactory consisting in vac. distillation of the NH_3 from alkaline solution into standard acid. NH_3 may be removed completely from alkaline cyanide solutions by prolonged aeration. R. C.

Apparatus for the detection and determination of arsenic by the Gutzeit and Beck-Merres methods. J. D. GNESSIN (Pharm. Zentr., 1934, 75, 719—722).—Simplified forms of apparatus are described. J. S. A.

Reducing action of mercurous chloride. Separation, detection, and determination of arsenic, gold, platinum, palladium, selenium, tellurium, and iodine. G. G. PIERSON (Ind. Eng. Chem. [Anal.], 1934, 6, 437—439).—By reducing HCl solutions of the compounds to the element by means of Hg_2Cl_2 and comparing the colours produced with a series of standards, it is possible to detect and approx. determine Au (0.00005 mg.), Pd (0.00005 mg.), Pt (0.0002 mg.), Se (0.0002 mg.), Te (0.0005 mg.), As (0.00002 mg.), and I (0.003 mg.). Methods of separation are indicated. E. S. H.

Determination of carbon in rocks and minerals. B. E. DIXON (Analyst, 1934, 59, 739—743).—A wet combustion method, based on Morgan's $\text{H}_3\text{PO}_4\text{-H}_2\text{CrO}_4$ method (J.C.S., 1904, 85, 1004), is described. CO_3'' and non- CO_3'' C are determined consecutively on the same sample in the same apparatus. All the typical C minerals tested were completely oxidised. The method is especially suited to the determination of C in rocks containing a considerable amount of CO_3'' . E. C. S.

Determination of carbon monoxide by Nicloux's method. (MME.) S. KAGAN (Bull. Soc. chim., 1934, [v], 1, 1201—1206).—With air containing 0.02—0.05 mg. of CO per litre, Nicloux's method (A., 1925, ii, 834) affords data in error by 50%. J. G. A. G.

Iodometric determination of phosgene. M. P. MATUSZAK (Ind. Eng. Chem. [Anal.], 1934, 6, 457—459).—The low results obtained by the usual method

are traced to side reactions. Modified procedure is recommended. E. S. H.

Micro-chemical detection of hydrogen cyanide. M. T. KOSLOVSKI and A. J. PENNER (*Arch. Pharm.*, 1934, 272, 792—794).—Directions are given for detection of HCN by its catalysis of the alloxan- NH_3 reaction observed by the microscope. NH_3 cannot be replaced by pure $\text{C}_5\text{H}_5\text{N}$ (cf. lit.). R. S. C.

Spectroscopic detection of argon in argon-nitrogen mixtures. J. A. M. VAN LIEMPT and S. H. R. VISSER (*Rec. trav. chim.*, 1934, 53, 1084—1086).—A can be detected in A- N_2 mixtures by observation on the line 4159 Å., excited in a discharge tube at 2 cm. pressure; the glow around the upper electrode is the best source of light. R. S. B.

Determination of radium emanation in the atmosphere. A. B. VERIGO (*Trav. inst. etat radium (U.S.S.R.)*, 1933, 2, 126—130).—A modification of Elster and Geitel's method of exposing a negatively charged wire to the atm. was employed. CH. ABS. (e)

Determination of the common and rare alkalis in mineral analysis. R. C. WELLS and R. E. STEVENS (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 439—442).—The chlorides are separated into two groups, (a) Li and Na, (b) K, Rb, Cs, by means of H_2PtCl_6 . Li and Na are determined by the usual methods. A modified method of separation of Rb and Cs from K is described and suitable procedure for their determination indicated. E. S. H.

Determination of potassium by the cobaltinitrite method. S. D. SUNAWALA and K. R. KRISHNASWAMI (*J. Indian Inst. Sci.*, 1934, 17A, 105—112).— $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ is pptd. by boiling 0.1 g. of KNO_3 in 5 c.c. H_2O and 1—2 c.c. AcOH with 2—3 c.c. each of 50% NaNO_2 (I) and 25% CoSO_4 (II). 1 g. of KNO_3 required 25—27 ml. each of (I) and (II). If the ratio of (I) to KNO_3 was diminished, the ppt. was contaminated with $\text{K}_2\text{Na}(\text{NO}_2)_6 \cdot 0.5\text{H}_2\text{O}$, and with excess of (I) the ppt. contained $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$. Variation of $[\text{CoSO}_4]$ had no effect on the composition of the ppt., which, in all cases, was stable at 100—110°. J. G. A. G.

Colorimetric determination of small quantities of sodium. K. L. MALJAROV and T. JUDENITSCH (*Zavod. Lab.*, 1934, 3, 904—906).—An equal vol. of 95% EtOH and excess of reagent (I) are added to the solution, and the ppt. is collected after 1 hr. in an unglazed porcelain filter, washed once with 4 c.c. of EtOH , and repeatedly with 2:5 $\text{EtOH-Et}_2\text{O}$, and the dry residue dissolved in 2% AcOH , H_2O added to 100 c.c., 1 c.c. of 20% $\text{K}_4\text{Fe}(\text{CN})_6$ added, and the brown coloration compared with that given by standard aq. $\text{UO}_2(\text{OAc})_2$ (II). (I) consists of equal vols. of a solution of 10 g. of (II) in 50 c.c. of 12% AcOH , and of 3 g. of $\text{Zn}(\text{OAc})_2$ in 50 c.c. of 6% AcOH ; 1.2 c.c. of (I) ppts. 1 mg. of Na. The experimental error is $\pm 2\%$ for 0.1—70 mg. Na. In presence of K the pptn. should be repeated, whilst MgCl_2 and CaCl_2 , and Fe, Al, SiO_2 , Cl' , SO_4'' , and CO_3'' in the concns. present in soil- H_2O do not interfere. R. T.

Metallic silver as an ultimate standard in volumetric analysis. C. W. FOULK and L. A.

PAPPENHAGEN (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 430—433).—A scheme for standardising HCl against Ag is put forward. The Ag is dissolved in HNO_3 , and the equiv. vol. of HCl is determined by the point at which two portions of the supernatant liquid above the AgCl ppt. give equal opalescence on treating one with excess Ag' and the other with excess Cl' .

E. S. H.

Photometric determination of calcium and oxalic acid. L. JENDRASSIK and F. TAKÁCS (*Biochem. Z.*, 1934, 274, 200—204).—Ca (e.g., in 2 c.c. of blood-serum) is pptd. in presence of aq. NaCl and NH_4Cl with $(\text{NH}_4)_2\text{C}_2\text{O}_4$, left for 10—24 hr., and centrifuged. The ppt. is dissolved, in the absence of daylight, in dil. $\text{HCl} + \text{FeCl}_3$, 2 drops of aq. $\text{KH}(\text{IO}_3)_2$ are added to prevent autoxidation, and the colour (I) produced on immediate addition of 2% aq. sulphosalicylic acid is measured with a step photometer. (I) inversely \propto the amount of CaC_2O_4 . The average error is $\pm 3\%$. $\text{H}_2\text{C}_2\text{O}_4$ (e.g., in gallstones) is determined in almost the same way, but a correction must be applied if H_3PO_4 is present. W. Mc.C.

Detection of calcium in presence of strontium and barium. E. R. CALEY (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 445—447).—The conc. chloride solution is acidified with HCl, boiled to expel CO_2 , and KI is added. The presence of Ca is indicated by the appearance of a white, cloudy ppt. on adding HgO to the boiling solution. The reaction involved is represented by $\text{CaCl}_2 + \text{HgO} + 4\text{KI} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{KCl} + \text{K}_2\text{HgI}_4$. Other metals forming insol. hydroxides, NH_4' , and oxidising anions (other than NO_3') must be removed. E. S. H.

Precipitation of barium in the copper-tin group of qualitative analysis. W. T. HALL and R. B. WOODWARD (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 478).—If the pptn. is carried out in presence of HNO_3 there is risk of BaSO_4 being pptd. E. S. H.

Determination of radium in rocks and minerals by the emanation method. I. E. STARIK and A. S. SMAGINA (*Trav. inst. etat radium (U.S.S.R.)*, 1933, 2, 104—116).—The sample is dissolved, Ra being pptd. with BaSO_4 , and converted into RaCl_2 with HCl. Fe or porcelain dishes may be used instead of Pt. Vals. are recorded for a series of minerals. CH. ABS. (e)

Colour reaction of the magnesium cation. S. AUGUSTI (*Annali Chim. Appl.*, 1934, 24, 531—534; cf. A., 1933, 1024).—A drop of the solution is evaporated to dryness on a clock-glass at a moderate temp., the cold residue being treated with a drop of the alkali hypoiodite reagent: a reddish-brown ppt. indicates Mg'' ; sensitivity 3×10^{-7} g. of Mg. Evaporation is unnecessary with amounts $\leq 6 \times 10^{-6}$ g. The reaction is disturbed by NH_4' , Co'' , Mn'' , or Al''' , but not by alkali or alkaline-earth cations. T. H. P.

Micro-determination of zinc. P. L. HIBBARD (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 423—425).—Zn (0.5—0.1 mg.) in plant material (5 g.) may be determined by igniting to remove org. material, extracting with HCl, and separating Zn by H_2S or $\text{H}_2\text{C}_2\text{O}_4$ and $\text{K}_4\text{Fe}(\text{CN})_6$. Details of the subsequent determin-

ation by (a) nephelometry, (b) iodometric titration, or (c) micro-titration with $K_4Fe(CN)_6$ are given.

E. S. H.

Fused beads on platinum wire as solvents for small particles of insoluble material. A. P. LAURIE (Analyst, 1934, 59, 746—747).—The particle is dissolved in a bead of $Na_2B_4O_7$, or microcosmic salt, or a mixture of the two. Sp. reactions for the metallic elements are given when the bead is immersed in the appropriate reagents. The metals can be electro-deposited from the bead on Pt wire.

E. C. S.

Determination of lead as periodate. H. H. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1934, 6, 425—426).—Pb can be separated from Ni, Cu, Zn, Cd, Al, Ca, and Mg by pptn. as $Pb_3H_4(IO_6)_2$ from 0.025*N*-HNO₃ by adding NaIO₃. The ppt. can be weighed or determined volumetrically by dissolving in conc. HCl containing excess of standard Na_3AsO_3 , and titrating the excess with standard NaIO₄, using $CHCl_3$ as indicator.

E. S. H.

Gravimetric determination of lead dioxide in red lead.—See B., 1934, 1056.

Flame determination of copper by carbon tetrachloride. P. GABRIEL (Ind. Eng. Chem. [Anal.], 1934, 6, 420).—The green flame produced by Cu turns blue when CCl_4 vapour is passed through the draught of the Bunsen burner. Other substances giving a green flame do not show this effect.

E. S. H.

Detection of mercury. E. STATHIS (Z. anal. Chem., 1934, 99, 106—108).—To the solution of Hg, KI and KOH are added, forming K_2HgI_4 , then 5 c.c. of 0.01% $AuCl_3$. In presence of Hg, reduction occurs, forming a violet colloidal solution of Au.

J. S. A.

Determination of mercury in medicinal preparations.—See B., 1934, 1083.

Apparatus for volumetric determination of aluminium. P. J. IVANNIKOV (Zavod. Lab., 1934, 3, 865).—The Al content is determined from the vol. of H_2 evolved with aq. NaOH.

R. T.

Spectrographic analysis of aluminium alloys.—See B., 1934, 1107.

Micro-colour reaction of the manganese cation. S. AUGUSTI (Annali Chim. Appl., 1934, 24, 535—538).—A drop of the Mn^{++} salt solution is treated with 1 drop of Na(or K)OH on a watch-glass, which is left in the air for a few min. and then heated gently. The cold, dry residue is treated with 1—2 drops of a 1% solution of strychnine in H_2SO_4 ; a violet-blue colour, changing to red, indicates Mn^{++} , 1.8×10^{-7} g. of which is detectable. Co^{++} interferes and may be removed either (1) by addition to the original solution of a few drops of 10% KCN, followed by heating, treatment with a few drops of HCl, and pptn. of $Mn(OH)_2$, or (2) by pptn. with 1:2 $NO \cdot C_{10}H_6 \cdot OH$. CrO_4^{--} , $Cr_2O_7^{--}$, $Fe(CN)_6^{--}$, and $Fe(CN)_6^{--}$ give colorations similar to Co^{++} , but are usually destroyed before the test is applied.

T. H. P.

Determination of manganate and permanganate present together. L. N. SOKOLOVA (Zavod. Lab., 1934, 3, 805—809).—2.5 g. of $KHSO_4$ are added

to 50 c.c. of solution, the washed ppt. of MnO_2 is dissolved in 25 c.c. of 0.1*N*- $Na_2C_2O_4$ (I) and 10 c.c. of 10% H_2SO_4 , and excess of (I) is determined by $KMnO_4$ titration. The filtrate + washings are made up to 250 c.c., and $KMnO_4$ is determined in 100 c.c. The MnO_4^{--} and MnO_4^+ contents are calc. from the equation $3K_2MnO_4 + 4KHSO_4 \rightarrow 2KMnO_4 + MnO_2 + 4K_2SO_4 + 2H_2O$.

R. T.

Titration with alkaline permanganate. H. STAMM (Angew. Chem., 1934, 47, 791—795).—The rapid reduction of MnO_4^{--} to MnO_4^+ in alkaline solution is utilised, further reduction being checked by pptg. MnO_4^{--} as $BaMnO_4$. Near the end-point, the action is catalysed by addition of Ni^{++} , Cu^{++} , or Co^{++} as O_2 carriers. HCO_2^+ may be so determined by direct titration against $KMnO_4$ at room temp. $H_2PO_3^+$, PO_3^{--} , and CNS^+ (oxidised to $CNO^+ + SO_4^{--}$) are determined by treating with excess of alkaline $KMnO_4$, then adding $BaCl_2$ and titrating back the excess of $KMnO_4$ with HCO_2Na . I^+ and IO_3^+ are determined similarly, being oxidised to IO_4^+ . CN^+ (oxidised to CNO^+) can be titrated directly or indirectly. $MeOH$ and CH_2O are titrated directly. $COMe_2$, fumaric acid, and erythritol are completely oxidised with alkaline $KMnO_4$, and the solution is acidified. Excess of $H_2C_2O_4$ is then added, and titrated back with $KMnO_4$ in acid solution.

J. S. A.

Systematic procedure for potentiometric analysis. I. General principles. W. HILTNER and W. GITTEL (Z. anal. Chem., 1934, 99, 97—105).—Potentiometric reduction-titrations of the following ions in presence of one another may be carried out with the appropriate reagents (given in parentheses), which will reduce all ions following in the series, but not those preceding. MnO_4^+ (with $H_2C_2O_4$); CrO_4^{--} (with As_2O_3); Hg^{++} , Fe^{+++} , UO_2^{++} (with Sn^{++}); Bi^{+++} , Cu^{++} , Sb^V (with Ti^{+++}); Sn^{IV} , Ti^{IV} (with Cr^{++}).

J. S. A.

Permanganometric investigations. II. J. H. VAN DER MEULEN (Chem. Weekblad, 1934, 31, 633—634; cf. A., 1931, 927).—For the determination of Mn^{++} , 50 c.c. of the solution are treated with 5 c.c. of conc. H_3PO_4 (*d* 1.5), 2 g. of $K_2S_2O_8$, 5 g. of $Na_3P_2O_7 \cdot 10H_2O$, 10 c.c. of 5*N*- H_2SO_4 , and 10 c.c. of 0.1*N*- $AgNO_3$. After gentle warming, the whole is refluxed for 5 min., cooled and diluted, treated with 10 c.c. of *N*-KI, and titrated with 0.1*N*- $Na_2S_2O_3$. The error is about 0.1%.

H. F. G.

Colorimetric determination of manganese in phosphorites and apatites.—See B., 1934, 1056.

Application of an old method for the removal of iron. E. WAINER (J. Chem. Educ., 1934, 11, 526—527).—Fe is converted into ferrocyanide by reducing the acid sulphate solution with SO_2 , removing excess of SO_2 , adding NaOH until most of the Fe is pptd., and quickly adding excess of powdered KCN. $(NH_4)_2SO_4$ is added, and the solution is diluted and made just alkaline to phenolphthalein. On adding aq. NH_3 no Fe is pptd., but other elements (e.g., Be, Al, In, rare earths, Cr, or Bi) are pptd. as hydrated oxides. Some Fe is adsorbed in the ppt.

CH. ABS. (e)

Volumetric determination of cobalt and nickel. J. T. DOBBINS and J. P. SANDERS (Ind. Eng. Chem. [Anal.], 1934, 6, 459—460).—The solution containing C_5H_5N is treated with excess of standard NH_4CNS ; $Co(C_5H_5N)_4(CNS)_2$ is pptd., and the excess of CNS determined by titration with $AgNO_3$. The results for Co and Ni compare favourably with those obtained by other methods.

E. S. H.

Oxidation-reduction indicators for use with dichromate. L. E. STRAKA and R. E. OESPER (Ind. Eng. Chem. [Anal.], 1934, 6, 465—466).—Among numerous org. compounds examined, phenyl-*p*- and -*m*-toluidine are satisfactory in absence of Hg salts, whilst naphthidine and an unidentified product, derived from the action of Et_2SO_4 on acetyldiphenylamine, are satisfactory even in presence of Hg salts.

E. S. H.

cycloHexanol in the colorimetric determination of molybdenum. L. C. HURD and F. REYNOLDS (Ind. Eng. Chem. [Anal.], 1934, 6, 477—478).—*cycloHexanol* is preferred to Et_2O as an extractor in the determination by the usual method.

E. S. H.

Separation and determination of metallic and phosphate ions in presence of one another. I. S. ISHIMARU (J. Chem. Soc. Japan, 1934, 55, 732—740).—Mo can be pptd. in presence of OAc' buffer as the 8-hydroxyquinoline derivative, $MoO_2(C_9H_6ON)_2$ (I), without disturbance due to presence of a phosphate. After collection the ppt. is decomposed by adding $KMnO_4$ acidified with HNO_3 . The phosphate is determined with NH_4 molybdate. The P in a steel can be separated as NH_4 phosphomolybdate, which is transformed into (I) and weighed. The P is thus determined indirectly.

CH. ABS. (e)

Volumetric determination of tungsten. Do-treppe's method. M. L. HOLT (Ind. Eng. Chem. [Anal.], 1934, 6, 476—477).—The method (Chim. et Ind., 1931, Spec. no., 173) gives low results, mainly because of the difficulty of reducing WO_3 .

E. S. H.

Analytical applications of the inhibition, under the influence of certain ions, of the fluorescence of the uranyl ion. VOLMAR and MATHIS (Bull. Soc. chim., 1934, [v], 1, 1266—1269; cf. A., 1933, 924).—Impurities containing ions active in suppressing the fluorescence (I) of UO_2^{2+} are detected in substances which do not inhibit (I). The concn. of known active ions is determined in terms of the vol. necessary to suppress (I).

J. G. A. G.

Pure titanium oxide as a standard in the volumetric determination of titanium. W. W. PLECHNER and J. M. JARMUS (Ind. Eng. Chem. [Anal.], 1934, 6, 447—448).—The prep. of pure TiO_2 from $TiCl_4$ and its use in standardising $Fe^{III}NH_4$ sulphate are described.

E. S. H.

Inclusion of rarer metals in elementary qualitative analysis. II. Inclusion of titanium and vanadium in group III. L. E. PORTER (Ind. Eng. Chem., 1934, 6, 448—449; cf. A., 1934, 502).—Suitable methods are indicated.

E. S. H.

Application of Schott glass filters for the determination of thorium by the emanation method. P. L. BOBIN (Trav. inst. etat radium (U.S.S.R.), 1933, 2, 54—61).—Emanation (I) is extracted from H_2O by placing the H_2O in a vertical glass tube constricted at both ends and fitted with a Schott glass filter above the lower constriction, and passing an air stream up the column. Addition of NaCl or EtOH to the H_2O facilitates the removal of (I).

CH. ABS. (e)

Detection of small quantities of germanium in presence of arsenic. S. A. COASE (Analyst, 1934, 59, 747—749; cf. A., 1934, 983).—0.05 mg. of GeO_2 can be detected in presence of $AsO_4^{'''}$ when Na amalgam is used as a reducing agent, or 0.16 mg. when Al and KOH are used. Devarda's alloy, NH_2OH , HCl, and $2N_2H_4 \cdot H_2SO_4$ are less sensitive.

E. C. S.

Determination of vanadium with potassium iodate, with notes on chloramine-T as an oxidising agent. A. J. BERRY (Analyst, 1934, 59, 736—739).—V is determined volumetrically by oxidation from V^{II} to V^{III} by the ICN method (I). Chloramine-T (II) can replace KIO_3 for the direct titration of various oxidisable substances in conjunction with KI. In particular, Ti^{IV} salts, for which (I) is unsuitable, can be determined by the ICl method, or by titration with (II) in presence of HCl and KBr.

E. C. S.

Determination of gold by photometric titration with potassium iodide. S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, 37, 561—562b).— $AuCl_3$ may be titrated photometrically with KI in $> 0.05N$ -acid. Excess of Cl_2 is added and breaks in the curve correspond with reduction of this and of $AuCl_3$, respectively. Small amounts of Pb, Cu, and Fe do not interfere.

A. G.

Micro-determination of platinum and iridium, and of associated chlorine and potassium. H. D. K. DREW, H. J. TRESS, and G. H. WYATT (J.C.S., 1934, 1787—1790).—5—20 mg. of the Pt compound are fused with 2 : 1 Na_2CO_3 - $NaNO_3$ mixture in a Pt or porcelain crucible. The product is mixed with H_2O and HNO_3 and is passed through a micro-Neubauer filter or a Pregl filter just previously washed with conc. HNO_3 and weighed. The Pt is washed with hot conc. HNO_3 and dried at 130° . Cl is determined in the filtrate from the above by pptn. with $AgNO_3$ in conc. HNO_3 (I) or on 5—12 mg. of substance by a micro-Carius method, the products of which are evaporated, and the halide extracted from the reddish insol. Pt compound by conc. aq. NH_3 and subsequently pptd. as $AgCl$. Since Ir is partly oxidised when heated in air, the product of the ignition with conc. H_2SO_4 of a K-Ir compound is cooled in CO_2 and weighed, and the loss in wt. after extracting with H_2O gives the K_2SO_4 . The partly oxidised Ir is then ignited in H_2 and weighed as the metal. Cl in the presence of Ir is determined as in method (I).

J. G. A. G.

M.-p. apparatus with rapid mechanical stirring. K. S. MARKLEY (Ind. Eng. Chem. [Anal.], 1934, 6, 475).—A modified Thiele tube is described.

E. S. H.

M.-p. determination. II. Evaluation of stem correction and the principle of simultaneous determination of m.p. by the capillary tube method. C. TSENG (Sci. Quart. Nat. Univ. Peking, 1934, 4, 283—324).—Stem corrections when using the capillary-tube method are best determined by comparison with results by the Dennis apparatus (A., 1930, 1265). CH. ABS. (e)

Apparatus for m.p. and micro-b.p. [determinations]. W. L. WALSH (Ind. Eng. Chem. [Anal.], 1934, 6, 468—469).—The substance, contained in a capillary tube, is observed through a low-power microscope. E. S. H.

Apparatus for b.p. and boiling range measurements. D. QUIGGLE, C. O. TONGBERG, and M. R. FENSKE (Ind. Eng. Chem. [Anal.], 1934, 6, 466—468).—A modification of the Cottrell apparatus is described. A side tube permits any quantity of material to be distilled off, so that mixtures may be examined. E. S. H.

Cryoscopy in concentrated solution at a low temperature. Method of successive equilibria. A. LALANDE (J. Chim. phys., 1934, 31, 498—510; cf. A., 1934, 1086).—The chief disadvantage of existing methods of determining the f.p. of two-component liquids is the difficulty of maintaining the system sufficiently close to the equilibrium point. A method is described in which, starting with the partly frozen liquid, the rises of temp. (Δt) produced, after attainment of the corresponding equilibria, by the development within the system of successive equal quantities of heat are measured. The val. of Δt for the interval in which the last trace of solid disappears is intermediate between the approx. equal smaller vals. which precede and the larger vals. which follow it, and a simple graphical construction permits the time, and hence the temp., at which the disappearance occurs to be determined with a high degree of accuracy. A full description of apparatus and procedure suitable for work at a low temp. (e.g., for a mixture of EtOH and Et₂O) is given. F. L. U.

Micro-calorimetry. B. WHIPP (Phil. Mag., 1934, [vii], 18, 745—759).—The max. sensitivity of a series of thermo-couples used with a galvanometer is discussed. The most favourable conditions are given by a low resistance in the galvanometer and the couples. The construction of a calorimeter with 5 couples of 1 ohm total resistance is described. The sensitivity is 1 mm. deflexion for 3×10^{-6} g.-cal. F. L. U.

Isothermal diphenylmethane calorimeter. A. N. SCHUKAREV, I. P. KRIVOBABKO, and L. A. SCHUKAREVA (Phys. Z. Sovietunion, 1934, 5, 722—724).—CH₂Ph₂ is substituted for H₂O in a Bunsen ice calorimeter. At the m.p. of CH₂Ph₂ (24.68°) the sensitivity was 0.140 g.-cal. per mm. of capillary. CH. ABS. (e)

Liquefaction of helium by an adiabatic method. P. KAPITZA (Proc. Roy. Soc., 1934, A, 147, 189—211).—An account is given of the liquefaction of He by means of an expansion engine which works without lubrication at low temp. The liquefier is pre-cooled by liquid N₂, further cooling of the He being effected down to 10° abs. by means of the expansion

engine, and finally down to liquefaction point by using the Joule-Thomson effect. It seems probable that the Joule-Thomson effect has a pressure inversion point at low temp., appearing at about 17 atm. The liquefier uses 1.5 litres of liquid N₂ to produce 1 litre of liquid He. L. L. B.

Sensitivity of thermopiles, micro-radiometers, radiometers, and bolometers. C. H. CARTWRIGHT (Z. Physik, 1934, 92, 153—171).—The vac. thermopile can be made most sensitive. Thermodynamics predicts that ideal thermo-electric metals would increase sensitivity at room temp. fivefold. A. B. D. C.

Application of Newton's law of cooling to the measurement of weak thermal effects. W. SWIENTOSLAWSKI and J. SALCEWICZ (Compt. rend., 1934, 199, 935—937).—Using a special type of calorimeter, the law was applied to the measurement of the heat emitted by a sample of pitchblende over varying periods. N. M. B.

Aluminium coating of gratings. C. P. BUTLER and F. J. M. STRATTON (Nature, 1934, 134, 810).—A speculum metal grating coated with Al showed an improvement in the shorter wave-lengths and an average increase in reflectivity of approx. 50%. L. S. T.

Two-crystal moving-film spectrometer. J. M. ROBERTSON (Phil. Mag., 1934, [vii], 18, 729—745).—Apparatus recording reflexions from any two crystal specimens on one film in one operation is described. Examples of results are given. F. L. U.

Light intensity for spectral apparatus, spectrographs, and monochromators. C. LEISS (Z. Physik, 1934, 91, 816—817).—Precautions for using apparatus of large focal aperture are given. A. B. D. C.

Practicality of etched quartz crystals for X-ray spectrometers. L. G. PARRATT (Rev. Sci. Instr., 1934, [ii], 5, 395—400).—The widths of the (1, -1) curves at half max. intensity, % reflexion, and coeff. of reflexion have been measured for quartz and etched calcite. The resolving power of X-ray spectrometers is increased 2—4 times by using quartz instead of calcite, but at the expense of considerable loss of intensity. C. W. G.

High-potential porcelain X-ray tube. R. CRANE and C. C. LAURITSEN (Physical Rev., 1933, [ii], 43, 212).—A tube operating up to 560,000 volts at 10⁻⁵ mm. is described. L. S. T.

Projection instrument for analysis of spectrographic plates. C. H. EDLIN (J. Sci. Instr., 1934, 11, 357—359).—Photographed spectra are projected side by side on a white screen. Wave-lengths can be read at ± 1 Å. between 2100 and 3000 Å. C. W. G.

Use of lithium for an X-ray window. R. E. CLAY (J. Sci. Instr., 1934, 11, 371—372).—The outer surface is covered with a thin layer of tap grease to prevent oxidation. The absorption is very small. C. W. G.

Equalisation of the temperatures of interferometer tubes. J. J. MANLEY (Proc. Physical Soc., 1934, 46, 745—746).—In one method the twin tubes

of the Jamin interferometer are wound with spirals of soft Cu wire; in the other they are enclosed in an Al chamber with removable ends. N. M. B.

Spectro-polariscopic method of Oumov applied to the microscopic examination of minerals. N. VEDENCEVA and S. GRUM-GRSHIMAILO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 583—588).—Applications of the method are described (cf. Umoff, A., 1912, ii, 1019). H. J. E.

Trichromatic colorimeter. H. P. J. VERBEEK (Physica, 1934, 1, 1082—1084).—Improvements have been made in a colorimeter previously described (*ibid.*, 1933, 13, 77). M. S. B.

Photometric method for optical spectral analysis. S. PIÑA DE RUBIES (Z. Physik, 1934, 92, 228—231).—The spectrum is projected on to a layer of several films, and the intensity is given by the logarithmic sum of the blackening of the different films. A. B. D. C.

Apparatus for photo-electric titration. W. W. RUSSELL and D. S. LATHAM (Ind. Eng. Chem. [Anal.], 1934, 6, 463—464).—Apparatus for the photo-electric determination of the end-point, using bromothymol-blue as indicator, is described. The error is about 0.05 c.c. of 0.01N-alkali. E. S. H.

Salt bridge for use in electrometric measurements. G. W. IRVING, jun., and N. R. SMITH (Ind. Eng. Chem. [Anal.], 1934, 6, 480).—Plugs are ground into the tapered ends of the bridge; electrical contact is maintained through the film of KCl solution in the ground-glass joints. E. S. H.

Simple pointer instrument for p_H measurements. W. HILTNER (Chem. Fabr., 1934, 7, 429—430).—A convenient form of potentiometer is described, the balancing current being read directly in terms of p_H . J. S. A.

Measurement of the current generated by a rectifier photo-electric cell. H. H. POOLE and W. R. G. ATKINS (Nature, 1934, 134, 810—811).—A modification of the Campbell-Freeth method (J. Sci. Instr., 1934, 11, No. 4) suitable for measuring illuminations ranging from full sunlight to a fraction of a metre candle is described. L. S. T.

Crystal spectroscopy with γ -rays. H. HULUBEI and (ILLE.) Y. CAUCHOIS (Compt. rend., 1934, 199, 857—859).—A new form of crystal spectroscope has been devised for studies with X-rays or γ -rays; it gives sharp definition and requires comparatively short exposures. J. W. S.

Electrostatic generation of high voltages for nuclear investigations. R. J. VAN DE GRAAFF, K. T. COMPTON, and L. C. VAN ATTA (Physical Rev., 1933, [ii], 43, 382). L. S. T.

Dielectric methods of investigation in the chemical laboratory. The dielkometer. R. BULL and J. H. MOC (Oesterr. Chem.-Ztg., 1934, 37, 183—185; cf. A., 1934, 749).—The principle and use of the instrument are described. The val. of determinations of dielectric const. in analysis is indicated, particularly in connexion with the determination of H_2O content by Exluan (dioxan) desiccating agents. R. S.

Electronography—a new method of examination of substances. M. M. UMANSKI (Zavod. Lab., 1934, 3, 810—818).—Known methods and apparatus are described. R. T.

Amplifier systems for the measurement of ionisation by single particles. J. R. DUNNING (Rev. Sci. Instr., 1934, [ii], 5, 387—394).—Detailed descriptions of circuits to measure the no. of ions suddenly produced by high-speed particles are given. C. W. G.

Electric manometer for pressures up to 3000 atmospheres. A. MICHELS and M. LENNSEN (J. Sci. Instr., 1934, 11, 345—347).—The variation of resistance of manganin with pressure is utilised. After annealing at 140°, when further change of resistance with time is negligible, the manometer is calibrated against a pressure balance. Results are reproducible to 0.05 atm. up to 1000 atm., to 0.1 atm. up to 1500 atm., and to 0.2 atm. up to 2500 atm. C. W. G.

Chemically fixed trace of electric waves. V. ARKADIEV (Z. Physik, 1934, 92, 194—203).—Coherers and paper sensitive to electric current can be used to trace the path of an electric wave. A. B. D. C.

Simple arrangement for the magnetic cooling method. N. KURTI and F. SIMON (Physica, 1934, 1, 1107—1108).—The paramagnetic substance to be cooled is loosely packed as a powder in a thin-walled glass capsule filled with He at 1 cm. pressure, cooled in liquid He, magnetised, and demagnetised. In this way $Mn NH_4$ sulphate was cooled from 1.2° to 0.1° abs. Some other substance might be cooled with it. M. S. B.

Apparatus for the production of small pressure differences. L. M. PARR (J. Sci. Instr., 1934, 11, 371).—Air escapes slowly through a capillary tube. C. W. G.

Microvolumenometer. H. HAUPTMANN and G. E. R. SCHULZE (Z. physikal. Chem., 1934, 171, 36—40).—An apparatus permitting determination of d on 0.01 c.c. of a substance with a precision of 1% is described. R. C.

Converted air-pump shaker. A. A. MORTON (Ind. Eng. Chem. [Anal.], 1934, 6, 469—470). E. S. H.

Sintered Pyrex glass aeration tubes. R. D. COOL and J. D. GRAHAM (Ind. Eng. Chem. [Anal.], 1934, 6, 479).—The prep. of a sintered Pyrex glass thimble is described. E. S. H.

Gas-absorption bulb for use with small amounts of reagent. J. A. SHAW (Ind. Eng. Chem. [Anal.], 1934, 6, 479—480).—The apparatus is designed to use < 5 c.c. of scrubbing solution. E. S. H.

Apparatus for observation of reactions at liquid interfaces. A. CLEMENTI (Biochem. Z., 1934, 274, 205—207).—By using test-tubes to which smaller tubes or dropping funnels (with or without stop-cock) are attached near the lower end, or by employing long-stemmed funnels with lateral opening or capillary at the jet, layers of miscible liquids of different d may be brought together without mixing when it is desired to observe reactions at the interface. W. McC.

Separation of isotopic mixtures by diffusion in streaming mercury vapour. G. HERTZ (Z. Physik, 1934, 91, 810—815). A. B. D. C.

Bunsen burner. ANON. (Chem. and Ind., 1934, 975—976).—The gas is controlled by a needle valve operated by an external screw and burns at a large perforated head; a handle is provided. A. G.

Application of the aërometer in investigating very small density changes of metals. A. E. BRUCHANOV (Metallwirts., 1934, 13, 206—208; Chem. Zentr., 1934, i, 3391).—Changes in d are observed by measuring changes in the depth at which a glass vessel (I) floats, the metal object to be examined being hung from the lower end of (I). H. J. E.

Apparatus and method for metallographic work at low temperatures. O. A. KNIGHT (Met. and Alloys, 1934, 5, 256—258).—The upper, unpolished face of the specimen forms the base of a chamber, the vertical walls of which are metal tubes screwed one within the other. Small specimens are mounted in Wood's metal. The chamber is supported above the microscope objective and connected to it by a short length of rubber tubing. A branch tube connects the air space so confined to a P_2O_5 bulb. When the air has been dried, Et_2O and solid CO_2 or liquid air is admitted to the upper chamber. Formation of martensite from austenite has been traced. E. H. B.

Micro-determination of vapour density. D. A. PEAK and R. A. ROBINSON (J. Physical Chem., 1934, 38, 941—943).—A method requiring only a few mg. of substance, which is vaporised under reduced pressure in an apparatus of the V. Meyer type, is described. Results are within 3—5% of calc. vals. F. L. U.

High-voltage vacuum tube. D. H. SLOAN (Physical Rev., 1933, [ii], 43, 213).—Absorption curves indicated 6×10^5 volts radiation with 5 millamp. emission from the apparatus described. L. S. T.

Attainment of high vacua in large metal chambers. M. S. LIVINGSTON (Physical Rev., 1933, [ii], 43, 214).—Pressures $< 5 \times 10^{-7}$ mm. can be maintained. L. S. T.

Rapid filtration of viscous liquids. E. B. MOSS (J. Sci. Instr., 1934, 11, 372).—A tight wad of

cotton-wool is pushed down through the liquid contained in a test-tube. C. W. G.

Ultra-centrifuge and its region of applicability. T. SVEDBERG (Ber., 1934, 67, [4], 117—129).—A lecture. H. W.

Efficient small-scale fractionating equipment. C. O. TONGBERG, D. QUIGGLE, and M. R. FENSKE (Ind. Eng. Chem., 1934, 26, 1213—1217).—Details are given of an all-glass still (I) of 50—100 c.c. capacity, and of a steel and Ni still (II) of 11 litres capacity. In (I) the column is lagged with a vapour jacket and packed with single-turn glass helices; the rate of reflux is measured with a small siphon cup. (II) is packed with Ni wire helices or staples and the rate of reflux is measured by the rate of flow of condenser H_2O and its temp. rise. A. G.

Packing materials for [laboratory] fractionating columns. M. R. FENSKE, C. O. TONGBERG, and D. QUIGGLE (Ind. Eng. Chem., 1934, 26, 1169—1177).—A no. of columns of varying diam. up to 2 in. and having varying types of packing were worked with suitable liquid pairs under total reflux until equilibrium was established. The height of a theoretical plate equiv. to the packing (I) was then determined. Such pairs as $CCl_4-C_6H_6$ which could be readily analysed by determination of n were chiefly used. The best results were given by one- and two-turn helices of wire or glass and carding teeth $\frac{1}{8}$ in. wide. Increase of height and of diam. tended to reduce efficiencies, partly owing to increase of channelling. Different hydrocarbon mixtures gave approx. the same results. The product of the no. of sq. in. of surface area per cu. in. and the % of free space, divided by 100, gives a no. parallel to the efficiency as determined by (I). Even slight corrosion greatly alters the behaviour of a packing, generally unfavourably. C. I.

Apparatus for vacuum distillation. A. W. STOUT and H. A. SCHUETTE (Ind. Eng. Chem. [Anal.], 1934, 6, 476—477).—A multiple receiver for collecting successive fractions of a condensate from a vac. distillation without interruption is described. E. S. H.

Determination of tie lines in ternary systems without analyses for the components. T. W. EVANS (Ind. Eng. Chem. [Anal.], 1934, 6, 408—409).—Mathematical. E. S. H.

Geochemistry.

Ozone and the sunspot cycle. F. E. FOWLE (Trans. Amer. Geophys. Union, 1933, 110—111).—The dependence of the amount of O_3 in the atm. on solar conditions, as indicated by sunspots, is not confirmed. CH. ABS. (e)

Luminescence of the upper atmosphere. J. CABANNES (Compt. rend., 1934, 199, 909—911).—An explanation is proposed for the presence in the least refrangible light emitted by the night sky of groups of radiations of atm. origin: bands of the first positive system of N_2 , and O_2 and H_2O bands. N. M. B.

Atmospheric ozone in the neighbourhood of Shanghai. P. LEJAY (Compt. rend., 1934, 199, 879—881).—Atm. $[O_3]$ near Shanghai, as measured by the ratio of the intensities of solar radiation within and outside the O_3 absorption band, shows an annual variation, being greatest in February and March and a min. in about November. J. W. S.

Determination of arsenic content of the air. O. M. FABER (Zentr. Gewerbehyg. Unfallverh., 19, 214—216; Chem. Zentr., 1934, i, 3888).—Counts of the no. of particles are made on photographs of a dust

sample before and after heating at 250°. At 250°, As₂O₃ is removed, but other constituents are unaltered.

H. J. E.

Mineral waters of Venice. Bromo-lithia water of Scorze. G. BRAGAGNOLO (*Annali Chim. Appl.*, 1934, 24, 493—495).—Composition and physico-chemical consts. are given. The H₂O contains mainly CaHCO₃, with 0.0003 g. Li and 0.0005 g. Br per litre.

T. H. P.

Analysis of the water of the Zomaro (Calabria) spring. B. RICCA and P. MEDURI (*Annali Chim. Appl.*, 1934, 24, 519—530).—This contains chiefly Cl⁻, HCO₃⁻, NO₃⁻, Na⁺, Ca⁺⁺, and SiO₂, and shows slight radioactivity. Composition, physico-chemical data, and results of bacteriological tests are given.

T. H. P.

Waters of L. Boza. V. CARCAMO (*Bol. Soc. Quím. Peru*, 1934, 1, 44—48).—A detailed analysis of the saline H₂O is given; the principal components are NaCl, Na₂CO₃, NaHCO₃, Na₂SO₄, KCl, and LiCl. H₃BO₃, I, and Br are also present.

E. L.

Radioactive content of water and its sedimentations in pit-hole No. 1 of Oukhta region. V. I. BARANOV and I. D. KURBATOV (*Trans. inst. état radium*, U.S.S.R., 1933, 2, 139—156).—The average content was 7.48×10^{-9} g. Ra and 2.1×10^{-11} g. Ms-Th I per litre.

CH. ABS. (e)

Relation between the temperature and the p_H of the bottom deposits from Takasukanuma pond. K. SUGAWARA (*Bull. Chem. Soc. Japan*, 1934, 9, 446—448).—The p_H remains const. for temp. below 18.7°, which is > the highest temp. (17.5°) of the bottom of the pond during the year. At higher temp. the p_H is lowered. The effect on benthic fauna and flora is mentioned.

W. R. A.

Radon content of mineral springs of Korea. S. IMORI, J. YOSHIMURA, and S. HATA (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, 13, 1363—1372).—Rn contents of 8 mineral springs of Korea have been determined.

R. S. B.

Origin of balthashite. L. D. SHTURM (*Khim. Tver. Topl.*, 1934, 5, 16—32).—Balthashite (H₂O 1.40—1.8, ash 4.3—8.4, and material extractable with C₆H₆+EtOH 9.65—33.0%) develops from seaweeds. The ash contains SiO₂ 28.61, Al₂O₃ 3.11, TiO₂ 0.35, Fe₂O₃ 7.30, CaO 20.00, MgO 16.22, K₂O 1.56, Na₂O 5.62, MnO 0.03, SO₃ 15.98, and P₂O₅ 0.34%. Analyses for sapropel are also given.

CH. ABS. (e)

Gold-bearing stony meteorite from Melrose, New Mexico. H. H. NININGER (*Amer. Mineral.*, 1934, 19, 370—374).—Analyses are given. The material (1 large, 4 small, stones) contained 0.24 oz. Pt metals and 0.02—0.32 oz. Au per ton.

CH. ABS. (e)

Processes of the formation of the earth, and periods of world drought. W. MATHESIU (*Naturwiss.*, 1934, 22, 787—792).—The variations in the composition of the earth and its atm. during the cooling process are described. The problem of periods of drought, and methods for preventing and alleviating them, are discussed.

A. J. M.

Petrological study of Malka river granodiorite laccolith (in Northern Caucasus) in connexion with its radium content. S. P. SOLOVIEV

(*Trans. inst. état radium*, U.S.S.R., 1933, 2, 223—245).

—Data for the Ra content of various rock samples are recorded.

CH. ABS. (e)

Nature and deposition relations of the quartzite schist of Kupferberg, Silesia. G. BERG (*Tsch. Min. Mitt.*, 1934, 46, 1—19).—The quartzites are related chemically and structurally to the Scandinavian leptites.

H. J. E.

Sanidinites of the Laacher lake region. G. KALB (*Tsch. Min. Mitt.*, 1934, 46, 20—55).—Two groups of sanidinites are described.

H. J. E.

Pseudoleucitic and epileucitic rocks. A. N. ZAVARITSKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 645—651).—Two specimens pseudomorphic with leucite, occurring with the alkaline rocks of the Ishim river (West Siberia), are described and discussed.

H. J. E.

Albite from Druzhnaya Gorka works with a small angle of optical axes. D. S. BELLANKIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 651—655).—Albite was found in the crusts from the arch of a regenerative chamber in a glass works. Optical properties are recorded. The angle of optical axes is small and negative, the abnormality being due to the high temp. of formation.

H. J. E.

Thermally metamorphosed diorite near Brookfield, Connecticut. W. M. AGAR (*Amer. J. Sci.*, 1934, [v], 28, 401—411).—The local rocks (granodioritic gneiss and gneissoid diorite) are described. Their formation is discussed.

H. J. E.

Limonite deposits at the Orient mine, Colorado. J. B. STONE (*Econ. Geol.*, 1934, 29, 317—329).—The limonite is formed by near-surface oxidation of replacement bodies of Fe-bearing carbonate in limestone. Analyses are given.

CH. ABS. (e)

Chloritoid from Dutchess County, New York. T. F. W. BARTH and R. BALK (*Amer. Mineral.*, 1934, 19, 345—350).—The mineral (H₂FeAl₂SiO₇) occurs as dark-green flakes scattered through a lens of sericite and quartz in a dark biotite-sericite schist.

CH. ABS. (e)

Unusual occurrence of asbestos. E. E. WAHLSTROM (*Amer. Mineral.*, 1934, 19, 178—180).—Fibrous and sheet-like masses of asbestos were found in a banded fissure-vein (Snowy Range mine, Boulder Co., Colorado), associated with Cu-bearing pyrite, galena, sphalerite, calcite, feldspar, quartz, and pyroxene.

CH. ABS. (e)

Oligonite, a manganosiderite from Leadville, Colorado. E. B. MAYO and W. J. O'LEARY (*Amer. Mineral.*, 1934, 19, 304—308).—Pale "taffy-coloured" crystals (MnO 35.28, FeO 26.18, CO₂ 37.98%) in radiating bundles of small columns were found associated with galena, chalcophyrite, and sphalerite.

CH. ABS. (e)

Vanadium, molybdenum, tungsten, and chromium in oxidised lead deposits. W. H. NEWHOUSE (*Amer. Mineral.*, 1934, 19, 209—220).—Analyses of sulphides found in Pb and Pb-Zn-Cu deposits indicate that they may contain small amounts of V, Mo, Cr, and W, and hence be the source of these elements in the oxidised Pb deposits.

CH. ABS. (e)

Selective incrustation of crystal forms. C. FRONDEL (Amer. Mineral., 1934, 19, 316—329).—Specimens of quartz, calcite, and galena are described and discussed. CH. ABS. (e)

Paragenesis of the Trafoss serpentine reaction aureole. F. WEINZEDL (Tsch. Min. Mitt., 1934, 46, 73—84).—The paragenesis is discussed. Analyses of the following minerals are recorded: andradite, diopside, epidote, hornblende, antigorite serpentine, and orthoamphibolite. H. J. E.

Classification of deformed shales by optical and X-ray means. B. SANDER (Z. Krist., 1934, 89, 97—124).—A general survey from the mineralogical viewpoint, with particular reference to those rocks in which owing to included fossils the deformation process can be followed. B. W. R.

Relation between phosphoric acid and fluorine contents of the Chibin apatite-nepheline deposits. E. N. ISAKOV (Zavod. Lab., 1934, 3, 796—799).—For Chibin apatite containing $> 38\%$ P_2O_5 , % F is given by $y/12.7062$, where y is the % P_2O_5 content; the results differ from experimental by $+0.06\%$. R. T.

Is the colour of the natural ruby due to iron? W. J. O'LEARY, G. L. ROYER, and J. PAPISH (Science, 1934, 80, 412—414).—Fe and Cr determinations of natural rubies show that (i) the total amount of pigmenting oxides (I) varies between 0.83 and 3.5%, (ii) apparently the depth of colour \propto the total amount of (I), irrespective of the Cr_2O_3 present, (iii) there is no fixed ratio of Fe : Cr, and (iv) the amount of (I) in the more deeply coloured natural rubies coincides with the amount which must be added to synthetic preps. in order to produce the same colour. L. S. T.

Distribution of arsenic in relation to rock structure in the Eastern Alps. R. SCHWINNER (Tsch. Min. Mitt., 1934, 46, 56—72).—A discussion. H. J. E.

Arsenic content of soils. J. E. GREAVES (Soil Sci., 1934, 38, 355—362).—The total and H_2O -sol. As of orchard soils varied widely. Vals. were unrelated to sol. salt or org. N contents. A. G. P.

Subdivision of the Upper Peninsula experimental forest on the basis of soils and vegetation. S. A. WILDE and H. F. SCHOLZ (Soil Sci., 1934, 38, 383—399).—An ecological study on 5 soil profiles. A. G. P.

Functional relationships between soil properties and rainfall. H. JENNY and C. D. LEONARD (Soil Sci., 1934, 38, 363—381).—In soils situate

along the 11° isotherm the CO_2 content decreases and the N content increases with rainfall. High rainfall favours colloidal clay formation. p_H vals. decline with increasing rainfall, neutrality being associated with an annual pptn. of 25 in. Exchangeable H^+ appears in areas having < 26 in. of rain and increases with rainfall, max. exchangeable bases being found in soils having 26 in. A. G. P.

Formation and stability of soil structure. P. I. ADRIANOV (Z. Pflanz. Düng., 1934, A, 36, 26—37).—The structure of soils is examined in relation to vol.-temp. changes and variations in internal cohesive forces. A. G. P.

Origin of brilliant coal (vitrain). M. LEGRAYE (Rev. Univ. Mines, 1934, [viii], 10, 352—354; Fuel, 1934, 13, 345—347).—Bright coal may consist of thin deposits of accumulated ulmic matter, which form the rarely-occurring structureless vitrain, or of lenticles of tissues ulmified *in situ*, forming structure vitrain. Dull coal is formed by accumulation of undecomposed vegetable debris, generally cuticles, spores, etc., which may be cemented together by a little ulmic matter. A. B. M.

Microscopical structure of vitrain. I. Band of vitrain occurring in bright coal. R. G. H. B. BODDY (Fuel, 1934, 13, 326—332).—A vitrain band occurring in a specimen of clarain from the Top Hard seam exhibited when examined microscopically a well-preserved structure which showed that it had once been a piece of coniferous-like wood. The structure is illustrated by photomicrographs. A. B. M.

Petrographic characteristic of Irkutsk sapropel coals. Y. A. ZHEMCHUZHNIKOV (Khim. Tver. Topl., 1934, 5, 97—107).—The coals are described and their formations discussed. CH. ABS. (e)

Origin of Barzass coals. Z. ERGOLSKAYA (Khim. Tver. Topl., 1934, 5, 32—39).—A discussion. CH. ABS. (e)

Petrographical investigation of the coal deposits of the Borovichi district. E. S. KORZHEVSKAYA (Khim. Tver. Topl., 1933, 4, 198—204).—The composition and formation of the deposits are discussed. CH. ABS. (e)

Occurrence of sal ammoniac at Tamaki, Auckland. J. A. BARTRUM (New Zealand J. Sci. Tech., 1934, 16, 80).—Formation of NH_4Cl results from the natural combustion of a thick bed of lignite. The salt is deposited on overlying clay strata.

Organic Chemistry.

[Pseudo-atoms.] H. ERLÉNMEYER (Helv. Chim. Acta, 1934, 17, 1558—1559; cf. A., 1933, 557).—Comments on papers by Perret and Perrot and by von Platz (A., 1933, 815; 1934, 1209). F. L. U.

Specific refractive dispersion as a method for distinguishing between different series of hydro-

carbons. A. L. WARD and W. H. FULWEILER (Ind. Eng. Chem. [Anal.], 1934, 6, 396—400).—The d and n (for 6563, 5893, 5461, 4861, and 4358 Å.) have been determined for several hydrocarbons and their mixtures. In general, the effect of substitution on dispersion is related to its effect in decreasing the benzenoid and increasing the paraffinoid character of the hydro-

carbon. Individual effects in paraffins, olefines, and aromatic hydrocarbons are described. The possibilities of the use of sp. dispersion data are discussed.

E. S. H.

Thermal decomposition of organic compounds from the viewpoint of free radicals. XI. Identification of methyl groups as dimethyl ditelluride. F. O. RICE and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1934, 56, 2472).—The fragments obtained by thermal decomp. of C_4H_{10} , $COMe_2$, or Et_2O at 800–900° combine with Te to give *dimethyl ditelluride* (I), b.p. 196° (decomp.), m.p. –19.5°, as the sole product; radicals other than Me are not produced. (I) is comparatively stable in air and has a low v.p. at room temp.

H. B.

Thermal decomposition of organic compounds from the viewpoint of free radicals. XI. Methylene radical. F. O. RICE and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1934, 56, 2381–2383; cf. A., 1933, 930).— CH_2 is formed when CH_2N_2 is decomposed at < 500° in a current of Et_2O or C_4H_{10} . At > 650° and < the decomp. temp. of Et_2O Me is formed. CH_2 reacts with Te, Se, As, and Sb, but not with Zn, Cd, Hg, Tl, Pb, and Bi. Me reacts with all these elements. The reaction of CH_2 with Te yields a red solid, $(CH_2Te)_n$, whilst Me yields Te_2Me_2 .

E. S. H.

Mechanism of the formation of methane and condensation products by the pyrolysis of ethane, ethylene, etc.—See this vol., 40.

Isomerisation of allene hydrocarbons by silicates. I. Isomerisation of asymmetric dimethylallene in presence of floridin. J. M. SLOBODIN (J. Gen. Chem. Russ., 1934, 4, 778–782).— $CPr^s:CH$ yields a mixture of isoprene (I) and $CH_2:CMc:CH:CH_2$ (II) when heated with floridin; the yields of (I) rise from 3.2% at 215° to 20% at 280°, above which they remain const., owing to polymerisation to the dimeride. The yields of (II) rise continuously from 25% at 215° to 60% at 334°.

R. T.

Preparation and cationoid reactivity of dichlorodinitromethane. E. DOWNING and W. B. ORR (J.C.S., 1934, 1671–1672).— $CCl_2(NO_2)_2$ [from $s-C_6H_2Cl_3NH_2$ and warm HNO_3 (d 1.42) followed by distillation] and $N_2H_4 \cdot H_2O$ in aq. $EtOH-NaOH$ react thus: $2CCl_2(NO_2)_2 + N_2H_4 \rightarrow 2CHCl(NO_2)_2 + N_2 + 2HCl$. In the absence of alkali, reduction continues slowly beyond this stage. In accordance with expectation, similar reductions of $CBBr_2(NO_2)_2$ occur more rapidly (cf. Macbeth and Pratt, *ibid.*, 1921, 119, 1356).

H. B.

Halogenation inhibition by oxygen. R. M. DEANESLY (J. Amer. Chem. Soc., 1934, 56, 2501–2502; cf. Bauer and Daniels, A., 1934, 1216).—Chlorination of C_3H_8 , C_4H_{10} , and pentanes is inhibited by O_2 even in presence of light or olefines (cf. B., 1933, 1046). Addition of Cl_2 to, e.g., Δ^2 -butene is not inhibited by O_2 even in the dark or absence of catalysts; reaction is very fast (accordingly, any retardation is not easy to detect).

H. B.

Catalysis in hydrogen bromide-olefine additions. V. N. IPATIEV, H. PINES, and R. C. WACKHER (J. Amer. Chem. Soc., 1934, 56, 2398—

2400).—When C_3H_6 is passed through $AcOH-HBr$, some of the C_3H_6 dissolves, but no reaction occurs. Addition of C_6H_{14} , cyclohexane, C_6H_6 , Bu^vBr , $EtBr$, or $PhBr$ to the $AcOH-HBr$ promotes reaction; H_2O and $EtOH$ have no effect. Reaction also occurs when an equimol. mixture of C_3H_6 and HBr is passed through C_6H_{14} . When an equimol. mixture of C_3H_6 and isobutene is passed through $AcOH-HBr$, the C_3H_6 reacts (slowly at first and then more rapidly) owing to the catalytic effect of the Bu^vBr produced. Reaction between C_4H_8 and $AcOH-HBr$ is similarly autocatalytic. All experiments are carried out at 5°.

H. B.

Rule relating to the formation of a double linking in aliphatic halogeno-compounds. S. C. J. OLIVIER (Rec. trav. chim., 1934, 53, 1093–1096).—The elimination of $HHal$ from aliphatic halogeno-compounds (saturated) involves the removal of the H attached to the C bearing the largest no. of negative atoms or groups. Various examples (lit.) are given. In $CHMeBr_2$, where the elimination of such a H cannot occur, reaction with KOH must be much slower than with CH_2Br-CH_2Br (cf. following abstract).

H. B.

Action of acids and bases on $\alpha\alpha$ - and $\alpha\beta$ -dibromoethanes. S. C. J. OLIVIER and A. P. WEBER (Rec. trav. chim., 1934, 53, 1087–1092).—Hydrolysis (method: A., 1934, 971) of $CHMeBr_2$ (I) and CH_2Br-CH_2Br (II) by aq. $COMe_2$ at 60° is not accelerated by H^+ . (I) and (II) are not hydrolysed (cf. Burkhardt and Cocker, A., 1931, 1031) by aq. KOH in various org. solvents, but are converted into CH_2^+CHBr (and to some extent into C_2H_2); in aq. $COMe_2$ at 30° the velocity coeffs. for (I) and (II) are 0.000023 and 0.0047, respectively.

H. B.

Chlorobutene C_4H_7Cl obtained in the action of phosphorus pentachloride on methyl ethyl ketone. P. CHARPENTIER (Bull. Soc. chim., 1934, [v], 1, 1407–1411).—The chlorobutene obtained, together with $CMcEtCl_2$, by the action of PCl_5 on $COMeEt$ (Dupont, A., 1909, i, 545) is a mixture of β -chloro- Δ^2 - (I) and Δ^2 - (II) n -butene, since, after careful fractionation, oxidation of the low fraction, b.p. 58.5–59°, with 2 mols. of alkaline $KMnO_4$ affords a mixture of $EtCO_2H$ and $AcOH$, and CO_2 (from HCO_2H), and is thus a mixture of (I) and (II); the fraction, b.p. 64–66°, gives only $AcOH$ and is thus almost pure (II). The composition of the mixed acids is determined by analysis of their Ba salts.

J. W. B.

Preparation of ψ -butylene chlorohydrin. V. S. BATALIN and P. G. UGRIMOV (J. Gen. Chem. Russ., 1934, 4, 871–874).—The chlorohydrin is obtained in 50–60% yield by Gomberg's method (A., 1919, i, 567), and in 60–65% yield by McElroy's method (U.S.P. 1,253,616; B., 1918, 167).

R. T.

Splitting of ditertiary alkylcarbinols by dehydration. Dehydration of *tert*-butyl*tert*-amyl- and *tert*-butyl*tert*-hexyl-carbinols. I. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 612–615; cf. A., 1934, 753).—Pinacolin with $NaNH_4$ and MeI or EtI gives, respectively, *tert*-butyl *tert*-amyl, b.p. 172–177°, and *tert*-hexyl ketone, b.p. 193–198°, which are reduced ($Na-EtOH$) to *carbinols*, b.p. 186–190° (I) and 206–211° (II), respectively. (I)

with 1:4- $C_{10}H_8BrSO_3H$ (III) at 150° affords a mixture of $CHMe:CHEt$, $CMe_2:CHMe$ (IV), and δ -methyl- Δ^2 -pentene (V). With $H_2C_2O_4$ at 150 – 160° , (I) affords some (IV) and a mixture of decenes, which with (III) gives products similar to the above. Similarly, (II) gives (IV), (V), γ -ethyl- Δ^2 -pentene, and higher-boiling hydrocarbons. J. L. D.

Synthesis of alldulcitol and dulcitol. R. LESPIEAU (Bull. Soc. chim., 1934, [v], 1, 1374–1376)

—When heated with H_2O the oxide $\left[\begin{array}{c} O < CH_2 \\ CH < CH_2 \end{array} \right]_2$ (not a mixture of stereoisomerides) affords the crude acetylenic $(OH)_4$ -derivative (I) from which by repeated extraction with $MeOH$ is isolated only a small amount of one stereoisomeride, m.p. 116 – 117.5° , reduced by $Pd-H_2$ to *cis*- Δ^2 -*n*-hexene- $\alpha\beta\epsilon\zeta$ -tetraol (II), m.p. 80 – 82° . Similar reduction of (I) and subsequent acetylation gives an Ac_4 derivative (III), b.p. $170^\circ/12$ mm. Oxidation of (II) with $AgClO_3-OsO_4$ gives almost exclusively alldulcitol, sinters 142° , m.p. 148° , but a trace not melting until 160° , most probably dulcitol (IV). Similar oxidation of (III) and acetylation of the product gives the Ac_8 derivative of (IV), and a substance, m.p. 50 – 59° . J. W. B.

Dry ether as a solvent for anhydrous aluminum chloride in organic synthesis. R. C. SHAH (Current Sci., 1934, 3, 157).—A solution (I) of anhyd. $AlCl_3$ in dry Et_2O may be used with advantage in Friedel-Crafts syntheses which occur under mild conditions, or in place of $ZnCl_2-Et_2O$ suspension in the Hoesch synthesis, examples being cited. In some cases Et_2O reacts to give ethers; e.g., $BzCl \rightarrow EtOBz$, $CPh_3Cl \rightarrow CPh_3 \cdot OEt \rightarrow CHPh_3 + MeCHO$. J. W. B.

Hydration of ethylene oxide. C. MATIGNON, H. MOUREU, and M. DODÉ (Bull. Soc. chim., 1934, [v], 1, 1308–1317).—By the action of $(CH_2)_2O$ (I) on $(CH_2OH)_2$ (II) in presence of 0.5% H_2SO_4 at 90° , pure specimens of tri- (III) and tetra- (IV) -ethylene glycol $HO \cdot CH_2 \cdot [CH_2 \cdot O \cdot CH_2]_n \cdot CH_2 \cdot OH$, are prepared, and the n_D -composition curves for synthetic mixtures of (II)-diethylene glycol (V), (III)-(V), and (IV)-(V) are determined. The compositions of the mixtures of glycols obtained when (I) is hydrolysed with varying amounts of H_2O (0.5% H_2SO_4 at 90 – 95°) are thus determined by measurement of n_D for the binary mixtures obtained by fractional distillation. Temp. and $[H^+]$ have little effect on the composition of the product, which is determined mainly by the mol. ratio $(R) H_2O/(I)$. As R is decreased successively from 10.5 to 0.61 the % of (II) decreases continuously from 82.3 to 15.7%; that of (V) increases from 12.7 to a max. of 34.5% at $R=2.1$ and then decreases to 26%. No (III) is formed until $R=4.2$ (2.3%), and it then increases to 19.8%; no (IV) is formed until $R=2.1$ (0.3%), increasing to 19%. Higher glycols are not formed until $R=1.40$. Thus to obtain pure (II), R must be ≤ 20 . J. W. B.

Complex platinum compounds with ter- and quinque-valent platinum. VII.—See this vol., 52.

Decomposition of neutral alkyl sulphites by heat. P. CARRE and D. LIBERMANN (Bull. Soc. chim., 1934, [v], 1, 1248–1250).—Alkyl sulphites (2

mols.) are decomposed by heat to give the olefine (1 mol.) and alcohol (1 mol.), if the alkyl group has a high mol. wt. The temp. of decomp. is lowered by approach of a substituent Ph nearer to S , by unsaturation in the alkyl, or addition of C_5H_5N . In the first case, the decomp. may take an alternative course. Thus, $SO(OBu^t)_2$ is stable at the b.p. (228°). *Decyl sulphite* (from $SOCl_2$ and the alcohol in C_5H_5N), b.p. about $250^\circ/15$ mm., decomposes to decene and $C_{10}H_{21}OH$ at 310° . $SO(OPr^i)_2$ gives C_3H_8 and Pr^iOH at 310° alone or 210° in C_5H_5N . β -*Phenyl-ethyl sulphite*, b.p. 238 – $240^\circ/15$ mm., at 290° gives $(CH_2Ph \cdot CH_2)_2O$, b.p. 194 – $195^\circ/20$ mm., and $SO(O \cdot CH_2Ph)_2$ (lit. b.p. 193 – $199^\circ/15$ mm.) decomposes at 130° to $(CH_2Ph)_2O$, b.p. 166 – $168^\circ/13$ mm., 295 – $298^\circ/760$ mm. *Allyl sulphite*, b.p. about $110^\circ/45$ mm., gives 45% of $CH_2 \cdot CH \cdot CH_2 \cdot OH$ and only a trace of olefine (most of that formed resinifies) at 190° alone or 110 – 120° in C_5H_5N . *Cinnamyl sulphite* decomposes at 100° (even in vac.) to form resins and cannot be distilled. R. S. C.

Cleavage of lecithin by heat. M. SATO and N. WADA (J. Soc. Chem. Ind. Japan, 1934, 37, 717–718b).—In agreement with Page and Schmidt (A., 1931, 1082) and contrary to Paal (A., 1929, 1337), lecithin (from soya-bean oil) is comparatively stable to heat in $EtOH$ solution, only 3–4% hydrolysis occurring after 3 hr. at 120° . H. N. R.

Fermentation of mannose by dried yeast.—See A., 1934, 1405.

Intramolecular transpositions. I. Influence of carboxyl, ester, and nitrile groups on allylic intramolecular transpositions. R. RAMBAUD (Bull. Soc. chim., 1934, [v], 1, 1206–1232).—A summary of experiments not yet described in detail. Formation during a reaction of $CH_2 \cdot CH \cdot CHYR$ (I) from $CH_2X \cdot CH \cdot CHR$ (II) is prevented if $R=CO_2H$, CO_2R' ($R'=H$, Me , Et , or Pr), or CN , and that of (II) from (I) is similarly rendered more difficult, but the formation of $CHMc \cdot CYR$ from (I) is facilitated; these rules apply only if X and $Y \neq H$. Replacement is termed "normal" if such changes are not involved. The following are exclusively "normal": acetylation in presence of H_2SO_4 or $NaOAc$ of (I) ($Y=OH$; $R=CO_2H$, CO_2Me , CO_2Et , or CN) and of *trans*- γ -hydroxycrotonic acid (the resulting Ac derivatives resist isomerisation); reaction of (II) ($X=Br$; $R=CO_2R'$) with $NaOAc$; alkaline hydrolysis of the Ac derivatives resulting from the above reactions; hydrolysis of (II) ($X=Br$; $R=CO_2R'$) by $AgOH$ in the cold (giving OH -esters) or KOH or $Ba(OH)_2$ cold (giving the Br -acid) or hot (giving the OH -acid) [$(CO_2H \cdot CH \cdot CH \cdot CH_2)_2O$ is also formed under certain conditions]; replacement of $X=Br$ by NEt_3 , and of X or $Y=OH$ ($R=CN$ or an ester) by Cl ($SO_2Cl \cdot C_5H_5N$). Anionotropic isomerism occurs in the following cases: α -hydroxy- Δ^2 -butenoic acid and its esters with PBr_3 give mixtures of α - and γ - Br -compounds with more or less decomp.; reaction of $Et \alpha$ -bromo- Δ^2 -butenoate with $NaOAc$ or $AgOH$ (cold) gives $Et \gamma$ -acetoxy- or γ -bromo-crotonate; α -chloro- Δ^2 -butenoates with $CaBr_2$ give α -bromocrotonates (the nitrile reacts similarly, but more slowly); $CH_2 \cdot CH \cdot CHCl \cdot CO_2Me$ and HCl give a little

$\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, which is the only case observed of anionotropy involving Cl. The following "abnormal" reactions involving prototropy are recorded. (a) Substances of type (I) in which $\text{Y}=\text{Cl}$: if $\text{R}=\text{CO}_2\text{R}'$ or CN , NaOH gives rapidly $\text{CHMe}\cdot\text{CCl}\cdot\text{CO}_2\text{H}$ (III); if $\text{R}=\text{CO}_2\text{R}'$, aq. NH_3 gives (III) or its amide, and anhyd. NH_4Et_2 gives its esters (with a 10% yield of $\alpha\text{-NEt}_2$ -ester), also formed (exclusively) by NaOAc in AcOH ; if $\text{R}=\text{CN}$ or an ester group, conc. HCl gives slowly (III) and oily by-products, but in this case the migration may have occurred after hydrolysis. (b) Substances of type (I) in which $\text{Y}=\text{OH}$; here migration of H gives $\text{CHMe}\cdot\text{CR}\cdot\text{OH}$, which ketonises to EtCOR ; α -hydroxy- Δ^2 -butenoic acid gives $\text{COEt}\cdot\text{CO}_2\text{H}$ more readily in aq. K_2CO_3 than in HCl ; the OH - and OAc -esters are similarly isomerised and hydrolysed (hydrolysis of $\text{CO}_2\text{R}'$ must precede that of OAc) by alkali, but not by acid; if $\text{R}=\text{CN}$, PBr_3 alone gives a complex mixture of Br-compounds, but in Et_2O acts catalytically to yield $\text{EtCO}\cdot\text{CN}$, which in presence of aq. acid forms EtCO_2H ; $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CN}$ and PBr_3 in Et_2O give, however, much Br-nitrile and little PrCO_2H . These and other results recorded in the lit. are interpreted as due to reaction of the unsaturated substance as a "tripolar ion," $\text{CH}_2\cdot\text{CH}\cdot\text{CHR}$, if $\text{R}=\text{H}$ or alkyl, but as a "pentapolar ion," $\text{CH}_2\cdot\text{CH}\cdot\text{CX}\cdot\text{C}(\text{OR}')\cdot\bar{\text{O}}$ or $\text{CH}_2\cdot\text{CH}\cdot\text{CX}\cdot\text{C}\cdot\text{N}$, if $\text{R}=\text{CO}_2\text{R}'$ or CN ; in the latter case prototropic ionisation is favoured and anionotropic ionisation is hindered by the electrical nature of R. Similar considerations apply to substances of type (II). The relative ease of fission as ion is Cl^- , $\text{OH}^- < \text{H}^+ < \text{Br}^-$. R. S. C.

Reaction between esters of organic acids and mixed organomagnesium compounds, especially with magnesium isopropyl chloride. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1934, [v], 1, 1419—1424).—The vol. of hydrocarbon evolved (tabulated) in the interaction of MgRX with esters depends on the mol. ratio ($r=\text{MgRX}/\text{ester}$), and is greatest with $\text{MgPr}^\beta\text{Cl}$ (I). By determination of the vol. of C_3H_8 (accompanied by a little C_3H_6) evolved in such interaction of (I) and various esters at 35° the following four types of reaction are recognised, examples being given in parentheses: (a) simple enolisation (max. $r=2:1$), $\text{CH}_2\text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{CHR}\cdot\text{C}(\text{OEt})\cdot\text{OMgX}$ [$\text{CH}_2(\text{CO}_2\text{Et})_2$, $\text{CHEt}(\text{CO}_2\text{Et})_2$, $\text{CHPh}_2\cdot\text{CO}_2\text{Et}$, and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Pr}^\alpha$]; (b) condensation and enolisation of the product ($\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$); (c) EtOAc affords COMePr^β , which enolises (max. $r=3:1$) [similarly with $\text{Et}\cdot\text{CO}_2\text{Et}$ and $(\text{CH}_3)_2\text{CO}_2\text{Et}$]; and (d) a combination of (a) (b), and (c) [$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, $\text{CHCl}_2\cdot\text{CO}_2\text{Et}$, $\text{CH}_2\text{Pr}^\beta\cdot\text{CO}_2\text{Et}$, $\text{Pr}^\alpha\text{CO}_2\text{Et}$, and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$]. Similar types of results are obtained with other MgRX compounds. J. W. B.

Mechanism of Kolbe's reaction. I. Electrolysis of free acetic acid.—See this vol., 45.

Lead acetato-chloride.—See this vol., 50.

Electrolysis of acetate solutions.—See this vol., 45.

Intramolecular transformations. II. Preparation and study of α -hydroxyvinylacetic acid and its derivatives. Experimental study of their normal reactions and the normal reactions of the isomeric γ -substituted crotonic acids. III. Abnormal reactions of α -substituted derivatives of vinylacetic acid. R. RAMBAUD (Bull. Soc. chim., 1934, [v], 1, 1317—1341, 1342—1355).—Experimental details of results previously summarised (A., 1933, 489, 1275, 1281) are given. The following appears to be new: the lactide, $\text{CH}_2\cdot\text{CH}\cdot\text{CH} < \text{CO} > \text{CH}\cdot\text{CH}\cdot\text{CH}_2$, m.p. $151\text{--}152^\circ$ (Br_4 additive compound, m.p. 225°); hydrolysis of esters of the *trans*- γ -Br-acid with NaOH at room temp. affords the ether $(\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2)_2\text{O}$, m.p. 195° (*Ag* and *Ba* salts), of *trans*- γ -hydroxy- Δ^2 -butenoic acid, and interaction with NH_4Et_2 in dry Et_2O gives *Et* γ -diethylamino- Δ^2 -butenoate, b.p. $111\text{--}111.5^\circ/15$ mm. (*picrate*, m.p. $97\text{--}98^\circ$); $\alpha\beta$ -dichlorobutyronitrile, b.p. $74\text{--}78^\circ/17.5$ mm. (*amide*, m.p. 121°). *Me*, b.p. $87^\circ/15$ mm., and *Pr* $^\alpha$, b.p. $108\text{--}109^\circ$, γ -bromo- Δ^2 -butenoate are described. J. W. B.

Toxic principle of croton oil. I. Acids of croton oil. B. FLASCHENTRAGER and R. VON WOLFFERSDORFF (Helv. Chim. Acta, 1934, 17, 1444—1452).—Analysis of croton oil gives the following results: toxic substances, 3.4%; unsaponifiable matter, 0.25%; oleic, 37.0%, linoleic, 19.1%, arachidic, 1.52%, stearic, 0.31%, palmitic, 0.89%, myristic, 7.45%, lauric, 0.05%, valeric, trace, tiglic acid, 0.03%; PrCO_2H , trace; AcOH , 0.6%; HCO_2H , 0.8%; acids insol. in light petroleum, 6.93%; undetermined acids, 0.64%; glycerol, 7.20%; loss, 13.83%. H. W.

Composition of cacao butter. Partial hydrolysis of mixed azelaic glycerides. J. BOUGAULT and G. SCHUSTER (Bull. Soc. chim., 1934, [v], 1, 1416—1419).—Contrary to the criticism of Hilditch *et al.* (A., 1933, 592), analytical data (C, 74.14; H, 11.95%) and mol. wt. (595) determinations for the product obtained by partial hydrolysis [cold aq. Na_2CO_3 or NaOH , or in Et_2O - EtOH - KOH (I)] of the triglyceride (II), m.p. 59° , from cacao butter confirm the original conclusion (A., 1931, 820) that it is glyceryl α -palmitate γ -stearate, m.p. $45\text{--}46^\circ$ (*loc. cit.*, m.p. 34°), and not *Et* stearate, although the latter is also formed in (I). (II) is therefore α -palmito- β -oleo- α -stearin (A., 1931, 1199). J. W. B.

Heneicosoic acid. S. SHIINA (J. Soc. Chem. Ind. Japan, 1934, 37, 721B).—*Et* nonadecoate is converted successively into *n*-nonadecanol, m.p. $61.8\text{--}62.0^\circ$, the iodide, m.p. $42.0\text{--}42.2^\circ$, *n*-nonadecylmalonic acid, and *n*-heneicosoic acid, m.p. $73.9\text{--}74.2^\circ$ (*Et*, m.p. $44.2\text{--}44.4^\circ$, and *Me*, m.p. $46.8\text{--}47.2^\circ$, ester). H. N. R.

Alkylation of acetoacetic, malonic, and succinic esters. B. WOJCİK and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 2424—2425).— $\text{CH}_2\text{R}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, where $\text{R}=\text{H}$, *Me*, *Pr*, hexyl, *Ph*, and furyl, are prepared by reduction (H_2 , Raney Ni at room temp.) of $\text{CHR}\cdot\text{C}(\text{CO}_2\text{Et})_2$ [from RCHO , $\text{CH}_2(\text{CO}_2\text{Et})_2$, and piperidine]. *Et* heptylidenemalonate has b.p. $143\text{--}145^\circ/5$ mm. *Et* itaconate is simi-

larly reduced to Et α -methylsuccinate; Et α -isopropylidenesuccinate [from $(\text{CH}_2\text{CO}_2\text{Et})_2$, COMe_2 , and EtOH-NaOEt] gives Et α -isopropylsuccinate; Et α -methylbenzylidenesuccinate affords Et α -methylbenzylsuccinate; Et α -heptylidene- and α -cinnamylidene-acetoacetates yield Et α -heptylacetoacetate and α -acetyl- δ -phenylvalerate, respectively. H. B.

Derivatives of glyoxylic acid and their use in the Hopkins-Cole reaction. P. P. T. SAH, C. H. KAO, and T. Y. CHANG (J. Chinese Chem. Soc., 1934, 2, 234—239).—The following compounds of glyoxylic acid (I) are described: *o*-nitrophenyl-, m.p. 213—214° (decomp.), and β -naphthyl-, m.p. 208°; 3-nitro-, m.p. 206—207°, 3:5-dinitro-, m.p. 223—224° (decomp.), *o*-, m.p. 199° (decomp.), and *p*-chloro-benzoyl-hydrazone, m.p. 210° (decomp.); phenyl-, m.p. 183—184°, *o*-, m.p. 194—195° (decomp.), and *p*-tolyl-, m.p. 217—218°, and α -naphthyl-semicarbazone, m.p. 190—191° (decomp.). These compounds in conc. H_2SO_4 give a violet coloration with tryptophan and are recommended as substitutes for (I) in the Hopkins-Cole reaction. J. L. D.

Acetolic condensations of ethyl acetoacetate with acetaldehyde. H. GAULT and T. WENDLING (Compt. rend., 1934, 99, 1052—1054; cf. A., 1934, 1332).— $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ is added gradually to a mixture of 33% MeCHO and K_2CO_3 at 0°. When the solution no longer gives a colour with FeCl_3 , the temp. is lowered to -15° and K_2CO_3 and a large excess of MeCHO are added, whereby Et di- α' -hydroxyethylacetoacetate (I), m.p. 33°, is prepared. (I) is too unstable to permit the isolation of derivatives and passes when kept in vac. over H_2SO_4 at $> 20^\circ$ into the unstable, non-cryst. Et α' -hydroxyethylacetoacetate (II) (phenyl-hydrazone, m.p. 92°; corresponding pyrazolone, m.p. 275°), also obtained directly from $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$, MeCHO , and K_2CO_3 . In presence of NH_4Et_2 at -10° (II) passes into non-cryst. Et δ -hydroxy- $\alpha\gamma$ -diacetyl- β -methylpentane- $\alpha\gamma$ -dicarboxylate (corresponding dipyrazolone, m.p. 267—268°), which slowly loses MeCHO on exposure to air, thereby passing into Et δ -ethylidenediacetoacetate, which isomerises spontaneously to Et δ -hydroxydimethylcyclohexanedicarboxylate, m.p. 80°. H. W.

Polymembered heterocyclic compounds. VI. Preparation of pure ambrettolide. Preparation of the lactones of λ -hydroxystearic acid and ν -hydroxypentadecic acid. M. STOLL and R. E. GARDNER (Helv. Chim. Acta, 1934, 17, 1609—1612; cf. A., 1934, 1201).—Oxidation of civetone with Caro's acid yields only traces of a lactone, $\text{C}_{17}\text{H}_{30}\text{O}_2$, b.p. 135—145°/0.3 mm., the greater part of the material being either unattacked or resinified. Similarly, a homogeneous lactone is not obtained from α -methyl-exaltone. Ambrettolic acid (isolation from musk-kernel oil described) is slowly added to a solution of PhSO_3H in much C_6H_6 , thus giving homogeneous ambrettolide, $\text{C}_{16}\text{H}_{28}\text{O}_2$, b.p. 154—156°/0.9—1.1 mm. (cf. Kerschbaum, A., 1927, 541). Similarly, λ -hydroxystearolactone, b.p. 140—145°/0.11 mm., and ν -hydroxypentadecolactone, b.p. 105—105.5°/0.1 mm., are obtained from the respective OH-acids. H. W.

Photometric determination of calcium and oxalic acid.—See this vol., 54.

Formation of active racemates as a method of resolving racemates and a means of determining relative configurations. M. DELÉPINE (Bull. Soc. chim., 1934, [v], 1, 1256—1265).—If two racemates, *dl*-A and *dl*-B, and the active components are isomorphous, and if "active racemates," and *d*-A, *l*-B, are formed, then crystallisation of mixtures of, e.g., *l*-A (1 mol.) and *dl*-B (2 mols.) may lead to a less sol. fraction which is partly or entirely the active racemate, *l*-A, *d*-B. Thus, *dl*-B will have been resolved without a chemical reaction. Presence or absence of resolution is decided by the α of the successive fractions. Resolutions were obtained with *dl*-(Rh en)₃Br₃ by *l*-(Co en)₃Br₃ and the following K_3 trioxalates, $[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]\text{K}_3$: *dl*-Ir by *d*-Rh, *dl*-Co^{III} by *d*- or *l*-Ir, and *dl*-Cr^{III} by *d*-Ir; no resolution occurred with the K_3 trioxalates of *dl*-Al or *dl*-Fe^{III} and *d*-Ir. The active and ordinary racemates of the K_3 trioxalates contain 4.5H₂O. Substances forming active racemates are enantiomorphous. It is thus proved that the various M^{III} trioxalates giving the less sol. strychnine salts are homeomorphous; homeomorphism in this series is not related to the sign of α , which changes with λ . R. S. C.

Norcaperatic acid and agaricic acid. M. ASANO and Z. OHTA (Ber., 1934, 67, [B], 1842—1845; cf. A., 1933, 823).—Condensation of Et₃ propane- $\alpha\beta$ -tricarboxylate (I) with *n*-tetradecyl iodide in presence of NaOEt-EtOH at 130°, followed by hydrolysis and heating of the product at 130—140°, leads to an anhydride (II), transformed by boiling KOH and EtOH with subsequent acidification into α -methyl- β -*n*-tetradecylsuccinic acid, m.p. 134—136°. (II) is transformed by NH_2Ph at 160—170° into α -methyl- β -*n*-tetradecylsuccinanil, m.p. 63.5—64.5°, identical with the anil from norcaperatic acid (*loc. cit.*). Agaricic acid is heated at 155—160° and the product is treated successively with HI (*d* 1.7) at 170—180° and Zn-HCl, thus giving methylhexadecylsuccinic acid (III), m.p. 133.5—135°, whence methylhexadecylsuccinanil (IV), m.p. 67.5—69.5°. The synthesis of (III) and (IV) from (I) and cetyl iodide is described. H. W.

Physical properties and chemical constitution. II. Esters of $\beta\beta$ -substituted glutaric acids. A. I. VOGEL (J.C.S., 1934, 1758—1765; cf. A., 1934, 475).—By comparison of substituted malonic esters with the corresponding $\beta\beta$ -substituted glutaric esters the parachor and mol. refraction coeff. differences for 2CH_2 are found to vary from 70.8 to 78.4 and 41.30 to 43.32, respectively, thus showing that these consts. are not purely additive (and often not identical for isomeric substances), but are affected by valency deflexion. Small, but irregular, divergences are shown by $[\text{R}]_D$ and sp. dispersions. Valency angles are in the order $\text{Pr}, \text{Pr} < \text{Et}, \text{Pr} < \text{Et}, \text{Et} < \text{Me}, \text{Pr} < \text{Me}$, $\text{Et} < \text{Me}, \text{Me} < \text{Me}, \text{H} < \text{H}, \text{H}$. Directions are given for the prep. (Guareschi) of 14 dicyano-imides and their hydrolysis. The following data are new or have been disputed. (a) $\beta\beta$ -Disubstituted glutaric acids: Me_2 -, m.p. 101°; MeEt -, m.p. 85° (*Me* ester, b.p. 124°/21 mm.); Et_2 -, m.p. 106°; MePr -, m.p. 92—93° (*Me* ester, b.p. 130°/17 mm.); EtPr -, m.p. 69° (*Me* ester, b.p. 142°/20 mm.); Pr_2 - (*Me* ester, b.p. 151°/

20 mm.). (b) 3-, m.p. 142°, and 4-Methylcyclohexane-1:1-diacetic acid, m.p. 158–159° (*Me*₂ ester, b.p. 164°/20 mm.). (c) *Me*₂ (and in parentheses *Et*₂) cycloparaffin-1:1-diacetates: cyclopentane-, b.p. 141°/17 mm. (b.p. 177°/21 mm.); 3-methylcyclopentane-, b.p. 148°/19 mm.; 3-, b.p. 155°/15 mm. (b.p. 177°/21 mm.), and 4-methylcyclohexane-, b.p. 164°/20 mm. (b.p. 178°/21 mm.); trans-decahydronaphthalene-, b.p. 193°/14 mm. (b.p. 208°/17 mm.); trans-hexahydrohydrindene-, b.p. 179°/12 mm. (b.p. 196°/14 mm.); and cyclohexane- (b.p. 165°/14 mm.). *Me* β-methylglutarate has b.p. 110°/19 mm. R. S. C.

Glutaconic acids. XXIV. Catalytic effect of alkalis on the rate of racemisation of *l*-trans-α-dimethylglutaconic acid. (Miss) J. E. BULL, J. S. FITZGERALD, J. PACKER, and F. J. THORPE (J.C.S., 1934, 1653–1657; cf. A., 1933, 789).—The velocity of racemisation of this acid (I) (0.125*M*) by aq. KOH or NH₃ at 100° rises to a max. at 0.075*M* [half-neutralisation of (I)] and falls to a min. at 0.25*M* (full neutralisation); thereafter it rises rapidly with KOH, but remains nearly const. with NH₃. The concns. of fully (*A*) and half-dissociated (*B*) and non-ionised (I) are calc. from *k*₁ and *k*₂. An equation is derived, which is accurate for HCl, KOH, and dil. aq. NH₃ solutions. The undissociated acid has prototropic mobility 10³ times that of (*A*) and 10⁵ times that of (*B*). R. S. C.

Constitution of antimony emetics and the hydroxy-acids from which they are derived. P. DUQUENOIS (Bull. Soc. chim., 1934, [v], 1, 1387–1396).—Whereas the complexes of polyhydroxylic compounds with B(OH)₃ and As₂O₃ are acidic (B>As), those with V₂O₅, Sb₂O₃, or Bi₂O₃ are not. The fixation of Sb₂O₃ (determined iodometrically; Volmar *et al.*, A., 1933, 376, 948) by various polyhydric alcohols [which show large conductivity increases with B(OH)₃] in 0.1*N* solution at 100° is small, and is but slightly increased in *N* solution, indicating the different nature of the B and Sb complexes. Much greater fixation occurs with α-OH-acids (I). On the basis of these results and others previously summarised (A., 1933, 1142; 1934, 187) it is concluded that in (I) when the OH is *tert.* the CO₂H is hydrated, e.g., oxalic HO·CO·C(OH)₂ and citric acid (CO₂H·CH₂)₂C(OH)·C(OH)₂, and, in agreement with experimental data, the max. fixation of Sb₂O₃ occurs when the fraction of acid H neutralised is that given by the ratio total no. of >C(OH)·CO₂H groups/total no. OH groups, e.g., oxalic 1/4; citric 1/6; tartaric [·CH(OH)·CO₂H]₂ 2/4. J. W. B.

Determination of citric acid as pentabromoacetone in aqueous citric acid solutions, citrates, fruit juices, and fruit-juice preparations. O. REICHARD (Z. anal. Chem., 1934, 99, 81–96).—A considerable excess of both Br and KMnO₄ in the determination of citric acid (I) as pentabromoacetone (II) is not harmful. Aq. solutions of (I) or its salts (dissolved in HCl if necessary) are acidified strongly with H₂SO₄, 50% aq. KBr is added, and the solution oxidised to (II) by addition of saturated aq. KMnO₄ at > 5°. Pptd. MnO₂ is removed by adding KBr. Small amounts of sugar (< 0.5 g. in sample), as in fruit juices, do not interfere. When larger amounts

are present (e.g., in syrups), sugar may be first removed by fermentation with yeast or, better, (I) may be separated as the Ba salt and then determined.

J. S. A.

Experimental verification of Sah's proposed synthesis of vitamin-C (*l*-ascorbic acid). P. P. T. SAH (J. Chinese Chem. Soc., 1934, 2, 288–290).—The work of Reichstein *et al.* (cf. A., 1934, 511) verifies Sah's prediction in a very large measure. J. L. D.

Colour reaction of isoascorbic acid (iso-vitamin-C).—See A., 1934, 1417.

Optical rotatory dispersion in the carbohydrate group. IV. Tetramethyl-γ-mannonolactone. T. L. HARRIS, E. L. HIRST, and C. E. WOOD (J.C.S., 1934, 1825–1829; cf. A., 1934, 1092).—The rotatory dispersion of tetramethyl-γ-mannonolactone (I) is simple in H₂O, but anomalous in Et₂O, COMe₂, EtOH, CHCl₃, C₆H₆, and dioxan. In the last 5 solvents it can be expressed by a two-term Drude equation with terms of opposite sign, the rotation depending on centres of absorption at about λ 1500 and 2500 (II). The former centre is identified with the aliphatic ether, the latter with the lactonic CO. (I) thus diverges from Hudson's rule in non-aq. solvents owing to the pronounced effect due to C2 in these solvents. The effect of solvent is further shown by variation of [α] with concn. in C₆H₆. (I) does not show absorption bands in H₂O, EtOH, or CHCl₃, but in H₂O and EtOH a step-up occurs at λ 2200, possibly correlated with (II). R. S. C.

Derivatives of *l*-α-rhamnohexonic acid. Synthesis of *l*-α-rhamnohexonolactone. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2455–2456).—*l*-Rhamnose is treated with NaCN and Ba(OAc)₂ in H₂O at about 0° for 70 hr.; subsequent hydrolysis [Ba(OH)₂] gives 55% of α-rhamnohexonolactone (I), m.p. 171–171.5° (all m.p. are corr.), [α]_D (in H₂O) +87.3° → +74.4° (after 67 days). α-Rhamnohexonic acid, m.p. 171° (lit. 174–175°), [α]_D²⁰ (in H₂O) +21.5° → +74° [calc. as (I)], its *Et* ester, m.p. 165–166° (decomp.), [α]_D (in H₂O) +12.9° → +74° [calc. as (I)], amide, m.p. 177.5–178° (decomp.) (lit. 194°), [α]_D²⁰ (in H₂O) –19.9° (lit. –47.3°), and phenylhydrazide, m.p. 205–206° (decomp.), [α]_D –5.2° in H₂O, are described. H. B.

Pharmacology of rare earths.—See A., 1934, 1400.

[Aldehyde of violet leaves.] H. WALBAUM and A. ROSENTHAL (Ber., 1934, 67, [B], 1804; cf. B., 1929, 1049).—A question of priority (cf. Späth *et al.*, A., 1934, 1204). H. W.

Substances with the odour of violets. IV. Oil of violet leaves. Constitution of the aldehyde of violet leaves. Δ^α-Nonadienal. V. Synthesis of the aldehyde of violet leaves. Δ^α-Nonadienal or a stereoisomeride thereof. L. RUTZICKA and H. SCHINZ (Helv. Chim. Acta, 1934, 17, 1592–1601, 1602–1608).—IV. The treatment of the oil by distillation with steam and by fractionation in vac. is described, the crude aldehyde being transformed into its semicarbazone (I), m.p. 157–158°, from which it is regenerated with difficulty. In presence of Pt-black (I) absorbs 2H₂ giving *n*-nonaldehyde-

semicarbazone (II), m.p. 97—98°, whereas in presence of PtO_2 it absorbs 3H_2 yielding *n-nonylsemicarbazide*, m.p. 104—106°, also obtained from (II). Ozonisation of (I) yields EtCHO (*p*-nitrophenylhydrazone, m.p. 120°), two substances, $\text{C}_{14}\text{H}_{14}\text{O}_6\text{N}_6$, red needles, m.p. 177—179°, and yellow crystals, m.p. 178—179°, apparently compounds of *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ and glyoxylic acid *p*-nitrophenylhydrazone, succinaldehydic acid *p*-nitrophenylhydrazone, incipient decomp. about 300°, and (?) glyoxaldisemicarbazone. The work of Spath *et al.* (A., 1934, 1204) is thus confirmed.

V. Energetic reduction of $\text{Et } \Delta^8\text{-hexenoate}$ with Na and EtOH at 100—110° gives a mixture of little hexenol and much hexyl alcohol and a substance, $\text{C}_8\text{H}_{18}\text{O}_2$, b.p. 88—89°/12 mm., whilst the regenerated acid is mainly hexoic acid. Similar treatment of Et sorbate at $\approx 80^\circ$ smoothly yields a hexenol, b.p. 62—63°/13 mm., proved by ozonisation to be essentially Δ^7 -hexenol (I). Treatment of (I) with SOCl_2 in $\text{CHCl}_3\text{-C}_5\text{H}_5\text{N}$ gives Δ^7 -hexenyl chloride (II), b.p. 59—61°/60 mm. (the corresponding bromide cannot be prepared analogously), converted by anhyd. NaI in COMe_2 into Δ^7 -hexenyl iodide (III), b.p. 62—63°/12 mm. The Grignard compound, best prepared from a mixture of (II) and (III), is converted by acraldehyde into the corresponding (impure) carbinol, b.p. 80—90°/12 mm., transformed by the successive action of PBr_3 and $\text{C}_5\text{H}_5\text{N}$ in light petroleum and of AgOBz in abs. Et_2O into nonadienyl benzoate (IV), b.p. 137°/0.3 mm. (IV) is hydrolysed to Δ^8 -nonadienol, b.p. 100°/13 mm. [ozonisation product, $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$], oxidised by CrO_3 to Δ^8 -nonadienal (semicarbazone, m.p. 156—157°, does not depress the m.p. of the similar product from oil of violet leaves). The synthetic and natural aldehydes may be *cis-trans*-isomerides. H. W.

Resolution of *r*-glyceraldehyde. M. BETTI and P. PRATESI (Biochem. Z., 1934, 274, 1—3).—A certain amount of resolution can be effected by means of β -hydroxynaphthylbenzylamine. P. W. C.

d-isopropylidenedioxysuccindialdehyde (*l*-isopropylidenetartardialdehyde). H. O. L. FISCHER and H. APPEL (Helv. Chim. Acta, 1934, 17, 1574—1582).—Triisopropylidenemannitol is converted by HCl in $\text{H}_2\text{O-EtOH}$ at 40° into $\gamma\delta$ -isopropylidenemannitol (I), m.p. 85°, $[\alpha]_D^{20} + 29.5^\circ$, which is oxidised by Pb(OAc)_4 in anhyd. C_6H_6 at 100° to *d*-isopropylidenedioxysuccindialdehyde (II), $[\alpha]_D^{18} + 26.6^\circ$ to $+5.2^\circ$ in abs. EtOH. Distillation of (II) under diminished pressure appears to be accompanied by polymerisation in varying degree, but by repeatedly interrupting the process, dissolving the residue in abs. CHCl_3 or COMe_2 , evaporating the solution, and immediately resuming the distillation, it is possible to volatilise all at $\approx 100^\circ/2$ mm. Within > 24 hr. (II) passes from a mobile liquid to a colourless glass. With CH_2N_2 (II) affords a liquid, b.p. 50—51°/0.025 mm., which is not the expected diketone. (I) is converted by Pb(OAc)_4 and treatment of the product with CH(OEt)_3 into *d*-isopropylidenedioxysuccindialdehyde Et_4 acetal, b.p. 88—89°/0.08 mm., $[\alpha]_D^{19} + 16.1^\circ$ in abs. EtOH. (II) yields a diphenylhydrazone ($+1\text{H}_2\text{O}$), m.p. 145°, $[\alpha]_D - 239.0^\circ$ in EtOH or (anhyd.), $[\alpha]_D^{22} - 250^\circ$ in EtOH. *d*-Dihydroxysuccindialdehydediphenylhydrazone has m.p. 181° (decomp.), $[\alpha]_D^{20} - 114.3^\circ$ in $\text{C}_6\text{H}_5\text{N}$.

Hydrolysis of (II) with 0.1*N*-HCl followed by oxidation of the product with Br leads to *l*-tartaric acid. Treatment of Me_2 *d*-tartrate with ZnCl_2 and much PhCHO and of the product with NaHSO_3 leads to *Me*, *d*-benzylidenetartrate, m.p. 74°, $[\alpha]_D^{20} - 44.2^\circ$ in EtOH (corresponding dihydrazide, m.p. 179—180.5°).

H. W.

Polymerisation and thermal decomposition of keten. A. T. WILLIAMSON (J. Amer. Chem. Soc., 1934, 56, 2216—2218).—Keten polymerises to diketene at 400—500°. Above 530° it decomposes, giving CO , CH_4 , and a C-like deposit. E. S. H.

Thermal decomposition of acetone. F. O. RICE, E. L. RODOWSKAS, and W. R. LEWIS (J. Amer. Chem. Soc., 1934, 56, 2497—2498).—Keten is not formed from COMe_2 containing approx. 1% of HgMe_2 (I) at 350—400°; $(\cdot\text{CH}_2\cdot\text{COMe})_2$ (II) [amount = (I) used] is produced: $\text{COMe}_2 + \text{Me} \rightarrow \text{CH}_4 + \text{COMe}\cdot\text{CH}_2\cdot$; $2\text{COMe}\cdot\text{CH}_2\cdot \rightarrow$ (II). At lower temp. the Me groups do not attack COMe_2 . Decomp. of COMe_2 or MeCHO in presence of small amounts of (II), diallyl, and dibenzyl does not give COMeEt , Δ^8 -butene, and PhEt, respectively. The production of Me from COMe_2 at 700°/200 mm. could not be detected by Te. H. B.

Formation of methylglyoxal from trioses at neutral p_H and body temperature under the influence of phosphate and arsenate. Z. DISCHE and S. S. ROBINS (Biochem. Z., 1934, 274, 42—44).—When a solution of glyceraldehyde or $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ in physiological saline is kept at body temp. for 24 hr. at p_H 7.2, a small amount of AcCHO is formed, the process being greatly accelerated by the presence of PO_4''' or AsO_4''' at p_H 7—7.2. $\text{Na}_4\text{P}_2\text{O}_7$ has only a slight effect. P. W. C.

Auto-condensations of methylglyoxal. I. Humic acids from three-carbon systems. G. HAHN and O. SCHALES (Ber., 1934, 67, [B], 1816—1826).—Oxidation of boiling COMe_2 with SeO_2 followed by distillation of the product in vac. gives a mixture of dimeric (I) and trimeric (II) AcCHO (the re-conversion of Se into SeO_2 is described). Particularly at low temp., (I) passes rapidly into a solid modification, $8\text{AcCHO}\cdot 4\text{H}_2\text{O}$, which is not hygroscopic, and hence is not identical with Harries' product. It can be kept unchanged for a long period, whereas (II) slowly passes into AcCO_2H when kept in a glass vessel. It is readily depolymerised when heated with H_2O or distilled in vac. Treatment of AcCHO with acid gives solutions which slowly when cold, but rapidly when heated, become yellow and then red and from which a dark brown, amorphous humic acid (III), m.p. 220° (decomp.), separates which is sol. in EtOH, COMe_2 , CHCl_3 , and dioxan and differs from the glucose-humic acid. The mother-liquors yield very small amounts of an acid, $\text{C}_{14}\text{H}_{14}\text{O}_8$, decomp. 248° (*d*-nitrophenylhydrazone, m.p. 320°). Optimum yields of (III) are obtained in solutions of p_H 5.9, these being far in excess of those achieved with carbohydrates, excepting xylose. Even after very protracted action, humic acids are not obtained from natural hexoses at p_H 6, but fructose gives a 2.4% yield. $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ reacts at about the same rate as AcCHO. It appears, therefore, that carbohydrates are first transformed by

bacteria into trioses, which then pass, most readily in the physiological p_H region, into humic acids.

H. W.

Determination of reducing sugars. C. GIORGIO (Ind. ital. conserv. aliment., 1934, 9, 100—103; Chem. Zentr., 1934, ii, 156).—The Cu solution contains CuSO_4 , NaOH, and glycerol. Following the customary reduction (hot) by the sugar solution, the liquid is filtered and the filtrate titrated with H_2SO_4 (Congored). Formation of Cu_2O utilises an equiv. wt. of NaOH.

A. G. P.

Reactions of carbohydrates in liquid ammonia.
II. Apparatus and methods. Alkyl, acyl, and metallic and non-metallic derivatives of diisopropylideneglucose. I. E. MUSKAT (J. Amer. Chem. Soc., 1934, 56, 2449—2454).—Details are given (cf. A., 1934, 512) for the prep. of alkali metal salts of carbohydrates. The K derivative (I) of diisopropylideneglucose (II) is prepared in liquid NH_3 (which is then evaporated and replaced by Et_2O ; general method). (I) and MeI or Me_2SO_4 give 97% of 3-methyldiisopropylideneglucose, b.p. $105^\circ/0.3$ mm., $[\alpha]_D^{25}$ -34.2° in EtOH; the 3-Et, b.p. $115^\circ/0.8$ mm., $[\alpha]_D^{25}$ -25.75° in COMe_2 , and 3-Pr, b.p. $120^\circ/1$ mm., $[\alpha]_D^{25}$ -29.2° in CHCl_3 , derivatives are similarly prepared in 90 and 30% yield using EtI(Br) or PrI. (I) and the requisite acyl chloride give diisopropylideneglucose 3-acetate, m.p. 62° , $[\alpha]_D^{25}$ -38.5° in CHCl_3 , 3-benzoate, m.p. 64° , $[\alpha]_D^{25}$ -50.2° in EtOH, and 3-p-toluenesulphonate, m.p. 120° , $[\alpha]_D^{25}$ -70.4° in CHCl_3 . (I) and PCl_3 (1 mol.) give [after hydrolysis (75% EtOH)] diisopropylideneglucose phosphite; with $\frac{1}{2}$ mol. of PCl_3 , tri(diisopropylideneglucose) phosphite, m.p. about 60° , $[\alpha]_D^{25}$ -19° in CHCl_3 , results. (I) and POCl_3 similarly afford mono- [also obtained from (II), POCl_3 , and $\text{C}_5\text{H}_5\text{N}$] and tri-(diisopropylideneglucose) phosphate, m.p. about 55° , $[\alpha]_D^{25}$ -44.4° in CHCl_3 . Tri(diisopropylideneglucose) arsenite and di(diisopropylideneglucose) disulphide are prepared from (I) and AsCl_3 and S_2Cl_2 , respectively. (I) also reacts with HgCl_2 , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{HgCl}$, SbCl_3 , BiCl_3 , CPh_3Cl , and acetobromoglucose. Carbohydrates containing free or potential CHO and CO are readily oxidised by I in liquid NH_3 : RCHO thus gives $\text{RCO}\cdot\text{NH}_2$.

H. B.

Preparation of α -aldose acetates from acetylated glycosides. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2465—2466).— α -Methylmannoside tetra-acetate is converted by conc. H_2SO_4 in Ac_2O - AcOH into α -mannose penta-acetate; the change is followed polarimetrically at 20° and is unimol. after 20 min. α -Glucose penta-acetate is obtained similarly from β -methyl-, β -phenylthio-, and β - β' -naphthylthio-glucoside tetra-acetates, whilst α -methyl- γ - d -mannoside tetra-acetate gives a d -mannose penta-acetate, m.p. 76° (corr.), $[\alpha]_D^{25}$ $+89.6^\circ$ in CHCl_3 . The changes with β -methyl-(β - d -galactoside) penta-acetate and β -phenylthio- d -xyloside triacetate have been followed polarimetrically.

H. B.

Synthesis of derivatives of glucose 2:3:6-tri- p -toluenesulphonate and their identification with the sugars obtained by fission of tri- p -toluenesulphonyl- and iododi- p -toluenesulphonyl-

starch. K. HESS and W. EYKING (Ber., 1934, 67, [B], 1908—1916; cf. A., 1933, 1279).—4:6-Benzylidene- β -methylglucoside 2:3-di- p -toluenesulphonate is converted by $\text{MeOH}\cdot\text{HCl}$ (improved prep.) into $\text{CHPh}(\text{OMe})_2$ and β -methylglucoside 2:3-di- p -toluenesulphonate (I), transformed by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 50° into β -methylglucoside 4:6-diacetate 2:3-di- p -toluenesulphonate, m.p. 136 — 137° , $[\alpha]_D^{25}$ -24.1° in CHCl_3 , $[\alpha]_D^{25}$ -21.2° in COMe_2 , $[\alpha]_D^{25}$ -53.9° in C_6H_6 . (I) is converted by the successive action of CPh_3Cl and Ac_2O in $\text{C}_5\text{H}_5\text{N}$ into 6-triphenylmethyl- β -methylglucoside 4-acetate 2:3-di- p -toluenesulphonate, m.p. 128 — 131° , $[\alpha]_D^{25}$ $+5.9^\circ$ in CHCl_3 , $+9.6^\circ$ in COMe_2 , -21.1° in C_6H_6 , which with $\text{AcOH}\cdot\text{HBr}$ at 0° yields non-cryst. 6-methylglucoside 4-acetate 2:3-di- p -toluenesulphonate (II), $[\alpha]_D^{25}$ -15.8° in CHCl_3 , -10.5° in COMe_2 . With $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$ at 50° (II) affords β -methylglucoside 4-acetate 2:3:6-tri- p -toluenesulphonate (III), labile form, m.p. 131 — 132° , stable variety, m.p. 149 — 150° , $[\alpha]_D^{25}$ -13.9° in CHCl_3 , -5.1° in COMe_2 , -32.7° in C_6H_6 , also obtained by the successive action of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and Ac_2O in $\text{C}_5\text{H}_5\text{N}$ on (I). Treatment of (III) with NaI in COMe_2 at 120° leads to 6-iodo-6-methylglucoside 4-acetate 2:3-di- p -toluenesulphonate, m.p. 162 — 163° , $[\alpha]_D^{25}$ $+11.1^\circ$ in CHCl_3 , $+3.1^\circ$ in COMe_2 , $[\alpha]_D^{25}$ -17.9° in C_6H_6 , identical with the product of degradation of iodostarch tri- p -toluenesulphonate.

H. W.

Determination of fructose in the presence of glucose and sucrose. M. NORDLUND (Suomen Kem., 1934, 7, 95b).—A measured amount of solution is treated with I and $N\text{-NaOH}$. After 20 min. at room temp., the solution is acidified with $5N\text{-H}_2\text{SO}_4$ and excess of I titrated with NaHSO_3 . Solid $\text{Pb}(\text{OAc})_2$ is added to ppt. the reaction products, and the solution filtered. A portion of the filtrate is used, after removal of excess of Pb with K_2SO_4 if necessary, for determination of fructose, e.g., by the Bertrand method. The accuracy of this method is unaffected by presence of large amounts of peptone, OH-acids, or alcohols.

J. W. S.

Decomposition of fructose by ultra-violet light in non-aqueous solution (methyl alcohol). R. CANTIENI (Helv. Chim. Acta, 1934, 17, 1528—1529).—Fructose in pure MeOH is decomposed by ultra-violet light with evolution of gas, mainly CO. Addition of H_2O to MeOH causes more copious evolution of gas. Acceleration of the evolution of gas by addition of H_2O is relatively greater as the quantity of H_2O diminishes.

H. W.

Decomposition of fructose in quartz light in presence of pyridine. Determination of pyridine in very dilute solution. R. CANTIENI (Helv. Chim. Acta, 1934, 17, 1492—1493).—Fructose solutions containing $<1\%$ of $\text{C}_5\text{H}_5\text{N}$ become brown and form a brown ppt. without evolving gas when irradiated. Those containing $>1\%$ of $\text{C}_5\text{H}_5\text{N}$ become yellow and evolve gas in amounts which increase with decreasing concn. of $\text{C}_5\text{H}_5\text{N}$. The intensity of the yellow colour diminishes with diminishing concn. of $\text{C}_5\text{H}_5\text{N}$. The concn. at which gas evolution ceases lies between 0.1 and 1% of $\text{C}_5\text{H}_5\text{N}$, whereas that at which interaction ceases lies between 0.001% and

0.0001% of C_6H_5N . A possible method of determining minute amounts of C_6H_5N is indicated. H. W.

Three crystalline hexa-acetates of d - α -mannoheptose. E. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1934, **56**, 2463—2464).—Contrary to previous results (A., 1924, i, 617), acetylation (Ac_2O - $NaOAc$) of d - α -mannoheptose (I) gives β - d -(α -mannoheptose) hexa-acetate (II), m.p. 107° , $[\alpha]_D^{20} +34.1^\circ$ in $CHCl_3$ (cf. *loc. cit.*), and aldehydo- d - α -mannoheptose hexa-acetate (III), m.p. 146° , $[\alpha]_D^{20} -34^\circ$ in $CHCl_3$. (II) is converted by conc. H_2SO_4 in Ac_2O - $AcOH$ into its α -isomeride, m.p. 75 — 76° , $[\alpha]_D^{20} +120.8^\circ$ in $CHCl_3$. d - α -Mannoheptose *Et mercaptal*, m.p. 188 — 190° , $[\alpha]_D^{20} -11.9^\circ$ in H_2O [from (I), $EtSH$, and 36% HCl], is acetylated (Ac_2O - C_6H_5N at 0°) to the hexa-acetate, m.p. 77° , $[\alpha]_D^{20} -2.2^\circ$ in $CHCl_3$, which is converted by $HgCl_2$ in aq. $COMe_3$ + $CdCO_3$ into (III). (III) is also formed from methyl- α -mannoheptoside penta-acetate and conc. H_2SO_4 in Ac_2O - $AcOH$.

H. B.

Alkaline conversion of β -glucoheptose. Y. KHOUVINE (Compt. rend., 1934, **199**, 869—870; cf. A., 1934, 513).—Treatment of β -glucoheptose (I) with aq. $Ca(OH)_2$ yields the same glucoheptulose as that obtained from the α -isomeride. The α - d -glucoheptulose from (I) gives, on reduction, α -glucoheptitol and α - d -glucoheptulitol.

A. G. P.

Configuration of isosucrose (sucrose- D of Pictet and Vogel) and a peculiarity of the β -glucosidase of mushrooms. A. GEORG (Helv. Chim. Acta, 1934, **17**, 1566—1574; cf. A., 1933, 260).—Hydrolysis (Zemplen) of isosucrose octa-acetate affords isosucrose (I), m.p. 179° (corr.) after softening at 175° , $[\alpha]_D^{20} +32.7^\circ$ to $+34.7^\circ$ in H_2O [Pictet and Vogel (A., 1928, 510, 741; 1929, 913) record m.p. 127° , $[\alpha]_D^{20} +19.0^\circ$ in H_2O , whereas Irvine *et al.* (A., 1929, 603) give m.p. 194° after softening at 152° , $[\alpha]_D^{20} +34.2^\circ$ in H_2O]. Application of Hudson's rules indicates that (I) is β -glucopyranosido- α -fructofuranoside. Unexpectedly, (I) is not hydrolysed by the β -glucosidase of emulsin from sweet almonds (analogous cases are cited), but is affected by the invertase of *Aspergillus niger*, although much less rapidly than is sucrose; this is shown to be due to the presence of both α - and β -glucosidase. Pure β -fructofuranosidase does not attack (I).

H. W.

α -Glucosidase of yeast. B. HELFERICH, U. LAMPERT, and G. SPARMBERG (Ber., 1934, **67**, [B], 1808—1811).—In contrast with the behaviour of β -glucosidase of almonds, increase in fission by α -glucosidase of yeast is not observed on passing from phenol- to saligenin- and thence to *o*-cresol- α - d -glucoside, thus further emphasising the great difference between the two enzymes. β - D -Glucose penta-acetate is converted by *o*-cresol and $ZnCl_2$ at 125 — 130° into *o*-cresol- α - d -glucoside tetra-acetate, m.p. 101 — 102° after softening, $[\alpha]_D^{20} +155^\circ$ in $CHCl_3$, catalytically hydrolysed by $NaOMe$ to *o*-cresol- α - d -glucoside, m.p. 170 — 172° , $[\alpha]_D^{20} +156^\circ$ in H_2O . ω -Bromo-*o*-cresol- α - d -glucoside tetra-acetate, m.p. 94 — 95.5° (corr.) after softening, $[\alpha]_D^{20} +145.6^\circ$ in $CHCl_3$, is converted by Ag_2CO_3 in $COMe_3$ - H_2O and subsequent hydrolysis by $NaOMe$ - $MeOH$ into saligenin- α - d -glucoside (α -salicin), $[\alpha]_D^{20} +118^\circ$ in H_2O .

H. W.

Glucoside from madder.—See A., 1934, 1420.

Structure of populin. N. K. RICHTMYER and E. H. YEAKEL (J. Amer. Chem. Soc., 1934, **56**, 2495—2497).—Synthetic populin (I), prepared by Dobbin and White's method (A., 1904, i, 905), is methylated (Ag_2O , MeI) to tetramethylpopulin, m.p. 134 — 135° , $[\alpha]_D^{20} -31.7^\circ$ in $CHCl_3$ (the Me_3 derivative, m.p. 148 — 150° , is probably formed also), debenzoylated ($MeOH$ - $NaOMe$) to ω :2':3':4'-tetramethylsalicin, m.p. 137 — 138° , $[\alpha]_D^{20} -46.4^\circ$ in $CHCl_3$, which is hydrolysed ($2N$ - HCl in $EtOH$) to 2:3:4-trimethylglucose. (I) is, therefore, 6'-benzoylsalicin. (I) is reduced (H_2 , Pd -black, $AcOH$) to deoxypopulin (β -*o*-cresolglucoside 6-benzoate), m.p. 148 — 149° , $[\alpha]_D^{20} -13.3^\circ$ in C_6H_5N , also prepared from *o*-cresolglucoside, m.p. 162 — 163° , $[\alpha]_D^{20} -68.4^\circ$ in H_2O (lit. $+61.75^\circ$) [prepared (cf. A., 1934, 992) by reduction (H_2 , Pd -black, H_2O) of salicin], and $BzCl$ in C_6H_5N .

H. B.

Nitrogenous glycosides. III. Preparation of a simple cyanophoric glycoside. L. R. BUEGER (J. Amer. Chem. Soc., 1934, **56**, 2494—2495).—Acetobromoglucose and $AgCN$ in xylene give 1-cyano- d -glucose 2:3:4:6-tetra-acetate (I), m.p. 76° , converted by $AcOH$ at 150° or Ac_2O at 200° into β -glucose penta-acetate. (I) is decomposed by digestion with 50% $AcOH$, 5% tartaric acid, or warm H_2O .

H. B.

Present position of *Digitalis* chemistry. W. BLADERGROEN (Chem. Weekblad, 1934, **31**, 674—680).—A review.

Colour reaction of digitoxin, gitoxin, and gitalin; application to colorimetric determination of these glucosides. J. A. SANCHEZ (Semana Med., 1934, II, 399—402).—Digitoxin in $AcOH$ is treated with a solution of vanillin in HCl and heated (100°). A red colour is formed and changes to a stable blue. Details for quant. use are given.

CH. ABS. (p)

Fructose anhydrides. XV. Constitution of graminin I. H. H. SCHLUBACH and K. KOENIG (Annalen, 1934, **514**, 182—196).—Details are given for the extraction and purification of graminin (I), M (in H_2O) 776 — 1183 , $[\alpha]_D^{20} -36.6^\circ$ (cf. Tanret, A., 1891, 661; Tillmans *et al.*, B., 1929, 70; use of the last method does not give a protein-free product), from rye flour. (I) is hydrolysed (N - H_2SO_4 at 20°) at the same rate as irisin (A., 1933, 938); the product obtained after 91% hydrolysis has an aldose val. of 0.59% (cf. A., 1932, 1021). These results indicate that (I) is built up solely of fructose units. Swelling of (I) in C_6H_5N at 75° and subsequent treatment with Ac_2O gives graminin acetate (II), $[\alpha]_D^{20} -7.2^\circ$ in $CHCl_3$, M (in C_6H_6) 2606 — 2792 ; the (I) recovered by hydrolysis ($MeOH$ - $NaOMe$) has a somewhat higher mol. wt. (1416 — 1537) than the original (I). These vals. indicate the presence of 9—10 C_6 units. Successive treatment of (II) with Me_2SO_4 and 30% $NaOH$ (in $COMe_3$) and MeI - Ag_2O affords methylgraminin, $[\alpha]_D^{20} -48^\circ$ in $CHCl_3$, hydrolysed ($H_2C_2O_4$ in 70% $EtOH$) to 1:3:4:6-tetramethyl-, (probably) 3:4:6-trimethyl-, b.p. $94^\circ/0.1$ mm., $[\alpha]_D^{20} +27.3^\circ$ in $CHCl_3$, and a dimethyl-fructose. A ring structure is suggested for (I).

H. B.

Esterification of starch and its degradation products. A. F. DAMANSKY (Ann. Chim., 1934, [xi], 2, 491—565).—Potato-starch (I) by Peiser's or Pringsheim's method gives poor yields (14—25%) of Ac derivatives with some degradation to biose. Haworth's and Fries's methods afford quant. yields of amylose triacetate (II). (I) with $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ at 0° or $\text{AcCl}-\text{C}_5\text{H}_5\text{N}$ first at -20° and then at $70-80^\circ$ gives a mixture of diacetate (III) and some (II). amec's amylopectin (IV) gives, particularly by AcCl , almost entirely (III), Ling and Nanji's (IV) also some (II). Amylose (V) gives entirely (III), whilst "sol. starch" (VI) gives an Ac_4 derivative. The amount of (II) obtained from (I) is increased by previous heating of (I) in H_2O (e.g., 30% after 30 min. at 90°). Since (III) is unaltered by further acetylation, it is concluded that (I) is a mixture of (IV) and (V); (V) is considered to be a degradation product formed during the isolation of (I), which, if pure, would consist entirely of (IV). Formation of (V) from (IV) renders a third OH group reactive, either by stereochemical change or by fission of a linking between glucose mols. 2% of (I) in 0.15% aq. NaOH at 0° gives after 3 days 3—4% of (V), and 40—50% are formed in 2 hr. at 50° ; in 0.5*N*- NaOH -abs. EtOH 2% of (V) are formed in 25 days at 0° and 3—4% in 4 days at 50° . 0.1—0.15*N*- NaOMe in dry MeOH , however, does not form (V) at 0° or 50° from (I) or (IV), and is used to hydrolyse the acyl derivatives (12—15 days at 0°); the process is catalytic, since esters are formed in quantity and $\approx 30\%$ of the NaOMe is neutralised. The relationship of (II) and (III) to (V) and (IV) is thus established. The following gelatinisation temp. are determined viscosimetrically: (I) 57.9° , Samec's (IV) 43.6° , Ling and Nanji's (IV), 45.9° , (II) and other di-esters $40.2-43.9^\circ$; the identity of the products recovered by hydrolysis of the esters is confirmed by this method. Results exactly similar to those given by AcCl are obtained with BzCl and cinnamoyl chloride in $\text{C}_6\text{H}_5\text{N}$. The following are described: tricinnamate of (V), $[\alpha]_D^{25} -186^\circ$ in CHCl_3 , sol. in CHCl_3 , etc. [from (I), maize starch, or (IV) previously heated to 90°], and the tribenzoate, $[\alpha]_D^{25} +80.3^\circ$ in CHCl_3 , sol. in CHCl_3 , etc. [from (I) or (V)]; dicinnamate and dibenzoate of (IV), insol. in org. solvents. By separation of its benzylation products (VI) is shown to consist of (I) (2.4%), (V) (3%), amylose B (8.5%), $[\alpha]_D^{25} +167.3^\circ$ in H_2O , non-reducing (Bz_3 derivative, m.p. 187° , $[\alpha]_D^{25} +95.3^\circ$ in CHCl_3) (reddish-brown colour with I), and a non-reducing biose (VII) (78.5%), $[\alpha]_D^{25} +152.6^\circ$ in H_2O (Bz_3 derivative, m.p. 181° , $[\alpha]_D^{25} +70.6^\circ$ in CHCl_3). (VII) is not maltose, but is hydrolysed directly to glucose only; it gives a brown colour with I. R. S. C.

Chemistry of cellulose. H. STAUDINGER (Naturwiss., 1934, 22, 797—803, 815—819).—A lecture.

Separation and fractional extraction of cellulose acetates. L. CLEMENT and C. RIVIÈRE (Bull. Soc. chim., 1934, [v], 1, 1075—1082).—Fractional pptn. of cellulose acetate in COMe_2 with mixtures of COMe_2 and H_2O , or fractional extraction with $\text{MeOH}-\text{H}_2\text{O}$, $\text{EtOH}-\text{H}_2\text{O}$, or $\text{EtOH}-\text{COMe}_2$, leads to a no. of fractions differing considerably in chemical and physical properties, e.g., degree of acetylation, m.p., and solubility in many org. solvents. F. S. H. H.

Preparation of *d*-glutamic acid. Y. C. CHENG and W. H. ADOLPH (J. Chinese Chem. Soc., 1934, 2, 221—224).—Hydrolysis of wheat gluten (I) is facilitated and affords increased yields of glutamic acid hydrochloride when Sn, Ni, Pb, or Cu is used as catalyst. Peanut proteins and soya beans give nearly as good yields as (I). J. L. D.

Catalytic hydrogenation of amides to amines. B. WOJCIK and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 2419—2424; cf. A., 1934, 283).—Amines (primary, sec., and tert.) are formed in good yield by reduction [usually with H_2 (200—300 atm.) at 250° in dioxan using a Cu—Cr oxide catalyst] of the appropriate amides. With $\text{RCO}\cdot\text{NHR}'$ and especially $\text{RCO}\cdot\text{NR}'_2$, the following reactions occur: $\text{RCO}\cdot\text{NHR}'_2 + \text{H}_2 \rightarrow \text{CH}_2\text{R}\cdot\text{NHR}' + \text{R}'\text{H} + \text{H}_2\text{O}$; $\text{RCO}\cdot\text{NR}'_2 + \text{H}_2 \rightarrow \text{RMe} + \text{NHR}'_2 + \text{H}_2\text{O}$. The reaction $\text{RCO}\cdot\text{NH}_2 + \text{H}_2 \rightarrow \text{CH}_2\text{R}\cdot\text{OH} + \text{NH}_3$ occasionally takes place; this change occurs almost exclusively on attempted reduction in aq. and EtOH media. The predominating secondary reaction is $2\text{NH}_2\text{R} \rightarrow \text{NHR}_2 + \text{NH}_3$; hydrolysis, ammonolysis, and aminolysis of the amide and alkylation (by alcohol produced) of the amine may occur. The amides used are prepared from RCO_2Et and liquid NH_3 or the appropriate amine at 250° in H_2 (50—100 atm.) or from the NH_4 or amine salt in dioxan at 250° .

Lauramide is thus reduced to 48% of *n*-dodecylamine (I) and 49% of di-*n*-dodecylamine (II), m.p. $55-56^\circ$ (hydrochloride, m.p. $207-208^\circ$); NH_4 laurate gives (I) (14%) and (II) (79%); heptamide affords 39% of mono- (III) and 58% of di- (IV) *n*-heptylamine; α -phenylbutyramide yields α -amino- β -phenylbutane (72%) and material (23%), b.p. $163-167^\circ/3-4$ mm.; salicylamide furnishes *o*-cresol (80%); tetrahydrofuroamide gives 60% of mono- and 33% of di-tetrahydrofurfurylamine; γ -hydroxyvaleramide (crude) affords valerolactone (74%) and α -amino- δ -hydroxypentane (16%), b.p. $119-121^\circ/8$ mm. (hydrochloride, m.p. $107-110^\circ$); $(-\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ yields pyrrolidine (25%), 1- δ -aminobutylpyrrolidine (14%), and *N*- δ -aminobutylsuccinimide (15%), b.p. $120-124^\circ/3$ mm. (hydrochloride, m.p. $89-90^\circ$); laur- β -phenylethylamine, m.p. 73° , furnishes PhEt (11%), $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$ (16%), (I) (13%), (II) (9%), and β -phenylethyl-*n*-dodecylamine (66%), b.p. $182-184^\circ/2$ mm. (hydrochloride, m.p. $232-233^\circ$); laurcyclohexylamine, m.p. 85° , gives mono- (15%) and di-cyclohexylamines, (I), (II) (24%), and cyclohexyl-*n*-dodecylamine (62%), b.p. $158-159^\circ/2$ mm. (hydrochloride, m.p. $204-205^\circ$); lauranilide affords NH_2Ph (29%), NHPH_2 (5%), (I) (14%), (II) (2%), and *n*-dodecylaniline (37%), b.p. $160-161^\circ/2$ mm. (hydrochloride, m.p. 206°); laur-*n*-amylamine, m.p. 78° , yields di-*n*-amylamine (8%), (I) (15%), (II) (42%), and *n*-amyl-*n*-dodecylamine (35%), b.p. $175-177^\circ/10$ mm. (hydrochloride, m.p. $240-241^\circ$); hepto- β -phenylethylamine, m.p. 78° , furnishes PhEt (5%), (III) (7%), (IV) (10%), $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$ (6%), and β -phenylethyl-*n*-heptylamine (56%), b.p. $153-156^\circ/9$ mm. (hydrochloride, m.p. $254-255^\circ$); adip-*n*-amylamine, m.p. $161-162^\circ$, gives di-*n*-amylamine (90%); 1-laurylpiperidine affords *n*-dodecyl alcohol (2%) and 1-*n*-dodecylpiperidine (92%), b.p. $139-140^\circ/2$ mm. (hydrochloride, m.p. $184-186^\circ$); 1-heptylpiperidine

yields heptyl alcohol (5%) and 1-*n*-heptylpiperidine (92%); 1- α -phenylbutyrylpiperidine, b.p. 145–146°/2 mm., furnishes β -phenylbutyl alcohol (32%) and α -piperidino- β -phenylbutane (65%), b.p. 134–135°/8 mm. (hydrochloride, m.p. 166–168°); 1-nonylpiperidine gives 1-*n*-nonylpiperidine (88%), b.p. 135–137°/11 mm. (hydrochloride, m.p. 186–187°); 1-furoylpiperidine affords tetrahydrofurfuryl alcohol (3%) and 1-tetrahydrofurfurylpiperidine (85%), b.p. 96–98°/9 mm. (hydrochloride, m.p. 180°); 1-benzoylpiperidine yields PhMe (79%) and $\text{CH}_2\text{Ph}\cdot\text{OH}$ (3%); 1- β -hydroxybutyrylpiperidine, b.p. 109–113°/9 mm., furnishes 1-butylpiperidine (56%); 1- β -hydroxy- α -dimethylbutyrylpiperidine, b.p. 86–88°/3 mm., gives piperidine (29%) and 1-isobutylpiperidine (64%); *sebacylpiperidine*, b.p. 255–256°/2 mm., m.p. 59–60°, affords decane- α -diol (4%) and α -*dipiperidinodecane* (94%), b.p. 181–183°/2 mm. (hydrochloride, m.p. 276–277°); succinylpiperidine yields $(\text{CH}_2)_4(\text{OH})_2$ (15%) and α -*dipiperidinobutane* (80%); *adipylpiperidine*, b.p. 221–223°/2 mm., m.p. 61–62°, furnishes $(\text{CH}_2)_6(\text{OH})_2$ (16%) and α -*dipiperidino*hexane (80%); *laurdiethylamide*, b.p. 166–167°/2 mm., gives (II) (30%) and *ethyl-*n*-dodecylamine* (64%), b.p. 124–129°/2 mm. (hydrochloride, m.p. 205–207°); *heptodiethylamide* affords (IV) (25%), *ethyl-*n*-heptylamine* (64%), b.p. 81–83°/16 mm. (hydrochloride, m.p. 188–190°), and *diethyl-*n*-heptylamine* (4%), b.p. 86–87°/16 mm. (hydrochloride, m.p. 105–106°); *N-n-amylsuccinimide*, b.p. 123–124°/3 mm., yields 1-*n*-amylpyrrolidine (79–88%); *N- β -phenylethylsuccinimide*, m.p. 134°, furnishes PhEt (13%) and 1- β -phenylethylpyrrolidine (65%), b.p. 113–115°/9 mm. (hydrochloride, m.p. 159–160°); *N-n-amylphthalimide* gives 3:4-hexahydrobenzpyrrolidine (V) (8%) and its 1-*n*-amyl derivative (52%), b.p. 104–106°/3 mm. (hydrochloride, m.p. 210–211°); *N- β -phenylethylphthalimide* affords PhEt (22%), (V) (16%), and 1- β -phenylethyl-3:4-hexahydrobenzpyrrolidine (39%), b.p. 167–168°/10 mm. (hydrochloride, m.p. 216–217°).

Piperidine (VI) and *o*-OH \cdot C₆H₄·CO₂Me at 250° in H₂ give *Ph piperidine-1-carboxylate*, b.p. 101–102°/3 mm., also prepared from (VI), PhOH, and CO₂ under similar conditions. *Buⁿ piperidine-1-carboxylate*, b.p. 98–99°/13 mm., is similarly obtained from (VI), BuⁿOH, and CO₂, whilst *n*-amylamine, PhOH, and CO₂ afford *Ph n-amylcarbamate*, b.p. 108–111°/5 mm.

H. B.

Action of hydrobromic acid on tri- β -hydroxyethylamine and tetra- β -hydroxyethylammonium bromide. V. PRELOG and Z. BLÁŽEK (Coll. Czech. Chem. Comm., 1934, 6, 476–486).—The *hydrobromide* (I), m.p. 196.5°, of $\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_3$ and $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{OH}$ in hot EtOH give *tetra- β -hydroxyethylammonium bromide* (II), cryst., hygroscopic (bromide of the *Ac*₄ derivative, m.p. 150.5°). Only three of the OH groups of (II) can be replaced by Br by use of HBr. (II) with HBr (9 mols. of 64% or 21 mols. of 71%) at 110° gives *NN-di- β -bromoethylmorpholinium bromide*, m.p. 243° (corresponding *picrate*, m.p. 146.5°), and *-spirodimorpholinium bromide*, m.p. 285° (decomp.) (corresponding *picrate*, m.p. 210°). When heated with 64% HBr first at 110° and then at 160–170°, (II) gives *tri- β -bromoethyl- β -hydroxyethylammonium bromide* (III), decomp. 228°, the *hydro-*

bromide (IV), m.p. 162°, of *di- β -bromoethyl- β -hydroxyethylamine* (*picrate*, m.p. 135.5°) (also formed by heating directly to 170°), and (at 160°) *N- β -bromoethylmorpholine hydrobromide* (V), m.p. 222–224° (*picrate*, m.p. 134.5°). (IV) is best obtained by use of 25 mols. of 71% HBr at 160°, but also from (I), (II), or (III) and 3 mols. of 64% HBr, and from (I) and HBr·AcOH at 170°. (IV) and NH₂Ph in hot MeOH give a substance, C₁₂H₂₀ON₂Br₂, m.p. 275° (decomp.) (*picrate*, m.p. 208°) (conc. alkali liberates a solid base), and *N- β -hydroxyethyl-di- $(\beta$ -phenylaminoethyl)amine hydrobromide*, decomp. about 294°. (V) and 64% HBr at 170–200° give $(\cdot\text{CH}_2\text{Br})_2$, (IV), and $\text{NH}(\text{CH}_2\cdot\text{CH}_2\text{Br})_2\cdot\text{HBr}$, m.p. 209–210° (lit. 202–204°). (V) and NH₂Ph in hot MeOH give *N- β -phenylaminoethylmorpholine* (*dihydrobromide*, m.p. 223–224°; *dipicrate*, m.p. 192°).

R. S. C.

Configurative behaviour of ψ -leucine in the Walden inversion and elimination of halogen by dilute alkali from stereoisomeric α -bromo- β -dimethylbutyrylamino-acids. E. ABDERHALDEN, W. FAUST, and E. HAASE (Z. physiol. Chem., 1934, 228, 187–197).— α -Amino- β -dimethylbutyric acid (*dl- ψ -leucine*) was prepared from pinacolin, the formyl derivative, m.p. 210°, was resolved by brucine, and the products were hydrolysed by 10% HBr, giving *l*(+)-(I), $[\alpha]_D^{20} + 10.01^\circ$ in H₂O, $[\alpha]_D^{25} - 8.19^\circ$ in 20% HCl, and *d*(-)- ψ -leucine (II), $[\alpha]_D^{25} - 10.16^\circ$ in H₂O, $+ 8.36^\circ$ in 20% HCl [*C*₆H₄Me·SO₂ derivative (III), m.p. 239–240°, $[\alpha]_D^{25} + 47.1^\circ$ in EtOH]. The active formyl derivatives were converted into *l*(-)-(IV), m.p. 66°, b.p. 115–120°/12 mm., $[\alpha]_D^{27} - 14.4^\circ$ in EtOH (acid chloride, b.p. 68–70°/10 mm., $[\alpha]_D^{27.5} - 14.7^\circ$), and *d*(+)- α -bromo- β -dimethylbutyric acid (V), m.p. 70°, b.p. 115–120°/10 mm., $[\alpha]_D^{23} + 14.0^\circ$ in EtOH (acid chloride, $[\alpha]_D^{25} + 14.5^\circ$). Amination of (IV) and (V) regenerated (I) and (II) of the same configuration as the original material. When (II) was injected into a dog, (III) was isolated from the urine, hence the + form has the *l*-configuration. The following were synthesised from the acid chlorides and the appropriate NH₂-acid ester: *l*(-)- α -bromo- β -dimethylbutyryl-*l*(-)-(VI), $[\alpha]_D^{27} + 7.35^\circ$, and *d*(+)-tyrosine (VII), $[\alpha]_D^{27} - 53.6^\circ$, and *l*(+)-(X), $[\alpha]_D^{23} + 5.37^\circ$, and *d*(-)- ψ -leucine (VIII), $[\alpha]_D^{23} - 14.8^\circ$; *d*(+)- α -bromo- β -dimethylbutyryl-*l*(-)-tyrosine (IX), $[\alpha]_D^{27} + 51.8^\circ$, and *d*(+)-tyrosine (X), $[\alpha]_D^{23} - 7.87^\circ$, and *d*(-)-(X), $[\alpha]_D^{23} - 5.02^\circ$, and *l*(+)- ψ -leucine, $[\alpha]_D^{23} + 15.1^\circ$ (all $[\alpha]$ in EtOH). Of these only (VI) and (VIII) are hydrolysed by trypsin. In the tyrosine series Br elimination by alkali occurs more rapidly with (VII) and (IX) than with (VI) and (X).

J. H. B.

Solubility of the stereoisomerides of cystine; identity of stone- and hair-cystine.—See A., 1934, 1381.

Additive compounds of halides of bivalent metals with organic bases. VIII.—See this vol., 49.

Additive compounds of alkali halides and organic bases.—See this vol., 48.

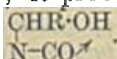
Acetylation of α -amino- and α -hydrazinosulphonic acids. H. J. BACKER and H. MULDER (Rec. trav. chim., 1934, 53, 1120–1127; cf. A., 1933,

702).—Acetylation (Ac_2O in H_2O) of the Na salt of α -aminoethane- α -sulphonic acid (from MeCHO , aq. NaHSO_3 , and aq. 25% NH_3 at about 70°) gives Na α -acetamidoethane- α -sulphonate. α -Amino- α -phenylmethanesulphonic acid (from PhCHO) similarly affords Na α -acetamido- α -phenylmethanesulphonate, which is resolved through the strychnine salt; the d-, $[\text{M}]_D^{25} +23^\circ$, and l-, $[\text{M}]_D^{25} -23.8^\circ$, -Ba salts are described. α -Amino- α -p-nitrophenyl- and - α -anisyl-methanesulphonic acids and K α -acetamido- α -p-nitrophenyl- and - α -anisyl-methanesulphonates are described. The above NH_2 -acids are all decomposed by aq. KCN, whereas the Ac derivatives are not. Na hydrazino-dimethanesulphonate, $(\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na})_2$ (Ac_2 derivative), prepared from $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$ and aq. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, is converted by aq. KCN into hydrazino-diacetonitrile (yield about 5%), m.p. $182-184^\circ$ (decomp.). $\text{NHPh}\cdot\text{NH}_2$ and $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$ similarly give K phenylhydrazinomethanesulphonate (NO- and Ac_2 derivatives), converted by aq. KCN into a little phenylhydrazinoacetonitrile, m.p. $34-35^\circ$. H. B.

Dehydration of acid amides to nitriles. C. H. KAO, J. Y. YEN, and S. L. CHIEN (J. Chinese Chem. Soc., 1934, 2, 240—242).—Amides are converted into nitriles best with PCl_5 or POCl_3 and NaCl.

J. L. D.

Constitution of ascorbic acid. Action of sodium hypochlorite on α -methoxy-acid amides. R. G. AULT, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1934, 1722—1726).—(a) $\text{OMe}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$ (I) (modified prep. from $\text{OMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$, b.p. $92^\circ/0.03$ mm.), m.p. $113-114^\circ$, with aq. NaOCl at 0° or 25° gives PhCHO , NH_3 , and CO_2 , but no NaCNO (II) (cf. A., 1934, 756). (b) In aq. MeOH 45% of $\text{OMe}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, which is formed as intermediate product, is isolated; in N-NaOH at 0° this gives PhCHO , NH_3 , and MeOH , but no (II). 2 : 3 : 5-Trimethyl-l-arabonamide, O-methyl-lactamide (modified prep.), m.p. 84° (lit. $79-81^\circ$), and 2 : 4-dimethyl-d-erythronamide with aq. NaOCl give similarly the aldehyde and NH_3 , but no (II). The formation of (II) is thus characteristic of α -OH-amides; it probably occurs by virtue of co-ordination, e.g.,



In (a) $\text{OMe}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}_2\text{H}$ is probably an intermediate product.

R. S. C.

Preparation of aldonic and saccharic acid amides in liquid ammonia. J. W. E. GLATTFELD and D. MACMILLAN (J. Amer. Chem. Soc., 1934, 56, 2481—2482).—dl-Erythronamide, m.p. 62.3° [which could not be prepared by Weerman's method (A., 1917, i, 546)], is obtained in quant. yield when dl-erythronolactone is dissolved in a little liquid NH_3 and the solution evaporated. The following are similarly prepared: dl- $\alpha\gamma$ -, m.p. $118.5-119.5^\circ$, and - $\beta\gamma$ -, m.p. 90.7° , -dihydroxybutyramides; d-, m.p. 94.8° , $[\alpha]_D^{20} +28.2^\circ$ in H_2O , and l-, m.p. 94.8° , $[\alpha]_D^{20} -28^\circ$ in H_2O , -erythronamides; d-galactonamide; d-glucosamine; d-mannonamide (from the γ - or δ -lactone). Coumarin is unaffected by liquid NH_3 . γ -Butyrolactone is also unaffected at the b.p.; ammonolysis occurs at room temp. in a sealed bomb. H. B.

Carbamide phosphate. C. MATIGNON and M. DODÉ (Bull. Soc. chim., 1934, [v], 1, 1114—1127).—

The physical and chemical properties of carbamide phosphate (I), $\text{CO}(\text{NH}_2)_2\cdot\text{H}_3\text{PO}_4$, m.p. 117.5° , are recorded. The salt $3\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_3\text{PO}_4$ was not obtained and the m.-p. curve of the system $\text{CO}(\text{NH}_2)_2$ -(I) yields no evidence of the existence of any combination other than (I). F. S. H. H.

Microchemistry of diethylbromocetylcarbamide (Adaline). M. WAGENAAR (Pharm. Weekblad, 1934, 71, 1261—1264).—Adaline gives characteristic micro-cryst. ppts. with HNO_3 , AgNO_3 (AgBr), and $\text{Pt}(\text{SO}_4)_2$ [$(\text{NH}_4)_2\text{PtBr}_6$]. S. C.

Azido-dithiocarbonic acid. VIII. Guanidine trinitride and azido-dithiocarbonate. J. CRAIK, K. H. BERGER, and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 2380—2381; cf. A., 1934, 735).— $\text{NH}_2\text{C}(\text{NH}_2)_2\cdot\text{HN}_3$, m.p. 93.5° , and $\text{NH}_2\text{C}(\text{NH}_2)_2\cdot\text{SH}\cdot\text{CS}\cdot\text{N}_3$, decomp. $88-90^\circ$, have been prepared. E. S. H.

Tautomeric transformations of certain organic phosphorus compounds. A. E. ARBUZOV and A. I. RAZUMOV (J. Gen. Chem. Russ., 1934, 4, 834—841; cf. A., 1929, 1129).—The Na salt of Et α -diisobutylphosphinoacetate, b.p. $170-171^\circ/10$ mm., prepared from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and $\text{P}(\text{O}^\text{Bu}^\text{is})_3$, exists in three tautomeric forms, which react with MeI as follows: $\text{PO}(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CHNa}\cdot\text{CO}_2\text{Et} + \text{MeI} \longrightarrow$

$\text{PO}(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ (I) + NaI;

$\text{P}(\text{ONa})(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CH}\cdot\text{CO}_2\text{Et} + \text{MeI} \longrightarrow$

$\text{PI}(\text{ONa})(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ —

$\text{PO}(\text{ONa})(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ (II) + BuI;

$\text{PO}(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CH}\cdot\text{C}(\text{ONa})\cdot\text{OEt} + \text{MeI} \longrightarrow$

$\text{PO}(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CHMe}\cdot\text{C}(\text{ONa})\cdot\text{OEt} \longrightarrow$

$\text{PO}(\text{O}^\text{Bu}^\text{is})_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Na}$ (III) + EtI. (I), b.p. $165-$

$168.5^\circ/7.5$ mm., is obtained in 43% yield, and (II) and (III) (not isolated) in 25% yields. $\text{P}(\text{OEt})_3$ or

$\text{P}(\text{ONa})(\text{OEt})_2$ (IV) and $\text{COPh}\cdot\text{CH}_2\text{Br}$ in Et_2O give a

mixture of products, from which the ketone,

$\text{PO}(\text{OEt})_2\cdot\text{CH}_2\cdot\text{COPh}$ (V), b.p. $174-176^\circ/2.5$ mm., is

isolated. The Na salt of (V) with MeI in Et_2O yields

the substance $\text{PO}(\text{OEt})_2\cdot\text{CHMe}\cdot\text{COPh}$, b.p. $171-180^\circ/$

3 mm. (IV) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Ph}$ in Et_2O yield Ph

α -diethylphosphinoacetate, b.p. $153.5-157^\circ/9$ mm., the

Na salt of which reacts with MeI to give Ph α -diethyl-

phosphinopropionate, b.p. $140-146^\circ/15$ mm. (50%

yield), EtI, and other products. PPh_2Cl and $\text{NaO}^\text{Bu}^\text{is}$

in Et_2O afford $\text{PPh}_2\cdot\text{O}^\text{Bu}^\text{is}$, b.p. $188^\circ/15$ mm., which

with $\text{COMe}\cdot\text{CH}_2\text{Cl}$ at 140° gives $\text{POPh}_2\cdot\text{CH}_2\cdot\text{COMe}$,

b.p. $220-224^\circ/10$ mm., m.p. 73° , in which H is not

replaceable by Na. R. T.

Sodium cacodylate. F. MARTIN (Bull. Sci.

pharmacol., 1934, 41, No. 36, 21—28; Chem. Zentr.,

1934, i, 3774—3775).—Chemically neutral Na cacody-

late (I) reacts alkaline to phenolphthalein (II); if

neutral to (II), 3% of free dimethylarsinic acid is

present. To test for Na methylarsinate (III), 1 g. of

(I) is dissolved in 5 c.c. of dil. H_2SO_4 , and 2 drops of

10% KI are added. With $\leq 0.1\%$ of (III), a ppt.

forms on mixing. J. S. A.

Radial esters of tetrathio-orthostannic acid.

II. H. J. BACKER and J. KRAMER (Rec. trav. chim.,

1934, 53, 1101—1112; cf. A., 1933, 1274).—The

following alkyl and aryl tetrathio-orthostannates,

$\text{Sn}(\text{SR})_4$, are prepared from SnCl_4 and RSNa as

previously described (*loc. cit.*): R—*n*-amyl, b.p. 162°/0.004 mm.; *n*-hexyl, decomp. on attempted distillation in cathode vac.; *n*-dodecyl, m.p. 35.5°; *n*-hexadecyl, m.p. 53—54°; *allyl*; β -methylallyl; cyclohexyl, m.p. 53—54° (crystallographic data given); *Ph*, m.p. 67°; *p*-tolyl, m.p. 100°; *p*-C₆H₄Cl, m.p. 189°; *p*-C₆H₄Br, m.p. 217°; *p*-C₆H₄Bu^v, m.p. 106°; *benzyl*, decomp. on attempted distillation in cathode vac. (SH·CH₂·CH₂)₂O (in EtOH—NaOEt) and SnCl₄ (in C₆H₆) give the spiro-compound,

$\text{Sn} \left(\begin{array}{c} \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \right) \text{O}$, m.p. 124°. Sn(SAlk)₄ are oxidised [warm HNO₃ (*d* 1.1)] to SnO₂ and (SAlk)₂. Sn(SET)₄ and Sn(SPr^δ)₄ with EtOH—HgCl₂ give compounds of the composition C₂H₅ClSHg and C₃H₇ClSHg, respectively. SnPh₂Br₂ (simplified prep.; cf. Chambers and Scherer, A., 1926, 629) and NaSPh in C₆H₆ afford *di*(phenylthiol)diphenylstannane, SnPh₂(SPh)₂, m.p. 65—65.5°. Slow addition of 60% oleum to cold PhBu^v (from C₆H₆, Bu^vCl, and a little AlCl₃) gives *p*-C₆H₄Bu^v·SO₃H (*K* salt + H₂O); the *chloride*, m.p. 83°, is reduced (Sn, conc. HCl) to *p*-tert.-butylthiophenol, b.p. 117°/10 mm. *p*-C₆H₄Cl·SH, *p*-C₆H₄Br·SH, and *p*-C₆H₄Me·SH are similarly prepared. CH₂:CH·CH₂·SH, b.p. 67—69°, and CH₂:CMe·CH₂·SH, b.p. 93.5°/760 mm. (which polymerises readily), are prepared by hydrolysis (aq. NaOH) of NH₂·C(=NH)·SR.

H. B.

Configuration of bisdimethylglyoximidamine cobaltic salts.—See this vol., 51.

Action of niobium and tantalum pentachloride on organic compounds. IV. H. FUNK (Ber., 1934, 67, [B], 1801—1804; cf. A., 1929, 1039).—NbCl₅ and TaCl₅ react readily with CH₂Ac₂ with evolution of HCl and formation of compounds contaminated by the products of decomp. of CH₂Ac₂. The complication can be avoided by use of a suitable solvent (MeOH, EtOH) in small amount, but the products then contain OAlk. They are colourless to dark yellow, those containing Nb being darker than the corresponding Ta compounds and those derived from CH₂AcBz darker than those obtained with CH₂Ac₂. They are much less sensitive to H₂O than the parent chlorides. The following salts are described: NbCl₂(OMe)₂·C₅H₇O₂, m.p. 128—129°;

TaCl₂(OMe)₂·C₅H₇O₂, m.p. 113—115°;

NbCl₂(OEt)₂·C₅H₇O₂, m.p. 74—76°;

TaCl₂(OEt)₂·C₅H₇O₂, m.p. 63—65°;

NbCl₂(OMe)₂·C₁₀H₉O₂, m.p. 144—145°;

TaCl₂(OMe)₂·C₁₀H₉O₂, m.p. 138—139°;

NbCl₂(OEt)₂·C₁₀H₉O₂, m.p. 110—112°;

TaCl₂(OEt)₂·C₁₀H₉O₂, m.p. 114—116°.

H

Recent researches on the cyclane series. M. GODCHOT (Bull. Soc. chim., 1934, [v], 1, 1154—1200).—A lecture.

Thermal decomposition of cyclohexane hydrocarbons. N. D. ZELINSKI, B. M. MICHAÏLOV, and J. A. ARBUZOV (J. Gen. Chem. Russ., 1934, 4, 856—865).—The yields of butadiene obtained by heating various hydrocarbons at 750° with or without H₂O are: cyclohexene 65.2; Δ³-methylcyclohexene 56.4; cyclohexane 40; methyl- 34.8, and ethyl-cyclohexane 41.2; decahydronaphthalene 11.6 mol.%; at the

same time, C₂H₄, C₃H₆, and H₂ are produced in various proportions. Under analogous conditions, Δ¹-methylcyclohexene affords isoprene in 36.2 mol.-% yield.

R. T.

Raman effect and organic chemistry. γ -cyclopentyl-Δ^α-propine and its derivatives. B. GRÉDY (Compt. rend., 1934, 199, 1129—1131).—Mg cyclopentyl bromide and CH₂Br·CBr·CH₂ give β-bromo-γ-cyclopentyl-Δ^α-propene, b.p. 75°/13 mm., converted by NaNH₂ in decahydronaphthalene at 150° into γ-cyclopentyl-Δ^α-propine (I), b.p. 132.5—133.5°/760 mm. (Ag, Cu, and Na derivatives). The Mg derivative of (I) is transformed by trioxymethylene into α-cyclopentyl-Δ^β-butin-α-ol (II), b.p. 117°/14 mm., and by MeCHO into ε-cyclopentyl-Δ^γ-pentin-β-ol (III), b.p. 114—115°/13 mm. Treatment of (I), (II), and (III) with Me₂SO₄ and NaNH₂ in anhyd. Et₂O affords, respectively, δ-cyclopentyl-Δ^β-butine, b.p. 164—165°/760 mm., α-methoxy-δ-cyclopentyl-Δ^β-butine, b.p. 96—97°/15 mm., and β-methoxy-γ-cyclopentyl-Δ^γ-pentine, b.p. 99.5°/17 mm. A cyclic nucleus separated by CH₂ from the C:C linking is without influence on the frequencies of the latter. The presence of cyclopentyl is characterised by a series of bands, and the band 1445, characteristic of CH₂, is resolved into two rays 1429 and 1450 in all derivatives of (I).

H. W.

Internal energy relationships and regularities of substitution among aromatic, carbocyclic compounds. O. SCHMIDT (Ber., 1934, 67, [B], 1870—1887).—The line of reasoning is based on the work of London (A., 1927, 923; 1928, 344, 1077; 1929, 1397) whereby it is assumed that homopolar union depends on the coupling of two electrons of opposite spin and that under these conditions the energy of union constitutes the main part of the total energy; also, the twist vectors of the valency electrons of an atom are parallel. Hence, the twist vectors of the valency electrons of consecutive C atoms of a chain or ring with an even no. of C atoms are anti-parallel. A single C·C linking vicinal to a C·C union is strengthened, whereas the next is weakened, and the alternation of strengthening and weakening continues with diminishing intensity through the whole mol.; it is strongly pronounced at a distance of 2.5 Å. and probably obvious at 5 Å. The C·C linking consists of two spin-valencies, one of which is weaker than the other. The electrons concerned with the stronger linking, localised in the direction of the line of nuclear union, are designated *A* electrons, whereas the others, inclined thereto, are *B* electrons. The latter are more feebly united because further distant from one another. The potential of the *B* electrons inversely ∝ to the distance. The *B* electrons at the terminations of a diameter of C₆H₆ are anti-parallel, whereas those with parallel spin are located at similar positions in cyclooctatetraene (I). Vectorial addition in C₆H₆ causes strong resultants directed inwards, whereas with (I) the effect is weak. Within the C₆H₆ nucleus there is therefore a ring of 6 *B* electrons co-planar with the 6 atoms, held together in the *o*- and *p*-position by coupling of electron pairs with opposed spin. This is the cause of aromatic character. The energy of relationships

of aromatic hydrocarbons and their partly hydrogenated products are calc. The results are in accord with thermochemical data and permit simple explanation of the reaction relationships of complex aromatic compounds. The regularities of substitution are in harmony with the author's conceptions. H. W.

Technical reactions. IV. Substitution rules in aromatic compounds. O. SCHMIDT (Z. Elektrochem., 1934, 40, 765—770).—Theoretical.

E. S. H.

Direct introduction of deuterium into benzene without heterogeneous catalysis. C. K. INGOLD, C. G. RAISIN, and C. L. WILSON (Nature, 1934, 134, 734).—When C_6H_6 is shaken with 90% H_2SO_4 of enhanced H^2 content part of the H^2 is transferred to the C_6H_6 , which gives H_2O on combustion. The amount of H^2 transferred increases with time of shaking. Certain substitution products of C_6H_6 undergo spontaneous exchange of their nuclear H atoms with the H of H_2O or acids more readily than does C_6H_6 itself. The existence of an aromatic substitution depending on "normal" polarisation, i.e., one corresponding with the ionisation, is thus demonstrated.

L. S. T.

Direct introduction of deuterium into benzene. J. HORIUTI and M. POLANYI (Nature, 1934, 134, 847).—A general mechanism for H exchange in unsaturated compounds involving the addition and subsequent elimination of H_2O or H halide is suggested. The interchange of H between C_6H_6 and 90% H_2SO_4 recently reported (preceding abstract) is regarded as a special case of this general principle.

L. S. T.

Direct introduction of deuterium into benzene. C. K. INGOLD, C. G. RAISIN, and C. L. WILSON (Nature, 1934, 134, 847—848).—Whilst the mechanism suggested by Horiuti and Polanyi (see above) often applies to unsaturated compounds it does not apply to the H exchange between aq. H_2SO_4 and C_6H_6 . This involves polarisations in which addition and subsequent removal of H_2SO_4 occur.

L. S. T.

Electrochemical chlorination of benzene.—See this vol., 45.

Reactive methyl group in toluene derivatives.

II. p-Nitrobenzotribromide. C. H. FISHER (J. Amer. Chem. Soc., 1934, 56, 2469—2470).— $p-NO_2 \cdot C_6H_4 \cdot CHBr_2$ (I) and aq. NaOBr give p-nitrobenzotribromide (II), m.p. 86—87°, which is stable to hot MeOH and cold alkali, and is hydrolysed (boiling H_2O or, more rapidly, aq. Na_2CO_3) to $p-NO_2 \cdot C_6H_4 \cdot CO_2H$ (III). (II) and PhOH at 135—145° afford a little (I) and an alkali-sol. coloured substance. Condensation products are obtained from (II) and $NPhMe_3$; (I) could not be isolated. (II) could not be dehalogenated by $COMe_2$ or $COPhMe$; treatment with N_2H_4 in EtOH gives N_2 (cf. Cox *et al.*, A., 1931, 1074). Prolonged treatment (8 days) of $p-C_6H_4Me \cdot NO_2$ with NaOBr affords a little (III). $CBR_3 \cdot NO_2$ is formed by the action of NaOBr on 2 : 4- $C_6H_3Me(NO_2)_2$ and s- $C_6H_2Me(NO_2)_3$.

H. B.

Fluoro-derivatives of butyltoluene and of butyl-m-xylene. Fluoronitro-derivatives with the

odour of musk. G. DARZENS and A. LEVY (Compt. rend., 1934, 199, 959—962).—3-Fluoro-5-tert.-butyltoluene (I), m.p. 96—98°/25 mm., and 4-fluoro-5-tert.-butyl-m-xylene (II), b.p. 97—98°/21 mm., are obtained from m- C_6H_4FMe and 4-fluoro-m-xylene with Bu^tCl and $AlCl_3$, respectively. 2-Fluoro-5-tert.-butyl-m-xylene (III), b.p. 100°/22 mm., is prepared through the borofluoride (cf. A., 1927, 654) from 2-nitro-5-tert.-butyl-m-xylene. With conc. $H_2SO_4-HNO_3$, (I), (II), and (III) give, respectively, 2 : 4 : 6- $(NO_2)_3$, m.p. 95°, 2 : 6-, m.p. 57.5°, and 4 : 6- $(NO_2)_2$ -derivatives, m.p. 89°, all of which possess the odour of musk.

J. L. D.

Volume effect of alkyl groups in aromatic compounds. VI. Constitution of the iodo-p-cymene formed by direct iodination of the hydrocarbon. S. N. GANGULY and R. J. W. LE FEVRE (J.C.S., 1934, 1697—1699; cf. A., 1934, 878).—Pure 2-aminocymene gives (diazo-reaction) 2-iodocymene (I), b.p. 122°/11 mm. [dichloride (II), m.p. 97°]. The Grignard reagent from 3-bromocymene affords p-cymene and a little 3-iodocymene, b.p. 125—126°/11 mm. (dichloride, m.p. 85—87°). Cymene, HIO_3 , and I in hot EtOH give (I) (cf. lit. and A., 1933, 1153) and substances halogenated in the side-chain; the former was identified by prep. of (II) and of 3 : 5-dinitro-2-piperidino-p-cymene and by the $[\alpha]$ therein of l-menthol (III). The $[\alpha]$ of (III) is slightly lower in solution in the 3- than in the 2-halogenocymenes.

R. S. C.

Preparation of styrene. H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1934, 53, 1133—1138).—Pure styrene (I), b.p. 145—145.8°/760 mm., 48°/20 mm., m.p. —33°, is prepared from β -bromo- α -phenylethyl Et ether, b.p. 96—100°/15 mm. (from $CH_2Br \cdot CHBr \cdot OEt$ and $MgPhBr$), and Zn—Cu in 90% EtOH, and subsequent vac. distillation (partial polymerisation occurs at atm. pressure) over anhyd. Na_2SO_4 . (I) can be kept for several months in the cold and darkness without polymerisation taking place. The physical consts. of (I), PhEt, and ethylcyclohexane are tabulated and compared with those in the lit.

H. B.

Determination of the mol. wt. of polystyrenes. A. SMAKULA (Angew. Chem., 1934, 47, 777—779).—The molar absorption coeff. at 260 m μ for polystyrenes \propto mol. wt. deduced from val. of (Staudinger).

A. G.

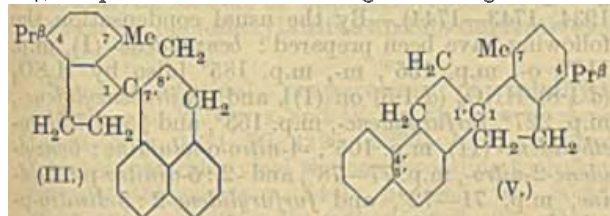
Relation between constituents of Japanese acid earth and its catalytic action [on naphthalene].—See this vol., 44.

Fluorene and triphenylmethane. XIII. Alcoholic potassium hydroxide as a reagent for fluorene hydrocarbons with a labile hydrogen atom. A. A. VANSCHIEDT (J. Gen. Chem. Russ., 1934, 4, 875—884).—Hydrocarbons containing the cyclopentadiene ring give characteristic colorations with EtOH—KOH.

R. T.

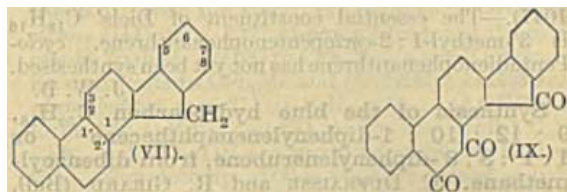
Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones. IV. Constitution of Diels' hydrocarbon, " $C_{25}H_{24}$," from cholesterol. J. W. COOK, C. L. HEWETT, W. V. MAYNEORD, and (Miss) E. ROE (J.C.S., 1934, 1727—1738; cf. A., 1934, 766).—The

Grignard reagent from 3-bromo-*p*-cymene and CH_2O give 3-*p*-cymylcarbinol (not obtained pure), b.p. 143—144°/25 mm. (3:5-dinitrobenzoate, m.p. 85—86°), which with SOCl_2 and NPhMe_2 give 3-chloromethyl-*p*-cymene (I), b.p. 129—130°/25 mm. The Grignard reagent therefrom with 1-keto-1:2:3:4-tetrahydrophenanthrene gives an oil, which with P_2O_5 at 145—150° yields a resin, b.p. about 260—270°/4—5 mm., dehydrogenated (Se) at 320—340° to 1-(3-*p*-cymylmethyl)phenanthrene, m.p. 115—116° [$\text{s-C}_6\text{H}_3(\text{NO}_2)_3$ complex, m.p. 134—135°], oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$) to 1-3'-methyl-6'-isopropylbenzoylphenanthraquinone, m.p. 208—209° (phenazine, m.p. 187°). (I) and $\text{CHNa}(\text{CO}_2\text{Et})_2$ in C_6H_6 give an ester, b.p. 195—200°/14 mm., which after hydrolysis yields at 180° β -3-(*p*-cymyl)propionic acid, m.p. 61—61.5°, dehydrated by SnCl_4 at 120° to 7-methyl-4-isopropyl-1-hydrindone (II), m.p. 46—48°, b.p. 165—167°/15 mm. (phenylhydrazone, m.p. 96—97°). This with the Grignard reagent from β -1-naphthylethyl chloride affords 1-hydroxy-1-(β -1'-naphthylethyl)-7-methyl-4-isopropylhydrindene, m.p. 115—116°, which with KHSO_4 at 160° gives 3-(β -1'-naphthylethyl)-4-methyl-7-isopropylindene, m.p. 92—93°, and with $\text{H}_2\text{SO}_4\text{-AcOH}$ at 100°, P_2O_5 at 160°, or AlCl_3 in CS_2 at 0° gives 7-methyl-4-isopropylhydrindene-1:1'-spiro-7':8'-dihydrophenalene (III), m.p. 82—83°. The Grignard reagent from

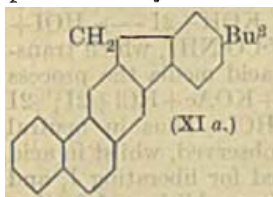


5-bromotetrahydronaphthalene and ethylene oxide give β -5-tetrahydronaphthylethyl alcohol, b.p. 120°/0.2 mm. (3:5-dinitrobenzoate, m.p. 128—129°), the chloride (IV) (by SOCl_2 and NPhMe_2), b.p. 155°/11—12 mm., of which with (II) gives (Grignard) 1-hydroxy-1-(β -5'-tetrahydronaphthylethyl)-7-methyl-4-isopropylhydrindene, m.p. 114.5—115°, which, when dehydrated with $\text{H}_2\text{SO}_4\text{-AcOH}$ at 100°, and then heated with Se at 320°, gives probably a little 5-methyl-8-isopropyl-naphthylfluorene, m.p. 198—200°, and much 7-methyl-4-isopropylhydrindene-1:1'-spiro(4':5'-benz)-hydrindene (V), an oil (picrate, m.p. 121.5—122°). Spiran formation in these dehydrogenations is prevented and yields in previous stages are improved if the β -position of the ethylenic linking is substituted. Thus, $\text{CH}_3\text{Ph}\cdot\text{CHMe}\cdot\text{COCl}$ [prep. of the acid from CH_2PhCl and $\text{CMeNa}(\text{CO}_2\text{Et})_2$] and AlCl_3 give an 82% yield of 2-methyl-1-hydrindone (VI), which with $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$ gives a carbinol, converted by distillation in vac. into 3- β -phenylethyl-2-methylindene (80%), b.p. 170°/1 mm. (picrate, unstable), which with AlCl_3 in CS_2 at 0° gives 10-methyl-3:4:10:11-tetrahydro-1:2-benzfluorene, b.p. 159°/0.8 mm., dehydrogenated by Se at 310—320° to give a 65% yield of chrysofluorene, m.p. 182—183°. Previous samples of tetrahydrochrysofluorene contained some spiran. (IV) and the Grignard reagent from (IV) give 3-(β -5'-tetrahydronaphthylethyl)-2-methylindene, m.p. 173°, b.p. 190°/0.3 mm. (picrate, m.p. 115°), which with AlCl_3

in CS_2 at 0° or $\text{H}_2\text{SO}_4\text{-AcOH}$ at 100° gives 10-methyl-3:4:10:11:5':6':7':8'-octahydro-2':1'-naphtha-1:2-fluorene, m.p. 123.5—124°, b.p. 195°/0.4 mm., converted by Se at 310—320° or 400—420° to 2':1'-naphtha-1:2-fluorene (VII), sublimes at 300°/0.3 mm., m.p. 327—328° (preheated to 300°) (2:7-dinitroanthraquinone complex, m.p. 249—251°), which with



$\text{Na}_2\text{Cr}_2\text{O}_7$ (best, an excess) in hot AcOH yields 2':1'-naphtha-1:2-fluorenone (VIII), m.p. 207—208°, sublimes at < 300°/0.3 mm., and some triketone (IX), m.p. 340—350° (decomp. from 280°), sublimes at 300—320°/0.3 mm. [also formed by oxidation of (VIII)]. (I) and $\text{CMeNa}(\text{CO}_2\text{Et})_2$ in C_6H_6 give an ester, b.p. 175°/2 mm., whence by hydrolysis and decarboxylation at 200° β -(3-*p*-cymyl)- α -methylpropionic acid, b.p. 160—162°/0.8 mm., was obtained. This acid with SnCl_4 at 120° gives 2:7-dimethyl-4-isopropyl-1-hydrindone, b.p. 160°/16 mm., m.p. 46—46.5°, which with (IV) affords 3-(β -5'-tetrahydronaphthylethyl)-2:4-dimethyl-7-isopropylindene, b.p. 218°/0.3 mm. (dipicrate, m.p. 119—119.5°), cyclised by AlCl_3 or $\text{H}_2\text{SO}_4\text{-AcOH}$ to 5:10-dimethyl-8-isopropyl-3:4:10:11:5':6':7':8'-octahydro-2':1'-naphtha-1:2-fluorene, b.p. 215—220°/0.3 mm., whence by Se at 310—325° was obtained 5-methyl-8-isopropyl-2':1'-naphtha-1:2-fluorene (X), m.p. 198°, sublimes at 230—240°/0.2 mm. (2:7-dinitroanthraquinone complex, m.p. 261—262°), which is not identical (mixed m.p.) with Diels' hydrocarbon, $\text{C}_{25}\text{H}_{24}$ (XI), from cholesterol. Oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$) of (X) affords 5-methyl-8-isopropyl-2':1'-naphtha-1:2-fluorenone, m.p. 197—198°. Absorption curves are given for (VII), (X), (XI), phenanthrene, and picene; the close similarity of those of the first three compounds indicates that (XI) has a ring system related to (VII). X-Ray spectra, however, show that (XI) has a longer mol. than (X), and it is suggested that (XI) may be 7-isobutyl-1':2'-naphtha-2:3-fluorene (XIa), the new ring system being produced by fission between C14 and C15 and



linking of C15 to C23 and of C21 to C12. Rearrangement of the ring structure during dehydrogenation is not observed with simple polycyclic hydroaromatic compounds, but is characteristic of the terminal 5-membered ring and labile side-chain of the sterols etc. It is caused by the high temp. used and not by any special reagent.

R. S. C.

Is Diels' hydrocarbon, " $\text{C}_{18}\text{H}_{16}$," a pure single substance? H. W. THOMPSON (Chem. and Ind., 1934, 1027—1028).—Diels' hydrocarbon, " $\text{C}_{18}\text{H}_{16}$," (from cholesterol), is recovered unchanged on distillation with Zn dust. Slow crystallisation from dil.

EtOH gave separation into two fractions, m.p. 150° and 142°. The former, recryst. repeatedly, showed m.p. 253° (12° depression with chrysene) and agreed with empirical formula $C_{17}H_{12}$. These facts suggest that " $C_{18}H_{16}$ " is a mixture. H. G. M.

Is Diels' hydrocarbon $C_{18}H_{16}$ a pure single substance? J. W. COOK (Chem. and Ind., 1934, 1047).—The essential constituent of Diels' $C_{18}H_{16}$ is 3'-methyl-1:2-cyclopentenophenanthrene. cyclo-Pentadienophenanthrene has not yet been synthesised. J. W. B.

Synthesis of the blue hydrocarbon $C_{30}H_{16}$, 9:12:10:1-diphenylenenaphthacene or 1:1':3:3'-diphenylenerubene, from dibenzoylmethane. C. DUFRAISSE and R. GIRARD (Bull. Soc. chim., 1934, [v], 1, 1359—1367).—The blue diphenylenerubene $C_{30}H_{16}$ (I) obtained by prolonged action of PCl_5 on CH_2Bz_2 thus: $CH_2Bz_2 - 4HCl \rightarrow$ yellow $C_{30}H_{20}Cl_4$ (II) $- 2HCl \rightarrow$ red dichlorodiphenyl-rubene $C_{30}H_{18}Cl_2$ (III) $- HCl \rightarrow$ violet chlorophenylphenylenerubene $C_{30}H_{17}Cl$ (IV) $- HCl \rightarrow$ (I), has an identical absorption spectrum (revised data; max. at 6100, 5650, and 5250 Å.), volatility (at 270—275°/0.01 mm.), and solubility, and gives the same reduction product, as a specimen of (I) obtained by the action of KOH at 325—330° on (IV) (A., 1933, 1284) in $C_{10}H_8$, or on (II) or (III), or obtained from $\alpha\alpha$ -triphenyl- Δ^2 -propinen- α -ol, thus confirming the structure previously assigned (Badoche, *ibid.*, 1154) to (I), and the elimination of 2Ph in the conversion of the colourless $C_{42}H_{26}$ into (I). The absorption spectra of (III) and (IV) closely resemble, respectively, those of tetraphenyl- and diphenylphenylene-rubene. J. W. B.

(A) Halogenation of organic compounds. Bromination and iodination of aromatic amines by means of *N*-chloroamides. (B) Mechanism of iodination of organic compounds by means of chloroamides and oxidising agents. M. V. LICHOSCHERSTOV, B. I. TSIMBALIST, and A. A. PETROV (J. Gen. Chem. Russ., 1934, 4, 557—562, 622—628).—(A) Arylamines may be conveniently halogenated by the reaction $NH_2 \cdot RH + MX + R' \cdot CO \cdot NHCl$ (I) \rightarrow $NH_2 \cdot RX + MCl + R' \cdot CO \cdot NH_2$ (II), where RH is an aromatic radical, R' is NHCl, Me, or some other radical, and MX is an alkali halide.

(B) In neutral solution the above reaction consists of the stages (I) + $H_2O \rightarrow$ (II) + HOCl; $HOCl + 2KI \rightarrow 2I + KCl + KOH$; $KOH + 2I \rightarrow HOI + KI$; (II) + HOI \rightleftharpoons $H_2O + R' \cdot CO \cdot NHI$, which transfers I to the compound. In acid media the process is (I) + $2KI + AcOH \rightarrow$ (II) + $KOAc + KCl + 2I$; $2I + (I) + \cdot RH \rightarrow 2 \cdot RI + (II) + HCl$. Thus in neutral solution liberation of I is not observed, whilst in acid solutions half of the (I) is used for liberating I, and iodination commences only after addition of further (I); the same effect is obtained by adding the theoretical amount of I, and half the total amount of (I), or by using $K_2Cr_2O_7$, KIO_3 , or $KMnO_4$ in place of (I). R. T.

Fission of aryltrimethylammonium chlorides in aqueous solution by means of sodium amalgam. P. GROENEWOUD and R. ROBINSON (J.C.S., 1934, 1692—1697).—The % of salt decomp.,

$+NArMe_3Cl^- \rightarrow NArMe_2 + CH_4$ or $\rightarrow ArH + NMe_3$, and the % of reacting mols. giving NMe_3 in the reductive fission of aryltrimethylammonium chlorides with 12 times the theoretical amount of 1% Na-Hg at 95—100° (CO_2 stream) under standard conditions are, respectively, given in parentheses after each salt: $Ar = Ph$, m.p. 220° (decomp.) (picrate, m.p. 123—124°) (44—46; 71.1); *o*- (88—90; 62.9), *m*- (picrate, m.p. 108°) (61—63; 60.1), and *p*- C_6H_4Me (picrate, m.p. 193—198°) (27—30; 30.8); *o*-, m.p. 140° (decomp.) (picrate, m.p. 125°) (34—37; 88.6), *m*-, m.p. 195° (decomp.) (picrate, m.p. 132.5—133.5°) (62.5—65.4; 64), and *p*- C_6H_4OMe , m.p. > 200° (decomp.) (picrate, m.p. 176—177°) (65—68; 20.2); 3-, m.p. > 200° (decomp.) (picrate, m.p. 166—167°) (89—91; 92.5), and 4- C_6H_4Ph , m.p. 205—208° (decomp.) (picrate, m.p. 153°) (93.5—96; 85.8), and 2-naphthyl, m.p. 173—174° (90—91; 94.7). With aq. Me_2SO_4 on a steam bath *m*- $C_6H_4Ph \cdot NH_2$ affords 3-dimethylaminodiphenyl, b.p. 171—173°/12 mm. (methiodide, m.p. 182—183°; 6-*NO*-derivative, m.p. 121—122°). It is suggested that increased unsaturation of the aryl group facilitates the reaction by increasing the rate of fission between the N atom and the aromatic nucleus. J. W. B.

Orientation problems. I. Effect of nitro-groups in Schiff's bases. A. MCGOOKIN (J.C.S., 1934, 1743—1744).—By the usual condensation the following have been prepared: benzylidene- (I), m.p. 116°, *o*-, m.p. 155°, *m*-, m.p. 185° [also by H_2SO_4 (*d* 1.8)— HNO_3 (*d* 1.5) on (I)], and *p*-nitrobenzylidene-, m.p. 227°, furfurylidene-, m.p. 153°, and $\beta\beta$ -trichloroethylidene- (II), m.p. 105°, 4-nitro-*o*-toluidine; benzylidene-2-nitro-, m.p. 77—78°, and -2:5-dinitro-*p*-toluidine, m.p. 71—72°, and furfurylidene-2:5-dinitro-*p*-toluidine, m.p. 208°. All are stable to acids, hydrolysis being effected only by heating with aq. NH_3 (*d* 0.880) under pressure. With aq. $KMnO_4$ (I) readily gives PhCHO and 4-nitro-*o*-toluidine, but in dry $COMe_2$ a colourless solid is isolated, which gives no PhCHO until H_2O is added. With HNO_3 (*d* 1.5) at 0° (II) gives a substance, m.p. 170°. J. W. B.

Rearrangement of alkylanilines. VI. Mechanism of rearrangement. W. J. HICKINBOTTOM (J.C.S., 1934, 1700—1705).—When heated together at 100—115° (H_2O excluded), $NPhMe_2$ and CPh_3Cl afford $CHPh_3$ and *p*- $C_6H_4 \cdot CMe_2 \cdot NMe_2$ (methiodide, m.p. 206—207°), $NPhMeAc$ at 140—150° similarly giving the *Ac* derivative, m.p. 191—192°, of *p*-triphenylmethylmethylaniline, m.p. 211—212° (prep. from $NHPhMe \cdot HCl$ and $CPh_3 \cdot OH$ in boiling $AcOH$). Thermal decomp. of $NHPhMe \cdot HBr$ at 305—310° gives up to 13.8% MeBr and a mixture of (mainly) NH_2Ph (11%) and *p*- $C_6H_4Me \cdot NH_2$, whereas the HI salt gives only 2—6% of MeI and a mixture of *o*- and *p*- $C_6H_4Me \cdot NH_2$. A general hypothesis, assuming the separation of an alkyl cation which reacts with a quinonoid form of the aniline, is developed to explain such migrations, and its extension to the rearrangements of $NClPhAc$, $NHPh \cdot OH$, and $(\cdot NHPh)_2$ is briefly discussed. J. W. B.

3-Halogeno-1-nitro-, -1-amino-, and -1-hydroxy-naphthalenes. H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1934, 1705—1707).—With Cl_2 - $AcOH$

at 100°, 4-nitroaceto- α -naphthalide gives its 2-Cl-derivative, m.p. 231°, converted by boiling 20% NaOH into 2-chloro-4-nitro- α -naphthol, m.p. 231°, and by boiling H_2SO_4 -aq. EtOH into 2-chloro-4-nitro- α -naphthylamine (I), m.p. 249°, from which, by diazotisation, 3-chloro-1-nitronaphthalene, m.p. 105°, is obtained. With Br- PhNO_2 at room temp. 4-nitro- α -naphthylamine (II) gives its 2-Br-derivative (III), m.p. 250° (hydrobromide). (II) and $\text{Hg}(\text{OAc})_2$ in hot AcOH afford a mercuriacetate [mercurichloride, m.p. 244° (decomp.); mercuribromide, m.p. 249° (decomp.); mercuri iodide, m.p. 259° (decomp.); mercurihydroxide], converted by the appropriate halogen into (I), (III), or the 2-I-derivative, all deaminated to the corresponding 3-halogeno-1-nitronaphthalene, suitable reduction of which affords 3-chloro-, m.p. 62° (hydrochloride, m.p. 219°; Ac, m.p. 197°, and Bz, m.p. 162°, derivatives), 3-bromo-, m.p. 70° (hydrochloride, m.p. 247°; Ac, m.p. 174°, and Bz, m.p. 166°, derivatives), and 3-iodo-, m.p. 84° (hydrochloride, m.p. 238°; Ac, m.p. 207°, and Bz, m.p. 174°, derivatives), - α -naphthylamine, from which, by the diazo-reaction, 3-chloro-(2:4- Br_2 -derivative, m.p. 112°), 3-bromo-, m.p. 61° (2:4- Br_2 -derivative, m.p. 133°), and 3-iodo-, m.p. 119° (2:4- Br_2 -derivative, m.p. 191°), - α -naphthol, are obtained. J. W. B.

Catalytic action of Japanese acid earth. VI. Action on cyclohexylamine and its derivatives.—See this vol., 44.

Electrochemical preparation of tolylhydrazines. E. W. COOK and W. G. FRANCE (J. Amer. Chem. Soc., 1934, 56, 2225—2226).—The toluenediazonium chlorides yield the corresponding hydrazines (current efficiencies α -, 74.9; p -, 58.5; m -, 35.6%) when reduced with a Hg cathode at 5—6°. Ease of reduction does not appear to be related to the polar properties of the compounds. E. S. H.

Preparation of 3:3'-ditrifluoromethylhydrazobenzene. M. GONZE (Bull. Acad. roy. Belg., 1934, [v], 20, 809—815).—3:3'-Ditrifluoromethylhydrazobenzene (I), m.p. 36.2°, is much more stable to heat, oxidation, and acids than (m - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot$)₂ (II), and is best prepared by reduction of (m - $\text{CF}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot$)₂ (III), m.p. 82.5° (A., 1923, i, 292), with SnCl_4 and 2% EtOH-HCl. With HCl (I) gives (III), m - $\text{CF}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and a solid, possibly the related tolidine. (All reductions in N_2 atm.) F. S. H. H.

Derivatives of β -naphthoylhydrazine. H. GOLDSTEIN and A. STUDER (Helv. Chim. Acta, 1934, 17, 1485—1487).—The β -naphthoylhydrazones of PhCHO, p - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, COMe_2 , and COPhMe have m.p. 230°, 228°, 143°, and 200°, respectively. With NaNO_2 , β - $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ affords β -naphthoazide, m.p. about 76° (violent decomp.), converted by 90% or 50% H_2SO_4 into β - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$ and by boiling abs. EtOH into β -naphthylurethane. H. W.

Occurrence of free radicals in chemical reactions. VIII. [Thermal fission of aryl- and acyl-azotriphenylmethanes.] H. WIELAND [with K. HEYMAN, T. TSATSAS, D. JUCHUM, G. VARVOGLIS, G. LABRIOLA, O. DOBBELSTEIN, and H. S. BOYD-BARRETT] (Annalen, 1934, 514, 145—181; cf. A., 1922,

i, 772; 1926, 61).—Decomp. of $\text{CPh}_3\cdot\text{N}\cdot\text{NPh}$ (I) in C_6H_6 and O_2 at 60—70° gives $(\text{CPh}_3\cdot\text{O}\cdot)_2$ (II) (50—60%), some PhOH, and a little Ph₂ (probably formed thus: $\text{CPh}_3\cdot\text{N}\cdot\text{NPh} + \text{C}_6\text{H}_6 \rightarrow \text{N}_2 + \text{CHPh}_2 + \text{Ph}_2$). Decomp. in PhMe and $\text{C}_5\text{H}_5\text{N}$ affords $\text{C}_6\text{H}_4\text{MePh}$ (o -+ p -) and phenylpyridine (probably 2-+4-), respectively. Decomp. of (I) in CCl_4 at 55° and then at the b.p. gives PhCl and $\alpha\alpha\alpha$ -trichloro- $\beta\beta\beta$ -triphenylethane (III), m.p. 237° (decomp.) [reduced (large excess of Zn dust, AcOH) to CPh_3Me ; a small amount of Zn dust leads to CPh_3Me and (probably) $\alpha\alpha\alpha\delta\delta\delta$ -hexaphenylbutane, m.p. 271°]; C_6H_6 , CPh_4 , and CHPh_3 are formed in $\text{C}_2\text{H}_2\text{Cl}_4$ and CO_2 at 55—65°, whilst C_6H_6 , CPh_4 , and $\text{CPh}_3\cdot\text{OH}$ are produced in boiling H_2O and CO_2 . Slow decomp. of (I) in presence of sand at 105—115°/high vac. gives C_6H_6 (probably formed from Ph radicals), CPh_4 , and CHPh_3 . (I) and benzoquinone (IV) in C_6H_6 and N_2 at 60—70° afford quinhydrone, phenylbenzoquinone (V), and p - $\text{C}_6\text{H}_4(\text{O}\cdot\text{CPh}_3)_2$, thus showing the production of active H in the decomp. and phenylation (cf. above). (V) is also obtained from PhN_2Cl , AgOAc , and (IV) in AcOH. Decomp. of $\text{CPh}_3\cdot\text{N}\cdot\text{NBz}$ (VI) in C_6H_6 and CO_2 and subsequent treatment of the red solution (A) with Br gives a compound (Br content about 36%), hydrolysed (EtOH-KOH) to a Br-free acid containing about 12.5% N; the free radical produced thus contains N (cf. loc. cit.). The main product obtained by decomp. of (VI) is $\text{COPh}\cdot\text{CPh}_3$ (VII); in one case, p -benzoyltriphenylmethane was isolated also. Decomp. of (VI) in C_6H_6 is accelerated by O_2 and proceeds exothermally; (II) (about 10%), (VII), and small amounts of BzOH , CO_2 , and PhOH, but no Bz_2O_2 , are produced: $2\text{CPh}_3\cdot\text{N}\cdot\text{NBz} + \text{O}_2 \rightarrow (\text{CPh}_3\cdot\text{O}\cdot)_2 + 2\text{N}\cdot\text{NBz}$. (II) is not produced when O_2 is passed into (A) (prepared in N_2). No volatile product is obtained by decomp. of (VI) in presence of sand in a high vac. (VI) and Br in C_6H_6 give BzBr and CPh_3Br . The mol. heats of combustion at const. pressure of (I), (VI), and (VII) are 3171, 3238, and 3181 kg.-cal., respectively. The differing rates of decomp. of (I) and (VI) are decided by the tenacity of the C-N linking; decomp. of (I) is best represented as: $\text{CPh}_3\cdot\text{N}\cdot\text{NPh} \rightarrow \text{CPh}_3 + [\text{N}\cdot\text{NPh}] \rightarrow \text{Ph} + \text{N}_2$.

α -1-Naphthyl- β -triphenylmethylhydrazine, m.p. 183° (decomp.) (from α - $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NH}_2$ and CPh_3Cl in C_6H_6), is oxidised ($\text{Br}\cdot\text{H}_2\text{O}$ in C_6H_6) to α -naphthalene-azotriphenylmethane (VIII), m.p. 117° (decomp.), which decomposes in C_6H_6 and N_2 at 50—60° or in presence of sand at 105—120°/high vac. to α - $\text{C}_{10}\text{H}_7\cdot\text{CPh}_3$, C_{10}H_8 , and CHPh_3 ; in C_6H_6 and O_2 , 32.3% of (II) is produced. (VIII) in CCl_4 and N_2 at 55° gives (III) and 1- $\text{C}_{10}\text{H}_7\text{Cl}$; in H_2O and CO_2 at 100°, α - $\text{C}_{10}\text{H}_7\cdot\text{CPh}_3$, C_{10}H_8 , $\text{CPh}_3\cdot\text{OH}$, and 9-phenylfluorene result. β -Naphthaleneazotriphenylmethane, decomp. 114°, in CCl_4 and CO_2 at 50—70° affords (III) and 2- $\text{C}_{10}\text{H}_7\text{Cl}$; in C_6H_6 and O_2 , 29% of (II) results. Benzeneazotridiphenylmethane, decomp. 118°, heated in xylene gives a violet solution (the colour fades on keeping) from which $\text{CH}(\text{C}_6\text{H}_5\text{Ph})_3$ (IX) is isolated; decomp. in "benzine," b.p. 120—150°, affords C_6H_6 , whilst in C_6H_6 and O_2 , 28% of $[\text{C}(\text{C}_6\text{H}_5\text{Ph})_3\cdot\text{O}\cdot]_2$ (X) results. Diphenylazotridiphenylmethane, m.p. 110° (decomp.), decomposes in xylene to (IX) and Ph_2 ; in C_6H_6 and O_2 , 34% of (X) is formed.

m-Di(triphenylmethylhydrazino)benzene, m.p. 173° (decomp.) [from *m*-C₆H₄(NH·NH₂)₂ and CPh₃Cl in C₆H₅N], is oxidised [alkaline K₃Fe(CN)₆ in CHCl₃] to *m*-di(triphenylmethylazo)benzene, m.p. 127° (decomp.), which in C₆H₆ and O₂ at 72° gives (II), CPh₃·OH, and resinous products; decomp. at 70°/vac. affords C₆H₆ (from C₆H₄ radicals) and CHPh₃. 2:3-Di(triphenylmethylhydrazino)-, m.p. 198°, and 2:3-di(triphenylmethylazo)-, m.p. 148° (decomp.), -naphthalene are similarly prepared. 2:2'-Di(triphenylmethylhydrazino)diphenyl (XI), m.p. 185° (decomp.), is oxidised [K₃Fe(CN)₆] to (probably) the 2-hydrazino-2'-azo-derivative, m.p. 165° (decomp.); decomp. in xylene and subsequent treatment with O₂ gives (II) (= >1 CPh₃ group) and a hydrocarbon (? 2-triphenylmethyl-diphenyl), m.p. 171°. Oxidation (Br-H₂O in CHCl₃) of (XI) affords (probably) 3-bromo-2-triphenylmethylhydrazino-2'-triphenylmethylazodiphenyl, decomp. 139°, which decomposes in xylene to CHPh₃ and a compound, C₃₁H₂₃N₂Br, m.p. 219—220° (darkening) [probably an *o*-phenyleneazine (cf. Tauber, A., 1896, i, 686)].

α -1-Naphthoyl- β -triphenylmethylhydrazine, m.p. 187° (decomp.), is oxidised (aq. CaOCl₂ in CHCl₃ or Et₂O) to α -naphthoylazotriphenylmethane, m.p. 59° (decomp.), which decomposes readily in C₆H₆ and N₂ at 30—35° to give (after atm. oxidation) α -naphthoyltriphenylmethane (XII), m.p. 176° (also formed in absence of solvent), and in C₆H₆ and O₂ to (II), (XII), and α -C₁₀H₇·CO₂H. β -Naphthoylazotriphenylmethane, m.p. 65° (decomp.) [hydrazo-derivative, m.p. 173° (decomp.)], similarly affords β -naphthoyltriphenylmethane, m.p. 202°, alone or with (II) and β -C₁₀H₇·CO₂H; decomp. in C₆H₆+ (IV) at 50—70° gives quinhydrone. Succinatriphenylmethylhydrazide, m.p. 241° (decomp.) [from (·CH₂·CO·NH·NH₂)₂ and CPh₃Cl in aq. C₅H₅N], is oxidised (CaOCl₂) to succinylbisazotriphenylmethane, m.p. 81—82° (decomp.), which decomposes in C₆H₆ and N₂ at 20—50° to β -diketo- $\alpha\alpha\alpha\zeta\zeta$ -hexaphenylhexane, m.p. 220°, also formed with (II) in C₆H₆+O₂. Terephthal-, m.p. 221° (decomp.), and *ox*-, m.p. 247° (decomp.), -triphenylmethylhydrazide and terephthalylbisazotriphenylmethane, m.p. 92° (decomp.), are similarly prepared. *Et* *p*-triphenylmethylhydrazinobenzoate, m.p. 152—153° (from *Et* *p*-hydrazinobenzoate, m.p. 115—116°, and CPh₃Cl in C₅H₅N), is oxidised (Br-H₂O in Et₂O) to *p*-carbethoxybenzeneazotriphenylmethane, m.p. 107° (decomp.). β -Phenylpropionylazotriphenylmethane, m.p. 55—56° (decomp.), undergoes fission to β -phenylethyl triphenylmethyl ketone, m.p. 135°; in C₆H₆+O₂, (II), CH₂Ph·CH₂·CO₂H, and a little PhOH are also formed. Cinnamatriphenylmethylhydrazide, m.p. 182° (decomp.), is oxidised directly to CHPh·CH·CO·CPh₃ (XIII) by Br-H₂O; with CaOCl₂, (XIII) and a Cl-containing compound, m.p. 185—186°, result. Phenylpropionylazotriphenylmethane, m.p. 70° (decomp.), is prepared by oxidation [K₃Fe(CN)₆] of phenylpropionyltriphenylmethylhydrazide, m.p. 158—159° (from CPh·C·COCl and CPh₃·NH·NH₂ in Et₂O).

Benzoylhydrazinodiphenylmethane, m.p. 179—180°, from NHBz·NH₂ and CHPh₃Br in C₅H₅N, is oxidised (I in Et₂O-CHCl₃) to benzoylazodiphenylmethane, m.p. 96—98° (decomp.) (which rearranges in PhMe at 100° to CPh₂·N·NHBz), thermal decomp. of which gives N₂ (75%) and a substance, C₂₂H₂₂O₂·N₂, m.p. 257—259°

(decomp.). Acetylhydrazinodiphenylmethane, m.p. 137°, is oxidised (Br-H₂O in CHCl₃) to CPh₂·N·NHAc; phenylhydrazinodiphenylmethane, m.p. 75—76°, could not be oxidised to CHPh₂·N·NPh. H. B.

Decomposition of normal diazotates. Z. E. JOLLES and W. CAMIGLIERI (Atti Congr. naz. Chim., 1933, 4, 491—495).—The reaction 4PhN₂OH = C₂₄H₁₈ON₂+3N₂+3H₂O, which takes place with diazobenzene in alkaline solution, and the corresponding reactions for *p*- and *m*-toluidine (I), *o*- and *p*-anisidine, and *p*-phenetidine (II), were verified by measuring the N₂ evolved. The min. duration of the reactions varied from 3½ to 70 hr., and the N₂ evolved differed considerably from the calc. quantities only for (I) and (II). The observation of Heller (cf. A., 1908, i, 300), that PhN₂Cl in alkaline solution was converted into PhOH, which coupled with more PhN₂Cl to form trisbenzeneazophenol, was not confirmed, the decomp. of PhN₂OH into PhOH or diazo-resin being governed by the alkali concn. R. N. C.

Amphoteric aromatic substitution. I. Reactions of sodium benzenediazoate and nitrosoacetanilide. W. S. M. GRIEVE and D. H. HEY (J.C.S., 1934, 1797—1806).—In the interaction of PhN₂ONa (I) or NPhAc·NO (II) with PhX (X=H, Me, Cl, NO₂, CO₂Et, CHO), mesitylene (III), *m*-xylene (IV), and *o*-C₆H₄Me·NO₂ (V) to give N₂ [and AcOH from (II)] and derivatives of the type Ph·C₆H₄X, Ph substitution always occurs in the *o*- and/or *p*-position to X, irrespective of whether X is a group normally *op*- or normally *m*-directing to cationoid reagents, and the reaction is not appreciably affected by the alkalinity of the medium. Since with (I) (V) gives only 4-nitro-3-methyldiphenyl, and the ratio nitrodiphenyls : methyldiphenyls is 4 : 1 when an equimol. mixture of PhNO₂ and PhMe (both in excess) is employed, substitution occurs more readily *op* to NO₂ than it does *op* to Me. It is suggested that the decomp. of (I) or (II) involves the production of free Ph radicals, which have amphoteric character, functioning as a cationoid or anionoid reagent at the reactive *op*-positions as occasion demands. In agreement with this view the velocity of N₂ evolution from (II) in homogeneous solution in C₆H₆ (461), (IV) (466), PhMe (344), (III) (507), CCl₄ (405), PhOMe (522), PhNO₂ (502), PhCl (400), and AcOH (100) is unimol., the vals. of the unimol. velocity coeffs. (*k* × 10⁵ min.⁻¹), given in parentheses, differing but slightly, since the essential reaction in all cases is the formation of free Ph; a similar mechanism is applied to the decomp. of diazonium salts. Only when (II) decomposes in C₆H₆ or in MeOH (C₆H₆ absent) is Ph₂ obtained, arising, in the latter case, from the reactions: 2Ph + MeOH → 2C₆H₆ + CH₃O (isolated as its 2:4-dinitrophenylhydrazone); Ph + C₆H₆ → Ph₂ + H. Decomp. of (II) occurs in AcOH, H₂O, or CCl₄ to give *p*-OH·C₆H₄·N₂Ph, and in EtOAc, CH₂(CO₂Et)₂, and Et₂O, although in these cases MeCHO is the only product identified. Decomp. of CH₂Ph·NAc·NO in C₆H₆, PhMe, or PhCl occurs only after addition of K₂CO₃. The main products are CH₂Ph·OAc and CH₂·CHPh, a small yield of CH₂Ph₂ (identified by oxidation to CPh₂) being the only definite substitution product isolated. The 2:4-dinitrophenylhydraz-

ones of *p*-methyl-, m.p. 199—200°, and *p*-chloro-, m.p. 184—185°, -benzophenone are prepared. J. W. B.

Esters of sulphurous acid. III. Metallic aryl sulphites. W. VOSS and M. LAX (Ber., 1934, 67, [B], 1916—1919; cf. A., 1931, 462).—Powdered Na and PhOH are allowed to react in xylene and the solution is treated at 0° with SO₂, whereby Na Ph sulphite is pptd. Na β-C₁₀H₇ sulphite is prepared similarly. Both substances are very unstable towards H₂O. Salts of aryl sulphites cannot therefore be intermediates in Bucherer's reaction. H. W.

Rotations of the nitrophenyl esters of disubstituted acetic and propionic acids and of the free acids.—See this vol., 14.

Addition of phenols to aryl[alk]enes. Synthesis of phenylthymol and its isomerides. J. B. NIEDERL and C. H. RILEY (J. Amer. Chem. Soc., 1934, 56, 2412—2414).—Equimol. quantities of CHPh:CHMe (from CHPhEt:OH and a trace of conc. H₂SO₄ at 150°), *o*-cresol, and conc. H₂SO₄ in AcOH give (probably) α-phenyl-β-4-hydroxy-3-methylphenylpropane (I), b.p. 200°/18 mm. (phenylcarbamate, m.p. 178°). α-Phenyl-β-2-hydroxy-5-methylphenylpropane (II), b.p. 215—220°/28 mm. (phenylcarbamate, m.p. 123°), and α-phenyl-β-2(or 4)-hydroxy-4(or 2)-methylphenylpropane ("phenylthymol" or "phenylisothymol") (III), b.p. 200—205°/22 mm. (phenylcarbamate, m.p. 125°), are similarly obtained from *p*- and *m*-cresol, respectively. The PhOH coeffs. (towards *S. aureus*) of (I), (II), and (III) are 59, 82, and < 10, respectively. H. B.

Diphenyl and its derivatives; new asymmetric 2:2'-disubstituted derivatives of diphenyl. L. MASCARELLI and D. GATTI (Atti Congr. naz. Chim., 1933, 4, 503—505).—*o*-Iodoanisole and *o*-C₆H₄I:NO₂ condense in presence of Cu powder to 2-nitro-2'-methoxydiphenyl, m.p. 80—81°, reduced (Sn, HCl) to 2-amino-2'-methoxydiphenyl, m.p. 80—81°. Diazotisation and treatment with KI gives 2-iodo-2'-methoxydiphenyl, m.p. 58—59°, with some diphenyleneiodonium iodide, in accordance with a characteristic reaction of 2-diazo-2'-substituted diphenyls with KI, which occurs when the 2'-substituting group is N₂Cl, NO₂, Cl, Br, I, or OMe, but not Me. 2-Methyl-2'-diazo-diphenyl is, however, decomposed by H₂O to fluorene. R. N. C.

Preparation and germicidal properties of 4-hydroxy-2-methylphenyl alkyl sulphides. C. M. SUTER and J. P. MCKENZIE (J. Amer. Chem. Soc., 1934, 56, 2470—2471).—*m*-C₆H₄Me:OMe and conc. H₂SO₄ (2 mols.) at room temp. give 74—86% of 3-methoxytoluene-6-sulphonic acid [*p*-toluidine salt, m.p. 204—205° (corr.)]; the chloride, b.p. 173—175°/17 mm. (cf. Haworth and Lapworth, A., 1924, i, 848), is reduced (method; Org. Synth., 1921, 1, 71) to 4-methoxy-2-methylthiophenol (I), b.p. 130—132°/22 mm. (cf. Shah *et al.*, A., 1933, 1292) [Bz derivative, m.p. 78—79° (lit. 84°)]. 4-Methoxy-2-methylphenylthiolacetic acid has m.p. 72—73°. 4-Methoxy-2-methylphenyl Me, b.p. 145—147°/26 mm., Et, b.p. 150—151°/23 mm., Pr^a, b.p. 162—163°/22 mm., Bu^a, b.p. 173—175°/23 mm., and *n*-amyl, b.p. 165—167°/15 mm., sulphides, prepared from (I) as previously described (A., 1932, 1244), are demethylated to 4-hydroxy-2-

methylphenyl Me, b.p. 148—151°/15 mm. (13, 12, 10), Et, b.p. 159—163°/20 mm. (20, 50, 40), Pr^a, b.p. 165—170°/20 mm. (23, 80, 80), Bu^a, b.p. 180—186°/27 mm. (14, 100, 80), and *n*-amyl, b.p. 193—197°/24 mm. (8, 250, 200), sulphides, respectively; the nos. quoted in parentheses are the PhOH coeffs. towards *B. typhosus*, *S. aureus*, and *Strep. haemolyticus*, respectively. H. B.

Preparation of veratryl chloride and formation of the 9:10-dihydroanthracene nucleus. P. CARRE and D. LIBERMANN (Compt. rend., 1934, 199, 791—793).—ClSO₂Et is added to veratryl alcohol (I) and C₅H₅N in anhyd. Et₂O and, after removal of C₅H₅N.HCl, SOCl₂ is introduced, whereby ClSO₂Et and SO₂Cl·CH₂·C₆H₃(OMe)₂ are produced, the latter of which when distilled affords SO₂ and 3:4-dimethoxybenzyl chloride (II), b.p. 152—156°/10 mm., m.p. 48—49°, in 60—70% yield. (I) is transformed by conc. HCl mainly into 2:3:6:7-tetramethoxy-9:10-dihydroanthracene (III), m.p. 237°, also obtained through 3:4:3':4'-tetramethoxydiphenylmethane, m.p. about 70°, by the action of CH₂O on veratrole in presence of HCl and ZnCl₂. (II) is stable towards gaseous HCl, but readily converted by conc. HCl into (III), probably owing to hydrolysis to (I). Piperonyl alcohol and conc. HCl give the corresponding chloride and 2:3:6:7-bis(methylenedioxy)-9:10-dihydroanthracene. H. W.

Preparation and germicidal properties of derivatives of 4-*n*-butylresorcinol. M. L. MOORE, A. A. DAY, and C. M. SUTER (J. Amer. Chem. Soc., 1934, 56, 2456—2459).—4-Chlororesorcinol (I), b.p. 147°/18 mm., m.p. 105° (lit. 89°), prepared by Reinhard's method (A., 1878, 276), and SO₂Cl₂ give the 4:6-Cl₂-derivative, m.p. 112—113° (lit. 77° and 101°), which affords the known Me₂ ether. (I) could not be prepared by Clark's method (A., 1933, 270). 4-Butylresorcinol and SO₂Cl₂ in Et₂O give 6-chloro-4-butylresorcinol (II), m.p. 84—85° [also prepared from (I), Pr^aCO₂H, and ZnCl₂ at 125—135°], which with Cl₂ in Et₂O affords the 2:6-Cl₂-derivative, m.p. 124—125°. (II) is reduced (Clemmensen) to 6-chloro-4-*n*-butylresorcinol (III), m.p. 70—71°, also prepared (less satisfactorily) from SO₂Cl₂ and 4-*n*-butylresorcinol (IV) (6-Br-, m.p. 67—68°, and 6-acetoxymercuri-, m.p. 164—165°, -derivatives). (IV) heated with aq. NaHCO₃ in CO₂ gives 2:4-dihydroxy-5-*n*-butylbenzoic acid (V), m.p. 172—173° (decomp.). Mercuration of (III) by Whitmore and Hanson's method (Org. Synth., 1925, 4, 13) affords the anhydro-compound, C₁₀H₁₁O₂ClHg, m.p. > 225°, converted (AcOH) into the 2-acetoxymercuri-, m.p. 153—154°, and thence (aq. EtOH-HCl) into the 2-chloromercuri-derivative (VI), m.p. 144—145°. (II) similarly gives a compound, C₁₀H₉O₃ClHg, m.p. 227—230°, convertible into the 2-chloromercuri-derivative, m.p. 218—220°. (IV) and an excess of Hg(OAc)₂ in EtOH afford a compound, C₁₂H₁₄O₄Hg₂ (?), m.p. > 230°. The m.p. of the Hg derivatives are uncorr.; all others are corr. Of several of the above compounds examined, (VI) possesses the highest PhOH coeff. (towards *B. typhosus* and *S. aureus*); (V) is inactive. H. B.

Relation between chemical constitution and purgative action. A. P. T. EASSON, J. HARRISON,

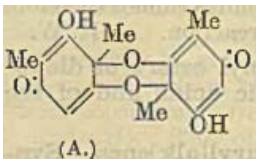
B. A. MACSWINEY, and F. L. PYMAN (Quart. J. Pharm., 1934, 7, 509—513).—Members of the two homologous series di-(*p*-hydroxyphenyl)- and di-(4-hydroxy-3-methylphenyl)-dialkyl-(or -aryl)-methanes were prepared by saturating mixtures of the appropriate aldehyde or ketone and an excess of PhOH or *o*-cresol with dry HCl and keeping at room temp. The following are new: (p-hydroxyphenyl)-*n*-butane, m.p. 124—125°; $\beta\beta$ -di-(p-hydroxyphenyl)-*n*-pentane, m.p. 150°; $\alpha\alpha$ -di-(4-hydroxy-3-methylphenyl)-*n*-heptane, m.p. 86—87°; $\beta\beta$ -di-(4-hydroxy-3-methylphenyl)-*n*-butane, m.p. 145—147°; $\alpha\alpha$ -di-(4-hydroxy-3-methylphenyl)- α -phenylethane, m.p. 142—143°; 1:1-di-(4-hydroxy-3-methylphenyl)cyclohexane, m.p. 191—192°. The (2-)lactones, m.p. 127—129° and 167—168°, respectively, of 2-hydroxy-5-methoxy- and of 2:4-dihydroxy-4':4''-dimethoxy-triphenylacetic acid were prepared by heating benzoic acid with *p*-OH-C₆H₄-OMe and *pp'*-dimethoxybenzoic acid with *m*-C₆H₄(OH)₂, respectively. α -(2-Hydroxy-5-methylphenyl)phthalide, m.p. 171°, was prepared by condensation of *p*-cresol with *o*-C₆H₄(CO)₂O followed by reduction. Most of the above have purgative properties. C. G. A.

Derivatives of 1:2:3:4-tetrahydroxybenzene. III. Synthesis of dill apiole, and extension of the Dakin reaction. W. BAKER, E. H. T. JUKES, and (in part) C. A. SUBRAHMANYAM (J.C.S., 1934, 1681—1684).—Gallacetophenone 3:4-Me₂ ether (improved prep.) is oxidised by 3% H₂O₂ in 10% NaOH in H₂ (Dakin reaction) to 1:2-dihydroxy-3:4-dimethoxybenzene, converted by CH₂:CH-CH₂Br and anhyd. K₂CO₃-COMe₂ into its 2-allyl ether, isomerised at 165° into 1:2-dihydroxy-3:4-dimethoxy-5-allylbenzene, b.p. 160—173°/14 mm. (1:2-Me₂ ether, m.p. 25°, b.p. 145°/12 mm.), converted by CH₂I₂-COMe₂-K₂CO₃ into its 1:2-CH₂O₂-derivative, identical with natural dill apiole. The following are similarly prepared: pyrogallol methylene ether, m.p. 65°, and 7-methoxy-8-acetyl-2-methylchromone, m.p. 161—162° (by Me₂SO₄ on the 7-OH-derivative, A., 1934, 410). The Dakin reaction is readily applicable to OH-aryl ketones; thus resacetophenone with 6% H₂O₂-12% NaOH at 50° in H₂ gives 1:2:4-C₆H₃(OMe)₃ (I); 2:4-C₆H₃(OH)₂-CO-CH₂Ph gives CH₂Ph-CO₂H (II) (95%) and (after methylation) (I); ononetin gives *p*-OMe-C₆H₄-CH₂-CO₂H (60%) and (I); homopiperonylresacetophenone affords β -piperonylpropionic acid (90%), and 2:4-C₆H₃(OH)(OMe)-CO-CH₂Ph gives (II) (50% yield). J. W. B.

Condensation of pyrocatechol with acetone. W. BAKER (J.C.S., 1934, 1678—1681).—The compound C₂₁H₂₄O₄ (Fabinyi *et al.*, A., 1905, i, 591), best obtained by heating together *o*-C₆H₄(OH)₂ (I) (2 mols.), COMe₂ (3 mols.), AcOH, and conc. HCl on a steam-bath at atm. pressure [also from 2 mols. of (I), CO(CH₃COMe)₂ (1 mol.), and AcOH-HCl], is 5:6:5':6'-tetrahydroxy-3:3:3':3'-tetramethylbis-1:1'-spirohydrindene (II) (Me. ether, α -form, m.p. 158°, and β -form, m.p. indef.

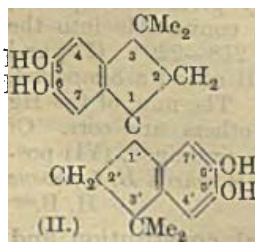
125—158°, with conversion into the α -form), converted by Br-AcOH into its 4:7:4':7'-Br₄-derivative, m.p. 231° (decomp.) (lit., m.p. 130°), which, contrary to the lit., is stable to H₂O at 100°. J. W. B.

Phenol dehydrogenation. V. Dehydrogenation of trimethylphloroglucinol. Structure of cedron. H. ERDTMAN (Svensk Kem. Tidskr., 1934, 46, 226—229).—The observations of Herzog *et al.* (A., 1914, i, 295) on cedron (I), C₁₈H₂₀O₆, the product of dehydrogenation of trimethylphloroglucinol with FeCl₃, are confirmed, but their structural conclusions do not accord with the facile reductive fission of (I), which is best represented as (A) and its tautomeric form, a mechanism of formation being suggested. The acidity is due to the system CO-C'C-OH. J. W. B.



Effect of strain in cycloalkylcarbinols on their reactivity with benzene in presence of aluminium chloride. R. C. HUSTON and K. GOODENOUGH (J. Amer. Chem. Soc., 1934, 56, 2432—2434).—cyclo-Hexylcarbinol (1 mol.), C₆H₆ (4—5 mols.), and AlCl₃ (0.66 mol.) at 75—80° give 7% of cyclohexylphenylmethane (I), b.p. 239.5—241.5°/736 mm.; cyclopentylcarbinol similarly affords 45% of cyclopentylphenylmethane (II), b.p. 234.5—236°/736 mm., and some di(cyclopentylmethyl)benzene, m.p. 101.5—102°. (I) and (II) are not similarly produced at 25—35°. cycloButylcarbinol gives 29 and 21% of cyclobutylphenylmethane (III), b.p. 218—219°/736 mm., at 25—35° and 75—80°, respectively. The reactivity of the carbinols decreases (in accordance with expectation) with increase in the size of the ring; when the strain is min. the reactivity is of the same order as that of CH₂Alk-OH. The mol. vols., parachors, and mol. refractions of (I), (II), (III), and allylbenzene are given. H. B.

Purification of alcohols through their *p*-nitrobenzoates. *cis*-2-Decahydronaphthol. W. HUCKEL and K. KUMETAT (Ber., 1934, 67, [B], 1890—1893).—Difficulties are met in the purification of alcohols through their *p*-nitrobenzoates (I), since hydrolysis frequently occurs unexpectedly slowly, the small amounts of regenerated alcohol are contaminated with ketone, and the liquid is coloured yellow to red by azoxy- or azo-compounds. These are avoided by reducing (I) by H₂ in presence of EtOH-HCl-PtO₂ to the NH₂-derivatives, which are hydrolysed by alkali. The separation of *cis*-, m.p. 18° (II), and *trans*-2- (III), m.p. 53°, from *trans*-2- (IV), m.p. 75°, -decahydronaphthol is described. (II) gives a *p*-nitrobenzoate, m.p. 77°, *p*-aminobenzoate, m.p. 155° [hydrochloride, m.p. 216° (decomp.)], and *H* succinate, m.p. 59°. (III) yields a *p*-nitrobenzoate, m.p. 112°, *p*-aminobenzoate, m.p. 118° [hydrochloride, m.p. 167—168° (decomp.)], and *H* succinate, m.p. 64°. The *p*-nitrobenzoate, m.p. 141°, and *p*-aminobenzoate, m.p. 103—104° [hydrochloride, m.p. 211—213° (decomp.)], of (IV) are described. *trans*-1-Decahydronaphthol, m.p. 49°, yields a *p*-aminobenzoate, m.p. 143° (hydrochloride, m.p. 180—182° (decomp.)). (II) exists in two forms, m.p. 18° and m.p. 31°, respectively, which very slowly pass into one another. Since they do not behave as nuclei, the



difference is not attributable to polymorphism and the existence of *d*+*l*- and *r*-forms is suggested. (II), almost free from (IV), is obtained by isomerisation of *cis*-2-decahydronaphthol, m.p. 105°, at 105–110° for 1 hr. in presence of Cu chromite and H₂ at 30 atm., whereby a mixture of *cis*-compounds readily separable through their H phthalates is produced. At 160° (IV) is also formed.

H. W.

***p*-Nitrobenzyl esters of organic acids.** T. L. KELLY and M. SEGURA (J. Amer. Chem. Soc., 1934, 56, 2497).—*p*-Nitrobenzyl glutarate, m.p. 69°, adipate, m.p. 105.6°, suberate, m.p. 85°, azelate, m.p. 43.8°, itaconate, m.p. 90.6°, diphenate, m.p. 182.6°, *o*-benzoylbenzoate, m.p. 100.4°, *p*-cyanobenzoate, m.p. 189.2°, 3 : 5-dinitrobenzoate, m.p. 156.8°, *o*-bromobenzoate, m.p. 109.8°, *m*-chlorobenzoate, m.p. 107.2°, and *o*-, m.p. 110.8°, *m*-, m.p. 121°, and *p*-, m.p. 140.6°, -iodobenzoates are prepared by Reid's method (A., 1917, i, 333). Cryst. esters were not obtained from hexoic, octoic, nonoic, and decoic acids.

H. B.

Synthetic ephedrine [isomeride]. J. LAM-BILLON (Bull. Soc. chim., 1934, [v], 1, 1411–1416).—CH₂Ph·MgCl reacts with CH₂Cl·CHCl·OEt to give [with (·CH₂Ph)₂] β-chloro-α-benzylethyl Et ether, b.p. 125°/12 mm., converted by the appropriate alkylamine at 100–110° into the corresponding β-methylamino-, b.p. 120–122°/12 mm. (hydrochloride; aurichloride) {together with some [OEt·CH(CH₂Ph)·CH₂]₂NMe, b.p. 220°/12 mm.}, β-ethylamino-, b.p. 126°/vac., β-dimethylamino-, b.p. 123–124°/12 mm., and β-diethylamino-, b.p. 147°/20 mm., -derivatives. These are converted by HBr (*d* 1.78) at 75° into ephedrine analogues of the type CH₂Ph·CH(OH)·CH₂·NHR, and thus are obtained β-hydroxy-γ-phenylpropyl-methyl-, b.p. 137–138°/12 mm. (hydrochloride), and -ethylamine, b.p. 146–148°/12 mm. (hydrochloride).

J. W. B.

Condensation of rosaniline with 1-chloro-2 : 4-dinitrobenzene. A. E. PORAI-KOSCHITZ and E. I. MANDELSCHTAM (J. Gen. Chem. Russ., 1934, 4, 842–846).—Rosaniline and 1 : 2 : 4-C₆H₃Cl(NO₂)₂ in AcOH or C₆H₅N give 4 : 4'-diamino-2'' : 4''-dinitrophenyl-fuchsonimide (I), m.p. 168–170° (98% yield), when heated for 5 hr. at 180–200°. (I) affords the corresponding 2'' : 4''-diamine (II), m.p. indef., on reduction (SnCl₂ or Zn–AcOH). (II) is an intense fast violet dye for wool, silk, or cotton (tannin).

R. T.

New isomeride of cholesterol. R. DE FAZI (Atti Congr. naz. Chim., 1933, 4, 476–480; Chem. Zentr., 1934, ii, 257).—The substance, m.p. 141–143°, obtained by heating cholesterol (I) hydrochloride (m.p. 136–137°) with NaOAc in EtOH is now established as an isomeride of (I). It is also produced with allocholesterol (II) by the action of NaOAc on the hydrochloride, m.p. 124–126° (A., 1933, 710). From both hydrochlorides HCl is eliminated from adjacent C atoms yielding the same isomeride. Similarly (II) is obtained from the two hydrochlorides, m.p. 158.5° and 124–126°.

A. G. P.

Structure of cholesterol. M. VANGHELOVICI (Chem. and Ind., 1934, 998).—Comparison of the structures of cholesterol (I) and squalene suggests that the second Me is at 9. The synthesis of (I) in the animal organism probably follows the course : carbohydrates

→ saturated fatty acids → unsaturated fatty acids → polyisoprenic-carotenoid compounds → (I). H. W.

Photochemistry of ergosterol. O. LINSERT (Med. u. Chem. Abh. med.-chem. Forsch. I.G. Farben-ind., 1934, 2, 281–287; Chem. Zentr., 1934, i, 3615).—A review.

R. N. C.

cycloPropane derivatives, and their reactions, in particular those of isomerisation. N. J. DEMJANOV (J. Gen. Chem. Russ., 1934, 4, 762–777).—A review of the lit. is given.

R. T.

New products of condensation of glycerol with aromatic compounds. P. P. SOHORIGIN and A. T. SMIRNOV (J. Gen. Chem. Russ., 1934, 4, 830–833).—Glyceryl α-2 : 4 : 6-trinitrobenzoate, m.p. 140–142°, prepared from C₆H₂(NO₂)₃·COCl and glycerol (I), yields C₆H₃(NO₂)₃·OH and (I) on hydrolysis with aq. KOH, whilst on nitration glyceryl α-2 : 4 : 6-trinitrobenzoate βγ-dinitrate, m.p. 123°, is obtained. The prep. of the corresponding α-picrate is described. Phenyl-βγ-dihydroxypropylamine, m.p. 40–42°, b.p. 200–203°/7–8 mm., is prepared by boiling glyceryl monochlorohydrin in NII₂Ph; under analogous conditions, CH₂Cl·CH₂·OH yields NPh·C₂H₄·OH and (NPh·CH₂)₂.

R. T.

Synthesis of tetrahydronaphthalenecarboxylic acids and naphthalenic hydrocarbons. G. DARZENS and A. LÉVY (Compt. rend., 1934, 199, 1131–1133).—Successive treatment of CHPh(CO₂Et)₂ with Na in PhMe and crotyl bromide in EtOH gives Et₂phenylcrotylmalonate, b.p. 160–162°/2 mm., hydrolysed to the corresponding non-cryst. acid, which passes at 180° into phenylcrotylacetic acid (I), m.p. 55°, b.p. 158°/3 mm. (I) is very slowly converted by 85% H₂SO₄ at room temp. (rise of temp. causes sulphonation) into 4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-1-carboxylic acid, m.p. 87°, which could not be dehydrogenated by S or Se without simultaneous loss of CO₂ with production of 1-C₁₀H₇Me.

H. W.

Action of acetic anhydride on β-naphthamidrazone. H. GOLDSTEIN and F. CHASTELLAIN (Helv. Chim. Acta, 1934, 17, 1481–1482).—β-C₁₀H₇·NH₂ is transformed into β-C₁₀H₇·CN (improved method), converted by HCl in EtOH into Et imino-β-naphthoate hydrochloride (I) in 85% yield. Successive treatment of (I) with NaOH and N₂H₄·H₂O gives β-naphthamidrazone (II), C₁₀H₇·C(NH)₂·NH·NH₂ or C₁₀H₇·C(NH₂)₂·N·NH₂, which, contrary to Pinner, does not give β-C₁₀H₇·NH·NH₂ under the influence of Ac₂O. (II) and cold Ac₂O containing NaOAc give a Ac₂ derivative, C₁₇H₁₇O₃N₃, m.p. 186°, which passes when heated into AcOH and acetyl-β-naphthylmethyltriazole, m.p. 135°.

H. W.

α-Naphthylacetic acid. A. HIGGINBOTTOM and W. F. SHORT (Rec. trav. chim., 1934, 53, 1141).—Crystallisation (from C₆H₆) of the acids obtained by oxidation (KMnO₄ in aq. EtOH at –1° to 0°) of 1-allylnaphthalene gives α-C₁₀H₇·CO₂H (I) and a mixture, m.p. about 106° (cf. Keach, A., 1933, 948), of α-naphthylacetic acid (m.p. 132°, when regenerated from the anilide, m.p. 156°) and 10–20% of (I).

H. B.

Knoevenagel reaction. H. LOHAUS (Annalen, 1934, 514, 137–144).—Exposure of a solution of

stable Et cinnamylidenecyanoacetate (I) in EtOH containing a little H_2SO_4 to sunlight (in Pyrex glass) gives the labile form (II), since further exposure of the cryst. material recovered affords the cyclobutane derivative (III), m.p. 125° , of Reimer (A., 1911, i, 447; 1913, i, 1060); in EtOH alone, (I) similarly gives the open-chain dimeride (IV), m.p. 165° , of Reimer (*loc. cit.*). Rapid conversion of (II) into (I) occurs when its solution in EtOH-I is exposed to sunlight (in quartz). $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ (0.2 g.-mol.), $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (0.2 g.-mol.), EtOH (20 c.c.), and piperidine (V) (1 drop) at $30\text{--}35^\circ$ (heat of reaction) give 71.5% of (I) [converted into (IV)]; twenty-fold increase in the amount of (V) results in a reaction temp. of 65° and a 60.4% yield of (II) [convertible into (III)]. Condensation occurs very slowly in presence of $\text{C}_5\text{H}_5\text{N}$ and gives (I) (80.5% yield). An 11.6% yield of (I) (?) is obtained in the absence of condensing agent after 20 months. These results conform to the "regulating law" of Skrabal (A., 1912, ii, 33; 1922, ii, 488). Prolonged interaction of PhCHO , $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and (V) in the cold gives the labile $\text{CHPh}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ (VI) (Bertini, A., 1901, i, 537); when the reaction mixture is made homogeneous with EtOH and kept at room temp. for 8 weeks the stable form (VII), m.p. 51° , begins to separate. (V) is considered to effect the change $(\text{VI}) \rightarrow (\text{VII})$. The production of (VII) using (V) in EtOH at $15\text{--}25^\circ$ or $45\text{--}48^\circ$ (according to the amount) or $\text{C}_5\text{H}_5\text{N}$ (no solvent) probably involves the rapid rearrangement of the intermediate (VI).

H. B.

5-Chloroveratrylidenehippuric acid and some of its derivatives. R. M. HANN (J. Washington Acad. Sci., 1934, 24, 464—466).—Hippuric acid and 5-chloroveratraldehyde with $\text{NaOAc}\cdot\text{Ac}_2\text{O}$ give 5-chloroveratrylidenehippuric acid azlactone, m.p. 161° , hydrolysed (NaOH) to 5-chloroveratrylidenehippuric acid (I), m.p. 192° (Me, m.p. 135° , and Et ester, m.p. 104° ; amide, m.p. $213\text{--}214^\circ$, and corresponding imide, m.p. $286\text{--}287^\circ$). All m.p. except that of (I) are corr.

H. G. M.

Chaulmoogric acids and their derivatives. L. TAUB (Med. u. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 295—302; Chem. Zentr., 1934, i, 3765).—Chaulmoogric acid undergoes decomp. on keeping even when pure, yellowing and forming HCO_2H . The Et ester is stable indefinitely. Hydno-carpic acid also decomposes on keeping. The use of mixed benzyl esters of the total fatty acids of chaulmoogra and hydnocarpus oils ("Antileprol By") is an improvement on the use of the Et esters.

J. S. A.

Influence of cyclisation on the colour of molecules. (MME.) RAMART-LUCAS (Bull. Soc. chim., 1934, [v], 1, 1133—1148).—The colour change which accompanies the cyclisation of an open-chain compound may be due to (1) changes in the chromophores due to an isomerisation or intramol. reaction, (2) an alteration in the relative positions of the chromophores, or (3) a change due to cyclisation alone. The change may be either bathochromic or hypsochromic and can be predicted in some cases.

The absorption spectra of phthalide, its mono- and di-aryl derivatives, of phthalin, its Me ether and Na

salt are discussed. On passing from an acyclic to a cyclic mol. containing one chromophore, if the chromophore is not modified and the valency angles remain about normal, the change of absorption should be small. The position of max. absorption of the following pairs of ketones is about the same: COEt , and cyclohexanone; COMeBu^r and camphor; COBu^r_2 and fenchone. The change from $\text{A}(\text{CH}_2)_n\text{B}$ (V)

($n > 1$) to $(\text{CH}_2)_n\text{A}'\text{B}'$ (VI) should be analogous to

that on passing from $(\text{EtA}+\text{EtB})$ (VII) to $\text{Et}\cdot\text{A}'\cdot\text{B}'\cdot\text{Et}$ (VIII). If the absorptions of (V) [or (VII)] and (VIII) are known, that of (VI) can be predicted approx. Thus since the esterification of phenols produces a hypsochromic effect, the same effect should be observed on passing from coumaric acid to coumarin, and the curves for these substances show that this is the case. Similar predictions are verified by the curves for $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (IX), NHPhAc (X), and oxindole (XI), [(IX) \rightarrow (XI), hypsochromic; (X) \rightarrow (XI), bathochromic] and for allylbenzene, isallylbenzene, and indene.

F. S. H. H.

Reaction between α -ketonic acids and α -amino-acids. R. M. HERBST and L. L. ENGEL (J. Biol. Chem., 1934, 107, 505—511).—In H_2O at 100° α -ketonic acids react with $\alpha\text{-NH}_2$ -acids thus: $\text{COR}\cdot\text{CO}_2\text{H}+\text{NH}_2\cdot\text{CHR}'\cdot\text{CO}_2\text{H}\rightarrow\text{CO}_2\text{H}\cdot\text{CR}\cdot\text{N}\cdot\text{CHR}'\cdot\text{CO}_2\text{H}\rightarrow\text{CO}_2\text{H}\cdot\text{CHR}\cdot\text{N}\cdot\text{CR}'\cdot\text{CO}_2\text{H}\rightarrow\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}+\text{R}'\cdot\text{CHO}+\text{CO}_2$. Such action between AcCO_2H and $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (I) [PhCHO , alanine (II), CO_2], glycine [CH_3O , $\text{CHO}\cdot\text{CO}_2\text{H}$, (II), CO_2], phenylalanine (III) [$\text{CH}_2\text{Ph}\cdot\text{CHO}$, (II), CO_2], *L*-aspartic acid, and *L*-cystine [both giving MeCHO , (II), CO_2] is investigated quantitatively, the isolated products being given in brackets. No action occurs with $\text{NHMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ or $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ (IV) and (I) afford PhCHO , CO_2 , and (III), and α -keto- γ -hydroxy- β -diphenylvalerolactone, obtained by self-condensation of (IV).

J. W. B.

cycloHexanedicarboxylic acids of the tartaric acid type. W. HUCKEL and U. LAMPERT (Ber., 1934, 67, [B], 1811—1816).—Et cyclohexanone-2-carboxylate is transformed by the successive action of NaCN and HCl into 1-hydroxycyclohexane-1:2-dicarboxylic acid (I), m.p. 178° , in 30% yield. The non-cryst. acid simultaneously obtained passes when distilled in vac. into Δ^1 -tetrahydro-*o*-phthalic anhydride (II), m.p. 74° , which is not obtained when homogeneous (I) is distilled, but is formed in 70% yield from (I) and Ac_2O . (II) is transformed by aq. Na_2CO_3 followed by AgNO_3 into *Ag*, Δ^1 -tetrahydro-*o*-phthalate, whence Et, Δ^1 -tetrahydro-*o*-phthalate, b.p. $147^\circ/10\text{ mm.}$ (I) and AcCl give 1-acetoxycyclohexane-1:2-dicarboxylic anhydride, m.p. 98° (corresponding acid, m.p. 141°). The action of $\text{Cl}_2\text{--H}_2\text{O}$ on (II) dissolved in NaOH , followed by addition of AcOH and $\text{Pb}(\text{OAc})_2$, leads to the salt, $\text{C}_8\text{H}_9\text{O}_5\text{ClPb}$, whence by means of conc. H_2SO_4 in EtOH, 1-chloro-2-hydroxycyclohexane-1:2-dicarboxylic acid (III), m.p. 186° , is obtained. (III) is very readily transformed by H_2O into 1:2-dihydroxycyclohexane-1:2-dicarboxylic acid [cis-form (IV), m.p. 184° , not resolved by bases; trans-variety, m.p. 178° (decomp.)], which with brucine in EtOH

yields a *brucine* salt, m.p. 237°, whence a *d*-acid, m.p. 182°, and a *brucine* salt, m.p. 226°, whence an *l*-acid]. Treatment of (III) with dil. NaOH leads to non-cryst. 1:2-oxidocyclohexene-1:2-dicarboxylic acid (V) (*Ba*, *Pb*, and *fenchylamine*, m.p. 176°, salts). (V) and H₂O give only (IV), whereas (V) and HCl-Et₂O yield (III). (III) and warm AcCl afford 1:2-diacetoxycyclohexane-1:2-dicarboxylic anhydride (VI), m.p. 174°, 1:2-diacetoxycyclohexane-1:2-dicarboxylic acid (VII), m.p. 200°, and (?) 1-chloro-2-acetoxycyclohexane-1:2-dicarboxylic acid, m.p. about 160°. (VI) and (VII) are also obtained from the stereoisomeric (OH)₂-acids with Ac₂O or AcCl and (VI) from (VII) by AcCl. H. W.

Isatogens and indoles. XV. *m*-Phenylenediacrylic acid. P. RUGGLI and A. STAUB (Helv. Chim. Acta, 1934, 17, 1523—1527).—*m*-C₆H₄(CHO)₂ is converted by prolonged treatment with NaOAc and Ac₂O at 150° into *m*-phenylenediacrylic acid (I), m.p. 280° (slight decomp.). Alternatively, CHCl(CO₂Et)₂ is treated successively with NaOEt and *m*-C₆H₄(CH₂Br)₂, giving essentially Et₂ *m*-xylylene-dichloromalonate, hydrolysed and decarboxylated to non-cryst. *m*-xylylenedi- α -chloropropionic acid, which is transformed by boiling KOH-H₂O into (I) [Me₂, m.p. 132°, and Et₂, m.p. 53.5°, esters]. H. W.

Rotenone. XXXI. Synthesis of 2-hydroxy-4:5-dimethoxyphenylacetic acid. L. E. SMITH and F. B. LAFORGE (J. Amer. Chem. Soc., 1934, 56, 2431).—The *azlactone*, red and yellow forms, m.p. 168°, from 4:5-dimethoxy-2-methoxy-methoxybenzaldehyde, m.p. 61° [from 2:4:5-C₆H₂(ONa)(OMe)₂-CHO and CH₂Cl-OMe in PhMe], is converted by successive hydrolysis (10% KOH), oxidation (H₂O₂), and steam distillation (of mixed acids to remove BzOH) into 2-hydroxy-4:5-dimethoxyphenylacetic acid, m.p. 138°. H. B.

Acetoacetic ester condensation. IX. Condensation of ethyl γ -isobutyryl- β -phenylpropane- α -dicarboxylate. R. F. B. COX and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 2459—2463).—Styryl Pr⁸ ketone (I) (0.34 mol.), CH₂(CO₂Et)₂ (II) (0.34 mol.), and EtOH-NaOEt (0.03 mol.) give Et γ -isobutyryl- β -phenylpropane- α -dicarboxylate (III), b.p. 192—194°/7 mm., m.p. 42°, which with an equimol. amount of NaOEt at 125—130°/vac. (cf. A., 1934, 756) affords COMePr⁸ and CHPh:C(CO₂Et)₂ (retrograde Michael) (II), Pr⁸CO₂Et, CHPh:CH-CO₂Et (IV), Pr⁸CO-CH₂-CO₂Et (V), 5-phenyl-2:2-dimethylcyclohexane-1:3-dione (VI) (Dieckmann and Kron, A., 1908, i, 388), and (probably) two diisobutyryldiphenylcyclobutanes, m.p. 155° (VII) and 180° (VIII) [presumably formed by dimerisation of (I)]. (III) is considered to undergo an internal acetoacetic ester condensation to Et 5-phenyl-2:2-dimethylcyclohexane-1:3-dione-4-carboxylate, which is then degraded to (VI), (IV), and (V); the results substantiate for the mechanism previously suggested (*loc. cit.*) for the acetoacetic ester condensation. (VI) is also obtained when Et 5-phenyl-2:2-dimethylcyclohexane-1:3-dione-4:6-dicarboxylate is heated with BzOH at 150°. (VII) is converted by Ac₂O at 140° into (VIII) and an isomeride, m.p. 182°; (VIII) is similarly unaffected. α -Methylstyryl Pr⁸ ketone, b.p. 140—141°/

12 mm., is prepared in 12% yield by Rupe and Hirschmann's method (A., 1931, 1050). H. B.

Sulphite liquor lactone and tsuga-resinol. H. EMDE and H. SCHARNER (Naturwiss., 1934, 22, 743—744).—The sulphite liquor lactone of Holmberg, m.p. 256° (decomp.), [α]_D²⁰ -54.5° in COMe₂, is identified with Kawamura's tsuga-resinol and to it is assigned the constitution $\begin{array}{c} \text{CH}_2\text{R}-\text{CH}-\text{CO} \\ \text{CH}_2\text{R}-\text{CH}-\text{CH} \end{array} > \text{O}$ [R=3:4-C₆H₃(OMe)-OH]. It is regarded as derived through a dehydrolactone by dimerisation and Cannizzaro reaction from coniferaldehyde. H. W.

Lichen substances. XLIV. Salazinic and norstictic acid. XLV. Identity of coccellic acid with barbatric acid. Y. ASAHINA and F. FUJIKAWA (Ber., 1934, 66, [B], 1789—1792, 1793—1795).—XLIV. Very mild treatment of norstictic acid (I) with KOH-K₂CO₃ yields K₂ norstictinate (+3H₂O), from which (I) is regenerated by dil. HCl at 0°. Salazic acid (II) similarly affords K₂ salazinate (+3H₂O), re-forming (II) when treated with dil. HCl. Similarity of absorption spectra indicates similar results with salazic acid α -Me ether (III). The formation of red crystals on treatment with KOH appears to depend on the presence of free phenolic OH *o*- to CHO and of a lactol group in the second nucleus. Action of more conc. KOH on the red crystals leads to dark red or brown resins. The red salts are best represented by A [R= Me, -CH₂-OH, and -CH₂-OMe, respectively, in the cases of (I), (II), and (III)].

XLV. Exhaustive extraction of the thalli of *Cladonia amaurocraea* with Et₂O gives *l*-usnic acid, m.p. 203°, [α]_D²⁵ -487° in CHCl₃, and coccellic acid (I), C₁₉H₂₀O₇ (instead of C₂₀H₂₂O₇), m.p. 186—187°, proved identical with barbatric acid by comparison of the Me esters, m.p. 173°. Alkaline hydrolysis of (I) affords CO₂, β -orcinol, and rhizonic acid, with which the coccellic acid of Hesse is probably identical. H. W.

Condensation of acraldehyde with cyclohexyl and aromatic rings. E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1934, 4, 866—870).—Hexahydrobenzaldehyde and MeCHO in aq. COMe₂ in presence of KOH at 70° yield hexahydrocinnamaldehyde (I), b.p. 92—94°/4 mm. [semicarbazone, m.p. 179—180° (decomp.); diacetate, b.p. 122—124°/13 mm.], readily polymerising to a glassy product at 100°. (I) is oxidised by KMnO₄ to hexahydrobenzoic acid, whilst Ag₂O affords hexahydrocinnamic acid. Piperonyl-acraldehyde is obtained in 15% yield by Ladenburg's method (A., 1895, i, 42). R. T.

Synthesis of γ -resorcylaldehyde dimethyl ether. D. B. LIMAYE (Proc. Indian Acad. Sci., 1934, A, 1, 163—165).—2:6-Dimethoxyphenylglyoxylic acid and NH₂Ph at 180° give (3—5 min.) the anil, hydrolysed (aq. NaOH) to γ -resorcylaldehyde Me₂ ether, m.p. 98—99°, b.p. 285° (semicarbazone, m.p. 190°; yields 2:6-dimethoxycinnamic acid, m.p. 146—147°), which with AlCl₃ in C₆H₆ at 100° gives

$m\text{-C}_6\text{H}_4(\text{OH})_2$, but under other conditions affords the $\text{OH}\cdot$ and $(\text{OH})_2$ -aldehydes. R. S. C.

Some phenolic derivatives of lignin. L. LEMMEL (Bull. Soc. chim., 1934, [v], 1, 1082—1085).—The cresols heated at 125° with pine sawdust (previously extracted with $\text{EtOH}\cdot\text{C}_6\text{H}_6$) and a trace of HCl give $o\cdot$, m.p. $220\text{--}225^\circ$, $m\cdot$, m.p. $210\text{--}220^\circ$, and $p\text{-cresol-lignin}$, $\{(\text{C}_6\text{H}_7\text{O})(\text{OMe})(\text{OH})[\text{C}_6\text{H}_3\text{Me}(\text{OH})]\}_x$, decomp. above 165° (Ac_2 derivatives, m.p. $165\text{--}173^\circ$, $160\text{--}165^\circ$, and $140\text{--}150^\circ$, respectively).

F. S. H. H.

Reactions involving ring closure. K. ZIEGLER (Ber., 1934, 67, [A], 139—149).—A lecture.

H. W.

Reactions of *trans*- β -decalone. I. E. LEHMANN and B. KRATSCHELL (Ber., 1934, 67, [B], 1867—1870).—Chlorination of *trans*-2-ketodecahydronaphthalene yields, in addition to much non-cryst. matter, *trans*-3-chloro-2-ketodecahydronaphthalene (I), m.p. 92° , *trans*-dichloro-2-ketodecahydronaphthalene, m.p. 137° , and a hydrocarbon, $\text{C}_{20}\text{H}_{26}$, m.p. 59° . Treatment of (I) with boiling aq. NaOH affords the two forms of *trans*-3-hydroxy-2-ketodecahydronaphthalene, m.p. 84° (II) and m.p. 134° (III), respectively (corresponding oximes, m.p. 183° and m.p. 192° , respectively). (II) is oxidised by KMnO_4 to cyclohexane-*trans*-1:2-diacetic acid, m.p. 167° . Reduction of (III) with $\text{Na}\cdot\text{Hg}$ in $\text{MeOH}\cdot\text{H}_2\text{O}$ affords 2:3-dihydroxydecahydronaphthalene, m.p. 141° . (III) is not acylated by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_6\text{H}_5\text{N}$, which converts it into (II); under similar conditions (II) remains unchanged. (II) with 80% H_2SO_4 at 60° yields *trans*-2-keto- Δ^3 -octahydronaphthalene, b.p. $126\text{--}127^\circ/12\text{ mm.}$ (oxime, m.p. 145°). (I), Na , and $\text{CH}_2(\text{CO}_2\text{Et})_2$ in boiling Et_2O afford *Et*, *trans*-2-ketodecahydronaphthyl-3-malonate, b.p. $162^\circ/0.5\text{ mm.}$, whence the corresponding acid, m.p. $149\text{--}150^\circ$, and *trans*-2-ketodecahydronaphthyl-3-acetic acid, m.p. 93° .

H. W.

Acetophenone- ω -sulphonic acid, and phenylglyoxal- α -sulphonic acids. G. D. PARKES and S. G. TINSLEY (J.C.S., 1934, 1861—1864).—Phenacyl bromide and aq. Na_2SO_3 give the *Na* salt of acetophenone- ω -sulphonic acid, m.p. $73\text{--}75^\circ$ [NH_4 , m.p. 207° , NH_4Ph , m.p. 181° , and $\text{NH}_2\cdot\text{NHPH}$, m.p. 208° (decomp.), salts], which is liberated by passing HCl into the dry Et_2O suspension. By condensation with the appropriate ArN_2Cl are obtained: phenylglyoxal- (I), m.p. 220° (decomp.) [*Ba* salt, m.p. 188° (decomp.)], *p*-bromo- (II), m.p. 240° (decomp.), 2:4-dibromo-, m.p. 245° (decomp.) [*Ba* salt, m.p. 270° (decomp.)], and 2:4:6-tribromo- (III), m.p. 210° (decomp.) (also a labile form), *o*- (IV), m.p. 238° (decomp.), and *p*-nitro-, m.p. 259° (decomp.), 4-bromo-2-nitro-, m.p. 242° (decomp.), *p*-chloro-, m.p. 240° (decomp.), 2:4-dichloro-, m.p. 248° (decomp.), and 2:4:6-trichloro-, m.p. 217° , phenylhydrazone- ω -sulphonic acid, all of type $\text{NHR}\cdot\text{N}\cdot\text{CBz}\cdot\text{SO}_3\text{H}$. With $\text{Br}\cdot\text{AcOH}$ (I) gives successively (II), $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{CBzBr}$, and 2:4- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}\cdot\text{N}\cdot\text{CBzBr}$; (III) with Br gives 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}\cdot\text{N}\cdot\text{CBzBr}$. Similarly are obtained ω -bromophenylglyoxal-*o*-nitro-, m.p. 128° , and 4-bromo-2-nitro-, m.p. 185° , phenylhydrazone [also by excess of

$\text{Br}\cdot\text{AcOH}$ on (IV)]. Similar reactions with Cl_2 give ω -chlorophenylglyoxal-*p*-chloro-, m.p. 133° , 2:4-dichloro-, m.p. 106° , and 2:4:6-trichloro-, m.p. 119° , phenylhydrazone. J. W. B.

Structure of metal ketyls. II. Dissociation of alkali metal pinacولات to metal ketyls in liquid ammonia solution. C. B. WOOSTER. III. Mechanism of reactions with alkyl halides. C. B. WOOSTER and W. E. HOLLAND (J. Amer. Chem. Soc., 1934, 56, 2436—2438, 2438—2442).—II. Decomp. of the product (A) from COPh_2 and Na (1 equiv.) in liquid NH_3 solution with NH_4Cl or NH_4Br gives 5—15% of benzpinacol, indicating that (A) consists largely of $\text{CPh}_2\cdot\text{ONa}$ (I) (cf. Bachmann, A., 1933, 505): $(\text{CPh}_2\cdot\text{ONa})_2 \rightleftharpoons 2\text{CPh}_2\cdot\text{ONa}$. The following results show that the change $2\text{CPh}_2\cdot\text{ONa} \rightarrow \text{COPh}_2 + \text{CNaPh}_2\cdot\text{ONa}$ (II) (cf. A., 1929, 928) occurs to little or no extent. Addition of $\text{CH}_2\text{Ph}\cdot\text{OH}$ (III) [which reacts rapidly (5 min.) with (II)] to (I) does not retard the reaction between (I) and EtBr (approx. 1 equiv.; added after 5 min.); reaction occurs more slowly with approx. 0.1 equiv. of EtBr [which does not promote reaction between (I) and (III)]. The results of Kraus and Bien (A., 1933, 1120) indicate that the anion $\text{CR}_2\cdot\text{O}^-$ exists in liquid NH_3 .

III. MeOAc (or Et_2CO_3) reacts slowly with (I) in liquid NH_3 ; (I) is probably hydrolysed by the ammonolysis products of the ester. Decomp. of (I) in liquid NH_3 by slow addition of EtBr gives 88—99% of COPh_2 (determined as oxime): $2\text{CPh}_2\cdot\text{ONa} + \text{EtBr} \rightarrow \text{COPh}_2 + \text{CPh}_2\text{Et}\cdot\text{ONa} + \text{NaBr}$. Rapid addition of EtBr with stirring affords only 20—45% of COPh_2 . These results indicate that COPh_2 is formed in a secondary reaction, which is suppressed during the rapid decomp. of (I): $\text{CPh}_2\cdot\text{ONa} + \text{EtBr} \rightarrow \text{NaBr} + \text{C}_{15}\text{H}_{15}\text{O}$; $\text{CPh}_2\cdot\text{ONa} + \text{C}_{15}\text{H}_{15}\text{O} \rightarrow \text{COPh}_2 + \text{CPh}_2\text{Et}\cdot\text{ONa}$. Possible side reactions (leading to the production of Et ethers) are discussed; the OEt content of the residue [freed from COPh_2 (19.9%)] from one experiment is not large enough to account for the diminution in the yield of COPh_2 . The reaction mechanism suggested by Schlenk and Weickel (A., 1911, i, 545) is considered to be disproved. The product ($? \text{CPh}_2\text{Br}\cdot\text{OEt}$) obtained from $\text{CHPh}_2\cdot\text{OEt}$ and Br in Et_2O in presence of light (Hg -vapour lamp) gives $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ when treated with $\text{NH}_2\cdot\text{OH}$ in alkaline solution. CPh_3 does not react with EtBr in liquid NH_3 . H. B.

Action of Grignard reagents on desyl chloride.

I. Aryl Grignard reagents. R. ROGER and A. MCGREGOR (J.C.S., 1934, 1850—1853).— CHPhClBz (I) and MgPhBr in Et_2O give mainly $\text{CHPh}_2\cdot\text{CPh}_2\cdot\text{OH}$ and some CHPh_2Bz ; $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ gives $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHPhBz}$ and a substance (?) $\text{C}_{22}\text{H}_{22}\text{O}_3$ (II), m.p. 185° , converted by heating at $130^\circ/\text{vac.}$ into a mixture, m.p. $45\text{--}75^\circ$, from which Bz_2 and CH_2PhBz (III) are isolated. With $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (I) gives (II) and a mixture which seems to contain $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHPhBz}$. Mechanisms are discussed, and since the intermediate formation of $\text{CPh} > \text{O}$ may be involved, the following attempts were made to prepare it from (I) (Madelung *et al.*, A., 1932, 62). (I) with KOH gives only $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ and (III), converted

by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (IV) into *phenyl-p-tolylbenzyl-carbinol*, m.p. 89.5—90.5°. (I) with $(\text{CH}_3\cdot\text{OH})_2$ and moist Ag_2O gave bidesyl and a little $\text{CHPhBz}\cdot\text{OH}$. Distillation of α -methoxy- $\alpha\beta$ -diphenyloxan in CO_2 at atm. pressure gives MeOH , Bz_2 , and a substance, m.p. 48—49°, converted by (IV) into a substance, m.p. 142—143°. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHPhBz}$ boiled with (IV) gives $\alpha\beta$ -diphenyl- $\alpha\beta$ -di- p -tolylethan- α -ol, m.p. 195—196°.

J. W. B.

Reactivity of unsymmetrical distyryl ketones. W. P. JENNINGS and A. MCGOOKIN (J.C.S., 1934, 1741—1742).—By condensation of the appropriate styryl Me ketone and substituted PhCHO are obtained 4'-hydroxy-2-methoxy-, m.p. 137°, 3:4'-dimethoxy-, m.p. 77—78°, 3- (I), m.p. 167°, and 4-chloro-4'-hydroxy- (II), m.p. 200—201°, and 3- (III), m.p. 115.5°, and 4-chloro-4'-methoxy- (IV), m.p. 157—157.5°, distyryl ketone. Condensed with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (I), (II), (III), and (IV) give, respectively, *Et* 3- p -hydroxyphenyl-5-m-, m.p. 202° (*Me* ether, m.p. 121°), and -5- p -chlorostyryl-, m.p. 200°, *Et* 3-m-, m.p. 123°, and 3- p -chlorophenyl-5- p -methoxystyryl-, m.p. 128°, Δ^6 -cyclohexen-1-one-2-carboxylate. J. W. B.

Stereoisomerism of indones. R. DE FAZI (Atti Congr. naz. Chim., 1933, 4, 481—482).—By the action of dry Cl_2 on a CHCl_3 solution of β -phenyl- α -ethylindone at -5° to -10° are obtained two stereoisomeric $\alpha\beta$ -dichloro- β -phenyl- α -ethylhydrindones, m.p. 92—94° and 115—116°, respectively. Similarly from β -phenyl- α -methylindone are obtained two $\alpha\beta$ -dichloro- β -phenyl- α -methylhydrindones, m.p. 92—93° and 110—111°, respectively. They are racemised by boiling with Cu in MeOH for 45 min. R. N. C.

α -Oximino- and α -amino-derivatives of o -hydroxypropiofenone. H. L. MASON (J. Amer. Chem. Soc., 1934, 56, 2499—2500).— $o\text{-OBz}\cdot\text{C}_6\text{H}_4\cdot\text{COEt}$, $\text{BuO}\cdot\text{NO}$, and HCl in Et_2O give o -benzoyloxyphenyl α -oximinoethyl ketone, m.p. 100—101°, which is hydrolysed (aq. $\text{EtOH}\cdot\text{NaOH}$) to the o -OH-derivative, m.p. 85—88°, and reduced (method: Hartung and Munch, A., 1929, 1066) to o -benzoyloxyphenyl α -aminoethyl ketone, m.p. 112—114° [hydrochloride (+0.5H₂O), decomp. 180°]. H. B.

Friedel-Crafts type reactions on diphenyl. S. L. SILVER and A. LOWY (J. Amer. Chem. Soc., 1934, 56, 2429—2431).— Ph_2 or $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{COMe}$, AcCl , and AlCl_3 give 4:4'-diacetyldiphenyl. $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ (I) is similarly prepared using 1 mol. of $\text{CH}_2\text{Cl}\cdot\text{COCl}$ (II) or $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$; with an excess of (II), 4:4'-di(chloroacetyl)diphenyl, m.p. 228—229° [oxidised (KMnO_4) to diphenyl-4:4'-dicarboxylic acid and $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$], also obtained from (I) and (II), results. Ph_2 and $(\text{COCl})_2$ give di- p -diphenyl ketone and 4:4'-diphenylbenzil. p -Benzenesulphonyldiphenyl, m.p. 148.5° [oxidised (CrO_3 , AcOH) to $p\text{-PhSO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$], and di- p -diphenyl sulfoxide, m.p. 207—208° [oxidised (10% KMnO_4) to the sulphone], are prepared using PhSO_2Cl and SOCl_2 , respectively. All the reactions are carried out in CS_2 . Complex products are obtained from Ph_2 , $\text{CH}_2\cdot\text{CHCl}$, and AlCl_3 in light petroleum at -5° to 5° . H. B.

New factor controlling certain chelations, with special reference to disubstitution in the res-

orcinol nucleus. W. BAKER (J.C.S., 1934, 1684—1692).—Analysis of the physical and chemical properties of certain diacetylresorcinols indicates that chelation between the carbonyl-O (donor) and the H (acceptor) of the adjacent OH occurs only when the OH and Ac are united to 2 mutually doubly-linked C atoms of the C_6H_6 nucleus (probably dependent on the electromeric effect), thus supplying confirmatory evidence that the aromatic character of C_6H_6 is not dependent on the rapid alternation of double linkings (Mills *et al.*, A., 1931, 83). Thus the 2:4-Ac₂ derivative (I) is doubly chelated, whereas in the 4:6-Ac₂ compound (II), only simple chelation is possible. Such fixation of the position of the double linkings determines the position of further substitution: thus whereas rearrangement of 2-*O*-acetylresacetophenone (no fixation) by AlCl_3 gives only (II) (usual p -migration), the 4-*O*-Ac derivative (double linkings fixed) affords a 45% yield of a mixture containing 58% of (I) (*Me*₂ ether, m.p. 65°, b.p. 187°/15 mm.) and 42% of (II), but on removal of the chelation reversion to p -migration occurs, since the 4-*O*-Ac derivative, m.p. 34°, of resacetophenone 2-*O*-Me ether (*isopæanol*, prep. with *pæanol* from $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ by rearrangement with AlCl_3 in PhNO_2 , or from $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ and MeCN with $\text{ZnCl}_2\cdot\text{Et}_2\text{O}\cdot\text{HCl}$), and subsequent methylation gives only the *Me*₂ ether of (II), the *Me*₂ ether of resacetophenone, and no (I). In the nitrophenols both O of the NO_2 can act as donors in chelation with OH, whether the C atoms, to which the groups are attached, are united by a single or double linking. Thus 2-nitroresorcinol (III) is doubly chelated and no essential difference is observed in the properties of 2:4- and 2:6-dinitroresorcinols. In the disubstitution of resorcinol the 4-derivative is always formed first and, in the absence of the disturbing factors discussed above, the second substituent enters position 6, and the formation of dihalogeno-, $(\text{CO}_2\text{H})_2$, $(\text{SO}_3\text{H})_2$, and $(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2$ derivatives (all 4:6-) and of $(\text{NO}_2)_2$, $(\text{CHO})_2$ (both 2:4-), and bisazo-(2:4- or 2:6- according to conditions) (chelation fixing the position of the double linkings in the last three), are discussed on this basis. Nitration of resacetophenone with HNO_3 (*d* 1.42) at 30—40° gives the 5- NO_2 -derivative, since oxidation (3% $\text{H}_2\text{O}_2\cdot\text{N}\cdot\text{NaOH}$ in H_2) and subsequent methylation affords 5-nitrohydroxyquinol *Me*₂ ether. Nitropæanol (Adams, A., 1919, i, 160) is 5-nitro-2-hydroxy-4-methoxyacetophenone, since its *Me*₂ ether, m.p. 180° (not the compound, m.p. 131°, *loc. cit.*), is identical with that of 5-nitroresacetophenone. With HNO_3 (*d* 1.42) at 80° (II) gives its 2- NO_2 -derivative. J. W. B.

Synthesis of methoxychalkones [methoxyphenyl styryl ketones] and methoxybenzylidene- β -coumaranones from methoxyacetophenones and nitrobenzaldehydes. D. PRICE and M. T. BOGERT (J. Amer. Chem. Soc., 1934, 56, 2442—2449).—2:3:4-(OMe)₃C₆H₂·COMe and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in aq. $\text{EtOH}\cdot\text{NaOH}$ give 2:3:4-trimethoxyphenyl *o*-, m.p. 125° (all m.p. are corr.), *m*-, m.p. 135°, and *p*-, m.p. 160.5°, -nitrostyryl ketones, which are reduced (SnCl_2 , $\text{AcOH}\cdot\text{HCl}$) to 2:2':3':4'-trimethoxyphenyl-quinoline, m.p. 105°, and 2:3:4-trimethoxyphenyl *m*-, m.p. 98°, and *p*-, m.p. 104°, -aminostyryl ketone, re-

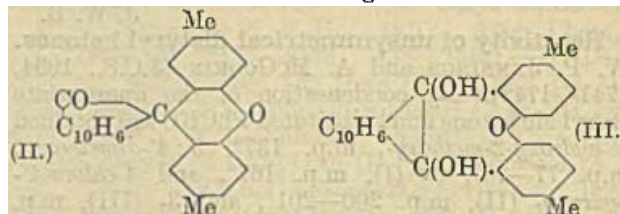
spectively. 2-Hydroxy-3:4-dimethoxyacetophenone (I) and *o*-NO₂-C₆H₄-CHO in MeOH-NaOMe give 2-hydroxy-3:4-dimethoxyphenyl β-hydroxy-β-*o*-nitrophenylethyl ketone (II), m.p. 132° [the *p*-NO₂-isomeride (III) has m.p. 156°], which when heated above its m.p. affords 2-hydroxy-3:4-dimethoxyphenyl *o*-nitrostyryl ketone (IV), m.p. 163.5° [Ac derivative, m.p. 115°, prepared from (II) or (IV) (or a mixture) and Ac₂O-NaOAc]. (I) and *m*-NO₂-C₆H₄-CHO in aq. EtOH-NaOH give 2-hydroxy-3:4-dimethoxyphenyl *m*-nitrostyryl ketone, m.p. 190.5° (Ac derivative, m.p. 99°), whilst crude (III) is dehydrated (Ac₂O) to 2-hydroxy-3:4-dimethoxyphenyl *p*-nitrostyryl ketone, m.p. 188.5° (Ac derivative, m.p. 173.5°). 2-Acetoxy-3:4-dimethoxyphenyl αβ-dibromo-β-*o*-, m.p. 143.5°, -*m*-, an oil, and -*p*-, m.p. 148°, -nitrophenylethyl ketones (from the above Ac derivatives and Br in CHCl₃) are converted by EtOH-KOH [independently of temp. (cf. von Auwers and Anschütz, A., 1921, i, 682)] into 2'- (V), m.p. 196—196.5°, 3'- (VI), m.p. 220°, and 4'- (VII), m.p. 265.5°, -nitro-5:6-dimethoxybenzylidenecoumaranone, respectively; (V) is accompanied by a Br-containing substance, m.p. 133°. (VII) is also prepared from 2-hydroxy-3:4-dimethoxyphenyl acyl chloride, m.p. 161.5° [from 1:2:3-C₆H₃(OMe)₃, CH₂Cl-COCl, and AlCl₃ in CS₂ under defined conditions; different conditions lead to 4:6-di(chloroacetyl)pyrogallol 2-Me ether, m.p. 154.5°], and *p*-NO₂-C₆H₄-CHO in alkali. Reduction (SnCl₂, AcOH-HCl) of (V), (VI), and (VII) at room temp. gives the corresponding NH₂-derivatives, m.p. 211—212°, 205.5°, and 174°, respectively; at 100°, (V) gives (mainly) dimethoxycoumarinoline, m.p. 179° (cf. Feist and Siebenlist, A., 1927, 671).

H. B.

Influence of chemical constitution on visible colour and other tinctorial properties in the case of structurally related methoxychalkones [methoxyphenyl styryl ketones] and methoxybenzylidenecoumaranones. D. PRICE, A. DINGWALL, and M. T. BOGERT (J. Amer. Chem. Soc., 1934, 56, 2483—2486).—The 2:3:4-trimethoxyphenyl nitro- and amino-styryl ketones [absorption spectra curves for the *m*- (I) and *p*- (II) -NH₂-derivatives given] (preceding abstract) and the 5:6-dimethoxy-nitro- and -amino-benzylidenecoumaranones [absorption spectra curves for the 3'- (III) and 4'- (IV) -NH₂-derivatives given; that for (III) appears to be anomalous] (*loc. cit.*) are generally yellow (varying shades). (III), (IV), and the 2'-NH₂-isomeride (V) are more intensely coloured than the NO₂-derivatives [which resemble the OH-analogues (Felix and Friedlander, A., 1910, i, 278)]; all dissolve in conc. H₂SO₄ to (usually) red solutions. There is not such a marked difference between (I) and (II) and the corresponding NO₂-derivatives. The 2-hydroxy-3:4-dimethoxyphenyl nitrostyryl ketones (*loc. cit.*) are more intensely coloured than their Ac derivatives and the β-hydroxy-β-nitrophenylethyl ketones. Passage from (II) to (IV) is accompanied by a marked deepening in colour; no such effect is observed with (I) and (III). The position of the NH₂-group has a much greater effect on the colour of the coumaranones than of the styryl ketones. (II), (IV), and (V) dye silk and wool (from dil. solutions in dil. AcOH) greenish-yellow, golden-yellow and orange-yellow, respectively.

H. B.

Condensation of acenaphthenequinone with cresols and naphthols; cyclic pinacols. I. MATEI and E. BOGDAN (Ber., 1934, 67, [B], 1834—1842).—Cautious addition of conc. H₂SO₄ (6 equivs.) to a molten mixture of acenaphthenequinone (I) and *p*-cresol gives anhydro-8-keto-7:7-di-2'-hydroxy-5'-methylphenylacenaphthene (II), m.p. 333°, which is insol. in alkali and does not give an Ac derivative.



With 1 equiv. of conc. H₂SO₄, (I) and *p*-cresol afford anhydro-7:8-di-2'-hydroxy-5'-methylphenylacenaphthene-7:8-diol (III), m.p. 225° (or +1EtOH, 1AcOH, or 1PhMe, m.p. 191°, 136°, and 148°, respectively), which is insol. in alkali and transformed by conc. H₂SO₄ into (II). (I), β-C₁₀H₇-OH, and a few drops of conc. H₂SO₄ yield anhydro-8-keto-7:7-di-2'-hydroxynaphthylacenaphthene (IV), m.p. 337°, whereas in boiling EtOH containing HCl anhydro-7:8-di-2'-hydroxynaphthylacenaphthene-7:8-diol [+1EtOH or +1AcOH, m.p. 180—182° (decomp.)] is obtained, transformed by boiling AcOH containing conc. H₂SO₄ into (IV). (I), and *m*-cresol in boiling EtOH-conc. HCl yield 8-keto-7:7-di-4'-hydroxy-2'-methylphenylacenaphthene, m.p. 165° (Ac₂ derivative, m.p. 229—230° after softening). Similarly (I) and *o*-cresol give 8-keto-7:7-di-4'-hydroxy-3'-methylphenylacenaphthene, m.p. 216—217° (Ac₂ derivative, m.p. 180°), whilst (I) and α-C₁₀H₇-OH yield 8-keto-7:7-di-4'-hydroxynaphthylacenaphthene, m.p. 218° (decomp.) [Ac₂ derivative, m.p. >192° (decomp.)].

H. W.

Constitution of dypnopinacone. D. IVANOV (Compt. rend., 1934, 199, 729—731; cf. A., 1933, 157).—Dypnopinacone (I) results from the condensation of dypnone with MgCl-CHPh-CO₂MgCl or related substances which are agents for ketolic condensation. From this fact, and also from the presence of one OH and one CO in the mol., (I) is considered to be βδζ-triphenyl-γ-benzoyl-Δ⁸-heptadien-δ-ol.

R. N. C.

Optical method for the study of reversible organic oxidation-reduction systems. IV. Aryl-*p*-benzoquinones. V. *o*-Benzoquinones. D. E. KVALNES (J. Amer. Chem. Soc., 1934, 56, 2478—2481, 2487—2489).—IV. *p*-Benzoquinone (I) and the appropriate ArN₂X in aq. EtOH-NaOAc at > room temp. give 55—85% of phenyl- (II), m.p. 114° (0.698), *p*-diphenyl-, m.p. 199° (0.719), β-naphthyl-, m.p. 173—174° (0.713), *p*-tolyl-, m.p. 138—139° (0.703), anisyl-, m.p. 120—121° (0.692), *p*-acetylphenyl-, m.p. 152—153° (0.715), *p*-carboxyphenyl-, m.p. 220—221° (decomp.), *p*-carbethoxyphenyl-, m.p. 123—124° (0.716), and *m*-, m.p. 105—107° (0.721), and *p*-, m.p. 137° (0.721), -nitrophenyl-*p*-benzoquinones. (II) and PhN₂X (III) similarly give poor yields of 2:5-diphenyl- (IV), m.p. 214° (0.689), and tetraphenyl-, m.p. 311—315°, *p*-benzoquinone. 2:5-Dichloro-*p*-benzoquinone and (III) (excess) in AcOH

afford 2 : 5-dichloro-3 : 6-diphenyl-*p*-benzoquinone, m.p. 208—209°, hydrolysed (MeOH-alkali) to the 2 : 5-(OH)₂-derivative (polyporic acid). *p*-Xyloquinone and *m*-NO₂·C₆H₄·N₂X (1 mol.) give 3-*m*-nitrophenyl-, m.p. 123—124°, and a little 3 : 6-di-*m*-nitrophenyl-, m.p. 241—242°, -2 : 5-dimethyl-*p*-benzoquinone. Some 2-phenyl-, m.p. 110°, and a little 2 : 3-diphenyl-, m.p. 135—136°, -1 : 4-naphthaquinone are obtained from (III) and 1 : 4-naphthaquinone [the 2-*p*-carboxyphenyl derivative, m.p. 303—305° (decomp.), is prepared in good yield using *p*-CO₂H·C₆H₄·N₂X; reductive acetylation of this gives 1 : 4-diacetoxy-2-*p*-carboxyphenyl-naphthalene, m.p. 200—201°]. 3-Phenyl-2 : 6-dimethyl-1 : 4-naphthaquinone, m.p. 114—115°, is prepared in poor yield. 3 : 4-Di-*p*-carboxyphenyl-1 : 2-naphthaquinone has m.p. 260—262°. The naphthaquinones are purified through the naphthaquinols. (IV) and Ac₂O-conc. H₂SO₄ give 1 : 2(? 3) : 4-triacetoxy-2 : 5-diphenylbenzene, m.p. 191—192°. Pure products could not be obtained from (I) and *o*-NO₂·C₆H₄·N₂X, 2 : 6-C₆H₃Me₂·N₂X, and α -C₁₀H₇·N₂X; 2-methoxy-1 : 4-naphthaquinone does not react with (III). 2-Hydroxy-1 : 4-naphthaquinone and (III) give the 3-benzene-azo-derivative, m.p. 225—226° (decomp.). *p*-Diphenyl-, m.p. 177—178°, *o*-naphthyl-, m.p. 172—174°, *p*-tolyl-, m.p. 123°, *anisyl*-, m.p. 111—112°, *p*-acetylphenyl-, m.p. 192—193°, and *p*-carboxyphenyl-(anhyd. and +H₂O), m.p. 230—231°, -quinols are described. The vals. quoted in parentheses after some of the above quinones are the relative oxidation potentials [(I)=0.711 volt] determined in C₆H₆ by the method previously described (A., 1932, 947; 1934, 527); the normal potentials are also determined electrometrically in 70% EtOH.

V. The relative oxidation potentials of the following are determined polarimetrically in C₆H₆ using the system *d*-camphor-10-sulphonyl-quinol and -quinone (improved prep.; cf. A., 1932, 947): (I)=0.711 volt; *o*-benzoquinone, 0.833; 4-chloro-, 0.810, 4-bromo-, 0.810, 4-methyl-, 0.796, 4-triphenylmethyl-, 0.804, 3 : 4-dimethyl-, 0.765, tetrachloro-, 0.860, and tetrabromo-, 0.860, -*o*-benzoquinones. The vals. are compared with those determined electrometrically in aq. solution. The effects of substituents are discussed briefly. 2 : 5 : 1-C₆H₃(OH)(OMe)·CHO is oxidised (method: Dakin, Proc. Chem. Soc., 1909, 194) to 4-methoxy-*pyrocatechol*, m.p. 48—50° (diacetate, m.p. 69—70°), oxidised (Ag₂O, Et₂O, Na₂SO₄) to 4-methoxy-*o*-benzoquinone (V), decomp. 88—90° (darkens at 85°). 4-Bromo-*o*-benzoquinone, m.p. 74—75°, is similarly prepared. The potentials of (V) and 3 : 5-dichloro-*o*-benzoquinone are 0.658 and 0.819 volt, respectively.

H. B.

Synthesis and properties of 2 : 7-tetramethyldiaminoanthraquinone, 2 : 7-tetramethyldiamino-10-hydroxy-10-phenylanthrone, and related compounds. D. C. R. JONES and F. A. MASON (J.C.S., 1934, 1813—1817).—Anthraquinone-2 : 7-disulphonic acid with KClO₃ in boiling dil. HCl affords a mixture of the 2 : 7-Cl₂-derivative (I) and 2-chloroanthraquinone-7-sulphonic acid (*sulphonyl chloride*, m.p. 205°), converted by 33% aq. NHMe₂ at 185—190° into the Na salt of 2-dimethylaminoanthraquinone-7-sulphonic acid (*hydrochloride*), the Na salt of the -6-sulphonic acid and the Na salt of 2-diethyl-

aminoanthraquinone-7-sulphonic acid being similarly prepared. By heating (I) or the 2 : 6-Cl₂-derivative with the appropriate 33% aq. NHR₂ and Cu powder at 180° are obtained 2-chloro-7-, m.p. 256°, and -6-dimethylamino-, m.p. 258°, and -7-diethylamino-, m.p. 254°, -anthraquinone, but with 50% aq. NHR₂ and Cu in C₅H₁₁·OH at 220° are obtained 2 : 7- (II), m.p. 317° (*Br*₁-derivative, m.p. 234°), and 2 : 6-tetramethyldiamino-, m.p. 289°, and 2 : 7-tetraethyldiamino-, m.p. 285°, -anthraquinone. With H₂SO₄-HNO₃ (II) gives a mixture of (NO₂)₁-derivatives, m.p. 260—282°, a compound, m.p. 264°, being obtained with warm 50% HNO₃. Reduction of (II) with Sn-AcOH-conc. HCl gives 2 : 7-tetramethyldiamino-9(or 10)-anthrone (III), m.p. 180° (*Ac* derivative, m.p. 173°), oxidised by aq. FeCl₃ in boiling AcOH to 2 : 7 : 2' : 7'-octamethyltetraamino-9(10) : 9'(10')-dianthrone, m.p. 330°. With MgPhBr in Et₂O or Na in boiling PhCl-PhMe (II) gives the dye salt from which the carbinol base, 2 : 7-tetramethyldiamino-10-hydroxy-10-phenylanthrone, m.p. 273° (zincchloride; hydrochloride in H₂O has chief absorption band at 650 m μ , and strong absorption at 450 m μ), is derived. Other dyes obtained by replacing PhCl by 1-C₁₀H₇Br, *p*-C₆H₄MeBr, *p*-C₆H₄Br·OMe, and MeI (anthranol base, m.p. 59—71°) are briefly described (no analytical data). With MgPhBr (III) gives 2 : 7-tetramethyldiamino-9(10)-hydroxy-9(10)-phenyldihydroanthracene, m.p. 190°. 3 : 3'-Tetramethyldiaminodiphenylmethane with 40% CH₂O-15% HCl at 90° gives 2 : 7-tetramethyldiamino-9 : 10-dihydroanthracene, m.p. 198°.

J. W. B.

Scammonium resin. K. H. BAUER and R. JUNGE (Arch. Pharm., 1934, 272, 841—848).—Scammonin (I) with H₂SO₄ in EtOH or MeOH gives the *Et*, m.p. 46°, b.p. 123°/4 mm., or *Me* ester, m.p. 49—50°, respectively, of scammonic acid (II), C₁₅H₃₀(OH)·CO₂H, m.p. 68° (Ba salt), and *d*-CHMeEt·CO₂H (III). With Ba(OH)₂ (I) yields (II) and (III). Scammonic acid (IV) (equiv. wt. about 1060) does not give (II) on acid hydrolysis; it contains 4 monosaccharide residues (I-titration), of which 2 are glucose (V) (quant. fermentation). > 1 mol. of (V) is obtained by hydrolysis of (IV) with emulsin, but no rhodose (VI) is liberated. (IV) is thus probably (II)-(VI)-rhamnose-(V)-(V), the OH of (II) being linked glucosidically. In (I) the CO₂H groups of (II) and (III) are esterified. Only these ester linkings are affected by Ba(OH)₂, but H₂SO₄ hydrolyses also the glucosidic linkings.

R. S. C.

Resinols. III. α - and β -Amyrone oxides and their derivatives. F. S. SPRING and T. VICKERSTAFF (J.C.S., 1934, 1859—1861).—Oxidation (BzO₂H in CHCl₃ at 0°) of α - and β -amyrone gives α -, m.p. 183°, [α]_D +125° in CHCl₃, and β -, m.p. 234°, -amyrone oxides II; those previously described (A., 1934, 776) are now designated α - and β -amyrone oxides I. β -Amyrin acetate is similarly oxidised to an oxide (I), m.p. 293° [identical with the previously described (A., 1933, 1299) "oxy- β -amyrin acetate"], also prepared by acetylation (Ac₂O-KOAc) of β -amyrin oxide (II) and by Rollett and Bratke's method (A., 1923, i, 588). Hydrolysis (KOH in EtOH-C₆H₆) of (I) gives (II), which is also formed by oxidation (BzO₂H in CHCl₃ at 0°) of β -amyrin; (II) is the "oxy- β -amyrin" of Rollett

and Bratke (*loc. cit.*) and Spring (A., 1933, 1299). The "oxy- β -amyronc" of Rollett and Bratke (*loc. cit.*) is now termed β -amyronc oxide III. The "oxy- α -amyryn" of Vesterberg (A., 1892, 290) is oxidised (CrO_3 , AcOH at 70°) to α -amyronc oxide I. H. B.

Digitalis glucosides. VIII. Degradation of the lactone side-chain of digitoxigenin. W. A. JACOBS and R. C. ELDERFIELD (Science, 1934, 80, 434).—Oxidation of the *sec.*-OH group with CrO_3 converts α -digitoxanoldiacid into the keto-acid, *digitoxanon diacid*, $\text{C}_{23}\text{H}_{34}\text{O}_5$; reduction (Clemmensen) yields *digitoxandiacid*, $\text{C}_{23}\text{H}_{36}\text{O}_4$. The Me_2 ester on treatment with a Grignard reagent followed by CrO_3 oxidation is degraded with the loss of 3 of the original C atoms of the lactone side-chain to the monobasic acid $\text{C}_{20}\text{H}_{32}\text{O}_2$, m.p. $219\text{--}219.5^\circ$ (*Me* ester, m.p. $97\text{--}98^\circ$; *Et* ester, m.p. $76.5\text{--}77.5^\circ$), which may be identical with α -tiocholanic acid. L. S. T.

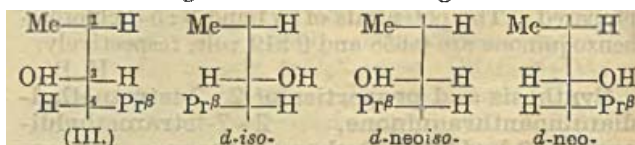
[Pterosantalol.] H. LEONHARDT and W. BUSCKE (Ber., 1934, 67, [B], 1888—1889; cf. A., 1934, 1007).—A question of priority (cf. Raudnitz, *ibid.*, 1223). H. W.

Dehydration of linalool and structure of the terpene obtained thereby. B. A. ARBUSOV and V. S. ABRAMOV (Ber., 1934, 67, [B], 1942—1946).—Linalool is dehydrated by distillation at $150\text{--}160^\circ/150\text{--}160$ mm. in presence of a trace of I, giving 33.7% of a hydrocarbon (I), b.p. $51\text{--}51.5^\circ/8.5$ mm. α -Naphthaquinone and (I) in EtOH give 7- δ -methyl- Δ^7 -pentenyl-5 : 8 : 9 : 10-tetrahydroanthraquinone, m.p. $58.5\text{--}59.5^\circ$, dehydrogenated to 7- δ -methyl- Δ^7 -pentenyl-anthraquinone, m.p. $80\text{--}81.5^\circ$, which is oxidised by HNO_3 (*d* 1:1) at 170° and subsequently at $200\text{--}220^\circ$ to anthraquinone-2-carboxylic acid, m.p. $285\text{--}286^\circ$ (*Et* ester, m.p. 144°). (I) is therefore identical with myrcene. (I) adds maleic anhydride readily, giving a non-cryst. anhydride, b.p. $186\text{--}191^\circ/8$ mm., transformed into an acid, $\text{C}_{14}\text{H}_{20}\text{O}_4$ (II), m.p. $111\text{--}113.5^\circ$. Ozonisation of (II) gives COMe_2 and an acid approximating to tetrahydrobenzene-1 : 2-dipropionic acid. Attempted isomerisation of (II) by HBr gave non-cryst. products. It is therefore possible that (I) contains small amounts of an isomeric hydrocarbon of the limonene type which hampers the purification of *iso*-hexenyltetrahydrophthalic acid and the products of its isomerisation. H. W.

Syntheses in sesquiterpene series. I. A. E. BRADFIELD, E. R. JONES, and J. L. SIMONSEN (J.C.S., 1934, 1810—1812).—*l*-Tetrahydrocarvone, -20.3° , $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn in C_6H_6 give *Et* 2-hydroxy-2-menthylacetate, b.p. $144\text{--}148^\circ/12$ mm., $[\alpha]_{5461} -18^\circ$ (free acid, m.p. $77\text{--}78^\circ$), dehydrated (KHSO_4 at $180\text{--}200^\circ$) to *Et* 2-menthylideneacetate, b.p. $133\text{--}136^\circ/12$ mm., $[\alpha]_{5461} -59.3^\circ$, which is reduced (H_2 , Pd -norit, EtOH) to *Et* 2-menthylacetate (I), b.p. $125\text{--}126^\circ/12$ mm., $[\alpha]_{5461} +7.2^\circ$ [free acid (II), b.p. $162\text{--}166^\circ/12$ mm. (*p*-toluidide, m.p. 133°)]. Bouveault reduction of (I) affords β -2-menthylethyl alcohol, b.p. $126\text{--}131^\circ/12$ mm., $[\alpha]_{5461} +9.8^\circ$, the bromide (III), b.p. $126^\circ/12$ mm., of which with $\text{CNaMe}(\text{CO}_2\text{Et})_2$ gives *Et* β -2-menthylethylmethylmalonate, b.p. $193^\circ/12$ mm. Hydrolysis (MeOH - KOH) and subsequent decarboxylation at $165\text{--}200^\circ$ affords

γ -2-menthyl- α -methylbutyric acid (IV), b.p. $160\text{--}163^\circ/2$ mm., $[\alpha]_{5461} +25^\circ$ in CHCl_3 [*p*-toluidide, m.p. 142° (sinters at 139°)]. Traces of a ketonic product are obtained from (IV) and P_2O_5 in Et_2O or xylene and from the chloride, b.p. $154\text{--}157^\circ/12$ mm., and AlCl_3 in CS_2 . (III) is converted (NaI , COMe_2) into the iodide and thence (EtOH - KCN) into β -2-menthylpropionitrile, b.p. $141\text{--}146^\circ/14$ mm., which with $\text{EtOH}\text{--}\text{H}_2\text{SO}_4$ gives *Et* β -2-menthylpropionate (V), b.p. $145\text{--}151^\circ/16$ mm., $[\alpha]_{5461} +17.3^\circ$. This and MgMeI afford γ -2-menthyl- α -dimethylpropyl alcohol, b.p. $144\text{--}147^\circ/17$ mm., $[\alpha]_{5461} +35^\circ$ in CHCl_3 , which is dehydrated (KHSO_4 at 180°) to a mixture, b.p. $127\text{--}128^\circ/19$ mm., of δ -2-menthyl- β -methyl- Δ^2 - and Δ^3 -butenes, since ozonolysis gives CH_3O , COMe_2 , (II), and impure β -2-menthylethyl *Me* ketone, b.p. $127\text{--}129^\circ/17$ mm. (2 : 4-dinitrophenylhydrazones, m.p. 113°). The mol. refractions of the above compounds are all normal except those of (I) and (V), which show an exaltation of approx. 1 unit. H. B.

Menthone series. XIII. Relative molecular configurations of menthols and menthylamines. J. READ and W. J. GRUBB (J.C.S., 1934, 1779—1783).—The ratios of the reaction velocities of *l*-menthylamine (I) and *d*-neomenthylamine (II) are determined by allowing equimol. mixtures to react with 0.67 mol. of various ArCOCl in CHCl_3 +aq. NaOH at 25° (with stirring); the resulting product is analysed polarimetrically. In each case, (II) reacts somewhat faster than (I). Similar competitive reaction of equimol. mixtures of various pairs of menthols in $\text{C}_5\text{H}_5\text{N}$ at 25° shows that *l*-menthol (III) reacts much more rapidly than *dl*-neomenthol (IV). With $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ [which can be used to separate a mixture of (III) and (IV)], the mean relative rates of reaction are: menthols 16.5, *isomenthols* 12.3, *neomenthols* (V) 3.1, *neomenthols* (VI) 1. If these differences are due to steric hindrance, then OH(3) and H(4) must be assigned a *trans*-configuration in (V) and (VI). This conclusion is supported by the formation of a predominance of *neomenthol* (VII) in the reduction of menthone (A., 1934, 413), and by the more rapid esterification (as above) of *trans*- than *cis*-cyclohexane-1 : 2-diol monobenzoate. The production of Δ^3 -menthene by dehydration of (V) and (VI) [and from the neo-amines and HNO_2 by way of (VII)] must be due to *trans*-elimination of H_2O between OH(3) and H(4), assuming that H(2) is unaffected. Modified configurations are now assigned as follows :



Analogous configurations (NH_2 replacing OH in above formulæ) are assigned to the menthylamines; the results with (I) and (II) are, incidentally, at variance.

The following reference compounds are described : *o*-, m.p. 188.5° , $[\alpha]_D -62.9^\circ$ (all rotations are in CHCl_3 at 17.5°), *m*-, m.p. 135° , $[\alpha]_D -59.4^\circ$, and *p*-, m.p. 170° , $[\alpha]_D -53.8^\circ$, -nitrobenzoyl-, 3 : 5-dinitrobenzoyl-, m.p. 193° , $[\alpha]_D -60^\circ$, and β -naphthoyl-, m.p. 180.5° , $[\alpha]_D -51.9^\circ$, -*l*-menthylamines; *o*-, m.p. 183° ,

$[\alpha]_D +36.5^\circ$, m., m.p. 131° , $[\alpha]_D +18.7^\circ$, and p., m.p. 151° , $[\alpha]_D +16.1^\circ$, *-nitrobenzoyl*-, 3:5-dinitrobenzoyl-, m.p. 164° , $[\alpha]_D +22.6^\circ$, and β -naphthoyl-, m.p. 165° , $[\alpha]_D +5.4^\circ$, *-d-neomenthylamines*. H. B.

[Isomerisation of α -pinene to an aliphatic terpene (*alloocimene*).] B. A. ARBUSOV (Ber., 1934, 67, [B], 1946; cf. A., 1934, 658).—The identity of the product obtained from α -pinene with *alloocimene* is confirmed by comparison of the additive compounds formed with maleic anhydride. H. W.

Spontaneous resolution of pinenenitrolbenzylamine. M. DELEPINE, R. ALQUIER, and (Mlle.) F. LANGE (Bull. Soc. chim., 1934, [v], 1, 1250—1252).—Pinenenitrolbenzylamine crystallises from EtOH in enantiomorphous crystals, which, when separated by hand, have $[\alpha] +76^\circ$ and -91.6° , respectively (cf. A., 1889, 1071). R. S. C.

Racemisation in the camphene transformation. S. S. NAMETKIN and A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1934, 4, 847—855).—Racemisation taking place during the transformation of camphene into isoborneol, or vice versa, and in other analogous cases, is explained by a combination of Nametkin and Brüssov's (A., 1928, 182) and Wagner's rearrangements. R. T.

New methods in stereochemistry. I. Preparation of *d*- and *l*-borneol. II. Resolution of *dl*-menthol. J. CLARK and J. READ (J.C.S., 1934, 1773—1775, 1775—1779).—I. Successive treatment of *d*-borneol (I), m.p. $200-201^\circ$, $[\alpha]_D +21.5^\circ$ in EtOH, with Na and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ in $\text{C}_5\text{H}_5\text{N}$ gives impure (III) (below), m.p. $70-72^\circ$, $[\alpha]_D +34^\circ$ in EtOH, converted (SOCl_2) into the chloride (II), b.p. $130-135^\circ/13$ mm. (I) and (II) in $\text{C}_5\text{H}_5\text{N}$ afford (after repeated crystallisation from aq. MeOH and MeOH) *d*-bornyl *d*-bornoxyacetate, m.p. 72° , $[\alpha]_D +63.3^\circ$ in CHCl_3 , hydrolysed (1% EtOH-KOH) to optically pure (I), m.p. $204.5-205^\circ$, $[\alpha]_D +37.6^\circ$ in PhMe, and *d*-bornoxyacetic acid (III), m.p. 76° , $[\alpha]_D +59.1^\circ$ in EtOH (which can be used repeatedly in an improved process). *l*-Borneol (IV), m.p. $190-197^\circ$, $[\alpha]_D -33.6^\circ$ in EtOH, is similarly converted into crude *l*-bornoxyacetyl chloride, b.p. $140-143^\circ/17$ mm., and thence into impure, m.p. $55-60^\circ$, and pure, m.p. 72° , $[\alpha]_D -63.3^\circ$ in CHCl_3 , *l*-bornyl *l*-bornoxyacetate; subsequent hydrolysis (as above) gives optically pure (IV), m.p. 205° , $[\alpha]_D -37.9^\circ$ in PhMe, and *l*-bornoxyacetic acid, m.p. 76° , $[\alpha]_D -59^\circ$ in EtOH. The (II) prepared (as above) from a specimen of (I) with $[\alpha]_D +28.4^\circ$ in EtOH, with *l*-menthol in $\text{C}_5\text{H}_5\text{N}$ affords optically impure *l*-menthyl *d*-bornoxyacetate, an oil, $[\alpha]_D -17.9^\circ$ in CHCl_3 . The corresponding *d*-bornyl, b.p. $206-208^\circ/0.5$ mm., $[\alpha]_D -37.7^\circ$ in CHCl_3 , and *l*-bornyl *l*-menthoxyacetate, $[\alpha]_D -76.1^\circ$ in CHCl_3 [from (IV) and *l*-menthoxyacetyl chloride in $\text{C}_5\text{H}_5\text{N}$], cannot be applied effectively to the purification of impure (I) and (IV).

II. *l*-Menthyl chloroacetate, b.p. $136^\circ/13$ mm., m.p. $-9-40^\circ$, $[\alpha]_D -77.5^\circ$ in CHCl_3 [from *l*-menthol (V) $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in C_6H_6], and *l*-menthylamine (VI) give *l*-menthyl *l*-menthylaminoacetate (VII), m.p. 63° , $[\alpha]_D^{19.6} -105.3^\circ$ in CHCl_3 [*N*-Ac (VIII), m.p. 96° , *N*-*p*-nitrobenzoyl, m.p. 146° , and

N-3:5-dinitrobenzoyl, m.p. 170° , derivatives; hydrochloride, m.p. 69° ; sulphate (X), m.p. 191° ; oxalate, m.p. 168.5°]. Et *l*-menthylaminoacetate [from (VI) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ in C_6H_6] has b.p. $139^\circ/10$ mm., $[\alpha]_D -56.1^\circ$ in CHCl_3 , *dl*-Menthyl chloroacetate, b.p. $130^\circ/9.5$ mm., and (VI) at $120-130^\circ$ afford *dl*-menthyl *l*-menthylaminoacetate (XI), a waxy solid, $[\alpha]_D -43^\circ$ in CHCl_3 , repeated crystallisation of which from MeOH gives *d*-menthyl *l*-menthylaminoacetate (XII), m.p. 82° , $[\alpha]_D -2^\circ$ in CHCl_3 , [*N*-Ac (XIII), m.p. 95° , *N*-Bz, m.p. $106-107^\circ$, *N*-*p*-nitrobenzoyl, m.p. 146° , and *N*-3:5-dinitrobenzoyl, m.p. 131° , derivatives; sulphate, m.p. 176°]. Hydrolysis (1% EtOH-KOH) of (VIII) affords *N*-acetyl-*l*-menthylaminoacetic acid (XIV), m.p. 154° , $[\alpha]_D -43.6^\circ$ in CHCl_3 , which is attacked only slowly by hot 50% H_2SO_4 or 10% NaOH; *N*-benzoyl-*l*-menthylaminoacetic acid, m.p. 118° , is similarly obtained from (IX). Hydrolysis of (XII) gives *l*-menthylaminoacetic acid, m.p. 191° , $[\alpha]_D -61.5^\circ$ in CHCl_3 , and *d*-menthol (XV), b.p. $98^\circ/12$ mm., m.p. $42-43^\circ$, $[\alpha]_D +50.6$ in EtOH (yield 36.6% based on *dl*-menthol originally used). Crystallisation (from COMe_2 and EtOH- COMe_2) of the sulphate of (XI) gives pure (X) [hydrolysed to (V) in 65.2% yield]; basification of the residue and subsequent crystallisation from MeOH affords (XII) [and thence (XV) in 55.9% yield]. The *N*-Ac derivative of (XI), prepared by acetylation of (XI) or from *dl*-menthol, (XIV), and SOCl_2 in C_6H_6 , on fractional recrystallisation from MeOH gives (XIII) [and thence (XV) in 7.5% yield]. (XIV) is decomposed by SOCl_2 in absence of solvent. *l*-Menthylamine H phthalate heated at $150^\circ/360$ mm. affords *phthal-l*-menthylimide, m.p. 109° , $[\alpha]_D -18.9^\circ$ in CHCl_3 , hydrolysed (5% EtOH-KOH) to *phthal-l*-menthylamic acid, m.p. 171° , $[\alpha]_D -71.8^\circ$ in CHCl_3 , which is readily dehydrated (SOCl_2 ; HCl) to the imide. H. B.

Chemistry and pharmacology of campherol and related compounds. Y. SAHASHI, K. TAKEUCHI, T. SHIMAMOTO, T. IKI, and T. TAKEBE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 47—109).—Fractionation by Et_2O of additive compounds of "campherol" from camphor-fed dog's urine with CaCl_2 in dry C_6H_6 yields *trans*- (but not *cis*-) π -(8- or 9-) (20%), 3- (15%), and 5-hydroxycampherol (55%). With (I) from rabbit's urine, 3- and 5- but not π -hydroxycampherol (II) are present. *p*-Diketocamphane, m.p. $208-210^\circ$ (uncorr.) (A., 1921, i, 257), prepared by various methods, differs in $[\alpha]$ with the solvent used. Further details of the prep. of 5-hydroxycampherol (A., 1934, 659) are given; with Ac_2O it yields 5-acetoxycampherol, b.p. $149-150^\circ/25$ mm. [semicarbazide, m.p. $223-224^\circ$ (uncorr.)]. Acetylation of *d*- π -bromocampherol (J.C.S., 1895, 67, 382) affords *d*- π -acetoxycampherol, b.p. $125^\circ/4-5$ mm. [semicarbazide, m.p. 233° (uncorr.)], hydrolysed to (II), m.p. 234° , $[\alpha]_D^{17} +64^\circ$ in abs. EtOH. Oxidation of (II) gives π -apocampher-7-carboxylic acid, m.p. 246° (uncorr.), and -aldehyde, m.p. $204-205^\circ$ (uncorr.) (semicarbazide, decomp. $>300^\circ$). β -(10-)Bromocampherol (J.C.S., 1902, 81, 1462) acetylates to β -acetoxycampherol, b.p. $128-130^\circ/3-4$ mm. [semicarbazide, m.p. 163° (uncorr.)], converted by

EtOH-KOH into β -hydroxycamphor (III), m.p. 216° (uncorr.) [semicarbazide, decomp. 213° (uncorr.)] (cf. J.C.S., 1913, 103, 63). (III) with AcOH-CrO₃ at low temp. yields β -apocamphor-1-aldehyde, m.p. 203—205° (uncorr.) [semicarbazide, m.p. 247° (uncorr.)]; disemicarbazide, m.p. 240° (uncorr.)], and, mainly, the β -hydroxycamphor ester of ketopinic acid, m.p. 164°. The cardiotonic action and toxicity of camphor, 3-, 5-, π -, and 10-hydroxycamphor, π -camphorcarboxylic acid, etc. indicate that (III) is the only compound to exhibit stimulating action without any initial systolic depression. The bearing of the data on the action of "vitacamphor" (cf. Tamura *et al.*, B., 1932, 960; A., 1930, 955; 1932, 948) is discussed.

F. O. H.

Active racemates. Fusion curve of mixtures of d - α -chloro- and α -bromo-camphor- π -sulphonamide. M. DELÉPINE, L. LABRO, and (MLLE.) F. LANGE (Bull. Soc. chim., 1934, [v], 1, 1252—1255).— d and l - (I) α -Bromocamphor- π -sulphonyl chloride, m.p. 140° (lit. 136—137°), [α]_D 130—131° in CHCl₃, give a *racemate*, m.p. 121° (eutectic m.p. 116.5°). (I) and d - α -chlorocamphor- π -sulphonyl chloride, [α]_D +111—112° in CHCl₃, are isomorphous and give an "active racemate" (II), [α]_D -18.8° (calc. 18°). d - (III) and l - α -Chloro-, m.p. 149—150°, and α -bromocamphor- π -sulphonamide (IV), m.p. 145—146°, give *racemates*, m.p. 154.5° and 175° with eutectic m.p. 135° and 137.5°, respectively. (III) and l - (IV) give an "active racemate" (V), m.p. 160.5° (eutectic m.p. 132°), [α] -18°, also obtained from (II). (V) is less sol. than its components. "Active" and ordinary racemates are thus strictly analogous.

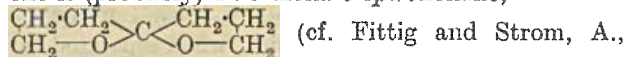
R. S. C.

Caryophyllenes. I. W. C. EVANS, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1934, 1806—1810).—Blue β -caryophyllene nitrosite (Deussen and Lewisohn, A., 1907, i, 945) is reduced (Na, EtOH) to aminodihydro- β -caryophyllene (I) (Semmler and Mayer, A., 1912, i, 120), b.p. 138—143°/2 mm. [3:5-dinitrobenzoate, m.p. 172—173° (softens at 163°)], which is probably a mixture of stereoisomerides. (I) is reduced (H₂, Pd-norit, EtOH) to aminotetrahydro- β -caryophyllene, b.p. 140—142°/12 mm., [α] -29.1°, converted by HNO₃ and subsequent dehydration (KHSO₄ at 190°) into dihydro- β -caryophyllene, b.p. 118—121°/14 mm., -47.15°, which differs from the isomeric dihydrocaryophyllenes of Deussen (A., 1928, 70). Humulene (α -caryophyllene) nitroschloride (II) and boiling C₅H₅N give a mixture of products from which a nitrosohumulene (III), m.p. 126—127°, separates. (III) [which is probably identical with the compound, m.p. 128—129°, obtained by Deussen *et al.* (A., 1909, i, 813) from (II) and NaOEt or NaOPr] is reduced (Na, EtOH) to aminodihydrohumulene, b.p. 141—142°/11 mm., [α]_D -0.64° (hydrochloride, m.p. 257°; Ac derivative, m.p. 142°; picrolonate, m.p. 232°), which is apparently homogeneous. Oxidation [KMnO₄, COMe₂ followed by HNO₃ (d 1.165) on acid fraction] of γ -caryophyllene, conversion of the acidic product into Me ester, fractionation, and subsequent hydrolysis gives *as*-dimethylsuccinic, *cis*-norcaryophyllenic (IV), C₈H₁₂O₄, m.p. 125—127° (sinters at 118°), [α]_D +137° in CHCl₃, and *cis*-caryophyllenic acid,

C₉H₁₄O₄, m.p. 80—81° (sinters at 76°), [α]_D +13.56° in CHCl₃ (cf. Ruzicka *et al.*, A., 1931, 735). (IV) affords a liquid anhydride, is stable to HCl at 120°, and is converted by successive treatment with PCl₅, Br (at 120°), MeOH, and EtOH-KOH into dehydronorcaryophyllenic acid, m.p. 193°. (IV) is probably a methylcyclopentanedicarboxylic acid.

H. B.

Structure of [the compound] C₇H₁₂O₂ from the hydrogenation of furylacraldehyde. M. FARLOW, H. E. BURDICK, and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 2498—2499).—The compound previously described (A., 1934, 416) as 1:5-dioxaoctahydroindene is (probably) 1:9-dioxa-5-spiroonane,



(cf. Fittig and Strom, A., 1892, 813), since it is converted by HI into di- γ -iodopropyl ketone, which is reduced (Zn, EtOH) to COPr₂ and with piperidine gives di- γ -piperidinopropyl ketone.

H. B.

Synthetical experiments in chromone group. XIII. Hydroxy-2-styrylchromones. K. C. GULATI, S. R. SETH, and K. VENKATARAMAN. XIV. Action of sodamide on 1-acyloxy-2-acetonaphthones. H. S. MAHAL and K. VENKATARAMAN. XV. Synthesis of forniononetin, daidzein, and ϕ -baptigenin. H. S. MAHAL, H. S. RAI, and K. VENKATARAMAN (J.C.S., 1934, 1765—1767, 1767—1769, 1769—1771).—XIII. 7-Methoxy-2-methylchromone, conveniently prepared from 2-hydroxy-4-methoxyacetophenone, Na, and EtOAc, is converted into 7-methoxy-, m.p. 189—190°, and 7:4'-dimethoxy-, m.p. 144°, -2-styrylchromone. Resacetophenone, CH₃PhCl, and anhyd. K₂CO₃ in COMe₂ give 2-hydroxy-4-benzoyloxyacetophenone, m.p. 111°, converted (method; A., 1932, 520) into 7-benzoyloxy-2-methyl- (I), m.p. 137°, and -2-styryl- (II), m.p. 161°, -chromone. (II) is debenzylated (AcOH-HBr) to 7-hydroxy-2-styrylchromone, m.p. 239°. (I) and *p*-CH₃Ph·O·C₆H₄·CHO (III) give the dibenzyl ether, m.p. 176°, of 7:4'-dihydroxy-2-styrylchromone, m.p. 332° (diacetate, m.p. 183°). Contrary to Sen and Ghosh (J.C.S., 1920, 147, 61), phloracetophenone (IV), m.p. (anhyd. or +H₂O), 219° [2:4-dinitrophenylhydrazine, m.p. 280° (decomp.)]; Ac₃ derivative, m.p. 103°, is not obtained from *s*-C₆H₃(OH)₃, AcOH, and ZnCl₂; a compound, C₁₈H₁₆O₈, m.p. > 290° (decomp.), is formed. (IV), CH₃PhCl, and K₂CO₃ in COMe₂ give (probably) 2:6-dihydroxy-4-benzoyloxy-3-benzylacetophenone, m.p. 121°, since it does not undergo a smooth styryl ketone or β -diketone condensation. (IV) and Ac₂O-NaOAc afford 5:7-dihydroxy-3-acetyl-2-methylchromone (V), m.p. 252°, and its diacetate, m.p. 131°. Hydrolysis (10% Na₂CO₃) of (V) and subsequent acidification gives 5:7-dihydroxy-2-methylchromone, m.p. 279° (lit. 290°) (7-benzyl ether, m.p. 148°, which does not react with PhCHO); the preceding results differ from those of Canter *et al.* (A., 1931, 962). 7-Benzoyloxy-5-methoxy-2-methylchromone, m.p. 156°, and (III) give a substance, C₃₂H₂₆O₅, m.p. 181°.

XIV. 1-Hydroxy- β -naphthyl *o*-methoxystyryl ketone, m.p. 155° [acetate, m.p. 93°; dibromide, m.p. 157°, converted by EtOH-KOH into a compound, C₂₀H₁₄O₃, m.p. 252° (decomp.)], is prepared from 2:1-C₁₀H₆·Ac·OH (VI) and *o*-OMe·C₆H₄·CHO in EtOH-

KOH. 2:1- $C_{10}H_6AcOBz$ and $NaNH_2$ in Et_2O at $\approx 22^\circ$ followed by decomp. of the solid reaction product with dil. $AcOH$ give 1-hydroxy- β -naphthyl phenacyl ketone, m.p. 147° , converted by conc. H_2SO_4 at room temp. into α -naphthaflavone, m.p. 157° . 2-Acetyl- α -naphthyl *o*-methoxybenzoate, m.p. 115° [from (VI) and o - $OMe \cdot C_6H_4 \cdot COCl$ in C_5H_5N], is similarly converted into 1-hydroxy- β -naphthyl *o*-methoxyphenacyl ketone, m.p. 113° , and thence by $EtOH$ -conc. H_2SO_4 into 2'-methoxy- α -naphthaflavone, m.p. 164° [sulpho-derivative, m.p. 326° (decomp.), formed using conc. H_2SO_4 alone]. 2-Acetyl- α -naphthyl 2:4-dimethoxy-, m.p. 126° , and 3:4:5-trimethoxy-, m.p. 143° , benzoates similarly give 1-hydroxy- β -naphthyl 2:4-dimethoxy-, m.p. 133° , and 3:4:5-trimethoxy-, m.p. 142° , phenacyl ketone, respectively, convertible into 2':4'-dimethoxy-, m.p. 214° , and 3':4':5'-trimethoxy-, m.p. 224° , α -naphthaflavone, respectively.

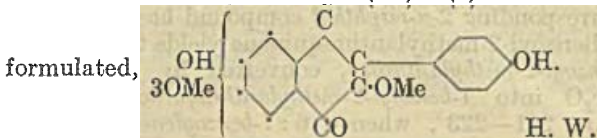
XV (cf. A., 1934, 660, 1107). 2-Hydroxy-4-benzyl-oxyphenyl *p*-methoxybenzyl ketone, m.p. 103° [from the 2:4-(OH) $_2$ -derivative, CH_2PhCl , and anhyd. K_2CO_3 in $COMe_2$], HCO_2Et , and Na give the benzyl ether, m.p. 182° , of 7-hydroxy-4'-methoxyisoflavone (formononetin) (VII), m.p. 257° (cf. Wessely *et al.*, A., 1933, 614). The Ac derivative, m.p. 170° (lit. 164 — 165°), of (VII) and HI (*d* 1.7) in Ac_2O at 140° afford 7:4'-dihydroxyisoflavone (daidzein), m.p. 322° (darkens $> 310^\circ$) [Ac_2 derivative, m.p. 187° (sinters at 184°) (lit. 182°)] (cf. Baker *et al.*, A., 1933, 510; Wessely *et al.*, loc. cit.). 2-Hydroxy-4-benzyl-oxyphenyl 3:4-methylenedioxybenzyl ketone, m.p. 94° (sinters at 86°) [from ψ -baptigenetin (Spath and Schmidt, A., 1929, 1458), CH_2PhCl , and K_2CO_3 in $COMe_2$], HCO_2Et , and Na give the benzyl ether, m.p. 168° , of 7-hydroxy-3':4'-methylenedioxyisoflavone (ψ -baptigenin), m.p. 292 — 293° (darkens $> 288^\circ$) [lit. 298 — 299° (vac.) and 303 — 304°] [Ac derivative, m.p. 176° (lit. 173°)]. H. B.

Chromone chlorides and dichromylenes. A. SCHONBERG and S. NICKEL (Ber., 1934, 67, [B], 1795—1798; cf. A., 1931, 1305).—8-Methylflavone is readily converted by $(\cdot COCl)_2$ into the corresponding chloride, which with Cu powder in boiling $PhMe$ affords 2:2-diphenyl-8:8'-dimethyldichromylene, m.p. 240° . Similarly, 8-methoxy-1-thioflavone successively yields the chloride and 8:8'-dimethoxy-2:2'-diphenyl-1:1'-dithiodichromylene, m.p. 292 — 293° . Reduction of xanthone in $AcOH$ containing Ac_2O and $NaClO_4$ by activated Zn wool gives the dimerchlorate of 9:9'-dihydroxydixanthyl, converted by $MgPhBr$ or $LiPh$ in Et_2O into dixanthylene. H. W.

Components of *Matteucia orientalis*. Optically active flavanones. S. FUJISE and T. KUBOTA (Ber., 1934, 67, [B], 1905—1908; cf. A., 1933, 832).—The difficulties met in the attempted identification of demethoxymatteucinol (I) with synthetic 5:7-dihydroxy-6:8-dimethylflavanone (II) are explained by observation that the natural material is optically active. Matteucinol (IV) (improved prep. from the roots of *M. orientalis*) has m.p. 175.5° , $[\alpha]_D^{25} -39.47^\circ$ in $COMe_2$ (Me ether, m.p. 103 — 103.5° , $[\alpha]_D^{14} -7.80^\circ$ in whilst the data, m.p. 202.5° , $[\alpha]_D -50.00^\circ$ in $COMe_2$, and m.p. 112 — 112.5° , $[\alpha]_D^{14} -22.47^\circ$, respectively, are recorded for (I) and its Me ether. (I) gives an oxime, m.p. 210 — 211° , $[\alpha]^{25} -62.1^\circ$ (corresponding

r-oxime, m.p. 232°), whilst the oxime of (III) has m.p. 202° , $[\alpha]_D^{18} -33.1^\circ$ (corresponding *r*-oxime, m.p. 228 — 229°). After being racemised by conc. H_2SO_4 the natural materials and their Me ethers are identical with the corresponding synthetic substances. H. W.

New flavone dye. W. KARRER (Helv. Chim. Acta, 1934, 17, 1560—1565).—Thapsin (I), $C_{19}H_{18}O_8$, m.p. 224° , is obtained as by-product of the extraction of digitoxin from (?) *Digitalis thapsi*, L. It contains 2 OH and 4 OMe. (I) is converted by Me_2SO_4 and NaOH into dimethylthapsin, prisms, m.p. 130° , or rhombohedra, m.p. 129° , transformed by boiling KOH - $EtOH$ into *p*- $OMe \cdot C_6H_4 \cdot CO_2H$ and 2-hydroxy-3:4:5:6: ω -pentamethoxyacetophenone (II), m.p. 66 — 67° . Since ethylation of (I) gives diethylthapsin, dimorphous, m.p. 130° , hydrolysed to *p*- $OEt \cdot C_6H_4 \cdot CO_2H$ and 2-hydroxytetramethoxyethoxyacetophenone (III), m.p. 63 — 64° , the C_6H_6 nucleus carries only 1 OH. Methylation of (II) yields 2:3:4:5:6: ω -hexamethoxyacetophenone, b.p. $210^\circ/14$ mm., oxidised by $KMnO_4$ to (impure) pentamethoxyphenylglyoxylic acid, whilst similar treatment of (III) leads to pentamethoxyethoxyacetophenone, b.p. $208^\circ/14$ mm., oxidised to an acid which differs from (IV). (I) is therefore



Dibenzfuran [diphenylene oxide]. III. Nuclear substitutions. H. GILMAN, G. E. BROWN, W. G. BYWATER, and W. H. KIRKPATRICK (J. Amer. Chem. Soc., 1934, 56, 2473—2477).—2-Acetamido- (I) or 2-diacetamido- (II) diphenylene oxide and Br (1 mol.) in $AcOH$ give 3-bromo-2-acetamidodiphenylene oxide, m.p. 194° ; the free base, m.p. 129° (hydrochloride, decomp. 236°), is de-aminated to 3-bromodiphenylene oxide (III) and converted by aq. $NH_3 + CuBr$ at 190° into 2:3-diaminodiphenylene oxide (IV) (quin-oxaline, m.p. 184 — 185°). (I) or (II) and HNO_3 in $AcOH$ afford 3-nitro-2-acetamidodiphenylene oxide, m.p. 196° [described by Borsche and Schacke (A., 1924, i, 161) as the Ac_2 derivative], which on hydrolysis and reduction gives (IV). 3-Aminodiphenylene oxide is prepared from the 3-Br-derivative (V), aq. NH_3 , and $CuCl$ at 200 — 210° ; its Ac_2 derivative (VI) and Br in $AcOH$ give the Ac_1 derivative, m.p. 240 — 241° , of 2-bromo-3-aminodiphenylene oxide, m.p. 172 — 173° , also convertible [as for (V)] into (IV). (VI) and fuming HNO_3 in $AcOH$ afford 2-nitro-3-acetamidodiphenylene oxide (Brumberg, Diss., Gottingen, 1925), which on hydrolysis and reduction gives (IV). Diphenylene oxide (VII) and Cl_2 (1 mol.) in $AcOH$ at 60° afford the 3-Cl-derivative, also prepared from (VII) and PCl_5 ; with Cl_2 (excess) in CCl_4 at 40° , the 3:6- Cl_2 -derivative, m.p. 185° , is formed. (VII) and I (1 mol.) in conc. $HNO_3 + CHCl_3$ give the 3-*I*-derivative, m.p. 112° ; with 2 mols. of I in the hot, the 3:6- I_2 -derivative, m.p. 173° , results. 2-Nitrodiphenylene oxide and Br in $AcOH$ at 70° give 3-bromo-7-nitrodiphenylene oxide (VIII), m.p. 250.5 — 251.5° , also prepared [together with a little of the $2NO_2$ -isomeride, m.p. 154.5 — 155.5°], from (III) and HNO_3 (*d* 1.52) in $AcOH$. 3:7-Diaminodiphenylene oxide is obtained by reduc-

tion of 7-nitro-3-aminodiphenylene oxide [from (VIII), aq. NH_3 , and CuCl at 208—210°] or from 3-bromo-7-aminodiphenylene oxide, m.p. 133—134°, aq. NH_3 , and CuBr at 205°. 2-Bromodiphenylene oxide and HNO_3 (d 1.5) in AcOH give (probably) the 7- NO_2 -derivative, m.p. 251°, converted by aq. $\text{NH}_3 + \text{CuBr}$ at 200° into (probably) 7-nitro-2-aminodiphenylene oxide, m.p. 133°. H. B.

Supposed aryloxyperhydrofurananthroxyls as derivatives of benzoylene- $\beta\beta'$ -benzofuran. II. R. SCHOLL and J. DONAT (Ber., 1934, 67, [B], 1919—1922; cf. A., 1933, 508).—Re-examination has been made of the following "aryloxyperhydrofurananthroxyls," now shown to be derivatives of benzoylene- $\beta\beta'$ -benzofuran. Anthraquinone-1-carboxyl chloride and PhOMe in presence of FeCl_3 at 130° give 1-anisoylanthraquinone, transformed by $\text{Na}_2\text{S}_2\text{O}_4$ in boiling aq. EtOH into 9-hydroxy-1-anisoylanthrone, which yields 6:7-benzoylene-2-anisyl- $\beta\beta'$ -benzofuran, m.p. 182°, with conc. H_2SO_4 . 1-p-Tolylanthraquinone, m.p. 205—206°, similarly affords 6:7-benzoylene-2-p-tolyl- $\beta\beta'$ -benzofuran, m.p. 186°. Diphenyl anthraquinonyl ketone, m.p. 234—235°, yields 6:7-benzoylene-2-p-diphenyl- $\beta\beta'$ -benzofuran, m.p. 220°. The corresponding 2- α -naphthyl compound has m.p. 209°. 1-Benzoyl-2-methylantraquinone yields 9-hydroxy-1-benzoyl-2-methylanthrone, converted by KOAc and Ac_2O into 1-benzoyl-2-methylantraquinol diacetate, m.p. 221—223°, whence 6:7-benzoylene-2-phenyl-3-methyl- $\beta\beta'$ -benzofuran, m.p. 206°. H. W.

Rotenone. XXX. Non-crystalline constituents of derris root. H. L. HALLER and F. B. LAForge (J. Amer. Chem. Soc., 1934, 56, 2415—2419).—The material extracted by light petroleum (b.p. 30—60°) from the ground root is freed from toxicarol by extraction of its Et_2O solution with aq. 5% KOH ; the Et_2O solution is then conc. and kept at 0°, when rotenone (I) separates. Evaporation of the residual solution gives amorphous "deguelin concentrate" (II), which contains 60—63% of (I) + deguelin (III) [as determined by Gross and Smith's method (A., 1934, 1017)]. Treatment of (II) with MeOH-KOH in H_2 affords 38.2% of optically inactive (III); successive treatment of the residue (after extraction of its Et_2O solution with 2% KOH) with air in MeOH-KOH and $\text{EtOH-H}_2\text{SO}_4$ gives (mainly) dehydrorotenone, some dehydrodeguelin, and a little of a compound, $\text{C}_{19}\text{H}_{14}\text{O}_6$, m.p. 240—250°. Reduction (H_2 , PtO_2 , EtOAc) of (II) affords tetrahydroroteneone (dihydroroteneone acid), 19.1% of β -dihydroroteneone (dihydrodeguelin) (IV), $[\alpha]_D^{20} -104^\circ$ in C_6H_6 , and (after treatment with MeOH-KOH in H_2) about 15% of optically inactive (IV). (II), therefore, contains < 19% of optically active (III). The 1-deguelin of Takei *et al.* (A., 1934, 194) is probably *dl*-deguelin contaminated with a little (I). isoRotenone (V), $[\alpha]_D^{20} -74.6^\circ$ in C_6H_6 , +13° in dioxan, is racemised by EtOH-KOH in H_2 ; (V) obtained by hydrolysis ($\text{EtOH-H}_2\text{SO}_4$) of acetylisorotenone (A., 1932, 950) has $[\alpha]_D^{20} -21.1^\circ$ in C_6H_6 . H. B.

Hydrogenation of derivatives of pyridine. H. ADKINS, L. F. KUICK, M. FARLOW, and B. WOJCIK (J. Amer. Chem. Soc., 1934, 56, 2425—2428).— $\text{C}_5\text{H}_5\text{N}$ and the following derivatives of $\text{C}_5\text{H}_5\text{N}$ are reduced [H_2 (150–300 atm.); usually Raney Ni; occasionally

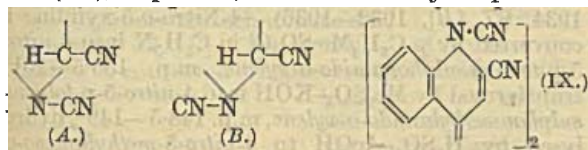
no solvent, but usually in EtOH , Et_2O , dioxan, or methylcyclohexane; 100—200°] to the corresponding piperidines: 2-Me, 2- and 4-Ph, 2- CH_2Ph , 2- $\text{CH}_2\text{Ph}\cdot\text{CH}_2$; 3- CO_2Et , 3- CO_2Bu , 2:6-Me₂, 2:6-Ph₂, 2:6-di- β -phenylethyl, 6-Ph-2-Me, 2- γ -phenylpropyl, 2- δ -phenylbutyl, 2:3- and 2:6-(CO_2Et)₂, 3- CO_2Et -2:6-Me₂, and 3-Ac (which gives 3-ethyl- and 3- α -hydroxyethyl-piperidines); the 2:6-derivatives are reduced most readily. Reduction of Et pyridine-3-carboxylate in EtOH gives Et piperidine-3-carboxylate, b.p. 79—80°/4 mm. (cf. McElvain and Adams, A., 1924, i, 417), and some of its 1-Et derivative, b.p. 113—116°/19 mm. (hydrochloride, m.p. 143°). Et piperidine-2:3-dicarboxylate [hydrochloride, m.p. 200—202° (decomp.)] has b.p. 119—121°/3 mm. (cf. Clemo *et al.*, A., 1932, 178). Et 2:6-dimethylpiperidine-3-carboxylate, b.p. 93—95°/10 mm. (hydrochloride, m.p. 162—163°), and Buⁿ pyridine-3-carboxylate, b.p. 119—120°/8 mm., and piperidine-3-carboxylate, b.p. 83—86°/2 mm., are new. Reduction (H_2 , Cu-Cr oxide, EtOH at 250°) of $\text{C}_5\text{H}_5\text{N}[\text{CH}_2]_n\text{CO}_2\text{Et}$ to $\text{C}_5\text{H}_{11}\text{N}[\text{CH}_2]_n\text{CH}_2\text{OH}$ occurs when $n=1$ or 4, to a much smaller extent when $n=3$, but not when $n=2$. H. B.

2-Aminopyridine series. II. Action of phthalic anhydride and salicyloyl chloride on 2-aminopyridine. K. FEIST and J. SCHULTZ (Arch. Pharm., 1934, 272, 785—791; cf. A., 1934, 417).—2-Aminopyridine (I) and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ at 180° give the *H* phthalate, m.p. 120°, and N-2-pyridylphthalimide (II), m.p. 225° (perbromide, XBr_2 , m.p. 162°; periodide, XI_3 , m.p. 128°), the constitution of which is proved (i) by its resistance to hydrogenation, and (ii) by its formation also from $o\text{-C}_6\text{H}_4(\text{CO})_2\text{S}$, $o\text{-C}_6\text{H}_4(\text{COCl})_2$, or $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NH}$. (II) and cold, aq. NaOH give N-2-pyridylphthalamic acid, m.p. 169° (*Na* salt, m.p. > 300°), which cannot be esterified, but regenerates (II) at the m.p. or when heated in 95% EtOH or AcCl . 6-Amino- α -picoline gives similarly the *H* phthalate, m.p. 168°, and N-6- α -picolinophthalimide, m.p. 192.5°. $o\text{-OAc-C}_6\text{H}_4\text{COCl}$ and (I) in Et_2O give a mixture of 2-salicyloyl, m.p. 203°, and 2-acetylsalicyloyl-amidopyridine, m.p. 140°, indifferent to hydrogenation. R. S. C.

Amino-acids and related compounds. VIII. Electrolytic oxidation of histamine and histidine. Y. TAKAYAMA and H. OEDA (J. Chem. Soc. Japan, 1934, 55, 649—654; cf. A., 1933, 1127).—On electrolytic oxidation, histamine yields NH_3 , CO_2 , $\text{CO}(\text{NH}_2)_2$, and β -alanine; histidine (I) similarly yields CO_2 , NH_3 , $\text{CH}_2(\text{CO}_2\text{H})_2$ (II), and a melanin-like substance. Aspartic acid is suggested as an intermediate in the formation of (II) from (I). CH. ABS. (r)

Quinoline dicyanide. Stereochemistry of ter-valent nitrogen. O. MUMM, H. LUDWIG, and (in part) D. H. LU and R. RADENHAUSEN (Annalen, 1934, 514, 34—60).—6-Methoxyquinoline (I) (2 mols.), CNBr (1 mol.), and anhyd. HCN (rather > 2 mols.) in cold C_5H_6 give (I) hydrobromide and a dicyanide (II), $\text{C}_{12}\text{H}_9\text{ON}_3$, m.p. 85—87°, which is converted by dil. EtOH-NH_3 into an isomeride, m.p. 169—170°; 3-methylquinoline (III) similarly affords analogous dicyanides, m.p. 139° (IV) and 125° (V), respectively. Dicyanides could not be obtained from 2- and 4-

methyl- or 2- and 4-phenyl-quinolines; the last-named gives 2-hydroxy-1-cyano-4-phenyl-1:2-dihydroquinoline, m.p. 150° (cf. below). α -Naphthquinoline similarly affords (at 150°) the 4-CN-derivative, m.p. 154—156°, hydrolysed (conc. HCl at 150°) to α -naphthquinoline-4-carboxylic acid, m.p. 278° (decomp.), which is oxidised (alkaline KMnO_4) to pyridine-2:3:4-tricarboxylic acid (VI). 4-Cyano-2-phenyl-, m.p. 138°, and 4-cyano-8-methyl-quinoline, m.p. 140—141° [corresponding acid, m.p. 276° (decomp.; darkens at 260°), also oxidised to (VI)], are similarly prepared from 2-phenyl- and 8-methyl-quinoline, respectively. The primary (more fusible) (VII) and sec. (less fusible) (VIII) quinoline dicyanides (A., 1914, i, 574) are both hydrolysed (conc. HCl at 150°) to quinoline-2-carboxylic acid [hydrochloride (+ H_2O), m.p. 202°]; the 8-naphthquinoline dicyanides (*loc. cit.*) similarly afford 8-naphthquinoline-2-carboxylic acid (hydrochloride). (VII) and (VIII) are considered to be *cis*- (A) and *trans*- (B) forms of 1:2-dicyano-1:2-dihydroquinoline. (VII) or (VIII) and I in $\text{EtOH}-\text{C}_6\text{H}_5\text{N}$ give the compound (IX), m.p. 347°, and a little 2-cyanoquinoline



(X). (IX) and Br in AcOH afford 2:2'-dicyano-4:4'-diquinolyl, m.p. 306°, hydrolysed (conc. HCl at 130°) to 4:4'-diquinolyl-2:2'-dicarboxylic acid (+ $2\text{H}_2\text{O}$), m.p. 232° [diamide, m.p. 355—356°, obtained from (IX) and cold conc. H_2SO_4], which when heated at 200—210° gives 4:4'-diquinolyl (picrate, m.p. 262—263°) (Clemo and Perkin, A., 1924, i, 1103). (IX) and conc. HNO_3 in AcOH afford 2:2'-diketo-1:1'-dicyano-1:2:1':2'-tetrahydro-4:4'-diquinolyl, m.p. 334°, hydrolysed (conc. HCl at 130°) to 2:2'-dihydroxy-4:4'-diquinolyl, m.p. 397—399°. (VII) or (VIII) and I in CHCl_3 +anhyd. NaOAc give (X). (VII) heated with AcOH affords quinoline (XI); similarly, (II) gives (I), (IV) yields (III), but (VIII) and (V) furnish 2-keto-1:2:3:4-tetrahydroquinoline (cf. *loc. cit.*) and its 3-Me derivative, m.p. 130°, respectively. Conversion of (VII) into (VIII) can be effected with NH_2R , NHR_2 , or NR_2 but not with $\text{EtOH}-\text{KOH}$ or acids; the change (VIII) \rightarrow (VII) has not been realised.

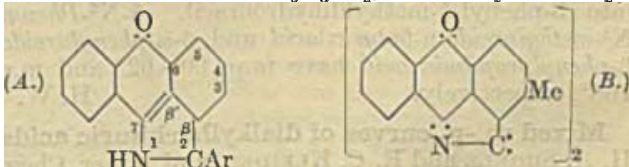
(XI) (1 mol.) and CNBr (1 mol.) in moist Et_2O or C_6H_6 give 2-hydroxy-1-cyano-1:2-dihydroquinoline (XII), m.p. 117°; in the absence of moisture di-(1-cyano-1:2-dihydro-2-quinolyl) ether (XIII), m.p. 150°, results. (XII) and (XIII) are converted by dil. HCl or 20% HClO_4 into (XI) and by 70% HClO_4 into 1-cyanoquinolinium perchlorate, m.p. 194°. The following are similarly prepared: 2-hydroxy-1-cyano-6-methyl-1:2-dihydroquinoline, m.p. 120°, the corresponding ether, m.p. 139°, and perchlorate, m.p. 191°; 2-hydroxy-1-cyano-1:2-dihydro- β -naphthquinoline (XIV), m.p. 121°, the corresponding ether (XV), m.p. 132°, and perchlorate, m.p. 200°; hydroxy-N-cyano-dihydroacridine and the corresponding ether. (XV) heated with the appropriate AlkOH gives the Me, m.p. 159°, Et, m.p. 128.5°, and Pr, m.p. 72°, ethers of (XIV). H. B.

Synthesis of periquinolinazole (N-N). I. Attempted synthesis of tetrahydropyridinquinolinazole. S. N. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1934, 3, 223—228).—The formyl derivative of N-aminodihydrocarbostyryl (I) [from (I) and HCO_2H at 180—200°] with POCl_3 in boiling PhMe gives a hydrochloride, m.p. 205—206°, of an oily base, reduced by Zn-dil. HCl to dihydrocarbostyryl, no cyclisation being effected. Condensation with CH_2O under usual conditions also failed. With BzCl and $\text{C}_6\text{H}_5\text{N}$ (I) gives its Bz derivative, m.p. 168.9°, converted by P_2O_5 in boiling PhMe into a substance, m.p. 212°. An improved prep. of quinoline-8-carboxylic acid by CrO_3 -30% H_2SO_4 oxidation of 8-methylquinoline is described. J. W. B.

Manufacture of carbazole compounds.—See B., 1934, 1095.

3:6-Dialkoxy-10-alkylacridinium derivatives with various types of amino-group in the 9 position. III. Mechanism of reaction of 9-chloro-3:6-dialkoxy-10-alkylacridinium chloride. K. ISHIIHARA (J. Chem. Soc. Japan, 1934, 55, 716—730).—Hydrolysis of 9-chloro-3:6-dialkoxy-10-alkylacridinium chlorides gives both the corresponding hydroxides (I) and 9-hydroxy-3:6-dialkoxy-10-alkylacridinium hydroxides (II). The stabilities of (I) \propto their dissociation consts. and inversely \propto stability of (II). CH. ABS. (r)

Supposed arylperipyrrolinoanthroxyls as derivatives of benzoylene- $\beta\beta'$ -benzopyrrole and the violet products of reduction of 1-cyanoanthraquinones. R. SCHOLL, O. BÖTTGER, and E. STIX (Ber., 1934, 67, [B], 1922—1931).—The recognition of the supposed aryloxypyrroloanthraquinones as derivatives of benzoylene- $\beta\beta'$ -benzofuran (A., 1933, 508; this vol., 92) implies the consideration of the pyrrolinoanthroxyls (formerly pyrrolinoanthranolazyls) as derivatives of benzoylene- $\beta\beta'$ -benzopyrroles (cf. A). This view is supported by fresh analyses; it explains the solubility in NH_3 and NaOH, the behaviour on oxidation and reduction, and the titration with CrO_3 . The arylperipyrrolinoanthranolazyls (A., 1928, 773) with $\text{Ar}=\text{Ph}$, $\text{C}_6\text{H}_4\text{Me}$, $m\text{-C}_6\text{H}_3\text{Me}_2$, $\text{C}_6\text{H}_4\text{OMe}$, $\text{C}_6\text{H}_4\text{Cl}$, the N-Me and Bz derivative with $\text{Ar}=m\text{-C}_6\text{H}_3\text{Me}_2$, and the aryl-2-methyl



derivatives with $\text{Ar}=\text{Ph}$ and $p\text{-C}_6\text{H}_3\text{Me}_2$ are re-described in accordance with A as 6:7-benzoylene-2-aryl- $\beta\beta'$ -benzopyrroles, their 1 Me and Bz derivative and 6:7-benzoylene-2-aryl-3-methyl- $\beta\beta'$ -benzopyrroles. The oxylammonium or oxylum salts are oxonium or NH_4 salts.

Mild reduction of 1-cyano-2-methylantraquinone by Zn dust and dil. NH_3 leads, as with $\text{Na}_2\text{S}_2\text{O}_4$, to 1-cyano-2-methylantraquinol. With conc. NH_3 for a long period at room temp. or for a short time in boiling solution the product is 6:7-benzoylene-3-methyl- $\beta\beta'$ -benzopyrrole (I), decomp. $> 200^\circ$ (isolated

through the *perchlorate*), oxidised by amyl nitrite in boiling PhNO_2 to the substance B, decomp. about 300° . Treatment of (I) in COMe_2 with Me_2SO_4 and 20% NaOH gives 6 : 7-benzoylene-1 : 3-dimethyl- $\beta\beta'$ -benzopyrrole, m.p. about 187° after softening (*perchlorate*). 1-Cyanoanthraquinone gives non-cryst. 6 : 7-benzoylene- $\beta\beta'$ -benzopyrrole, oxidised by amyl nitrite in PhNO_2 to the substance $\text{C}_{30}\text{H}_{14}\text{O}_2\text{N}_2$, m.p. 508 — 509° after darkening at about 490° when rapidly heated. H. W.

Synthesis of paraberine. I. Synthesis of 8 : 17-diketo-6 : 17-dihydroparaberine. S. N. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1934, 3, 208—215).—When heated with $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ isocoumarincarboxylic acid (Bamberger *et al.*, A., 1894, i, 192) affords N-benzylisocarbostyryl-3-carboxylic acid [1-keto-2-benzyl-1 : 2-dihydroisquinoline-3-carboxylic acid], m.p. 207° , the chloride of which is converted by AlCl_3 in PhNO_2 into 8 : 17-diketo-6 : 17-dihydroparaberine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{CO} \\ \text{CO}\cdot\text{N}\cdot\text{CH} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, m.p. 189° (oxime, m.p. 306°), which could not be reduced to tetrahydroparaberine (I). $\text{NH}_2\cdot\text{CH}(\text{CH}_2\text{Ph})_2$ (or its formyl derivative) could not be converted into (I) by ring closure with CH_2O . J. W. B.

β -Ureidocarboxylic acids and dihydrouacils. I. β -Phenylureidocarboxylic esters and 3-phenyldihydrouacils. K. MORSCH (Monatsh., 1934, 64, 333—340).— PhNCO in Et_2O is added to the NH_2 -ester in Et_2O , whereby the ω -phenylureido-ester is obtained in 85—95% yield; it is converted by HCl into the corresponding dihydrouacil. The following transformations are recorded : $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ into Me β - N^2 -phenyl- N^1 -methylureidopropionate, m.p. 58 — 59° , and thence into 3-phenyl-1-methyldihydrouacil, m.p. 130.5 — 131.5° ; Et β - N^2 -phenyl- N^1 -methylureido-n-butyrate, m.p. 111.5 — 112.5° , whence 3-phenyl-6-methyldihydrouacil, m.p. 209 — 209.5° ; $\text{NHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ into Et β - N^2 -phenyl- N^1 -methylureido-n-butyrate, m.p. 67° , whence 3-phenyl-1 : 6-dimethyldihydrouacil, m.p. 154° . Et β - ω -phenylureido- β -phenylpropionate, m.p. 116.5 — 117.5° , and Et β - N^2 -phenyl- N^1 -methylureido- β -phenylpropionate, m.p. 102 — 102.5° , are described. PhNCO and an alkaline solution of $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ yield a non-cryst. product transformed by dil. HCl into 3-phenyl-1-methyldihydrouacil. β - N^2 -Phenyl- N^1 -methylureido-n-butyric acid and β - ω -phenylureido- β -phenylpropionic acid have m.p. 60 — 62° and m.p. 168° , respectively. H. W.

Mixed m.-p. curves of dialkylbarbituric acids. H. A. SHONLE and E. C. KLEIDERER (J. Amer. Chem. Soc., 1934, 56, 2489—2490).—M.-p. curves for the following pairs of dialkylbarbituric acids are given: (i) 5-ethyl-5- α -ethylpropyl- and 5-ethyl-5- α -methylbutyl- (ii) 5- α -ethylpropyl-5-allyl- and 5- α -methylbutyl-5-allyl-, (iii) 5-ethyl-5-isoamyl- and 5-ethyl-5- α -methylbutyl- (optically active). H. B.

Barbituric acids containing a sec.-amyl group. SHONLE (J. Amer. Chem. Soc., 1934, 56, 2490).—5-alkyl-5- α -ethylpropylbarbituric acids previously prepared (A., 1930, 1047) contain some of the 5- α -methylbutyl derivative (cf. Tabern and Volwiler, A., 1934, 183). Further details are given for

the prep. of 5- α -ethylpropyl-, m.p. 196 — 197.5° , 5-ethyl-5- α -ethylpropyl-, m.p. 161 — 161.5° , 5- α -ethylpropyl-5-allyl-, m.p. 131 — 132° , and 5- α -methylbutyl-5-allyl-, m.p. 99 — 100° , -barbituric acids. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{CHEt}_2$ has m.p. 43 — 45° (lit. 32 — 35°). Pharmacological data are given. H. B.

Antineuritic vitamin.—See A., 1934, 1415.

6 : 7-Dimethyl- and 1 : 3 : 6 : 7-tetramethylalloxazine. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1826—1829).—Condensation of 4 : 5-diamino-o-xylene hydrochloride (I) with alloxan in H_2O leads to 6 : 7-dimethylalloxazine, decomp. 360° after darkening at 335° , identical in cryst. form, absorption spectrum, colour reactions, and fluorescence with the Na_2CO_3 -sol. product (II) of the degradation of lumilactoflavin. It is transformed by CH_2N_2 into 1 : 3 : 6 : 7-tetramethylalloxazine, m.p. 252° (corr.), also obtained from (I) and dimethylalloxan and from (II), thus confirming the structure of (II). H. W.

Synthesis of 6 : 7 : 9-trimethylflavin (lumilactoflavin). R. KUHN and K. REINEMUND (Ber., 1934, 67, [B], 1932—1936).—4-Nitro-o-5-xylydine is converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ into 4-nitro-5-p-toluenesulphonamido-o-xylene, m.p. 150.5 — 151° , transformed by Me_2SO_4 - KOH into 4-nitro-5-p-toluenesulphonmethylamido-o-xylene, m.p. 148.5 — 149° , hydrolysed by H_2SO_4 - AcOH to 4-nitro-5-methylamino-o-xylene (I), m.p. 139° . (I) is reduced by SnCl_2 and conc. HCl to 4-amino-5-methylamino-o-xylene (II), m.p. 79 — 80° , the dihydrochloride, decomp. 180 — 185° when rapidly heated, of which condenses with alloxan tetrahydrate (III) in H_2O at 50 — 60° to 6 : 7 : 9-trimethylflavin (lumilactoflavin) [also $+0.5\text{HCO}_2\text{H}$]. (II) and (III) in EtOH at 15 — 20° yield alloxanyl-4-amino-5-methylamino-o-xylene, m.p. 251 — 252° (decomp.), transformed by boiling $2\text{N}\cdot\text{Na}_2\text{CO}_3$ into 2-keto-1 : 6 : 7-trimethyl-1 : 2-dihydroquinoxaline-3-carboxylic acid, m.p. 214° (decomp.), which passes by loss of CO_2 into 2-keto-1 : 6 : 7-trimethyl-1 : 2-dihydroquinoxaline, m.p. 176° ; these substances are identical with those obtained by the alkaline degradation of lumilactoflavin. H. W.

Synthesis of 6 : 7-dimethyl-9-n-amyflavin. R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 1941—1942).—4-Nitro-o-5-xylydine is heated at 140° with $n\text{-C}_5\text{H}_{11}\text{I}$ and the product is reduced by SnCl_2 - AcOH - HCl to 4-amino-5-n-amyllamino-o-xylene, which, with excess of alloxan in boiling AcOH , affords 6 : 7-dimethyl-9-n-amyflavin, decomp. 295 — 300° (corr.). H. W.

Syntheses of substances resembling lactoflavin. II. P. KARRER, E. SCHLITTLER, K. PFAEHLER, and F. BENZ (Helv. Chim. Acta, 1934, 17, 1516—1523; cf. A., 1934, 1233).—Colamine, $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, and anhyd. NaOAc at 100 — 120° yield o-nitrohydroxyethylaniline, m.p. 76° , reduced (Pt and H_2) to the diamine, which with alloxan tetrahydrate (I) yields 9- β -hydroxyethylisalloxazine (II), m.p. 310° (decomp.) after becoming discoloured about 300° . Since irradiation of (II) in neutral or alkaline solution causes formation of alloxazine and methylisalloxazine, the presence of 1OH in the β -position is sufficient to induce the typical flavin photo-sensitiveness. 5-Chloro-4-nitro-o-xylene, from 4-nitro-o-5-xylydine

(Sandmeyer), is converted by α -aminopropane- β - γ -diol and anhyd. NaOAc at 125—130° into 4-nitro- α - β - γ -dihydroxypropylamino-*o*-xylene, m.p. 102°, which is reduced and condensed with (I) to 6:7-dimethyl-9- β - γ -dihydroxypropylisalloxazine, m.p. about 294° (decomp.) after darkening. p -C₆H₄BrAc is reduced (Clemmensen) to p -C₆H₄BrEt, transformed by HNO₃ (d 1.49) at $\geq 0^\circ$ into a mixture of NO₂-compounds, b.p. 132—134°/9 mm., which with NH₃-EtOH at 150° yields 3-nitro-4-aminoethylbenzene (III), b.p. 126—130°/0.4 mm. (III) is reduced (SnCl₂ and HCl) and condensed with (I) to 6(or 7)-ethylalloxazine. The fluorescence colours of alloxazine derivatives are so characteristic that they may be used for purposes of identification.

H. W.

Ovoflavin e. P. KARRER and K. SCHOPP (Helv. Chim. Acta, 1934, 17, 1557—1558).—Irradiation of ovoflavin (I), from dry, technical ovalbumin, in 75% MeOH leads to 6:7-dimethylalloxazine. (I) therefore contains the 3-ring skeleton of lactoflavin (II), but the identity of the sugar-like side-chains in (I) and (II) remains unestablished.

H. W.

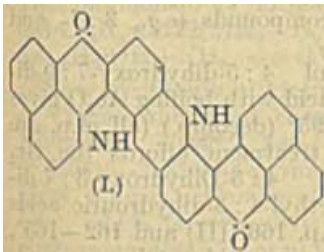
N-Dihydrobenzanthroneazine. E. J. MULLER (Ber., 1934, 67, [B], 1799—1800).—N-Dihydrobenzanthroneazine is converted by glycerol and H₂SO₄ at 120°

into the compound (I), which does not yield a vat with Na₂S₂O₄, is largely unchanged by molten alkali at 300°, but decomposed at 400°, and is oxidised by conc. H₂SO₄ to the azine. Anthroneazine could not be transformed into

benzanthroneazine. Indanthrene in presence of NH₂Ph does not yield a cryst. product, although the formation of a dihydroazine is established.

H. W.

Dicarbazyls. VI. Synthesis of 1:1'-dicarbazyl. (MISS) (J. G. DUNLOP, T. F. MACRAE, and S. H. TUCKER (H.C.S., 1934, 1672—1678).—2:2'-Diaminodiphenyl (I), 2:4-(NO₂)₂C₆H₃Cl (II), and anhyd. K₂CO₃ at 140° for 4 hr. give 80% of 2:2'-di-(2'':4'':4''-dinitroanilino)diphenyl (III), brick-red, m.p. 238—241° (corr.) (yellow 1:1-compound with C₅H₅N); at 190° for 10 min. (cf. Le Fevre, A., 1929, 705), a 60% yield of (III) results, whilst at 140° for 5 min., 10% of 2-amino-2'-(2'':4'':4''-dinitroanilino)diphenyl (IV), m.p. 168—170° (corr.; slight softening at 162°), is obtained. (IV) is also prepared in 38% yield from (I), (II) (slight excess), and K₂CO₃ in xylene. The *salicylidene* derivative, m.p. 181—182.5° (corr.), of (IV) is probably the (III) of Le Fevre (*loc. cit.*). Carbazole, (II), and K₂CO₃ at 170—180° give N-2':4'-dinitrophenylcarbazole, m.p. 188—190° [the substance described as this by Le Fevre (*loc. cit.*) is probably (III)]. (III) is reduced (EtOH-NH₄HS) to 2:2'-di-(4''-nitro-2''-aminoanilino)diphenyl, m.p. 126°, converted by NaNO₂ in AcOH into 2:2'-di-(5''-nitro-1'':2'':3''-benzotriazolyl)diphenyl, m.p. about 140°, reduction of which gives unworkable products. p -C₆H₄Cl·CO₂H (V) (from p -C₆H₄ClMe and Na₂Cr₂O₇ in aq. AcOH-H₂SO₄) and warm HNO₃ (d 1.5) afford 4-chloro-3-nitrobenzoic acid [*amide*, m.p. 153—154°, dehydrated



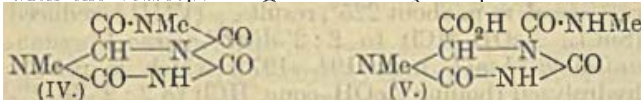
(P₂O₅ at 170°) to 4-chloro-3-nitrobenzonitrile (VI), m.p. 101° (lit. 110°), also obtained from (VI) and boiling HNO₃ (d 1.42). p -C₆H₄Cl·CN (VII) and HNO₃ (d 1.51) give (VI); nitration is slower with HNO₃ (d 1.5) and does not occur with HNO₃ (d 1.49). (VII) and boiling HNO₃ (d 1.42) afford (V). p -C₆H₄Cl₂ and (V) are nitrated by HNO₃ (d 1.48), indicating that the directing power of CN is $<$ that of Cl or CO₂H. (I), (VI), and K₂CO₃ at 160—185° give 2:2'-di-(2'':4'':4''-cyanoanilino)diphenyl (VIII), m.p. 243—248° (1:1-compounds with C₆H₅N, PhNO₂, and C₆H₆); at 150° or in xylene, 2-amino-2'-(2'':4'':4''-cyanoanilino)diphenyl, m.p. 143° [which with (VI) affords (VIII)], is obtained. (VIII) is hydrolysed (AcOH—conc. HCl at 200°) to 2:2'-di-(2'':4'':4''-carboxyanilino)diphenyl, m.p. $> 300^\circ$, which with Cu-bronze at 320° in an evacuated Pyrex tube gives 2:2'-di-*o*-nitroanilinodiphenyl (IX). Hydrolysis (EtOH—NaOH at 160°) of (VIII) affords a compound, m.p. $> 300^\circ$, and 3:4-(NH₂)(OH)C₆H₃·CO₂H; with HNO₃, a polynitrocompound, m.p. about 225°, results. (VIII) is reduced (SnCl₂, AcOH—HCl) to 2:2'-di-(2'':4'':4''-amino-4''-cyanoanilino)diphenyl, m.p. 194—197°, which is readily hydrolysed (boiling AcOH—conc. HCl) to 2:2'-di-(2'':4'':4''-carboxyanilino)diphenyl (X), m.p. 280° (decomp.; softens at 265° and blackens at 275°). (X) is decarboxylated (as above) to 2:2'-di-*o*-aminoanilinodiphenyl, the intermediate in the synthesis (A., 1934, 86) of 1:1'-dicarbazyl. 2:2'-Di-(5'':4'':1'':2'':3'':benzotriazolyl)diphenyl, m.p. 269°, heated at 320° gives (probably) 6:6'-dicyano-1:1'-dicarbazyl, m.p. 305—307°; hydrolysis (EtOH—NaOH at 160°) affords 2:2'-di-(5-carboxy-1'':2'':3'':benzotriazolyl)diphenyl, m.p. $> 330^\circ$.

Contrary to Le Fevre (*loc. cit.*), complete absence of steric hindrance during *NN'*-disubstitution is considered not to be proved. The steric effect is often negligible in comparison with the polar effect; thus, (IX) can be acetylated, whereas (III) cannot (under same conditions). Furthermore, the ease of acetylation and ethylation of NHPh₂, *o*-NO₂·C₆H₄·NHPh, and 2:4-(NO₂)₂C₆H₃·NHPh [which with Et₃SO₄ and KOH in EtOH (not COMe₂) gives a little of the *N*-Et derivative] decreases in the order quoted.

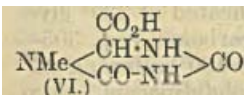
H. B.

Theobromuric acid degradation of theobromine. H. BILTZ [with M. HEYN, H. MUNDT, and P. DAMM] (Ber., 1934, 67, [B], 1856—1866).—The varying results obtained in analysis of the product of the action of Cl₂ on theobromine suspended in boiling CHCl₃ free from EtOH are due to the presence of 1/4CHCl₃, which is somewhat readily lost. The solvent-free substance is N-2:4:5:5-tetrachloro-1-methyl- Δ^2 -iminazolinyl-N-methylcarbamide-N'-carboxyl chloride, NMe·CCl₂ \rightarrow CCl=NMe·CO·NH·COCl. It is converted by H₂O into theobromuric acid [N-methyl-N-2:4-diketeto-1-methyl- Δ^3 -iminazolinyl-4-carbamide-N'-carboxylic acid] (I), $\text{NMe}\cdot\text{CO}\cdot\text{CO}\cdot\text{N}\rightarrow\text{C}\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{H}$. This constitution explains its ready conversion by warm H₂O into CO₂, methylparabanic acid, and NHMe·CO·NH₂, and the greater stability of the Me (II), m.p. 202°, and Et₂, m.p. 210°, esters and of the NH₄, m.p. 125° (decomp.), and Na, m.p. 105—106°

(decomp.), salts. The presence of NH in (I) is shown by the transformation of (II) into the Ag salt, converted by MeI and a little Ag₂O into *Me N-methyltheobromurate*, decomp. 175—177°, reduced by HI to (?) 3-methylhydantoin, m.p. 184—185°, and oxidised by K₂Cr₂O₇ and H₂SO₄ to a substance, C₈H₁₀O₅N₄, m.p. 205° (slight decomp.). Hot conc. HCl or hot NH₃-H₂O transforms (I) into N¹N³-dimethyl-*s*-dicarbamyl-carbamide (III), NH₂·CO·NMe·CO·NH·CO·NHMe, m.p. 200—201° (converted by boiling 20% into NH₂Me and *N*-methylcyanuric acid, m.p. 290°), and *N*H₄ dimethylureidoglycollate, NH₂·CO·NMe·C(OH)(CO₂NH₄)·NH·CO·NHMe, m.p. 196—197°. Reasons are advanced against the symmetrical formula for (III) proposed by Fischer *et al.* Reduction of (I) with HI leads to hydrotheobromuric anhydride (IV), m.p. 264° (decomp.), or hydrotheobromuric acid (+H₂O) (V). The identity of (IV) with 1 : 7-dimethylspirohydantoin and of its Me derivative with the corresponding 1 : 3 : 7-Me₃ compound is ex-



cluded, and the observation that (V) does not possess the lability of (I) indicates the absence of CO₂H attached to N. General considerations of the course of the reduction lead to the structures shown for (IV) and (V), according to which (IV) is not a true anhydride of (V), a conclusion supported by the observation that esters cannot be obtained from it in the same manner as from (V).



The constitution (V) readily explains the transformation, best by Na₂CO₃, of (V) by loss of NH₂Me and CO₂ into theuric acid, which is therefore (VI).

H. W.

Synthesis of pyridylpyrazoles. G. R. CLEMO and T. HOLMES (J.C.S., 1934, 1739—1741).—Et pyridine-3-carboxylate (I), EtOAc, and EtOH-NaOEt at 77° give Et nicotinoylacetate (β-keto-β-3-pyridyl-propionate) (II), b.p. 125—135°/1 mm., hydrolysed (10% H₂SO₄) to 3-pyridyl Me ketone, b.p. 106°/12 mm. (*oxime*, m.p. 130.5°). (II) and CH₂Cl·CHCl·OEt in aq. NH₃ (or NH₂Me) afford γ-keto-β-carbethoxy-γ-3-pyridylbutaldehyde, m.p. 116°, which reduces aq. NH₃-Ag₂O, restores the colour to Schiff's reagent, and is unaffected by EtOH-NH₃ or -HCl. (II) and NHPh·NH₂ in AcOH at 100° afford 1-phenyl-3-(3'-pyridyl)-5-pyrazolone, m.p. 188°. 3-(3'-Pyridyl)-5-pyrazolone, m.p. 268° [from (II) and N₂H₄·H₂O in MeOH], and POCl₃ at 180° give 5-chloro-3-(3'-pyridyl)-pyrazole, m.p. 190°, which with fuming HNO₃ affords the 4-NO₂-derivative, m.p. 220.5°. This is reduced (red P and 20% HI at 170°) to 4-amino-5(or 3)-(3'-pyridyl)pyrazole (III), m.p. 176° [*dipicrate*, m.p. 205°; *Ac* derivative, m.p. 183° (*dihydrochloride*, m.p. 254°)]. The *hydrazide*, m.p. 260°, of 5-(3'-pyridyl)pyrazole-3-carboxylic acid (*Et* ester, m.p. 170°) [prepared by Gough and King's method (A., 1933, 616)] and amyl nitrite in aq. EtOH-HCl give (after subsequent treatment with EtOH) Et 5-(3'-pyridyl)pyrazole-3-carbamate [*dihydrochloride* (+EtOH), m.p. 302° (after loss of EtOH at 126°)], which is hydrolysed (conc. HCl) to 3-amino-5-(3'-pyridyl)pyrazole (IV) (*hydrochloride*,

m.p. 301°; *Ac* derivative, m.p. 308—309°; *dipicrate*, m.p. 219°). (IV) is identical with the supposed (III) of Gough and King (A., 1932, 68; *loc. cit.*; cf. Lund, A., 1933, 840). The nitro-5-(3'-pyridyl)pyrazole produced during HNO₃-oxidation of nicotine is, therefore, the 3-derivative; introduction of NO₂ occurs before the formation of the final pyrazole ring (cf. Gough and King, *loc. cit.*). H. B.

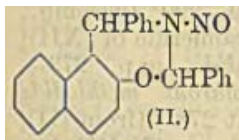
Action of acetic anhydride on uric acid glycols and their ethers. Introduction. H. BILTZ. I. 1 : 3-, 3 : 7-, and 7 : 9-Dimethyl- and 7 : 9-diethyl-uric acid [glycols]. H. BILTZ and L. LOEWE (J. pr. Chem., 1934, [ii], 141, 218—224, 225—240).—Introduction. The dialkyl ethers of uric acid glycols [4 : 5-dihydroxy-4 : 5-dihydrouric acids] are not converted by boiling Ac₂O into *spiro*dihydantoin (I); acetylation occurs at position 7 (in the case of the 1 : 3-Me₂ derivative, 5-alkoxy-1 : 3-dimethylisouric acid is formed). Similarly, the 5-alkyl ethers do not give (I); acetylation occurs at C₄-OH and then at >N₇-H, but prolonged treatment causes fission of the N₃-C₄ linking and the production of 5-alkoxy-hydantamides. 9-Methyl- and 3 : 9-dimethyl-uric acid glycols are acetylated at >N₇-H; subsequent rearrangement into (I) occurs. (I) are not obtained from the 7-substituted compounds (e.g., 3 : 7- and 7 : 9-Me₂).

I. Short treatment of 4 : 5-dihydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid with boiling Ac₂O gives an *Ac* derivative, m.p. 195° (decomp.) (all m.p. are corr.); more prolonged treatment affords the *Ac*₂ derivative, m.p. 165°. 4 : 5-Dihydroxy-3 : 7-dimethyl- (I) and -7 : 9-diethyl-4 : 5-dihydrouric acids afford *Ac*₂ derivatives, m.p. 166° (II) and 162—165°, respectively; *Ac*₁ derivatives could not be prepared. (II) is hydrolysed (conc. aq. NH₃) to (I); with MeOH- and EtOH-NH₃, the 5-Me ether (III) (*Na* salt, decomp. 90—120°; 4-*Ac* derivative, m.p. 180°) and 5-*Et* ether (IV), respectively, of (I) are produced. Prolonged treatment of (I) with Ac₂O gives 5-acetoxy-3 : 7-diacetyl-1-methylhydantamide,

$\begin{array}{ccc} \text{CO-NMe} & & \\ | & & \\ \text{NAc-CO} & \text{---} \text{C} & \text{(OAc)-CO-NHAc} \end{array}$ m.p. 150—152°; (III) and (IV) similarly afford 5-methoxy-, m.p. 126°, and 5-ethoxy-, m.p. 151°, -3 : 7-diacetyl-1-methylhydantamide, respectively. 4 : 5-Dihydroxy-1 : 3-dimethyl-4 : 5-dihydrouric acid (V) and Ac₂O-conc. H₂SO₄ give the *Ac*₂ derivative, m.p. 160—165° (decomp.), converted by boiling Ac₂O into 5-acetamido-5-acetoxy-1 : 3-dimethylbarbituric acid (VI), m.p. 180° (decomp.) (also prepared from acetyl-1 : 3-dimethyluramil and Cl₂ in Ac₂O), and by anhyd. EtOH into 4-acetoxy-5-ethoxy-1 : 3-dimethyl-4 : 5-dihydrouric acid, m.p. 175—180° (becoming red), decomp. 190°. (VI) and EtOH similarly give 5-acetamido-5-ethoxy-1 : 3-dimethylbarbituric acid, m.p. about 210°, reduced (conc. HI) to 1 : 3-dimethyluramil; an analogous reaction does not occur with MeOH. The Me₂ and Et₂ ethers of (V) are converted by Ac₂O into 5-methoxy-, m.p. 207°, and 5-ethoxy-, m.p. 195°, -1 : 3-dimethyl-Δ⁴⁻⁹-isouric acid, respectively. H. B.

Optical absorption of porphyrins.—See this vol., 10.

Action of nitrous acid on phenyl-2-hydroxy- α -naphthylmethylamine. II. N. AHMED and M. G. HEMPHILL [with F. E. RAY] (J. Amer. Chem. Soc., 1934, 56, 2403—2405; cf. A., 1933, 155).—The compound previously obtained (A., 1932, 263) from phenyl-2-hydroxy- α -naphthylmethylamine (I) and HNO_2 is now shown to a mixture of 3-nitroso-2:4-diphenyl-5:6-naphtho-(2':1')-isooxazine (II), m.p.



163°, and 1:6-dinitro- β -naphthol (III), m.p. 194° (decomp.) (Ag salt). Condensation of β - $\text{C}_{10}\text{H}_7\text{OH}$, PhCHO , and NH_3 gives (cf. Betti, A., 1929, 1063) 2:4-diphenyl-5:6-naphtho-(2':1')-isooxazine (IV), m.p. 150°, and not 2:1-

$\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{N}\cdot\text{CHPh}$. (IV) could not be methylated; with HNO_2 it gives (II), whilst its *Ac* derivative, m.p. 170°, is hydrolysed (cold conc. HCl) to 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{NHAc}$, which is methylated to the *Ac* derivative of phenyl-2-methoxy- α -naphthylmethylamine (V) (A., 1933, 1157) [$\text{N}\cdot\text{CO}_2\text{Et}$ derivative (VI), m.p. 132°, obtained by methylation (Me_2SO_4 , aq. $\text{EtOH}\cdot\text{KOH}$) of the $\text{N}\cdot\text{CO}_2\text{Et}$ derivative, m.p. 201°, of (I)]. (IV) and N_2O_3 in PhMe give (III). (V) is converted by HNO_2 into the corresponding carbinol. The mechanism of formation of (II) from (I) is: $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHPh}\cdot\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{PhCHO} + \beta\text{-C}_{10}\text{H}_7\cdot\text{OH} + \text{NH}_3 \rightarrow \text{(IV)} \rightarrow \text{(II)}$. H. B.

New synthesis of ricinine. J. REITMANN (Med. u. Chem. Abh. med.-chem. Forschungsstaten I.G. Farbenind., 1934, 2, 384—388; Chem. Zentr., 1934, i, 3597).—3-Nitro-4-pyridone with PCl_5 and POCl_3 gives 3-nitro-4-chloropyridine, m.p. 45°, b.p. 95°/5 mm., which is converted by NaOMe into 3-nitro-4-methoxypyridine (I), m.p. 73°, b.p. 127°/1 mm., with some 3-nitro-*N*-methyl-4-pyridone (II), m.p. 233°. (I) is converted into (II) at 170°. (I) is reduced by Fe and aq. AcOH to 3-amino-4-methoxypyridine, which by diazotisation and CuCN and NaCN gives 3-cyano-4-methoxypyridine (III), m.p. 124°. Ricinine is obtained from (III) by addition of Me_2SO_4 and oxidation with $\text{K}_3\text{Fe}(\text{CN})_6$. R. N. C.

Alkaloids of *Anabasis aphylla*. X. Reduction of aphyllidine. A. OREKHOV and S. NORKINA [with T. MAXIMOVA] (Ber., 1934, 67, [B], 1845—1849; cf. A., 1932, 405).—Aphyllidine (I), $\text{C}_{15}\text{H}_{22}\text{ON}_2$, after purification through the perchlorate, m.p. 210—212°, $[\alpha]_D^{25} +15.0^\circ$ in MeOH , has m.p. 112—113°, $[\alpha]_D^{25} +6.50^\circ$ in MeOH ; the hydrochloride has m.p. 235—237°, $[\alpha]_D^{25} +30.0^\circ$ in H_2O . (I) is strongly unsaturated; it combines with Br in ligroin- CHCl_3 with loss of HBr and production of bromoaphyllidine, m.p. 150—152° (hydrobromide, m.p. 210—211°; perchlorate, m.p. 234—235°), which is not reduced by Zn dust- AcOH or H , (PtO_2) and is stable towards boiling $\text{KOH}\cdot\text{MeOH}$. Electrochemical reduction of (I) in 50% H_2SO_4 at Pb electrodes leads to pachycarpine (II) (identified by the methiodide, hydriodide, dipicrate, and perchlorate). Catalytic hydrogenation (PtO_2) of (I) slowly affords aphylline (III) at room temp., whereas at 80—90° (II) is produced. (I), (III), anagryne, and lupanine are, therefore, derivatives of (+)-sparteine, whereas matrine, sophocarpine, and sophoridine belong to a different series. H. W.

Lupine. VIII. Alkaloids of *Lupinus palmeri*, S. Wats. J. F. COUCH (J. Amer. Chem. Soc., 1934, 56, 2434—2436; cf. A., 1934, 310).—Details are given for the extraction of lupinine (I) (hydrochloride, m.p. 207—209°; hydriodide, m.p. 140—141°; aurichloride, m.p. 211—213°; platinichloride, m.p. 166—166.5°; methiodide, m.p. 295—296°; methochloride, m.p. 212—213°; picrate, m.p. 136—137° and 196—197°; phenylcarbamate, m.p. 98—99°; d-camphorsulphonate, m.p. 181—182°), tetralupine (II), $\text{C}_{19}\text{H}_{19}\text{ON}$, m.p. 81—83°, $[\alpha]_D^{25} +4.63^\circ$ [d-camphorsulphonate (+ H_2O), m.p. 164—165°], and pentalupine, $\text{C}_{16}\text{H}_{30}\text{ON}_2$, b.p. 175—182°/2 mm., from the air-dried plant; sparteine could not be found. (II) is isomeric with (I) and is not identical with isolupinine, m.p. 77—79° [from (I) and Na in C_6H_6]. H. B.

Sophora alkaloids. VI. Bases of high b.p. from the foliage of *Sophora pachycarpa*. Sophoridine and sophocarpine. A. OREKHOV, M. RABINOVITSCH, and R. KONOVALOVA (Ber., 1934, 67, 1850—1855; cf. A., 1933, 617).—Sophocarpine (I) and sophocarpidine are isolated from the bases of high b.p. obtained from the foliage of *Sophora pachycarpa*. The proportion is approx. the same as in the alkaloid mixture from the seeds, which differs therefore from that of the foliage only in the absence of pachycarpine. Interaction of (I) or sophoridine (II) (from *S. alopecuroides*) with CNBr or MgMeI or under the conditions of the Hofmann degradation gives unchanged material or non-characteristic products. Electrochemical reduction of (I) in 50% H_2SO_4 at a Pb cathode yields a volatile, cryst. base, $\text{C}_{15}\text{H}_{26}\text{N}_2$, b.p. 153—154°/5 mm., $[\alpha]_D^{25} -26.2^\circ$ in EtOH (dimethiodide, m.p. $\geq 260^\circ$). Similar treatment of (II) gives a non-cryst. base, $\text{C}_{15}\text{H}_{26}\text{N}_2$, b.p. 172—173°/4 mm., $[\alpha]_D^{25} -37.1^\circ$ in EtOH (dimethiodide, m.p. $\geq 260^\circ$). H. W.

Samandarine, the principal alkaloid in the poison of fire and alpine salamanders. C. SCHÖFF and W. BRAUN (Annalen, 1934, 514, 69—136).—The crude poison (method of isolation described) from *Salamander maculosa* and *S. atra* is digested with pepsin- HCl at 37° during 13—16 days, the acidic solution is extracted with peroxide-free Et_2O [which removes oil and a sterol, probably $\text{C}_{30}\text{H}_{52}\text{O}$, m.p. 139° (sinters at 120°) (acetate, m.p. 107—108°)], and then basified (aq. NH_3). Subsequent extraction with Et_2O gives samandarine (I), $\text{C}_{19}\text{H}_{31}\text{O}_2\text{N}$ (cf. Faust, A., 1900, i, 186; Gessner and Craemer, A., 1930, 1204), $+\text{H}_2\text{O}$ (from aq. COMe_2), $+\text{MeOH}$ (from MeOH), m.p. 187—188°, $[\alpha]_D^{17} +43.7^\circ$ in COMe_2 {*N*-*NO*-derivative (?+0.5 EtOH), decomp. 111—113°, re-solidifying with m.p. 164—165°; *O*-*Ac* derivative [hydrochloride, m.p. 300—302° (decomp.)], obtained during attempted reduction (Zn dust, AcOH) of (I); *ON*-*Ac*, m.p. 167—168°, *O*-*HCO* (+ H_2O), m.p. 148—150°, and *ON*-(*HCO*)₂, m.p. 256—258°, derivatives}, and amorphous products [from which (I) is separated as its hydrochloride, m.p. 321—322°]. (I) is also obtained from the "substances III, IV, VIII, and IX" of Gessner and Craemer (*loc. cit.*). The samandaridine of Faust (*loc. cit.*) was not found; the samandarine of Netolitzky (A., 1904, i, 770) is probably impure (I). (I) contains 2 active H (Zere-

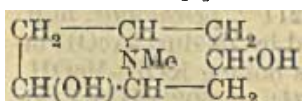
vitinov in PhOMe at 95°; general procedure). The presence of a *sec.*-OH in (I) is shown by its oxidation (CrO₃, dil. H₂SO₄) to *samandarone* (II), C₁₉H₂₉O₂N, m.p. 191—192° (sinters at 189°) (*N*-Bz derivative, m.p. 249—250°; α -, m.p. 277—278°, and β -, m.p. 288—289°, *oximes*). (I) and MgMeI in Et₂O give *methylsamandiol* (III), C₂₀H₃₅O₂N, m.p. 170—172° [*hydrochloride*, m.p. 288—289°; *Ac.* derivative (+H₂O), m.p. 188—190°], oxidised [as (I)] to *methylsamandione*, C₂₀H₃₁O₂N, m.p. 124—126° (sinters at 118°) [*dioxime*, decomp. 268—270° (sinters at 265°); *N-Me* derivative *methiodide* (+2H₂O), m.p. 258—260° (decomp.)]. (I) and MgPhBr afford *phenylsamandiol* (IV), C₂₅H₃₇O₂N, 0.5MeOH, m.p. 194—196° [*hydrochloride*, decomp. 314—316° (sinters at 311°); *Ac.* derivative, m.p. 95—102° (decomp.; sinters at 60°)], which contains 3 active H. The production of (III) and (IV) indicates that the second O of (I) is present as >CH·O·C—, which with MgRX

gives >CH·OH CR—. (I) probably also contains 3 reduced C-rings; CMe groups are present, since oxidation of (I) by Kuhn and L'Orsa's method gives 1.07 mols. of AcOH. (IV) is oxidised [as (I)] to α -*phenylsamandione* (V), C₂₅H₃₃O₂N, m.p. 184—185° [*hydrochloride* (+0.5H₂O), m.p. 250—252° (decomp.)]; *N-Ac* derivative, m.p. 232—233°; *semicarbazone*, m.p. 236—237° (decomp.; sinters at 234°); *oxime*, m.p. 203—204° (decomp.; sinters at 198°)], which contains 1 active H, and the isomeric β -*phenylsamandione* (VI), m.p. 112—113° (sinters at 106°) [*hydrochloride*, m.p. 275—277° (decomp.)]; *N-Ac* derivative, m.p. 194—198°]. (V) and (VI) afford the same *dioxime*, m.p. 227—228° (decomp.; sinters at 224°) [*Ac* derivative, m.p. 149—151° (decomp.; sinters at 142°)] (which is formed only in strongly alkaline solution); they are probably stereoisomerides. Rearrangement of (V) or (VI) could not be effected with NaOEt or 3% H₂SO₄. (V), MeI, and 1.5*N*-Na₂CO₃ give some *N*-methyl- α -*phenylsamandione*, (mainly) its *methiodide* (VII) (+H₂O), m.p. 192—194° (decomp.; sinters at 190°), and small amounts of *de-N*-dimethyl- α -*phenylsamandione* (VIII), C₂₇H₃₇O₂N, m.p. 216—217° (sinters at 206°) [*methiodide* (+MeOH), m.p. 256—258°], and the isomeric *isode-N*-dimethyl- α -*phenylsamandione*, m.p. 146° (sinters at 140°) [*methiodide hydriodide* (+0.5MeOH), m.p. 219—220° (decomp.; sinters at 216°)]. (VII) is degraded by aq. NaOH or Ag₂O to (VIII) and an amorphous base [*methiodide*, C₂₈H₄₀O₂Ni (+MeOH), m.p. 269—270° (sinters at 266°)]. *N*-Methylsamandarine *methiodide* (+H₂O), m.p. 271—272° [from (I), MeI, and aq. Na₂CO₃], is unaffected by aq. alkali, but is converted by Ag₂O-H₂O into *de-N*-dimethylsamandarine (IX), C₂₇H₃₅O₂N, m.p. 190—191° [α]₂₀^D -121.3° in EtOH [*hydrochloride*, m.p. 275—276° (decomp.; sinters at 270°)], which contains 1 active H, and a little *N*-methylsamandarine, not obtained cryst., [α]_D²⁰ -21.1° in C₅H₅N [*hydrochloride*, m.p. 300—302° (decomp.); *perchlorate*, m.p. 250—254° (decomp.; sinters at 220°)]. The *methiodide* (+H₂O), m.p. 320—321°, of (IX) is similarly converted into (mainly) (IX). Reduction (H₂, colloidal Pd, dil. AcOH) of (IX) gives a *dihydro*-derivative (X), m.p. 149—150° [*Ac* derivative, m.p. 93—94° (sinters at 88°); *methiodide*, m.p. 321—322°, con-

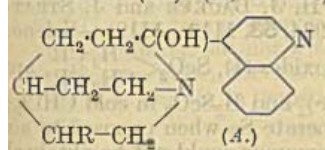
verted by Ag₂O-H₂O into (mainly) (X)]. (IX) and 3% H₂SO₄ at 100° (bath) afford *hydroxydihydrode-N*-dimethylsamandarine (XI), C₂₁H₃₇O₃N, m.p. 167—168° (sinters at 165°) [*perchlorate* (+0.5EtOH), m.p. 222—225° (sinters at 216°); *hydrochloride* (XII), m.p. 270—271° (decomp.) (sinters at 265°); *Ac* derivative, m.p. 141—143° (sinters at 139°)], which contains 2 active H; the products from the Zerevitinov reaction are a base [*hydrochloride*, m.p. 289—290° (decomp.; sinters at 287°), probably a stereoisomeride of (XII)] and a base, C₂₂H₄₁O₃N [*hydriodide*, m.p. 273—275° (decomp.)]. *N*-Methylsamandarone *methiodide* (+H₂O), m.p. 282—283° (sinters at 278°) [from (II), MeI, and 10% Na₂CO₃], is stable to aq. NaOH, but is degraded by Ag₂O-H₂O to *de-N*-dimethylsamandarone (XIII), C₂₁H₃₃O₂N, m.p. 147—148° [*hydriodide*, decomp. 260—262° (sinters at 257°); *methiodide*, m.p. 323° (slight decomp.; sinters at 320°), similarly converted into (XIII) and (mainly) a neutral resin], which is reduced (H₂, Pd, dil. AcOH) to a *dihydro*-derivative, m.p. 144—146°, [α]₂₁^D -159° in 2*N*-AcOH [*hydriodide*, m.p. 268—270° (slight decomp.)]; *oxime*, m.p. 246—247° (sinters at 237°)], also prepared by oxidation (CrO₃, dil. H₂SO₄) of (X). (XIII) and 3% H₂SO₄ at 100° (bath) give *hydroxydihydrode-N*-dimethylsamandarone (XIV), m.p. 139—140° (sinters at 135°) [*hydriodide*, decomp. 245—248° (sinters at 239°)], which contains 1 active H, also prepared by oxidation of (XI). (XIII) is reduced (Na, EtOH) to (IX) (thus showing that the double linking is not $\alpha\beta$ to the CO) and a product, which when treated with 3% H₂SO₄ and then oxidised gives *samandesone* (XV), C₂₁H₃₃O₂N, m.p. 190—192° (sinters at 188°) [*oxime*, m.p. 274—276° (sinters at 273°)]. (XV) is also prepared by energetic oxidation (CrO₃, dil. H₂SO₄) of (XI) and (XIV); it is unaffected by boiling 2*N*-NaOH (in which it is sol.) or 50% KOH, and is not acetylated by Ac₂O-NaOAc. The Zerevitinov reaction with (XV) gives only a little CH₄; a base, C₂₄H₄₅O₃N, m.p. 175—176°, is formed. Reduction (Na, EtOH) of (XV) affords *samandesol* (XVI), C₂₁H₃₅O₃N, m.p. 170—172° (sinters at 168°), which is isomeric with (XIV), and *samandesolic acid* (XVII), C₂₁H₃₇O₄N, m.p. 208—210° (decomp.) (sinters at 205°). (XVI) and (XVII) are also obtained from (XV) and EtOH-NaOEt. (XVI) and MgMeI (Zerevitinov) give a base, C₂₃H₄₃O₃N, m.p. 223—224°. H. B.

New tropan derivative from coca leaves. O. WOLFES and O. HROMATKA (Merck's Jahresber., 1934, 47, 45—53; Chem. Zentr., 1934, ii, 1307).—A *dihydroxytropan*, C₈H₁₅O₂N [probably (I)], m.p. 209—209.5°, [α]₂₇^D -22° in EtOH (*hydrochloride*, [α]_D²⁰ +1.15 in H₂O; *picrate*, decomp. 253°), is isolated from the alkaloid fractionless sol in Et₂O than tropine and ψ -tropine. On benzylation (I) yields a *bis*(benzoyloxy)tropan [sulphate, [α]_D²⁰ +52.1° in EtOH; *mono-hydrochloride*, m.p. (+2H₂O) 115° (anhyd.) 205°, [α]_D²⁰ +41.8° in aq. EtOH; *nitrate*, m.p. 197°]. Reduction of (I) with HI and red P yields tropan; with POCl₃, (I) affords a *tropen oxide*, b.p. 188°/752 mm. [*picrate*, m.p. 177° (decomp.)].

H. N. R.



Cinchona alkaloids. XXIX. Stereochemical investigations. IV. Hydrocinchonine of H. Emde and epicinchonine of J. Suszko and A. Tomanek. P. RABE, H. HAEUSZLER, and W. HOCHSTÄTTER (Annalen, 1934, 514, 61—68).—The dihydrocinchonine (—hydrocinchotoxin) (I), m.p. 112°, of Emde (A., 1932, 759) is impure *epihydrocinchonidine* (II) [prep. from hydrocinchonidine (III) and 25% HCl described (cf. *loc. cit.*)]. Contrary to Emde, (I) is not produced from hydrocinchonine (IV) and 25% HCl; *epihydrocinchonine* (V) results. Emde's conclusions regarding the stereochemical configuration of (II)—(V) are thus invalid. The present results confirm the structures previously assigned (A., 1932, 289). The *epicinchonine* of Suszko and Tomanek (A., 1933, 288) is considered to be *heterocinchonine* (A, R=CH₂CH₂). This is reduced (H₂, Pd-black, 3% H₂SO₄) to the *dihydro-*derivative (VI) (A, R=Et).



is converted by KOBz in EtOH into the benzoate, oil, of (VI). The bromide (A, R=Et, OH=Br) (which is neutral towards litmus) is obtained (no details) as a by-product from (IV) and PBr₅; hydrolysis gives (VI). H. B.

Alkaloids of calumba root. V. Absorption spectra of the alkaloids of calumba root and of some derivatives of berberine. K. FEIST, W. AWE, and H. ETZRODT (Arch. Pharm., 1934, 272, 817—826; cf. A., 1932, 177).—The prep. of *palmatinium* (I), m.p. 240—242° (decomp.), and *jatro-rhizinium iodide* (II), m.p. 210—212° (decomp.), from calumba root (III) is described. The quaternary sulphates of berberine and the alkaloids of (III) are reduced to the *tert.* bases by amalgamated Zn and AcOH. *Corydaline* and Hg(OAc)₂ lead to 2:3:11:12-tetramethoxy-16-methyl-8:9:16:17-tetradehydroberbinium (8:9:16:17-tetradehydro-corydalinium) iodide (IV), m.p. about 230° (decomp.). The absorption spectra of berberinium iodide (V), (I), (II), and the iodide of the new alkaloid from (III) (*loc. cit.*) are very similar (max. at 265 and 335 mμ), but (V) differs by not showing also a subsidiary max. at 280 mμ. 16:17-Dihydrodeoxyberberine and 9-CH₂Ph, -ψ-CH₂Ph, and -o-C₆H₄Me derivatives give a broad band below 315 mμ (max. 290 mμ), but the corresponding reduced (III) alkaloids have no absorption above 305 mμ and a max. at about 280 mμ. The absorptions of 9-*m*-tolyldeoxyberberine and its hydriodide differ somewhat, which supports the view that the ethylenic linking wanders during salt formation. The absorption spectra of oxyberberine and oxypalmatine (modified preps.) are similar, showing a max. at 340 and a min. at 285 mμ; the effect of the CO group is thus very pronounced. R. S. C.

Reduction in morphine series. IV. Codeine. R. E. LUTZ and L. SMALL (J. Amer. Chem. Soc., 1934, 56, 2466—2468).—*allo-ψ*-Codeine (I)

(Speyer and Krauss, A., 1923, i, 1115) [salicylate, m.p. 202°; *hydrochloride*, m.p. 256—258° (decomp.)] is reduced (hydrochloride; H₂, PtO₂, AcOH) to 80% of the non-phenolic *dihydroallo-ψ-codeine* (II), m.p. 78—79°, [α]_D²⁵ -105° in EtOH [*H tartrate* (+2H₂O), m.p. 124—125°, re-solidifying with m.p. 160—163°; *hydriodide*, m.p. 255° (decomp.); *perchlorate* (+3H₂O), m.p. 265—270°], 18% of *tetrahydroallo-ψ-codeine* (III), m.p. (anhyd.) 145.5°, [α]_D²⁵ -58° in EtOH [*perchlorate* (+H₂O), m.p. 102—104°; *methiodide*, m.p. 241—242° (decomp.)], and a trace of *tetrahydrodeoxycodine* (IV). Reduction (H₂, Pd-CaCO₃, EtOH) of (I) affords approx. equal parts of (II) and (III). Reduction (Na, EtOH) of (I) gives 36% of the phenolic *dihydroallo-ψ-codeine*, not obtained *cryst.* [*perchlorate* (+H₂O), m.p. 145—147°; *methiodide*, m.p. 247—248° (decomp.)], and 44% of the previously described (A., 1934, 1117) mixture (V) of *dihydrodeoxycodines-B* and *-C*. (IV) and (V) probably result from 1:6 addition of H₂ to (I); the intermediate *deoxycodine-A* is then reduced. The *methiodide* of (II) is converted by hot alkali into the non-phenolic *dihydro-ζ-methylmorphimethine*, m.p. 99°, [α]_D²⁵ +117° in EtOH (*salicylate*, m.p. 175°), hydrogenated to the non-phenolic *tetrahydro-ζ-methylmorphimethine*, m.p. 110°, [α]_D²⁵ -26° in EtOH (*salicylate*, m.p. 175—175.5°). Phenolic *tetrahydro-ζ-methylmorphimethine* (*hydriodide*, m.p. 249°), prepared by Speyer and Krauss' method (*loc. cit.*), is hydrogenated to the hexahydro-derivative [*hydriodide*, m.p. 279—281° (decomp.)] of *ζ-methylmorphimethine* (Speyer and Koulen, A., 1925, i, 59) [*H tartrate* (+2H₂O), m.p. 99—101° (decomp.); *perchlorate* (+H₂O), m.p. 117—118°; *salicylate* (+H₂O), m.p. 118—120°]. All m.p. are corr.

H. B.


Oxidation of strychnine. A. BERNARDI (Atti Congr. naz. Chim., 1933, 4, 389—396; Chem. Zentr., 1934, ii, 251).—Oxidation of strychnine (I) in AcOH by CrO₃ yields a product C₄₂H₄₂O₈N₄, m.p. 301—302°, which on reduction again gives colour reactions of (I).

A. G. P.

Arsenated phenoxyalkanols. L. A. SWEET and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 2409—2412).—*p*-OH·C₆H₄·AsO₃H₂ and CH₂Cl·CH₂·OH in *N*-NaOH give *β*-*p*-arsinophenoxyethyl alcohol (I), m.p. 147—148° (softens at 127°) [*Na salt* (+2H₂O); *nitrate* (II), m.p. 145°], which with HNO₃ (*d* 1.5) and conc. H₂SO₄ at 20° affords *β*-2-nitro-4-arsinophenoxyethyl nitrate (III), m.p. 217—218° (decomp.; softens > 160°), hydrolysed (2.5*N*-HCl) to *β*-2-nitro-4-arsinophenoxyethyl alcohol (IV) [*3-nitro-4-β-hydroxyethoxyphenylarsinic acid*], m.p. 138°. (IV) is reduced [Fe(OH)₂, dil. NaOH] to *β*-2-amino-4-arsinophenoxyethyl alcohol (V) (+H₂O), m.p. 96—98°, m.p. (anhyd.) 156—157° [*Na salt*; *anhydride*, m.p. 208—210° (decomp.); softens at 145—150°]; *hydrochloride*, m.p. 171—172° (decomp.); *N-Ac derivative*, m.p. 207° (decomp.). (I) and HNO₃ (*d* 1.5) in conc. H₂SO₄ at 95° give *β*-2:6-dinitro-4-arsinophenoxyethyl alcohol, m.p. 212—215° (decomp.) [*nitrate*, m.p. 188—189°; corresponding (NH₂)₂-derivative, m.p. 205° (decomp.)], and 3:5-dinitro-4-hydroxyphenylarsinic acid, m.p. > 275°. (I) and HNO₃ (*d* 1.5) at 25—30° for 24 hr. afford 2-nitro-4-arsinophenoxyacetic acid, m.p. > 250° (*Me*

ester, m.p. 225—226°), which is reduced to 3-hydroxy-1:4-benzisooxazine-6-arsinic acid (Newbery *et al.*, A., 1929, 83). Hydrolysis (6*N*-HCl) of a mixture of (II) and (III) gives 2-chloro-4-arsinophenoxyethyl alcohol, m.p. 141° [nitrate, m.p. 205° (decomp.; softens at 136°)] [formed from (I) and Cl₂ from HCl+HNO₃], and (IV) (removed by reduction). 4-β-Hydroxyethoxyphenylarsenoxide and its 3-Cl- and 3-NH₂-derivatives, all m.p. > 250°, are prepared by reduction (H₂SO₃, HI) of the corresponding arsinic acids. 3-Amino-4-β-hydroxyethoxyphenyldichloroarsine hydrochloride has m.p. 174°. 3:3'-Dinitro-4:4'-di-β-hydroxyethoxyarsenobenzene and its dinitrate are prepared by reduction (25% H₃PO₂ at 95°) of (IV) and (III), respectively; (V) similarly gives 3:3'-diamino-4:4'-di-β-hydroxyethoxyarsenobenzene. γ-p-Arsinophenoxypropyl alcohol, m.p. 146° [2-NO₂-derivative (nitrate, m.p. 207°); 2-NH₂-derivative hydrochloride, m.p. 136°], is prepared [as (I)].

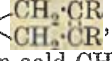
Arsenicals derived from 6-nitro-β-naphthylamine. L. A. SWEET and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 2408—2409).—6-Nitro-2-naphthylarsinic acid, prepared by the usual method from 6-nitro-β-naphthylamine (Bz derivative, m.p. 206°), is reduced [Fe(OH)₂] to 6-amino-2-naphthylarsinic acid (Ac and N-CO₂Et derivatives), which with (CH₂)₂O in 0.5*N*-Na₂CO₃ gives 6-β-hydroxyethylamino-2-naphthylarsinic acid. All the above have m.p. > 250°. 2:6-C₁₀H₆(NH₂)₂ has m.p. 220°. H. B.

Constitution of neoarsphenamine. W. J. C. DYKE and H. KING (J.C.S., 1934, 1707—1718).—Na formaldehydesulphoxylate and the appropriate NH₂Ar in H₂O and N₂ at 50—80° give Na anilino- (I), o-toluidino- (II) (tetrahydrate), o- (III) and p-carboxyanilino- (tetrahydrates), and 2-hydroxy-5-carbomethoxyanilino- (IV) (+3.5H₂O), -N-methylenesulphoxylates. Na 2-hydroxy-5-carbomethoxyanilino-N-methylenesulphite (V) (+2H₂O) is prepared using OH·CH₂·SO₃Na. (I)—(IV) do not reduce methylene-blue (VI) to any appreciable extent in neutral NaOAc-buffered solution in O₂-free N₂. (VI) is reduced to the extent of 71% by (IV) in aq. EtOH-NaOAc at 70—75°; in almost boiling 0.1*N*-AcOH, about 90% reduction occurs: NHR·CH₂·O·SONa+(VI) ⇌ NHR·CH₂·O·SO₂Na+leuco-(VI). (IV) absorbs 0.1*N*-I until 90% of the S is converted into SO₄''; a small amount of (V) (which is not acted on by I except in presence of acid) is probably first formed, viz.: (i) (subsidiary) NHR·CH₂·O·SONa+I₂→NHR·CH₂·O·SO₂Na+HI; (ii) (main) NHR·CH₂·O·SONa+HI→NH₂R+OH·CH₂·O·SONa  CH₂O+Na₂SO₄. These results completely invalidate the conclusions of all previous workers [except possibly Freedman (cf. B., 1926, 767)] on the quant. action of I on neoarsphenamine (VII) [which consumes 7.2 I (As:As requires 8), a considerable proportion of which is used in forming SO₄ at the expense of AsO₃H₂ (which then reverts to AsO:RAsO₃H₂+2HI→RAsO+I₂+2H₂O)]. Unlike (I)—(IV), (VII) reduces (VI) in neutral solution at room temp.; this is attributed to activation by the As:As group, which does not take part in the reaction. Na diaminodihydroxyarsenobenzene-NN'-dimethylenesulphite has no action on (VI) at room

temp.; reduction (ascribed to As:As) occurs on warming. Little reaction (which is catalysed by light) occurs between (VI) and OH·CH₂·O·SONa at room temp.; quant. oxidation occurs at approx. *pH* 3 and 100°.

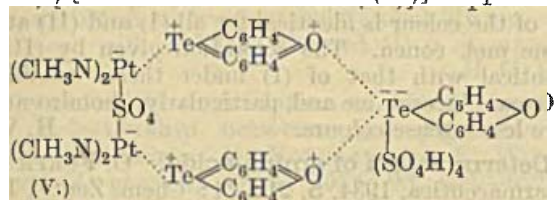
Determinations of As, total S (by Elvove's method, B., 1926, 27), S [by titration with (VI)], and free SO₄ in various commercial samples of (VII), and of As, S (Elvove), S [(VI)], and Na in the products obtained by pptn. from aq. solutions with AcOH in absence of O₂ (apparatus used described) show that some samples contain ·NH·CH₂·O·SONa groups only, whilst others also contain ·NH·CH₂·O·SO₂Na; all the samples contain uncombined salts. The analogous results obtained with products synthesised (as standards) from salvarsan base and OH·CH₂·O·SONa (2 mols.), OH·CH₂·SO₃Na (2 mols.), and an equimol. mixture of the two salts are given. H. B.

Cyclic selenones. H. J. BACKER and J. STRATING (Rec. trav. chim., 1934, 53, 1113—1119).—Seleno-

Δ³-cyclopentene 1:1-dioxides (I), SeO₂  are obtained from (CH₂:CR·)₂ and H₂SeO₃ in cold CHCl₃; (I) are unstable and liberate Se when exposed to air and light. Similar compounds could not be obtained from butadiene and αβγδ-tetramethyl- and αδ-dimethyl-βγ-diethyl-butadienes. The following are described: 3-methyl-, m.p. about 67° (decomp.) (from isoprene); 3:4-dimethyl-, m.p. about 66° (decomp.) [from (CH:CMc·)₂]; 3-tert.-butyl-, m.p. about 81—82° (decomp.) (from CH₂:C(Bu)⁺·CH:CH₂); 3:4-ditert.-butyl- (II), m.p. 132° (decomp.); 3-phenyl-, m.p. 90° (decomp.); 3:4-diphenyl-, m.p. 89—90° (decomp.), and 3-chloro-4-methyl-, m.p. about 110° (decomp.) (from CH₂:CCl·CMc:CH₂), -seleno-Δ³-cyclopentene 1:1-dioxides. (II) and SO₂ in Et₂O give a compound, C₁₂H₁₄O₆Se, m.p. about 143° (decomp.): C₁₂H₂₂O₆Se+SO₂+H₂O+O→C₁₂H₂₄O₆Se. H. B.

Interpretation of the phenoxtellurine dibisulphate reaction with platinous compounds. Micro-analysis of platinum and tellurium. H. D. K. DREW (J.C.S., 1934, 1790—1797).—Phenoxtellurine dibisulphate (I) is ground with (NH₄)₂PtCl₄ or K₂PtCl₄ and the product then triturated successively with cold H₂O, conc. H₂SO₄, and cold H₂O; subsequent extraction with boiling AcOH and drying at 105° in air gives the black phenoxtellurium platichloride (II), C₁₂H₈OCl₄TePt (alternative structures discussed), which is decomposed by aq. HCl or aq. KCl to phenoxytellurine dichloride (III) and H₂PtCl₄ or K₂PtCl₄, respectively. (III) and Ag₂O in H₂O afford phenoxtellurine oxide, which when heated gives phenoxtellurine and Ph₂O. Some (II) is also produced from (I) and Magnus' green salt, probably owing to the dissociation, [Pt(NH₃)₄]PtCl₄→[Pt(NH₃)₄]Cl₂+PtCl₂. Plati-ammines and Pt^{IV} salts do not give colours with (I). The product from (I) and β-Pt(NH₃)₂Cl₂ (IV) is extracted with cold 75% (vol.) H₂SO₄; cautious addition of H₂O to the resulting solution ppts. the purplish-black triphenoxtellurium tetrabisulphate diamminodichloroplatosulphate (V) (dotted lines represent ionised linkings). (V) is decomposed by warm H₂O to phenoxtellurine salts, H₂SO₄, and (IV); with warm AcOH or cold Ac₂O,

phenoxtellurine sulphate, (II), and a ppt. of (VI) (below) [mixed or combined with (IV)] are produced.



Impure *diamminodichloroplatosulphuric acid* (VI), $\text{H}_2[\text{Pt}(\text{NH}_3\text{Cl})_2 \cdot \text{SO}_4 \cdot \text{Pt}(\text{NH}_3\text{Cl})_2]$, black, is prepared from (IV) and fairly conc. H_2SO_4 ; use of too conc. H_2SO_4 gives (probably) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{SO}_4$. (VI) is decomposed by aq. NaCl to (IV). The results support the view that the relationship between the α - and β -plato-diammine dichlorides is not merely that between *trans*- and *cis*-isomerides but is also structural; α -(IV) does not form compounds of the types (V) and (VI). (I) forms purple complexes with PAr_3 , AsAr_3 , and SbAr_3 , but not with NAr_3 or BiAr_3 .

Details are given for the micro-determination of Pt, Te, Cl, and S in substances containing all 4 elements. H. B.

Mixtures of casein and native ox serum-albumin. M. FREEMAN (Austral. J. Exp. Biol., 1934, 12, 155—160).—When casein is pptd. near its isoelectric point in presence of serum-albumin the ppt. is partly sol. in 1% aq. NaCl . The sol. fraction, which contains less P than the original casein and somewhat resembles euglobulin, increases in amount as the p_{H} of pptn. is increased. W. O. K.

Ultra-violet absorption spectra of certain denatured proteins. C. S. HICKS and H. F. HOLDEN (Austral. J. Exp. Biol., 1934, 12, 91—97).—The ultra-violet absorption of various proteins undergoes considerable change when the protein is denatured by EtOH or in alkaline solution; hot denaturation in acid solution has little effect except with serum-albumin, when secondary chemical changes may occur. W. O. K.

Allocation of free amino-groups in proteins and peptides. S. GURIN and H. T. CLARKE (J. Biol. Chem., 1934, 107, 395—419).—By the action of PhSO_2Cl - NaOH on the NH_2 -acid are obtained the *benzenesulphonyl* derivatives of *dl*-phenylalanine, m.p. 127—128°, *dl*-methionine, m.p. 104°, and *l*-histidine, m.p. 236° (decomp.), $[\alpha]_{\text{D}}^{25} -27.2^\circ$ in 0.1N- NaOH . Such derivatives are readily characterised as their cryst. Bu^a esters. The Bu^a esters of benzenesulphonyl-glycine, m.p. 26—27°, *dl*-alanine, m.p. 113°, *l*-leucine, m.p. 50—51°, $[\alpha]_{\text{D}}^{21} -16.1^\circ$ in 95% EtOH, *dl*-alanylglycine, m.p. 76.5°, *glycyl*-*dl*-alanine, m.p. 101°, and *glycyl*-*l*-leucine, m.p. 107°, and the Bu^a esters of benzenesulphonyl-*d*-glutamic, m.p. 58—59°, $[\alpha]_{\text{D}}^{20} 0^\circ$ in EtOH, and *i*- β -hydroxyglutamic acid, m.p. 76° (Bu^a ester, m.p. 169—170°), are new. Hydrolysis of such derivatives of simple dipeptides with 50% HCO_2H containing a little conc. HCl at 90—100° proves that under such conditions complete fission of the peptide linkings can be effected without hydrolysis of the $\cdot\text{SO}_2\text{Ph}$, and hence this method is applied to determine the location of free NH_2 in various

polypeptides. Thus hydrolysis of the *benzenesulphonyl* derivative, m.p. 123°, of oxidised glutathione affords, after esterification, Bu^a benzenesulphonyl-glutamate, confirming the location of the free NH_2 in the glutamic acid residue. The benzenesulphonyl derivative of gelatin (I) (S, 2.0%; control 0.20%: $\text{NH}_2\text{-N}/\text{total N}=0.1$; control 4.0; p_{H} titration curve with glass electrode shifted as for deaminised gelatin) affords a hydrolysate from which is isolated a 50% yield of the *Cu* salt of ϵ -benzenesulphonyl-*d*-lysine, characterised as its *phenylhydantoin* (II), m.p. 138°, $[\alpha]_{\text{D}} -31.4^\circ$ in 95% EtOH, identical with a specimen synthesised thus: hydrolysis of its ϵ -Bz derivative (Karrer *et al.*, A., 1926, 603) affords the *phenylhydantoin* of *d*-lysine, isolated as its *platinichloride*, m.p. 210—211° (decomp.), converted by grinding with finely-divided Ag and treatment with PhSO_2Cl - NaOH into (II), which is different from ϵ -*phenylureido*- α -benzenesulphonyl-*d*-lysine, m.p. 145°, $[\alpha]_{\text{D}}^{20} +11.9^\circ$ in 95% EtOH [prepared by PhNCO and α -benzenesulphonyl-*d*-lysine (III), m.p. 249—251° (decomp.), $[\alpha]_{\text{D}}^{23} -22.8^\circ$ in 0.1N- NaOH , obtained by *N*- NaOH hydrolysis of its ϵ -Bz derivative, m.p. 168° (from PhSO_2Cl and ϵ -benzoyl-*d*-lysine)]. Hydrolysis (HCl) of the *dibenzenesulphonyl* derivative of *d*-lysine affords (III). At least 50% of the free NH_2 in (I) is due to the ϵ - NH_2 in lysine, and $>0.5\%$ of the free $\text{NH}_2\text{-N}$ can be allocated to $(\text{NH}_2)_1$ -acids. J. W. B.

Electric furnace with automatic temperature regulation for semi-micro-determination of carbon and hydrogen (ter Meulen). B. HEINEMANN (Chem.-Ztg., 1934, 58, 991—992).—An apparatus is described and advantages are enumerated. E. S. H.

Argentometric semi-micro-determination of chlorine and bromine in organic substances. B. BROBAŃSKI (Z. anal. Chem., 1934, 99, 108—109).—Polemical against Holscher (A., 1934, 671). J. S. A.

Determination of chlorine in presence of bromine in organic substances. F. BOCK and G. LOCK (Chem. Fabr., 1934, 7, 406—407).—Modified technique for Rose's method is described. The mean error is <0.0002 g. E. S. H.

Determination of small amounts of organic arsenic compounds in air. M. JUREČEK (Coll. Czech. Chem. Comm., 1934, 6, 468—475).—Volatile As compounds are removed from air by sorption on SiO_2 gel; the gel is then heated under MgO , covered with Na_2O_2 - Na_2CO_3 . Dusts of As compounds are absorbed from air by washing with COMe , or Et_2O ; the solution is evaporated and the residue heated with H_2SO_4 - HNO_3 - H_2O_2 . The aq. extract of the melt or the diluted acid solution is reduced and the AsH_3 formed determined colorimetrically; suitable apparatus is described. R. S. C.

Determination of carbonyl compounds by means of 2:4-dinitrophenylhydrazine. H. A. IDDLIS and C. E. JACKSON (Ind. Eng. Chem. [Anal.], 1934, 6, 454—456).—An aq. solution of the CO-compound is allowed to react with an excess of a saturated solution of 2:4-dinitrophenylhydrazine in 2N- HCl (I) at 0° for 1 hr. The ppt. is washed with (I) and dried in a vac. The average yields obtained with the follow-

ing are given in parentheses: MeCHO (95.04), COMe₂ (97.49), COMeEt (97.87), COMePr^a (98.29), PhCHO (99.15), *p*- (99.39) and *o*-OH·C₆H₄CHO (98.7), *o*-OMe·C₆H₄CHO (100.2), vanillin (102.18%). S. C.

Determination of aldehydes by the hydrogen sulphite method. A. E. PARKINSON and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1934, 6, 433—436).—More accurate results are obtained by adding the aldehyde H sulphite (I) solution to an excess of I and back-titrating immediately with Na₂S₂O₃. If (I) dissociates too rapidly at room temp. the solution is cooled in ice before and during contact with I. The following aldehydes were tested and the % purity of the samples is given in parentheses: CH₂O (100), MeCHO (98.9), EtCHO (98.6), Pr^aCHO (98.5), Pr^bCHO (95.8), Bu^aCHO (96.3), Bu^bCHO (97.6), *n*-C₆H₁₃·CHO (97.2), PhCHO (97.1), acetal (97.2), *o*-OH·C₆H₄·CHO (96.1), vanillin (97.3), piperonal (100.6). Unsatisfactory results were obtained with paraldehyde, croton- and cinnam-aldehydes. S. C.

Determination of lactic acid in presence of methylglyoxal. J. O. GIRŠAVIČIUS and P. A. HEYFETZ (Biochem. Z., 1934, 274, 95—96).—The method of Simon and Neuberg (A., 1931, 662) is favoured. P. W. C.

Determination of amino-acids and polypeptides. E. CHERBULIEZ and A. HERZENSTEIN (Helv. Chim. Acta, 1934, 17, 1440—1443).—Blood serum (1 c.c.) is treated with so much powdered (NH₄)₂SO₄ that the vol. attains 1.5 c.c. and then with saturated (NH₄)₂SO₄ until the vol. is 4 c.c. After thorough shaking the mixture is passed through a dry filter and 1 c.c. of the filtrate is boiled for 2 min. with 0.2 c.c. of 1% aq. ninhydrin. The mixture is shaken with amyl alcohol until the aq. solution is perfectly clear and the alcoholic extract is agitated with 0.5% NaOH until it is pure blue in colour. The intensity is matched against that of a standard solution obtained from glycine. Under these conditions the reaction is sp. for the group ·CO·CH(NH₂)· and hence is shown by all NH₂-

acids (I) and the polypeptides (II) derived from them, by α-NH₂-aldehydes and -ketones (III). The intensity of the colour is identical for all (I) and (II) at the same mol. concn. The coloration given by (III) is identical with that of (I) under these conditions, whereas glucosamine and, particularly, chondrosamine give less intense colours. H. W.

Determination of amino-acids. O. FURTH (Sci. Pharmaceutica, 1934, 5, 21—24; Chem. Zentr., 1934, i, 3600).—A review of recent work. R. N. C.

Identification of aromatic nitro-compounds by optical crystallographic methods. E. S. DAVIES and N. H. HARTSHORNE (J.C.S., 1934, 1830—1836).—Crystallographic data are given for 20 NO₂-compounds. Some binary and ternary mixtures of these compounds were rapidly identified under the polarising microscope. R. S. C.

Determination of *m*-cresol. A. WADA and I. KAWAI (J. Soc. Chem. Ind. Japan, 1934, 37, 702B).—An improvement of Raschig's process for determining *m*-cresol as its (NO₂)₃-derivative (A., 1900, ii, 694) is described. H. N. R.

Determination of nicotine by the silicotungstic acid method. N. H. PIZER (J.S.C.I., 1934, 53, 356—357T).—The method is trustworthy for solutions containing from 0.1% to 0.005% of nicotine. Ignition of the nicotine silicotungstate at 1000° gives const. wt.

Determination of quinine hydrobromide by the cupro-hydrogen bromide reaction. G. DENIGES (Bull. Soc. Pharm. Bordeaux, 71, 251—254; Chem. Zentr., 1934, ii, 1343).—A simple colour reaction for the detection of Br⁻ in the presence of quinine is described; the process may be made quant. H. N. R.

Alkaloidal reagents. V. Aconite alkaloids. J. C. MUNCH and H. J. PRATT (J. Amer. Pharm. Assoc., 1934, 23, 968—973).—The behaviour of aconitine, benzoylaconine, and aconine towards 71 alkaloidal reagents is recorded. Aconite alkaloids are excreted chiefly into the liver. A. E. O.

Biochemistry.

Case of deficient acclimatisation to low oxygen pressure. J. BARCROFT, R. H. E. ELLIOTT, F. R. FRASER, W. HERKEL, B. H. C. MATTHEWS, and M. TALAAT (J. Physiol., 1934, 82, 369—376).—A normal subject kept in a reduced O₂ partial pressure for 5 days attained a poor degree of acclimatisation, alveolar O₂ pressure and total metabolism falling and CO₂ pressure remaining high. The O₂ dissociation curve was shifted to the right. The arterial blood at the end of the experiment was > 65% saturated with O₂. R. N. C.

Anhydrase activity of the blood and coelomic liquid of invertebrates. M. FLORKIN (Bull. Acad. roy. Belg., 1934, [v], 20, 922—930).—A method is described for determination of the relative anhydrase activity, which catalyses the liberation of CO₂ from blood, of various body-fluids. This enzyme has been found in the blood of Annelids, but not in Arthropods or Molluscs. H. G. R.

Direct chemical determination of "carb-amino-bound" carbon dioxide in hæmoglobin solution. J. K. W. FERGUSON and F. J. W. ROUGHTON (Proc. Physiol. Soc., J. Physiol., 1934, 81, 21—22P).—Much CO₂ in blood is not pptd. by alkaline BaCl₂. The proportion is higher in reduced than in oxy-hæmoglobin solutions. Carbamino-compounds are probably important in the transport of CO₂. CH. ABS. (p)

Determination of hæmoglobin in blood. B. DEUTSCH (Biochem. Z., 1934, 274, 299—304; cf. Denes, A., 1933, 174).—The hæmoglobin (I) content of blood is determined spectrophotometrically, without loss of accuracy, after (I) is converted into hæmochromogen. W. McC.

Fluorescence of the blue pigments of the blood of the wrass. M. FONTAINE (Compt. rend. Soc. Biol., 1934, 117, 420—422).—In ultra-violet light the

pigments show a red fluorescence (I) and the absorption spectrum shows a band at 665—631 m μ . The (I) spectrum shows bands at 666.5 and at 516 m μ . By treatment with *N*-KOH, the red (I) is changed to green.

H. G. R.

Physiological degradation of blood-pigment.
IV. Relationship between the pigments of blood and urine. R. NOTHAAS and F. WIDENBAUER (Z. ges. exp. Med., 1934, 93, 644—652).—The production from hæmin of a substance having the same chemical and physical properties as urochrome-B (I) is described. (I) is a derivative of hæmoglobin.

NUTR. ABS. (m)

Bilirubin in the serum of vertebrates. B. VARELA-FUENTES and A. MUNILLA (Compt. rend. Soc. Biol., 1934, 117, 555—557).—Bilirubin has been found in small quantities in dog- and ewe-serum (I) and in considerable quantities in horse-(I). It is not present in rabbit-, pigeon-, guinea-pig-, hen-, pig-, duck-, or turkey-(I).

H. G. R.

Differentiation of the pigments of human blood-serum. F. VERZAR, H. SULLMANN, and A. VISCHER (Biochem. Z., 1934, 274, 7—15).—A method for the differentiation of serum-pigments which depends on the spectrophotometric determination of total absorption, of absorption of bilirubin (I) (as azo-dye), of lipochromes sol. in light petroleum [carotene (II) and xanthophyll ester (III)], and of an "X" fraction of pigments (xanthophyll, flavin, and EtOH-sol., light petroleum-insol. non-diazotisable pigment) is elaborated and applied to a no. of normal and pathological sera. Of the total absorption of normal serum, 74% is due to (I), 8% to (II), 3% to (III), and 15% to the "X" fraction.

P. W. C.

Clinical colour measurements. XII. Spectrophotometric pigment analysis of blood-serum, with respect to the bilirubin and carotene spectra. L. HEILMEYER and H. TOOP (Z. ges. exp. Med., 1934, 80, 603—632; Chem. Zentr., 1934, i, 3774).—Bilirubin is identified from the extinction curve as the principal yellow pigment of normal and pathological sera, with absorption max. at 460 m μ . Carotenoid pigments, traces of hæmoglobin, and an unidentified yellow pigment are also present.

State of combination of protein degradation products on passage into the blood. B. LUSTIG (Biochem. Z., 1934, 274, 313—319).—Determination of N in the filtrate from heat-coagulated blood-sera (I) to which degradation products of protein have previously been added shows that about 25% of added proto- and deuto-albumoses, a much smaller proportion of peptone, and no NH₂-acids are adsorbed by the serum-proteins (II). (I) kept for 24 hr. before treatment lose $\frac{1}{2}$ of their adsorbing power (III). Longer keeping leads to no further diminution of (III). (III) is unaffected when (I) are heated at 38° for several hr. or inactivated by heating for 1—2 hr. at 60°. Different (I) have different (III). (III) is greatly reduced by dilution to half concn. and destroyed by further dilution. After a meal rich in protein (I) have increased (III). It is the globin fraction of (II) which is responsible for (III).

W. McC.

Determination of creatinine (and creatine) in blood. O. FOLIN (Z. physiol. Chem., 1934, 228, 268—272).—A criticism of Lieb and Zacherl's method (A., 1934, 543). The author's method is described.

J. H. B.

Formation of acetylcholine in serum and embryonal extract. R. AMMON and H. KWIATKOWSKI (Pflüger's Archiv, 1934, 234, 269—272; Chem. Zentr., 1934, ii, 1330).—The results of previous workers are confirmed. Hydrolysis of acetylcholine is inhibited by use of a Ringer's solution containing eserine.

H. N. R.

Ammonia content and formation in blood.
XI. J. K. PARNAS (Biochem. Z., 1934, 274, 158—162).—A table shows the amount of NH₃-N eliminated from 3 samples of human blood as determined by the author's distillation method both with Folin's oxalate-carbonate buffer (I) and with borate buffer (II). In the first distillation with (II) much less NH₃ is obtained than with (I), and on carrying out a second distillation with (II) the amount of NH₃ falls to nil, whereas with (I) a further significant amount is obtained. (II) therefore removes completely the NH₃ present and further NH₃ formation is small. Long keeping with (II) leads to the formation of a small amount of NH₃.

P. W. C.

Alkali reserve and fat content of the blood.
R. F. OGILVIE (Edinburgh Med. J., 1934, 41, 448—451).—In rabbits the acid-base balance in blood does not control the fat content of the blood or its migration from the fat depôts.

CH. ABS. (p)

Cholesterol content and cholesterolytic power of the serum of the aged. M. ECK and J. DESBORDES (Compt. rend. Soc. Biol., 1934, 117, 428—429).—The sera of atheromatous cases are frequently supersaturated with cholesterol.

H. G. R.

Cholesterolytic power of serum in a study of the metabolism of cholesterol. M. ECK and J. DESBORDES (Compt. rend. Soc. Biol., 1934, 117, 429—431; cf. preceding abstract).—Cholesterol (I) is dissolved by serum in a definite proportion, influenced by various factors, so that (I) may be deposited in the arteries and may then be redissolved, possibly in excess.

H. G. R.

Relation between the cholesterolytic power of a serum and its protein content. M. ECK and J. DESBORDES (Compt. rend. Soc. Biol., 1934, 117, 615—618).—The power (I) of a serum to dissolve excess cholesterol (II) is dependent on the ratio (III) of the total serum-protein pptd. by NaCl to the amount of (II) carried down by the pptn. In normal sera, (I) is zero when (III) is 50—65, becoming positive and negative, respectively, when (III) rises above or falls below these limits. (I) rises as the protein/urea-N ratio falls. The relation between (I) and (III) does not hold in pathological cases.

R. N. C.

Maternal and foetal oxalæmia. F. P. DONEDDU (Arch. Farm. speriment., 1934, 58, 201—232).—Blood-H₂C₂O₄ rises slightly during the first four months of pregnancy, and falls suddenly in the fifth, then rises gradually to the ninth, when it falls sharply again. It rises considerably during parturition (I), falling again in puerperium. H₂C₂O₄ in the umbilical cord

is high compared with blood- $\text{H}_2\text{C}_2\text{O}_4$; it is lower in premature than in normal (I), and seems to be related to the wt. and length of the foetus. Some results in pathological cases are given. R. N. C.

Micro-determination of lactic acid in blood. M. BOURDEAU (J. Pharm. Chim., 1934, [viii], 20, 342—353).—Neutralised serum freed from albumins and globulins is oxidised in a special apparatus (A., 1934, 384) with dil. KMnO_4 solution in presence of MnSO_4 , when lactic acid is converted into MeCHO , which is collected in Nessler's reagent. The latter is finally reoxidised with 0.5 c.c. of 0.05*N*-I, the excess being titrated with 0.005*N*- $\text{Na}_2\text{S}_2\text{O}_3$. Ketones or β -hydroxybutyric acid do not interfere. S. C.

Micro-determination of acetone in blood. O. CANTONI (Biochem. Z., 1934, 274, 45—50).—A colorimetric method based on Frommer's reaction is described. P. W. C.

Colorimetric determination of blood-sugar by the Creceleius-Serfert method. L. ARNOLD (Med. Welt, 1934, 8, 364; Chem. Zentr., 1934, i, 3627).—The method is suitable for clinical purposes. A. G. P.

Significance of phosphoric esters in the course of blood-glycolysis. I. Degradation of hexose phosphates to triose phosphates as the first stage of glycolysis. Formation of fructose phosphate from glucose and glyceraldehyde by intact erythrocytes. Explanation of the Harden-Young fermentation equation. Z. DISCHE (Biochem. Z., 1934, 274, 51—74).—Washed erythrocytes convert glucose into a fructose phosphate (I) probably identical with the Harden-Young ester. (I) is then degraded by a rapid reaction to triose phosphate and subsequently by a slow reaction to lactic acid. Glucose phosphate (II) is not converted into (I), but probably is degraded to glyceraldehyde and $\text{CO}(\text{CH}_2\text{OH})_2$ phosphates, intact cells converting the latter into lactic acid and haemolysed cells into (I). Degradation of (II) is reversible, erythrocytes being able to synthesise (II) from glyceraldehyde and glucose. $\text{CO}(\text{CH}_2\text{OH})_2$ is not esterified under these conditions. P. W. C.

Glass electrode for determining the p_{H} of venous blood. I. HARRIS, E. L. RUBIN, and W. J. SHUTT (J. Physiol., 1934, 81, 147—152).—A modified electrode is designed to avoid glycolysis and change of p_{H} in the sample, loss of CO_2 , and variation of temp. CH. ABS. (p)

Influence of neutral salts on the ultrafilterability of serum-calcium. L. BRULL, R. POVERMAN, and A. LAMBRECHTS (Compt. rend. Soc. Biol., 1934, 108, 1165—1166; Chem. Zentr., 1934, i, 3759).—The ultrafilterability of serum-Ca is raised by neutral salts according to their position in Hofmeister's ion series, SO_4^{--} and K^+ being most effective. J. S. A.

Variations in serum-magnesium. L. VELLUZ and J. VELLUZ (Compt. rend. Soc. Biol., 1934, 117, 417—418).—In 92% of the normal cases examined serum-Mg varied between 18 and 22 mg. per 1000 c.c. and showed no variation with age. H. G. R.

Regulation of the mineral composition of the blood in the crayfish (*Astacus fluviatilis*, L.).

M. BOGUCKI (Arch. internat. Physiol., 1934, 38, 172—179).—The mineral content of the normal blood-serum is Cl 6.21, Ca 0.48, Mg 0.06, Na 3.49, and K 0.11 mg. per ml. When the fish is placed in sea- H_2O the concn. of the electrolytes in the haemolymph increases with the concn. of the sea- H_2O . As long as the proportion of sea- H_2O is $> 50\%$ the ratio of the different ions remains unchanged. The degree of hydration of the muscles diminishes with the increase of the concn. of the external medium, although the wt. of the fish remains const. NUTR. ABS. (m)

Micro-determination of sulphate in plasma. E. ØLLGAARD (Biochem. Z., 1934, 274, 181—188).— SO_4^{--} in > 2 c.c. of blood-serum or -plasma (but not in whole blood) is determined (error 5%), after deproteinisation with $\text{CCl}_3\text{CO}_2\text{H}$, by pptn. with freshly prepared COMe_2 solution of benzidine, dissolution of the ppt. in aq. EtOH containing NH_4Cl and MgCl_2 , and immediate titration with 0.02*N*- BaCl_2 using Na rhodizonate as indicator. A blank determination must be made. Large amounts of PO_4^{--} do not interfere. W. McC.

Determination of bromine in blood and in animal tissues. I. BELLUCCI [with L. BALDANZI] (Gazzetta, 1934, 64, 696—702).—The org. matter is ashed and the I and Br are then determined as described in A., 1934, 1321. O. J. W.

Determination of iodine in blood and thyroid gland. I. BELLUCCI and R. VIGNI (Gazzetta, 1934, 64, 634—643).—After destruction of org. matter with KOH and H_2O_2 , KI is extracted with EtOH and oxidised with alkaline KMnO_4 , HNO_2 is destroyed with urea and AcOH, and after addition of H_2SO_4 and KI, the I is titrated with 0.002*N*- (for blood) or 0.004*N*- $\text{Na}_2\text{S}_2\text{O}_3$ (for thyroid), with CS_2 as indicator. The method will measure 10^{-5} g. of I in 100 c.c. of blood. R. N. C.

Determination of fibrinogen and thrombin. J. O. W. BARRATT (J. Physiol., 1934, 80, 422—428).—Fibrinogen (I) is determined by measuring the coagulation time of a dil. citrated plasma to which thrombin (II) has been added. Human plasma is used as standard. (II) is determined by means of the time of clotting when the unknown (II) solution and normal human citrated plasma are mixed in proportions just sufficient to convert all (I) into fibrin with no excess of (II). CH. ABS. (p)

Mechanism of the anticoagulant action of azo-dyes in blood-clotting. A. ST. G. HUGGETT (Quart. J. Pharm., 1934, 7, 372—378).—The azo-dyes chlorazol-sky-blue FFS (Chicago-blue 6B) and chlorazol-fast-pink BKS act as anticoagulants by inhibiting the action of thrombokinase and thrombase. C. G. A.

Anticoagulating properties of gold and other salts. A. LUMIERE and S. SONNERY (Compt. rend. Soc. Biol., 1934, 117, 443—444).—The thiosulphates of the alkalis and alkaline earths, particularly Na and Mg, are most effective in preventing the coagulation of blood. Whereas the thio-derivatives of Pb, Zn, and Sn are anticoagulants, other salts (except citrates) are not. H. G. R.

Combination of tetanus- and diphtheria-toxin with blood-proteins. E. KYLIN (Arch. exp. Path. Pharm., 1934, 177, 93—102).—Tetanus toxin (I) in Ringer's solution migrates cataphoretically towards the anode at a velocity > that of the blood-proteins (separated by cataphoresis). The migration of (I) is diminished by human serum, (I) tending to accompany the slowly moving globulin and to leave the more rapidly migrating albumin (II) (I)-free. Diphtheria (I) behaves similarly, although at high concns. it partly migrates with (II). The results indicate that the transport function of serum-proteins holds for bacterial (I). F. O. H.

Separation of haptens by adsorption on inorganic colloids. H. RUDY (Klin. Woch., 11, 1312—1313; Chem. Zentr., 1934, i, 3874).—Wassermann extracts can be adsorbed from a mixture of brain (I) and heart extracts (II) with $\text{Al}(\text{OH})_3$. Spirochaete extracts can be adsorbed from a mixture with (I) by kaolin, and from one with (II) by kaolin and fuller's earth. R. N. C.

Immuno-chemistry of the pyrazolone series. H. ERLENMEYER and E. BERGER (Arch. exp. Path. Pharm., 1934, 177, 116—118).—Of a series of pyrazolone derivatives (I), only those with the grouping $\cdot\text{NPh}\cdot\text{NMe}\cdot$ functioned as a hapten in sp. antibody-formation in horse-serum as indicated by the inhibition of flocculation with the appropriate antigen of fowl-serum and (I). This immuno-property is correlated with the antipyretic action. F. O. H.

Total and thyroxine-iodine of the lion's thyroid. L. BLANCHARD (Bull. Soc. Chim. biol., 1934, 16, 1372—1373).—The left gland of a lion's thyroid contained 0.0683 g. of total and 0.0219 g. of thyroxine-I per 100 g. of fresh tissue. A. L.

Mol. wt. of thyroglobulin. M. HEIDELBERGER and T. SVEDBERG (Science, 1934, 80, 414).—At p_H 4.8—11.3 the sedimentation const. (I) of pig thyroglobulin (II) is 19.2×10^{-13} , indicating a mol. wt. of approx. 8×10^5 . At p_H 3, (II) is incompletely split into two components, for the lighter of which (I) is approx. 10×10^{-13} . At p_H 12, there is a similar fission. Human thyroglobulin has essentially the same (I) as (II). L. S. T.

Carotenoids of the integuments of some insects. E. LEDERER (Compt. rend. Soc. Biol., 1934, 117, 413—416).—The femur of *Aedipoda* contains a mixture of pigments similar to that of the wings, whilst the blue wings of *O. caerulea* contain only traces of carotenoid (I). The pigment of the red elytrons of the Coleoptera *Mylabris* is not a (I). H. G. R.

Glycogen and total carbohydrate content of the human heart. H. BLUME (Beitr. path. Anat., 1934, 93, 20—35).—The % of glycogen (I) in the ventricles and in the septum of the normal human heart are practically identical; some time after death small differences were detected due to unequal glycogenolysis. In long-standing cardiac hypertrophy, (I) storage is increased in the affected part. (I) is more conc. in the infant than in the adult heart. The total carbohydrate of the adult hearts examined (at various times after death) was 0.45—1.46 g. per

100 g. of wet tissue, of which about 70% was (I); in infants probably more (I) is present. A (I) content > 1.5 g. per 100 g. is regarded as pathological. *Post-mortem* glycogenolysis is most rapid during the first 5 hr.; after 3½ hr. about 50%, and after 9 hr. 90% of the original (I) disappears. Within 3 hr. of death it is possible to compute the amount of original (I), but not subsequently. NUTR. ABS. (b)

Structure and origin of corpora lutea in some of the lower vertebrata. J. T. CUNNINGHAM and W. A. M. SMART (Proc. Roy. Soc., 1934, B, 116, 258—281). H. G. R.

Bombicesterol. W. BERGMANN (J. Biol. Chem., 1934, 107, 527—532).—The unsaponifiable portion (1.5—1.6%) of the chrysalis oil of *Bombyx mori* contains, in addition to a large hydrocarbon fraction, 33% of sterols, isolated as their 3:5-dinitrobenzoates. Separation by the usual bromination of their acetates affords cholesterol (I) (85%) and sitosterols (II) (15%), no trace of bombicesterol (III) (Menozzi *et al.*, A., 1908, i, 265) being detected. (III) is probably a mixture of (I) and (II). J. W. B.

Changes in the acid-base coefficient of meat during storage. I. A. SMORODINCEV and N. N. KRYLOVA (Bull. Soc. Chim. biol., 1934, 16, 1344—1351).—The factors *A* and *B* of the acid-base ratio *A/B* (I) (cf. A., 1934, 322) of meat change in opposite directions during autolysis, (I) increasing to a max. val. 5—6 times that given after 1 hr. After 72 hr. at 4° or 48 hr. at 36°, (I) becomes const. at a val. three times that shown in 1 hr., but at both temp. the process follows the same course. The addition of acid accelerates the process. A. L.

Determination of reduced glutathione in tissue. L. BINET and G. WELLER (Bull. Soc. Chim. biol., 1934, 16, 1284—1296).—A method for the determination of reduced glutathione (I) in tissue by pptn. with Cd lactate from the $\text{CCl}_4\text{CO}_2\text{H}$ extract is described. To the ppt. I is added, and the excess titrated with aq. $\text{Na}_2\text{S}_2\text{O}_3$. The results by this method indicate a lower (I) content than that given by other methods. The method may be used when ascorbic acid and ergothione are present, and a modification to avoid interference by cysteine is suggested. A. L.

Comparison of the surface tension of lymph and blood of the dog. N. L. COSMOVICI and P. JITARIU (Compt. rend. Soc. Biol., 1934, 117, 520—521).— γ of lymph-plasma is > that of the corresponding blood-plasma, but those of whole lymph and blood are practically the same. H. G. R.

Pyralin content of human saliva. A. GERHARD (Z. klin. Med., 124, 153—167; Chem. Zentr., 1934, ii, 452—453).—Saliva (I) is obtained by the method of Delhougne; maltose (II) is determined by the Willstätter-Waldschmidt-Leitz-Hesse method. There is no relation between the quantity of enzyme used and the (II) formed for as much as 50—60 mg. of (II). The most favourable results are obtained with 1 c.c. of (I) diluted to 1:8. With this material in young normal subjects 48—133 mg. of (I) are obtained; the vals. fluctuate considerably in pathological cases. Fluctuations are also dependent on

age, young men tending to have a lower ptyalin content. R. N. C.

Chlorine content of gastric juice. G. DELRUE and J. VAN DAMME (Compt. rend. Soc. Biol., 1934, 117, 488—490).—When the secretion of acid is small total Cl is const., but this increases with increased secretion of acid. H. G. R.

Chloride concentration of gastric secretion from fundic pouches and from the intact whole stomach. C. M. WILHELMJ, L. C. HEINRICH, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1934, 108, 197—202).—Stomach fluid comprises (a) fundic secretion containing 578 mg. of Cl' per 100 c.c. irrespective of rate of secretion or p_{H} of gastric contents, (b) pyloric and mixed duodenal secretions containing 340 mg. per 100 c.c. CH. ABS. (p)

Elimination of iodine in human colostrum and milk. A. W. ELMER and W. RYCHLIK (Compt. rend. Soc. Biol., 1934, 117, 530—532).—I in colostrum increases after the first day and is const. in the milk ($20-47 \times 10^{-6}$ g. per 100 c.c. per 24 hr.). H. G. R.

Effect of salts on cell permeability as shown by studies of milk secretion. (A) G. L. PESKETT. (B) S. J. FOLLEY and G. L. PESKETT (Proc. Roy. Soc., 1933, B, 114, 167—180; 1934, B, 116, 396—402).—A. A definite correlation between the ratio of Na to diffusible Ca in the blood and that of solids-not-fat to fat in milk was observed in cows. It is suggested that variations in these salts affect the relative permeability of the mammary cell membranes to lipins and non-lipins.

B. This has been confirmed in cows of different breeds and is suggested as the factor governing the difference in milk composition between the breeds. H. G. R.

Relation between quantity of milk, absolute fat production, and the percentage of fat in milk. J. KŘÍŽENECKÝ (Vestn. czechoslov. Akad. Zemed., 1934, 10, 6—8; Chem. Zentr., 1934, ii, 155).—Relationships for different breeds of cows show close correlation between milk yield and fat yield. A. G. P.

Influence of the stage of lactation on fat determination by the Gerber method. J. LYONS and M. O'SHEA (Sci. Proc. Roy. Dublin Soc., 1934, 21, 123—131).—A low val. for the fat content of cow's milk towards the end of lactation is due to the presence of a fraction in the form of very small globules. This amounts to about $4\frac{1}{2}$ lb. for a 45-week period. P. G. M.

Arachidonic acid in butter-fat. A. W. BOSWORTH and E. W. SISSON (J. Biol. Chem., 1934, 107, 489—496).—By fractionation of the Me esters of the fatty acids from butter, a " C_{20} " fraction was obtained which contained stearic, behenic, and arachidonic (I) acids [(I) separated as octabromide], but no arachidic acid. Linoleic and linolenic acids cannot be detected as tetra- and hexa-bromides, respectively, in presence of (I), since (I) forms isomeric bromides with similar properties. A. E. O.

Effect of feeding irradiated dried yeast on the yield and composition of milk with special reference to its nutritional value. F. DUSCH

(Diss., Techn. Hochschule, Munchen, 1933, 112 pp.).—Feeding of the yeast slightly increases the fat content of milk and definitely increases solids-not-fat. Sp. gr., acidity, catalase, reductase, and leucocyte contents and rennin test are unaltered. The vitamin-D content of the milk is increased so that 0.5 g. of butter-fat prevents rickets in rats. No detectable rise in the antineuritic factor occurs. The growth factor appears to increase. NUTR. ABS. (m)

Sugar content of bile. Z. ASZÓDI (Biochem. Z., 1934, 274, 146—153).—Bile of fasting dogs contains a reducing substance, the amount of which increases after a carbohydrate diet and after adrenaline, decreases after insulin, and is little altered by a flesh or fat diet. Bile undergoes glycolysis. The reducing substance is probably glucose. P. W. C.

Does glycogen occur often in urine? F. N. SCHULZ and H. BECKER (Arch. Pharm., 1934, 272, 795—796).—Cappenberg's evidence (A, 1934, 797) that this is the case is invalid, the tests applied not being sp. R. S. C.

Evaluation of urinary glucose. A. CASTILLA (Bol. Soc. Quím. Peru, 1934, 1, 49—50).—Urinary analyses must relate to the whole output of the 24-hr. day. Iodometric determination of sugar was satisfactory. E. L.

Pentose produced during chronic pentosuria. P. BALINT (Biochem. Z., 1934, 274, 305—312).—The pentose had $[\alpha]_{\text{D}}^{20} + 32.4^\circ$ (*p*-bromophenylhydrazone, m.p. 128—129°; osazone, m.p. 162—163°). It was probably $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{OH}$. W. McC.

Renal excretion of sucrose, xylose, urea, and inorganic sulphates in normal man; comparison of simultaneous clearances. N. M. KEITH, M. H. POWER, and R. D. PETERSON (Amer. J. Physiol., 1934, 108, 221—228).—Relative clearances were in the descending order sucrose, xylose, urea, and inorg. SO_4^{--} . CH. ABS. (p)

Urea excretion and renal function. T. BJERRING (Acta Med. Scand., 1934, 82, 213—227).—There is a constant relationship in human patients between the concn. index of urea and of creatinine (I) in the same individual during variations of the (I) concn. from 10 to 150 and between blood-urea vals. of 13—90 mg. per 100 ml. The ratio of the max. clearance of urea to that of (I) is therefore const. in the same individual and, within the known limits of the (I) concn., independent of the diuresis. Provided the blood-urea is const., the urea content of the reabsorbed fluid remains const. and independent of the concn. index so long as this index is < 150 . NUTR. ABS. (b)

Economy of water in renal function referable to urea. J. L. GAMBLE, C. F. MCKHANN, A. M. BUTLER, and E. TUTHILL (Amer. J. Physiol., 1934, 109, 139—154).—The requirement of H_2O for renal elimination of substances is additive except where urea is a constituent. CH. ABS. (p)

Creatinine clearance as a measure of glomerular filtration in dogs, with particular reference to the effect of diuretic drugs. L. F. DAVENPORT, M. N. FULTON, H. A. VAN AUKEN, and R. J. PARSONS (Amer. J. Physiol., 1934, 108, 99—106).—Constancy

of normal creatinine excretion is undisturbed by exercise, diet, diuresis, or disease. CH. ABS. (p)

Effect of magnesium halides on the p_H of urine. P. DELBET and FRANCESCO (Bull. Acad. Méd., 1934, 108, 1470—1475; Chem. Zentr., 1934, i, 3760). The urine of cancerous, but not normal, subjects showed variation between p_H 5 and 7 in one day; the cancerous condition tends towards alkalosis. NaHCO_3 , H_3PO_4 , and AlCl_3 affect the p_H by direct transport, whilst Mg halides produce a sp. indirect acidifying effect. J. S. A.

Urobilin excretion and destruction of blood. A. LICHTENSTEIN (Nederland. Tijdschr. Geneesk., 1934, 78, 1522).—The average excretion (I) of urobilin (II) in the faeces of an average European of 70 kg. wt. is 135—150 mg. daily; in a Javanese, (wt. about 55 kg.) it was 75—80 mg. This lower rate of excretion may be due to diet poor in animal protein, since in healthy European vegetarians (I) of (II) is 75.4 mg. daily. Constipated individuals show low (I) of (II). Determination of (I) of (II) cannot be used to calculate the average time of survival of the red blood-corpuscle. NUTR. ABS. (m)

Pathological skin pigmentation and "pigment-vitamins." P. MORAWITZ (Klin. Woch., 1934, 13, 324—327; Chem. Zentr., 1934, i, 3762).—Prolonged treatment of Addison's disease with adrenal cortex often produces a disappearance of pigmentation without affecting the other symptoms. Similarly, administration of sweet-orange- or lemon-juice to a scorbutic patient with a chloasma-like melanosis (I) causes the disappearance of (I), suggesting a connexion between (I) and avitaminosis-C. R. N. C.

Chloride, carbohydrate, and water metabolism in adrenal insufficiency and other conditions. H. SILVETTE (Amer. J. Physiol., 1934, 108, 535—544).— H_2O retention and salt loss in muscles of adrenalectomised animals are related to deficiency of glucose and glycogen in the tissues. CH. ABS. (p)

Presence of the anti-anæmic factor in preparations of dried stomach from the cardia, fundus, and pyloric regions. E. MEULENGRACHT (Ugeskr. Laeger, 1934, 96, 179—187; Acta Med. Scand., 1934, 82, 352—374).—Powder from the fundus (pig) (defatted and dried) region is inactive; that from the pyloric region is strongly active. The anti-anæmic factor appears to be associated with the function of the pyloric glands (I). In pernicious anæmia the mucous membrane of the stomach is more or less atrophic and its secretory function impaired. Hence the disease may be due to atrophy and inactivity of (I). NUTR. ABS. (m)

Guinea-pig as a hæmatopoietic test animal. J. W. LANDSBERG and M. R. THOMPSON (J. Amer. Pharm. Assoc., 1934, 23, 964—968).—The active constituent of liver extract producing a reticulocyte response in the guinea-pig is not readily destroyed by heating. A. E. O.

Calcium in beriberi and in fowls with similar symptoms due to calcium deficiency. H. Y. OH (W. Chosen Med. Assoc., 1934, 24, 40—41).—Patients

with beriberi (I) have low serum-Ca, and show marked clinical improvement after intravenous injections of 20 ml. of 5% aq. CaCl_2 daily. A condition resembling (I) in fowls kept on a low-Ca diet containing vitamin-B is relieved by Ca injections. Ca deficiency is an important factor in the etiology of (I). NUTR. ABS. (m)

Biochemical control of cancer. M. COPISAROW (Chem. and Ind., 1934, 1047—1048).—Recent results indicate that protracted enzyme depletion causes suppressed oxidation and resultant formation of carcinogenetic dehydrogenated products *in situ*. Corrective measures therefore involve (1) inhibition of tumour formation, (2) inactivation of unsaturated carcinogenetic substances, (3) counteraction of conditions detrimental to normal enzyme equilibrium, and (4) restoration of the glutathione oxidation-reduction. Substances possessing such properties are $(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{S}$, methylthionine chloride, $\text{Na}_2\text{S}_2\text{O}_3$, $\text{Na}_2\text{S}_4\text{O}_6$, colloidal S, Ph_2SO , and cysteine sulphoxide. J. W. B.

Retention of glyoxalines in cardio-renal conditions. M. LOEPER, M. PERRAULT, and A. LESURE (Compt. rend. Soc. Biol., 1934, 117, 433—435).—Retention of glyoxalines in cardio-renal affections, particularly in cases of œdema, with striking elimination at the crises, is demonstrated. H. G. R.

Glyoxaline compounds in spinal fluids. M. LOEPER, M. PERRAULT, E. BLOY, and A. LESURE (Compt. rend. Soc. Biol., 1934, 117, 576—578).—Glyoxaline compounds are found in large quantities in cerebrospinal fluid in pregnancy, in cases of nervous reaction with spinal hypertension, and in acute meningitis. In normal and other pathological conditions they are absent, or present only in traces. R. N. C.

Glyoxalinæmia of parenteral origin. M. LOEPER, M. PERRAULT, and A. LESURE (Compt. rend. Soc. Biol., 1934, 117, 578—579).—Glyoxalinæmia (I) occurs in many pathological conditions, produced probably by fever, release of leucocyte debris, destruction of erythrocytes, and from tissue-protein. Injection of serum increases (I) and also glyoxalinuria. Ascitic fluid in cirrhotics contains glyoxaline compounds even when albumin and cellular elements are low. R. N. C.

Effect of adrenaline on the alimentary lipæmia of diabetes. M. SULLIVAN and P. CAMERON (Amer. J. Med. Sci., 1934, 187, 457—462).—In diabetes, adrenaline depresses the curve of increasing blood-fat (Ruckert's method) following fat ingestion. NUTR. ABS. (b)

Action of hexose diphosphate and phosphates on the diabetic organism. V. S. ILJIN, N. N. JAKOVLEV, and V. M. VESSELKINA (Z. ges. exp. Med., 1934, 93, 679—684).—Subcutaneous injection of Na hexose diphosphate (I) or intravenous administration of a phosphate mixture (p_H 7.0) produces in cats with partial pancreatectomy a reduction in blood-sugar, an increase in the lactacidogen (II) content of the muscles, but no significant change in the glycogen. The increase in (II) is very much less marked in completely pancreatectomised cats. The action of (I) is explained by the production of inorg. phosphate,

the effect of which on the diabetic animal is only partly accounted for by the increase in (II).

NUTR. ABS. (m)

Does glycosuria influence the silicon in the pancreas and liver? A. S. E. VON HERMANY (Münch. med. Woch., 1934, 81, 554; Chem. Zentr., 1934, i, 3760).— CaSiO_3 gel lowers blood- and urine-sugar. It is suggested that diabetes is due to a lowering of the SiO_2 content of the pancreas and liver.

J. S. A.

Behaviour of blood-sugar during sulphur (sulfosin) treatment of dementia praecox. S. IZIKOWITZ (Acta Med. Scand., 1934, 82, 567—578).—The blood-sugar decreased 5.5 hr. after injection of sulfosin; during the later period of fever hyperglycaemia was observed.

NUTR. ABS. (b)

Methylglyoxal in infantile food disorders; relations with avitaminosis- B_1 . G. POPOVICIU and N. MUNTEANU (Compt. rend. Soc. Biol., 1934, 115, 897—899).—In a no. of cases of summer infantile food disorders, AcCHO (I) in varying quantities was excreted in the urine. On recovery, (I) excretion ceased. No (I) was excreted in cases of avitaminosis- B_1 which were free from summer food disorders.

R. N. C.

Acid-base equilibrium in patients with convulsions. J. MADSEN (Compt. rend. Soc. Biol., 1934, 117, 625—630).—The mean p_H of the nocturnal urine in starvation of epileptic patients (I) is 6.05 as compared with 5.83 in controls (II). The matutinal alkaline tide, which rises steadily to the neutral point in (II), fluctuates towards the alkaline side in (I). Ingested NaHCO_3 is excreted more rapidly in (I) than in (II).

R. N. C.

Ammonia content of the urine in convulsive patients. J. MADSEN (Compt. rend. Soc. Biol., 1934, 117, 630—633).—Total urinary N is practically identical in normal persons (I) and epileptics (II). Urinary NH_3 at a const. p_H in (II) is $>$ in (I).

R. N. C.

Ratio of acids and ammonia in the urine of normal persons and convulsive patients. J. MADSEN (Compt. rend. Soc. Biol., 1934, 117, 633—635).—The ratios $\text{NH}_3/\text{inorg. acid}$, $\text{NH}_3/\text{SO}_4^{--}$, and $\text{NH}_3/\text{org. acid}$ are all increased in the urine of epileptics as compared with normal persons.

R. N. C.

Causes of alimentary glycosuria in infective diseases. N. A. NIELSEN (Acta Med. Scand., 1934, 82, 306—310).—In rabbits, fever, unaccompanied by toxæmia, does not affect the glycaemic response to administered glucose. The alimentary glycosuria of acute infectious disease is therefore caused by toxic liver damage.

NUTR. ABS. (n)

Carbohydrate metabolism in infectious fevers. S. LEITES, L. S. LIFSCHITZ, and A. ODINOV (Z. ges. exp. Med., 1934, 93, 803—815).—In febrile infections (I), oral and intravenous administration of glucose are followed by a more prolonged rise of blood-sugar (II) with no hypoglycaemic phase (III). (III) becomes very marked during the fall of the temp. Intravenous injection of adrenaline produces a very slight rise in (II) and occasionally a fall; its effect is not changed by previous administration (oral or intravenous) of

glucose. Fever has no definite effect on the glycaemic reaction to 10 units of insulin. In (I) utilisation and storage of carbohydrate are impaired as a result of defective cellular metabolism and hypofunction of the islet tissue.

NUTR. ABS. (m)

Hæmochromatosis. J. H. SHELDON (Lancet, 1934, 227, 1031—1036).—A lecture.

L. S. T.

Creatine metabolism in children with hypothyroidism. H. G. PONCHER, M. B. VISSCHER, and H. WOODWARD (J. Amer. Med. Assoc., 1934, 102, 1132—1135).—Hypofunction of the thyroid causes decrease or complete cessation of creatine excretion, which can be restored to normal by administration of thyroid extract.

NUTR. ABS. (m)

Modifications of phosphorus, sodium, and nitrogen-exchange in the blood in renal and thyroid deficiency. R. MESSINA (Arch. Farm. sperim., 1934, 58, 187—199).—In rabbits with $\text{UO}_2(\text{NO}_3)_2$ nephritis (I) total and inorg. P and Na fall slowly and steadily, whilst the N exchange also diminishes. Thyroidectomy (II) causes similar diminutions whilst with (I) and (II) together the fall is more considerable in all cases.

R. N. C.

Basal metabolism and impedance angle in thyrotoxicosis and myxoedema. J. D. ROBERTSON and A. T. WILSON (Lancet, 1934, 227, 1158—1159).—In Graves' disease the impedance angle (I), an electrical property of the body (J. Inst. Elect. Eng., 1933, 73, 203), deviates from the normal. Administration of I produced a fall in pulse and basal metabolic rates but no alteration in (I). In myxoedema (I) is normal and treatment with thyroid extract produced no change.

L. S. T.

Hyperthyroxinaemia in thyrotoxicosis. A. W. ELMER, W. RYCHLIK, and M. SCHEPS (Compt. rend. Soc. Biol., 1934, 117, 533—534).—In exophthalmic goitre thyroxine (I)-I is increased and varies between 8.5 and 16.1×10^{-8} g. per 100 c.c. in the peripheral venous blood and the total (I) between 0.75 and 1.25 mg.

H. G. R.

Transmission of influenza by a filterable virus. T. FRANCIS, jun. (Science, 1934, 80, 457—459).—Previous observations (A., 1933, 1071) on the transfer of a filterable transmission agent from human cases of epidemic to ferrets are confirmed. Experiments with mice also indicate that the disease is produced by a filterable virus.

L. S. T.

Enzootic marasmus. Iron content of kidney, liver, and spleen. E. J. UNDERWOOD (Australian Vet. J., 1934, 10, 87—92).—The Fe content of all three organs in diseased sheep and calves was $>$ normal. The absence from the diet of some factor necessary for the utilisation of Fe in the body is indicated as the cause of the disease.

CH. ABS. (p)

Diurnal changes in liver during pregnancy. T. W. GOODWIN and G. M. HIGGINS (Amer. J. Physiol., 1934, 108, 567—572).—Changes in wt. and in glycogen and H_2O contents of livers of pregnant rats (I), after feeding, resemble those of normal animals except that peak vals. occur earlier and the glycogen recovered at the peak is less in (I).

CH. ABS. (p)

Residual reducing substances of the blood in puerperium. E. BRANDSTRUP (Acta Med. Scand., 1934, 82, 329—337).—During the first 10 days of the puerperium lactose is not present in the blood in demonstrable amounts. NUTR. ABS. (m)

Chemotherapy. I. Action of sodium formaldehydesulphoxylate in bacterial infections. S. M. ROSENTHAL (U.S. Pub. Health Rep., 1934, 49, 908—911).—Subcutaneous injection of the sulphoxylate (I) gave a high degree of protection of mice against pneumococci (II). Death occurred only with dosages of 4 g. per kg. (I) produced no bactericidal or bacteriostatic effects in broth cultures of (II).

CH. ABS. (p)

Change in the antirachitic activity of orthophosphoric acid by esterification with phenol. R. LECOQ and M. L. BARBAN (Compt. rend., 1934, 199, 1255—1257).—Phenolic esterification decreases the antirachitic potency of H_3PO_4 . Na phosphite, Ph_3PO_4 , and guaiacol phosphate or phosphite do not relieve rickets, but Na_3PO_4 (2%) does. J. L. D.

Chemotherapy of syphilis and other infectious diseases. I. Experimental chemotherapy of preparation No. 1717, formaldehydesulphoxylate of 3-amino-4-hydroxyphenylarsinic acid. G. W. RAIZISS, M. SEVERAC, and A. KREMENS (J. Chemotherapy, 1934, 11, 34—45).—Prep. and properties are described. Efficiency against syphilis is > that of tryparsamide and approx. equal to that of acetarsone.

CH. ABS. (p)

Changes in serum-proteins in general paralysis and correlations with serological reactions. A. PRUNELL and J. GALMES (Compt. rend. Soc. Biol., 1934, 117, 551—552).—Wassermann and Kahn reactions progressively decrease as the serum-globulin increases and are often negative when this reaches 5—6 g. per 100 c.c. H. G. R.

Effect of hyperglobulinæmia on the Wassermann and Kahn reactions. A. PRUNELL (Compt. rend. Soc. Biol., 1934, 117, 552—554; cf. preceding abstract).—The ppt. obtained in the Kahn reaction is independent of the globulin (I) and does not contain N. Paralytic serum (II) with a negative Wassermann reaction and an increased content of (I) has a lytic power > that of normal (II). H. G. R.

Manometric determination of oxygen uptake and carbon dioxide evolution of tissue sections. H. RUSKA (Arch. exp. Path. Pharm., 1934, 177, 38—41).—An improved type of vessel suitable for use in Warburg's manometric method is described.

F. O. H.

Mechanism of intracellular oxido-reduction. P. JOYET-LAVERGNE (Compt. rend., 1934, 199, 1159—1161).—The catalysis of intracellular oxido-reductions is due to the conjoint action of glutathione and vitamin-A.

H. W.

Capillaroscopy and acid-base equilibrium in mental work. R. MESSINA (Arch. Farm. sperim., 1934, 58, 242—251).—Mental fatigue from prolonged study is accompanied by a fall in blood- p_H and N exchange.

R. N. C.

Viscosity of protoplasm. A. M. FREDERIKSE (Chem. Weekblad, 1934, 31, 593—595).—Methods

which have been used for determining the viscosity (η) of protoplasm are reviewed. In order to obtain a val. representative of the undisturbed living material it is necessary to calculate η from measurements of Brownian movement; improved methods are outlined. Measurements with *Amœba verrucosa* show η to be different in different parts of the cells and to depend greatly on the physiological conditions prevailing at the time of the measurement. Narcotics in small quantities reduce, and in larger quantities increase, η , particularly of the ectoplasm. H. F. G.

Viscosity and plasticity in muscle. H. J. JORDAN (Chem. Weekblad, 1934, 31, 590—593).—Smooth muscle is regarded as a colloidal system consisting of micelles surrounded by a viscous liquid, contraction involving first an elastic deformation of the micelles and then plastic propagation. The interrelationships of the elastic and plastic changes are discussed. H. F. G.

Relationships between the chemical and physical processes in muscular contraction. O. MEYERHOF (Ann. Inst. Pasteur, 1934, 53, 565—590).—A lecture.

Chemical changes associated with muscular contraction in normal and adrenalectomised animals. O. COPE, A. B. CORKILL, H. P. MARKS, and S. OCHOA (J. Physiol., 1934, 82, 305—320).—The formation of lactic acid from glycogen and hexose phosphates by muscle extracts (I) shows no great differences between (I) from normal (II) and adrenalectomised cats (III). When stimulated anaerobically and isometrically the isometric coeffs. (IV) for lactic acid in (II) and (III) are similar, but (IV) for phosphagen (V) in (III) is > in (II), whilst the heat coeff. is decreased in (III), and the muscle performs less work, this decrease being probably due to its diminished capacity to resynthesise (V). During activity the rate of (V) breakdown is decreased.

R. N. C.

Rôle of phosphocreatine in fundamental chemical changes in contracting mammalian muscle. J. SACKS and W. C. SACKS (Amer. J. Physiol., 1934, 108, 521—527).—In rabbits fed with oats the alkali reserve of tissues decreased, and the amount of base liberated by hydrolysis of phosphocreatine (I) and conversion into hexose phosphate is equiv. to the lactic acid formed in muscle contraction. (I) tends to preserve a const. p_H .

CH. ABS.

Transformation of adenosinetriphosphoric acid (adenyl pyrophosphate) in the isolated frog heart. A. N. PARSCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 630—633).—Perfusion of the isolated frog heart with Ringer's solution results in a change in the adenyl pyrophosphate (I) content. NaF , CH_2I-CO_2H , and KCN have practically no effect on the rate of change of (I). J. L. D.

Phospholipin content and activity in muscle. W. R. BLOOR and R. H. SNIDER (J. Biol. Chem., 1934, 107, 459—470).—By comparison of skeletal muscles of different extent of usage in the same animal and of the same muscle (I) in different animals subject to different amounts of use, it is found that the more used (I) has a higher phospholipin content

(II) than less used (I). Similar but smaller differences are found in cholesterol content (III) so that the (II) to (III) ratio is $>$ in more used (I). Smooth (I) (gizzard and stomach) has normal (II) but high (III). The I val. is the same in much- or little-used (I).

C. G. A.

Sources of energy in muscular work performed in anaerobic conditions. R. MARGARIA and H. T. EDWARDS (Amer. J. Physiol., 1934, 108, 341—348).—Lactic acid production from glycogen is one probable source of energy corresponding with approx. 66% of anaerobic work. CH. ABS. (p)

Anaerobic breakdown of carbohydrate in the isolated frog ventricle. R. GADDIE and C. P. STEWART (J. Physiol., 1934, 80, 457—479).—Frog ventricle (I) exhausted by contracting in the absence of O_2 repeatedly recovers on addition of glucose and mannose to the perfusion fluid. Fructose, galactose, various pentoses and other sugars, glycogen, glycine, and alanine are ineffective. Oleate and linoleate cause a little recovery at first, but the effect cannot be repeated. Partial recovery (II) is caused by AcCHO and glyceraldehyde, the latter being eventually toxic. $AcCO_2H$ (III), glycerophosphate (IV), and dihydroxyacetone added separately have no effect, but (III) and (IV) together cause partial (II). Contraction of (I) in the absence of O_2 is inhibited by $CH_2I \cdot CO_2H$ and $CH_2Br \cdot CO_2H$ and not restored by washing. Addition of glutathione (V) and cysteine prevent this inhibition, and partial (II) of an already affected heart is effected with (V). (I) which have been treated with $CH_2I \cdot CO_2H$ and partly restored by (V) are poisoned by addition of glucose, perhaps because a toxic breakdown product of it accumulates under these conditions. Dil. aq. Na_2AsO_3 slowly stops the contractions in N_2 but not in O_2 ; addition of glucose and reduced (V) restores them.

There are probably two paths of glucose breakdown in the heart, one through AcCHO and one through (III). NUTR. ABS. (m)

Existence of two types of lactic fermentation in dog's muscle. E. AUBEL and E. SIMON (Compt. rend. Soc. Biol., 1934, 117, 400—402).—Lactic acid is formed from hexose diphosphate in two ways. After the production of triose phosphate, in one case AcCHO is the intermediate product, in the other an equilibrium of Wurmser's type occurs. H. G. R.

Influence of muscular work on urinary lipase. K. MATOBA (Archi Igakkai Zasshi, 1933, 40, 1523).—Urinary lipase (I) in meat-fed rats is more resistant to quinine and more sensitive to atoxyl and NaF than that of rice-fed rats. Increased (I) during muscular work is not derived from the blood.

CH. ABS. (p)

Ammonia content and ammonia formation in muscle. XXI. Inhibition of ammonia formation by various alkaline buffer solutions. T. MANN and P. OSTERN (Biochem. Z., 1934, 274, 154—157).—Deamination of adenylic acid by muscle deaminase is inhibited with increasing p_H , but to a different extent with different buffers. Thus the deamination at p_H 8.85 is reduced to 20% with PO_4^{4-} and borate buffer, but only to 70% by veronal-carbonate buffer. P. W. C.

Occurrence of decomposition products of chlorophyll. II. Decomposition products of chlorophyll in stomach walls of herbivorous animals. P. ROTHMUND, R. R. McNARY, and O. L. INMAN (J. Amer. Chem. Soc., 1934, 56, 2400—2403; cf. A., 1933, 168).—Extraction of the mucous membrane of the third and fourth stomachs of freshly-killed cows with $COMe_2$ and subsequent fractionation of the Et_2O -sol. pigments with 0.35—38% HCl gives small amounts of deuterio- and proto-porphyrins (both formed by decomp. of blood-pigment), phylloerythrin (obtained in max. amount), phaeopurpurin 18, phaeophorbide α , and phaeophytin (detected spectroscopically). These compounds have a definite erythropoietic effect on rats when administered *per os* in small doses (0.1—2 mg. per rat per day). H. B.

Metabolic rate, blood-sugar, and the utilisation of carbohydrate. H. T. EDWARDS, R. MARGARIA, and D. B. DELL (Amer. J. Physiol., 1934, 108, 203—209).—The R.Q. in man during severe exercise (I), designed to deplete the carbohydrate store, did not, even at the beginning, indicate that carbohydrate was the sole fuel. With continued (I) the R.Q. fell to a val. which represented an energy metabolism mainly of fat. It rose again after ingestion of glucose, but not until some time after the max. hyperglycemia had been attained. With alternating rates of work the R.Q. rose when the rate was increased. The blood-sugar remained at the normal resting level during continuous (I). A difference between the rates at which the usage and mobilisation of glucose are diminished on stopping exercise may explain the hyperglycemia resulting from discontinuous severe (I). NUTR. ABS. (b)

Blood-sugar curve after administration of glucose in children. S. A. SRWE (Jahrb. Kinderheilk., 1934, 142, 344—350).—In children, especially in young and nervous children, a marked hypoglycemic phase frequently occurs 1½—2½ hr. after oral administration of glucose (I) (1 g. per kg. of body-wt.). In severe rickets, the fasting blood-sugar level is often high, and oral administration of (I) may produce a flat curve which is abnormally sustained. The response of healthy young children, however, to (I) ingestion is normally very variable. NUTR. ABS. (b)

Variation in sugar content of blood and urine after administration of glucose. A. SZEPESHELYI (Arch. wiss. pr. Tierheilk., 1934, 67, 405—409).—The blood-sugar curve after ingestion of various amounts of glucose following a 24-hr. fast had its max. after 45—75 min. in dogs and after 105—150 min. in horses, reaching the original level after 135—180 and 210—360 min., respectively. The assimilation limit for dogs was 12—13 g. per kg. of body-wt. and that for horses 11—12 g. NUTR. ABS. (b)

Influence of exercise on the blood-sugar, especially in connexion with glucose ingestion. B. STRANDELL (Acta Med. Scand., 1934, Suppl. 55, 245 pp.).—If the ingestion of glucose (I) in man is immediately followed by exercise of long duration the hyperglycemic response is considerably diminished or replaced by a fall in blood-sugar (II). This is due to

increased removal of (I) from the blood rather than to deficient absorption from the intestine. If exercise is begun when the glycaemic response to ingested (I) is at its max., the (II) level falls rapidly, but rises again if the exercise is discontinued. This latter rise is due to absorption of (I) remaining in the gut. Discontinuation of fasting exercise is often followed by a transitory rise in (II), probably due to hepatic glycogenolysis partly caused by adrenaline secretion. Subcutaneous adrenaline administration, however, has little effect on the (II) curve during exercise. NUTR. ABS. (b)

Sugar threshold and renal function. I, II. T. BJERRING and P. IVERSEN (*Acta Med. Scand.*, 1934, **82**, 193—212, 228—250).—I. The renal threshold is defined as that sugar concn. of the blood (or glomerular filtrate) at which the glucose (I) concn. of the re-absorbed fluid passes over from a higher level than that of the blood to a lower one, or conversely. Two threshold vals. must be considered, one for the rising and another for the falling blood-sugar (II) curve.

II. At the same (II) level, (I) re-absorption in the kidney is less with a falling (II) curve than with a rising one. The (I) concn. and total (I) excretion in the urine are dependent both on the (II) level and on the concn. index. When the latter remains const., changes of (II) concn. are paralleled by those of the urine, but an increased (I) excretion may be accompanied by a fall in the concn. index. In acidosis the tubules are poisoned so that the re-absorption of (I) is decreased. NUTR. ABS. (b)

Glucose tolerance and the glycogen storage capacity of the dog. W. L. BUTSCH (*Amer. J. Physiol.*, 1934, **108**, 639—642).—Continuous intravenous injection of glucose in the dog caused the liver-glycogen to increase until a level of 20% was reached, when the sugar tolerance of the animal markedly decreased. The muscle-glycogen attained a level of 3—4%. The time necessary to reach this max. was decreased by increasing the rate of administration of glucose. NUTR. ABS. (b)

Effect of diet on the distribution of glycogen in the skeletal muscle of the rat. M. SAHYUN, A. SIMMONDS, and H. WORKING (*Amer. J. Physiol.*, 1934, **108**, 708—712).—The glycogen content of the muscles varied directly with the quantity of carbohydrate fed. The gastrocnemius contained about 18% more glycogen than the quadriceps femoris, triceps brachii, and pectoralis major. A variation occurred from animal to animal. The right leg gave vals. > the left, which is unexplained. NUTR. ABS. (b)

Glycogen metabolism in the rat after partial hepatectomy. K. MACKENZIE (*Caduceus*, 1933, **12**, —11).—After removal of 30—50% of the liver of the rat, insulin more readily produces hypoglycaemic symptoms, and the % but not the total increase in liver-glycogen is greater. NUTR. ABS. (b)

Carbohydrate exchange in splenectomised R. DEL ZOPPO (*Arch. Farm. speriment.*, 1934, **5**—186).—Blood-sugar (I) is raised considerably 7—8 days after splenectomy (II), but returns to normal after approx. 21 days. The glycaemic curve (III) is higher and more extended during the hyperglycaemic

period. The (III) resulting from administration of adrenaline is also higher after (II), this increase persisting even when (I) has returned to normal.

R. N. C.

Intermediary metabolism of carbohydrates from angiostomy data. I. E. S. LONDON, E. F. IVANENKO, and M. J. PROCHOBOVA (*Z. physiol. Chem.*, 1934, **228**, 243—248).—AcCHO (I) and AcCO₂H (II) were determined in the inflowing and outflowing blood of various organs of the dog, fasting, and after administration of glucose. There is no parallelism between the curves for (I) and (II). The highest vals. for (I) and (II) are given by the brain sinus. (I) is probably an intermediary metabolic product of glucose, (II) definitely so. J. H. B.

Significance of bile acids in carbohydrate metabolism. XXI (ii). Glycolysis and degradation of glycogen in liver and muscle following administration of cholic acid and adenylypyrophosphoric acid. K. WATANABE (*Biochem. Z.*, 1934, **274**, 268—273; cf. A., 1933, 88).—Administration of cholic acid (I) to rabbits causes increase, whilst that of adenylypyrophosphoric acid (II) (from rabbit muscle) causes decrease, in the glycogen content of the liver (III) and muscle (IV). Lactic acid production in (III) and (IV) is restricted by administration of (I) and increased by that of (II). (I) and (II) act antagonistically. W. McC.

Bile acids and carbohydrate metabolism. XXXII. Influence of bile acids on liver-glycogenesis and on [H'] of urine. K. OHASHI (*J. Biochem. Japan*, 1934, **20**, 319—326).—The *p*_H of rabbit's urine gradually decreases during hunger to a min. val., when a slight increase sometimes occurs; it subsequently increases on subcutaneous injection of Na cholate. A similar phenomenon occurs with liver-glycogenesis. F. O. H.

Biochemistry of carbohydrates. V. Micro-determination of chondroitinsulphuric acid in cartilage. VI. Chondroitinsulphuric acid in cartilage and bone. T. MIYAZAKI. VII. Enzyme hydrolysing glucosamine. VIII. Distribution and renal threshold of glucosamine after injection into animals. K. KAWABE. IX. Fermentation of chondroitinsulphuric acid by *B. pyocyaneus*. Pyocyanine. T. MIYAZAKI. X. Fate of glucosamine in the animal body. K. KAWABE. XI. Constitution and specific enzyme of benzoylglycuronic acid. H. MASAMUNE (*J. Biochem. Japan*, 1934, **20**, 211—222, 223—231, 233—241, 243—251, 287—292, 293—310, 311—317).—V. Dried cartilage (I) (approx. 5 mg.) is hydrolysed with *N*-HCl (10 c.c.) for 30 min., the hydrolysate is evaporated to dryness, and glucosamine (II) in the residue determined colorimetrically by alkali and Ehrlich's reagent (A., 1931, 1081; cf. A., 1932, 532).

VI. The content of chondroitinsulphuric acid (III) (determined approx. by the reducing val. after hydrolysis) varies with the type of (I), viz., hyalin->elastic->fibro-(I); that of costal (I) is low owing to early ossification. With rabbits, the incidence of rickets increases (approx. ×3) the (III) content of the femur.

VII. An enzyme hydrolysing (II) occurs in the

lung, kidney, intestinal mucosa, pancreas, and, to a smaller extent, blood and gastric mucosa of rabbits, dogs, and cats, but not of guinea-pigs. Injection of (II) appears to increase the body-content of the enzyme.

VIII. (II) hydrochloride orally administered to rabbits (2 g. per kg. body-wt.) appears only in traces in the blood, but is excreted in the urine, a max. occurring 5—7 hr. after ingestion; the renal threshold is very low. Subcutaneous administration produces rapid excretion, the blood level being max. 2—3 hr. after injection. Temporary accumulation occurs in the liver, kidney, and mucosa of stomach and intestine.

IX. *B. pyocyaneus*, *Streptococcus haemolyticus*, and *Staphylococcus flavus* hydrolyse (III) with liberation of a reducing substance but not of $\text{SO}_4^{''}$. Pyocyanine is formed, its solution in HCl giving absorption bands at 470, 380, and 275 μ .

X. Subcutaneous injection of (II) into normal rabbits produces liver-glycogenesis to an extent < that occurring after administration of the equiv. amount of glucose. The urinary lactic acid, $[\text{H}^+]$, and urea levels increase, but the total N, including that due to excreted (II), is < the total N administered; fructose is not excreted.

XI. Benzoylglycuronic acid (IV) treated with aq. NaHCO_3 exhibits mutarotation, whilst no Bz is liberated (cf. A., 1926, 1056); the Bz is probably attached to C2 or C4. $\text{CHCl}_3\text{--H}_2\text{O}$ extracts of kidney contain an enzyme (optimum p_{H} 5.4—5.8, inactivated at 80°) which hydrolyses (IV). Differences in the rates of hydrolysis of tributyrin and (IV) by various enzyme preps. indicate that the enzyme is not an esterase.

F. O. H.

Food value of mannitol and sorbitol in relation to the balance of the ration. R. LECOQ (Compt. rend., 1934, 199, 894—896).—When comprising 35% of a pigeon's ration, mannitol (I) and sorbitol are completely utilised and in the case of (I) the vitamin-B (II) requirement is reduced. With 66% in the ration nutritional disturbances occur and polyneuritis intervenes however great the supply of (II). A. G. P.

Utilisation of inulin from *Arctium lappa* and certain soluble inulins by the rat. C. J. CARR and J. C. KRANTZ, jun. (Proc. Soc. Exp. Biol. Med., 1934, 31, 675—678).—No significant differences are noted in the absorption and utilisation of the insol. inulin from burdock root and in the sol. inulins from the roots of camas and wild onion.

NUTR. ABS. (m)

Carbonic acid assimilation by animal cells. W. LOELE (Virchow's Archiv, 286, 167—169; Chem. Zentr., 1934, i, 3602).— MeCHO occurs in alkaline solutions of glycine and H_2O_2 after passage of CO_2 .

A. G. P.

Acetaldehyde and trimethylamine in human pulmonary expiration. W. LIBBRECHT and L. MASSART (Compt. rend. Soc. Biol., 1934, 117, 495—496).— MeCHO and NMe_3 have been detected in expired air after absorption in H_2O . H. G. R.

Relationship between oxygen consumption and nitrogen metabolism. IV. C. W. BALDRIDGE (Arch. Int. Med., 1934, 54, 517—539).—In dogs

the O_2 consumption is decreased during recovery from acute haemorrhagic anaemia. Blood transfused into dogs is lost from the peripheral circulation, during which time the basic metabolic rate is increased. The pigment of haemolysed blood is rapidly excreted and is accompanied by an increase in gaseous metabolism (whether the blood is haemolysed *in vivo* or obtained from another animal). Phloridzin diabetes in dogs is accompanied by a great increase in endogenous protein catabolism and O_2 consumption, followed by a marked storage of N. C. G. A.

Protein and energy metabolism of wild and albino rats during prolonged fasting. F. G. BENEDICT and E. L. FOX (Amer. J. Physiol., 1934, 108, 285—294).—Wild rats have the higher basal metabolism. Towards the end of fasting protein metabolism increased, the animals deriving increased proportions of total heat from proteins. The effect was greater in wild rats. CH. ABS. (p)

Relative value of proteins in feeding. E. F. TERROINE (Compt. rend. Soc. Biol., 1934, 117, 574—576).—A criticism of Lesne and Clément's work.

R. N. C.

In what form is protein of food resorbed? I. E. S. LONDON and N. KOTSCHNEV (Z. physiol. Chem., 1934, 228, 235—242).—The arterial and portal blood (I) of angiotomised dogs was analysed for polypeptide-(II) and $\text{NH}_2\text{-N}$ after introduction of various types of protein (III) into the stomach. (III) is resorbed as a mixture of $\text{NH}_2\text{-acids}$ and (II), the proportion varying with the (III). In fistula dogs the gastric (IV) and small-intestinal chyme (V) was examined. The (II) quotients of (I) and (V) are similar (65%); that of (IV) is higher (88%). The products of (III) digestion pass unchanged through the intestinal wall into the portal vein. The $\text{NH}_2\text{-acids}$ in the portal blood resorbed from the small intestine are found chiefly in the corpuscles, the (II) in the plasma. After exercise there is a decrease in resorption, a decrease in $\text{NH}_2\text{-acids}$, and an increase in (II) of the plasma, with only small changes in the erythrocyte-(II) quotient. J. H. B.

Chemistry of the intestine. I. Intestinal juice. II. Perfusion of the intestine with urea. III. Perfusion of the intestine with glycine. IV. Perfusion of the small intestine with *D*-alanine. G. IKEDA (J. Biochem. Japan, 1934, 20, 253—259, 261—269, 271—278, 279—285).—I. Juice from the upper part of the small intestine (I) of pilocarpinised dogs with fistulae contained (average of 2 samples) 2.34% of solids, the inorg. (0.96%) including K (0.05%), Na (0.32%), Cl (0.47%), Ca, Mg, S, P, and Si and the org. (1.38%) urea, NH_3 , $\text{NH}_2\text{-acids}$, creatine, and creatinine.

II. Normal blood (II) perfused through an isolated loop of (I) shows a decrease in urea-N and an approx. corresponding increase in $\text{NH}_3\text{-N}$. With (II)+added urea, the decrease in urea-N is much > the increase in $\text{NH}_3\text{-N}$.

III. The $\text{NH}_2\text{-N}$ of (II) perfused through (I) is approx. normal; the $\text{NH}_3\text{-N}$ slightly increases. With (II)+added glycine, the $\text{NH}_2\text{-N}$ is greatly diminished, whilst the increase in $\text{NH}_3\text{-N}$ is more marked; a volatile acid is also formed. Glycine is subsequently

found in the muscle and mucosa of (I). With both types of perfusion, the urea-N decreases.

IV. The greater part of *D*-alanine added to (II) perfused through (I) is decomposed in an unknown manner, small amounts being fixed in the tissue or converted into lactic acid. F. O. H.

Feeding experiments with mixtures of highly purified amino-acids. VI. Relation of phenylalanine and tyrosine to growth. M. WOMACK and W. C. ROSE (J. Biol. Chem., 1934, 107, 449—458).—Phenylalanine is an essential dietary component for rats and cannot be replaced by tyrosine. C. G. A.

Metabolic effect of cystine. C. DOLFF (Z. ges. exp. Med., 1934, 93, 532—540; Chem. Zentr., 1934, ii, 88).—Peroral and parenteral administration of cystine (I) causes a lowering of blood-sugar \propto the amount of (I) to a max. of 23%, an increase of total N in urine, and a decrease below normal in the tissues. R. N. C.

Oxidation of the sulphur of the acetyl and formyl derivatives of *D*- and *L*-cystine in the animal body. V. DU VIGNEAUD, H. S. LORING, and H. A. CRAFT (J. Biol. Chem., 1934, 107, 519—525).—Acetyl- and formyl-*D*-cystine, unlike the corresponding derivatives of *L*-cystine, are, in the rabbit, far more resistant to oxidation than the parent acid. A. E. O.

Comparative availability of *D*- and *L*-histidine for growth. G. J. COX and C. P. BERG (J. Biol. Chem., 1934, 107, 497—503).—*D*-Histidine is rather less efficient than *L*-histidine in promoting growth of rats when fed as a supplement to a histidine-deficient diet. A. E. O.

Origin of specific dynamic action. I. ABELIN (Naturwiss., 1934, 22, 758).—From fresh organs (liver and kidney) of animals which have been fed with meat shortly before death, an active protein-free extract can be isolated, which when injected into rats subcutaneously promotes heart and respiratory activity, a sensitiveness towards high external temp., and sometimes increased perspiration. It is suggested that after taking up proteins, a highly active substance is formed in the organs, which assists in the sp. dynamic action. A. J. M.

Course of specific-dynamic increase in metabolism. M. CARMENA (Arch. exp. Path. Pharm., 1934, 177, 85—92).—The basal metabolism of men frequently varies from day to day. Ingestion of meat produces a regular increase in O_2 consumption [indicating heat-formation due to the sp. dynamic action (I)] and a return to normal vals. with some subjects, whilst in others the curve is irregular; for each person, (I) due to protein is remarkably const. F. O. H.

Deaminating power of the lungs. L. BINET and D. BARGETON (Compt. rend., 1934, 199, 1245—1247).—The NH_3 -N in the blood-perfusate of an isolated lung increases from 1.09 to 3.04 mg. N per 100 c.c. during 3 hr. Alanine in the fluid is deaminated to $AcCO_2H$. Concurrently, the R.Q. falls from about 1 to 0.68 in 3 hr. J. L. D.

Purine metabolism. III. Fate of guanosine and adenosine in the dog. L. R. CERECEDO and

F. W. ALLEN (J. Biol. Chem., 1934, 107, 421—424).—Guanosine (I) and adenosine (II) up to 3 g. are completely metabolised. $\frac{1}{2}$ to $\frac{2}{3}$ of the N of (I) is metabolised to allantoin (III), the remainder increasing the urinary urea (IV), this being $>$ can be accounted for by the NH_2 of (I). (II) causes a similar increase of (III), but no more (IV) than is accounted for by deamination. It seems that (I) but not (II) is broken down beyond the (III) stage. C. G. A.

Nitrogen metabolism. Series 2. U. LOMBROSO (Arch. internat. Physiol., 1934, 38, 404—415).—A reply to Terroine's criticism of the postulation of an "azote injustifié" (N not determined by Kjeldahl method and loss through skin, intestinal putrefaction, and in collecting excreta) to explain the discrepancy between N balance and body-wt. balance. NUTR. ABS. (b)

Nitrogen metabolism. Series 2. I. Nutritive value of ammonium salts. G. SARZANA and A. GATTO (Arch. internat. Physiol., 1934, 38, 416—427).—The addition of org. NH_4 salts to a diet rich in carbohydrates, vitamins, salts, and lipins, but poor in protein, and of such a nature as to produce a gradual and progressive fall in wt. of albino rats, was incapable of conserving wt. or permitting longer survival. NUTR. ABS. (b)

Metabolic rhythm. Daily variations in the temperature of the body and the excretion of water, nitrogen, urea, and urobilin in the urine. E. FORSGREN and R. SCHNELL (Acta Med. Scand., 1934, 82, 155—169).—In two afebrile cases agreement was found between the daily variations in body-temp. and excretion of total N, urea, urobilin, and H_2O . The course of the curves was relatively independent of meal times and of sleep. The administration of an antipyretic to a febrile case affected only the temp. curve. NUTR. ABS. (b)

Cyclic changes in the lipin content of the liver of the rat. B. OHLSSON and G. BLIX (Skand. Arch. Physiol., 1934, 69, 182—188).—Independently of food intake, the neutral fat content of the rat-liver in the morning is $>$ in the evening. There is no cyclic change in phosphatides or H_2O . NUTR. ABS. (b)

Esterification of cholesterol during absorption from the intestine. E. FRÖLICHER and H. SULLMANN (Biochem. Z., 1934, 274, 21—33).—Normal intestinal lymph of rabbits contains free (I) and esterified (II) cholesterol in the ratio of 1 : 1. During absorption of (I) from the intestine, both the (I) and (II) contents of the lymph are increased. Esterification must therefore occur during absorption. The cholesterol (especially (I)) content of the lymph is also increased after absorption of a pure fat diet due to accelerated passage of (I) back to the intestine for excretion. P. W. C.

Fate of plant sterols in the animal organism. I. H. DAM and U. STARUP (Biochem. Z., 1934, 274, 117—121).—Phytosterol (I) after intravenous injection in oil emulsions into rabbits can be detected by a considerable increase in the m.p. of the sterol acetate of the liver and lung, but not of the brain. Stored (I) is not esterified and very slowly disappears. (I) administered to rats by mouth causes a slight increase in

the m.p. of body-sterol acetate and with rabbits in 1 case gave a slight but in 2 cases no increase.

P. W. C.

Change of xanthophylls in the body after absorption from the intestine. H. SULLMANN and A. VISCHER (Biochem. Z., 1934, 274, 16—20).—After administration to man of egg-yolk [which contains a large amount of xanthophylls (I) and only traces of carotene and (I) ester], an increase occurs in the light petroleum-sol. fraction of the serum, but there is no increase in free (I). (I) are therefore changed during absorption and in part esterified.

P. W. C.

Digestion of foods. IV. Digestion of synthetic fats. II. S. SUZUKI and K. NISHINA (J. Agric. Chem. Soc. Japan, 1934, 10, 510—516).—The real digestion coeff. (I) of tripalmitin (II) is intermediate between that of triolein and tristearin. With large administration of (II) the difference between the apparent and the real (I) was small.

CH. ABS. (p)

Metabolism of isolated fat-tissue. I. Tissue of normal and starved animals. H. RUSKA and T. OESTREICHER (Arch. exp. Path. Pharm., 1934, 177, 42—52).—The protoplasm of the fatty tissue (I) of rat's testes and epidermis (II) has an O_2 uptake, respectively, 50 and 90% of that of the liver. The R.Q. of normal (I) is > 1.0 and indicates aerobic glycolysis. Starvation causes periodic increases in the respiration (III) and N and fat content of (I) which can be correlated with the disappearance of fat from the depôts; the R.Q. (in Ringer's solution) of (II) during max. (III) is < 1.0 .

F. O. H.

Oxidation of metabolites. III. Mechanism of the oxidation of fatty acids in an alkaline phosphate-hydrogen peroxide system. E. J. WITZEMANN (J. Biol. Chem., 1934, 107, 475—487; cf. A., 1926, 270).—When many fatty acids are treated with H_2O_2 and Na_2HPO_4 at p_H 8—9 the chief product is CO_2 [83.3% from decanoic acid (I)], together with $AcOH$ [6.3% from (I)] and $MeCHO$ and other CHI_3 -yielding substances. $AcOH$ is the only volatile acid formed, being resistant to oxidation, and $COMe_2$ and homologues are almost entirely absent. Crotonic acid (II) and $PrCO_2H$ (III) yield both $COMe_2$ and $AcOH$; $OH\cdot CHEt\cdot CO_2H$ (IV) yields much $AcOH$; and $OH\cdot CHMe\cdot CH_2\cdot CO_2H$ (V) much $COMe_2$. At p_H 6—7, (III) and (V) are similarly oxidised, but (II) behaves as if largely composed of (IV). The mechanism of the oxidation of the C_4 acids is discussed in the light of the above results.

A. E. O.

Nutrition with edible tubers. I. Effects of common edible tubers and polished rice on breeding. T. TAKAHASHI and H. YOKOYAMA (J. Agric. Chem. Soc. Japan, 1934, 10, 451—458).—When fed to rats in the proportion of 20 parts of dry powdered tuber to 100 parts of polished rice, potato, sweet potato, taro, and yam did not improve growth. Radish produced rapid increases in wt., but the life cycle was shortened. Carrot prolonged life, but the live-wt. increase was slow.

CH. ABS. (p)

Effect of feeding rations varying in their mineral, vitamin, and protein contents on growth, reproduction, and lactation of dairy

cattle. I. R. JONES (Minutes 18th Ann. Meeting Amer. Dairy Sci. Assoc., 1932, 46—54).—Customary rations containing sufficient Ca and P for growth were inadequate for satisfactory reproduction. Administration of cod-liver oil in addition to steamed bone flour did not further improve reproduction, but increased yields of milk and butter-fat. CH. ABS. (p)

Mineral metabolism of horses and cows. O. BANG and C. R. DAHM (Skand. Arch. Physiol., 1934, 69, 1—32).—When receiving dry hay as sole ration the horse excretes in the urine two thirds, the dry cow only one fortieth, of the total Ca excreted. In neither animal is there any appreciable amount of P in the urine. Both have a negative Ca balance (I) which is not affected by addition to the ration of H_2SiO_3 , which should not, therefore, be taken into account in calculating the acid-base equiv. of the ration. In the cow addition of 200 g. of sucrose daily improves the Ca (I). In a cow giving 5 litres of milk per day and showing negative Ca and P (I), addition of sugar has no effect, but addition of wheat bran results in positive Ca and P (I). Changing the ration to green lucerne gives a positive P but a negative Ca (I). In a horse fed on bran alone and showing negative P and Ca (I), addition of $NaHCO_3$ improves the Ca (I) but has little effect on the P (I). Addition of $Ca_3(PO_4)_2$ causes equilibrium with respect to Ca and P.

NUTR. ABS. (m)

Mineral metabolism. XXXI. Minimum mineral requirements of cattle. II. P. J. DU TOIT, A. I. MALAN, and J. W. GROENEWALD (Onderstepoort J. Vet. Sci., 1934, 2, 565—606).—Daily requirements for (2 gal.) milk productions were Cl 14 g., Na_2O 15 g., K_2O 0.38 g. The Na content of S. African pastures is often $<$ min. requirements. Mg deficiency is probably not important in animal nutrition.

CH. ABS. (p)

Effect of addition of minerals and sucrose to milk diet on growth, fertility, and lactation in the rat. H. L. KEIL, H. H. KEIL, and V. E. NELSON (Amer. J. Physiol., 1934, 108, 215—220).—Female rats on a milk diet supplemented with $CuSO_4$ and $FeCl_3$ grow almost as well as those on a stock ration, but reproduction (I) does not proceed beyond the 2nd generation (II). Addition of the Daniels and Hutton salt mixture (III) (B., 1925, 331) allowed normal growth (IV), but (I) proceeds only to the 5th (II). Of the constituents of (III), only $MnSO_4$ permits favourable (IV) and (I) to the 3rd (II). The addition of sucrose gives results that are poorer than on milk, Fe, and Cu alone.

NUTR. ABS. (m)

Agriculture, cows, and magnesium. P. DELBET (Bull. Acad. Med., 1934, 111, 393—415; Chem. Zentr., 1934, i, 3760).—The Mg content of foodstuffs is considered to be deficient.

J. S. A.

Nitrogen, calcium, magnesium, phosphorus, and iron balances in children of 7—8 years. A. PETRUNKINA (Z. Kinderheilk., 1934, 56, 219—226).—For each of the elements studied the balance rises or falls with the intake (I) of the particular element and in no case is max. retention attained. Reasonably good Ca balances are obtained only with a daily (I) of 30—40 mg. per kg. body-wt., 450—500 c.c. of milk being consumed. The Mg balance is negative with (I)

of < 10 mg. per kg. The daily milk (I), or the absence of milk from the diet, has no marked influence on the P balance, which is good with (I) of 60—70 mg. per kg. The Fe balances are positive. NUTR. ABS. (m)

Availability of iron in biological materials. W. C. SHERMAN, C. A. ELVEHJEM, and E. B. HART (J. Biol. Chem., 1934, 107, 383—394).—The availability of the Fe as determined by the 2 : 2'-dipyridyl method (I) is > 60% in ox and pig liver and cardiac muscle and in soya beans, 50% in beef skeletal muscle, and < 25% in oysters (II), spinach (III), lucerne (IV), and blood, agreeing with the vals. obtained by the acid extraction method (V) except in the cases of (II), (III), and (IV), where (V) gives considerably higher vals. Hæmoglobin regeneration in anæmic rats cc the amount of available Fe determined by (I).

C. G. A.

Influence of fruit and vegetable feeding on iron metabolism of the infant. F. W. SCHLUTZ, M. MORSE, and H. OLDHAM (J. Pediat. St. Louis, 1933, 3, 225).—Vegetable [spinach (I)] or fruit (apricots) in addition to milk has no significant effect on the amount of Fe retained by the infant or on the hæmoglobin (II) level. In an anæmic infant, fed exclusively on milk, no effect was produced by dried (I), but apricots or Fe NH₄ citrate caused a marked increase in the retention of Fe, but scarcely affected (II) and erythrocyte count.

NUTR. ABS. (m)

Influence of the ingestion of iron caseinogenate on body-weight and carbon and nitrogen content of the urine of the non-anæmic adult dog. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1934, 116, 784—787).—Two healthy adult dogs received a diet of milk, rice, and NaCl for 50 days. There was much loss of wt., and the C : N ratio in the urine was 1.0. Early symptoms of vitamin-B deficiency appeared and the animals were given 6 g. of fresh yeast daily. Growth was resumed for a time, but ceased after 25 days. The C : N ratio was now 0.78. The addition of FeCl₃ (40 mg. daily), administered simultaneously with the milk, so that Fe caseinogenate was formed, resulted in rapid growth, an improved N balance, and a urinary C : N ratio of 0.96. CaCO₃ did not have the same effect.

NUTR. ABS. (b)

Alkali losses after administration of sodium and potassium. H. GLATZEL (Z. ges. exp. Med., 1934, 93, 666—678).—Oral administration of KCl leads to marked and rapid increase in the alkalinity of the urine and its content of K and Na and a very slight fall in the alkali reserve (I) of the blood : the changes are to some extent dependent on the dose. After NaCl there is a very gradual increase in Na output, little change in K or urinary reaction, and slight rise in (I). The liver plays an important part in these changes, which are in part due to the necessity for maintaining the Na+K concn. of the blood const.

NUTR. ABS. (m)

Chlorine metabolism. J. BOTTIN (Rev. belge Sci. med., 1934, 6, 173—211).—Dogs on a mixed diet maintain a steady level of Cl in whole blood (I) and plasma. Most of the ingested Cl is excreted in the urine. During starvation excretion of Cl ceases, and the Cl in (I) is reduced by about 10%, whilst the level in plasma and corpuscles remains const. The no. of

red blood corpuscles increases and the decrease in Cl in (I) is probably a function of the reduction in plasma-vol. After re-feeding with a mixed diet the excretion of Cl rises rapidly and for a time exceeds the intake. Equilibrium is then reached and maintained, and Cl in (I) and plasma-vol. return to normal. There is no difference between venous (II) and arterial (III) blood as regards Cl level, but in the gastric vessels the Cl is higher in the (III) and varies with the changes taking place in the Cl content of the gastric juice during digestion. In the renal vessels the Cl level is lower in the veins, the difference between (II) and (III) being greatest when digestion is at its height and urinary excretion of Cl at its max. In the superior mesenteric vessels (II) contains more Cl than does (III), the difference reaching a max. when intestinal digestion is fully active.

NUTR. ABS. (m)

Increasing the chlorine content of young dogs. G. TORÖK and L. NEUFELD (Arch. Kinderheilk., 1934, 102, 35—45).—Administration of NaCl, in addition to the usual food, to very young puppies produces an increased Cl content of liver, muscle, and brain, but not of skin and lungs, whether or not nutritional disturbances occur. "Dry" retention of Cl may occur.

NUTR. ABS. (m)

Excretion of iodine in the urine after ingestion of inorganic iodine, thyroxine, and di-iodotyrosine. A. W. ELMER and W. RYCHLIK (Compt. rend. Soc. Biol., 1934, 115, 1719—1722).—About 31% of the I ingested as KI is excreted in 24 hr., 23% appearing in 6 hr. After ingestion of pure cryst. thyroxine, thyroxine in alkaline solution, and di-iodotyrosine, the amounts excreted are 1, 7, and 9%, respectively, in 6 hr., and 6, 14, and 32%, respectively, in 24 hr.

NUTR. ABS. (m)

Absorption of iodine from baths through the skin and its fate in the organism. H. ANTHER and F. SALZMANN (Z. ges. exp. Med., 1933, 91, 100—105; Chem. Zentr., 1934, ii, 465).—No connexion has been found under the conditions employed between the blood-I following KI baths and the [I] of the bath, nor has any increased I excretion in the urine been noticed.

R. N. C.

Role of the liver in the regulation of blood-iodine. A. W. ELMER and Z. LUCZYNSKI (Compt. rend. Soc. Biol., 1934, 115, 1717—1718).—After a meal the amount of I in the bile of rabbits is increased fivefold, whereas the level in the blood is almost unaltered. The liver holds back the I absorbed from the alimentary tract and returns it by way of the bile, thereby establishing a cycle and preventing any large increases in blood-I.

NUTR. ABS. (m)

Chemical transmission of nerve impulses. H. H. DALE (Science, 1934, 80, 450).—A correction (A., 1934, 1386).

L. S. T.

Physico-mathematical aspects of the conduction of nervous impulse. N. RASHEVSKY (Physical Rev., 1933, [ii], 43, 372).

L. S. T.

Action of acetylcholine on the brain and its occurrence therein. B. B. DIKSHIT (J. Physiol., 1934, 80, 409—421).—A substance resembling acetylcholine (I) occurs in brain (principally in basal ganglia) and occasionally in cerebrospinal fluid after vagal

stimulation. (I) may be concerned in transmission of nerve stimulus to the brain. CH. ABS. (p)

Does vagus stimulation cause an increase in the acetylcholine content of heart muscle? A. VARTAINEN (J. Physiol., 1934, 82, 282—292).—Extracts of heart muscle with $\text{CCl}_3\cdot\text{CO}_2\text{H}$ show no evidence of increased acetylcholine content as the result of vagus inhibition. R. N. C.

Influence of the vagus nerves on sugar tolerance in dogs. R. C. RANQUIST (Amer. J. Physiol., 1934, 108, 210—214).—The lowered sugar tolerance and fall in blood-sugar following double vagotomy (I) result, not from (I) *per se*, but from the associated operative procedure. NUTR. ABS. (m)

Humoral control of the secretion by the sub-maxillary gland of the cat following sympathetic stimulation. J. SECKER (J. Physiol., 1934, 82, 293—304).—Stimulation of the cervical sympathetic nerve or injection of adrenaline induces a secretion of saliva containing a "cholinergic" substance. Secretion resulting from either stimulus is enhanced by eserine and inhibited by atropine. The active substance is similar to acetylcholine in being inactivated by alkali. R. N. C.

Function of sympathetic nerves in relation to skeletal muscle. Evidence for humoral action. O. W. TIEGS (Proc. Roy. Soc., 1934, B, 116, 351—375).—Stimulation of the sympathetic nerves sets free a substance with adrenaline-like action, which is probably responsible for the Orbeli phenomenon. H. G. R.

Identification of the substance liberated in the nictating membrane of the cat by sympathetic stimulation. Z. M. BACQ and H. FREDERICQ (Bull. Acad. roy. Belg., 1934, [v], 20, 931—947).—*L*-Adrenaline is the only known substance which has an effect similar to stimulation of the sympathetic system. H. G. R.

Anaphylactic metabolic reaction of isolated tissues. G. BOSTROM (Klin. Woch., 1934, 13, 399—403).—The glycolysis and O_2 uptake of the liver and skin of sensitised animals are increased by very high dilutions of the antigenic protein, whilst rather more conc. solutions cause a decrease. True sensitisation or immunisation occurs. NUTR. ABS. (m)

Colloidal nature of anaphylactic precipitates. A. LUMIÈRE and P. MEYER (Bull. Soc. Chim. biol., 1934, 16, 1266—1283).—The addition of antigen to the sera of the rabbit and the guinea-pig previously sensitised to horse-serum causes in both cases a ppt. consisting mainly of globulins. The supernatant liquid shows a decrease in osmotic pressure and surface tension, and an increase in viscosity, compared with the corresponding vals. of the sensitised sera. These effects may be due to an increase in size of the globulin aggregates. A. L.

Histamine test-meals on normal students. F. P. L. LANDER and N. F. MACLAGAN (Lancet, 1934, 227, 1210—1213).—Results of 100 test-meals on normal males are recorded, the highest free acidity, the vols. of gastric juice and free acid per hr. being used as characteristics of the test. L. S. T.

Effect of histamine on blood-sugar in adren-alectomised rats. L. C. WYMAN and C. T. SUDEN (Amer. J. Physiol., 1934, 108, 424—427).—Injection of small amounts of histamine caused hyperglycaemia in normal rats and hypoglycaemia in those the adrenals of which had been removed with or without transplanted cortical tissue. CH. ABS. (p)

Effect of the acid secretion of the stomach on blood-sugar after histamine stimulation. S. MARINO and F. ROMEO (Arch. Farm. speriment., 1934, 58, 233—241).—The hyperglycaemia resulting from injection of histamine has no relation to the acidity of gastric secretion in starvation, and is frequently increased by introduction of gastric juice into the stomach. R. N. C.

Histamine and blood-cholesterol. F. GOEBEL (Compt. rend. Soc. Biol., 1934, 117, 535—537).—Intramuscular injection of histamine causes hypercholesterolaemia in the dog lasting for 2 hr. This does not occur if the gastric juice, secreted owing to the injection, does not pass into the duodenum. H. G. R.

Toxicity of some esters of diethylaminoethyl alcohol. H. VINCENT and J. DETRIE (Compt. rend. Soc. Biol., 1934, 117, 597—598).—The ratios of the toxicities of the esters and salts of $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ with AcOH , $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ are respectively 6, 9, and 13 when injected intravenously in mice, and approx. half these vals. when injected subcutaneously. R. N. C.

Influence of "octinum" on bile excretion. G. BALTĂCEANU, H. ANGELESCU, and C. VASILEU (Arch. exp. Path. Pharm., 1934, 177, 29—33).—Subcutaneous injection of small doses (0.2 g. daily) of "octinum" [octenylamine (?)] into dogs has little influence on the vol., viscosity, and dry wt. of the bile; with larger doses (0.8 g. daily), the vol. is reduced by 30%, whilst viscosity and dry wt. are unchanged. F. O. H.

Influence of cholagogues on the respiration of liver tissue. H. NAKAGAWA (J. Biochem. Japan, 1934, 20, 327—342).—The respiration (I) of mouse liver tissue is inhibited by *in-vitro* application, and increased (max. after 15 min.) by intravenous administration, of atophan. Bile salts *in vitro* inhibit or increase (I) according to their concn., whilst *in vivo* a marked rise (max. after 30 min.) occurs. Diuretics which are also cholagogues (II) generally increase the *in-vivo* (I); avertin and chloral hydrate are exceptions. The relation between (I) and (II) is discussed. F. O. H.

Micro-determination of ethyl alcohol in blood and tissues. M. NICLOUX, E. LE BRETON, and A. DONTCHEFF (Bull. Soc. Chim. biol., 1934, 16, 1314—1332).—A modification of the method of Nicloux (A., 1931, 752) permits the determination of 0.8—10 $\times 10^{-4}$ g. of EtOH with an error $\pm 2\%$. A. L.

Absorption, distribution, and elimination of ethyl alcohol. I. Determination in air, blood, and urine by iodine pentoxide. II. Excretion in urine and expired air. Distribution between air and water, blood, and urine. III. Rate of oxidation in the body. H. W. HAGGARD and L. A.

GREENBERG (J. Pharm. Exp. Ther., 1934, 52, 137—149, 150—166, 167—178).—I. EtOH vapour [liberated from urine (I) or blood (II) by heat] is passed over I_2O_5 at 150—180°, the liberated $HI+I$ being absorbed successively in H_2O and aq. KI and determined by titration. The error is approx. 2.5 and 10% for samples of 1.0 and 0.1 c.c., respectively.

II. The ratio of the relative solubilities of EtOH in (I) and (II) (calc. from the air-fluid partition) is 1:144:1. After ingestion of EtOH by dogs, the concns. in (I) and arterial (II) agree with this ratio; hence EtOH passes through the kidneys by simple diffusion. With the exception of that of the peripheral veins (which is markedly < normal), the concn. of EtOH in (II) from different blood vessels after ingestion is approx. the same. During the first 16 hr., 2.1—4.3% of the vol. ingested is excreted in (I), whilst approx. 8% occurs in the expired air; the distribution between alveolar air and arterial (II) gives the same ratio as that of the air-(II) distribution *in vitro*.

III. The rate of oxidation of EtOH intravenously injected into dogs is not const., but \propto the amount of EtOH in the body; the (II)-EtOH diminishes, however, by an approx. const. % each hr. (cf. Mellanby, M.R.C. Rep., 1919). The solubility of EtOH in (II) is > that in the tissues as a whole (1:0.62). Data for (II)-EtOH after ingestion of EtOH and the derived curve for EtOH absorption from the stomach are discussed. F. O. H.

Alcohol content of the blood of different vessels in the rabbit after its administration. B. FALCONER and H. GLADNIKOFF (Skand. Arch. Physiol., 1934, 68, 245—251; Chem. Zentr., 1934, ii, 267).—No differences were established between the EtOH contents of arterial and venous blood, but portal blood after administration of EtOH contained more EtOH than that of the vena cava. R. N. C.

Experimental alcoholism. Mechanism of alcohol tolerance. J. LEVY (Compt. rend., 1934, 199, 973—975).—The concns. in the brain, kidney, and liver after a given time of EtOH (I) injected into normal rats and those accustomed to (I) are comparable, as are the rates of oxidation of (I). Normal rats are anaesthetised by smaller doses than the latter, the brain cells of which are probably hyposensitive. J. L. D.

Effect of physical work on the fate of alcohol in the organism. E. NYMAN and A. PALMLOV (Skand. Arch. Physiol., 1934, 68, 271—294; Chem. Zentr., 1934, ii, 89).—The increase in respiration due to physical exertion has no effect on the removal of EtOH. Similarly the amount of EtOH in urine or sweat is not increased. The immediate augmentation in the blood at the commencement of muscular activity recedes after abs. rest. R. N. C.

Chemistry and pharmacology of campherol and related compounds.—See this vol., 89.

[Pharmacology of] phenanthrene derivatives. Disubstitution products. N. B. EDDY (J. Pharm. Exp. Ther., 1934, 52, 275—289).—Disubstituted derivatives are in general less active than monosubstituted containing the same groups, except

when the two substituents are in the 9:10- or 3:4-positions. H. G. R.

Chemical changes accompanying muscle contraction and fever. IV. Changes in composition of muscle, blood, and liver in fever. T. CAHN. V. Muscle metabolism unit and hypotheses on carbohydrate breakdown in muscle. T. CAHN and J. HOUGET (Ann. Physiol. Physicochim. biol., 1933, 9, 393—426, 427—450; Chem. Zentr., 1934, ii, 88).—IV. In hyperthermia (I) in dogs from intravenous injection of 2:4-dinitrophenol, and in "spontaneous" (I), the muscular system was fully atonic, and a considerable disappearance of carbohydrate occurred in the muscles (II) and liver (III), with occasional hyperglycæmia. (II)-lactic acid was only slightly raised, whilst fats and lipins fell in (II), but rose in blood (IV) and (III). Creatinephosphoric acid was extensively broken down in (III), adenyphosphoric acid less extensively; inorg. PO_4''' in (II) rose. Urea rose more in (II) than in (III). Creatine and creatinine increased in (II), (III), and (IV); Na, K, and Ca were unchanged.

V. Theoretical.

R. N. C.

Pharmacological and chemical studies of the digitalis group. I. *Adonis*, *Apocynum*, and *Convallaria*. J. C. MUNCH and J. C. KRANTZ, jun. (J. Amer. Pharm. Assoc., 1934, 23, 988—996).—Biological assays show that the potencies of *Adonis*, *Apocynum*, and *Convallaria* are, respectively, 1, 2, and 3 times that of *Digitalis*. A. E. O.

Excretion of glucose, creatinine, and urea following phloridzin administration. P. GOVAERTS and P. CAMBIER (Bull. Acad. roy. Méd. Belg., 1934, 14, 226—243).—Excretion of glucose runs parallel with that of creatinine in dogs given phloridzin.

NUTR. ABS. (m)

Grayanotoxin, the active principle of *Leucothoe grayana*.—See A., 1934, 1359.

Toxic material in *Lathyrus* peas. R. STOCKMAN (J. Hygiene, 1934, 34, 145—153).—The material (I) consists of H_2O -sol. phytic acid salts precipitable by $Pb(OAc)_2$, $Hg(OAc)_2$, and conc. EtOH. (I) is toxic to monkeys, rabbits, and frogs and causes lathyrism in man.

NUTR. ABS. (m)

Cardiac activity and toxicity towards rats of red and white squill from Cyprus. F. WOKES and S. G. WILLIMOTT (Quart. J. Pharm., 1934, 7, 565—573).—Cultivated and wild red squill and white squill have approx. equal cardiac activity, but red squill is 10—15 times as toxic as the white. C. G. A.

Action of piperidinomethyl-3-benzodioxan on glycæmia in the dog. E. ZUNZ and J. PERLA (Compt. rend. Soc. Biol., 1934, 117, 473—476).—Intravenous injection raises the blood-sugar (I), which later falls below the initial val. Intramuscular injection increases (I) slightly, with a return to normal after 5—6 hr. H. G. R.

Can chlorogenic acid be formed in coffee poisoning? M. KOCHMANN (Med. Welt, 1934, 8, 577—578; Chem. Zentr., 1934, ii, 279).—Free chlorogenic acid (I) is toxic to mice in doses of 70 mg. per 20 g. body-wt. injected intraperitoneally, but not

subcutaneously. Orally, 70—85 mg. per 20 g. has no action in mice, nor 1.0 g. per kg. in rabbits. (I) is effective only in the free state; it ppts. protein, and when injected subcutaneously in 7% solution causes local necrosis and suppuration, which can lead to death. Equiv. quantities of HCl exhibit the same effect as free (I). The neutral Na salt is not toxic even when injected intraperitoneally in 7% solution. The Na caffeine salt has the same effect as the corresponding dose of caffeine, the toxic effect of (I) in coffee indulgence being due to neither its concn. nor its total quantity. R. N. C.

Relation between chemical constitution and purgative action.—See this vol., 79.

Excretion of eucodal. K. SCHUBEL (Arch. exp. Path. Pharm., 1934, 177, 34—37).—With dogs, subcutaneously injected eucodal (I) (B., 1931, 945) appears (up to 12%) in the urine. With animals and men, (I) is excreted in urine and faeces. The detection of (I), depending on the appearance in mice of typical tail and respiratory movements lasting for some hr. and not given by morphine or thebaine (cf. A., 1934, 556), is described. F. O. H.

Detection of barbituric acid derivatives in blood. P. CHÉRAMY and R. LOBO (J. Pharm. Chim., 1934, 20, [viii], 461—462).—The blood after treatment with COMe_2 is acidified with tartaric acid, boiled for 20—30 min., and filtered. The filtrate is concd., treated with aq. $(\text{NH}_4)_2\text{SO}_4$, filtered, and the filtrate extracted with Et_2O . The extract is examined for barbituric acid. E. H. S.

Characterisation of barbituric derivatives in urine. FOUCHET (J. Pharm. Chim., 1934, [viii], 20, 403—406).—A modification of Zwikker's reaction (A., 1931, 1328) is described. Barbiturates (I) give a violet ppt. with a 3% aq. solution of CuSO_4 containing sufficient $\text{C}_5\text{H}_5\text{N}$ to redissolve the hydroxide first pptd. The (I) may be recovered by sublimation of the ppt. Derivatives containing *N*-Me (prominal, evipan) do not react. C. G. A.

Extraction of barbituric derivatives from viscera by acetone. P. CHÉRAMY and R. LOBO (J. Pharm. Chim., 1934, [viii], 20, 400—403).— COMe_2 is preferable to EtOH for the extraction of barbiturates in toxicological work. C. G. A.

Detection of barbital in human viscera. C. STRZYZOWSKI (Ann. Med. lég. Criminol., 1933, 13, 49—53).—Crude barbital from liver, kidneys, etc. is dissolved in H_2O , made alkaline with NaOH , and filtered. The Et_2O extract of the filtrate is decolorised with C, and crystallised from HCl solution. The product is examined by micro-sublimation, by the cryst. form of the Ag salt, and by colour reactions of the Cu and Hg salts. A. G. P.

[Pharmacology of] barbiturates. VIII. Distribution in the brain. T. KOPPANYI, J. M. DILLE, and S. KROP. IX. Effect on the embryo and on pregnancy. J. M. DILLE. X. Acute barbital poisoning in dehydration and diuresis. T. KOPPANYI, W. S. MURPHY, and S. KROP (J. Pharm. Exp. Ther., 1934, 52, 121—128, 129—136, 223—230).—VIII. Various barbiturates (I), intravenously adminis-

tered in anaesthetising doses to dogs, are recoverable from every part of the central nervous system in approx. equal concn. and from the organs and tissue fluids. The classification of (I) as thalamic hypnotics must therefore be rejected. Lecithin interferes with the determination of (I) in nerve tissue and must first be removed.

IX. With pregnant rabbits, cats, and guinea-pigs, intravenously injected (I) are detectable in the embryo (II) 15 min. after injection; after some time (II) is freed from (I) by maternal elimination. Whilst small single doses of (I) are not harmful, repeated dosage produces abortion or absorption of (II).

X. With dogs poisoned by (I), treatment with diuretics (Na_2SO_4 , glucose, CaCl_2 , or 0.9% aq. NaCl) does not increase their excretion. Intravenously injected NH_4Cl increases the urinary excretion of barbital, but recovery from the narcosis is not hastened. F. O. H.

Metabolic processes during growth. I. Metabolism of isobarbituric acid in the growing dog. L. R. CERECEDO and J. A. STEKOL (J. Biol. Chem., 1934, 107, 425—428).—In contrast with adult dogs, puppies do not metabolise isobarbituric acid (I) to urica. The fall in inorg. S and corresponding rise in ester-S indicate partial excretion of (I) in conjunction with SO_4^{--} . No change in the neutral S fraction is observed after feeding small amounts of (I). C. G. A.

Comparative effects of anaesthetics on the isolated nervous system of the frog (*Rana esculenta*). A. RABRENO and V. RUFFINI (Arch. int. Pharmacodyn. Ther., 1933, 46, 425—445; Chem. Zentr., 1934, i, 3879).—The reflex excitability of the Herlitzka prep. can be used to compare anaesthetics and other depressors; it is sensitive to concn. differences between 10^{-15} and 10^{-5} . The effect is dependent on the chemical nature of the drug; the strongest effects being given by sandoptal (Na isobutylallylmalonylurea) and $\text{CCl}_3\text{-CHO}$, and the weakest by Et urethane and Na veronal. R. N. C.

Relative anaesthetic effects. (a) Urea derivatives. E. J. DEBEER and A. M. HJORT. (b) Aliphatic ureas. E. J. DEBEER, J. S. BUCK, and A. M. HJORT (J. Pharm. Exp. Ther., 1934, 52, 211—215, 216—222).—(a) The toxicity (I) and anaesthetic action (II) in mice were determined for a series of alkylaryl derivatives of urea and barbituric acid. The position of MeO has no consistent influence on (I) or (II), whilst (II) with low (I) occurs with relatively simple urea derivatives.

(b) The (I) and (II) in mice of a series of *n*- and *iso*-alkylureas [including *n*-amylurea, m.p. 100° (corr.)] increase with increasing mol. wt., the rise in (II) being > that in (I). F. O. H.

Tobacco smoking in relation to blood-sugar, blood-lactic acid, and metabolism. D. B. DILL, H. T. EDWARDS, and W. H. FORBES (Amer. J. Physiol., 1934, 109, 118—122).—The smoking of one cigarette produced no change in blood-sugar or -lactic acid or R.Q., but increased the metabolic rate in some cases. CH. ABS. (p)

Nicotine content of milk from women who smoke. L. NAGY (Pharm. Zentr., 1934, 75, 737—

740).—100—150 c.c. of milk are coagulated by warming for 20 min. with a few c.c. of 1% HCl, 4 c.c. of 20% CaCl₂, and 10 c.c. of 25% CCl₃·CO₂H solutions. The ppt. of caseinogen is extracted thrice with 40 c.c. of boiling 0.5% HCl and the extracts are combined with the whey. The combined liquids are evaporated to 20—25 c.c. and the nicotine (I) is separated by distillation in presence of MgO into 10 c.c. of 0.1N-H₂SO₄, which is then evaporated to 1 c.c. and treated with 1% silicotungstic acid solution. The results are accurate within $\pm 2 \times 10^{-6}$ g. of (I). Human milk from patients smoking 50—60 cigarettes per day contained a negligible amount of (I) ($13\text{--}15 \times 10^{-6}$ g. per litre). S. C.

Pharmacological assay of nicotine with rats and mice. F. J. NIEUWENHUYZEN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 575—578).—Nicotine (I) produces catatonic symptoms accompanied by tremor in mice (II) and rats. The action on (II) may be used for the determination of (I).

W. O. K.

Absorptive action of aconitine ointments. Biological detection and determination of aconitine. P. PULEWKA and H. GREVENER (Arch. exp. Path. Pharm., 1934, 177, 74—84).—Methods of assay of aconitine (I) and veratrine, based on characteristic changes in the respiration and body movement and on their toxicity in mice, are described. Inunction of mice with 50 mg. of ointment containing 3—5% of (I) produces the same effect as, but much more slowly than, subcutaneous injection of 0.0012 mg. of (I) nitrate. F. O. H.

Experimental catatonia by means of derivatives of mescaline and adrenaline. L. NOTEBOOM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 562—574).—Of various compounds allied to mescaline, β -3 : 4-dimethoxyphenylethylamine gave the most strongly marked symptoms of catatonia in cats. A no. of sympathomimetic bases including ephedrine, sympathol, and norsympathol produced superficial catatonic reactions. W. O. K.

Atropine tolerance in infants and children. Negative action of serum of tolerant subjects. J. D. PILCHER (J. Pharm. Exp. Ther., 1934, 52, 196—205).—The serum of atropine-tolerant children does not neutralise the action of atropine as indicated by dialysis and subsequent testing of the cutaneous reaction or by the cat's pupil response (cf. A., 1926, 1267). Phenomena associated with atropine tolerance are described. F. O. H.

Comparative actions of atropine and *l*- and *d*-hyoscyamine in infants and very young children. J. D. PILCHER (J. Pharm. Exp. Ther., 1934, 52, 206—210).—The relative activities (as indicated by both central and peripheral action) of atropine and *l*- and *d*-hyoscyamine are approx. 20 : 40 : 1—2, respectively. F. O. H.

Fate of azo-dyes in the organism. G. HECHT (Med. Chem. Abh. med.-chem. Forsch. I.G. Farben-ind., 1934, 2, 167—176; Chem. Zentr., 1934, i, 3877).

In the cat and rabbit, acid mono- and bis-azo dyes containing ≥ 3 SO₃H are taken up in the gall-bladder. R. N. C.

Effect of insulin and other factors on iodoacetate hyperglycaemia. J. T. IRVING (J. Physiol., 1934, 80, 360—368).—CH₂I·CO₂H causes hyperglycaemia by mobilising liver-glycogen and interfering with the disappearance of sugar in the tissues.

CH. ABS. (p)

Kinetics of penetration. IX. Models of mature cells.—See this vol., 42.

Asphyxial arrest of the isolated frog's ventricle. A. J. CLARK, R. GADDIE, and C. P. STEWART (J. Physiol., 1934, 82, 265—277).—Total lactic acid (I) of the ventricle (II) rises sharply on asphyxiation (III); the (I) of the ventricular fluid rises more steadily, is relatively higher, and on aeration falls less rapidly than that of (II) itself. (I) production and mechanical response (IV) fall together in (III); (I) production appears to be the only source of energy available in (III), and the amounts produced are adequate for the maintenance of the (IV) observed. Failure of (IV) is not due solely to (I) accumulation, since it occurs prior to this. Fall of p_H increases rate of fall of (IV) in (II), and inhibits aerobic recovery. Most of the (I) excreted by a fresh heart in the first 10 min. of (II) is in neutral form, so that the (I) excretion cannot be calc. from the p_H .

R. N. C.

Effect of cyanide and other substances on the oxygen uptake of rat tissue. E. MUNTWYLER and D. BRINNS (Amer. J. Physiol., 1934, 108, 80—90).—The O₂ uptake (I) of tissues and the degree of inhibition of (I) by KCN are unrelated to the indophenol-oxidase colour. KCN and pyrophosphate decrease O₂ consumption and inhibit the ability of the tissue to take up O₂ in presence of p -C₆H₄(NH₂)₂ (II). Urethane and AsO₃''' decrease (I), but do not inhibit the absorption of additional O₂ in the presence of (II).

CH. ABS. (p)

Urinary elimination of bismuth after injection of bismuth preparations. J. POUZERGUES (Ann. Inst. Pasteur, 1934, 53, 535—553).—The absorption of Bi after intramuscular injection of insol. compounds in guinea-pigs is very low. Bi metal is the least, and Na tartrobismuthate the most, readily absorbed; Bi camphorcarboxylate is intermediate between the two. Death follows in < 8 days after injection of lethal doses of sol. compounds which give rise to acute uraemia, whilst insol. compounds lead to diarrhoea with ultimate death. P. G. M.

Toxicity and fixation in the organism of magnesium thiosulphate. R. E. CARRATALA and C. L. CARBONESCHI (Semana méd., 1934, II, 25—29).—The protective action of MgS₂O₃ (I) in HCN intoxication is much < that of Na₂S₂O₃. Toxicity of (I) is examined. The normal Mg of the organism is increased by repeated narcosis with (I). CH. ABS. (p)

Rôle of copper in the setting, metamorphosis, and distribution of the American oyster, *Ostrea virginica*. H. F. PRYTHERCH (Ecol. Monographs, 1934, 4, 47—107).—The duration of the setting process varied with the salt concn. (optimum 1.60—1.86‰). Setting was most pronounced at the stage of tide when Cu content was max. (0.05—0.60 mg. per litre) and in this range \propto the amount of Cu present. The oyster larva is stimulated through ingestion of Cu as

a colloidal ppt., and its further development depends on further ingestion of Cu. Distribution of oysters is examined in relation to concns. of salt and Cu.

CH. ABS. (p)

Biologically electronegative nature of potassium. R. KELLER (Arch. Phys. Biol. Chim.-Phys. Corps organisés, 1933, 11, 31—39; Chem. Zentr., 1934, ii, 257).—The significance of the nature of the electric charge on the intake, transport, and accumulation of substances in plant and animal organisms is examined.

A. G. P.

Investigations on lipins in view of a theory of the pharmacodynamic effect of alkalis and alkaline earths. J. WĄJZER (Compt. rend. Soc. Biol., 1934, 115, 830—833).—The min. concn. of CaCl_2 to ppt. a 1% soap solution is 0.003—0.006*N*, that of NaCl is 0.125—0.25*N*, whilst KCl does not ppt. soap. Mixed solutions of the salts show simple additive effects. The surface tension of 0.001*N*- NaOH is lowered by 0.001*N*- Na oleate to the same extent as the corresponding KOH solution is by K oleate.

R. N. C.

Microchemical examination of blood-serum for the detection of industrial poisoning. E. A. PRIBRAM (Arch. Gewerbepath. Gewerbehyg., 1934, 5, 345—354).—The fixation of simultaneously injected sugar, urea, and PO_4''' by blood-serum is normally controlled by definite equilibrium relationships, but is decreased by injections of As , Hg , or Pb chlorides and increased by FeCl_3 . Use is made of this phenomenon in detecting incipient industrial poisoning by heavy metals.

A. G. P.

Behaviour of residual nitrogen in blood following administration of arsenic, phosphorus, and sodium chlorate and in oxygen deficiency. H. E. BUTTNER (Z. ges. exp. Med., 1934, 93, 391—401; Chem. Zentr., 1934, ii, 1323).—Small dosages of As , P , and NaClO_3 or slight reduction in atm. O_2 reduce, and large dosages or great reduction in O_2 increase, residual N .

A. G. P.

Avidity determination of new arsenobenzene preparations (myosalvarsan, solusalvarsan). R. SCHNITZER (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 253—262; Chem. Zentr., 1934, i, 3764).—The avidity index is defined as the ratio N/F of the chemotherapeutic indices of preps. towards normal strains of trypanosomes (N) and towards strains resistant to salvarsan (F). The therapeutic vals. of compounds are high as N/F approaches 1. Vals. obtained are arsenophenylglycine 1/3, solusalvarsan 1/4—1/10, myosalvarsan 1/23, neosalvarsan 1/62, salvarsan 1/80. J. S. A.

Colloidal chemical properties of chemotherapeutically active substances and their relationship to constitution. R. LABES and F. BILLMANN (Biochem. Z., 1934, 274, 75—86).—Of a no. of acid and basic dyes, those substances which are most active chemotherapeutically (germanin, a trypan dye) exert the greatest colloidal chemical action on caseinogen, their effect being still apparent at dilutions which correspond with the chemotherapeutically active dose.

P. W. C.

Significance of amines in chemotherapy. I. K. KINDLER (Arch. Pharm., 1934, 272, 811—817).—A lecture. The "toxic val.," T.V., of a substance against *Paramecia* (I) is defined as x/t , where x is the no. of mg. of solution containing 1 mg. of the substance and t is the time in sec. required for death of at least 90% of (I). The "relative toxic val.," R.T.V., of a substance is defined as its T.V. compared with that of quinine (II) taken as 1000. x must be chosen so that t is 1—10 min., since otherwise irregular results for T.V. are obtained; thus T.V. for (II) is 3000 if $x=1000$, 1300—1100 if $x=2000$ —10,000 ($t=1.5$ —16 min.), and approx. 25 if $x=30,000$. Aliphatic amines have a low R.T.V., e.g., NH_3 1—2 < NH_2R ($\text{R}=\text{Me}$, Et , Pr , or *iso*amyl), NHMe_2 , $\text{NH}(\text{Et})_2$, NHPy , NMe_3 , piperidine, and *dl*-2-methylpiperidine (all 1—2), scopolamine and coniine < 1, atropine 3. Introduction of aryl groups increases R.T.V. greatly, e.g., R.T.V. for $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$ is 10—20, $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ 50—100, and $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{NH}_2$ 100—200, although $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ has R.T.V. only slightly > 2. Introduction of two or more aryl groups increases R.T.V. still further, and substituents, such as OH and OR , often have a profound influence. Similarly, 1-aryl-*iso*quinolines, -di- and -tetra-hydro-*iso*quinolines are much more toxic than their 1-Me analogues. Numerous examples are given. The most potent substance recorded is 1-*p*-methoxycinnamyl-3:4-dihydro-*iso*quinoline (R.T.V. 10,000). $\beta\text{-C}_{10}\text{H}_7$ and α -thienyl groups have effects similar to those of Ph . There is no relation between toxicity to mammals and to (I) (cf. coniine etc.), but probably between toxicity to the latter and to protozoa in general. R. S. C.

Physical basis of the biological effects of high-voltage radiations. W. V. MAYNEORD (Proc. Roy. Soc., 1934, A, 146, 867—879).—The importance of the range of the secondary electrons produced in living materials by high-voltage X- and γ -rays is discussed.

L. L. B.

Susceptibility of infusoria to ultra-violet rays as related to the colloidal properties of their protoplasm changed by different physico-chemical methods. V. V. ALPATOV and O. K. NASTIUKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 595—600).—The resistance of *Paramecium caudatum* to the destructive action of ultra-violet light (I) was increased by colloid-condensing electrolytes (Na_2SO_4). KCNS produced the opposite effect. Narcosis renders the infusoria less resistant to (I). Increase in the viscosity of the protoplasm produced by an electric current increases the resistance to (I).

H. J. E.

Relation of substances of the cell nucleus to the lethal action of ultra-violet light. F. F. HEY-ROTH and J. R. LOOFBOUROW (Bull. Basic Sci. Res., 1933, 5, 13—22).—Ultra-violet irradiation (I) in the range 295—200 $\text{m}\mu$ destroys pyrimidines (II) and purines. Curves showing absorption by (II) and lethal action on micro-organisms rise abruptly at 295 $\text{m}\mu$ and show max. at 260 $\text{m}\mu$. In bacteria, action of (I) on nuclear substances is more important than its effect on proteins. Stimulative effects in the range 320—295 $\text{m}\mu$ correspond with increased absorption of thymus-nucleic acid and may produce growth-promoting substance.

CH. ABS. (p)

Effect of ultra-violet light on carbohydrate metabolism. P. KALLÓS and L. KALLÓS-DEFFNER (Strahlenther., 1934, 50, 191—192).—In rabbits the rise in blood-sugar after intravenous injection of glucose is less when the animals are irradiated than when they are kept in the dark. Prolonged irradiation increases sugar tolerance, which remains high for 8—10 days. NUTR. ABS. (m)

Enzymes, vitamins, and the zone of maximum colloidal. J. B. SUMNER (Science, 1934, 80, 429).—A criticism (A., 1934, 1136). L. S. T.

Enzymic oxidation and reduction systems. H. VON EULER (Ergebn. Enzymforsch., 1934, 3, 135—162; Chem. Zentr., 1934, ii, 258).—A discussion. A. G. P.

Biological oxidations. III. Oxidation-reduction potential of the system lactate-enzyme-pyruvate. E. S. G. BARRON and A. B. HASTINGS. **IV. Mechanism of the catalytic effect of reversible dyes on cellular respiration.** R. H. DE MEIO, M. KISSIN, and E. S. G. BARRON (J. Biol. Chem., 1934, 107, 567—578, 579—590).—III. When α -hydroxyoxidase from gonococci is added to lactate+pyruvate in presence of a dye only partly reduced by this system, a stable, reproducible potential is reached in 1—2 hr. For the above system at 35°, the normal potential is $+0.248 \pm 0.002$ volt, the free energy change ΔF is 11,440 g.-cal., and the heat of reaction ΔH is 21,639 g.-cal.

IV. Reversible dyes (I) influence the O_2 consumption of cells containing no haemoglobin (II) only when respiration has been inhibited by HCN or CO. (I) evidently act as catalysts for the oxidation of lactic acid. In the case of cells containing (II), (I), if sufficiently positive, also oxidise (II) to methaemoglobin, which then oxidises, irreversibly and stoichiometrically, a portion of the substrate. A. E. O.

Acceleration of an enzymic dehydrogenation by irradiation. H. VON EULER and E. KLUSMANN (Naturwiss., 1934, 22, 777).—The reduction of methylene-blue at 30° in presence of yeast extract with EtOH as H donor is accelerated by exposure to Hg light. With liver succinodehydrogenase as enzyme and Na succinate as H donor, a similar acceleration not produced by irradiation. W. O. K.

Thermodynamics of the fumarase system. K. P. JACOBSON, F. B. PEREIRA, and J. TAPADINHAS (Biochem. Z., 1934, 274, 167—180).—The dependence of the fumaric-malic acid equilibrium in presence of fumarase on the temp. is investigated, similar results being obtained by both gravimetric and polarimetric methods. P. W. C.

Co-enzymes. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1934, 274, 112—116).—1 g. of a substance (I) has been isolated (no details) from the erythrocytes of 250 litres of horse blood, 0.0001 mg. of which added to a system in which hexose monophosphate is being oxidised by O_2 , causes an increased absorption of O_2 by 1 c.c. per min. Useful characterisation of (I) is obtained in terms of the velocity coeff. of destruction by acids and alkalis. (I) fluoresces blue in acid and yellow-green in alkaline solution and contains 10% of organically bound PO_4'''

and 11% of N. It is similar in elementary composition to the co-enzyme of yeast, but cannot replace the latter in its action on fermentation either with or without PO_4''' . (I) is a mixture of phosphoric esters and on hydrolysis yields 70% of its N as adenine. After removal of adenine, two other bases have been isolated, one of which is contained in larger amounts in the more active preps. P. W. C.

Enzymes of *Bombyx mori*, L. VII and VIII. Catalase of the eggs. IX. Blood-protease and -amylase. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1934, 10, 112—116, 116—118, 119—127; cf. A., 1934, 559, 1032).—VII. Treatment of aq. extracts of silkworm eggs with EtOH and $CHCl_3$, adsorption on $Ca_3(PO_4)_2$ followed by elution, and dialysis yields a catalase (I) prep. the unimol. reaction coeff. of which gradually diminishes. (I), with optimum temp. and p_H of 25° and 6.8, respectively, is inactivated at $> 55^\circ$. Max. thermostability, which increases with increasing concn., occurs at p_H 6.8. Data for the affinity const. and temp. coeffs. are given.

VIII. The action of (I), purified by adsorption on $Al(OH)_3$ and elution with Na_2HPO_4 , is inhibited by the following anions in increasing order of activity: butyrate, SO_4 , PO_4 , Cl, lactate, OAc, NO_3 , F, oleate, SH, S, CN.

IX. The blood-protease activity of the male larva is somewhat $>$ that of the female; the level is also influenced by health, starvation, and type. The content of protease-a (p_H optimum 2.3) increases during the five larval stages, decreases after cocoon-spinning, and increases again to a max. at the end of the pupal stage; that of protease-b (p_H optimum 8.8), which is less evident than -a, follows an almost opposite course. The blood-amylase in the male larva is $<$ that in the female, is independent of growth, and increases with starvation. Its level during development follows a course approx. parallel with that of protease-a. F. O. H.

Action of trypsin and amylokinase on the amylase content of grains. T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1934, 274, 274—284; cf. A., 1934, 1258).—Different grains [barley (I), wheat (II), rye, oats, buckwheat, maize, millet (III)] exhibit great differences as regards the extent to which their power to convert starch into dextrin and sugar is increased by trypsin (IV). The starch-liquefying powers remain weak. As regards saccharifying effect (V), (IV) acts in virtue of its proteolytic power, its effect being great with (I), less with rye and (II), and quite weak with the other grains. The increase in dextrin-forming power (VI) is due to the amylokinase (VII) (produced during germination) in (IV). Variations in (VI) with const. (V) are due to variations in the amount of (VII). The activity of the amylase of (III) is not reduced by (IV). Inactive (IV) may act like an eluto-substance. The assumptions of Ohlsson (A., 1932, 303) and Oparin (A., 1934, 1258) are not justified. W. McC.

Absorption-spectrographic examination of invertase preparations. H. ALBERS and I. MEYER (Z. physiol. Chem., 1934, 228, 122—140).—Highly purified invertase preps. were obtained from yeast autolysates by adsorption with $Al(OH)_3 C_7$. Tryptop-

phan (I) was detected in the preps. by the ultra-violet adsorption spectrographic method even when not shown by the colorimetric method of von Fürth and Lieben. The (I)-peptide concn. \propto the difference between the absorption max. and min. Higher absorption coeffs. are shown as the preps. become inactive (by ageing), owing to aggregation of the high-mol. carrier, accompanied by a masking of the active group. J. H. B.

Autolysis of placental glycogen. A. DAVY and A. ST. G. HUGGETT (J. Physiol., 1934, 81, 183—193).—In minced rabbit placenta no change in total carbohydrate occurred on autolysis for 24 hr. in Ringer's solution, at 37°, in presence of air, O₂, or N₂. As with liver, lactic acid remained unchanged, and of the glycogen (I) which disappeared, one third was accounted for as dextrin, the remainder as glucose. Change in p_H did not affect the disappearance of (I) but an acid reaction inhibited glucose formation. The enzymes concerned were in the placental cells, not in the blood, and were unaffected by F' or PO₄'''. NUTR. ABS. (6)

Antiglyoxalase. J. O. GIRŠAVIČIUS, P. H. EFENDI, and A. P. RYZHOVA (Biochem. Z., 1934, 274, 87—94).—Glyoxalase (I) is inhibited both by histidine and pancreatin (II) and the inhibition is reversed in both cases by addition of glutathione, whilst the inhibition by (II) is dependent on the presence of sufficient protein. These facts support the view of Ochoa and Dudley, according to whom antiglyoxalase is the protease of (II) under the action of which NH₂-acids arise, of which especially histidine has a powerful inhibitory action on (I). P. W. C.

Relation between the synthesis of adenosinetriphosphoric acid and the oxido-reductive transformation of dihydroxyacetonephosphoric ester during glycolysis. Z. DISCHE (Naturwiss., 1934, 22, 776—777).—The disappearance of hexose diphosphate in presence of hæmolysed washed human erythrocytes and phosphate at 40° which takes place without production of triose phosphate is accelerated by adenylic acid. Addition of phosphoglyceric acid causes a similar acceleration, in this case with an increased formation of AcCO₂H. The acceleration is accompanied by increased formation of lactic acid and formation of easily split phosphoric esters. The increased esterification is associated with an increased oxido-reductive activity of the intermediate triose esters. Erythrocytes with glucose at 0° synthesise the Harden-Young hexose diphosphate, for which the P appears to come from adenosinetriphosphoric acid and a relatively stable ester. W. O. K.

Enzymic decomposition of adenosinetriphosphoric acid (adenyl pyrophosphate) in heart muscle. A. N. PARSHIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 626—630).—Adenyl pyrophosphate (extraction described) from the heart muscle of a frog or white rat is hydrolysed nearly completely in 0.5 hr. at 20° in 0.9% KCl. 0.5—0.05*N*-NaF partly inhibits the hydrolysis, whereas 0.005*N* is without action. 0.004*N*-CH₂I-CO₂H accelerates hydrolysis, but 0.02*N* has no effect. Analogous results are obtained with skeletal muscle. KCN results in immediate hydrolysis. J. L. D.

Influence of the hydrogen-ion concentration of the medium on the hydrolysis of α - and β -glycerophosphoric acids by grain phosphatases. J. COURTOIS (Compt. rend., 1934, 199, 1252—1254; cf. A., 1934, 927).—The phosphatase (I) of white or black mustard hydrolyses both isomerides (II) at any p_H , but the rates of hydrolysis are different. The (I) of sweet almonds hydrolyses the (II) (as an emulsion) at equal rates (max. at p_H 5.8), although the affinity of the (I) for the substrate diminishes with increase in p_H . Contrary to taka-diastase, these (I) hydrolyse both (II) in mixtures. J. L. D.

Enzymic activity of the phosphatase of cobra venom. E. ROUSSEAU (Compt. rend. Soc. Biol., 1934, 117, 565—566).—The activity is not destroyed by heating at 70° for 30 min. R. N. C.

Specificity of phosphatase. R. HOTTA (J. Biochem. Japan, 1934, 20, 343—360).—The following new substrates were prepared: NH₄ sec.-Bu phosphate and its Ph ester (as K salt); NH₄ cyclohexyl phosphate, its 1:2- and 1:3-Me₂ derivatives (as Ba salts), and the Ph ester of the former (as K salt); bis-sec.-Bu phosphate (as K salt); biscyclohexyl phosphate (as K salt). The action of various mono- and di-phosphatase preps. (from dialysed kidney autolysate, taka-phosphatase, pig's liver, rice bran, snake venom, etc.) on these and other substrates indicates that the specificity of phosphatases depends not only on linking of H₃PO₄, but also on the nature of the ester-forming alcohol (cf. A., 1932, 650; 1933, 426). F. O. H.

Determination of plasma-phosphatase. A. BODANSKY (Proc. Soc. Exp. Biol. Med., 1934, 28, 760—762; Chem. Zentr., 1934, i, 3604).—Errors in Kay's method are corr. by addition of Na diethylbarbiturate (0.1*M*). To 1 c.c. of centrifuged plasma are added 7 c.c. of H₂O, 2 c.c. of veronal solution, and 1 c.c. of glycerophosphate solution. After 2 hr. at 37° the liquid is rapidly cooled, and 5 c.c. of 10% solution of CCl₃-CO₂H are added. Total inorg. PO₄''' is determined in the filtrate. Phosphatase activity is expressed as mg. inorg. PO₄ formed per 100 c.c. of plasma per hr. A. G. P.

Crystalline proteins: hormones and enzymes. E. GORTER (Chem. Weekblad, 1934, 31, 682—685).—An account is given of measurements on unimol. films of ovalbumin, insulin (I), trypsin (II), and pepsin (III) at various p_H vals. (I), (II), and (III) are protein complexes, the protein in (II) being combined with a strong base and that in (III) with a strong acid. S. C.

Proteolytic enzymes in plants. R. SCHAEDE (Ber. Deut. bot. Ges., 1934, 52, 378—383).—The distribution of gelatin-liquefying enzymes in the roots, rhizomes, and leaves of a no. of plants is recorded. A. G. P.

Activation of plant proteinases. E. MASCHMANN (Z. physiol. Chem., 1934, 228, 141—186).—The activation of papain (I) on gelatin substrate by Fe''' [for which ascorbic acid (II) is not necessary] is due to the activation of a concomitant (III) (not present in all preps.) which is removed by pptn. of (I) with 90% EtOH. (III) is apparently not a SH-compound,

since it is more quickly activated, neither is it a flavin. In the hydrolysis of peptone with (I) the specificity range is broadened by Fe^{++} . Peptone is almost unattacked by (I), but after treatment with Fe^{++} it becomes susceptible to hydrolysis. (III) immediately accelerates the hydrolysis in presence of Fe^{++} , no pre-treatment being necessary. (II) promotes hydrolysis only after long "incubation" with (I), treatment of the substrate with (II) produces immediate fission. The favourable effect of HCN is probably due to reduction of $\cdot\text{S}\cdot\text{S}\cdot$ groups. The effect of Pd-C in inactivating gelatin hydrolysis is incompletely removed by H_2 . Bromelin behaves similarly to and is probably identical with (I). The proteinase activity of a yeast autolysate towards gelatin is not affected by (II) or Fe^{++} either singly or together. (III) treated with Fe^{++} has no effect on this reaction.

J. H. B.

Activation of papain, applied to the determination of physiologically active substances in blood. A. PURR and M. RUSSEL (Z. physiol. Chem., 1934, 228, 198—206).—Cysteine hydrochloride and glutathione solutions of equal $\cdot\text{SH}$ content show the same power of activation of papain. This is the basis of a method for determination of active or potential $\cdot\text{SH}$ groups in blood (I). Carcinomatous (I) shows a lower activating power than normal (I). The activator in (I) occurs exclusively in the (I)-cells. Cathepsin is also activated by (I)-cells, an important fact in considering intracellular proteolysis.

J. H. B.

Enzymic components of the proteinase from pancreas. E. WALDSCHMIDT-LEITZ and S. AKABORI (Z. physiol. Chem., 1934, 228, 224—234).—The activity of cryst. trypsin (I) towards caseinogen (II) is < that of pancreas-proteinase (III), towards sturin and clupein about the same, towards clupean markedly greater. (I) together with chymotrypsin (IV) has about the same effect as (III). Hence (III) contains (IV), which may also be inferred from the milk-coagulating properties of (III); the Ca^{++} required to produce clotting gives a measure of (IV). In a purified (III) prep. the ratio of "trypsin" to (IV) was about 9:1 calc. on this basis. (IV) in (III) was separated by adsorption on $\text{Al}(\text{OH})_3$. A. J. H. B.

Activation of pancreas extract by acidification. LISBONNE, R. SEIGNEURIN, and A. FRANK (Bull. Soc. Chim. biol., 1934, 16, 1306—1313).—The pancreas excretion of rabbits and dogs, having no proteolytic activity, when brought within the p_{H} range 4.2—3.8 by addition of 0.125N-HCl and kept at 42° for 12 hr., develops tryptic activity. The activation may be connected with the pptn. of the protein carrier of the enzyme, since within the active range considerable pptn. takes place.

A. L.

Activation of the pancreatic juice of the rabbit by enterokinase. Rapid diminution at 30° of curdling power. M. GUILLAUME (Compt. rend. Soc. Biol., 1934, 117, 604—607).—The curdling power (I) of rabbits' pancreatic juice (II) activated by enterokinase (III) at 30° rises to its max. after a time lag, which decreases as the amount of (III) increases. (I) reaches its max. before the proteolytic activity (IV), and then falls rapidly to a low val.;

(IV) on reaching its max. falls only slowly. Further addition of (III) to a mixture comparatively poor in it after its (I) has begun to fall increases (I) only slightly, but (IV) considerably. These results suggest that (I) and (IV) are due to separate enzymes. The (II) of the dog has (I) three times as high as that of the rabbit, for quantities with equal (IV).

R. N. C.

Biochemical micro-methods. V. Nephelometric micro-determination of trypsin and cathepsin. B. J. KRIEGSMAN (Z. physiol. Chem., 1934, 228, 256—266).—Trypsin is determined on a caseinogen (I) substrate, cathepsin best on (I), but also on edestin or by means of the protein in the enzyme extract.

J. H. B.

Ground Congo-red-fibrin for testing rates of action of enzymes. H. HARTRIDGE (Proc. Physiol. Soc., J. Physiol., 1934, 81, 11 p).—Fibrin is treated with Congo-red, washed, dried, and powdered. Enzyme activity is indicated by the rate of liberation of colour from the dry powder added to the test solution.

CH. ABS. (p)

Properties of uricase. H. KLEINMANN (Bull. Soc. Chim. biol., 1934, 16, 1252—1265).—Uricase (I) preps. made from powdered pigs' liver (II) by the author's method (A., 1933, 864) decompose uric acid in blood even in the absence of air. Evaporation in vac. of the preps. destroys the activity. Whilst (I) may be extracted from (II) by aq. NH_3 , $\text{Na}_2\text{B}_4\text{O}_7$, NaOH, and NaCl, the ppt. obtained from such extracts by addition of acids, EtOH, or COMe_2 is inactive. NH_4 salts catalyse the decomp. of uric acid in aq. solution, but not in human blood. A. L.

Biochemical hydrogenations. I. Hydrogenation of unsaturated α -keto-acids, aldehydes, and alcohols by fermenting yeast. F. G. FISCHER and O. WIEDEMANN (Annalen, 1934, 513, 260—280).—An actively fermenting mixture of brewer's bottom yeast (I), sucrose, and aq. NaH_2PO_4 reduces $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ (concn. about 1%) to $\text{Bu}\cdot\text{OH}$ and a little $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ (also similarly reduced to $\text{Bu}\cdot\text{OH}$); repeated additions of (I) are necessary to maintain fermentation. $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ similarly gives $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (II) and a little $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ [also similarly reduced to (II)]; $\Delta^{\alpha\gamma}$ -hexadienal (concn. \approx 0.5%) affords $\Delta^{\beta\delta}$ -hexadien- α -ol (which undergoes slow reduction) and a mixture of $\Delta^{\gamma\epsilon}$ and Δ^{δ} -hexen- α -ol; $\Delta^{\alpha\gamma\epsilon}$ -octatrienal (concn. \approx 0.5%) yields $\Delta^{\beta\gamma\epsilon}$ -octatrien- α -ol (III) [the action of impoverished yeast (IV) gives this as the main product] and octadienol (V). ζ -Methyl- Δ^{ϵ} -hepten- β -ol is similarly unaffected. $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ (as Na salt) undergoes decarboxylation and reduction to (II); little or no change occurs with (IV). α -Keto- $\Delta^{\beta\gamma\epsilon}$ -nonatrienoic acid and (I) give (III) and then (V); (III) and $\Delta^{\alpha\gamma\epsilon}$ -octatrienoic acid are formed using (IV). The main type of reduction appears to be $\alpha\beta$.

H. B.

Ion antagonism and activation in alcoholic fermentation. V. KULIKOV and A. POROVA (Mikrobiologiya, 1933, 2, 51—56).—In 25—30% sugar solutions, 10% of K_2SO_4 retarded fermentation. Subsequent addition of CaSO_4 accelerated the process.

CH. ABS. (p)

Reduction of hyposulphite by yeasts. M. P. KORSKOVA (Mikrobiologiya, 1933, 2, 251—259).—Reduction of hyposulphites is unrelated to the fermentative process. A substance resembling glutathione is the causative agent. CH. ABS. (p)

Death of a yeast culture as registered by electrical resistance. B. J. LUYET (Proc. Soc. Exp. Biol. Med., 1934, 31, 800—801).—Resistance-temp. effects in yeast cultures were reversible between 15° and 62°. An irreversible fall in resistance occurs at > 62°. CH. ABS. (p)

Resistance of individual cells of micro-organisms of the same species to the action of ultra-violet rays. J. BEAUVERIE (Compt. rend., 1934, 199, 881—883).—Resistance is associated with the thickness of the glycogen layer in yeast cells.

A. G. P.

Effects of inositol, crystalline vitamin-B₁, and "pantothenic acid" on the growth of different strains of yeast. R. J. WILLIAMS and D. H. SAUNDERS (Biochem. J., 1934, 28, 1887—1893).—The addition of 0.000008 mg. of a highly conc. prep. of "pantothenic acid" (A., 1933, 982; 1934, 254) to each ml. of a synthetic medium containing sucrose, asparagine, and all essential inorg. constituents results in a striking increase of growth with 5 out of 6 strains of *Saccharomyces cerevisiae* tested, and a slight but definite increase with "old process" yeast (I). The effect was usually enhanced by inositol (II) (in relatively large amount), by vitamin-B₁ (III) (in extremely minute amount), or both. (II) has little effect alone, and (III) alone produces a striking effect only with (I) and one other strain of yeast tested. An unknown basic factor, not (III), promotes the growth of Wildier's yeast. "Pantothenic acid" is the most important constituent of "bios."

A. E. O.

Yeast as an indicator for growth-promoting substance. E. ALMOSLECHNER (Planta, 1934, 22, 515—542).—By means of single-cell drop cultures of yeast the presence of growth-promoting substance is established in *Boletus edulis*, *Rhizopus suinus*, and in urine. The active agent is insol. in Et₂O, sol. in H₂O and EtOH, and resistant to heat and oxidation, but has no action on the growth of *Avena coleoptiles*. It is probably of the group of growth-substances-B of Nielsen.

A. G. P.

Influence of antiseptics on yeast autolysis. H. HAEHN and H. LEOPOLD (Woch. Brau., 1934, 51, 353—356).—Autolysis was carried out by heat-treatment (I) (50—52°), with PhMe, CHCl₃, or with EtOAc. With (I), p_H fell from 5.9 to 5.3 in 21 days; with PhMe or CHCl₃ changes were smaller, due to the presence of buffer substances, despite considerable development of titratable acidity. EtOAc gave abnormal results, due to its own hydrolysis. Volatile acids are formed chiefly during the first 12 hr. of autolysis, but there is considerable prolonged liberation of inorg. PO₄'''. Proteolysis is hindered by CHCl₃ and EtOAc, as compared with (I) and PhMe. At the close of autolysis, all the yeast-P appears to be in solution, although not necessarily in the inorg. form. Alkaline autolysis gave reduced liberation of inorg. PO₄''' as compared with (I).

I. A. P.

α - and β -Glucosidase.—See this vol., 69.

Soil protozoa. F. S. BODENHEIMER and K. REICH (Soil Sci., 1934, 38, 259—265).—The annual cycle of protozoa in soil and the heat-tolerance of various cysts is examined.

A. G. P.

Micro-moving pictures showing the lethal effects of ultra-violet radiation on certain living protozoa. R. FRANKLIN, A. J. ALLEN, and E. McDONALD (Physical Rev., 1933, [ii], 43, 1041).—Ultra-violet radiation below 2900 Å. causes immediate cessation of all motion of *Entosiphon*, *Euglena*, *Colpoda*, and *Paramecia*. Some light is thrown on the mechanism of death caused by the photochemical changes which occur.

L. S. T.

Microphotography and some radiation effects on living organisms with various wave-lengths of monochromatic ultra-violet light. A. J. ALLEN, R. FRANKLIN, and E. McDONALD (Physical Rev., 1933, [ii], 43, 1041; cf. preceding abstract).—Absorption of wave-lengths below 2900 Å. by nuclei of the cells of different kinds of tissue produces an effect similar to staining. Photomicrographs of cancer tissue taken 5 min. and 3 hr. after the death of an animal show a marked change in the micro-absorption spectra of the cells.

L. S. T.

Soluble enzymes secreted by *Hymenomycetes*. Cytolysis of cellulose. L. LUTZ (Compt. rend., 1934, 199, 893—894).—Decomp. of cellulose (cotton) by *Stereum purpureum* involves the successive stages, cellulose, hydrocellulose, erythrocellulose, xanthocellulose, insol. gums, sol. gums, intermediate products, cellobiose, monoses.

A. G. P.

Occurrence of tyrosine in the protein of *Aspergillus niger*. M. VORBRODT (Bull. Acad. Polonaise, 1934, B, 85—88).—0.3% of tyrosine has been isolated from the protein, containing 9% N, of the mycelium.

H. G. R.

Chemistry and enzyme chemistry of acid formation and degradation by moulds. XI. Formation of oxalic acid from formic, glycollic, succinic, and other acids by *Aspergillus niger*. K. BERNHAUER and F. SLANINA (Biochem. Z., 1934, 274, 97—111).—Using dil. solutions of HCO₂Na (I) a yield of > 60% of H₂C₂O₄ (II) was obtained [calc. on amount of (I) disappearing], whilst with more conc. solutions the yield of (II) was halved, the chief reaction being the degradation of (I) to CO₂ + H₂O. Under parallel conditions AcOH, succinic, fumaric, glycollic, aconitic, and citric acids gave 77.6, 68, 67.2, 65.6, 60, 61.1% yields, respectively, of (II). The bearing of these results on the mechanism of the degradation of sugar is discussed. The views of Butkewitsch (A., 1934, 1139) on the mechanism of the formation of citric acid from AcOH and EtOH are critically examined and repudiated.

P. W. C.

Citric acid fermentation. W. P. DOELGER and S. C. PRESCOTT (Ind. Eng. Chem., 1934, 26, 1142—1149).—A standard mineral salt-acid-sucrose medium is used for citric acid (I) fermentation by a selected variety of *Aspergillus niger*, care being taken to limit the hydrolysis of sucrose during the preliminary sterilisation. Adjustment of the initial p_H to 1.6—

2.2 gives improved yields of (I), HCl being best used for this purpose. The optimum temp. for (I) production is 26–28°. Titratable acidity (II) increases rapidly from the 6th to the 12th day of fermentation, and thereafter increases more slowly, (I) being converted into other products. Repeated transference of spores to new fermentations gives increasing (II), and spore-formation decreases as ability to produce (I) increases. The efficiency of the process increases with the ratio surface area/depth of medium. For a 9–12-day fermentation, 14% of sucrose in the medium gives the most satisfactory yield of (I); addition of other sugars gives a decreased yield. Shallow containers of 99.8–99.98% Al with Cu covers and min. air circulation may be used; the use of open containers necessitates a high R.H. I. A. P.

Glucose metabolism of *Trypanosoma equiperdum* in vitro. L. REINER and C. V. SMYTHE (Proc. Soc. Exp. Biol. Med., 1934, 31, 1086–1088).—Glucose is converted by suspensions of *T. equiperdum* into 1 mol. each of glycerol and AcCO_2H (I) anaerobically and into 2 mols. of (I) aerobically. Aerobically glycerol gives 1 mol. of (I) and utilises 1 of O_2 . Neither CO_2 nor lactic acid is produced. C. G. A.

Action of arsenopyridine derivatives on resistant strains of trypanosomes. H. SCHLOSSBERGER and R. SCHUFFNER (Angew. Chem., 1934, 47, 768–771).—The action of various arsenopyridine derivatives on strains of *T. brucei* resistant to trypanarsamide or to the Na salt of 2-pyridone-5-arsinic acid was determined in mice (cf. A., 1930, 1213). The data are compared with those from corresponding arsenophenyl derivatives. F. O. H.

Malarial pigment (hemozoin). III. Action of solvents and of oxidising and reducing agents on optical properties and on crystallisation. J. A. SINTON and B. N. GHOSH (Rec. Malaria Survey, India, 1934, 4, 205–221).—The pigment was obtained from the centrifuged Na_2CO_3 extract of the parasites by pptn. with $\text{H}_2\text{C}_2\text{O}_4$. Chemical and physical properties were identical with those of hæmatin. CH. ABS. (p)

Cytochrome and the respiratory systems of bacteria. W. FREI, L. RIEDMULLER, and F. ALMASY (Biochem. Z., 1934, 274, 253–267).—Bacteria (I) may be divided into 4 groups on the basis of the presence or absence of respiratory catalysts. (I) of the first group contain hæmochromogen (II) (cytochrome) and indophenol-oxidase (III); (I) of the second, (II) but no (III); (I) of the third, (III) but no (II); and (I) of the fourth, neither (II) nor (III). Cytochrome scarcely ever occurs unless (III) is also present. With increase of age or for other reasons some (I) may pass from one group to another. (I) of the first three groups always, and (I) of the fourth group which can act anaerobically usually, contain peroxidase and catalase. Not all aerobically grown (I) contain detectable amounts of hæmatin. In special cases pigments (IV) other than those mentioned are encountered. (IV) are probably respiratory. W. McC.

Fermentation of cellulose. V. PEROVSKANSKI and Y. CHELTZOVA (Brodilnaya Prom., 1933, 3, 3–6).

—With Langwell's process, thermophilic organisms isolated from horse manure increased their capacity for cellulose decomp. on repeated subculturing, and produced max. yields of 25% of EtOH in 3 days. HCO_2H and PrCO_2H are also formed.

CH. ABS. (p)

Role of a cellulolytic bacterium of the stomach in the conversion of cellulose into glucose in the alimentary canal of ruminants. J. POCHON (Compt. rend., 1934, 199, 983–985).—Fermentation of cellulose *in vitro* by *Plectridium cellulolyticum* in a neutral medium (cf. A., 1934, 812) gives (80%) mainly HCO_2H , AcOH , and some PrOH , but by Pringsheim's method affords glucose (I) (10%), which indicates the presence of a cellulase. (I) is formed in small amounts when the fermentation liquor becomes gradually acid, and in optimum concn. at p_{H} 4.8. A symbiosis of bacteria is unnecessary to account for cellulose digestion.

J. L. D.

Fermentation product of galactose by acetic acid bacteria. Production of galactonic and comenic acids. T. TAKAHASHI and T. ASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 604–607).—Bacteria isolated from "sanboka" (citrus) fruit, grown in yeast extract containing 5% of galactose, produced galactonic and comenic acids.

CH. ABS. (p)

Restriction of butyric acid fermentation by carbon monoxide. F. KUBOWITZ (Biochem. Z., 1934, 274, 285–298; cf. A., 1934, 113).—The degradation of glucose (I) by *Clostridium butyricum* (II) is unaffected by CO , which, however, affects some degradation product (III) in such a way that PrCO_2H fermentation (IV) is replaced by lactic acid fermentation (V). The consumption of (I) is decreased only about 25%. The degree of restriction of (IV) by CO depends on $[\text{H}^+]$, increasing from 23.5% at p_{H} 5.6 to 71% at 7.15. 0.01M-HCN acts like CO , but higher concns. also restrict (V). H_2 reversibly restricts (IV), but does not affect consumption of (I). CO reversibly restricts (53% at p_{H} 4.5, 25% at 6.64) fermentation (VI) of AcCO_2H by (II). H_2 also acts thus. Restriction by CO of (VI) by (II) is counteracted by irradiation. The enzyme in (II) which attacks AcCO_2H seems to be identical with that which produces PrCO_2H from (I). W. McC.

Action of sodium salicylate on the fermentation of salicin and glucose by streptococci. E. VALENTINE and L. REINER (Proc. Soc. Exp. Biol. Med., 1934, 31, 926–929).—Na salicylate inhibits the fermentation of salicin and glucose by streptococci, but has little or no effect on the viable count, although the chains of organisms are shorter.

C. G. A.

Chemistry and pharmacology of fermented foodstuffs. II. W. KEIL and E. KUNZ (Arch. exp. Path. Pharm., 1934, 177, 25–28; cf. A., 1934, 1134).—The juice of salted cucumbers contained putrescine, choline, and acetylcholine (0.002%), but not histamine.

F. O. H.

Sulphur bacteria. II. Cyanophytes accompanying sulphur bacteria. III. Cell structure in sulphur bacteria. I. TUROWSKA (Bull. Acad.

Polonaise, 1933, B, 135—138, 139—148).—Organisms from various sources are examined in relation to H_2S assimilation. A. G. P.

Cultivation of organisms concerned in the oxidation of thiosulphate. R. L. STARKEY (J. Bact., 1934, 28, 365—386).—Development of *Th. thio-parus* (I) and *Th. novellus* (II) is favoured by initial alkalinity in media. The latter become increasingly acid with the growth of the bacteria. Strong buffering increases the oxidation of $S_2O_3^{--}$ by (II). Association of organisms producing acidity with those producing alkalinity in media frequently effects more rapid oxidation of $S_2O_3^{--}$ than either species alone. Growth of (II) was improved by org. matter, but the rate of its action on $S_2O_3^{--}$ was not increased. (II) utilises various forms of org. N, whereas (I) uses only NH_3 , NO_2^- , and NO_3^- . Forms of S other than $S_2O_3^{--}$ are oxidised very slowly or not at all. A. G. P.

Production of polythionates from thiosulphate by micro-organisms. R. L. STARKEY (J. Bact., 1934, 28, 387—400).—Organisms producing dithionates from $S_2O_3^{--}$ were more active in media containing org. matter. Heterotrophic species alone are concerned. A. G. P.

Neutralising power of anti-tuberculosis sera with respect to tuberculin. W. SCHAEFER and C. ZOBOLI (Compt. rend. Soc. Biol., 1934, 117, 404—405).—Anti-tuberculosis sera cannot neutralise tuberculin. H. G. R.

Chemical composition of virulent, avirulent, and weakened bovine and human tubercle bacilli. E. REMY (Z. Immunitat., 1932, 75, 527—536).—Cultures of BCG and weakened bovine (I) and human (II) strains of tubercle bacillus were compared with a virulent (I) as regards chemical composition (III). The composition of the medium affected (III), particularly in the case of egg medium (IV). (I) always had a higher fat content than (II), the use of (IV) increasing it still further; (II) contained more unsaturated fat than (I). The $KMnO_4$ val. for (I) was < for (II). From (II) was isolated a glucoprotein containing 10.75% N, which gave on hydrolysis a reduction val. corresponding with 13% of glucose. R. N. C.

Specific polysaccharide of the anthrax bacillus. J. TOMCSIK and H. SZONGOTT (Z. Immunitat., 1932, 76, 214—233).—A polysaccharide (I) is extracted from both capsulated and capsuleless strains of anthrax bacillus (II) by the following method. The EtOH-pptd. bacilli are boiled with 1% KOH, nucleoproteins pptd. with AcOH, the neutralised solution is filtered through a Seitz filter, and the (I) extracted with EtOH and purified by repeated pptn. with EtOH and $COMe_2$. (I) contains 0.8% N, and on hydrolysis gives 60% of glucose. It is a hapten, and gives a precipitin reaction. There is no relation between virulence and hapten activity. No carbohydrates can be extracted from (II) capsules, but only a $CuSO_4$ -precipitable protein (I) exhibits no "agressin" reaction in anthrax. R. N. C.

Specificity changes in immune sera after chemical pre-treatment. F. BREINL and F. HAUROWITZ (Z. Immunitat., 1932, 77, 176—186).—

Coupling of agglutinating horse-serum (I) with diazotised atoxyl, NH_2Ph , or metanilic acid reduces agglutinins (II) and type-specificity (III). Introduction of I into the protein mol. lowers (II) > (III). CH_2O in suitable concn. destroys selectively secondary (II) and the fine-flocculating primary (II) of dysentery, but (III) is unaltered. Strong alkalis destroy the antibodies and (III) completely. Diphtheria antitoxin and typhus vaccine behave similarly to (I). R. N. C.

Analysis of pyocyanase. L. BIRCH-HIRSCHFELD (Z. Hyg., 1934, 116, 304—314).—The bactericidal action of pyocyanase (I) is dependent on its content of high-mol. fatty acids. These occur largely as sol. salts and only to a small extent as free acids. The activity of (I) is a function of its surface tension effects and can be determined by means of its action in increasing the drop no. at appropriate dilution. A. G. P.

Ionic effects [on micro-organisms], especially anion phenomena. F. BOAS (Planta, 1934, 22, 445—461).—The selective action of SCN^- on micro-organisms results from its inhibitory effect on the catalase system of the cell. The reverse effect is shown by SO_4^{--} . In both cases the anions are active in hypo- and in hyper-tonic concns. Purple bacteria are relatively resistant to the action of SCN^- and SO_4^{--} . A. G. P.

Silver picrate. J. C. BIRD and A. BAROL (J. Amer. Pharm. Assoc., 1934, 23, 996—1000).—Ag picrate is readily sol. in certain glycol ethers, and, as an antiseptic, combines the effects of Ag and of picric acid. A. E. O.

Antiseptic and growth-inhibiting power of benzene and its halogen derivatives. A. MOREL, A. ROCHAIX, and Y. DUMAS (Compt. rend. Soc. Biol., 1934, 117, 445—447).—The antiseptic power of C_6H_6 is insignificant, but is increased by halogen substitution ($Cl > Br$ and I) and depends on the no. of halogen atoms present. H. G. R.

Preparation and germicidal properties of 4-hydroxy-2-methylphenyl alkyl sulphides.—See this vol., 79.

Preparation and germicidal properties of some derivatives of 4-n-butylresorcinol.—See this vol., 79.

Apparatus for purification of air. P. HAUDUROY (Compt. rend. Soc. Biol., 1934, 117, 431—433).—An apparatus for the sterilisation of air is described. H. G. R.

Counting bacteria in suspension by means of a photo-cell. E. S. AVTONOMOVA and T. A. STESSEL (Biochem. Z., 1934, 274, 220—230; cf. Andreev, A., 1930, 1115).—Suspended micro-organisms (I) are counted with the help of a modification of Andreev's apparatus, using a formula applicable to other than spherical particles. If the shape and dimensions of (I) do not vary beyond certain limits results more accurate than those obtained by other methods are obtained within a few sec. W. McC.

Melanophoric hormone in colostrum. S. KONSULOFF (Endokrinol., 1934, 13, 323—324; Chem. Zentr., 1934, i, 3759).—The presence of melanophoric

hormone in colostrum (I) was shown by darkening of the skin of frogs on subcutaneous injection of (I), and of fish placed in H_2O containing (I). J. S. A.

Adrenaline oxidation and stabilisation. A. D. WELCH (Amer. J. Physiol., 1934, 108, 360—372).—At physiological p_H and temp. glutathione or cysteine protects adrenaline (I) from irreversible oxidation. In autooxidation of (I) the O_2 consumption is 8—9 atoms of O per mol. CO_2 is produced in the later stages.

CH. ABS. (p)

Relation between blood-pressure, blood-urea-nitrogen, and fluid balance in the adrenalectomised dog. W. W. SWINGLE, J. J. PFIFFNER, H. M. VARS, and W. M. PARKINS (Amer. J. Physiol., 1934, 108, 428—437).—Blood pressure and blood-urea-N (I) are inversely related during the cycle of insufficiency and recovery after hormone treatment. High (I) is related to dehydration following disturbance of the mechanism for blood dilution with fluid, and salt mobilisation.

CH. ABS. (p)

Effect of diverting adrenal-vein blood into the portal vein on the blood-sugar of dogs. L. R. DRAGSTEDT (Amer. J. Physiol., 1934, 108, 42—45).—A persistent increase in blood-sugar is recorded without glycosuria or increased tolerance to insulin.

CH. ABS. (p)

Influence of adrenaline on the exchange of sugar between blood and muscle. S. SOSKIN, W. S. PRIEST, and W. J. SCHUTZ (Amer. J. Physiol., 1934, 108, 107—117).—In amyotomised dogs, arterio-venous blood-sugar differences have no quant. significance as regards sugar utilisation (I) by the muscles unless measurement is also made of blood flow and H_2O retention. When allowance is made for these, constantly injected adrenaline does not decrease (I) by the muscles.

NUTR. ABS. (b)

Action of insulin on the respiratory quotient, oxygen utilisation, carbon dioxide production, and sugar utilisation in the mammalian diabetic heart. E. W. H. CRICKSHANK and C. W. STARTUP (J. Physiol., 1934, 81, 153—161).—Insulin administration increases CO_2 production and sugar oxidation, but does not affect O_2 consumption. The glycogen of the heart is not markedly altered.

CH. ABS. (p)

Effect of crystalline insulin on substances of the residual carbon group. BURGER (Zentr. inn. Med., 1934, 55, 487—490).—An improved method for determining the non-protein-C of the serum is described. Injection of insulin into the mesenteric vein of dogs anaesthetised by somnifen caused a reduction in serum-C which was not accounted for by the fall in blood-sugar, so that the reduction in carbohydrate is not accompanied by the production of lipid substances. Subcutaneous injections of insulin into diabetic patients caused a reduction of C in the serum fraction sol. in light petroleum; the reduction was less marked in patients with the more severe types of diabetes, although none of the subjects had acidosis.

NUTR. ABS. (b)

Effect of insulin on amino-acid metabolism. A. LACQUET, P. DE NAYER, and J. P. BOUCKAERT (Arch. internat. Pharmacodyn., 1934, 47, 318—348).—The effects of massive and slow continuous injections

of glycine on the NH_2 -acid (I) content of the blood of depancreatized and normal dogs and rabbits receiving insulin indicate that insulin inhibits N metabolism directly or indirectly, most probably by affecting the catalysis of reactions which take place at a stage more complex than that of (I).

NUTR. ABS. (m)

Physiological variations in the internal secretion of the pancreas. XIII. Internal pancreatic secretion during experimental hyperamino-acidaemia. J. LA BARRE (Arch. internat. Physiol., 1934, 38, 37—51).—Intravenous injection of glycine (150—500 mg. per kg.) resulted, in the dog, in hyperglycaemia sometimes followed by hypoglycaemia (I). The latter is more marked when the dose is large. After removal of the adrenals, glycine no longer caused appreciable changes in blood-sugar, although (I) might still occur about 5 hr. after the injection. Cross-circulation experiments showed that the (I) could be attributed largely to an increased output of insulin from the pancreas.

NUTR. ABS. (b)

Absorption of insulin. K. THIEL, A. RUHNAU, and A. UNGER (Deut. med. Woch., 1934, 60, 975—978).—The absorption of insulin is considerably delayed if it is injected admixed with gelatin. By this means large doses of insulin could be given without the risk of hypoglycaemic symptoms.

NUTR. ABS. (b)

Standardisation of parathormone and its antagonistic effect on oxalic acid poisoning. M. KOCHMANN (Deut. med. Woch., 1934, 60, 406; Chem. Zentr., 1934, ii, 267).—The toxic effect of oxalate can be wholly or partly annulled by introduction of Ca into the blood, and also by injection of parathormone, which increases serum-Ca.

R. N. C.

Action of thyroxine on carbohydrates and proteins in the liver. R. STERNHEIMER (Compt. rend. Soc. Biol., 1934, 117, 422—424).—Glycogen (I) disappears from the liver without an increase in free sugar (II) or in the blood-(II) or in basal metabolism. During the lowering of (I) an increase in protein was observed, and this was followed by a second phase in which the phenomena were reversed.

H. G. R.

Action of thyroxine and thyroidin on lipin and fat metabolism. L. PASTERNAK and I. H. PAGE (Biochem. Z., 1934, 274, 122—145).—The following changes are detected in the blood and organs after subcutaneous administration of thyroxine (I) or after feeding thyroidin (II) to rabbits and rats. In muscle, the phosphatide (III) content was increased in rats after (II) by 96%, in rabbits after (I) by 100%, and in rats after (I) by 70%, the I val. was increased, the total fat and fatty acid content decreased, the dry wt. increased, and after (II) but not after (I) there was a considerable increase of cholesterol (IV). In heart muscle the same changes occur with the exception of the increase in (III). In liver there is a fall of dry wt. The (IV) content increases in rabbits after (I), in rats only after (II), whilst the effect on the (III) content is variable. In brain the changes are small, whilst in blood the chief alteration is in respect to the (III) and (IV) contents. Adminis-

tration of bromiodotyrosine reverses the (III) increase after (II). P. W. C.

Adenotropic hormones of the pituitary. C. L. LAUTENSCHLAGER (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 19—38; Chem. Zentr., 1934, i, 3608).—The general term "adenotropic" (I) is used for hormones influencing other internal secretions. The (I) hormones of the pituitary are reviewed. R. N. C.

Diuretic effect of posterior pituitary extract in the anaesthetised animal. E. E. NELSON (J. Pharm. Exp. Ther., 1934, 52, 184—195).—With rabbits anaesthetised by morphine-urethane and rendered diuretic by rapid intravenous administration of aq. sucrose or, after phloridzin, of aq. glucose, injection of posterior pituitary extract produces a transient diuresis due to an increased rate of filtration. The increase in relative and abs. [Cl'] of the urine indicates an increased flow through the tubules. F. O. H.

Changes in blood-lactic acid after injection of posterior pituitary extract. A. D. MARENZI (Compt. rend. Soc. Biol., 1934, 117, 457—458).—Subcutaneous or intravenous injection raises the blood-lactic acid. H. G. R.

Effect of anterior pituitary extract on blood-lactic acid. A. D. MARENZI (Compt. rend. Soc. Biol., 1934, 117, 464—465).—An alkaline extract which produces hyperglycaemia in the dog raises the blood-lactic acid. H. G. R.

Effect of anterior pituitary extracts on ketone excretion in the rat. P. T. BLACK, J. B. COLLIP, and D. L. THOMSON (J. Physiol., 1934, 82, 385—391).—Injection of anterior pituitary extracts in rats, either fasting or on a filtered butter diet, increases ketonuria (I). The effect is obtained with growth hormone (II) fractions free from thyrotropic hormone (III), or (II)-free (III) fractions, but not with adrenotropic fractions. (I) occurs also with thyroidectomised animals, and is not produced by thyroxine in normal animals. Prolonged pretreatment of rats with the Anderson-Collip (III) extracts containing the ketogenic principle (IV) renders them insensitive to (IV), due to the formation in the serum of an inhibitory principle which can also be produced in horse-serum. R. N. C.

Gonadotropic anterior-pituitary hormone (prolan). F. LAQUER, K. DOTTL, and H. FRIEDRICH (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 117—122; Chem. Zentr., 1934, i, 3608).—Rats are as suitable as mice for repeated assay of prolan (I). Vals. with 13 different preps. of (I) during a year vary \pm 15—20%. (I) in small doses appears to ripen the follicle, and in larger doses to influence the corpus luteum; there is no definite proof that it contains two active substances. R. N. C.

Gonadotropic hormone in the pregnant mare (pituitary or placental origin). C. HAMBURGER (Endokrinol., 1934, 13, 305—311; Chem. Zentr., 1934, i, 3608—3609).—Injection of the serum of pregnant mares (I) has a strong stimulating effect on the testis and comb growth of young cocks; the ovaries of young mice increase in wt.; the increase \propto the amount

of serum injected, up to a high dose. These changes are not produced at all, or only imperfectly, by the gonadotropic hormone (II) of the urine of pregnancy, and hence must be due to a (II) of pituitary origin in (I). R. N. C.

Preparation of gonadotropic extracts of urine of pregnancy by tungstic acid precipitation. P. A. KATZMAN and E. A. DOISY (J. Biol. Chem., 1934, 107, 513—518).—The ppt. (I) formed on addition of Na tungstate to acidified urine is decomposed by brucine in aq. suspension to yield all the active material in aq. solution, from which it is then pptd. by COMe₂. Theelin and theelol may be recovered from the filtrate from (I). A. E. O.

Influence of gonads on metabolism. I. Change in metabolism due to castration. T. INABA (Aichi Igakkai Zasshi, 1930, 40, 119, 423).—Ovariectomy in dogs caused a decrease in total urinary N and S. The subsequent increase in body-wt. is due to decreased general and N metabolism. CH. ABS. (p)

Absorption and excretion of folliculin in man. II. Excretion in urine and faeces. H. ENG (Biochem. Z., 1934, 274, 208—211; cf. A., 1934, 1039).—Since the amount of folliculin (I) excreted becomes very low when the diet is free from (I) support is given to the view that, in men, excreted (I) is derived chiefly from the diet. W. McC.

Development of tolerance by the ovary to the prolonged action of folliculin. C. J. CALATRONI (Compt. rend. Soc. Biol., 1934, 117, 452—453).—After 30 days' treatment the ovaries are atrophied, but become normal if the treatment is continued for 90 days. H. G. R.

Specific action of oestrin. P. G. 'ESPINASSE (Nature, 1934, 134, 738).—A sp. effect of oestrin on the Müllerian duct of the mouse (cf. A., 1934, 1412) is described. L. S. T.

Synthesis of the corpus luteum hormone. E. FERNHOLZ (Ber., 1934, 67, [B], 1855).—Stigmasterol is converted into 3-acetoxybismorcholenic acid and thence into the OH-ketone, C₁₂H₂₂O₂. The latter substance is transformed into the dibromide, which is oxidised by KMnO₄ to the diketone, m.p. 129° [dioxime, m.p. 246—248° (decomp.)], probably identical with luteosterone-C. H. W.

Preparation of homogeneous hormones from the corpus luteum. III. Constitution of luteosterone-C and -D. K. H. SLOTTA, H. RUSCHIG, and E. BLANKE [with, in part, A. NEUHAUS] (Ber., 1934, 67, [B], 1947—1954; cf. A., 1934, 1268).—Luteosterone-D (I) or its mixture with luteosterone-C (II) absorbs 3H₂, giving a mixture of several diols also obtained by saturation of the double linking and reduction of CO of the OH-ketone, m.p. 190°, derived from stigmasterol. The mixture from either source is converted by gentle oxidation into the same diketone, m.p. 188° (corr.). The corpus luteum hormones have therefore the tetracyclic ring system of the sterols and the CO and Ac groups are at 3 and 17, respectively. The double linking is in conjugation with CO. The possibility is discussed that (I) is a monohydrate of (II). H. W.

Corpus luteum hormone. I, II. K. H. SLOTTA and H. RUSCHIG (Z. physiol. Chem., 1934, 228, 207—223).—Fresh pig's corpora lutea are minced and extracted with EtOH. The extract, after removal of EtOH, is extracted with Et₂O and treated with COMe₂ to ppt. phosphatides. This yields a "crude oil" (dose, 300 mg. per unit), which is then dissolved in MeOH containing 10—12% of glycerol. The solution is extracted with petroleum (benzine), which removes lipoid substances. The hormone is transferred to 70% aq. EtOH, and the solution is again extracted with benzine. An "intermediate oil" (I) (dose, 40—50 mg.) is thus obtained. (I) is further purified by dissolution in glycerol (impurities insol.) and transferred to C₆H₆, followed by adsorption of impurities with Al(OH)₃, which yields the "pure oil" (dose, 4 mg.). J. H. B.

Mechanism of the action of the male hormone. R. FUSSGANGER (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 194—204; Chem. Zentr., 1934, i, 3607).—The method of inunction is recommended for the standardisation of commercial preps. of the hormone. R. N. C.

Vitamin-A content of various foodstuffs. K. WALTNER (Z. Vitaminforsch., 1934, 3, 245—247).—The contents of 40 common foodstuffs are tabulated. F. O. H.

Sterols as a source of vitamin-A. N. K. BASU (Biochem. Z., 1934, 274, 4—6).—The author claims that from liver-oil, egg-yolk, and fish-oil, sterol fractions (I) can be isolated, m.p. 62—67°, which are precipitable with digitonin (II), give a faint Salkowski and a negative SbCl₃ reaction, but after irradiation for 30 min. (λ 275—300 mμ) gave products no longer precipitable with (II) and showing an ultra-violet absorption band 328 mμ, a negative Salkowski and a strongly positive SbCl₃ reaction (absorption bands 620, 572 mμ). No details are given of the prep. of (I), but the activity of the irradiated (I) is confirmed by feeding to rats. (I) therefore as well as carotene may act as the precursor of vitamin-A. P. W. C.

Fluorescence of some substances containing vitamin-A.—See this vol., 12.

Difference in the vitamin-A content of cow- and bull-liver. F. ENDER (Z. Vitaminforsch., 1934, 3, 247—253).—With full-grown cattle, the livers of cows have a vitamin-A (or carotene) content approx. 5 times that of the livers of bulls. Both sexes, however, show individual variations. F. O. H.

Vitamin-A of serum following administration halibut-liver oil in normal children and in chronic steatorrhea. J. CHESNEY and A. B. MCCOY (Proc. Soc. Exp. Biol. Med., 1934, 31, 887—888).—Administration of halibut-liver oil to fasting children, subsequently given low-vitamin diet, increased the vitamin-A of the serum to a max. val. after 4 hr. CH. ABS. (p)

Local vitamin action with cod-liver oil bandages. W. VON DRIGALSKI (Z. Vitaminforsch., 1934, 3, 260—268).—Experimental skin-wounds in guinea-pigs heal more satisfactorily with application of an ointment containing cod-liver oil than with that of

a control ointment. The effect is attributed to vitamin-A. F. O. H.

Unit of vitamin-D. O. SCHULTZ (Z. Vitaminforsch., 1934, 3, 257—260).—Curative treatment of rats in the assay of vitamin-D must be started after the 12th and before the 21st day of feeding the rachitogenic diet. During this period the healing tendency is not influenced by the no. of days during which the diet has been fed. Sub-curative doses have no effect even with continued administration. F. O. H.

Absorption of vitamin-D through the skin. M. E. FODOR (Z. Vitaminforsch., 1934, 3, 241—244).—Rickets in rats can be cured by inunction with irradiated ergosterol (10 times the oral curative dose) in olive oil solution. F. O. H.

Effect of vitamin-D on the oxygen consumption of growing rats. E. LANDELIUS and G. LJUNGKVIST (Skand. Arch. Physiol., 1934, 68, 252—270; Chem. Zentr., 1934, ii, 464).—The O₂ consumption (I) of normal growing rats per sq. m. body-surface is reduced about 9% between the 6th and 11th weeks of life, but in vitamin-D deficiency the reduction is 20%. R. N. C.

Experimental production of hypercalcemia in man by means of irradiated ergosterol. T. D. SPIES and R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1934, 31, 747—750).—Administration of large doses of irradiated ergosterol, together with NaH₂PO₄ and Ca lactate, to four hopelessly diseased young adult patients, during 9—25-day periods preceding death caused a rise in blood-Ca, unaccompanied by tissue calcification. NUTR. ABS. (b)

Convulsions due to excessive dosage of biosterol. M. MATSUOKA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1267—1283).—Subcutaneous or intraperitoneal injection of 0.5 c.c. of a 25% solution of biosterol (A., 1925, i, 1365) in olive oil into rats produces clonic convulsions (I) within 20—30 min. Removal of vitamin-A (II) by hydrogenation or oxidation has no effect on the occurrence of (I), whilst the (II) fraction obtained by distillation is inactive. Injection of large doses of camphor, but not of cholesterol, ergosterol, carotene, squalene, etc., produces a similar effect. F. O. H.

Vitamin-E. II. Stability of concentrates towards oxidising and reducing reagents. H. S. OLCOTT (J. Biol. Chem., 1934, 107, 471—474).—Vitamin-E (I) is destroyed by O₃, BzO₂H, KNH₂, KOEt, and Cl₂. Chlorinated and brominated concentrates may be reactivated by boiling with Zn and HCl in MeOH. HBr does not attack (I). Cottonseed oil is as satisfactory as wheat-germ oil for the prep. of active concentrates. (I) concentrates exhibit an absorption band at 2940 Å. not apparently connected with the vitamin activity. C. G. A.

Vitamin-E. F. C. GELLER and C. SCHUSTER (Arch. Gynakol., 1934, 155, 363—380; Chem. Zentr., 1934, ii, 87).—Rats on a diet containing yeast or "vitox" and cod-liver oil, vitamin-A, or "vigantol," undergo degeneration of the testes (I) after 6 months, and loss of fertility (II) earlier. Addition of 8% of butter (III) retards (I) and prevents (II). (I) does

not occur with a diet of barley germ (IV) with vitamin-*A* and -*D*, but it occurs in animals fed with vitamin-*E* adsorbate (V). Female rats produce no young with yeast or "vitox" as the sole vitamin source, or with vitamin-*A* and -*D* in addition, but the oestrous cycle is normal. Addition of (III) has no effect, but with (IV) or wheat-germ oil, young are produced. (V) has no inhibitory effect. The ovaries are normal in all cases except in the animals fed on the diet containing yeast only. R. N. C.

Possible relation of vitamin-*E* to unrestricted cell division. F. B. ADAMSTONE (Science, 1934, 80, 450).—Evidence which indicates that vitamin-*E* is intimately associated with, and probably exerts an indirect controlling influence over, the cell nucleus during division has been obtained. L. S. T.

Association of fat-soluble vitamins and anti-oxidants in plant tissues. E. M. BRADWAY and H. A. MATTILL (J. Amer. Chem. Soc., 1934, 56, 2405—2408; cf. A., 1931, 773, 776).—The unsaponifiable matter of the material extracted by hot 90% MeOH from dried (vac. at 100°), canned tomatoes is freed [essentially as previously described (*ibid.*, 1931)] from carotenoid pigments and sterols, and then separated by diphasic distribution between 92% MeOH and light petroleum (I) into vitamin-*E* (II) and anti-oxidant (III) fractions. Distillation of the (III) (MeOH-sol.) gives a fraction, b.p. 90—115°/0.1—0.2 mm., possessing high (III)-activity. The (III) in carrots [which contain little (II)] is similarly separated. The (III) present in wheat-germ oil is sol. in (I) and could not be separated from (II) by fractional distillation. The various specimens of (III) obtained are probably all different. Lycopene, like carotene, shortens the induction period of autoxidation (of fat) (cf. Franke, A., 1933, 49). H. B.

Pyruvic acid and the avitaminotic brain. R. A. PETERS and R. H. S. THOMPSON (J. Physiol., 1934, 81, 22P).—AcCO₂H occurs in avitaminotic (but not in normal) pigeon brain during respiration in lactate solutions, but disappears on addition of vitamin-*B*.

CH. ABS. (p)

Biological reduction. VI. Oxidation of sugar by striated and cardiac muscle in *B*-avitaminosis. Effect of adrenal cortex. VII. Oxidation of lactic acid in *B*-avitaminosis. T. SAKAI (J. Biochem. Japan, 1934, 20, 193—203, 205—209).—VI. With fowls suffering from *B*-avitaminosis (I) induced by a diet of polished rice and H₂O, the contents of H donator [probably hexose phosphate (A., 1932, 1062)] in leg- and heart-muscle and of dehydrogenase co-enzyme in the hypertrophied adrenal cortex (II) are reduced. Administration of vitamin-*B*₁ (III) produces a rapid return to normal vals., whilst the onset of (I) is delayed by administration of extracts of (II) but not of liver, kidney, or brain. The rôle of (II) and (III) in carbohydrate metabolism is discussed.

VII. Determinations of methylene-blue reduction and of reduction-oxidation potentials indicate that (I) in fowls produces a marked diminution in the content of lactic acid dehydrogenase in the cardiac muscle. O. H.

Sparing action of fat on vitamin-*B*₁. VI. Influence of the levels of protein and vitamin-*B*₂. VII. Effectiveness of natural fats in sparing vitamin-*B*₁. H. M. EVANS, S. LEPKOVSKY, and E. A. MURPHY (J. Biol. Chem., 1934, 107, 429—437, 439—442).—VI. For fat to exert optimal sparing action on vitamin-*B*₁ both protein and vitamin-*B*₂ must be high. The relationship of the three factors is discussed.

VII. The order of effectiveness of the fats is coconut oil, lard, hydrogenated cottonseed oil, butter-fat, synthetic lard, hydrogenated coconut oil, maize oil, olive oil, hydrogenated sesamé oil (I), sesamé oil. Solid fats are more effective than liquid fats with the exception of (I). C. G. A.

Sparing action of fat on vitamin-*B*₂. H. M. EVANS, S. LEPKOVSKY, and E. A. MURPHY (J. Biol. Chem., 1934, 107, 443—447).—Although variable the results seem not to indicate a beneficial effect of fat on diets low in vitamin-*B*₂, but otherwise adequate. C. G. A.

Concentration and chemical nature of vitamin-*B*₂. L. E. BOOHER (J. Biol. Chem., 1934, 107, 591—597).—A 200—300-fold concn. of vitamin-*B*₂ (I) from whey is accomplished by adsorption of the 50-fold concentrate (A., 1933, 1213) on Lloyd's reagent followed by extraction with dil. C₅H₅N and elimination of H₂O-insol. material. The orange-red powder so obtained contains 3000—3500 (I) units per g. The H₂O-sol., yellow, fluorescent pigment of whey is either (I) or an integral part of (I). A. E. O.

Mode of action of vitamin-*B*₂ and the participation of flavoproteins in enzymic dehydrogenations. T. WAGNER-JAUREGG, H. RAUEN, and E. F. MOLLER (Z. physiol. Chem., 1934, 228, 273—276).—Dehydrogenation of *l*-malic acid in presence of frog-muscle extract, the co-enzyme from horse-erythrocytes, and methylene-blue is greatly accelerated by lactoflavin. J. H. B.

Growth-promoting properties of vitamin-*B*₂ concentrates. L. E. BOOHER, H. M. BLODGETT, and J. W. PAGE (J. Biol. Chem., 1934, 107, 599—605).—Vitamin-*B*₁ and -*B*₂ together do not constitute the whole of the vitamin-*B* complex and, in order to promote continuous growth in rats, the addition of a supplementary factor (I), occurring in an 80% EtOH extract of whole wheat and probably also in autoclaved yeast, is necessary. (I) is Et₂O-insol., and is only partly destroyed when autoclaved at 120° for 5 hr. in alkaline solution. A. E. O.

Ascorbic acid and its determination. J. P. SPRUYT and W. F. DONATH (Med. Dienst Volksgezond. Ned.-Indie, 1934 No. 2—3, 117—128).—Aq. ascorbic acid (I) is unstable; the stability is greater in 0.25% CCl₃·CO₂H, especially when kept under H₂S. Oxidised (I) in orange juice [content of normal (I)=0.056—0.071%] is reduced by H₂S. The titration of (I) with 2:6-dichlorophenol-indophenol is independent of p_H and is not influenced by the presence of 0—20% of CCl₃·CO₂H. F. O. H.

Identification reactions for *l*-ascorbic acid (vitamin-*C*). R. FISCHER (Pharm. Ztg., 1934, 79, 1207—1208, 1263).—In the presence of ascorbic acid

(I), $\text{NHPh}\cdot\text{NH}_2$ (II) in 20% EtOH gives dibenzoylhydrazine. (I) after oxidation (by air, methylene-blue, or I solution) gives crystals, m.p. 192–194°, with (II) in aq. solution. Conditions for the use of these reactions for the micro-detection of (I) are described. The tests can be used for vitamin-C in botanical preps. H. G. M.

Synthesis of ascorbic acid (vitamin-C) by means of tissues *in vitro*. B. C. GUHA and A. R. GHOSH (Nature, 1934, 134, 739).—The production of ascorbic acid (I) by means of the liver, kidney, and spleen tissues of the rat from glucose, fructose, galactose, mannose (II), arabinose, and xylose at 37° in phosphate buffer (III) (p_H 7.4) or in a mixture of (III) and Ringer-Locke solution has been investigated. Only (II) is converted into (I) by all these tissues; significant amounts of (I) are formed. L. S. T.

Vitamin-C and plasma-proteins. A. BOGER and H. SCHRODER (Klin. Woch., 1934, 13, 842–843).—In mild hæmophilia prolonged treatment with "Nateina" (I), a prep. of plant origin containing vitamin-A, -B, -C, and -D with added $\text{Ca}_3(\text{PO}_4)_2$ and lactose, causes a decrease in the coagulation time of the blood to below normal, accompanied by increase in plasma-protein (II) (chiefly albumin). Daily intravenous injections of 100 mg. of ascorbic acid cause a rise in (II) after 3–4 days' treatment, in selected cases of *peliosis rheumatica*, pseudohæmophilia, and simple jaundice. In severe focal nephritis with hæmaturia (I) (8 tablets daily) stops the bleeding and causes (II) to rise in 14 days from 2.9 to 5.1 g. per 100 c.c. The styptic effect of vitamin-C is due to its power of raising the plasma-albumin.

Nutr. Abs. (m)

Urinary excretion of vitamin-C. A. F. HESS and H. R. BENJAMIN (Proc. Soc. Exp. Biol. Med., 1934, 31, 866–868).—Under normal conditions vitamin-C (I) is not excreted in appreciable amounts in human urine and occurs only in small amounts in that of guinea-pigs, rabbits, and rats. Children receiving large amounts of (I) excrete only the surplus after complete saturation of body tissues.

Ch. Abs. (p)

Parallelism between vitamin-C and chlorophyll. A. GIROUD, R. RATSIMAMANGA, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1934, 117, 612–614).—The ascorbic acid (I) contents of plant leaves and tissues vary with their chlorophyll (II) contents. (I) is absent from plants grown in darkness, and diminishes in leaves in the autumn as (II) disappears. R. N. C.

Significance of the reduction of silver salts at the surface of chloroplasts. A. GIROUD, C. P. LEBLOND, and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1934, 117, 614–615).—Chloroplasts (I) reduce a AgNO_3 solution at p_H 4 in a similar manner to that of animal tissues containing ascorbic acid, indicating that it is contained in (I). R. N. C.

Sunlight and the action of vitamins. N. K. BASU (Z. Vitaminforsch., 1934, 3, 254–256).—With rats and guinea-pigs, sunlight enhances the efficacy of vitamin-C and the conversion of carotene into vitamin-A. F. O. H.

Pea test method for auxin, the plant growth-hormone. F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 547–555).—Pea shoots split medially constitute suitable test objects for the detection and determination of auxin (I); the rate of curvature of the split portions approx. \propto the logarithm of the (I) concn. The method is simple and sp. and less sensitive to the effect of light and temp. variations than is the *Avena* coleoptile reaction.

W. O. K.

Effect of ionised air on respiration of green plants. G. B. PORTSMOUTH (Ann. Bot., 1934, 48, 1013–1027).—In ionised air respiration of barley seedlings increased by approx. 2%. A. G. P.

Characteristics of green plants which develop in air enriched with carbon dioxide. M. MOLLARD and A. CRÉPIN (Compt. rend., 1934, 199, 1077–1080).—As the proportion of CO_2 increases in the ratio 1, 5, 25, 100, and 50 the yield of dry substance increases as 1, 2.4, 4.7, 6.5, and 8.8. Sucrose and CO_2 are simultaneously utilised, but the former diminishes the effect of the latter, the ratio being 1, 1.8, 2.6, 3.6, and 3.2. The H_2O content of plants diminishes gradually with increasing CO_2 content of the atm. H. W.

Physiology of apples. XV. Relation of carbon dioxide output to loss of sugar and acid in Bramley's Seedling apples during storage. H. K. ARCHBOLD and A. M. BARTER (Ann. Bot., 1934, 48, 957–966).—Sugar concn. in apples is higher on the "blushed" than on the "unblushed" side, and increases from stalk to calyx and from inside to outside. The decline in sugars and acids of stored apples was > could be accounted for by CO_2 production. A. G. P.

Development of sugar-beet in the first year of growth. A. I. SMIRNOV (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R., 1932, No. 8, 120–125).—The dry matter content of immature leaves varies irregularly, but that of mature leaves increases steadily. The H_2O -absorbing capacity of young leaves is > that of mature ones. Osmotic pressure, d , and viscosity of juice from leaves and roots increase with growth to a max. (in roots) at the ripe stage. Leaves have low starch but high sol. carbohydrate contents. Monosaccharides decrease and disaccharides (I) increase with leaf-growth. Of (I) only sucrose occurs in roots. Ch. Abs. (p)

Nutritional physiology of sugar-cane. T. H. VAN DER HONERT (Arch. Suikerind. Nederl.-Ind., 1932, No. 23, 1539–1608; Bied. Zentr., 1934, A, 4, 485–486).—The effects of variation in concn. of the nutrient media and of deficiency of essential nutrients on the growth of sugar-cane are examined in sand and H_2O cultures. A. G. P.

Nutrient intake of plants (maize and mustard) from undisturbed and from flowing nutrients. E. UNGERER (Z. Pflanz. Düng., 1934, A, 36, 15–26).—Plants grown in dil. flowing media produced less dry matter, and absorbed more Ca and P but less K and N, than those in conc. but stationary media. A. G. P.

Influence of temperature during germination on the subsequent development of certain winter

cereals and its relation to the effect of length of day. O. N. PURVIS (Ann. Bot., 1934, 48, 919—955).—Reduction of the N supply checked vegetative growth but did not affect flowering (I) at any day-length examined. (I) was not affected by limitation of K supply after germination at 1°, but was retarded after germination at 18°. Variation in N and sugar contents of leaves is an effect rather than a contributory cause of flower formation. A. G. P.

Germination of cereal seed in media of different hydrogen-ion concentration and the resultant changes in reaction. F. AICHELE (Diss., Tübingen, 1931; Bied. Zentr., 1934, A, 4, 513).—The influence of the reaction of the medium on germination depends not only on $[H^+]$, but also on the degree of dissociation of other ions involved. In very acid solutions PO_4''' is more injurious to germination than other anions in media of the same p_H . In all cases germinating seeds tend to change the reaction of the medium towards neutrality. A. G. P.

Influence of plants on the concentration of hydrogen ions in the medium. A. KOSLOWSKA (J. Ecol., 1934, 22, 396—419).—Plant species of sp. associations occurring in soils having a relatively narrow range of p_H are able to change the p_H of more alkaline or more acid media towards a mean val. Curves showing the p_H changes by any individual species are of similar character irrespective of the reaction of the soil from which the plants were taken. Species having a wide range of occurrence and not attached to sp. associations produce curves intermediate in type between those of definitely "alkalising" and those of "acidifying" species. Seeds of individual species taken from soils of widely different produce, in garden soils of given p_H , the same curve. Saps from strongly alkalising plants have high buffer power, especially in the acid range. Those of plants widely distributed are but weakly buffered. A. G. P.

Influence of sodium chloride content in the nutrient medium on the development of *Salicornia herbacea* and on the composition of the cell salts of these plants. M. VAN ELJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 556—561).—As $[NaCl]$ in the nutrient medium increased from 0 to 3%, the concn. in the cells of both Na and Cl' increased, but Na/Cl, which was < 1 with 0% NaCl, became > 1 with the higher concns. of NaCl. The $[Ca]$ in the cells decreased with increasing $[NaCl]$, although $[Ca]$ of the medium remained const. W. O. K.

Relation between the hydrogen-ion concentration of soil and plant distribution. H. E. G. EMMETT and E. ASHBY (Ann. Bot., 1934, 46, 869—876).—In soils having p_H 4.7—6.2, the occurrence of *Pteridium aquilinum* and *Vaccinium myrtillus* is unrelated to p_H . A. G. P.

Introduction of heavy hydrogen into the growing organism. O. REITZ and K. F. BONHOEFFER (Naturwiss., 1934, 22, 744).—Algae (*Chlamydomonas*) could assimilate H^2 from H_2O containing $H_2^{18}O$, although the rate of assimilation was about one fifth of that of H_2 . The H^2 after assimilation were directly

linked to C, and could not be exchanged for H^1 by continued washing with H_2O . A. J. M.

Ecological and physiological action of ammonium salts on the clover content of turf. G. E. BLACKMAN (Ann. Bot., 1934, 48, 975—1001).—Reduction in the proportion of clover (I) in frequently cut turf following treatment with $(NH_4)_2SO_4$ is attributed to the toxicity of NH_4^+ . Simultaneous treatment with sucrose delayed the disappearance of (I). Differences between the amount of N applied as NH_4^+ or NO_3^- and that recovered in grass are > the residual NH_4^+ - or NO_3^- -N of soil. Utilisation by bacteria is indicated. A. G. P.

Bursting of cells by polarised sunlight. E. S. SEMMENS (Nature, 1934, 134, 813).—When a hyacinth leaf is exposed to polarised direct sunlight the rapidly-increased turgor due to hydrolysis ruptures the cell wall and the guard-cells burst. Starch disappears. L. S. T.

Effect of elliptically-polarised light on the formation of carbohydrates in leaves. R. H. DASTUR and L. K. GUNJIKAR (Ann. Bot., 1934, 48, 1003—1012).—Carbohydrate in leaves exposed to elliptically polarised light was < that in leaves in non-polarised light. A. G. P.

Avitaminosis in plants and its elimination by vitamin additions. H. BURGEFF (Ber. Deut. bot. Ges., 1934, 52, 384—390).—The transmission of vitamin between host and symbiont is examined. A. G. P.

Evolutionary status of plant families in relation to some chemical properties. J. B. MCNAIR (Amer. J. Bot., 1934, 21, 427—452; cf. A., 1932, 99, 663).—Relationships between the distribution and nature of the alkaloids, fats, and volatile acids in plant families, their habitat, and stage of botanical evolution are examined. A. G. P.

Chemical investigation of Indian medicinal plants. IV. *Teramus labialis*. S. N. CHAKRAVARTI and K. GANAPATI (J. Annamalai Univ., 1934, 3, 216—222).—From the light petroleum (b.p. 30—50°) extract (0.88%) of dry powdered *T. labialis* are isolated a substance, $C_{27}H_{46}O_2$ (I), m.p. 83—84°, and a cryst. substance, $C_{27}H_{46}O_2$ (II), m.p. 129° (reduces Fehling's solution after hydrolysis); the Et_2O extract (0.79%) contains (I) and acidic material; the $CHCl_3$ extract (0.49%) contains an acid and a substance, m.p. 92—93°, and the $EtOH$ extract (2.39%) affords a substance, m.p. 123°, a crude acid, m.p. 169—175°, and (?) a Ca salt; the extract (4.61%) with 70% aq. $EtOH$ also contains protein, carbohydrate, K and Ca salts. An attempt to isolate the glucoside by extraction with $CaCO_3$ -boiling 70% or 95% $EtOH$ afforded a cryst. substance, m.p. > 300°, a substance, m.p. 83°, and a mixture, m.p. 85—101°, the presence of glucose being indicated by the formation of an osazone, m.p. 209°. (I) with warm HNO_3 - H_2SO_4 gives a (?) NO_2 -derivative, m.p. 102°, and with boiling Ac_2O -1 drop H_2SO_4 , a crude product, m.p. 167°. With material collected at a different period of the year (II) could not be detected, but a substance, m.p. 143° (C 82.55; H 17.6%), was obtained, other variations also being observed. J. W. B.

[Constituents of] *Canchalagua Panamena*. R. A. BENEDETTI (J. Amer. Pharm. Assoc., 1934, 23, 1012—1013).—Extraction of the dried plant (therapeutically important as a febrifuge) by Et_2O , EtOH , and H_2O yields a bitter glucoside, free acids, sugar, wax, gum, tannin, and green pigment. Alkaloids are absent.

A. E. O.

Chemical constituents of Irish lichens. *Buellia canescens*. I. T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1934, 21, 67—72).—The dried lichen (300 g.) gave 9.0 g. of Et_2O extract. The portion insol. in light petroleum after washing with Et_2O and crystallisation from C_6H_6 and EtOH gave a yellow cryst. product, m.p. 205—206°, and *diploicin* (colourless needles from C_6H_6), $\text{C}_{16}\text{H}_{10}\text{O}_5\text{Cl}_4$ (.), m.p. 232° (*Ac* derivative, m.p. 234—235°). A compound, m.p. > 250°, was obtained by further EtOH extraction of the Et_2O -extracted residue.

P. G. M.

Chemical composition of maize kernels. N. V. VOITCHISHIN (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R., 1932, No. 9, 26—33).—Vals. for protein, starch, and fats in grain with and without embryo are recorded for 3 successive year's crops. CH. ABS. (p)

Chemical examination of the liana "Efiri." I. Localisation in the plant of a substance showing reactions of alkaloids. II. Presence of *cyclohexanepentaol* in "Efiri" stems. E. CASTAGNE (Congo, 1934, 41—48, 341—347; Chem. Zentr., 1934, ii, 76).—I. Stems and leaves of this antipyretic plant contain materials giving alkaloid reaction with I in KI.

II. *d*-Quercitol was obtained by extraction of leaves with boiling 95% EtOH .

A. G. P.

Variations in the alkaloid content of lupins. N. IVANOV and M. LAVROVA (Trudy prikl. Bot., 1931, 25, 291—303; Bied. Zentr., 1934, A, 4, 488).—The N content of blue lupins ranged between 3.9 and 6.1%, and of yellow lupins, 5.3—7.2%. The alkaloid (I) contents showed parallel variations. Plants from northern areas contained less N and (I). The latter is probably a by-product of increased N nutrition.

A. G. P.

Alkaloids accompanying nicotine and methods for determining them. A. SCHMUCK (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 63—66).—Various methods for determining nicotine indicate the presence of other alkaloids in *N. americana*.

CH. ABS. (p)

Decomposition of nicotine in the tobacco plant. G. S. ILJIN (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1933, No. 104, 141—145).—Treatment of etiolated leaves and seedlings with PhMe vapour caused decomp. of nicotine which was taken up by the metabolic activities of the plant.

CH. ABS. (p)

Conductivity determinations of nicotine and ammonia in tobacco. A. N. KHARIN (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 31—45).—The conductivity method of titrating nicotine and NH_3 in aq. distillates from tobacco is rapid, but results may be 10% > those of the pptn. method.

CH. ABS. (p)

Determination of nicotine in tobacco by measuring surface tension. G. A. KORZHENOV-

SKI (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 47—61).—Tobacco distillates are examined by the capillary manometric titration method. Results were > those of the gravimetric method.

CH. ABS. (p)

Fractionation of resins of tobacco and makhorka. A. SCHMUCK and V. SHIROKAYA (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 77—87).—The residue from citric acid extraction of makhorka resin contains melanin 11.5, hydrocarbons 9.1, varnish-like substances 10.5, α -, β -, and γ -tabacenic acids 1.2, 9.0, 5.9, phenols 3.3, complex Et_2O fraction 39.2%.

CH. ABS. (p)

Determination of citric acid in tobacco. M. P. PIATNITZKI (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 67—70).—In the pentabromoacetone (I) method the formula used should be, wt. citric acid = $0.424 \times \text{wt. of (I)} + 7$. CH. ABS. (p)

Determination of citric and malic acids in tobacco and makhorka. A. SCHMUCK (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 71—75).—Piatnitzki's method is modified by use of HCl for H_2SO_4 and of COMe_2 for Et_2O . The solution containing citric (I) and malic (II) acids is divided. Total acidity is determined in one portion and (I) in the second. (II) is calc. by difference.

CH. ABS. (p)

Carbohydrates of tobacco. A. SCHMUCK (Vsesoy. Inst. Tabachn. Prom. Krasnodar, 1934, No. 109, 3—14).—In dry and fermented tobaccos fructose is the primary sugar. Amounts of glucose, mannose, galactose, and other sugars present are negligible.

CH. ABS. (p)

Carbohydrates and carbohydrate metabolism in leaves. III. Determination of glucose and fructose in mixed solutions; application to extracts of plant organs. H. SCHROEDER and F. HERMANN (Planta, 1934, 22, 468—489).—A no. of analytical methods are compared. The distribution of hexoses and sucrose in *Tropaeolum majus* is examined.

A. G. P.

Intracellular processes during formation of mucilage in the seeds of *Linum usitatissimum*, L., and in the roots of *Althaea officinalis*, L. R. JARETZKY and H. ULBRICH (Arch. Pharm., 1934, 272, 796—811).—By examination of stained sections mucilage is shown to be formed at the expense of starch in the materials named in the title, but an intermediate, "pre-mucilage" stage intervenes. The nuclei, however, also play some part in the process, possibly by providing activating substances.

R. S. C.

Crystalline erythrodextrin. L. KÖHLER-HOLLANDER (Z. physiol. Chem., 1934, 228, 249—255).—Hydrolysis of amyloamylose by salivary amylase to a "maltose val." of 16% yields a cryst. *erythrodextrin*, chars at 220—250°, $[\alpha]_D^{25} + 170^\circ$ in H_2O , giving a reddish-violet I colour and comprising 18 glucose units (from reduction val.). Other non-cryst. fractions contain 24 and probably 12 glucose units, respectively.

J. H. B.

Starch of the *Floriaceae*. H. COLIN (Compt. rend., 1934, 199, 968—970).—Starch grains (I) of

Lithothamnion calcareum are birefringent and give a brownish-red colour with I, but not after treatment with pancreatic enzyme at 40° during some min. (I) closely resembles glycogen. J. L. D.

Rubber resins. A. J. ULTEE (Rec. trav. chim., 1934, 53, 953—960).—In addition to substances already isolated, the latex of *Plumiera acutifolia*, Poir., contains cerotyl- and acetyl-lupeol, β -amyryn, and lupeol (I); of *Ficus Benjaminia*, Linn., α -acetyl-amyryn (II); of *F. glomerata*, Roxb., principally (II), some β -acetyl-amyryn (III) and (I); of *F. superba*, Miq., an alcoholate of cinnamic acid; and of *F. toxicaria*, Linn., and *F. fulva*, Reinw., compounds of stearic acid and (III). F. R. S.

Occurrence of furan derivatives in volatile oils. B. S. RAO and K. S. SUBRAMANIAN (Proc. Indian Acad. Sci., 1934, 1, A, 189—200).—Oil from leaves of *Clausena willdenovii* consists principally of 3 furan derivatives, α -clausenan (I) $C_{10}H_{12}O$, di- α -clausenan $C_{20}H_{24}O_2$, and β -clausenan $C_{10}H_{14}O$. Reactions and properties are described. (I) is determined as the ferro- or ferri-cyanic additive compound. A. G. P.

Acids of croton oil.—See this vol., 64.

Fat of *Cortinellus Shiitake*, P. Henn. M. SUMI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1257—1264).— Et_2O -extraction of the dried material yielded 1.6% of fat [30% unsaponifiable, the saponifiable fraction yielding palmitic (16%), cerotic (2%), linoleic (64%), and oleic acid (8%)]. Small amounts of fungi-, neo-, and ergo-sterol, and ceryl alcohol (?), but not of stearic or linolic acid, were isolated. F. O. H.

Fat in barley and its malting products. G. GAMPERL (Diss., Munich, 1931; Bied. Zentr., 1934, A, 4, 485).—From the fat of barley, malt, and spent grains are isolated sitosterol, palmitic acid, trilinolein, and a monoaminomonophosphatide. A. G. P.

Identity of globulins from the seeds of some *Cucurbitaceae*. H. LEONTJEV (Biochem. Z., 1934, 274, 163—166).—The similarity in vals. for viscosity, refraction, surface tension, tyrosine and tryptophan contents, and of the racemisation curves of globulin (I) solutions prepared from water-melons, melons, and gourds indicates that the (I) of the various types of *Cucurbitaceae* are probably identical. P. W. C.

Glutamine in the tomato plant. H. B. VICKERY, G. W. PUCHER, and H. E. CLARK (Science, 1934, 80, 459—461).—Glutamine (I) is formed in considerable amount in tomato plants grown in media which provide NH_3 as the sole source of N. (I) accumulates in the stems and more is formed in NH_3 than in NO_3^- cultures. L. S. T.

Solubility of phosphorus compounds of wheat flour and the ability of phytin to combine with protein substances therein. H. WIAZOWNICKA (Bull. Acad. Polonaise, 1933, B, 107—122).—The distribution of inorg., phytin-, nuclein-, and lecithin-P and of sol. N in flour is examined by extraction with NaOH and HCl of varying concn. The isoelectric point of extracted gliadin (I) was p_H 6.2—6.4. The

phytin prep. corresponded with a Ca_2 inositoltetraphosphate. Phytin and (I) form insol. compounds. A. G. P.

Hydrolysis of phytin compounds from seeds of hemp, beans, flax, horse chestnut, and wheat and from rye embryos. W. JAROSZ (Bull. Acad. Polonaise, 1933, B, 123—133).—Effects of acid and of heating on seed extracts are examined in relation to determinations of org. and inorg. P (I) by the molybdate method. The (I) in aq. extracts is $>$ that of 0.1% HNO_3 extracts, and increases steadily on boiling (to 70—80% of total P in 64 hr.). Heating at 60° for 5 hr. produces little change. Decomp. of org. P on boiling with $<$ 0.1% HNO_3 was more rapid than with higher concns. In alkaline solutions decomp. was much less rapid than in equiv. acid solutions. A. G. P.

Radiotropism in plants as shown by seedlings of *Pharbitis hispida*. V. KILLIAN (Planta, 1934, 22, 462—467).—Unilateral exposure to radioactive emanation results initially in a positive and later in a negative curvature of the seedlings. A. G. P.

Photometric determination of nitrogen. R. A. CLEGHORN and L. JENDRASSIK (Biochem. Z., 1934, 274, 189—193).—N in org. matter (e.g., urine) is determined by conversion into NH_3 by heating with H_2SO_4 and H_2O_2 as in the Kjeldahl method (complete removal of CO_2 essential) and treatment with Nessler solution containing 8 g. of KI per 100 c.c. The colour is measured with the step photometer. W. McC.

Determination, with the glass electrode, of the hydrogen-ion concentration of biological fluids. G. HAUGAARD (Biochem. Z., 1934, 274, 231—252).—If made of suitable glass the electrode (I) gives satisfactory results (II) in determining the $[H^+]$ of biological fluids. (II) differ by only 0.02—0.03 p_H unit from those obtained with the H_2 electrode (III). (I) may be used in cases where it is difficult or impossible to use (III). W. McC.

Electrometric determination of chlorides in the ash and sap of plants and in ground waters.—See this vol., 52.

Photometric determination of calcium and oxalic acid.—See this vol., 54.

Modification of Macallum's method for histochemical detection of potassium. V. D. MARZA and L. CHIOSA (Compt. rend. Soc. Biol., 1934, 117, 524—526).—After pptn. with $Na_3Co(NO_2)_6$ the sections are washed with 50% EtOH, treated with $(NH_4)_2SO_4$, and mounted in Canada balsam. H. G. R.

Determination of potassium in body-fluids. L. JENDRASSIK and F. TAKACS (Biochem. Z., 1934, 274, 194—199; cf. A., 1933, 687; 1934, 269).—Improvements in previously described procedure enable the K content of body-fluids to be determined without destruction of org. matter. The ppt. is separated by filtration or by centrifuging and the subsequent determination is volumetric, colorimetric, or photometric (step photometer). W. McC.

Determination of amino-acids and polypeptides.—See this vol., 102.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1935.

General, Physical, and Inorganic Chemistry.

Excitation of Balmer series by electrodeless discharge. H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1934, 10, 450—451).—Dry H_2 was circulated at low pressure through a tube 10 cm. diam., surrounded by a coil of thick wire. Discharges from a 125-kv. transformer of frequency 6×10^6 cycles per sec. were passed between Zn balls. C. W. G.

Influence of the Stark effect on the fine structure of the Balmer lines of hydrogen. N. P. HEYDENBURG (Physical Rev., 1934, [ii], 46, 1069—1075).—The possibility of small electric fields, present in a discharge tube, accounting for the discrepancies between observed and calc. doublet splitting of the Balmer lines is investigated. Doppler curves are plotted for each component and superimposed. For the H_β line, fields > 100 volts per cm. do not explain Houston's results (cf. A., 1934, 467). A field of 500 volts per cm. agrees with Gibbs' results (cf. *ibid.*, 575) for H_α , but not for H_β . N. M. B.

Spectrum of the hydrogen molecule. I. The $3, 4d^3\Sigma, \Pi, \Delta \rightarrow 2p^3\Pi$, and $3s^3\Sigma \rightarrow 2p^3\Pi$ systems. O. W. RICHARDSON and T. B. RYMER (Proc. Roy. Soc., 1934, A, 147, 24—47).—Several new bands and a new band system ending on the lowest triplet state are described. These include: (1) the $4d^3\Delta_a \rightarrow 2p^3\Pi$ system; (2) the substitution of new $v' = 2$ and 3 levels for those given by Richardson and Davidson (A., 1933, 1219); (3) the non-diagonal lines of $4d^3\Sigma, \Pi, \Delta_a$, and $\Delta_b \rightarrow 2p^3\Pi$; (4) extension of the $3s^3\Sigma \rightarrow 2p^3\Pi$ system to the $v' = 0, 2, 3$, and 4 (?) levels; and (5) extension of the $3d^3\Sigma\Pi\Delta$ complex $\rightarrow 2p^3\Pi$ to the $v', v'' = 4', 4''$ levels. L. L. B.

Spectrum of H_2 . II. Band systems due to transitions from four new triplet states to $2p^3\Pi$. III. New bands and band systems ending on $2s^3\Sigma$ and an extension of the singlet system $^1Q \rightarrow 2p^1\Sigma$. O. W. RICHARDSON and T. B. RYMER (Proc. Roy. Soc., 1934, A, 147, 251—272, 272—292).—II. Four new band systems from hitherto undiscovered upper triplet states to $2p^3\Pi$ are described. The consts. and properties of the upper states are worked out and the possible electronic configurations considered.

III. Three new band systems ending on $2s^3\Sigma$ and coming from hitherto undiscovered upper states are described. An account is given of the $v' = 0$ progression of the singlet system $^1Q \rightarrow 2p^1\Sigma$, and the progression previously known (A., 1929, 616, 731) is shown to be $v' = 1$. The band consts. and properties of the upper states are worked out. L. L. B.

Heat of dissociation of hydrogen molecule deduced from a new ultra-violet resonance band sequence. Heats of dissociation of HH^2, H_2^2 , and HCl . H. BEUTLER (Z. physikal. Chem., 1934, B, 27, 287—302).—Discharge through A containing traces of H_2 reveals lines due to H_2 which constitute a resonance-band system leading from $2p\sigma^1\Sigma_u^+, v' = 10, K' = 2 \rightarrow 1s\sigma^1\Sigma_u^+, v'' = 1 - 14, K'' = 1$ and 3. Excitation is effected by absorption of the A line 1066.4 \AA . by mols. at the level $v'' = 2, K'' = 1$. The extension of the series of vibrations v'' by $v'' = 13$ and 14 shows the no. of v'' vibrational levels to be finite and permits a more exact extrapolation giving heat of dissociation of $H_2, 102.68 \pm 0.12 \text{ kg.-cal}$. The vals. $103.50 \pm 0.12, 104.48 \pm 0.12$, and $101.63 \pm 0.22 \text{ kg.-cal}$. are calc. for the heats of dissociation of HH^2, H^2 , and HCl , respectively. R. C.

Fine structure of $H^2\alpha$. F. H. SPEDDING, C. D. SHANE, and N. S. GRACE (Physical Rev., 1933, [ii], 44, 58).—Spectroscopic measurements of H_2O containing 50% H^2O show that $H^1\alpha$ and $H^2\alpha$ are widely separated, each showing its own system of interference fringes. Preliminary vals. for e/m are $< 1.758 \times 10^7 \text{ e.m.u}$. L. S. T.

Spectrum of deuterium? F. SANFORD (Science, 1934, 80, 478). L. S. T.

Influence of the polarisation of the inner electron in the field of the outer [electron] on the spectral terms of a two-electron system (especially helium). G. LUDWIG (Helv. phys. Acta, 1934, 7, 273—284; Chem. Zentr., 1934, ii, 722).—Theoretical. H. J. E.

Inert gas molecules. K. G. EMELEUS and O. S. DUFFENDACK (Physical Rev., 1933, [ii], 44, 945).—The behaviour of the He band spectrum in discharge tubes carrying small currents indicates that the He mol. is actually produced under discharge conditions from one normal and one metastable He atom according to the scheme $He(1^1S) + He(2^1S) \rightarrow He_2(2^1\Sigma)$. The possibility of observing the visible He band spectrum is closely associated with the metastability of the $2^3\Sigma$ level. The band spectra of the mols. Ne_2, A_2 , etc. will be difficult, if not impossible, to excite. L. S. T.

Li^+ fine structure and wave functions near the nucleus. J. A. WHEELER and G. BREIT (Physical Rev., 1933, [ii], 44, 948).—The fine structure of the $(1s 2p)^3P$ level of Li^+ has been calc. L. S. T.

Be III $1snp \ ^1P_1 - 1s^2S_0$ series. P. G. KRUGER and F. S. COOPER (Physical Rev., 1933, [ii], 44, 418).—

Wave-lengths, term vals., and the series limit are calc. The ionisation potential of Be III is 153.012 volts. L. S. T.

Ionisation potential of Be III. B. EDLEN (Physical Rev., 1933, [ii], 44, 778).—New investigations confirm the author's previous val. (A., 1931, 539) for the series limit, which is $1s^2\ ^1S_0 = 1,241,180\text{ cm.}^{-1}$ (see above). L. S. T.

Magnetic dipole radiation and the atmospheric absorption bands of oxygen. J. H. VAN VLECK (Astrophys. J., 1934, 80, 161—170).—The atm. bands of O_2 are best interpreted as magnetic dipole radiation rather than as ordinary dipole or quadrupole radiation. L. S. T.

Regularities in the radiation emitted by the positive column in the neon discharge. H. KREFFT and E. O. SEITZ (Physikal. Z., 1934, 35, 980—983).—The spectral energy distribution of the red Ne lines in the positive column is characteristic and easily reproducible, but the abs. efficiency depends on experimental conditions. A. J. M.

Widening and displacement of absorption lines. C. FUCHTBAUER [with P. SCHULZ, A. F. BRANDT, and F. GOSSLER] (Physikal. Z., 1934, 35, 975—977).—The displacement of the absorption line of the principal series of K, Na, and Cs up to the 23rd and 26th members by the addition of He, Ne, and A was investigated. The curves for He and Ne show max. in the violet, whilst A produces only red displacement. The limiting vals. are the same for Na and K. The effective cross-section of He for very slow electrons obtained from the above data is $15.5\text{ cm.}^2\text{ per cm.}^3$. The effect of A and He on the width of the higher series lines of Na was investigated. The width attains a max at about $1s - 6p$. A. J. M.

Isotope effect in the spectrum of neon. II. H. NAGAOKA and T. MISHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 223—231; cf. A., 1930, 1337).—The relative intensities of the lines of Ne^{20} and Ne^{22} are not in the ratio of the relative amounts present. The isotope effect ($\delta\nu/\nu$) is 47.2×10^{-7} for $1s_2 - 2p_h$ terms and is almost const. at 34.8×10^{-7} for $1s_{3,4,5} - 2p_h$ terms. The relative intensities of some lines, especially the 5852 Å. ($1s_2 - 2p_1$) line, vary with changes in frequency of excitation between 50 and 167 cycles. Lines of the Ne isotopes form good wave-length standards if the difficulty of self-reversal is overcome. J. W. S.

Effect of pressure on the higher terms of the alkalis. E. AMALDI and E. SEGRÈ (Nuovo Cim., 1934, 11, 145—156; Chem. Zentr., 1934, ii, 724).—Data for the displacement of the higher terms in the Na and K absorption series, due to addition of H_2 , N_2 , He, and A, are recorded and discussed. H. J. E.

Pressure displacement of the higher lines of spectral series. E. FERMI (Nuovo Cim., 1934, 11, 157—166; Chem. Zentr., 1934, ii, 724).—A theoretical discussion of Amaldi and Segrè's results (see above). H. J. E.

Absorption spectrum of rhombic sulphur in polarised light. H. G. SMITH and R. H. CRADDOCK (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 173—

176).—The absorption spectrum and pleochroism of rhombic S between 4000 and 5800 Å. have been observed for 4 directions of the electric vector of the incident light relative to the crystal axes. The differences of the fractional transmissions for the various directions are relatively small, despite the marked anisotropic structure of the crystals, but the change in the long wave-length limit of the ultra-violet absorption exhibits marked variations. H. F. G.

Structure of discontinuities in the absorption of some gases in the region 10—100 Å. J. A. PRINS (Physica, 1934, 1, 1174—1180; cf. A., 1934, 712).—Measurements for A, CCl_4 , and N_2 are recorded and discussed. H. J. E.

Hyperfine structure of spectrum lines of manganese arc in vacuum. I. W. MOHAMMAD and P. N. SHARMA (Phil. Mag., 1934, [vii], 18, 1144—1149; cf. White, A., 1930, 970).—Structure data for 20 lines in the visible region are reported. N. M. B.

Persistence of some lines due to impurities in iron. R. BRECKPOT and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 290—298).—In connexion with quant. spectral analysis, the spectra obtained when known amounts of impurities (Cu, Ba, Pb, Bi, Sn, Sb) in an Fe base are used in the method (A., 1934, 857, 858) are examined. A. J. M.

Hyperfine structure of the arc lines of molybdenum and copper. L. SIBAIYA (Proc. Indian Acad. Sci., 1934, 1, A, 321—324).—Lines arising from transitions to the ground state in the arc spectra of Cu and Mo in a Schüller tube are self-reversed, but give correct vals. for the hyperfine structure components. Cu^{63} and Cu^{65} each have a nuclear spin of $3/2$, and the m^2D terms show positive isotope shift. The Mo lines $4d^5 4s^7 S_3 - \gamma^7 P_{2,3,4}$ and $4d^5 4s^7 S_3 - z^7 P_{2,3,4}$ are all singlets, whereas a nuclear moment of $\frac{1}{2}$ for Mo^{95} and Mo^{97} demands at least two satellites. It is concluded that the interval factors are negligibly small. J. W. S.

Standard wave-lengths in the copper spectrum in the region 80—650 Å. F. S. COOPER and P. G. KRUGER (Physical Rev., 1933, [ii], 44, 324).—Several hundred lines in the spectrum of Cu VI, VII, VIII, and IX have been photographed, and standard wave-lengths calc. The spectra of Co, Ni, Cu, and Zn have also been photographed in this region, and a partial analysis has been made. L. S. T.

Absorption spectrum of arsenic. G. E. GIBSON and A. MACFARLANE (Physical Rev., 1934, [ii], 46, 1059—1068; cf. Swings, A., 1933, 823).—Data and vibrational analyses for 80 band heads in the range 2200—2750 Å., when ultra-violet light is absorbed by As vapour heated to 1100° , are given. N. M. B.

Arc spectrum of selenium. J. E. RUEDY and R. C. GIBBS (Physical Rev., 1934, [ii], 46, 880—888).—Measurements for 510 lines in the range 300—11,000 Å. of the arc spectrum of Se excited by a positive column discharge in He, and classifications for 391 of these lines, are tabulated. All known Se I terms and numerical vals. and perturbations are listed. N. M. B.

Arc spectrum of selenium. K. R. RAO and S. G. KRISHNAMURTY (*Current Sci.*, 1934, 3, 200).—Four of the levels of Se I previously reported (*A.*, 1934, 935) are now definitely assigned. L. S. T.

Resonance series in selenium vapour. I. S. PASIERBIŃSKI (*Acta phys. polon.*, 1932, 1, 503—511; *Chem. Zentr.*, 1934, ii, 199).—Three new resonance series are recorded. H. J. E.

Spectrum of niobium IV. R. J. LANG (*Physical Rev.*, 1933, [ii], 44, 325).—The spectrum of Nb has been photographed from 2500 to 250 Å. in the vac. spark and from 2500 to 1250 Å. in the spark in N₂. The lines of Nb III and Nb IV have been separated, and further terms for Nb IV located. L. S. T.

Hyperfine structure and nuclear moment of niobium. N. S. GRACE and S. S. BALLARD (*Physical Rev.*, 1933, [ii], 44, 128).—The hyperfine structure of the lines 4059, 4675, 5344, and 4672 Å. in the spectrum of Nb I indicates a nuclear moment $\geq 7/2$ for Nb. L. S. T.

Nuclear spin of iodine. S. TOLANSKY (*Nature*, 1934, 134, 851—852).—The greater detail given by the arc and spark spectra of I excited in a cooled hollow cathode discharge establishes the nuclear spin as $5/2$ (cf. *A.*, 1932, 787). L. S. T.

Absorption of light in gases. R. W. DITCHBURN and H. J. J. BRADDICK (*Nature*, 1934, 134, 935).—Addition of He reduces the absorption of light by Cs vapour. In general, the absorption of a gas cannot be assumed \propto the concn. of the active atom or mol. (cf. this vol., 138). Many photochemical and astrophysical calculations may thus need revision. L. S. T.

Series of caesium atoms in an electric field. N. T. ZÉ and C. S. PRAW (*Nature*, 1934, 134, 1010).—The effect of an electric field on the absorption spectrum of Cs is described. L. S. T.

Hyperfine structure of the rare earths. N. S. GRACE (*Physical Rev.*, 1933, [ii], 44, 603).—A discussion of King's results (*A.*, 1931, 7, 780; 1932, 440). L. S. T.

Arc spectrum of europium. H. N. RUSSELL and A. S. KING (*Physical Rev.*, 1934, [ii], 46, 1023—1024).—Term vals. and lines, intensities, and temp. classifications are tabulated. The principal ionisation potential is 5.64 volts. N. M. B.

Nuclear moment of thulium (Tu¹⁶⁹), yttrium (Y⁸⁹), and rhodium (Rh¹⁰³). H. SCHÜLER and T. SCHMIDT (*Naturwiss.*, 1934, 22, 838—839).—Hyperfine structure investigations of the spectrum of Tu in the wave-length range 6500—4000 Å. indicate that the splitting is considerably smaller than in the case of other rare-earth elements of odd at. no., the greatest val. being 55×10^{-3} cm.⁻¹ Many lines consist of two equally strong components. The nuclear moment of Tu is $\frac{1}{2}$. It is probable that Tu has a very small nuclear magnetic moment (I). Within the same wave-length range the spectra of Y and Rh show a trace of a structure. These elements must have a very small (I). A. J. M.

Structure of spectra of hafnium and tungsten. A. T. WILLIAMS (*Compt. rend.*, 1934, 199, 1201—1202).—Data are classified. H. J. E.

Second spectrum of hafnium (Hf II). W. F. MEGGERS and B. F. SCRIBNER (*J. Res. Nat. Bur. Stand.*, 1934, 13, 625—657).—Data for > 1000 lines and Zeeman data for 207 lines are tabulated and classified. The ionisation potential of Hf is 14.8 volts. H. J. E.

Hyperfine structure and nuclear spin of tantalum. N. S. GRACE and E. McMILLAN (*Physical Rev.*, 1933, [ii], 44, 325, 949—950).—Most of the Ta arc lines have structure. The structures of the lines, especially of 5997.24 and 6020.69 Å., show that the nuclear moment of Ta is $7/2$. L. S. T.

Hyperfine structure and nuclear moment of gold. J. WULFF (*Physical Rev.*, 1933, [ii], 44, 512).—Many of the lines in the spectra of Au I and Au II show four components. The levels involved can be relegated to a hyperfine term system if a nuclear moment of $3/2$ be assumed (cf. *A.*, 1931, 1103). The interval rule is better satisfied in a no. of levels for a val. of $5/2$, but from the nature of the coupling involved this val. is unlikely. The splitting of the resonance lines agrees with previous results. L. S. T.

High series terms in the arc spectrum of mercury. I. WALTERSTEIN (*Physical Rev.*, 1934, [ii], 46, 874—879).—Wave-lengths, wave-nos., and term vals. are tabulated for the higher members in the singlet and triplet diffuse and sharp series in the spectrum of luminous Hg vapour drawn into a low-pressure chamber. The 3S_1 , 1S_0 , 1D , and 3D terms develop as series following a Ritz formula. N. M. B.

Paschen-Back effect. II. JJ-coupling (approx.). J. B. GREEN and R. A. LORING (*Physical Rev.*, 1934, [ii], 46, 888—893; cf. *A.*, 1934, 467).—The Paschen-Back effect of the $\lambda\lambda$ 5789—5790, 3662—3663, 3131—3132, and 2967—2968 Hg lines was in good agreement with Houston's theory. The red shift of the central component of λ 5790 at several field strengths approx. \propto (field strength)². g -vals. are calc. from Zeeman effect measurements of several other Hg lines. N. M. B.

Role of absorption of the exciting line in resonance spectra. W. KESSEL (*Acta phys. polon.*, 1933, 2, 91—95; *Chem. Zentr.*, 1934, ii, 198).—The contribution of the various components of the green Hg line to the excitation of the resonance series of I and Te vapour has been examined. H. J. E.

Second-order Zeeman effect in the arc spectrum of mercury. J. B. GREEN and R. A. LORING (*Physical Rev.*, 1933, [ii], 44, 325). L. S. T.

Physical properties of the radiation from the discharge in mercury vapour. H. KREFFT (*Physikal. Z.*, 1934, 35, 978—980).—The abs. radiation efficiency of 29 series lines in the Hg discharge was determined for definite current strengths, the pressure of the Hg vapour being varied continuously between 0.01 and 1000 mm. The radiation emission is a reproducible property of the Hg discharge with respect to spectral energy distribution and abs. efficiency.

The behaviour of the continuous background with regard to changes of v.p. and current strength was investigated.
A. J. M.

Re-emission in the fluorescence bands of mercury vapour. (MISS) A. FATERSON (Bull. Acad. Polonaise, 1934, A, 239—241).—Hg vapour at 450° and 100 mm., excited by Zn and Cd sparks, shows re-emission of the 2139, 2100, and 2164 Å. Zn lines and of the 2144 Å. Cd line, all in the region of intense mol. absorption. The re-emission varies in intensity with pressure in the same way as the fluorescence bands. The phenomenon is not due to anomalous at. diffusion because the separation of re-emitted and resonance lines is too great (200 Å.).
J. W. S.

Effect of hydrogen on the afterglow in mercury vapour. M. M. MANN and W. M. NIELSEN (Physical Rev., 1934, [ii], 46, 991—994).—With no potential applied to a grid in the luminous Hg vapour stream, the introduction of H₂ at a pressure $\times 4 \times 10^{-4}$ mm. slightly decreased the intensity of the afterglow; at higher pressures the lines increase in density. With grid potentials of 3.5—4 volts, H₂ at a pressure $\times 4 \times 10^{-4}$ mm. markedly decreased the intensity of the afterglow.
N. M. B.

Influence of nitrogen and carbon dioxide on the absorption spectrum of mercury vapour. R. W. WOOD and H. W. STRAUB (Physical Rev., 1933, [ii], 44, 1030).—The absorption spectra of Hg vapour with added gases has been investigated at 170—370°. A broad absorption band appears on the short-wave side of the resonance line 2536 Å. when CO₂ or N₂ is added.
L. S. T.

Isotope shift of thallium. G. BREIT (Physical Rev., 1933, [ii], 44, 418—419).—Shifts are appreciable only for $6p_{1/2}$ and $6p_{3/2}$ and are nearly the same for these two terms (cf. A., 1933, 2, 760).
L. S. T.

Forbidden lines in the arc spectrum of lead. H. NIEWODNICZANSKI (Physical Rev., 1933, [ii], 44, 854).—The forbidden lines 4618.0, 5312.7, 4659.4, and 7330 Å. have been observed when undamped high-frequency discharges are excited in rarefied Pb vapour + He or Ar.
L. S. T.

Specific isotope effect in the lead spectrum. B. H. DICKINSON (Physical Rev., 1933, [ii], 44, 329).—The sp. isotope effect for the separation of Pb²⁰⁶ and Pb²⁰⁸ levels in four different configurations of the Pb atom has been calc.
L. S. T.

Spectrum and ionisation potential of radium. H. N. RUSSELL (Physical Rev., 1934, [ii], 46, 989—990).—Term vals. and designations confirm a new interpretation of the connexion between the two groups of terms in Ra I (cf. Rasmussen, A., 1934, 340). The first ionisation potential is 5.252 volts.
N. M. B.

Bands at 4450 and 4180 Å. in the spectra of the night sky and of the aurora. H. HAMADA (Nature, 1934, 134, 801).—In addition to well-known bands, the spectrum of N₂ excited by weak currents at low pressure has bands at 4723.5 (weakest), 4432.3, and 4165.9 Å., each with apparently four intensity max. Addition of He or Ne has no effect, but A almost quenches the bands. At low temp. their intensity is

enhanced. The last two may be identical with the Rayleigh bands X₁ and X₂ of the night sky, and possibly of the aurora.
L. S. T.

Spectra and latent energy in flame gases. A. EGERTON and A. R. UBBELOHDE (Nature, 1934, 134, 848).—The luminosity or afterglow of flame gases is probably due to metastable mols., but the energy associated with them is probably < that ascribed to them by David (A., 1934, 1288).
L. S. T.

Spectra and latent energy in flame gases. W. T. DAVID (Nature, 1934, 134, 848).—A reply (see above).
L. S. T.

Sparking potentials at low pressures. S. S. CERWIN (Physical Rev., 1934, [ii], 46, 1054—1056).—Sparking potentials were determined as a function of air pressure in the range 1—0.06 mm. for spark lengths 2—10 mm. between outgassed Ni electrodes in air, and gave vals. up to 80,000 volts, agreeing approx. with Paschen's law.
N. M. B.

Classical analogue of electron spin. W. WESSEL (Z. Physik, 1934, 92, 407—424).
A. B. D. C.

Origin of K_α satellites. E. H. KENNARD and E. RAMBERG (Physical Rev., 1934, [ii], 46, 1040—1046).—Proposed explanations and conditions affecting these are examined for various elements.
N. M. B.

Structure of the K line of beryllium and conductivity electrons. A. HAUTOT (Compt. rend., 1934, 199, 1399—1401).—The width and intensity of the K line of Be can be interpreted satisfactorily on the hypothesis of free electrons.
J. W. S.

Self-consistent field and some X-ray terms of the sodium atom. E. H. KENNARD and E. RAMBERG (Physical Rev., 1934, [ii], 46, 1034—1040).—Self-consistent field functions are tabulated for neutral Na and for six internally ionised states. The corresponding calc. at. energies lead to agreement within 0.1% for the observed and calc. frequency of Na K_α.
N. M. B.

Direct and fluorescence excitation of the K level in thick copper targets. K. B. STODDARD (Physical Rev., 1934, [ii], 46, 837—842; cf. A., 1933, 657).
N. M. B.

Depth distribution of origins of characteristic X-rays from thick targets. P. KIRKPATRICK and D. G. HARE (Physical Rev., 1934, [ii], 46, 831—836).
N. M. B.

Widths of the L series lines and of the energy levels of Au (79). F. K. RICHTMYER, S. W. BARNES, and E. RAMBERG (Physical Rev., 1934, [ii], 46, 843—860).—An expression is found, based on the Weisskopf-Wigner theory of the shape of spectral lines, for the shape of an X-ray absorption discontinuity. Data are given, in the range 7.6—20.8 volts, on the widths of 23 Au L series lines; from these the widths of the several L, M, N, and O states of Au are calc.
N. M. B.

Probabilities of L ionisations of Au by cathode rays. D. L. WEBSTER, L. T. POCKMAN, and P. KIRKPATRICK (Physical Rev., 1933, [ii], 44, 130—131).—Probabilities of ionisation of L₂₂ and L₂₁ electrons have been measured as functions of cathode-

ray energy by intensities of the $L\alpha$ and $L\beta_1$ lines from Au leaf.

L. S. T.

Secondary structure of X-ray absorption edges from elements in certain cubic crystals. G. P. BREWINGTON (Physical Rev., 1934, [ii], 46, 861—864).—The K X-ray absorption spectra of K, Cl, Ca, and S were photographed, using KF, KCl, KBr, KI, LiCl, NaCl, RbCl, and CaS. Separation data for secondary structure on the short wave-length side of the K edge of each element are tabulated.

N. M. B.

X-Ray absorption coefficient of xenon. T. N. WHITE (Physical Rev., 1934, [ii], 46, 865—867).—Mass-absorption coeffs. for the range 0.18—1.5 Å. are tabulated and plotted, and an equation is deduced.

N. M. B.

X-Ray levels and atomic constants. H. R. ROBINSON (Phil. Mag., 1934, [vii], 18, 1086—1099; cf. A., 1934, 1149).—Energy data for photo-electrons characteristic of various X-ray levels of Au, Pt, W, Sn, Ag, and Cu are tabulated from magnetic spectrometer measurements, using $Cu K\alpha$ and $Cr K\alpha$ radiations in turn. Comparisons with X-ray data and relations with at. consts. are discussed.

N. M. B.

Ionised gases. T. V. IONESCU (J. Phys. Radium, 1934, [vii], 5, 578—584).—Mathematical. A study of self-induction and capacity is applied to the investigation of the characteristic frequency of ionised gases, the action of positive grid gas-filled lamps, and the propagation of energy in tubes of ionised gas.

N. M. B.

Measurement of shot voltage used to deduce the magnitude of secondary thermionic emission. E. B. MOULLIN (Proc. Roy. Soc., 1934, A, 147, 100—118).—The theory of shot effect is reviewed, and the experimental method is described and illustrated by measurements of the electron charge, in conditions where secondary emission is absent, both in the presence and absence of space charge.

L. L. B.

Direction of polarisation and selectivity of external photo-electric effect of metals. F. HLIVČKA (Z. Physik, 1934, 92, 359—366).—Normal and tangential light components have sensitivity max. at different wave-lengths for the metals Ag, Au, Pt, Cu, and Zn. The absence of parallel component max. for alkali metals is due to their optical properties.

A. B. D. C.

Velocity distribution of photo-electrons in thin metal foils. E. VASSER (Physikal. Z. Sovietunion, 1934, 5, 645—658).—The proportion of high velocities increases with increase in time under vac. With change of thickness a Fermi distribution is obtained.

CH. ABS. (e)

Electron-optical images with photo-electrically liberated electrons. J. POHL (Physikal. Z., 1934, 35, 1003—1005).—An apparatus for obtaining images of photo-cathodes with the electrons liberated from them is described. The method was applied to it to discover the effect of absorption of gas, and crystal structure, on the geometrical distribution of light and thermo-electric emission.

A. J. M.

Relativistic quantum electro-dynamics and radiation emission on collision of electrons of

high energy. G. WATAGHIN (Z. Physik, 1934, 92, 547—560).

A. B. D. C.

Elastic electron scattering in potassium. J. H. McMILLEN (Physical Rev., 1934, [ii], 46, 983—988).—An improved method of measuring slow electron scattering in vapours was applied to obtain angular distribution curves from 25° to 160° for 5- to 150-volt electrons elastically scattered by K atoms. Characteristic shifting max. and min., similar to those of A for energies > 50 volts, were obtained.

N. M. B.

Sensitivity of light counters. M. W. KAREV and S. F. ROBIONOV (Z. Physik, 1934, 92, 615—621).—Spectral electron emission efficiency of light counters registering single electrons was determined for Al, and compared with photo-current efficiency.

A. B. D. C.

Experiments with positrons. E. RUPP (Physikal. Z., 1934, 35, 999—1003).—A satisfactory artificial source of positrons (I) is described. A thin layer of Li on Al foil is bombarded with fast protons. Photographs of the tracks of the rays were obtained by means of the cloud chamber method. The majority of (I) had velocities between 800 and 1000 kv. An apparatus for the determination of e/m for (I) is described. The ratio of e/m for (I) to that for electrons (II), both of 800 kv. velocity, is 0.95 ± 0.05 . A slight modification of the e/m apparatus serves to separate (I) from (II) of equal energy. Diffraction experiments with (I) at Al and Au foils gave only a continuous scattering. The proportion of elastically to inelastically scattered particles is much smaller in the case of (I) than (II) of the same velocity. The absorption coeffs. of (I) and (II) of 800 kv. velocity were obtained for Al, Cu, and Au. The absorption of (I) \propto mass, to a first approximation. The velocity loss in Al was determined for various velocities. (I) give, with all substances investigated, almost pure monochromatic X-rays with absorption coeffs. $0.18 \pm 0.08 \text{ cm.}^{-1}$, one absorbed (I) giving 1.8—2.2 X-ray quanta. (I) give 35—50 times more X-ray quanta than the same no. of (II).

A. J. M.

Artificially excited positrons. E. RUPP (Z. Physik, 1934, 92, 485—512).—Positrons were emitted by Li, less by Mg and Be, and not at all by Cu, Hg, and Au, on bombardment by fast protons; an Al-N layer on Al is a particularly good emitter. Absorption measurements are given for positrons. For each positron absorbed two quanta of X-rays are emitted. e/m for positrons is 0.95 ± 0.05 that for electrons.

A. B. D. C.

Production of the positive electron. J. R. OPPENHEIMER and M. S. PLESSER (Physical Rev., 1933, [ii], 44, 53—55; cf. A., 1934, 468).—Theoretical.

L. S. T.

Recombination of electrons and positrons. E. FERMI and G. E. UHLENBECK (Physical Rev., 1933, [ii], 44, 510—511).—Theoretical. The explanation of the hard component observed by Gray and Tarrant (A., 1932, 791) as due to the destruction of positrons cannot easily be reconciled with the Dirac theory.

L. S. T.

Dirac's theory of the positron. W. HEISENBERG (Z. Physik, 1934, 92, 692).—A correction (cf. A., 1934, 1150).

A. B. D. C.

Formation of negative ions in gases by electron attachment. I. NH_3 , CO , NO , HCl , and Cl_2 . N. E. BRADBURY. II. CO_2 , N_2O , SO_2 , H_2S , and H_2O . N. E. BRADBURY and H. E. TATEL (J. Chem. Physics, 1934, 2, 827—834, 835—839).

—I. The gases were ionised by a stream of electrons from a photo-electric source, accelerated by X volts per cm., in an apparatus previously described (A., 1934, 126), and the probability h of capture of an electron by a mol. of gas at pressure p mm. was determined. X/p was plotted against h . In NH_3 negative ions are formed for $X/p > 7.5$. It is assumed that the gas dissociates first to NH and H_2 and NH then combines with an electron. CO does not form negative ions and has, therefore, no electron affinity. NO forms negative ions by direct electron attachment, h increasing with decrease in X/p . There is also a linear variation of h with p which is explained by collision of an electron with a lightly bound polymeride N_2O_2 . NO^- is formed and the remaining NO mol. carries off the excess energy. Negative ions are formed in HCl and Cl_2 , h increases with X/p , indicating that dissociation of the mol. probably occurs, due to the excess energy produced in the electron attachment process. Of the possible methods of dissipation of the excess energy in electron attachment, that most generally occurring appears to be the removal of the energy by a third body involved in the process.

II. No negative ions are formed in CO_2 . In N_2O they are formed when X/p is > 2 , with probable dissociation, $\text{N}_2\text{O} + e \rightarrow \text{N}_2 + \text{O}^-$. In SO_2 attachment definitely occurs for electrons of low energy, and increases rapidly as the energy of the electrons decreases, indicating a true electron affinity and a radiation process for the dissipation of energy. As X/p increases h decreases to a min. and then increases, due to dissociation and formation of SO^- . H_2S probably forms HS^- for $X/p > 6$ and H_2O gives HO^- for $X/p > 10$. Negative ion formation in H_2O is also observed at low X/p for sufficiently high vals. of p . This may be due to the formation of negative ions from small mol. aggregates existing near the point of condensation of H_2O . M. S. B.

Intensities of molecular rays diffracted by rigid crystal surfaces. W. LENZ (Z. Physik, 1934, 92, 631—639).—The geometric-optical and Huygen's methods are applied to diffraction by an ideal rigid periodic surface. A. B. D. C.

Geometric-optical and wave-theoretical methods of calculating intensities of diffraction of molecular rays by rigid crystal surfaces. E. BRANDT (Z. Physik, 1934, 92, 640—660; cf. preceding abstract).—The wave method is applied, and practical approximations are given for the two methods. A. B. D. C.

Sources of positive ions. Thermionic properties of the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. E. J. JONES and S. B. HENDRICKS (Physical Rev., 1933, [ii], 44, 322).—The mixture $3\text{Li}_2\text{O} + \text{Al}_2\text{O}_3 + 3\text{SiO}_2$ gives const. emission of large currents (4×10^{-4} amp. per sq. cm.) for 40 hr. A similar mixture containing K is a satisfactory source of K^+ ions. The various compounds of Li_2O , SiO_2 , and Al_2O_3 have been prepared as

homogeneous crystals; their thermionic properties are much superior to those of the above mixture. The nature of the lattice changes accompanying emission of positive ions has been determined by X-ray analysis. L. S. T.

Production of intense beams of positive ions. R. D. FOWLER and G. E. GIBSON (Physical Rev., 1934, [ii], 46, 1075—1086).—Theory of excitation and apparatus for the production of beams of several milliamps. of ions from H_2 , He , N_2 , and CO_2 from the low-voltage arc arc described. Data on the influence of gas pressure and c.d. in the arc, and of extractor voltage on the density of the beams, are given. Electrostatic divergence and magnetic convergence and magnetic analyses of the beams are discussed. Beams from H_2 consist of H_2^+ , H_3^{+1} , H_3^{+2} , H_2^+ , H_2^{+1} , and H^+ , depending on pressure. N. M. B.

At. wt. of tantalum. O. HONIGSCHMID and R. SCHLEE (Z. anorg. Chem., 1934, 221, 129—141).—The mean of 14 determinations of the Br content of TaBr_5 by nephelometric titration with AgNO_3 gives $\text{Ta } 180.88 \pm 0.01$, in agreement with Aston's val. F. L. U.

At. wt. of radium. O. HONIGSCHMID and R. SACHTLEBEN (Z. anorg. Chem., 1934, 221, 65—82).—The at. wt. of Ra has been determined from the ratio $\text{RaBr}_2 : \text{RaCl}_2$ using a comparatively large quantity of highly purified RaBr_2 . The mean of 8 determinations gave $\text{Ra} = 226.05$ ($\text{Cl} = 35.457$, $\text{Br} = 79.916$). The pure RaCl_2 was afterwards used for the prep. of standards. M. S. B.

Masses of the lithium isotopes. K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 44, 56—57).—The mass of Li^6 referred to O^{16} , measured from five spectra by comparison with H^2 by the doublet method, is 6.0145 ± 0.0003 ; that of Li^7 is 7.0146 ± 0.0006 . The mass ratio of the Li isotopes obtained does not agree with the val. from band spectrum analysis (A., 1933, 994), but agrees with that obtained from earlier mass-spectrograph measurements (A., 1925, ii, 1021). L. S. T.

Redetermination of the mass ratio of the lithium isotopes from the band spectrum. F. A. JENKINS and A. MCKELLAR (Physical Rev., 1933, [ii], 44, 325—326).—From new spectrograms of the $^1\Pi \leftarrow$ bands of Li_2 , accurate wave-length data for the (0,0), (0,1), and (0,2) bands from both the isotopic mols. Li^7Li^7 and Li^6Li^7 have been obtained. The mass ratio Li^7/Li^6 is 1.1690 ± 0.0003 , which is $>$ previous vals. Using 7.015 as the mass of Li^7 , this gives 6.001 for Li^6 . L. S. T.

Relative abundance of the isotopes of lithium, potassium, and rubidium. A. K. BREWER and P. D. KUECK (Physical Rev., 1934, [ii], 46, 894—897). From mass-spectrograph measurements, using artificial Al silicates of Li , K , and Rb as a source of ions, the abundance ratio, mass ratio, m of the two isotopes, and packing fractions p are: $\text{Li}^7/\text{Li}^6 = 12.14 \pm 0.4$, $m = 7.016 \pm 0.002$ and 6.016 ± 0.002 , $v = 23 \pm 3$ and 26 ± 3 ; $\text{K}^{39}/\text{K}^{41} = 13.88 \pm 0.4$, $m = 38.96 \pm 0.003$ and 40.96 ± 0.003 , $p = -9.85 \pm 0.9$ and -9.37 ± 0.9 ; $\text{Rb}^{85}/\text{Rb}^{87} = 2.59 \pm 0.04$, $m = 84.88$ and 86.88 , $p =$

— 14.1 ± 0.7 and -13.8 ± 0.7 . Vals. for Rb diverge from those due to Aston. N. M. B.

Isotopic constitution of lithium in the sun. E. McMILLAN (Physical Rev., 1933, [ii], 44, 240).—Microphotometric measurements of the Li line of the sun-spot spectrum show that the whole line 6707.8 \AA . can be accounted for by Li^7 alone. The presence of Li^6 cannot definitely be confirmed, but if present its relative abundance is not much $>$ on earth. L. S. T.

Relative abundances of elements of even and odd mass number and atomic number. T. E. STERNE (Physical Rev., 1933, [ii], 44, 238—239).—Band spectra of homonuclear mols. indicate that nuclei of even mass no. obey the Einstein-Bose statistics and those of odd mass no. the Fermi-Dirac statistics. This explains the general preponderance of nuclei of even mass no. and even at. no. pointed out by Harkins. L. S. T.

Faraday effect at high frequencies. G. P. HARNWELL, W. BLEAKNEY, S. N. VAN VOORHIS, and J. B. H. KUPER (Physical Rev., 1933, [ii], 44, 785).—Preliminary experiments show the feasibility of investigating the Faraday effect for isotopes with continuous oscillations. L. S. T.

Spectro-analytical investigations. XIII. Spectrographic test of purity of the new primary radium standard. W. GERLACH and (FRL.) E. RIEDL (Z. anorg. Chem., 1934, 221, 103—108).—A method for the spectral analysis of very small quantities of an element is described. Using 0.61 mg. of the RaCl_2 prepared by Honigschmid as standard (cf. this vol. 140), the Ba content was found to be $0.002\text{—}0.004 \text{ at.-%}$, the actual quantity detected being $1.6 \times 10^{-9} \text{ g.}$ M. S. B.

Failure to detect radioactivity in beryllium with the linear amplifier. R. D. EVANS and M. C. HENDERSON (Physical Rev., 1933, [ii], 44, 59).—The radioactivity of Be reported by Langer and Raitt (this vol., 6) could not be confirmed using a linear amplifier responsive to the α -particles emitted from a granite containing 10^{-12} g. of Ra per g. of rock. The results indicate that Be is stable. L. S. T.

Failure to detect the radioactivity of beryllium with the Wilson cloud chamber. D. M. GANS, W. D. HARKINS, and H. W. NEWSON (Physical Rev., 1933, [ii], 44, 310).—The radioactivity of Be recently reported (this vol., 6) could not be confirmed (see above). L. S. T.

Energies of α -, β -, and γ -rays. H. A. WILSON (Proc. Roy. Soc., 1934, A, 147, 240—250; cf. A., 1934, 579).—The energies of β -rays from elements with the same at. no. are approx. equal, in accordance with theory. Pairs of β - and γ -ray energies having sums equal to multiples of 3.85 are found for several elements. The internal conversion coeffs. for Ra-C' γ -rays are consistent with theory. L. L. B.

Ionisation curves of Po α -rays in rare gases. R. NAIDU (J. Phys. Radium, 1934, [vii], 5, 575—577; cf. A., 1934, 1053).—Curves for the velocity variation along trajectories and for retarding effect are given

for air, He, Ne, A, Xe, and Kr. Velocities corresponding with max. ionisation are calc. N. M. B.

Disintegration of beryllium by γ -rays. W. GENTNER (Compt. rend., 1934, 199, 1211—1213).—Szilard and Chalmers' result (cf. A., 1934, 1152) was confirmed using a mesothorium source. The optimum γ -ray energy was $0.9 \times 10^6 \text{ e.v.}$ The calc. mass of Be^9 was 9.013. H. J. E.

γ -Rays accompanying artificial nuclear disintegrations. E. McMILLAN (Physical Rev., 1934, [ii], 46, 868—873).—The excitation function and absorption of γ -rays from the bombardment of F, Li, B, and Be by protons, and of γ -rays and neutrons from the bombardment of Be, C, Li, B, F, Mg, and Al by deutons were investigated, as was the absorption of the "annihilation radiation" accompanying the radioactivity excited in C. N. M. B.

Absorption of γ -rays of radium by radioactive salts. F. BEHOUNEK (Z. Physik, 1934, 92, 533—542).—Absorption of Ra-C γ -rays is given for a no. of compounds, and the absorption coeff. is related to the no. of electrons per c.c. A similar relation is shown to hold for elements. A. B. D. C.

γ -Radiation from slow neutrons. R. FLEISCHMANN (Naturwiss., 1934, 22, 839).—The absorption of γ -rays and neutrons from Be-Rn was investigated. On passage of the rays through paraffin, H_2O , or substances containing H_2O , the proportion of γ -rays was considerably increased. The intensity of the γ -rays at first increases rapidly with the thickness of paraffin traversed up to 2.5 cm., reaching saturation at 6 cm. and then decreasing. The radiation from the paraffin is the same in both forward and backward directions. The neutrons pass through a certain thickness of paraffin where they are rapidly retarded, and combine with H^1 nuclei to form H^2 nuclei, with liberation of γ -rays, thus accounting for the rapid increase in intensity. A. J. M.

Fermi effect. M. DANYSZ, J. ROTBLAT, L. WERTENSTEIN, and M. ŻYW (Nature, 1934, 134, 970—971).—The intensities of the Fermi effect obtained under identical geometrical conditions when screens of Pb and Au are placed between the Be-Rn source and Si, Al, Ag, or I, in which the effect is excited, are recorded. With Ag and I, the effect increases when the screen is interposed, showing a transformation of the exciting rays. It is concluded that the capture of a neutron (I) by a heavy nucleus without emission of a heavy particle takes place only when the energy of (I) is $>$ a certain val. If the energy of (I) is too high it loses in a nuclear encounter a part of its energy, which is emitted as a γ -radiation. The increased effect observed with Ag and I would then be due to the production of slow (I) in a no. $>$ the loss of primary slow (I) due to absorption. L. S. T.

Emission of α -particles from various targets bombarded by deutons of high speed. G. N. LEWIS, M. S. LIVINGSTON, and E. O. LAWRENCE (Physical Rev., 1933, [ii], 44, 55—56).—Using H_2 containing 50% H_2^+ , H^1H^2+ ions have been given energies of $2 \times 10^6 \text{ volts}$. On striking a target these yield $6.6 \times 10^{-5} \text{ volt-protons}$ and $1.33 \times 10^{-6} \text{ volt-H}^2$

nuclei, deutons. When bombarded by these particles the N from a target of NH_4NO_3 yields approx. 10^9 α -particles (I) of range 6.8 cm. per 10^9 deutons and the min. deuteron energy for this disintegration is 6×10^5 volts. Li from a LiF target gives a large no. of (I) of 8.2 cm. range probably due to the accompanying protons, and some of 14.5 cm. range of 12.5×10^6 volts energy. Assuming the process $\text{Li}^6 + \text{H}^2 \rightarrow 2\text{He}^4$, the total energy liberated is 23.4×10^6 volts. With a Be target (I) of range 3.3 cm. are obtained and the no. of disintegrations per deuteron is < 100 times the no. per proton. The bombarding particle probably causes disintegration of the unstable Be nucleus without capture. Al and Mg targets, and CaF_2 and NaCl give a small no. of particles. SiO_2 , NaPO_3 , C, CuS, $\text{Ca}(\text{ClO}_3)_2$, Au, Pt, brass, and mica give no detectable (I). L. S. T.

Emission of protons from various targets bombarded by deutons of high speed. E. O. LAWRENCE, M. S. LIVINGSTON, and G. N. LEWIS (Physical Rev., 1933, [ii], 44, 56).—When deutons (I) of 6×10^5 — 1.33×10^6 volts are directed against different targets (see above), in addition to α -particles protons with ranges up to approx. 40 cm. are emitted in large nos. Each target, including Au and Pt which are unlikely to undergo disintegration, gives protons of approx. 18 cm. range. This group can be explained only by assuming that the (I) breaks up, presumably into a proton and a neutron. In all cases, proton emission is not observed when the (I) energy is $< 8 \times 10^5$. L. S. T.

Liberation of neutrons from beryllium by hard X-rays. Production of radioactive elements. A. BRASCH, F. LANGE, A. WALY, T. E. BANKS, T. A. CHALMERS, L. SZILARD, and F. L. HOPWOOD (Naturwiss., 1934, 22, 839, and Nature, 1934, 134, 880).— 1.5×10^6 -volt X-rays were passed on to Be, and the neutrons liberated were directed on to CHBr_3 , which was then found to have mols. containing radioactive (I) and ordinary Br. (I) has a half-life period of 6 hr. Increase of voltage on the X-ray tube caused a much more powerful activity; with both Br and I, activity sufficiently powerful to be indicated on an electroscope could be obtained. A. J. M.

Neutrons from a beryllium-radon source. J. R. DUNNING and G. B. PEGRAM (Physical Rev., 1933, [ii], 44, 317).—Absorption curves for C, Al, Pb, Cu, and paraffin up to 21 cm. in thickness and single points for other elements have been obtained. Scattering measurements have been made for C, Al, Cu, Sn, and Pb at angles between 35° and 135° . A beam of neutrons is not deflected by passage through a magnetic field of 10^4 gauss, indicating that it does not possess the properties of a free magnetic pole of any large multiple of unit strength. L. S. T.

Atom disintegration, atomic structure, and artificial radioactivity. H. MARK (Oesterr. Chem.-Ztg., 1934, 37, 200—203).—A lecture.

Artificial radioactivity and the scheme of Lande. I. KURTSCHATOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 202—207). E. S. H.

Experimental proof of layers of neutrons in the nucleus. W. YEH (Compt. rend., 1934, 199, 1209—1211).—The reciprocal of the log. of the period of radio-elements produced by neutrons plotted against the no. of protons in the nucleus shows a periodic variation for a series of elements. The interpretation of nuclear structure from this observation is discussed.

H. J. E.

Radioactivity induced by neutrons. W. YEH (Compt. rend., 1934, 199, 1404—1406; cf. preceding abstract).—When $10/\log T$ (T =half-life period of the atoms) is plotted against the no. of protons contained in radioactive elements formed by the inductive action of neutrons, the curve shows max. corresponding with the end of each complete layer of neutrons in the nucleus, the max. decreasing with increasing no. of layers of neutrons. The val. for K accords with theory. J. W. S.

Nuclear structure and artificial radioactivity. G. GUÉBEN (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 215—223).—The nuclear constitution of elements produced artificially which show radioactivity is deduced in terms of α -particles (α), dipions (π_2), protons (π), and neutrons (n). Those elements which disintegrate with emission of a positive electron have nuclei of the form $(x\alpha + \pi)$, $(x\alpha + \pi_2)$, or $(x\alpha + \pi_2 + \pi)$, where x is an integer. Those which disintegrate with emission of a negative electron have nuclear constitutions of the type $(x\alpha + \pi_2 + zn)$, z being even. The fact that these particular arrangements are unstable may be used to predict nuclear changes. A. J. M.

Disintegration of the elements by swiftly moving protons. M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Physical Rev., 1933, [ii], 44, 316).—When bombarded by 6×10^5 to 1.6×10^6 volt-protons, all the elements investigated give evidence of disintegration. Li yields α -particles (I) of 8.9 and 9.1 cm. range with 6×10^5 and 1.4×10^6 volt-protons, respectively. The process involves capture of the proton. Be yields 3.3 cm. (I) and a few of ranges up to 6.1 cm. NaCl yields (I) of ranges up to 3.4 cm. with 1.1×10^6 volt-protons. Al and Mg give a few 2.7 cm. (I) and NH_4NO_3 still fewer 2.2 cm. (I) with 7.5×10^5 volt-protons. L. S. T.

Three types of nuclear disintegration of calcium fluoride by bombarding protons of very great energy. E. O. LAWRENCE and M. S. LIVINGSTON (Physical Rev., 1933, [ii], 44, 316—317).—When bombarded by protons CaF_2 yields α -particles (I) of 2.8 cm. range with 6 — 9.5×10^5 volt-protons, 2.8 cm. and 5.6 cm. (I) with 9.5×10^5 — 1.35×10^6 volt-protons, and an additional (I) group of 6.8 cm. range with 1.35 — 1.60×10^6 volt-protons. The excitation threshold is sharp and the yields increase rapidly in a linear manner with an increase in proton range above the threshold val. L. S. T.

Interaction of neutrons and protons. I. TAMM (Nature, 1934, 134, 1010—1011).—The emission or absorption of two neutrinos by the neutron or proton, although less probable than emission of a γ -ray by the excited proton, may possibly occur. The electric charge and the spin of the heavy particle would be unchanged. This would not be the case when a

single neutrino is given off, as postulated by Fermi to account for the emission of β -rays by some radioactive materials. L. S. T.

Neutrons from beryllium bombarded by deutons. M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Physical Rev., 1933, [ii], 44, 782—783; cf. A., 1934, 6).—Neutrons (I) result from the disintegration of Be bombarded by deutons (II), apparently from the disintegration of Be⁹ with capture of a (II) to form Be¹⁰ and a (I). The yield of (I) increases linearly with the range 1—9 cm. of (II). Hence the probability that (II) will disintegrate the Be nucleus on collision is independent of (II) energy, and the increase in yield with (II) range is due only to the increased frequency of collisions. L. S. T.

Mass of the neutron. W. D. HARKINS and D. M. GANS (Nature, 1934, 134, 968—969).—For the present it is suggested that the val. 1.006 should be used for the mass of the neutron. A probable lower limit is 1.0052. L. S. T.

Passage of very fast protons through matter. H. J. BHABHA (Nature, 1934, 134, 934).—Theoretical. L. S. T.

Investigations of ultra-radiation corpuscles. H. KULENKAMPFF (Physikal. Z., 1934, 35, 996—997).—The absorption of ultra-radiation corpuscles (I) in Fe placed between or above two counter-tubes was investigated. The weakening of (I) on passing through an absorbent is due to gradual energy loss, absorption processes playing only a subordinate part. A. J. M.

Cosmic ray nuclear disintegrations. W. F. G. SWANN and C. G. MONTGOMERY (Physical Rev., 1933, [ii], 44, 52—53). L. S. T.

Absorption of cosmic rays by different substances. H. TIELSCH (Z. Physik, 1934, 92, 589—614).—Absorption measurements are given for Pb, Hg, Fe, Al, H₂O, air, and C. A. B. D. C.

Counter calibration and cosmic-ray intensity. J. C. STREET and R. H. WOODWARD (Physical Rev., 1934, [ii], 46, 1029—1034).—Observations with a set of counters calibrated absolutely gives the no. of ionising cosmic rays as 0.80 ± 0.028 per cm.² per min. from unit solid angle at the vertical at sea level. The no. of rays from all directions is 1.48 ± 0.055 cm.⁻² min.⁻¹, giving an average sp. ionisation of 100 ± 3.7 ion pairs per cm. path of a ray. N. M. B.

Distribution of cosmic ray nuclear disintegration in time. C. G. MONTGOMERY and D. D. MONTGOMERY (Physical Rev., 1933, [ii], 44, 779).—Experimental results support the hypothesis that the nuclear disintegrations produced by cosmic rays are randomly distributed in time. L. S. T.

Structure of ionised layer of the atmosphere. R. L. SCU and C. MIHUL (Compt. rend., 1934, 199, 1301—1303). H. J. E.

Constitution of the atmospheres of the giant planets. A. ADEL and V. M. SLIPHER (Physical Rev., [ii], 46, 902—906).—By duplicating the spectra of the gaseous envelopes of Jupiter, Saturn, Uranus, and Neptune, using an absorption cell 22.5

m. long and comparing band photographs of CH₄, approx. 40 rotation-vibration bands in the spectra of these planets are identified as due to CH₄, which appears to be the major constituent of their atm. The absence of appreciable amounts of other hydrocarbons is shown. N. M. B.

Constitution of elementary particles and nuclear forces. W. M. ELSASSER (Compt. rend., 1934, 199, 1213—1215).—Theoretical. H. J. E.

Genesis of the elements. G. N. LEWIS (Physical Rev., 1934, [ii], 46, 897—901).—It is suggested that a large part of the matter in the universe is composed, like the metallic meteors, chiefly of Fe and Ni, and that such material, thermodynamically stable against spontaneous transmutations except at very high temp., is superficially attacked by cosmic radiation to produce the material represented by the earth's crust and by stony meteors. This view is supported by comparison of the relative abundance of the chief at. species in the two types of meteors. The main disintegration processes undergone by the Fe and Ni nuclei are: splitting off of O₂, splitting into two identical parts, and splitting of He from the products of the preceding processes. N. M. B.

Jacyna's selection theorem for helium. V. JACYNA, S. DEREJANKIN, A. OBNORSKI, and T. PARFENTJEV (Z. Physik, 1934, 92, 675—679).—The selection theorem is verified for He (cf. A., 1934, 1070). A. B. D. C.

Wave theory of the neutrino. G. RUMER (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 21—24). A. B. D. C.

Mass of the neutrino. T. TAKEUCHI (Proc. Phys.-Math. Soc. Japan., 1934, 16, 294—295).—The mass of the neutrino differs from that of the anti-neutrino by the mass of a photon (4×10^{-64} g.). The spins are $\frac{1}{2}$ and respectively. CH. ABS. (e)

Equivalence of mass and energy. K. T. BAINBRIDGE (Physical Rev., 1933, [ii], 44, 123). L. S. T.

Expression for [energy] density in terms of the new theory of the photon. L. DE BROGLIE (Compt. rend., 1934, 199, 1165—1168; cf. A., 1934, 1054).—Theoretical. H. J. E.

Relativistic invariant perturbation theory of the Dirac electron. I. Scattered and retarded radiation. E. C. G. STUECKELBERG (Ann Physik, 1934, [v], 21, 367—389). A. J. M.

Atomic energy relations. I. R. F. BACHER and S. Goudsmit (Physical Rev., 1934, [ii], 46, 948—969).—Mathematical. Approx. energies of at. levels are calc. from linear relations which express the unknown energy in terms of observed energy vals. of the atom and its ions. Results are tabulated for *s* and *p* electrons and are applied to the spectra of C, N₂, and O₂. N. M. B.

Collision of two light quanta. G. BREIT and J. A. WHEELER (Physical Rev., 1934, [ii], 46, 1087—1091).—Mathematical. The production of positron-electron pairs as a result of collision of two light quanta, and the formation of photons due to recombination, are examined. Results are applied to the

collision of high-energy photons of cosmic radiation with the temp. radiation of interstellar space.

N. M. B.

Breakdown of the Coulomb law for the hydrogen atom. E. C. KEMBLE and R. D. PRESENT (Physical Rev., 1933, [ii], 44, 1031—1032).

L. S. T.

Magneto-ionic theory. H. G. BOOKER (Proc. Roy. Soc., 1934, A, 147, 352—382).—Several new features of Appleton's magneto-ionic theory of the propagation of wireless waves in the ionosphere (A., 1932, 670) appear if damping due to electronic collisions be taken into account, and incidence is not necessarily vertical.

L. L. B.

Electronic states of the N_2^+ molecule and their energies of dissociation. H. H. BRONS (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 793—801).—Potential energy-distance curves have been calc. for the electronic states of N_2^+ . The products of dissociation and the symmetry of the states are discussed.

R. S. B.

Magnetic moment of the proton. A. LANDE (Physical Rev., 1933, [ii], 44, 1028—1029).—The magnetic properties of higher nuclei indicate that the magnetic moment of a proton is approx. two magnetons. This differs from Stern's val. (A., 1933, 996) by 20%. The proton appears to circle around inside or on the surface of the neutron shells.

L. S. T.

Calculation of the perturbation of a hydrogenoid atom by a free electron. P. BRICOUT (Compt. rend., 1934, 199, 1392—1394).—Mathematical.

J. W. S.

Planck quanta and the atomic field of force. M. BRILLOUIN (Compt. rend., 1934, 199, 1345—1349).—Mathematical.

J. W. S.

Electronic at. wt. and e/m ratio. R. C. GIBBS and R. C. WILLIAMS (Physical Rev., 1933, [ii], 44, 1029).—The at. wt. of the electron, determined from measurements of the interval between corresponding components of the $H^1\alpha$ and $H^2\alpha$ lines (A., 1934, 575), is $(5.491 \pm 0.002) \times 10^{-4}$. This gives a val. of $(1.757 \pm 0.001) \times 10^7$ e.m.u. per g. for e/m for the electron.

L. S. T.

Band spectra measurements of mass. A. BRAMLEY (Physical Rev., 1933, [ii], 44, 309—310).—A discussion.

L. S. T.

Chemical reactivity and absorption of light. N. R. DHAR and P. N. BHARGAVA (Nature, 1934, 134, 848—849).—Absorption in the visible region for mixtures of reacting substances, e.g. $H_2 + Cl_2$, $H_2 + Br_2$, $MeOH + Br_2$, and $EtOH + Br_2$, is $>$ that by the separate constituents. Increased absorption may be a measure of the reactivity of a system, and is due to the weakening of the binding forces of the mols.

L. S. T.

Spectrum of $O^{16}H^2$. H. L. JOHNSTON and D. H. DAWSON (Physical Rev., 1933, [ii], 44, 1031).—Approx. 500 new lines (8 bands) have been identified and assigned in the spectrum of OH^2 produced in H_2O vapour containing 35% of the H as H^2 .

L. S. T.

Emission and fluorescence spectra of sulphur dioxide. H. D. SMYTH (Physical Rev., 1933, [ii], 44, 690).—A comparison of the results of Chow (A., 1933, 1227) and Lotmar (*ibid.*, 886). L. S. T.

Molecular spectra of boron and aluminium halides. E. MIESCHER (Helv. phys. Acta, 1934, 7, 462—464; Chem. Zentr., 1934, ii, 908—909).—Band spectrum data for BCl , BBr , $AlCl$, $AlBr$, and AlI (in a Geissler tube) are recorded.

H. J. E.

Band spectra of the halides of aluminium. F. H. CRAWFORD and C. F. FFOLLIOTT (Physical Rev., 1933, [ii], 44, 953—954).— $AlCl_3$ gives a well-developed group of red-degraded bands (approx. 75) from 2550 to 2900 Å., and $AlBr_3$ one from 3065 to 2745 Å., presumably due to $AlBr$. AlI_3 gives an intense continuous spectrum with a faintly-banded appearance in places extending from the visible to 2300 Å.

L. S. T.

Spectroscopic investigation of indium halide vapours and gallium halide vapours. M. WEHRLI and E. MIESCHER (Helv. phys. Acta, 1934, 7, 298—330, 331—359; Chem. Zentr., 1934, ii, 725—727).—Data on the emission and absorption spectra of $InCl$, $InBr$, and InI are recorded and classified. Three band systems were observed in each case. A new In isotope of mass 113 was detected. Data for $GaCl$, $GaBr$, and GaI are also recorded and classified. The bands resemble those of In halides.

H. J. E.

Absorption spectrum of thallium fluoride vapour. Z. V. BORTZOVA and K. V. BUTKOV (Physikal. Z. Sovietunion, 1934, 5, 765—776).—At low temp. a continuous absorption, attributed to Tl_2F_6 , was observed. At higher temp. the spectrum of TlF is observed. The dissociation energy of TlF is 106 kg.-cal.

CH. ABS. (e)

Absorption spectra of the samarium ion in solids. V. Absorption spectrum and energy levels of the Sm^{+++} ion as it exists in monoclinic crystals of $Sm_2(SO_4)_3 \cdot 8H_2O$. F. H. SPEDDING and R. S. BEAR (Physical Rev., 1934, [ii], 46, 975—983; cf. A., 1934, 1154).—Full data for the spectra at 20°, 78°, 169°, and 298° abs., and an energy level diagram are given. Results are similar to those for $SmCl_3 \cdot 6H_2O$. The existence of low-lying levels separated from the basic level by 160, 188, and 225 cm^{-1} is proved.

N. M. B.

Transparency of the atmosphere in the ultra-violet and a possible means of extending the Solar spectrum in the regions 2200—2000 Å. K. R. RAMANATHAN and L. A. RAMDAS (Proc. Indian Acad. Sci., 1934, 1, A, 308—314).—The absorption band of O_3 , which produces the short-wave limit of the solar spectrum, has relatively low intensity at 2200—2000 Å., whilst the Schumann-Runge absorption band system of O_2 begins at about 2000 Å. Hence it is calc. that, provided that the sun emits black-body radiation, and there is no other absorbing agent present in the atm., it should be possible to detect solar radiation between 2200 and 2000 Å. at heights of < 16 km. in the tropics.

J. W. S.

Ultra-violet absorption of methane. A. B. F. DUNCAN and J. P. HOWE (J. Chem. Physics, 1934, 2,

851—852).— CH_4 shows true continuous absorption in the region 1450—850 Å., and all excited states up to the first ionisation potential are repulsive. Continuous ultra-violet absorption spectra may be general for mols. with tetrahedral symmetry. M. S. B.

Absorption of ultra-violet light by some organic substances. XXXVII. L. MARCHLEWSKI and J. ZGLECZEWSKI. XXVIII. W. GOSELAWSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1934, A, 256—260, 261—279).—XXXVII. *o*-Hydroxycarb-anilide and its *N*-Et ether show similar absorption curves, that for the latter being shifted slightly towards longer λ . The *O*-Et ether shows weaker absorption, and a different type of absorption curve, with two max., indicating a difference in structure from the parent compound and its *N*-ether (cf. A., 1926, 9).

XXXVIII. Methyl-, ethyl-, amyl-, meta-, methyl-meta-, acetyl-, and alkali-lignins all show strong absorption bands with max. at 2795—2835 Å. The absorption increases with increased concn. of acid used in prep. of lignin, the length of time of reaction, and rise of temp. With the alcohol-lignins it increases with rise of temp. and pressure of formation. The selective absorption is unaffected by acidity, but the continuous absorption is increased considerably in alkaline solution. J. W. S.

Spectrum of acraldehyde. H. W. THOMPSON and J. W. LINNETT (Nature, 1934, 134, 937—938).—The ultra-violet spectrum of acraldehyde (I) has a region of absorption from 4000 to 2800 Å. approx. consisting of bands with no overlapping continuum, and a region of continuous absorption from 2300 Å. to higher frequencies. The relation of these bands to mol. structure is discussed. Illumination of (I) vapour at room temp. with light of wave-length corresponding with the first region leads to a polymerisation. L. S. T.

Ultra-violet absorption of binary liquid mixtures. V. System acetone-hexane. M. PESTEMER (Monatsh., 1934, 65, 1—5; cf. A., 1934, 952).—Results for the whole range of compositions of the system support the conclusions reached in the examination of other binary systems. E. S. H.

Band position of chlorophyll in different media. HUBERT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 694—699).—Determinations of the absorption band max. of chlorophyll (I) in different solvents indicate that the shift follows Kundt's law. Comparison with the shift in leaves indicates that, if (I) is dissolved in plastid, it must be in a medium of very high refractive index. Certain observations favour the adsorption theory. M. S. B.

Chlorophyll spectrum. L. G. M. BAAS-BECKING and (Miss) H. C. KONING (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 674—678).—Preliminary. The approx. positions of the absorption and fluorescence bands of solutions of chlorophyll (I) in different org. solvents have been determined. In general Kundt's rule is obeyed, since the higher is the refractive index the greater is the shift of the band max towards longer wave-lengths. The results indicate that (I) cannot be present in the living

plastid in ordinary solution. Intensities have been determined in aq. colloids and paraffin-oil solutions and measurements of diffusion in different solvents have also been made. From absence of fluorescence in the colloidal solution, it is probable that (I) is not present in the colloidal state in plastid. M. S. B.

Temperature classification of infra-red iron lines. A. S. KING (Astrophys. J., 1934, 80, 124—135).—The spectrum of Fe from 6400 to 10,500 Å. has been observed at temp. between 2100° and 2700° in the vac. furnace and in the arc, and 367 lines have been classified according to temp. L. S. T.

Temperature variation of infra-red absorption of crystals. I. Fluorspar and calcite. F. MATOSSI and H. BRIX. II. Sulphates and micas. F. MATOSSI and H. KINDLER (Z. Physik, 1934, 92, 303—311, 312—336).—I. Transmission spectra were obtained from -168° to 300° in the near infra-red. Combination bands become less intense and broader with rising temp., due to damping effects exceeding excitation of the fundamental; for calcspar this is at 41.4μ .

II. Absorption spectra are given for muscovite, clinochlore, anhydrite, celestine, and baryta from 0 to 20μ , and between -125° and 300° .

A. B. D. C.

Infra-red spectrum of heavy ammonia, NH_3 . S. SILVERMAN and J. A. SANDERSON (Physical Rev., 1933, [ii], 44, 1032).—Calc. and observed vals. of the four bands of the infra-red spectrum of 90% NH_3 are recorded. L. S. T.

Infra-red spectrum of methyl chloride. A. H. NIELSEN and E. F. BARKER (Physical Rev., 1934, [ii], 46, 970—974).—Data are tabulated for new infra-red absorption bands mapped in the region 0.7 — 7.0μ . Theoretical predictions and anomalous spacing are confirmed. Bands at 5900 and 4200 cm^{-1} indicate interaction between the levels ν_1 and $2\nu_4$ thought to exist in some Me compounds. N. M. B.

Polarisation and intensity measurements in the Raman spectrum of carbon dioxide. A. LANGSETH and J. R. NIELSEN (Physical Rev., 1934, [ii], 46, 1057—1058; cf. Dickinson, A., 1929, 1215; Hanson, A., 1934, 1056).—For the principal Raman bands at 1286 and 1389 cm^{-1} , the depolarisations (for unpolarised incident light) are 0.18 and 0.14 , respectively, and the relative intensities 0.61 . N. M. B.

Raman spectrum of gaseous carbon dioxide. A. ADEL (Physical Rev., 1933, [ii], 44, 691; cf. A., 1933, 661). L. S. T.

Raman spectra of some linear triatomic molecules. A. LANGSETH and J. R. NIELSEN (Physical Rev., 1933, [iii], 44, 326; cf. A., 1933, 208).—Raman spectra of N_2O , CO_2 , CS_2 liq., and the ions SCN' and N_3' in aq. solution have been photographed with high dispersion, and the depolarisations of certain lines and relative intensities measured. The results support a linear structure for these mols. L. S. T.

Raman effect with triatomic molecules. VI. Constitution of nitrite ion. A. LANGSETH and E. WALLIS (Z. physikal. Chem., 1934, B, 27, 209—218; cf. A., 1931, 1353).—Raman lines 1331.3 ± 1.0 ,

1240 \pm 2, and 813.2 \pm 1.0 cm.⁻¹ have been observed, with NaNO₂, and their states of polarisation measured. The relative intensities are the same at 15° as at 95°. The results indicate that NO₂' is isosteric with O₃ and has a ring structure. NO₂' is apparently pale yellow. R. C.

Raman spectrum of deuterio-methyl alcohol and deuterio-chloroform. O. REDLICH and F. PORDES (Naturwiss., 1934, 22, 808).—The Raman spectrum of MeOH² indicates that the frequency to be ascribed to the OH vibration in the ordinary mol. is 3388 cm.⁻¹ For CH₂Cl₃ lines were found at 649, 905, and 2253 cm.⁻¹ The results do not agree with those calc. on the basis of the central force system of Bjerrum and Dennison. A. J. M.

Raman spectra [of *n*- and *sec*.-butylamine and *n*-heptylamine]. P. L. BAYLEY (Physical Rev., 1933, [ii], 44, 510).—Frequencies and relative intensities are recorded. A weak line at approx. 2725 cm.⁻¹ is new for amines. Preliminary vals. for the frequencies of furan are also given. L. S. T.

Raman spectra of tartaric acid and tartrates in aqueous solution. I. PEYCHES (Compt. rend., 1934, 199, 1121—1123).—Data are recorded for the acid and for Li, Na, NH₄, K, Rb, Cs, and Et tartrates. H. J. E.

Raman effect of acetylenes. I. Methyl-, dimethyl-, and vinyl-acetylene. G. GLOCKLER and H. M. DAVIS (J. Chem. Physics, 1934, 2, 881—889).—An improved technique has resulted in slightly different vals. for the CMe₂CH frequencies (cf. A., 1933, 1229). Frequencies are also given for the other two compounds and the modes of vibration discussed. Faint rotation lines accompany the C₂C vibration in liquid CMe₂CMe. They are interpreted as due to rotation of the 6 H around the figure axis of the mol. The moment of inertia is 10⁻³⁹ g. × cm.² M. S. B.

Linking frequency of heavy acetylene Y. MORINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 232—234).—Theoretical. Assuming the force consts. to be the same as for C₂H₂, and the mass of H² to be 2.014, the frequencies of C₂H₂² are calc. A hitherto unobserved Raman line at 2680 cm.⁻¹ and an infra-red absorption band at 2408 cm.⁻¹ are predicted. J. W. S.

Raman spectra of cyclopentene derivatives. Synthesis of Δ^1 -benzylcyclopentene. L. PIAUX (Compt. rend., 1934, 199, 1127—1128; cf. A., 1934, 942).—Data are recorded for Δ^1 -cyclopentenylmethyl acetate, b.p. 73—75°, and bromide (I), b.p. 56—59°, and Δ^1 -1-benzylcyclopentene, b.p. 113—117° [from (I) and MgPhBr, or from cyclopentanone and CH₂Ph.MgCl and dehydration of the resulting 1-benzylcyclopentanol, m.p. 54—55°]. H. J. E.

Rotational Raman effect in liquids. A. V. RAO (Proc. Indian Acad. Sci., 1934, 1, A, 274—280; cf. A., 1934, 345, 1056).—C₆H₆, CS₂, cyclohexane, molten salol, and CCl₄ all show a high intensity near the Rayleigh line, and a weak but definite extension of the wing beyond the theoretical limit. The intensity distribution remains almost unchanged at temp. near the b.p. of the liquids. It is suggested that the

extreme wings arise from groups which cannot rotate, but oscillate about their equilibrium positions.

J. W. S.

Examination of molecularly scattered light with a Fabry-Perot etalon. I. Liquid benzene. B. V. R. RAO (Proc. Indian Acad. Sci., 1934, 1, A, 261—268).—Two fine structure components have been identified in the Rayleigh line due to mol. scattering in C₆H₆, their displacement being in agreement with theory. The variation of the frequency shift of the displaced components from the main line with the frequency of the incident radiation is in agreement with Brillouin's equation (Ann. Physique, 1922, [ix], 17, 88). J. W. S.

Rotational Raman scattering in benzene vapour. S. C. SARKAR (Nature, 1934, 134, 850—851).—Measurements of the distribution of intensity in the rotational wing due to C₆H₆ at 210° and approx. 16.6 atm. support the theory of Placzek and Teller (A., 1933, 446). L. S. T.

Raman spectrum of fluorobenzene. J. W. MURRAY and D. H. ANDREWS (J. Chem. Physics, 1934, 2, 890).—The data of Crawford *et al.* (A., 1934, 1155) for the Raman frequencies of PhF differ from those of the authors (*ibid.*, 473) for 4 of the lines. The former used a filter of I in CCl₄ which does not permit an unambiguous assignment of some of the lines. A numerical error in the earlier paper is corr. Polarisation data are given for the Raman lines of PhF. M. S. B.

Raman effect. XXXVII. Raman spectra of molecules of the type XCOY. K. W. F. KOHLRAUSCH and A. PONGRATZ (Z. physikal. Chem., 1934, B, 27, 176—195).—The Raman spectra of compounds of the type XCOY, principally amides and crotonyl derivatives and compounds having X=Br or SH and Y=alkyl, have been studied. Normal vibration frequencies are identified by means of approximation formulae for a valency-force system (cf. A., 1933, 209). The effect of X and Y on the CO frequency appears to be connected with their dipole moments. R. C.

Raman effect. XXXVI. Raman spectrum of organic substances. (Poly-substituted benzenes. V.) K. W. F. KOHLRAUSCH and A. PONGRATZ (Monatsh., 1934, 65, 6—17; cf. A., 1934, 1290).—Data are recorded for 1:3:5-, 1:2:3-, and 1:2:4-C₆H₃Me₃, 1:2:4:5- and 1:2:3:5-C₆H₂Me₄, C₆HMe₅, C₆Me₆, 1:2-, 1:3-, and 1:4-C₆H₄(OH)₂, 1:2:3- and 1:3:5-C₆H₃(OH)₃, PhOMe, 1:2-, 1:3-, and 1:4-C₆H₄(OMe)₂, 1:2:3- and 1:3:5-C₆H₃(OMe)₃. E. S. H.

Combination scattering and association of molecules. S. I. LEFTMAN and S. A. UCHODIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 12—14).—Scattering was investigated for solutions PhNO₂ in CCl₄, and AcOH in H₂O; a displacement at 623 cm.⁻¹ is ascribed to association of the AcOH mols. A. B. D. C.

Rayleigh scattering in crystals. F. MATOSSI (Z. Physik, 1934, 92, 425—461).—The theory of depolarisation is developed for rhombic, trigonal, hexagonal, and tetragonal crystals; trigonal crystals do not show symmetry normal to the single optic

axis, as elastic consts. have a lower symmetry than optical consts. Depolarisation was observed for glass, rock-salt, topaz, calcspar, and quartz; quartz shows the lower symmetry of elastic consts. A. B. D. C.

Topography of surfaces deduced from the coefficient of diffusion of light. Application in the study of corrosion. F. CANAC (Compt. rend., 1934, 199, 1117—1118).—The reflexion of light by the surface is correlated with the surface conditions.

H. J. E.

Fluorescence of platinocyanide solutions. I. A. CHVOSTIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 14—20).—Fluorescence of K, Ba, and Mg salts was observed. The K salt fluorescence appears as bands at 525 and 555 m μ , absorption bands appearing near 254, 279, and 350 m μ . Variation of polarisation with viscosity is used to calculate the half-life period of emitting centres.

A. B. D. C.

Crystallisation fluorescence. H. DORING (Naturwiss., 1934, 22, 838).—CaC₂O₄, freshly separated from plant cells, shows fluorescence, whilst more aged crystals do not. A similar phenomenon is observed in the separation of thymol and similar phenols, and vanillin, from supercooled melts.

A. J. M.

Luminescence and crystal structure of solidified gases. L. VEGARD (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 780—788).—The bands in the luminescence spectrum produced by bombarding solid Kr and A with cathode rays have been studied, and many have been referred to an impurity of N₂. The infra-red luminescence from A, A + 3.5% N₂, and N₂, in the solid state, has also been studied. From X-ray measurements solid β -N₂ has a hexagonal elementary cell, containing 2 mols. capable of rotation in the lattice, with a 4.039 Å., c/a 1.651. In α -N₂ the mols. are fixed on trigonal axes, space-group $\bar{4}2_1$, and the mol. centres are approx. arranged in a face-centred cubic lattice. It is suggested that in α -N₂ the excited state is kept undisturbed for sufficient time for transition to the normal to occur, and a band system is emitted, but with β -N₂ no phosphorescence can be emitted, since the excited state is disturbed by rotation. Solid O₂ exists in two forms, I stable between -229° and the m.p., II from -249° to -229°. There is some indication that the mols. rotate in form I.

R. S. B.

Efficiency of chemiluminescence accompanying the Wedekind reaction. W. L. ASLING and A. I. DUFFORD (Physical Rev., 1933, [ii], 44, 315).—The chemiluminescence (I) accompanying the reaction between chloropicrin and certain Grignard reagents has been quantitatively investigated. The efficiencies, which range from 4.4×10^{-8} to $10^{-9}\%$, are discussed in relation to the possible origin of (I).

L. S. T.

Luminescence on agitating mercury in impure neon at low pressure. G. DEJARDIN and E. SCHWÉGLER (Compt. rend., 1934, 199, 1110—1112).—The spectrum, which contains mainly and bands, resembles the aurora spectrum.

H. J. E.

Experiments the Kunsman anode. G. VILLE (Ann. Physik, 1934, [v], 21, 443—456).—The

Kunsman anode (mixture of Fe₂O₃, Al₂O₃, and alkali salt) was used to investigate the variation of velocity (I) of Cs ions emitted from it with temp. (I) was const. between 650° and 900°, increased by 0.5 volt between 900° and 1100°, and was again const. from 1100° to 1300°. The variation of (I) is due to a change in the thermo-electric emission work, a satisfactory explanation for which has not been found, although it may be connected with the β - γ Fe transformation in the anode.

A. J. M.

Outer photo-electric effect of composite photocathodes at low temperatures. R. SUHRMANN and D. DEMPSTER (Physikal. Z., 1934, 35, 973—975).—Photo-electric cells with K-KH-K (I) and K-C₁₀H₈-K (II) cathodes show increased sensitivity at the temp. of liquid air, when irradiated with light of the selective max. [430 m μ for (I), and 290 m μ for (II)]. It is assumed that the increased sensitivity is due to the presence in excited states of light-absorbing centres, of which the life is considerable at low temp., but is shortened at room temp. owing to thermal vibration.

A. J. M.

Photo-electric conductivity in silver chloride. A. ARSENEVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 118—120).—The photo-electric current is independent of temp. between -110° and -170°.

E. S. H.

Radiation from cells formed of semi-conductors. G. DÉCHÈNE (J. Phys. Radium, 1934, [vii], 5, 553—562).—The emission of absorbable electromagnetic radiation is confirmed. Investigation of the absorption in air, and analysis by the tangent grating method, showed that semi-conducting cells of yellow HgO, PbCl₂, and Na₂CO₃ emit an ionising radiation situated in a region 12—600 Å. thick; its suggested origin is the thin air film in contact with the semi-conductor.

N. M. B.

Barrier layer cells. R. H. VARIAN (Physical Rev., 1934, [ii], 46, 1051—1054).—Frenkel and Joffe's theory of the photovoltaic effect in cells containing a semiconductor (I), a thin barrier to the passage of electrons, and a metal, does not adequately explain the direction of current flow, but can be made adequate if the difference in the rate of loss of velocity of photo-electrons in (I) and in the metal is taken into account.

N. M. B.

External photo-electric effect and chemical constitution. A. POCHETTINO (Nuovo Cim., 1934, 11, 213—223; Chem. Zentr., 1934, ii, 910—911).—Data are recorded for several C₆H₆ derivatives using λ 2536 Å. for irradiation. The presence of a C₆H₆ ring combined with one or more other 6-rings, or containing active groups (e.g., NH₂), is necessary for a high photo-effect (I). Halogens, CO₂H, NO₂, or :C:O produce a low val. For isomerides the substances with the highest dipole moments have the highest (I), except when NO₂ is present. In C₁₀H₈ derivatives the val. is higher with α - than with β -substitution. Some dyes were studied and showed a high effect.

H. J. E.

Motion of ionic lattices of insulators at extreme field intensities. A. GUNTHER-SCHULZE and H. BETZ (Z. Physik, 1934, 92, 367—374).—Unaged oxide

layers on Al and Ta show three regions of current flow: a pure electron current at low field intensities, and an electron and ion current of the same order at higher intensities; at still higher intensities the ionic current follows a different exponential law. The ionic current is due to interpenetration of metal and O ions.

A. B. D. C.

Ionisation of liquid carbon disulphide by X-rays. F. L. MOHLER and L. S. TAYLOR (J. Res. Nat. Bur. Stand., 1934, 13, 659—664).—Data are recorded. The no. of ions produced in the liquid per quantum absorbed is approx. the same as in the vapour, but the current resulting from the ionisation is much reduced by intracolumnar recombination.

H. J. E.

Photovoltaic effect. R. T. DUFFORD (Physical Rev., 1933, [ii], 44, 315; cf. A., 1933, 915).—The behaviour of photovoltaic cells, especially those containing Grignard reagents, is compared with that of other types of cell. Current theories of electrode potential must be extended in order to explain the results.

L. S. T.

Effect of temperature and of visible and [near] infra-red radiation on the electrical resistance of boron. R. FREYMAN and A. STIEBER (Compt. rend., 1934, 199, 1109—1110).—Weintraub's results for the temp. effect are confirmed (cf. Ind. Eng. Chem., 1913, 5, 112). The resistance diminishes on irradiation.

H. J. E.

Ionic mobilities in dielectric liquids. I. ADAMCZEWSKI (Bull. Acad. Polonaise, 1934, A, 217—230).—A third ion has been detected in ionised C_6H_{14} , and three ionic mobilities each in C_5H_{12} , C_5H_{16} , and C_8H_{18} . The ionic mobilities are related empirically with the viscosity coeff. X-Rays furnish a better source of ions than Ra preps. for mobility investigations, owing to the stronger ionising effect and the absence of errors due to mechanical disturbance.

J. W. S.

Atomic polarisation of carbon monoxide. L. A. MATHESON (Physical Rev., 1933, [ii], 44, 604).—A discussion.

L. S. T.

Dipole moment of heavy water. F. H. MULLER (Physikal. Z., 1934, 35, 1009—1011).—The dipole moment of H_2O in C_6H_6 solution determined by a modified Williams method is $1.78 \pm 0.02D$, which agrees within experimental error with the val. for H_2O . The theoretical consequences are discussed.

A. J. M.

Determination of dipole moment of sucrose. E. LANDT (Naturwiss., 1934, 22, 809).—The dipole moment of sucrose in polar solvents has been determined. In C_5H_5N the val. is 2.8, in NH_4Bu^+ 3.4, and in NH_4Et 3.4 (all $\times 10^{-18}$). Interaction with the solvent is neglected.

A. J. M.

Refractive index and molecular refractivity of hydrogen selenide for the D_3 line (5875.6 Å.). O. and O. HASSEL (with J. LOHNE) (Z. physikal. Chem., 1934, B, 27, 316—318).— $(n_D - 1) \times 10^6$ measured at 8—27 mm. pressure is 788.0 mol. refractivity is calc. as 11.77.

R. C.

Refractivity of cellulose and its derivatives. III. Influence of adsorbed water on refractivity of cellulose fibres. IV. Refractive indices of cellulose nitrate and cellulose acetate. K. KANAMARU (Helv. Chim. Acta, 1934, 17, 1425—1429, 1429—1440; cf. A., 1934, 1292).—III. During absorption of H_2O by dried ramie fibres the refractive index perpendicular to the fibre axis (n_a) remains approx. const., whereas n_v (parallel to axis) passes through a min. An explanation is suggested.

IV. The linear relationship between double refraction and N content of cellulose nitrate has been established by direct measurement of n_a and n_v . The relationship is observed only when the nitration process gives rise to a homogeneous product. When cellulose (I) is acetylated so as to preserve the fibre structure the product is always heterogeneous, and consists of a mixture of the triacetate with unchanged (I). The diminution of n_a and n_v on esterification of (I) indicates that n is influenced by the polarity of the side-chains.

F. L. U.

Corrections to the refractive indices of quartz in the infra-red. D. G. DRUMMOND (Nature, 1934, 134, 937).—Corr. vals. for n are given for wavelengths between 3 and 3.8 μ .

L. S. T.

Optical anisotropy, form, and inner movements of organic molecules. H. A. STUART and H. VOLKMANN (Physikal. Z., 1934, 35, 988—990).—The optical anisotropy of n - and branched-chain hydrocarbons (C_2 — C_{12}) in the vapour state, calc. from the Kerr const., indicates that these mols. do not form extended zig-zag chains, and are not spiral. The introduction of polar groups ($\cdot O \cdot O$, $\cdot C \cdot O$), however, causes an extension of the chain.

A. J. M.

Anisotropy of the optical polarisation field in liquids. M. RAMANADHAM (Proc. Indian Acad. Sci., 1934, 1, A, 281—287).—The refractivities of a no. of org. vapours, calc. from the vals. of n for the liquid state on the basis of the theory of the anisotropic polarisation field developed by Raman and Krishnan (A., 1928, 113), agree with observed vals. better than those calc. by the Lorentz formula.

J. W. S.

Ultra-violet rotatory dispersion of camphor in sulphuric acid solution. J. LECOMPTE and J. PERRICHET (Compt. rend., 1934, 199, 1202—1205).—Data are recorded for varying concns. for $\lambda\lambda$ 4047, 3650, 3341, 3130, 3022, and 2967 Å. Measurements in conc. H_2SO_4 indicate that a third form or a compound of camphor exists in the solution.

H. J. E.

Magnetic rotation of salts of higher fatty acids and evidence in favour of the formation of ionic micelles. S. S. BHATNAGAR and P. L. KAPUR (J. Indian Chem. Soc., 1934, 11, 767—772).— $M[\omega]$ of Na and K oleates in H_2O in the concn. range 3—19% vary in a manner consistent with the formation of ionic micelles.

J. G. A. G.

Verdet constant of heavy water. F. G. SLACK (Physical Rev., 1934, [ii], 46, 945—947).—Verdet consts. for H_2O containing 0, 31.1, and 99.7% H^2 , measured for $\lambda\lambda$ 5893 and 5460.7 Å. at 20°, give a val. for the const. 3.93% < that of H_2O for both wave-lengths. Non-linearity of the Verdet const.-concn. relation gives an apparent const. for H^1H^2O

0.85% < that for H_2O . Vals. of the relative mol. rotatory power and magnetic rotatory dispersions are given. N. M. B.

Superposition of electric and magnetic birefringence. M. SCHERER and A. PIEKARA (J. Phys. Radium, 1934, [vii], 5, 568—570).—Investigations on CS_2 , PhMe, $1\text{-C}_{10}\text{H}_7\text{Me}$, and solutions of PhNO_2 in PhMe show that the two effects are without mutual influence, agreeing with Pockels' theory. N. M. B.

Magnetic double refraction of organic liquids. E. MATULL (Ann. Physik, 1934, [v], 21, 345—366).—The Cotton-Mouton consts. (I) of PhMe, C_6H_6 , and CHCl_3 , 7.28, 6.80, and -0.77 (all $\times 10^{-13}$), respectively, differ from those recorded. The principal magnetic polarisabilities (II) were calc. from (I). For CCl_4 , the three vals. of (II) are identical, confirming the tetrahedral form of the mol. For CHCl_3 , the negative sign of (I) indicates that the max. optical polarisabilities and (II) are coincident. The axis of max. (II) lies in the plane of the three Cl atoms, whilst that of least (II) coincides with the direction of the C-H moment. For C_6H_6 , (I) is relatively large, indicating considerable magnetic anisotropy. The max. optical polarisability and (II) are perpendicular to each other. A. J. M.

Thermal variation of magnetic birefringence of paramagnetic solutions of rare-earth salts. C. HAENNY (Compt. rend., 1934, 199, 1207—1209).—Vals. are recorded for salts of Ce and Tb. H. J. E.

Allison magneto-optic effect. L. B. SNODDY (Physical Rev., 1933, [ii], 44, 691).—Modifications in technique are described. L. S. T.

Isotopes of hydrogen by the magneto-optic method. Existence of H^3 . W. M. LATIMER and H. A. YOUNG (Physical Rev., 1933, [ii], 44, 690).—A solution of HCl in H_2O gives min. at 15.74 and 15.85 Allison units; the latter, due presumably to H^1 , is much stronger. With H_2O (2 and 4%) as solvent, these two min. are practically equal in intensity. A third min. at 15.65 corresponds with H^3 . Similar results are obtained when HBr replaces HCl. L. S. T.

Isotopes of chlorine. E. R. BISHOP and F. ALLISON (Physical Rev., 1933, [ii], 44, 419—420).—When HF, H_3PO_4 , or KBr is added to a saturated solution of Cl_2 in H_2O , min. corresponding with Cl uronde, Cl phosphate, and Br chloride, but not Cl bromide, respectively, were obtained by the magneto-optic method. $\text{Cl}_2\text{-H}_2\text{O}$ gives min. corresponding with Cl chloride. The min. observed are due to Cl^{35} , Cl , and probably Cl^{39} . L. S. T.

Isotopes of calcium by the magneto-optic method. W. M. LATIMER and H. A. YOUNG (Phys. Rev., 1933, [ii], 44, 61).—Many of the min. reported by Allison (A., 1930, 1541) have been confirmed. With Ca, a third faint min., probably due to Ca^{41} is always obtained. L. S. T.

Lead isotopes by the magneto-optic method. (Physical Rev., 1933, [ii], 44, 420).—In agreement with other investigators (A., 1933, 204) min. between 36 and 38 Allison units have been

obtained with aq. PbCl_2 by the magneto-optic method. L. S. T.

Constitution of hypophosphoric acid. A. HANTZSCH (Z. anorg. Chem., 1934, 221, 63—64).—The reactions of $\text{H}_4\text{P}_2\text{O}_6$ and its Na salt support Nylen and Stelling's formula (A., 1934, 854) $(\text{HO})_4\text{P}_2\text{O}_2$. It is not a mixed acid anhydride of H_3PO_3 and H_3PO_4 . M. S. B.

Magnetic properties of free radicals. Xanthyl- α -naphthylmethyl. (MME.) S. ALLARD (Compt. rend., 1934, 199, 1125—1126).—Measurements of the susceptibility are used to calculate the degree of dissociation in C_6H_6 solution of dioxanthylid- α -naphthylethane. H. J. E.

Dependence of the diamagnetism of water on temperature. A. P. WILLS and G. F. BOEKER (Physical Rev., 1934, [ii], 46, 907—909).—Anomalous results previously reported (cf. A., 1933, 212) are partly explained. Variation of susceptibility with temp. is plotted for the range 20—66°, and a parabolic formula is deduced. N. M. B.

Diamagnetic susceptibilities of salts forming ions with inert gas configurations. I. Halides of sodium and potassium. F. E. HOARE (Proc. Roy. Soc., 1934, A, 147, 88—100).—The diamagnetic susceptibilities of the Na and K halides have been measured at 20—22° by Gouy's method, in which the force on the specimen in an unhomogeneous magnetic field is measured with a sensitive balance. L. L. B.

Nickel cyanide and complex derivatives: magneto-chemical studies. L. CAMBI, A. CAGNASSO, and E. TREMOLADA (Gazzetta, 1934, 64, 753—772).— $\text{Ni}(\text{CN})_6$ and its complex salts containing H_2O , NH_3 , $(\text{CH}_2\text{-NH}_2)_2$, and other org. bases give vals. of $\chi_{\text{Ni}}=11$ Weiss magnetons approx., whereas for the halides NiX , and their complex salts the vals. =16 approx. It is suggested that the complex cyanides contain the complex cation $[\text{Ni}, \text{M}]$, which is paramagnetic with $\chi_{\text{Ni}}=16$ ($\text{M}=\text{a mol. of NH}_3$ etc.), and the complex diamagnetic anion $\text{Ni}(\text{CN})_4$. O. J. W.

Magnetic susceptibility of the ferrous salts of pyridine- and quinoline-2-carboxylic acids. L. CAMBI and A. CAGNASSO (Gazzetta, 1934, 64, 772—773; cf. A., 1934, 241).—The data given for the Fe salt of quinolinic acid in the previous paper are wrong. The correct val. of χ_{Fe} for the compound $\text{Fe}(\text{C}_7\text{H}_4\text{O}_4\text{N})_2 \cdot 3\text{H}_2\text{O}$ is 26.7 Weiss magnetons at 291° abs. O. J. W.

Paramagnetic rotation of tysonite. J. H. VAN VLECK and M. H. HEBB (Physical Rev., 1934, [ii], 46, 929; cf. A., 1934, 944).—A correction. N. M. B.

What is known of ferromagnetism with small changes of field? H. JORDAN (Ann. Physik, 1934, [v], 21, 405—424).—A criticism of the work of Gans and Wittke (A., 1934, 14). A. J. M.

[What is known of ferromagnetism with small changes of field?] R. GANS (Ann. Physik, 1934, [v], 21, 425).—A reply to Jordan (preceding abstract). A. J. M.

Chemical linking. (A) R. F. HUNTER and R. SAMUEL (*Nature*, 1934, **134**, 971). (B) ANON. (*ibid.*, 971—972).—Polemical. L. S. T.

Models for the demonstration of the exact space occupied by molecules. H. A. STUART (*Physikal. Z.*, 1934, **35**, 990—991).—Models in which parts of spheres are used instead of complete ones are described. A. J. M.

Constants of the HCl molecule. P. GOMBAS and T. NEUGEBAUER (*Z. Physik*, 1934, **92**, 375—384).—Theoretical. The ionic model with Hartree's proper function leads to an interat. separation 3.8% too great, a dipole moment 19% too great, and fundamental frequency 3.9% too small. A. B. D. C.

Interatomic forces and oscillation frequencies of atoms in lattices. S. FRANCHETTI (*Atti R. Accad. Lincei*, 1934, [vi], **20**, 186—191).—Mathematical. O. J. W.

Role of the electron in chemical combination. J. SAVARD (*Helv. Chim. Acta*, 1934, **17**, 1466—1480).—A lecture in which simple mols. are considered from the point of view of ionisation potential (*cf. A.*, 1934, **11**, 347, 577, 584, 943). F. L. U.

Collision phenomena in the recombination of hydrogen atoms to molecules. H. SENFTLEBEN and W. HEIN (*Physikal. Z.*, 1934, **35**, 985—986).—The effect of pressure and addition of inert gases on the recombination of H to H₂ has been investigated. The reaction is one involving triple collisions. The activity of the third participant in the reaction varies with its nature, and it is found that the heavier inert gases (A and Kr) are more effective than the lighter (He and Ne) and H₂ itself. A. J. M.

Electronic configuration of molecules and their electron affinity. N. E. BRADBURY (*J. Chem. Physics*, 1934, **2**, 840).—The relation between the electronic configuration of a mol. and its ability to form a stable negative ion by electron attachment is discussed. M. S. B.

Fundamental oscillations of molecules of the type X₆ and X₆Y₆. M. VAN DEN BOSSCHE and C. MANNEBACK (*Ann. Soc. Sci. Bruxelles*, 1934, **54**, B, 230—279).—Mathematical. The general method of symmetrical co-ordinates is used to calculate the frequencies of the fundamental oscillations of mols. of the type X₆ and X₆Y₆ (C₆H₆). The forms of the degenerate motions are also obtained. It is proposed to utilise the results to calculate the fundamental frequencies of C₆H₆. A. J. M.

Reactions of atoms. W. HELLER and M. POLANYI (*Compt. rend.*, 1934, **199**, 1118—1121).—A summary and discussion. H. J. E.

Intramolecular statistics, especially for chain molecules. I. E. GUTH and H. MARK (*Monatsh.*, 1934, **65**, 93—121).—Theoretical. M. S. B.

Potential function for the vibrations of diatomic molecules. M. F. MANNING and N. ROSEN (*Physical Rev.*, 1933, [ii], **44**, 953).—Mathematical. L. S. T.

Dynamical theory of the diamond lattice. I. N. S. N. NATH (*Proc. Indian Acad. Sci.*, 1934, **1**, A,

333—345).—Mathematical. The equations of vibratory motion of the diamond lattice are formulated. A typical factor of the secular equation corresponds with the vibration of the two face-centred cubic lattices composing the diamond lattice relative to one another, this vibration being triply degenerate. This vibration is Raman-active but optically inactive, since all atoms are homonuclear, and accounts for the principal Raman frequency (1332 cm.⁻¹) being absent from the infra-red spectrum. J. W. S.

Nuclear forces. W. M. ELSASSER (*Compt. rend.*, 1934, **199**, 1406—1408).—Theoretical. J. W. S.

Effect of dispersion and of lattice distortion on the atomic scattering factor of copper for X-rays. G. W. BRINDLEY and F. W. SPIERS (*Nature*, 1934, **134**, 850).—The at. scattering factor (I) for the (220) spectrum at room temp. of Cu pptd. from CuSO₄ by Zn is > that of Cu filings from chill-cast rod or hard-drawn wire. Distortions in a metal thus lower the val. of (I). The lowering of (I) due to dispersion is 3.3. L. S. T.

Angular variation of the refractive index for X-rays. J. A. PRINS (*Z. Physik*, 1934, **92**, 690—691).—Polemical, against Jentsch (*A.*, 1934, 1295). A. B. D. C.

Measurement of absolute X-ray intensities and absolute sensitivity of X-ray film with a Geiger-Müller counter. G. L. LOCHER (*Physical Rev.*, 1934, [ii], **46**, 1047—1051).—A special counter containing Kr is described, and a "standard beam" of fluorescent Zr X-rays is calibrated. Using this beam, the min. exposure of X-ray film for detectable blackening is 0.72 × 10⁶ quanta cm.⁻², incident on the film, or 4.1 × 10⁴ quanta cm.⁻², absorbed in the emulsions. The total absorption coeffs. of the film, celluloid, and emulsion, for Zr X-rays, are 8.63, 1.66, and 13.0 cm.⁻¹, respectively. N. M. B.

Structure determination by the Fourier method. A. HETTICH (*Z. Physik*, 1934, **92**, 528—532).—The Fourier method may be applied in general to structural and chemical problems of crystals. A. B. D. C.

Property of structure analysis. N. SELJAKOV (*Z. Physik*, 1934, **92**, 543—546).—X-Ray photographs taken by the rotating-crystal method depend very much on the crystal position for both large and small angles of reflexion. A. B. D. C.

Significance of surface forms for determination of symmetry and habit of crystals. G. KALB (*Z. Krist.*, 1934, **89**, 400—409).—The general geometry of a crystal is not always sufficient to fix its symmetry completely; an additional study of surface forms (including etch markings) is necessary. Detailed examples are given. B. W. R.

New evidence, setting an upper limit of 500 Å. or less, to dimensions of mosaic blocks (if any) in a crystal. H. E. BUCKLEY (*Z. Krist.*, 1934, **89**, 410—415).—Crystal plates (order of 0.3 mm. thick) can be grown or cleaved so perfectly as to give interference bands in monochromatic light between front and back surfaces over considerable areas. This is taken to disprove the existence of mosaic

structures such as have been required by various authors. B. W. R.

X-Ray investigations at high pressures. W. M. COHN (Physical Rev., 1933, [ii], 44, 326—327).—Changes in the modifications of crystals occurring in a Bridgman bomb at pressures up to 3000 atm. have been investigated by means of X-rays. L. S. T.

Theory of real crystals. A. SMEKAL (Z. Krist., 1934, 89, 386—399).—A summary of existing theories, with special reference to strength properties of crystals. B. W. R.

Theory of real crystals. A. G. SMEKAL (Physical Rev., 1933, [ii], 44, 308—309).—Polemical (cf. this vol., 19). L. S. T.

Strength and real structure of crystals. E. OROWAN (Z. Krist., 1934, 89, 327—343).—A perfect lattice cannot explain such properties as crystal breaking strength, plastic slip, and electrical strength, nor can any regularly modified lattice (e.g., block or secondary structures). The crack-broadening theory of Griffith with certain modifications is more satisfactory when applied to these properties. B. W. R.

X-Ray reflexion and real structure in rock-salt. M. RENNIGER (Z. Krist., 1934, 89, 344—374).—With a double-crystal spectrometer the reflexion width and the integrated intensity were determined for various crystals and surfaces of rock-salt. An artificial crystal gave the theoretical width and intensity; i.e., over regions of order 1 mm. the lattice was perfect. This is discussed in relation to the usual theories of secondary structure. B. W. R.

Theory of the plasticity of crystals. G. I. TAYLOR (Z. Krist., 1934, 89, 375—386).—The observed strength of crystals is highly dependent on the past history, i.e., on previous plastic distortions. A simple picture of plastic distortion is suggested, in which "dislocations" move through the lattice as slipping takes place. The dislocation moves freely only in a perfect lattice, and has a "mean free path"; this leads immediately to (a) a parabolic stress-strain relationship agreeing with experiment, and (b) a "mean free path" of about 10^{-4} cm., agreeing with the spacing of the dislocations or cracks postulated by Goetz, Zwicky, Smekal, *et al.* B. W. R.

Group phenomena in metal crystals. A. GOETZ (Z. Krist., 1934, 89, 310—326).—A survey of the experimental distinction between real and ideal crystals, especially referring to metal crystals. Proper verification of a group or swarm theory is difficult, but an assumption of this kind removes many arbitrary hypotheses which are otherwise required. B. W. R.

Hooke's law and crystal structure. A. E. CASWELL (Physical Rev., 1933, [ii], 44, 320).—Theoretical. L. S. T.

X-Ray rotation crystal and fibrous structure diagrams. I. Expressions of the X-ray spot and the crystal plane. II. Expressions of the X-ray spot and the crystal plane in triclinic

system. III. Limit of X-ray reflexion. M. ISHIHARA (J. Soc. Chem. Ind. Japan, 1934, 37, 562—566B, 566—568B, 568—570B).—Mathematical. J. W. S.

Crystallisation of polymorphous substances. I. K. LARK-HOROVITZ and S. E. MADIGAN (Physical Rev., 1933, [ii], 44, 320).—The cubic form of ZnS has been evaporated in a vac. at temp. < the transition point $\alpha \rightarrow \beta$ -ZnS and deposited on different surfaces at 20°. The deposit is cubic on all surfaces with a cubic lattice (Cu, Al, diamond, etc.), on amorphous surfaces such as glass and fused quartz, and on Zn, mica, and cryst. quartz. A mixture of the hexagonal with excess of the cubic modification is formed on ZnO. On hexagonal CdS (I), the deposit is also wholly hexagonal (wurtzite). When deposited simultaneously on (I) surrounded by Cu, the ZnS is hexagonal on (I) and cubic on the Cu. When evaporated in a vac., wurtzite is deposited on cubic surfaces as Zn blende, but remains hexagonal on hexagonal ZnS. L. S. T.

Transition of antimony into the vitreous amorphous state. G. TAMMANN and W. MÜLLER (Z. anorg. Chem., 1934, 221, 109—112).—By the addition of Sb₂Se₃ to molten Sb the crystallisation velocity may be reduced, so that, by rapid chilling to -180° of droplets of approx. 0.4 mm. diameter, amorphous particles are formed. By heating for $\frac{1}{2}$ hr. at 520° the particles become cryst. This result is not obtained in the absence of Se. M. S. B.

Nucleus formation on crystals of copper sulphate pentahydrate. N. F. H. BRIGHT and W. E. GARNER (J.C.S., 1934, 1872—1877; cf. A., 1934, 720).—The no. of nuclei (I) formed on the (110) face of crystals of CuSO₄·5H₂O when dehydrated in a high vac. was determined. After an induction period (II), (I) increases linearly with time. As a rule a few visible (I) are present during (II). (I) were star-shaped, with two main directions of growth in the (110) face, and a third into the crystal in the form of a thin disc making an angle of 56° with the face. The occurrence of (II) indicates that (I) when small do not grow at a uniform rate. The crit. increment of (II) is 16 kg.-cal. A. J. M.

Cell dimensions of ordinary and "heavy" ice. H. D. MEGAW (Nature, 1934, 134, 900—901).—The structure of cryst. H₂O is the same as that of ordinary ice, the difference between the cell dimensions being extremely small. There appears to be a small, real difference (< 0.1%) in *a* at 0°. Ordinary H₂O has its mols. more closely packed than H₂¹⁸O, which has a more ice-like structure. L. S. T.

Diffuse scattering of X-rays from sylvine. G. E. M. JAUNCEY and W. D. CLAUS (Physical Rev., 1934, [ii], 46, 941—945).—Improved experimental determinations of *S* vals. agree with calc. results. N. M. B.

Crystal structure of LaMg and CeMg. A. ROSSI (Gazzetta, 1934, 64, 774—778).—LaMg and CeMg have a cubic-centred lattice with *a* 3.952, 3.884 Å., *d*_{obs.} 4.36, 4.48, 4.36, 4.63, respectively. The Hume-Rothery rule is discussed. O. J. W.

Crystal structure of PrSn_3 and PrPb_3 . A. ROSSI (Gazzetta, 1934, 64, 832—834).— PrSn_3 and PrPb_3 have the same face-centred cubic structure as the corresponding La compounds (A., 1933, 1003) with a 4.704, 4.857 Å., $d_{\text{obs.}}$ 7.60, 10.60, $d_{\text{calc.}}$ 7.88, 10.98, respectively. O. J. W.

Crystal structure of stannite $\text{Cu}_2\text{FeSnS}_4$. L. O. BROCKWAY (Z. Krist., 1934, 89, 434—441).—The cell is tetragonal, a_0 5.46, c_0 10.725 Å., containing 2 mols. of $\text{Cu}_2\text{FeSnS}_4$. Space-group chosen as D_{2d}^{11} ; there is, however, a possibility of a structure based on the point-group \bar{S}_4 . At. positions are deduced from intensity considerations. The structure resembles, but is not identical with, that of chalcopyrite. B. W. R.

Crystal lattice of ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and the structure of the persulphate group. R. C. L. MOONEY and W. H. ZACHARIASEN (Physical Rev., 1933, [ii], 44, 327; cf. A., 1934, 1060).— NH_4 and Cs persulphates, monoclinic, have 4 mols. per unit cell; space-group $P2_1/n$ (C_{2h}^2). $(\text{NH}_4)_2\text{S}_2\text{O}_8$ has a 7.80, b 7.98, c 6.12 Å., β $95^\circ 9'$. The S_2O_8 group can be regarded as 2 SO_4 joined together by a linking across a centre of symmetry between 2 O atoms. Each S is tetrahedrally surrounded by 4 O at a distance of 1.50 Å. The distance between the 2 O connected by the valency linking is 1.31 Å., and the angle between the two linkings of these O is 128° . NH_4 is surrounded by 12 O at a mean distance of 3.15 Å. L. S. T.

Crystal structure of sodium thioantimonate. CHING-YEUNG HUI (Physical Rev., 1933, [ii], 44, 327).—X-Ray investigations show that $\text{Na}_2\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, cubic, a 11.835 Å., has 4 mols. per unit cell; space-group $P2_13$ (T^4); d 1.927. L. S. T.

Crystal structure of potassium uranyl acetate. I. FANKUCHEN (Physical Rev., 1933, [ii], 44, 327).—X-Ray investigations indicate that K uranyl acetate is dimorphous, both forms being hexagonal. One has a 14.38, c 25.80, and the other a 13.99, c 27.70 Å. Both body-centred unit cells have approx. the same vol. and contain 16 mols.; space-group, probably $I4_12$ (D_{10}^1). The U atoms are approx. in a face-centred lattice 0.25 the height of the actual unit cell. L. S. T.

Crystal structure of $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$. J. M. BIJVOET and C. H. MACGILLAVRY (Nature, 1934, 134, 849—850).—The unit cell, 4.06 Å.³, contains only 0.5 mol. Structure is discussed. L. S. T.

Crystal structure of chalcopyrite. S. KÔZU and K. TAKANÉ (Proc. Imp. Acad. Tokyo, 1934, 10, 498—501).—The cell dimensions and axial ratio of crystals from Arakawa, Ugo, Japan, are a_0 5.28, c_0 5.22 Å. c_0/a_0 0.989; space-group $P\bar{2}_1$; 2 mols. CuFeS_2 in unit cell. C. W. G.

Structural fine-structure of barium succinate. E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1934, B, 27, 282—286).—The unit cell has I_a 7.57, I_c 10.28 Å. and contains 4 $\text{BaC}_4\text{H}_4\text{O}_4$ mols.; space-group D_{2h}^{12} . The lattice is a typical ionic lattice. R. C.

Guanidine mono-, di-, and tri-chromates. Crystallographic study. A. SWARYCZEWSKI (Bull.

Acad. Polonaise, 1934, A, 246—255).—Crystallographic data are given. J. W. S.

Crystal lattice of oxalic acid dihydrate and the structure of the oxalate radical. W. H. ZACHARIASEN (Z. Krist., 1934, 89, 442—447).—This is monoclinic, a_0 6.12, b_0 3.61, c_0 12.03 Å., β $106^\circ 12'$, space-group $P2_{1/n}$. The 12 parameters (neglecting the H atoms) are uniquely and accurately determined. The oxalate radical is planar. B. W. R.

X-Ray studies of the molecular arrangement in liquids. S. KATZOFF (J. Chem. Physics, 1934, 2, 841—851).—An improved method for taking X-ray diffraction photographs of weakly absorbing liquids is described. Photographs of H_2O , C_7H_{16} , $\text{C}_{10}\text{H}_{22}$, C_6H_6 , and C_6H_{12} have been made. The results are explained on the assumption that adjacent mols. in a liquid are held together similarly to those of a crystal, but are otherwise of random arrangement. M. S. B.

X-Ray investigation of crystals of m -azotoluene. M. PRASAD and P. H. DALAL (Current Sci., 1934, 3, 200—201).—The rotation method gives a 11.88, b 13.75, c 7.52 Å.; space-group Q_1^1 . L. S. T.

Cholesteryl salicylate. S. B. HENDRICKS (Z. Krist., 1934, 89, 427—433).—The prep. of the pure salicylate is described; X-ray data give a_0 9.68, b_0 12.52, c_0 6.31, α $92^\circ 56.5'$, β $101^\circ 58.5'$, γ $95^\circ 14'$, for the cell, which is triclinic, space-group $P1$. There are possible alternative units, and it is argued that in general the dimensions of units of structure are not necessarily related to the mol. dimensions. The salicylate forms a liquid crystal phase below its m.p., perhaps due to the presence of orthogonal N and O valencies. B. W. R.

M.p. and long crystal spacings of the higher primary alcohols and n -fatty acids. S. H. PIPER, A. C. CHIBNALL, and E. F. WILLIAMS (Biochem. J., 1934, 28, 2175—2188).—The m.p. and long crystal spacings of several pure C_{26} to C_{36} alcohols, acids, acetates, and Et esters and binary and ternary mixtures of known composition are recorded. Methods are indicated for using the data in determining the composition of mixed alcohols and acids present in waxes. C. G. A.

Crystals of hydrochlorides, hydrobromides, and hydriodides of methylephedrine. Crystallographic relations between dl -compounds and their components. B. GOSSNER and H. NEFF (Z. Krist., 1934, 89, 417—426).—Crystallographic descriptions, d , cleavage, consts. of unit cell (X-ray), and space-group are given for the hydrochloride and hydrobromide of l - and dl -methylephedrine, and the dl -hydriodide. Two modifications of the dl -hydrobromide are described. The constitution of these racemates is discussed from the viewpoint of a "double salt" of the d - and l -compounds. B. W. R.

X-Ray observations on lower and higher polypeptides. K. H. MEYER and Y. Go (Helv. Chim. Acta, 1934, 17, 1488—1492).—Powder diagrams of n -glycylglycine ($n = 3-7$), compared with those of a polyglycylglycine of mol. wt. about 2000, show that as n increases the arrangement of atoms in the former

approximates to that in the latter. The atoms are mostly arranged in lattice planes at a distance of 4.15 Å. F. L. U.

Structure of rubber as shown by the time lag of fibering. W. E. SINGER, J. D. LONG, and W. P. DAVEY (Physical Rev., 1933, [ii], 44, 319).—X-Ray investigation shows that there is a time lag between the time rubber is stretched and the time a fibre structure is produced. The view that rubber consists of a tangle of spiral or zigzag-shaped mols. with firmly fixed ends, the lengths of which can be temporarily untangled by application of an external force, explains the properties of the time lag. L. S. T.

Directional effects in electron diffraction from single crystals. G. A. MORTON (Physical Rev., 1933, [ii], 44, 952).—Electron diffraction photographs from the cleavage surfaces of NaCl and NaF show that the resolution of the diffracted spots varies with the azimuth of the crystal. L. S. T.

Interpretation of electron-diffraction photographs of gas molecules, with results for benzene and carbon tetrachloride. L. PAULING and L. O. BROCKWAY (J. Chem. Physics, 1934, 2, 867—881).—The accuracy of the visual method of interpreting electron-diffraction photographs has been tested in 4 different ways. When carefully applied it can give vals. of intercat. distances accurate to about 1%. The regular plane hexagon model for the C_6H_6 mol. has been verified. The C—C separation in C_6H_6 is 1.390 ± 0.005 Å. and the C—Cl separation in CCl_4 is 1.760 ± 0.005 Å. M. S. B.

Bloch theory applied to the study of alloys and of the properties of bismuth. H. JONES (Proc. Roy. Soc., 1934, A, 147, 396—417).—The Bloch theory is applied to binary alloys which form ϵ - and η -phases both having a close-packed hexagonal structure, and to alloys of Bi with small concns. of other metals in solid solution. A Brillouin zone is found for Bi containing 5 electrons per atom. The conductivity of Bi—Sn and Bi—Pb alloys, and the diamagnetic properties of the solid solutions of Sn, Pb, Te, Se, in Bi are considered. L. L. B.

Ferromagnetic transformation and catalytic activity. J. A. HEDVALL, R. HEDIN, and O. PERSSON (Z. physikal. Chem., 1934, B, 27, 196—208).—A more detailed account of work already reported (A., 1934, 608). There is no evidence of a change in the macro-structure of Ni at the Curie point (cf. A., 1933, 574). There is an increase in the rate of oxidation of Ni at this point. R. C.

Thermal expansion and the ferromagnetic change in volume of nickel. C. WILLIAMS (Physical Rev., 1934, [ii], 46, 1011—1014).—The coeff. of expansion of single and polycryst. specimens of Ni of known (varying) purity was measured at 2.5° intervals in the range 200—500°. The ferromagnetic change in vol. per unit vol. of pure Ni is $3.24 \pm 0.15 \times 10^{-4}$. N. M. B.

Gyromagnetic effect for a ferromagnetic substance above its Curie point. W. SUCKSMITH (Nature, 1934, 134, 936).—The mass susceptibilities of three Ni—Cu alloys (Ni approx. 56%) with Curie

points at -14° , -9° , and -2° range from 98 to $180 (\times 10^{-6})$. g is approx. 2, indicating that the paramagnetism of the Ni is due to spin alone, as in the ferromagnetic state. L. S. T.

Magnetostriction of pure and alloyed Bi single crystals. A. WOLF and A. GOETZ (Physical Rev., 1934, [ii], 46, 1095—1107).—The existence of a magnetostrictive effect for steady moderate fields is shown. Using 99.97% Bi single crystals the modulus of magnetostriction is $+5.7 \times 10^{-16}$ parallel to the trigonal axis, and -7.0×10^{-16} normal to the trigonal axis. Bi crystals with Pb, Sn, and Te in concn. within the solubility range were studied. Sn and Pb first diminish the contraction normal to the trigonal axis, and with increasing concn. cause an elongation, Sn being four times as effective as Pb. Parallel to the axis small concns. of Sn decrease, and larger concns. increase, the elongation; the effect of Pb is small. Te causes a much larger sp. effect, but no change in sign. The change of the stress coeff. of the susceptibility with the concn. of foreign atoms is discussed. Results support the assumption of the existence of two types of insertion of foreign atoms in the crystal lattice: selective adsorption for small concns. and vol. absorption for larger concns. N. M. B.

Electrical properties of materials at high radio frequencies. J. S. McPETRIE (Nature, 1934, 134, 897—898). L. S. T.

Mechanism of electrical conductivity. R. W. POHL (Z. Metallk., 1934, 26, 217—219).—A brief account of recent work of the author and his collaborators with especial reference to electronic condition in salt crystals. A. R. P.

Direct determination of the free paths of electrons in metals. A. EUCKEN and F. FORSTER (Z. Metallk., 1934, 26, 232—235).—An apparatus is described for determining the diameter (d) of very thin metal wires by measuring the torsional vibration in vac. If the sp. electric resistance of the wire (ρ_d) is then determined, the free path (l) of the electrons is given by $\rho_d = \rho_\infty (1 + 8l/3\pi d)$. For Bi at 0° l is 11μ , showing that the no. of free electrons at this temp. is only 1 for every 10^6 Bi atoms, i.e., that the classical theory and not the Sommerfeld—Fermi theory (I) applies to Bi. For Ag at 0° l is 57.7×10^{-7} cm. ($\pm 1.5\%$), a val. which is in accordance with (I) and shows that every Ag atom provides a free electron. At very low temp. the equation does not apply, the const. $8/3$ —being replaced by another factor varying with the temp. A. R. P.

Interaction of electrons in metals. E. WIGNER (Physical Rev., 1934, [ii], 46, 1002—1011; cf. A., 1934, 1283).—Mathematical. N. M. B.

Reflexion of light from silver mirrors on transition from the amorphous to the crystalline state at low temperatures. R. SUHRMANN and G. BARTH (Physikal. Z., 1934, 35, 971—973).—The electrical resistance and reflexion of thin layers of Ag formed by vac. condensation at 20° abs. were determined up to 390° abs. The variation of resistance is parallel to that of reflecting power (I). As the resistance decreases (I) increases first in the long-

wave region, and later in the visible and ultra-violet. In the transition from the amorphous to the metallic state, first the weakly bound, and then the more strongly bound, electrons play the part of metal electrons. A. J. M.

Susceptibility measurements of aluminium mixed crystals. H. AUER (Z. Physik, 1934, 92, 283—290).—The susceptibility of Al with small quantities of Mn, In, Ge, Ga, Cu, Ag, Zn, Li, and Mg does not follow the additivity law; deviations are towards diamagnetism, and are dependent on the solvent metal. Extent of impurity may be determined spectroscopically, so that these measurements can be used to elucidate metallic constitution. A. B. D. C.

Reflecting power of aluminium and its alloys in different regions. D. H. CLEWELL and J. WULFF (Physical Rev., 1933, [ii], 44, 952).—The reflecting powers of Al, Be, Mg, Si, and Ag alloys have been measured throughout the region 2000—7000 Å. and compared with those of films of the same metals. L. S. T.

Absorption and reflexion of gold between 380 and 1400 Å. I. LIBEN and H. M. O'BRYAN (Physical Rev., 1933, [ii], 44, 952).—Reflexion from Au mirrors at various angles of incidence, and transmission of thin Au films, have been determined in a vac. spectrograph. Sputtered Au mirrors give more reproducible reflexion than evaporated surfaces. L. S. T.

Use of model substances for the investigation of metal mechanics. A. SMEKAL (Z. Metallk., 1934, 26, 220—224).—An account is given of the results obtained in studying the elastic properties and recrystallisation of NaCl and of their application to the problems of the mechanism of metal deformation and recrystallisation. A. R. P.

Elastic moduli of rock-salt. L. BALAMUTH (Physical Rev., 1934, [ii], 46, 933; cf. A., 1934, 836).—A correction. N. M. B.

Elastic moduli for different textures of regular metals. D. A. G. BRUGGEMAN (Z. Physik, 1934, 92, 561—588).—Elastic moduli for polycryst. solids may be calc. from vals. for the single crystal. A. B. D. C.

X-Ray analysis of the deformation textures of metallic materials. F. WEVER (Kolloid-Z., 1934, 69, 363—368).—A review of published work on the X-ray structure of cold-worked metals. E. S. H.

Allotropy and crystallisation of vitreous substances. P. MONDAIN-MONVAL (Ann. Chim., 1935, [xi], 3, 5—72).—An abrupt change in the thermal expansion and sp. heat of vitreous Se and S takes place at the softening temp. θ ($\theta_{Se} = 32^\circ$; $\theta_S = -29^\circ$). θ has been determined by following the rate of change of penetrability of the substance by a metal point with change of temp. Below θ the rate of penetration, and therefore the fluidity, is practically zero. θ has also been determined for a no. of other vitreous substances (sucrose, glycerol, B_2O_3 , a black wax, colophony, and glass). It is found that the transformation of the metastable cryst. varieties of

S and Se into the respective stable forms takes place above θ , but not below. M. S. B.

Thermo-electric force of thin films. E. A. JOHNSON and L. HARRIS (Physical Rev., 1933, [ii], 44, 944—945).—The e.m.f. of thin sputtered thermo-couples of Sb and Bi varies with the thickness of Bi ($Sb\ 3 \times 10^{-5}$ cm.) up to 10^{-4} cm. Varying the thickness of Sb (5×10^{-6} cm. to 10^{-4} cm.) has no effect with 2×10^{-4} cm. of Bi. Thicknesses $>10^{-4}$ cm. give a thermal e.m.f. corresponding with that of massive Bi-Sb. Different cryst. orientation in thin layers of Bi may be the cause of this effect. L. S. T.

Thermal conductivities of bismuth single crystals as influenced by a magnetic field. M. T. RODINE (Physical Rev., 1934, [ii], 46, 910—916).—Thermal and electrical conductivities of two specimens of Bi single crystals were determined as a function of temp., in the range -170° to -50° , and orientation of magnetic field relative to the crystallographic axes. N. M. B.

Electrical resistance of gold, copper, and lead at low temperatures. W. J. DE HAAS, J. DE BOER, and G. J. VAN DEN BERG (Physica, 1934, 1, 1115—1124).—Measurements are recorded between 1° and 20° abs. The val. for Au has a min. at 3.70° abs. The transition temp. of Pb is 7.20° abs. H. J. E.

Superconductivity of thin films. E. F. BURTON, J. O. WILHELM, and A. D. MISENER (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 65—79).—The temp. of transition (I) to the superconducting state of thin films of Sn varies with the thickness, there being a limiting thickness (about 2×10^{-5} cm.) for which (I) is $< 2^\circ$ abs. The anomalous behaviour of such thin films is not due to irregularities of structure. The pronounced sensitivity to current strength varies with the thickness. A superconducting film $< 40 \times 10^{-5}$ cm. thick is no longer superconductive (above 2° abs.) when it is covered with non-superconducting metal. Since alloy formation could not have occurred under the conditions of the experiment, it appears that a free surface is necessary for the occurrence of superconductivity, although a layer of definite thickness is also required. H. F. G.

Superconductivity. A. PAPAPETROU (Z. Physik, 1934, 92, 513—522).—Theoretical. A. B. D. C.

Recent work on superconductivity. W. MEISSNER (Physikal. Z., 1934, 35, 931—938).—A review of recent work on the occurrence of superconductivity in metals, thin metallic layers, and alloys, and the magnetic behaviour of superconductors, with a discussion by various investigators. A. J. M.

Thermodynamics of the superconducting state. C. J. GORTER and H. CASIMIR (Physikal. Z., 1934, 35, 963—966).—The assumption that the superconducting phase is a two-phase system is extended. A. J. M.

Electronic theory of superconduction. R. SCHACHENMEIER (Physikal. Z., 1934, 35, 966—969).—In a superconductor, the two outer electrons are supposed to have different functions. One is attached to the core, the other is a conductivity

electron (I), this being responsible for the superconductivity. The wave-function corresponding with (I) is unchanged by the application of a weak magnetic field.

A. J. M.

Excitation of nuclear vibrations of oxygen by molecular collision (according to determinations of absorption of sound). H. O. KNESER (Physikal. Z., 1934, 35, 983—984).—The connexion between excitation of nuclear vibrations and absorption of sound waves (I) is discussed. The dependence of (I) in O_2 on the frequency of the waves and on the purity of the gas has been determined. With very pure O_2 there is no (I), but when foreign gases are present (H_2O , $EtOH$, NH_3 , C_6H_6 , C_2H_2 , H_2S , H_2 , He) (I) increases to a max. and then decreases to zero as the concn. of impurity (II) is increased. Extrapolation of the (I)–(II) curve to zero concn. indicates that the cessation period of the vibrational heat in pure O_2 is < 0.001 sec. The probability of collision between two O_2 mols. is very small, but is greater between O_2 and foreign mols.

A. J. M.

Collision excitation of intramolecular vibrations in gases and gas mixtures studied by sound dispersion measurements. I. Experimental method and results of precise measurements of velocity of sound in ultrasonic region. II. Dispersion of sound at various temperatures in chlorine and carbon dioxide, pure and with admixed foreign gases. A. EUCKEN and R. BECKER (Z. physikal. Chem., 1934, B, 27, 219—234, 235—262; cf. A., 1933, 554).—I. An apparatus for the precise determination of the wave-length of ultrasonic waves and depending on the principle of the acoustic interferometer is described. This may be used even with corrosive gases over a wide temp. range. The derivation of the vals. of c_p/c_v reduced to zero pressure for the components of a gas mixture from the velocity of sound is described, the error being 0.4—1%.

II. The velocity of sound of frequencies 58, 145, and 292 kilohertz has been measured in Cl_2 and CO_2 , pure and with admixed foreign gases, at -33° to 145° . The results show that the no. of collisions necessary to withdraw one energy quantum from a vibrating mol., Z , is very high for pure Cl_2 and CO_2 at room temp., but may be reduced considerably by the presence of reactive foreign mols. It is deduced theoretically that $Z \propto 1/T^{n'}$, where n' depends on the index of repulsion of the mols. and a quantity expressing the increase, on mutual approach of the mol. centres, of the probability of loss of a vibrational quantum. The experimental data confirm this conclusion. In general, light mols. are more effective than heavier mols. in inducing excitation by collision.

R. C.

Velocity of sound in neon gas. W. H. KEESOM and J. A. VAN LAMMEREN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 614—615, and Physica, 1934, 1161—1170).—The velocity of sound in Ne has been measured by a resonance method between 0° and the temp. of liquid Ne (-247°). A new vapour cryostat has been designed for the lower temp. Down to liquid O_2 temp. C_p/C_v calc. for $p=0$ is 1.667 to $\pm 0.2\%$. The dependence of sound on pressure

has been investigated at 27.80° and 26.25° abs. C_p and C_v at these temp. and at pressures 0—1 atm. have been calc.

M. S. B.

High-frequency sound waves in Kundt's tube. O. BRANDT and H. FREUND (Z. Physik, 1934, 92, 385—389).

A. B. D. C.

Difference between the specific heats of solid and liquid tin in the neighbourhood of the m.p. L. D'OR and C. DEGARD (Bull. Soc. chim. Belg., 1934, 43, 510—512).—By application of Fischer's equation (cf. A., 1927, 615) to Sn–Bi solid solutions it is calc. that C_p (solid)– C_p (liquid) = $+0.44 \pm 0.06$ g.-cal. per g.-atom for Sn.

E. S. H.

Properties of condensed heavy hydrogen. K. CLUSIUS and E. BARTHOLOME (Physikal. Z., 1934, 35, 969—971).—The following data have been obtained for H_2 and H^2 (first val. in each case refers to H_2): m.p. 13.95° , 18.59° abs., heat of fusion 28.0, 47.0 g.-cal., pressure at triple point 58.3, 127 mm., mol. vol. at triple point 26.13, 23.15 c.c., characteristic temp. 0 for C_p (solid) 91° , 89° . The differences in these vals. are explained by the difference in zero-point energy of the two gases, and the anharmonicity of the lattice vibrations.

A. J. M.

Phase equilibria of the third kind. E. JUSTI and M. VON LAUE (Physikal. Z., 1934, 35, 945—953).—Phase equilibria of the third kind, as shown by O_2 at the transition point (44° abs.), are considered. Transformations of the NH_4Cl type (NH_4 salts, HI, HBr, PH_3), where the sp. heat-temp. curve shows a sharp max., are considered.

A. J. M.

Transformations of state of a higher kind. A. EUCKEN (Physikal. Z., 1934, 35, 954—959).—The continuation of the v.-p. curve above the crit. point is discussed as an example of a transformation of the third kind. Phase transformations (I) of the NH_4Cl type are considered as masked (I) of the first kind. They are due either to changes in the mol. arrangement in the crystal, or to the appearance or disappearance of rotation in the mols. Since in these cases the rotational state changes over a very small temp. range, the rotational hindrance exerted by the mols. on each other is the smaller the more mols. there are rotating. The variation of sp. heat with temp. of mixed crystals of CH_4 and A has been investigated. It was found that the max. was displaced to lower temp. and its width was considerably increased, showing decreased hindrance.

A. J. M.

F.p. of gallium. W. F. ROESER and J. I. HOFFMAN (J. Res. Nat. Bur. Stand., 1934, 13, 673—676).—The f.p. was $29.780 \pm 0.005^\circ$. Ga does not dissolve its oxide appreciably.

H. J. E.

Experimental determination of the heat capacity of explosive gases. A correction. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 890).—The heat capacity of O_3 cannot be calc. by the method previously given (A., 1934, 846).

M. S. B.

Determination of the specific heat of gases at high temperatures by the sound velocity method. I. Carbon monoxide. G. G. SHERATT and E. GRIFFITHS (Proc. Roy. Soc., 1934, A,

147, 292—308).—Working with > one frequency and correcting the data for the effect of frequency on the velocity of sound in the gas, the sp. heat of CO determined up to 1800° is in good agreement with that deduced from spectroscopic data. The discrepancy, even at fairly high temp., between sp. heats determined by sound velocity methods and those deduced from spectroscopic data is attributed to the use of a single frequency. L. L. B.

Heat capacity of gadolinium sulphate octahydrate below 1° abs. W. F. GLAUQUE and D. F. MACDOUGALL (Physical Rev., 1933, [ii], 44, 235—236).—The heat capacity has been determined by means of a series of adiabatic demagnetisations at 1.7° to 0.287° abs. in fields up to 8000 gauss. The results are compared with a theoretical curve obtained by considering the interaction of two Gd⁺⁺⁺ ions treated as simple magnets. L. S. T.

Real gases according to the thermodynamic equation of state. III. Specific heats c_v and c_p and the compressional and expansion coefficients, β and α , of helium. V. JACZYNA (Z. Physik, 1934, 92, 661—674).—Theoretical (cf. A., 1934, 1070). A. B. D. C.

Thermal behaviour of metals at very low temperatures. W. H. KEESOM (Physikal. Z., 1934, 35, 939—944).—The vals. of $\theta = 7.745TC^{-1}$ (C = at. heat), which should be const. if the Debye T^3 law is accurate, show an increase and then a sudden fall as the temp. is decreased below 4° abs., in the case of Ag, Zn, Sn, Pb, and Bi. The effect is not due to the desorption of He used in the cooling from the surface of the metal. The corresponding increase in sp. heat at very low temp. is due to free electrons. The sudden change of sp. heat of a metal on transition from the superconducting to the ordinary state was investigated for Sn and Tl, and the results are compared with thermodynamic theory. A. J. M.

Discontinuities in the energy and the specific heat. A. BIL (Physica, 1934, 1, 1125—1142).—A general theoretical discussion of association, illustrated by reference to gaseous condensation and the transition of NaNO₃ at 275°. H. J. E.

Rate of vaporisation of molybdenum in a vacuum. L. NORRIS and A. G. WORTHING (Physical Rev., 1933, [ii], 44, 323).—The changes in wt. of various long filaments of Mo heated in a vac. to various incandescence temp. give an empirical equation of the form $\log m = A + BT^{-1} + CT^{-2}$ for the rate of evaporation (m). Contrary to the case of W, operation at const. current results in a const. temp. L. S. T.

Effect of a magnetic field on the passage of heat through gases. H. SENFLEBEN and J. PIETZNER (Physikal. Z., 1934, 35, 986—988).—The variation of the effect of a magnetic field on the thermal conductivity of a gas with the nature of the gas is investigated. This effect increases until the lines of force are perpendicular to, and then decreases as they become parallel to, the direction of heat flow. A. J. M.

Melting parameters of nitrogen and argon under pressure, and the nature of the melting

curve. P. W. BRIDGMAN (Physical Rev., 1934, [ii], 46, 930—933).—The pressure-temp. co-ordinates of the melting curve and change of vol. were measured up to 5500 kg. per sq. cm., and latent heats of fusion are calc. There is no evidence of a crit. point between liquid and cryst. phases, or of a max. or of an asymptotic temp. N. M. B.

Isotopic ratio in hydrogen. Precise density comparisons on water from various sources. II. H. J. EMELEUS, F. W. JAMES, A. KING, T. G. PEARSON, R. H. PURCELL, and H. V. A. BRISCOE (J.C.S., 1934, 1948—1950; cf. A., 1934, 1062).—A no. of samples of H₂O have been found, by the flotation method, to be heavier than normal H₂O. The vals. of $\Delta\gamma d$ (p.p.m.) for the different samples are: Polar H₂O, +1.36 and +4.2, the more northerly being the heavier; deep-seated H₂O from the Asmari limestone of the Persian oilfields, +1.9; H₂O obtained by burning permanent gas driven off from charcoal absorbers used for extracting C₆H₆ from coal-gas, +4.6; ox-blood, +2.10, +2.52, +2.31; ox-bile, +1.47; H₂O from combustion of Trinidad cane-sugar, +7.56. The distribution of heavy H of beet-sugar and mixed molasses after fermentation was also investigated. A. J. M.

Density of liquid iodine. T. NAYDER (Bull. Acad. Polonaise, 1934, A, 231—238).—Liquid I has d_{420}^{20} 3.94916 (buoyancy method), and its temp. coeff. —0.003267 per 1°. J. W. S.

Thermal expansion of bismuth single crystals near the m.p. J. W. BUOHTA and A. GOETZ (Physical Rev., 1934, [ii], 46, 1092—1095; cf. A., 1932, 796).—Highly purified Bi single crystals showed no decrease in the coeff. of expansion as the m.p. was approached. Traces of impurities (Pb, Ag, Cd, Sn) caused a decrease to negative vals. in a range of 10° or 20° below the m.p. Discrepancies between previous data are discussed in the light of these results. N. M. B.

Interpretation of the pressure-volume-temperature relations of single and composite gases. G. A. LINHART (J. Physical Chem., 1934, 38, 1091—1097).—A formula previously deduced for the p - v - T relations of several gases over a large range of temp. and pressure (A., 1933, 668) has been applied to mixtures of these gases and over a much larger pressure range. M. S. B.

Pressure-volume-temperature relations for six [mineral] oils. R. B. DOW (J. Washington Acad. Sci., 1934, 516—526).—Relative vols. at 25°, 40°, and 75°, and pressures nearly up to apparent solidifying pressures, have been determined for 6 light oils of different composition. Compressibility, thermal expansion, and various thermodynamic functions have been deduced. Similar vals. are, in general, found for all the oils. Thermal expansion varies most with temp. and pressure, and in a manner contrary to that for pure liquids at low pressures. M. S. B.

Molecular size of crystalline carbon tetrachloride and tetrabromide, and of ethylene dichloride and dibromide. E. O. K. VERSTRAETE (Bull. Soc. chim. Belg., 1934, 43, 513—544).—The v.p. of CBr₄

at low temp. and the f.p. of solutions of CBr_4 and CCl_4 in CHCl_3 and C_2HCl_5 have been determined. The m.p. of the stable forms of CBr_4 and CCl_4 have been obtained by extrapolation and the heats of transformation calc. The d of the modifications of CBr_4 , CCl_4 , $\text{C}_2\text{H}_4\text{Br}_2$, and $\text{C}_2\text{H}_4\text{Cl}_2$ have been determined. The results indicate that the two forms of CCl_4 and CBr_4 are bimol. and the two modifications of $\text{C}_2\text{H}_4\text{Br}_2$ unimol. E. S. H.

Vapour pressure of hydrocarbons. SCHMITT (Compt. rend., 1934, 199, 1299—1301).—Vals. for $n\text{-C}_6\text{H}_{14}$, methylcyclopentane, C_6H_6 , and PhMe are represented by formulæ. H. J. E.

Dependence of vapour pressure on temperature above the critical point. J. E. VERSCHAFFELT (Physikal. Z., 1934, 35, 1013—1014).—The continuation of the v.-p. curve above the crit. point observed by Trautz and Ader (A., 1934, 723) is derived analytically. A. J. M.

Statistical mechanics applied to the calculation of the entropy of rigid gas molecules. (MLLE.) G. SCHOOLS (Bull. Acad. roy. Belg., 1934, [v], 20, 1014—1022).—Mathematical. N. M. B.

Two-dimensional equation of state and structure of surface layers. II. Surface layer of pure liquids. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1934, 9, 475—493; cf. A., 1934, 1304).—An equation of state for the surface layer of pure liquids is developed in which the surface tension (σ) is represented as the sum of the static cohesion, thermal energy, and intermol. forces. Eötvös' formula is derived, and the const. shown to depend on temp. and on the nature of the substance, increasing with increase in cohesive forces. The abnormal behaviour of anisotropic liquids is explained, and vals. of the dipole moment of *p*-azoxy-anisole and -phenetole agreeing with those experimentally determined are calc. by assuming that at the transition temp. σ =cohesive forces. F. L. U.

Equation of state. I. R. BECKER (Z. Physik, 1934, 92, 680—682, 689). G. SCHWEIKERT (*ibid.*, 683—688, 689).—Polemical. A. B. D. C.

General form of the equation of state for a monatomic ideal gas. G. POLVANI (Physical Rev., 1933, [ii], 44, 123).—A claim for priority (cf. A., 1933, 551). L. S. T.

Fusion. K. F. HERZFELD and (Miss) M. G. MAYER (Physical Rev., 1934, [ii], 46, 995—1001; cf. A., 1934, 241).—Mathematical. As a type of the simplest crystal, the equation of state of frozen A is developed. The pressure as a function of the vol. at a given temp. has a min., indicating the breakdown of the crystal. The temp. for this min. at zero pressure is interpreted as the m.p. The case of He and substances of high m.p. is considered. N. M. B.

Compressibility of helium gas between 2.6° and 4.2° abs. W. H. KEESOM and H. H. KRAAK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 746—747).—Isotherms of He have been determined at 4.224°, 3.095°, and 2.581° abs., and virial coeffs. calc. R. S. B.

Viscosity and conductivity of molten glasses. K. LARK-HOROVITZ and C. L. BABCOCK (Physical Rev., 1933, [ii], 44, 321).—The conductivity and η of molten glasses as a function of temp. have been determined at 50° intervals up to 1400°. There is no sudden break in the curves. Resistivity and η can, in most cases, be represented by $\eta = A\rho^B$ for temp. from the softening point to 1400°. A and B change from glass to glass. L. S. T.

Transport phenomena in Einstein-Bose and Fermi-Dirac gases. II. E. A. UEHLING (Physical Rev., 1934, [ii], 46, 917—929; cf. A., 1933, 551).—Mathematical. Equations for the heat conductivity and viscosity coeffs. of gases as a function of temp. and density are obtained for the case of mols. acting as rigid elastic spheres, and are evaluated for H and He. N. M. B.

Evaporation of binary liquid mixtures. A. PAKSCHVER and G. LURIE (Chem. Fabr., 1934, 7, 448—452).—The velocity of evaporation of a binary mixture of const. composition is expressed in terms of its surface area, the v.p. of the components, and the atm. pressure. The speed of evaporation in an air stream of velocity v follows the empirical law $V = V_0(1 + k\sqrt{v})$, where k is a coeff. dependent on temp. and on the composition of the mixture. The theory has been verified for EtOH-Et₂O mixtures. J. W. S.

Volatility at 20° of heptane-alcohol-benzene mixtures. R. SALMONI (Annali Chim. Appl., 1934, 24, 539—549).—The two binary EtOH systems show marked max. volatility (I) in the EtOH-poor region, owing to dissociation of the associated EtOH mols. on dilution with the inert component. The triangular diagram for the ternary mixtures shows that the (I) of binary mixtures containing 20% of EtOH is further increased by addition of 20% of C_6H_6 . At 20° the (I) of all the mixtures is sufficient to give an inflammable air-vapour mixture and, with mixtures rich in C_6H_6 or C_7H_{16} , much > sufficient. The ternary mixtures are of val. especially for starting up a motor engine at about 0°. T. H. P.

Azeotropism in relation to polymerisation and solvation, and negative azeotropism from the functional viewpoint. M. LECAT (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 283—290).—The connexion between positive (max. in v.p.-composition curve) (I) and negative (min. in curve) (II) azeotropism and the mol. condition of the components is discussed. Polymerisation may give rise to either (I) or (II), and not exclusively (I). The effect depends on the degree of polymerisation. Solvation is not strictly necessary for (II), but is favourable to it. All negative binary azeotropic mixtures (about 200 are known) contain either an acid, an organic halogen derivative with >1 halogen atom, or a phenol. These are discussed in detail. A. J. M.

Frequency of azeotropism without the Bancroft point, and limited azeotropism. M. LECAT (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 212—215).—Theoretical. A. J. M.

Temperature-viscosity measurements in the systems CaO-SiO_2 and $\text{CaO-SiO}_2\text{-CaF}_2$. C. H.

HERTY, jun., F. A. HARTGEN, G. L. FREAR, and M. B. ROYER (Bur. Mines, Rept. Invest., No. 3232, 1934, 31 pp.).—The concentric-cylinder method for high-temp. η determinations has been applied to the mixtures CaO-SiO_2 (36–57% CaO , 1464–1688°) and $\text{CaO-SiO}_2\text{-CaF}_2$ (12.64–61% CaO , 10.6–52.5% SiO_2 , and 0.39–76.7% CaF_2 , 1010–1740°). There is a ridge of max. η sloping from the 50:50 CaO-SiO_2 binary towards the CaF_2 apex. The decrease in η with fluorspar content is continuous over the range studied, but is greatest near the CaO-SiO_2 binary line. CH. ABS. (e)

Active oxides. LXXXII. Changes in the magnetic properties of mixtures of $\text{CdO/Fe}_2\text{O}_3$, $\text{CuO/Fe}_2\text{O}_3$, and $\text{PbO/Fe}_2\text{O}_3$ during chemical combination. H. KITTEL (Z. anorg. Chem., 1934, 221, 49–55).—On heating, the magnetic susceptibilities remain fairly const. until combination of the oxides begins to take place, generally above 500°, when paramagnetism increases. At still higher temp. ferromagnetism appears, indicating the presence of a ferrite. M. S. B.

Mobility of gold in solid lead. W. SEITH and H. ERTZOLD (Z. Elektrochem., 1934, 40, 829–832; cf. A., 1933, 1110).—The diffusion coeff. of Au in solid Pb, measured between 113° and 300°, $\propto e^{-14,000/RT}$, and is not affected by pressures up to 1000 atm. When a current is passed through a rod of homogeneous Pb-Au alloy at 150–180°, Au accumulates at the positive end. The transport no. of Au in solid Pb at this temp. is about 10^{-10} . F. L. U.

Compression of metals in the formation of intermetallic compounds. W. BILTZ (Z. Metallk., 1934, 26, 230–232).—Differences between the mol. vol. of intermetallic compounds and the sum of the at. vols. of their components show that readily compressible metals undergo a considerable contraction on combination; the contraction is slight when the metals are much less compressible. A. R. P.

Character of metallic solid solutions and compounds. U. DEHLINGER (Z. Metallk., 1934, 26, 227–230).—Recent work on the nature of intermetallic compounds is critically reviewed with especial reference to the influence of valency and affinity. A. R. P.

X-Ray analysis of iron-aluminium alloys. II. A. OSAWA (Kinz. no Kenk., 1933, 10, 432–445; cf. A., 1934, 137).—From X-ray analysis the phases existing at room temp. are $\alpha\text{-Fe}$, FeAl , (rhombohedral; a 6.314 Å., α 87° 24' 28"; 18 atoms per unit cell), Fe_2Al_3 (monoclinic; a 9.910, b 10.811, c 8.824 Å., β 124° 59' 53"; 56 atoms per unit cell) and FeAl_3 (rhombohedral; a 15.804, b 11.870, c 8.088 Å.; 104 atoms per unit cell). $(\text{FeAl})_n$ (parameter 5.980 Å.; 16 atoms per unit cell) was obtained by quenching from > 1080° in H_2O . The parameter of the α -solid solution increases from 2.854 Å. for Fe to 2.891 Å. with 46.7 at.-% Al. No deformation structures such as Fe_3Al or FeAl are present in the α -solid solution. CH. ABS. (e)

Equilibrium diagram of aluminium-magnesium system. M. KAWAKAMI (Kinz. no Kenk., 1933,

10, 532–554).—Al and Mg are mutually sol., forming α - and ϵ -phases. The γ , and δ intermetallic phases consist mainly of Al_3Mg_5 , AlMg , and Al_3Mg_4 , respectively. CH. ABS. (e)

Equilibrium relations in aluminium-nickel alloys of high purity. W. L. FINK and L. A. WILLEY (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Publ. 569, 1934, 11 pp.).—Alloys with 0–18% Ni have been examined. NiAl_3 and solid solution form a eutectic mixture (639.9°, 5.7% Ni). The solid solubility of Ni in Al decreases from 0.05% at the eutectic temp. to 0.005% at 500°. Al-Ni alloys exhibit age-hardening. CH. ABS. (e)

Effect of quenching strains on lattice parameter and hardness values of high purity aluminium-copper alloys. A. PHILLIPS and R. M. BRICK (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Publ. 563, 1934, 19 pp.).—Quenched Al-Cu alloys of high purity may have abnormally large lattice parameters which increase with rapidity of cooling, specimen diameter (up to 0.5 in.), and with Cu content of the solid solution. Alloys with 5.4% Cu in solution when rapidly quenched have a max. age-hardening capacity at room temp. The greater is the degree of strain the sooner does pptn. occur at 275–325°. CH. ABS. (e)

High zinc region of the copper-zinc phase-equilibrium diagram. E. A. ANDERSON, M. L. FULLER, R. L. WILCOX, and J. L. RODDA (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Publ. 571, 1934, 29 pp.).—Data obtained by X-ray, electrical conductivity, and microscopical methods are recorded, confirming earlier results. CH. ABS. (e)

Equilibrium in the lead-zinc system with special reference to liquid solubility. R. K. WARING, E. A. ANDERSON, R. D. SPRINGER, and R. L. WILCOX (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Publ. 570, 1934, 10 pp.).—The solubility is > and the temp. of complete miscibility < previously reported. The monotectic temp. is 417.8° (0.7% Pb). CH. ABS. (e)

Magnetic, electric, and spectroscopic investigation of gold-silver alloys. H. AUER, E. RIEDL, and H. J. SEEMANN (Z. Physik, 1934, 92, 291–302).—Magnetic susceptibility and electrical resistance show no change after heating in vac. or in N_2 , or after remelting in vac. (cf. Shimizu, A., 1933, 455). A. B. D. C.

Ternary system copper-silver-cadmium. L. LOSANA and C. GORIA (L'Ind. Chimica, 1934, 9, 1603–1615).—M.-p. data and photomicrographic observations are recorded and a few X-ray photographs are appended. No ternary compounds are formed. The structure of the alloys is influenced considerably by the rate of cooling. The composition of several alloys which are particularly resistant to oxidation is given. D. R. D.

Ternary aluminium-silver-magnesium alloys. B. OTANI (Kinz. no Kenk., 1933, 10, 262–276).—The equilibrium diagram for mixtures of Al with AgMg is recorded. The ternary compound AlAgMg is formed at 570°. Its solubility in Al is 14% at 538° and 0.4% at 300°. The combined effects of

AgMg and Cu, Si, Mn, and Ni on Al have been examined. The alloy with AgMg 6 and Cu .4% has excellent mechanical properties after suitable heat-treatment.
CH. ABS. (e)

New magnetic alloy with a very large coercive force. V. DROZZINA and R. JANUS (Nature, 1935, 135, 36—37).—Nd containing approx. 7% Fe is strongly ferromagnetic. The large coercive force, which is > that of Fe or its alloys, indicates that a new alloy is present.
L. S. T.

Critical solution temperatures of some hydrocarbons in sulphur dioxide. R. T. LESLIE (J. Res. Nat. Bur. Standards, 1934, 13, 589—597).—From miscibility temp. curves for various hydrocarbons the following crit. solution temp. in SO₂ have been determined: *n*-C₅H₁₂ 2°, *β*-methylpentane 10°, *n*-C₆H₁₄ 12°, methylcyclopentane 8°, cyclohexane 12°, *β*-methylhexane 18°, *n*-C₇H₁₆ 19°, methylcyclohexane 15°, *β*-methylheptane (I) 24°, ethylcyclohexane 25°, *n*-C₈H₁₈ 25.5°, nonanaphthene (II) 27°, hexahydromesitylene (III) 30.5°, *n*-C₉H₂₀ 32°, *n*-C₁₀H₂₂ 36.5°, *n*-C₁₁H₂₄ 42°, and *n*-C₁₂H₂₆ 47°. Vals. for NH₃Ph are (I) 75°, (II) 57°, and (III) 56.9°. SO₂ and NH₃ are considered unsuitable for separating const.-boiling mixtures of hydrocarbons, but NH₃Ph is more promising.
A. R. P.

Distribution equilibrium between alcohol, benzene, and water. F. SPAUSTA (Mitt. tech. Versuchsanst., 1933, 22, 9—17; Chem. Zentr., 1934, ii, 1559).
H. J. E.

Passage of helium through apparently compact solids. (LORD) RAYLEIGH (Nature, 1935, 135, 30).—He passes through gelatin, celluloid, and Cellophane at room temp., probably by penetration between the constituent crystals. It does not pass through single crystals of quartz; beryl, which has a more open crystal structure, appears to be permeable.
L. S. T.

Solubility of lead sulphate in water and aqueous solutions of sulphuric acid. H. D. CROCKFORD and D. J. BRAWLEY (J. Amer. Chem. Soc., 1934, 56, 2600—2601).—Data are recorded for 0°, 25°, 35°, and 50°. The solubility falls rapidly with the addition of minute quantities of H₂SO₄, but increases again at about 70% H₂SO₄. The solid phase in equilibrium throughout is PbSO₄.
E. S. H.

Saturated solutions of carbamide in liquid ammonia. Vapour pressures and compositions from -26.4° to 101.0°. W. SCHOLL and R. O. E. DAVIS (Ind. Eng. Chem., 1934, 26, 1299—1301).—The compositions and v.p. of saturated solutions of CO(NH₂)₂ in NH₃, determined by use of an isothermoscope, agree well with the data of Janecke. A break occurs in the temp.-composition curve at -3.6° and 74.6% CO(NH₂)₂, corresponding with the transition from CO(NH₂)₂.NH₃ to CO(NH₂)₂; a similar break occurs in the temp.-pressure curve.
A. G.

Ammoniates of calcium and barium nitrates. PORTNOV and B. B. VASSILIEV (Z. anorg. Chem., 1934, 221, 149—153; cf. A., 1934, 1185).—The solubility of Ca(NO₃)₂ in liquid NH₃ has been

determined between -70° and 70°, and of Ba(NO₃)₂ between -27° and 51°. With both substances unstable (probably tetra-)ammoniates are formed.
F. L. U.

Solubilities and activity coefficients of the three nitroanilines in aqueous solutions of typical salts at 85°. J. N. PEARCE and L. J. GARWOOD (Proc. Iowa Acad. Sci., 1932, 39, 161).—Solubilities have been determined at 25° in H₂O, and in aq. NaCl, BaCl₂, K₂SO₄, and MgSO₄. Activity coeffs. are calc. These increase for the four salts in the above order and also increase with salt concn.
CH. ABS. (e)

Velocity of crystallisation of sucrose. K. SMOLENSKI and A. ZELAZNY (Bull. Acad. Polonaise, 1934, A, 172—189).—The formation of secondary germ crystals after inoculation is attributed to the presence of crystal dust. Crystallisation of super-saturated solutions of sucrose (I) induced by the addition of (I) crystals of known size and no. has been followed refractometrically. For pure unstirred solutions at 25°, $dx/dt = KF(n_0 - x)^2/n_0$, where n_0 is the initial crystallisable (I), F is the surface, and x the amount of (I) crystallised, per 100 g. of H₂O, after t min. dx/dt is diminished by impurities.
R. S.

Distribution of trichloroacetic acid between two contiguous liquid phases. N. A. DE KOLOSOVSKI and F. S. KULKOV (J. Gen. Chem. Russ., 1934, 4, 915—926).—The partition coeff., y , of CCl₃.CO₂H for the systems H₂O-PhMe, -cumene, -CHCl₃, -CCl₄, -EtBr, -PhNO₂, -*n*- and *sec*.-C₅H₁₁.OH, and -CH₂Ph.OH, at 25° is given by $y = k_1c - k_2$, where k_1 and k_2 are consts., and c is the total concn. of CCl₃.CO₂H.
R. T.

Role of intergranular fissures in the occlusion and evolution of hydrogen by palladium. D. P. SMITH and G. J. DERGE (J. Amer. Chem. Soc., 1934, 56, 2513—2525).—The absorption and desorption of H₂ have been studied, particularly with respect to time of decay, annealing temp., rate of cooling, grain size, effect of air, and deformation. Variations in the metal other than those caused by mechanical deformation affect absorption and desorption in the same sense. Mechanical deformation may affect absorption and desorption in the same or opposite senses, according to its severity. The rate of absorption at atm. temp. and pressure is independent of time for both worked and unworked metal. Diffusion appears to occur primarily along slip-plane fissures and secondarily through the unstrained lattice.
E. S. H.

Sorption of sulphur dioxide by active charcoal. II. Effect of heating on the sorptive power of coconut charcoal. III. Sorption equilibrium at high temperatures. IV. Hysteresis. K. ARII (Bull. Inst. Phys. Chem. Res. Tokyo, 1934, 13, 1428—1434, 1435—1438, 1439—1445; cf. A., 1934, 1066).—II. The absorptive power of coconut charcoal (I) activated at 690° increases with time of activation. At 800°, max. activity is reached in 2 hr. and is unchanged on further heating. (I) activated at 990° for 30 min. has very high adsorption, but the activity decreases on further heating. X-Ray

analysis and the change in magnetic susceptibility show that the loss of activity is due to graphitisation.

III. The adsorption isotherm of SO_2 at low pressures is expressed by $a=10.47p^{0.435}$ and $2.67p^{0.917}$ at 90° and 100° , respectively.

IV. A hysteresis effect is observed at $20\text{--}30^\circ$ with (I) activated at 800° for 1 hr. This is attributed to difficulty in escape of SO_2 from the interior of (I).

J. W. S.

Chemisorption on charcoal. V. **Influence of ultraporosity on adsorption.** A. KING (J.C.S., 1934, 1975—1980; cf. A., 1934, 1067).—It is suggested that activation of charcoal by O_2 or CO_2 increases the pore diameter in agreement with the result that the max. size of mol. adsorbed increases with the degree of activation. The density also increases with the time of oxidation. Traube's rule is obeyed if the pores are sufficiently enlarged by oxidation or evacuation. The theory of sp. adsorption by charcoals is discussed.

R. S.

Vapour pressure isotherms of water on active charcoal applied to its behaviour towards carbonyl chloride. H. ENGELHARD and W. STILLER (Z. Elektrochem., 1934, 40, 833—836).—Specimens of active C containing equal quantities of adsorbed H_2O , prepared (I) by dehydrating wet material and (II) by allowing previously dried material to absorb H_2O , are not equally effective in removing COCl_2 vapour from air; (II) becomes ineffective sooner than (I). The difference in the resistance times (*i.e.*, duration of capacity to remove COCl_2 beyond the limit of detection under standard conditions) corresponds with the difference between the v.p. shown by the adsorption and desorption isotherms of the C- H_2O system. This behaviour is considered to be due to liquid H_2O partly blocking the pores in (II) and thus hindering entry of the vapour.

F. L. U.

Equation for the kinetics of activated adsorption. S. ROGINSKY (Nature, 1934, 134, 935).—The equation $q-\alpha^{-1}\log(t+t_0)+C$, where q is the amount of gas adsorbed during time t , and α and C are consts. for a given system, reproduces the data of various investigators for the sorption of gases on metals or metallic oxides. It does not agree with Taylor's theory of activated adsorption.

L. S. T.

Sorptional and catalytic properties of active manganese dioxide, with reference to vapours and gases. I. E. V. ALENKEVSKI and Z. E. GOLBRAICH (J. Gen. Chem. Russ., 1934, 4, 936—947).—The adsorptive power of active MnO_2 , prepared from KMnO_4 and MnSO_4 , increases with the mol. wt. of the members of a homologous series of adsorbates. For CCl_4 and PhCl , breaks in the adsorption isotherms indicate capillary condensation. NH_2Ph is converted into NPh:NPh (48% yield at room temp.) by MnO_2 , which is reduced to Mn_3O_4 , whilst PhCN is hydrolysed to NH_2Bz . C_6H_{14} and C_5H_{12} at 40° react violently with MnO_2 , with production of CO , CO_2 , H_2O , and of small quantities of unsaturated hydrocarbons; under analogous conditions, MeOH yields CO , CO_2 , H_2O , and traces of CH_2O , whilst PhMe affords PhCHO . NH_3 is adsorbed without oxidation at 0° , whilst at $>50^\circ$ the reaction $4\text{NH}_3+9\text{MnO}_2\rightarrow 2\text{N}_2+3\text{Mn}_2\text{O}_3+6\text{H}_2\text{O}$ takes place.

R. T.

Effect of air on the condensation of water vapour. E. F. M. VAN DER HELD (Physica, 1934, 1, 1153—1160).—Theoretical. The retarding effect of air on condensation is attributed to the resistance offered to diffusion by an air-rich boundary layer.

H. J. E.

Adsorption of phenol and resorcinol from aqueous solution by carbon. A. BOUTARIC and (Mlle.) P. BERTHIER (Bull. Soc. chim., 1934, [v], 1, 1549—1560).—The adsorption by animal, activated, vegetable, and gas C has been investigated interferometrically. There is no evidence of discontinuities in the adsorption isotherms, which in all cases conform to the Freundlich equation and not to that of Perrin. In general, added solutes which are only weakly adsorbed by C do not affect the adsorption of PhOH (I) and resorcinol (II), but >0.53 g. per litre of K phosphate (III) diminishes the adsorption, although (III) is adsorbed to only a small extent. The diminished adsorption of (I) and (II) in the presence of >0.25 g. of BzOH (IV) and >0.5 g. of succinic acid (V) per litre is probably related to the marked adsorption of (IV) and (V).

J. G. A. G.

Interchange of adsorbed ions. E. J. W. VERWEY (Chem. Weekblad, 1934, 31, 789—795).—A review of recent work on the interchange of ions between a solution and an adsorbed layer.

D. R. D.

Adsorption and catalysis. I. Carbon disulphide-water reaction. L. A. MUNRO and J. W. MCCUBBIN (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 29—33).—The quantity of CS_2 adsorbed from saturated air at 25° by Al_2O_3 gels of different H_2O contents, and the quantity of H_2S produced, have been determined. The adsorption rises to a pronounced max. (at about 8%) with decrease of the H_2O content, but the catalytic activity is a max. at 9—16% H_2O and shows no direct relation to the adsorptive power.

H. F. G.

Surface and interfacial tension of mercury by the sessile drop and drop-weight methods. H. BROWN (J. Amer. Chem. Soc., 1934, 56, 2564—2568).—A modification of the sessile drop apparatus is described, and the results obtained thereby are compared with those of the drop-wt. method. The interfacial tension of Hg against H_2O is 374.3 dynes per cm. at 25° ; the surface tension of Hg in dry air or in vac. is $473 (\pm 0.3\%)$ dynes per cm. at 25° . Irreversible adsorption effects and the difference between results obtained by static and dynamic methods are explained on the basis that surface oxidation of Hg in air occurs only in the presence of H_2O vapour.

E. S. H.

Validity of Antonow's rule for the solid-liquid interface, and the measurement of the surface tension of solids. R. LOMAN and N. P. ZWIKKER (Physica, 1934, 1, 1181—1201).—Antonow's rule has been verified by measurements of angles of contact for H_2O and Hg drops on 56 stones, minerals, etc. The relation is applied to calculate the surface tension of specimens of Fe, steel, and granite. The pre-treatment of the solid surface is discussed.

H. J. E.

Influence of atmospheric carbon dioxide on the surface tension of aqueous solutions of sodium salts of fatty acids. A. LOTTERMOSER and B. BAUMGURTEL (*Kolloid-Beih.*, 1934, **41**, 73—94).—In solutions of Na salts of the lower fatty acids, CO_2 reduces the surface tension (I) slightly, the effect increasing with increasing concn. of the solution, whilst with the soaps CO_2 reduces (I) markedly, the effect decreasing with increasing concn. of the soap. In all cases after a time (I) begins to rise again. The influence of temp. and concn. has been studied quantitatively. O_2 reduces the (I) of Na oleate solutions only slightly, whilst CO_2 reduces (I) markedly. The influence of temp. and concn. on the (I) of Na oleate in absence of O_2 and CO_2 has been determined. CO_2 coagulates Na abietate and causes a slight rise of (I). E. S. H.

Interface equilibria and inner equilibria in heterogeneous systems. III. Significance of molecular structure of salt-like compounds for charging adsorption on their surfaces. L. IMRE (*Z. physikal. Chem.*, 1934, **171**, 239—256; cf. A., 1933, 671).—Measurements of the adsorption of Pb^{++} on BaSO_4 and sparingly sol. Pb salts at low concns. of adsorbate have shown that the elementary vol., v , occupied by each adsorbed ion on the various adsorbents falls in the order $\text{BaSO}_4 > \text{PbSO}_4 > \text{PbCl}_2 > \text{PbI}_2 > \text{PbBr}_2$. The abs. vals. of v deduced by means of Boltzmann's distribution law, however, are the normal at. dimensions. The explanation is that in applying the Langmuir-Hückel isotherm to such systems the vol. term involved is not the vol. of the solution, but the much smaller phase vol. of the dissolved mols. Theoretical considerations show that the more polar is the lattice the larger is v , and this is confirmed experimentally. R. C.

Structure investigations of interfaces by means of X-rays and electrons. E. RUPP (*Kolloid-Z.*, 1934, **69**, 369—378).—Published work is reviewed. E. S. H.

Energetics of surface phenomena. W. KOSSEL (*Ann. Physik*, 1934, [v], **21**, 457—480).—The mechanism of the growth of crystals according to the Gibbs theory and the mol. theory is discussed. A. J. M.

Laminar systems. I. Uni- and multi-molecular sulphide and hydroxide layers at phase boundaries. S. G. MOKRUSCHIN (*Kolloid-Z.*, 1934, **70**, 48—55).—Published work is reviewed, and preliminary observations of the characteristics of sulphide and hydroxide films formed on metals are recorded. E. S. H.

Orientation of oxide films on metals. R. F. E. L. McCANDLESS, and F. N. RHINES (*Nature*, 1934, **134**, 1009).—Thin films of FeO and Cu_2O grown on Fe and Cu, respectively, have an at. arrangement definitely related to the lattice structure of the metal on which they are formed. L. S. T.

Structure of surface films. XXI. Surface potentials of dibasic esters, alcohols, aldoximes, and ketones. N. K. ADAM, J. F. DANIELLI, and J. HARDING (*Proc. Roy. Soc.*, 1935, **A**, **147**, 491—499).—const. val. of μ is obtained for mols. with $-\text{CO}_2\text{Et}$ groups at opposite ends of a long chain, so long

as the mols. are flat and the films gaseous. The val. is much lower for these groups when the mols. are standing on end (in the condensed state). For alcohols, Me ketones, and aldoximes, μ changes but slightly on transition from the expanded to the condensed state. It thus appears that there is no necessary reorientation of the end groups as the mols. come closer together. L. L. B.

Electron microscope and its application, especially to the study of thin films on metals. E. BRUCHE (*Kolloid-Z.*, 1934, **69**, 389—394).—Apparatus and technique are described and the application of the method to the study of metallic surfaces is illustrated. E. S. H.

Spreading of complex proteins. E. GORTER, H. VAN ORMONDT, and T. M. MEIJER (*Biochem. J.*, 1935, **29**, 38—47).—The influence of the introduction of a prosthetic group into a protein mol. on its spreading (I) is studied. Combination of tartrazine (II) with ovalbumin (III) does not influence the (I) at the isoelectric point (IV), whilst the min. at p_H 2.7—3.0 disappears. Combination of spermidine (V) with pepsin (VI) decreases (I) on the acid side of (IV) and increases it on the alkaline side. Nucleic acid is without influence on the (I) of (III). Acetylation of (VI) modifies the min. on the acid side of (IV). Additions of (II) and (V) produce similar effects with (III) and (VI), respectively. These effects are similar to those produced by adding negative and positive bivalent ions, respectively. H. D.

Influence of time on the spreading of proteins. E. GORTER and G. T. PHILIPPI (*Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 788—793).—The velocity of spreading of ovalbumin on acetate buffer has been determined by following the boundary of the film by means of a Po electrode. The time for the boundary to reach its final val. is a min. at p_H 1.0, p_H 13.0, and at the isoelectric point, and reaches high vals. on both sides of this point. This explains the W-shaped curve obtained when area, reduced to zero pressure, is plotted against p_H and the measurements are made at a const. time after the formation of the film. R. S. B.

Spreading of myosin. E. GORTER and H. VAN ORMONDT (*Biochem. J.*, 1935, **29**, 48—52).—Myosin is made to spread on H_2O by previous treatment with trypsin (I); the area-time curve is dependent on (I) concn. and the time of treatment with (I). H. D.

Effect of carbonic acid on the spreading of ovalbumin on the surface of water and variations in the thickness of these films in uni-molecular layers. H. DEVAUX (*Compt. rend.*, 1934, **199**, 1352—1354).—The variations observed in the spreading of ovalbumin on pure H_2O are due to variation in p_H , the observer's breath yielding sufficient CO_2 to cause inaccuracies. Unimol. films can be obtained which vary from 0.9 to 8 μ in thickness, according to the p_H . If these variations are due to orientation, the albumin mol. must be long and narrow. J. W. S.

Flow potentials of barium sulphate. H. R. KRUYT and R. RUYSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 624—632).—Measurements

were made on natural barytes and on 4 differently prepared samples of pptd. BaSO_4 . All the samples had exactly the same cryst. structure, but the degree of development of the active surface differed and influenced the electrokinetic potential (ζ). Natural barytes retained a negative charge in presence of aq. BaCl_2 and the ζ -concn. curve is similar to that of paraffin. Pptd. BaSO_4 , of dimensions 10μ approx., has a negative charge in contact with pure H_2O , but is charged positively by BaCl_2 and negatively by sol. sulphates. Chlorides of Sr, Ca, Mg, Zn, and Cd impart a positive charge, whilst NaCl and KCl increase the negative charge. M. S. B.

Theory of cataphoresis and electro-osmosis. J. J. BIKERMAN (Z. physikal. Chem., 1934, 171, 209—220).—The rate of formation of the double layer has been derived from considerations based on the theory of the diffuse double layer. The relation between cataphoretic and electro-osmotic velocity, the ζ -potential vals. deduced from electro-osmotic measurements with membranes having very fine pores, and the effect of proximity to the wall on surface conductivity and the methods of measuring it are examined. R. C.

Does electrokinetic potential measured by the electro-osmotic method with ceramic diaphragms vary with the current strength? J. VELIŠEK and A. VAŠIČEK (Z. physikal. Chem., 1934, 171, 281—285).—Measurements with aq. KCl solutions have shown that the amount of solution transported in 1 sec. \propto the current strength, I , so that, contrary to Schonfeldt's findings (A., 1933, 776), the ζ potential calc. in the usual way is independent of I . R. C.

Spherulites. A. WIELER (Kolloid-Z., 1935, 70, 79—94).—The production of spherulites and pptn. membranes by the interaction of solutions is described, and their relation to org. forms is discussed. E. S. H.

Theory of apparent molecular volume. III. Apparent molecular volume of sucrose. O. REDLICH and H. KLINGER (Monatsh., 1934, 65, 137—140).—In agreement with theoretical considerations, the apparent mol. vol. of sucrose in dil. solution varies linearly with the sucrose concn. (c) and not with \sqrt{c} as is the case with strong electrolytes. Deviations from the linear relation are found when c is large. M. S. B.

Cryoscopy and association in *p*-chlorotoluene. R. P. BELL, E. C. BAUGHAN, and M. W. VAUGHAN-JACKSON (J.C.S., 1934, 1969—1972).—The cryoscopic const. of $p\text{-C}_6\text{H}_4\text{MeCl}$ (I) is 5.53° per kg. $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, $\text{CHCl}_2\cdot\text{CO}_2\text{H}$, and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ are bimol. and the mol. refractivities are const. in (I) over the range 0.05—0.35 mol. per kg. R. S.

Diffusion of copper sulphate. L. W. ÖHOLM (Finska Kem. Medd., 1934, 43, 121—135; cf. A., 1934, 1170).—The diffusion coeffs. for Cu, Zn, Cd, and Mg sulphates have approx. the same val. R. S.

X-Ray diffraction in ionic solutions. J. A. PRINS (Physica, 1934, 1, 1171—1173).—The diffraction pattern of saturated aq. $\text{Th}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$ shows a ring, which shifts to smaller angles and

decreases in intensity with dilution. It indicates a more or less regular arrangement of the ions in the liquid. This effect is not observed with aq. AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, or $\text{Ba}(\text{NO}_3)_2$. Aq. LiI , LiBr , RbBr , and other alkali halides give a broad ring, unaffected by dilution, and this is attributed to interference between the scattering from a heavy ion and that from adjacent H_2O mols. H. J. E.

Refractometric investigation of the formation of compounds in aqueous solution, hitherto designated as double salts. G. SPACU and E. POPPER (Bul. Soc. Stiinte Cluj, 1934, 7, 400—520; Chem. Zentr., 1934, ii, 704).—Data are recorded for aq. solutions of 16 pairs of salts (*e.g.*, $\text{HgCl}_2 + \text{NaCl}$, $\text{HgCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7$, $\text{CdCl}_2 + \text{KCl}$, $\text{NaNO}_3 + \text{KNO}_3$) in varying proportions. H. J. E.

Observation of the Brownian movement with the unaided eye. E. LAU and J. JOHANNESON (Physikal. Z., 1934, 35, 1013).—A similar observation to that of Andreev (A., 1934, 361) has been made. If a point source is viewed through a thin layer of milk between two glass plates, a variation in the light scattered by the milk is observed. If, however, the cell is placed horizontally, the variations cease, showing that they are not due to the Brownian movement, but to alteration in the position of the scattering centres caused by currents. It is suggested that Andreev's observation is similarly explained. A. J. M.

Linear problems of the theory of Brownian movement. III. G. A. KRUTKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 120—124).—Theoretical. E. S. H.

Ultracentrifugal measurements with synthetic highly polymerised substances. R. SIGNER (Kolloid-Z., 1935, 70, 24—26).—Observations on the influence of concn. and mol. wt. on sedimentation of polystyrenes are reported. The variation of mol. wt. in the fractions of a specimen of polystyrene having a mean mol. wt. 80,000 has been determined. E. S. H.

X-Ray and electron analysis of disperse systems, fibres, films, and interfaces. W. OSTWALD (Kolloid-Z., 1934, 69, 264—266).—A lecture. E. S. H.

X-Ray analysis of difform and disperse systems (with special reference to electron interference). E. SCHIEBOLD (Kolloid-Z., 1934, 69, 266—301).—A lecture. E. S. H.

Determination of particle size by X-ray and electron analysis. R. BRILL (Kolloid-Z., 1934, 69, 301—312).—A lecture. E. S. H.

X-Ray and electron analysis of inorganic gels, especially hydroxides and oxides. R. FRICKE (Kolloid-Z., 1934, 69, 312—324).—A summary of published work. E. S. H.

X-Ray analysis of organic gels. F. HALLE (Kolloid-Z., 1934, 69, 324—340).—A lecture. E. S. H.

X-Ray analysis of protein fibres. W. T. ASTBURY (Kolloid-Z., 1934, 69, 340—351).—Published work is reviewed. E. S. H.

X-Ray analysis of lamellar disperse systems. U. HOFMANN (Kolloid-Z., 1934, 69, 351—357).—A review of published work, especially on graphite and certain minerals. E. S. H.

Highly polymerised compounds. CI. Connexions between solvation, solubility, and viscosity of polystyrenes. H. STAUDINGER and W. HEUER [with E. HUSEMANN] (Z. physikal. Chem., 1934, 171, 129—180).—The solubility, S , of two polystyrenes in various solvents has been examined by determining how much MeOH or COMe₂ must be added to the solutions just to cause pptn. Good solvents for polystyrenes (I) solvate all the groups of the mol., whilst poor solvents solvate principally the aromatic groups. S for polymeric-homologous (I) falls with rising mol. wt., M , very rapidly with the hemi-colloids and slowly with the meso- and eu-colloids. The sp. viscosity, η , of a solution in a good solvent is $>$ that of an equally conc. solution in a poor solvent. A mixture of a good solvent and a precipitant behaves like a poor solvent. For a given solute in various solvents, the vals. of η_{sp}/c , where c is the basic molarity, for a given temp., T , approach as T rises. The vals. for the M of a given solute deduced from η_{sp} for solutions in C₆H₆ and COMeEt by $\eta_{sp}/c = K_m M$ agree for hemi- and meso-colloids, but not for eu-colloids. For gel solutions and conc. sol solutions $\log(\eta_{sp}/c) = K_{St} \cdot c + [\log(\eta_{sp}/c)]_{c \rightarrow 0}$, where for a given (I) K_{St} has a const. val. independent of solvent and temp. This leads to a new equation for the M of (I): $M = (K_{St} - 0.17)/1.5 \times 10^{-5}$. Conc. solutions of homopolar org. substances with thread mols. are associated sol solutions if M is $>$ 1000 and gel solutions if M is larger. R. C.

Viscosity properties of synthetic highly polymerised substances. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1934, 37, 473—474B).—The character of viscous solutions of complex synthetic (polystyrene and polymerised ω -hydroxydecoic acid) (I) and natural (cellulose nitrate, starch, and rubber) (II) substances is compared by means of the consts. α and ϕ in the equation for η . Since α increases with an increase of η (I) and is independent of η for (II), it is inferred that solutions of (I) and (II) differ fundamentally in respect of the shape of the particles. A. J. H.

Specific volume and the form and electric charge factors of colloidal particles of cellulose nitrate and acetate. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1934, 37, 468—470B).—For cellulose nitrate solutions of decreasing viscosity the form and electric charge factor α vary irregularly, but the sp. vol. ϕ decreases regularly; both α and ϕ increase with increasing viscosity for cellulose acetate solutions. Cellulose nitrate and acetate particles are concluded to be spherical and chain-like, respectively. A. J. H.

Influence of temperature on the viscosity of a very syrupy and concentrated solution of a lyophilic colloid [cellulose nitrate]. F. HIRATA and T. DAIMON (J. Soc. Chem. Ind. Japan, 1934, 37, 459—462B).—Variations in η of a 22.88% solution of cellulose nitrate (11.4% N) in COMe₂ as determined by measurement of the rates of fall of carborundum

particles between 8° and 40° are expressed by $\eta = 12,740e^{-0.04649t}$ (cf. Busse and Karrer, A., 1934, 28).

A. J. H.

Particle form in colloidal rubber solutions. I. SAKURADA and K. TANAKA (J. Soc. Chem. Ind. Japan, 1934, 37, 470—473B).—Measurement of the variation of the sp. viscosity with the concn. of rubber in 8 different solvents shows that the colloidal particles are nearly spherical; particles of masticated rubber are uniform in shape, but not spherical or chain-like. A. J. H.

Colloid chemical researches on soaps. W. PROSCH (Kolloid-Z., 1935, 70, 106—108).—A discussion. E. S. H.

Colloid chemistry of metal soaps. II. Structure viscosity in benzene solution. Wo. OSTWALD and R. RIEDEL (Kolloid-Z., 1935, 70, 67—74; cf. A., 1934, 1305).—The viscosity and structure viscosity of Al soaps in C₆H₆ at 25° have been determined. With the middle members (laurate and myristate) the increase of viscosity with concn. is very marked, and the abs. viscosity shows a pronounced max. in very dil. solutions (0.00667M) and at high concns.; these members form gels at concns. at which the other members are fluid. These anomalies are discussed in relation to dielectric properties.

E. S. H.

Hydration of the crystalline fibres of soap curd. J. W. MCBAIN, H. I. BULL, and L. S. STADDON (J. Physical Chem., 1934, 38, 1075—1084).—The dew-point method of measuring v.p. has been employed to determine the hydration of curd fibres of NaP (P=palmitate) and NaL (L=laurate) at 20°. In presence of saturated aq. Na₂C₂O₄, NaP fibres have the composition NaP, 2.6H₂O and NaL fibres probably NaL, 1.2H₂O. Dehydration curves in absence of a salt indicate the existence of NaP, 8—10H₂O, NaP, 30H₂O, and possibly NaP, 2.6H₂O, but part of the apparent H₂O of hydration may be adsorbed H₂O. Curd fibres obtained from liquid-cryst. anisotropic soap solution have the composition NaP, 4.4—4.9H₂O. M. S. B.

Lyophilic colloids, their theory and application. M. H. FISCHER and M. O. HOOKER (Kolloid-Beih., 1934, 40, 241—412).—A comprehensive discussion, with special reference to the aq. systems containing soaps, gelatin, casein, and SiO₂, particularly from the point of view of gelation and solvation. E. S. H.

Specific heats and densities of hydrophobic sols. M. ANNETTS and H. SIMS (Canad. J. Res., 1934, 11, 665—666).—Sp. heats of Au and Cu hydro-sols containing 40 mg. per 100 c.c. differ from that of H₂O by $>$ 1 part in 400 at 25—30°. Vals. of d agree, within 4 parts in 100,000, with those calc. from the wt. of the residue on evaporation. F. L. U.

Dielectric measurements with eu-colloids. Wo. OSTWALD and R. RIEDEL (Kolloid-Z., 1935, 70, 75—79).—The dielectric and optical polarisations of ethyl- and benzyl-cellulose and caoutchouc in C₆H₆ have been determined. The calc. dipole moments for the cellulose derivatives are 10—40 $\times 10^{-18}$ and for caoutchouc 10—50 $\times 10^{-18}$, according to the assumed mol. wt. E. S. H.

Precipitation of ferric oxide hydrosol in solutions of moranyl. H. GOLDIE (Compt. rend. Soc. Biol., 1934, 117, 622—624).— Fe_2O_3 hydrosol is pptd. from FeCl_3 solutions containing moranyl (I) in the p_H zone 5—7, in the form of heavy yellow hydrophobic flakes (II), negatively charged, and poor in intermicellary liquids containing acid FeCl_3 . This pptn. occurs in (I) solutions as dil. as 1 : 100,000, and can be used to detect traces of (I) in protein-free solutions. Conc. strong acids interfere by destroying (I), conc. strong alkalis by changing the structure of the micelles. A (I)-free suspension of (II) in H_2O "sensitises" Fe_2O_3 to pptn. in the acid zone as (II), a phenomenon not exhibited by suspensions of brown alkali-pptd. Fe_2O_3 hydrosol. R. N. C.

Coagulation of colloids. X. Viscosity variation during mutual coagulations of positive ferric oxide sol and colloid arsenious sulphide, manganese dioxide, and antimony sulphide. S. S. JOSHI and K. P. N. PANIKKAR (J. Indian Chem. Soc., 1934, 11, 797—804; cf. A., 1934, 1171).—When Fe_2O_3 sol is mixed with the oppositely charged colloids As_2S_3 , MnO_2 , and Sb_2S_3 coagulation usually occurs with comparable quantities of the two colloids. In the case of slow coagulation there is an initial fall in η of approx. 6.5% and the η -time curve shows irregularities. For rapid coagulation the initial fall in η is insensible, and η increases rapidly with time without irregularities. In some cases variations in η occur when no coagulation is apparent, and it is suggested that η is a more sensitive property for studying coagulation than degree of turbidity. R. S. B.

Theory of coagulation. N. FUCHS (Z. physikal. Chem., 1934, 171, 199—208).—The fundamental equation of Smoluchowski's theory of rapid coagulation has been deduced by a new method, and doubts of its validity are unfounded. An important correction is, however, required in the theory, the magnitude of which depends on the val. of λ/a , where a is the particle radius and λ the mean path of the particle in a particular direction. For dispersions with a liquid dispersing medium the correction is negligible, but for aerosols it cannot be neglected. Smoluchowski's theory of slow coagulation requires complete reconstruction. Whereas Smoluchowski assumed the rate of coagulation, v , to be \propto to the fraction, α , of the collisions which are effective, it is found that v depends less on α as λ/a diminishes. This is important for the interpretation of experimental data on the stabilisation of sols. Harper's theory of coagulation (A., 1934, 960) is rejected. R. C.

Reversible opalescence changes in gum sols. N. PESKOV and E. PREIS (Kolloid-Z., 1935, 70, 62—67).—The opalescence-temp. curves of the sols exhibit hysteresis. The S-shaped character of the curves is less pronounced the greater is the EtOH content of the dispersion medium. E. S. H.

Influence of the nature of impurities on the formation of Liesegang rings in gelatin (silver chromate). M. F. TABOURY and R. ECHARD (Bull. Soc. chim., 1934, [v], 1, 1525—1531; cf. A., 1933, 224, 225).—Rings are produced in the system gelatin

(I)— K_2CrO_4 — AgNO_3 in the presence of a limited concn. range of sp. impurities, and it is inferred that these must give a ppt. with AgNO_3 . The impurities are divided into three classes: (1) those which induce ring formation in washed (I) include KCl, KBr, and KCN, which are effective in the ranges 0.5—2%, 1—5%, and 2—8%, respectively, and afford data conforming to Jablczynski's relation, (2) those which are without influence, e.g., NaF, and (3) those which prevent ring formation in unwashed (I), e.g., $\text{Na}_2\text{S}_2\text{O}_3$, which dissolves AgCl , and KI which reacts with chromate. J. G. A. G.

Fluidities of thixotropic gels. Bentonite suspensions. H. A. AMBROSE and A. G. LOOMIS (Physical Rev., 1933, [ii], 44, 320).—Flow measurements on bentonite suspensions (I), showing the property of thixotropy and of fluidity varying with shearing stress, have been carried out in capillary tubes, brass pipes, and a rotary apparatus (II) of special design. (II) showed that the structure of such gels must be broken down or built up until an equilibrium state of flow is reached in order to obtain reproducible measurements. No slip at the walls occurs in non-plug flow. Turbulent flow of (I) was also investigated. (I) behave as a viscous liquid in the turbulent region, and the vol. of flow at any pressure gradient may be assumed to be the same as that of H_2O . L. S. T.

Swelling of gelatin in deuterium oxide. H. Q. WOODARD and L. C. CHESLEY (J. Amer. Chem. Soc., 1934, 56, 2562—2563).—Gelatin swells less in H_2O than in D_2O . The ratio is 86% (wt.) in 90% H_2O and 93% (wt.) in 42% H_2O . E. S. H.

Relative flocculation value of alcohols towards protein solutions. W. S. EISENMENGER (Kolloid-Z., 1935, 70, 94—96).—The flocculating power (I) of the aliphatic alcohols increases with increasing mol. wt. and shows a relation with the b.p. In a series containing the same no. of C atoms, (I) decreases in the order *n*, *iso*, *sec.*, *tert.*, which is also the order of decreasing toxicity. $\text{CH}_2\text{Ph}\cdot\text{OH}$ has a particularly high (I) towards blood serum. E. S. H.

Precipitation power and dielectric polarisation of alcohols. W. OSTWALD (Kolloid-Z., 1935, 70, 96—100).—The relative pptn. power α of alcohols for protein solutions (cf. preceding abstract) increases rapidly with increasing polarisation in accordance with the expression $(\alpha + \frac{P_2}{P_1}) = k_2$, where P_1 is the limiting polarisation for the highest homologous alcohol sol. in H_2O , P_2 the mol. polarisation of the pure alcohol in question, and k_2 are consts. characteristic of the protein solution. E. S. H.

Aqueous solutions of proteins. M. PIETTRE, A. BOUTARIC, and M. ROY (Compt. rend., 1935, 200, 94—95).—The degree of polymerisation of the following proteins, as determined by the amount of charcoal necessary for complete adsorption from solution, increases in the order given: serum-albumin (ox), lactalbumin, serum-albumin (heifer), mammary albumin, myosin, liver-albumin, ox serum-myoxo-protein, ovalbumin, ricin. C. G. A.

Pressure and the water relations of proteins. I. Isoelectric gelatin gels. (Miss) D. J. LLOYD

and T. MORAN (Proc. Roy. Soc., 1934, A, 147, 382—395).—When isoelectric gelatin gel is submitted to pressure, pure H_2O is forced out of the gel, and the concn. of the residual gel is a function of the pressure. The effects of varying the pressure (up to 48,000 lb. per sq. in.), the temp. (0° and 20°), and the initial concn. of the gel (4.5—41.4%) have been examined. The relationship between the activity of H_2O and concn. of gel, calc. by applying the Katz equation to the pressure data, agrees with that obtained from an analysis of the f.p.-concn. curve of gelatin gel (A., 1932, 694). The results confirm the suggestion that the H_2O in gelatin gels is to be regarded as existing in two states: (1) firmly held H_2O , most of which is removed only at low activities (< 0.2), and (2) loosely held H_2O , present only at high activities (> 0.7). The nature of the forces holding the different types of H_2O to the gelatin mol. is discussed.

L. L. B.

Crystalline proteins: hormones and enzymes. —See this vol., 122.

Effect of hydrogen ions and thrombase on the coagulation of fibrinogen. G. CRUT (Compt. rend., 1935, 200, 95—98).—Fibrinogen is sol. at p_H 1—2.6. At higher p_H there is pptn. (different from the normal coagulation) which is max. at p_H 4.4—4.6. Above p_H 6 the solution remains clear. Up to p_H 6 the phenomena are the same in presence of thrombase, but above p_H 6 coagulation occurs, with max. velocity between p_H 7 and 8. Coagulation is followed by fibrinolysis.

C. G. A.

Colloidal behaviour of sericin. VII. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 510—520; cf. this vol., 33).—The different forms of N present in the hydrolysis products of sericin-A and -B have been determined. A summary of previous papers is given.

F. L. U.

Plant colloids. XL. Reaction of starches with proteins. M. SAMEC [with A. DURJAVA] (Kolloid-Beih., 1934, 40, 449—457; cf. A., 1934, 843).—Amylopectin, pptd. from starch solution by electro dialysis, neutralises solutions of gelatin or ovalbumin, reducing the H^+ activity to $10^{-6}N$. Simultaneously the viscosity falls, and the solution becomes more easily pptd. by EtOH and less easily by electro dialysis.

E. S. H.

Colloid chemistry of chlorophyll. H. A. KKER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 37, 688—694).—Cataphoresis of a suspensoid of chlorophyll (I) in H_2O showed it to be negatively charged. Flocculation by electrolytes was observed depended on the valency. A suspensoid of phaeophytin also showed a negative charge. A fluorescent sol and coacervate of lecithin (II) with (I) have been prepared. Since lecithinoids may be important components of plastid, it is not impossible that (I) may occur as coacervate of (II) in the living plant.

M. S. B.

Application of physico-chemical analysis to investigation of peptisation. II. Peptisation of wheat-flour proteins. A. DUMANSKI and HELOVA (Gen. Chem. Russ., 1934, 4, 951—957).—The peptising action on wheat proteins

of NaCl, EtOH, and AcOH, alone or in pairs, has been studied by the methods previously described (A., 1932, 910). The presence of > 1 protein is indicated, and methods for their separation are suggested.

R. T.

Physical chemistry of starch and bread making. XXIV. Hindering of X-ray diagram retrogression of starch paste and starch solutions by heating. J. R. KATZ and A. WEIDINGER (Z. physikal. Chem., 1934, 171, 181—189; cf. this vol., 33).—Retrogression is hindered by rise of temp. and inhibited above 60° . At each temp. a state of equilibrium is ultimately reached. At higher temp. the equilibrium state is the fresh state, at lower temp. the retrogressed state; at 20 — 60° the X-ray diagram shows superimposed V- and B-spectra. The increases on retrogression in opacity, viscosity, and proportion of substance resisting malt run approx. parallel with the change in X-ray diagram.

R. C.

Fine structure of wood. I. Volume swelling of pine wood and lignin in different media. H. SAECHTLING and H. ZOCHER (Kolloid-Beih., 1934, 40, 413—448).—The swelling phenomena of wood are discussed in the light of the spiral arrangement of anisotropically swelling cellulose micelles. The dimensional changes have been measured during swelling in C_6H_6 , Et_2O , $COMe_2$, C_5H_5N , MeOH, and H_2O . The amount of the swelling liquid taken up increases in the order given, excepting C_5H_5N , which has a sp. effect probably connected with its basic character.

E. S. H.

Use of photo-cells for the determination of the degree of dissociation in the gaseous equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ from the degree of absorption of light. K. BERGWITZ and O. E. SCHWECKENDIEK (Physikal. Z., 1935, 36, 35).—The method allows the simultaneous variation of pressure and temp., the amount of NO_2 present at any temp. being determined by the intensity of the light absorbed by it.

A. J. M.

Chemical equilibrium between hydrocarbons. VIII. Equilibria of the reactions $C_6H_{14} \rightleftharpoons C_6H_{12} + H_2$; $C_8H_{18} \rightleftharpoons C_8H_{16} + H_2$. A. A. VEDENSKI and P. J. IVANNIKOV (J. Gen. Chem. Russ., 1934, 4, 975—978).—Empirical formulæ connecting the equilibrium const. with temp. are given.

R. T.

Relation between molecular interaction and the thermodynamic properties of solutions. R. P. BELL and O. GATTY (Phil. Mag., 1935, [vii], 19, 66—82).—Theoretical.

H. J. E.

Chemical constitution and the dissociation constants of monocarboxylic acids. II. J. F. J. DIPPY and F. R. WILLIAMS (J.C.S., 1934, 1888—1892; cf. A., 1934, 364).—Classical and thermodynamic dissociation consts. of AcOH, BzOH, *p*-anisic acid, *o*- and *m*-chloro-, *o*-bromo-, *m*-nitro-, 2:4-dinitro-, *p*-methoxy-, and 3:4-dimethoxy-phenylacetic acid are given. *K* is increased by introduction of a 3-alkoxy-group into BzOH or $CH_2Ph\cdot CO_2H$, but diminished by a 4-alkoxy-group.

R. S.

Anomalous strength of salicylic acid. G. E. K. BRANCH and D. L. YABROFF (J. Amer. Chem. Soc., 1934, 56, 2568—2570).—The dissociation consts. of

o-, *m*-, and *p*-OH·C₆H₄·CO₂H, and *o*-, *m*-, and *p*-OMe·C₆H₄·CO₂H in 25% EtOH at 25° have been determined. That of salicylic acid (I) is abnormally large. An explanation based on H linking, which gives rise to a chelate ring, is put forward; this explains also the low second dissociation const. of (I).
E. S. H.

Dissociation constants of acetoacetic, glycollic, and acetic acids in solutions of sodium chloride. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 993—998).—The ratios of the dissociation consts. of CH₃Ac·CO₂H (I) to those of AcOH (II) and OH·CH₂·CO₂H (III), respectively, have been determined by the quinhydrone electrode at 0° and 18° in aq. NaCl of concn. 0—0.5*M*. The dissociation consts. at 0° and 18° and at infinite dilution have been calc.: (I) 2.57 and 2.62×10⁻⁴, (II) 1.70 and 1.79×10⁻⁵, (III) 1.36 and 1.48×10⁻⁴. M. S. B.

Dissociation constants of formic and acetic acids in concentrated salt solutions. Å. VON KISS and A. URMANCZY (Z. physikal. Chem., 1934, 171, 257—267).—The dissociation consts., *K_c*, in solutions of various neutral salts have been determined at 25° by e.m.f. measurements. At salt concns. $\propto N$, log *K_c* is a linear function of the concn. Except for CaCl₂, the salts show the same order in respect of the neutral salt effect for both acids. The ratio *K_a*/*K_c* for AcOH, compared with that for HCO₂H, varies with the salt and its concn.
R. C.

Strengths of phenolic ketimines and their methyl ethers as bases. J. B. CULBERTSON, P. BIEBER, and A. ZAVODSKY (Proc. Iowa Acad. Sci., 1932, 39, 177).—The ionisation consts. of monohydroxydiphenylketimines and their Me ethers are recorded.
CH. ABS. (r)

Combination scattering and "association of molecules." S. I. LETTMAN and S. A. UKHOLIN (J. Chem. Physics., 1934, 2, 825—826).—The association of PhNO₂ in CCl₄ and of AcOH in H₂O has been studied by the combination-scattering (Raman spectrum) method. Although PhNO₂ is known to be associated in CCl₄ the solution shows no evidence of the formation of complexes. In the spectra of aq. AcOH, however, the lines corresponding with the wave-no. 623 cm.⁻¹ change in relative intensity with change of concn. This wave-no. appears, therefore, to be characteristic of complex mols. of AcOH. Reasons for the difference in behaviour of the two solutions are discussed.
M. S. B.

Association of phenol in different solvents. F. A. PHILBRICK (J. Amer. Chem. Soc., 1934, 56, 2581—2585).—By a modification of the KBrO₃—KI procedure, 3—10 mg. of PhOH can be determined to within ±0.05%. The distribution of PhOH between H₂O and PhMe, PhCl, C₆H₆, PhNO₂, and CCl₄, respectively, at 25° shows that PhOH is present in these solvents as single and double mols. Differences in the calc. association consts. are ascribed to solvation of single PhOH mols.; the effect of substituents in the benzene ring is in the order: Me, Cl, (H), NO₂, OH.
E. S. H.

Activity coefficients of salts in ethylene dichloride from solubility measurements. R. P.

SEWARD (J. Amer. Chem. Soc., 1934, 56, 2610—2612).—The solubility of NMe₄Cl in C₂H₄Cl₂ in the presence of quaternary NH₄ salts has been determined at 25°. The decrease in the activity coeff. varies with the added salt and is greater the smaller are the added ions.
E. S. H.

Cyanide solutions. R. M. WICK (Monthly Rev. Amer. Electroplaters' Soc., 1934, 20, No. 10, 10—16).—Solutions of K Ag cyanide contain Ag(CN)₃^{''} and Ag(CN)₂['], the relative amounts depending on [CN[']].
CH. ABS. (e)

Condition of sodium dissolved in fused sodium hydroxide. F. HALLA and H. TOMPA (Z. anorg. Chem., 1934, 221, 18—20).—The authors' previous conclusions (cf. A., 1934, 1166) are in agreement with Rinck's observations (A., 1933, 228) on the variation of the equilibrium const. of the reaction NaOH+K ⇌ Na+KOH. The upper temp. limit for which the equilibrium const. for the reaction K₂O+Na=Na₂O+K can be determined is 400°.
M. S. B.

Compound of glucose and potassium chloride. S. MATSUURA (Sci. Rep. Hiroshima Higher Tech. School, 1929, 1, 217—221).—The system glucose—KCl—H₂O reveals no mol. compound such as is found with NaCl (A., 1927, 518).
CH. ABS. (r)

Constitution of phosphate complexes of iron and aluminium. K. A. JENSEN (Z. anorg. Chem., 1934, 221, 1—5).—The solubility of FePO₄ and AlPO₄ in acid solution containing Cl['] and PO₄^{'''} increases with the concn. of PO₄^{'''}, but is practically independent of the concn. of Cl[']. The phosphate complexes formed contain, therefore, no Cl. The rapid increase in mol. conductivity, with dilution, of aq. FeCl₃ decomposed by H₃PO₄ appears to be due to the formation of colloidal FePO₄ and free acid.
M. S. B.

Condensation reactions of boric acid. W. C. SCHUMB and W. H. HARTFORD (J. Amer. Chem. Soc., 1934, 56, 2613—2615).—The prep. of MoO₃ and WO₃ is described, and their solubilities at 28° have been determined. Solubility and *p_H* measurements for saturated solutions of MoO₃ and WO₃ in aq. Na₂B₄O₇, Na₂CO₃, and Na₃PO₄, respectively, show that boromolybdate ions do not exist, although the existence of borotungstate ions is demonstrated.
E. S. H.

Complex formation between aniline and picrate ion. Solubility measurements. K. J. PEDERSON (J. Amer. Chem. Soc., 1934, 56, 2615—2619).—Two forms of anilinium picrate have been prepared; the metastable form is 28% more sol. in H₂O at 18°. From solubility data it is concluded that the picrate ion forms complexes with 1 and 2 mols. of NH₂Ph. There is no evidence of complex formation between NH₂Ph and NH₃Ph⁺.
E. S. H.

Dielectric constants of solutions of amphoteric electrolytes. I. Existence of zwitter ion. O. BLÜH. II. O. BLÜH and J. KROCZEK (Z. physikal. Chem., 1934, B, 27, 263—269, 270—281).—I. Published data for the dielectric const., ϵ , of solutions of amphoteric electrolytes and its bearing on the existence of zwitter ions are reviewed. Reasons are given for rejecting the claim that the ϵ of an aq. solution of an aromatic amphoteric electrolyte is < that of the solvent.

II. Measurements of the ϵ of aq. solutions of amphoteric aromatic electrolytes (A., 1923, ii, 823) have been repeated using a method permitting comparison with solutions of strong electrolytes of the same high-frequency conductivity. The ϵ of almost all the solutions is $>$ that of H_2O , proving the presence of zwitter ions. In solutions of $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ and $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ these are present in considerable amount, whilst in solutions of o - and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and hippuric acid there are few, if any. R. C.

Colours appearing in the systems cupric chloride-hydrogen halide-water-alcohol (ether, aldehyde, ketone, acid, ester). E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 65, 82—90).—Many alcohols, ethers, and other org. liquids give a green colour with CuCl_2 and HBr under certain conditions, leaving a purple residue after evaporation; *sec*- and *tert*-alcohols give the effect at room temp. Cone. HCl gives a yellow colour, whilst HF discharges the colour. The influence of temp. and concn. of the reagents on these effects has been studied. E. S. H.

Complex salts of 2:2'-dipyridyl with bivalent copper. II. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 618—623; cf. A., 1934, 1317).—If an EtOH solution containing 1, 2, or 3 equiv. of dipyridyl (dip) is added to aq. $\text{Cu}(\text{NO}_3)_2$ the corresponding complex (dip) salts are deposited on slow evaporation, viz., $[\text{Cu}(\text{dip})(\text{H}_2\text{O})_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$ (I), dark blue, dichroitic, thick, tabular crystals or smaller needles; $[\text{Cu}(\text{dip})_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$ (II), dark blue, weakly dichroitic, thick, imperfect, triclinic crystals; $[\text{Cu}(\text{dip})_3](\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (III), flat, hexagonal, dark blue crystals, plastic owing to gliding planes, and red in thin layers. Crystallographic data are given. (II) and (III) are much less sol. than (I). From aq. $\text{Cu}(\text{OAc})_2$ with 1, 2, or 3 equiv. of (dip) the following salts are obtained: $[\text{Cu}(\text{dip})(\text{H}_2\text{O})_2](\text{OAc})_2\cdot 3\text{H}_2\text{O}$ (IV), dark blue prismatic needles with reddish reflexions; $[\text{Cu}(\text{dip})(\text{H}_2\text{O})_{0.66}](\text{OAc})_2\cdot 5\text{H}_2\text{O}$ or a mixture of 1 mol. of (IV) with $2[\text{Cu}(\text{dip})_2](\text{OAc})_2\cdot 6\text{H}_2\text{O}$; $[\text{Cu}(\text{dip})_{1.33}(\text{H}_2\text{O})_{1.24}](\text{OAc})_2\cdot 2\text{H}_2\text{O}$. M. S. B.

Complex metal-thiocarbamide salts. II. Equilibrium in trithiocarbamide-cuprous chloride solution. III. Conductivity and viscosity measurements on trithiocarbamide-cuprous chloride solutions. IV. Direct displacement of copper in trithiocarbamide cuprous chloride by other metals. G. WALTER and E. STORFER. V. Electrochemical relations of complex metal-thiocarbamide salts. G. WALTER, M. ADLER, and G. REIMER (Monatsh., 1934, 65, 21—35, 38—52, 53—58, 59—81; cf. A., 1931, 831).—II. $\text{Cu thi}_3\text{Cl}$ (I) in conc. solution is pptd. by aq. KCl or HCl ; at lower concns. $\text{Cu thi}_3\text{Cl}$ (II) is pptd., and Cu thiCl (III) is pptd. from dil. solutions. Small quantities of CH_2O ppt. in presence of medium amounts of CH_2O addition of KCl causes pptn. of (III). In presence of conc. CH_2O , KCl ppts. (III) from freshly prepared solutions of (I), but not from old solutions. On ageing, the conductivity and $[\text{H}^+]$ of the solution vary; p_{H} is on the acid side, and the conductivity changes anomalously with dilution. It is suggested that solutions of (I) contain (II) and (III).

III. Addition of CH_2O to (I) produces a decrease in electrical conductivity and an increase in viscosity, to a degree depending on the age of the solution. The CH_2O undergoes a stepwise reaction with the three bound $\text{CS}(\text{NH}_2)_2$ groups.

IV. The following compounds have been prepared by direct replacement of Cu in (I): $\text{MnCl}_2\cdot 10\text{CS}(\text{NH}_2)_2$, $\text{ZnCl}_2\cdot 10\text{CS}(\text{NH}_2)_2$, $2\text{CdCl}_2\cdot 5\text{CS}(\text{NH}_2)_2$, m.p. 203—206°, $\text{PbCl}_2\cdot 4\text{CS}(\text{NH}_2)_2$, decomp. 116—120°, $2\text{SnCl}_2\cdot 5\text{CS}(\text{NH}_2)_2\cdot 2\text{H}_2\text{O}$, m.p. 175° (decomp.).

V. Measurements of the potentials of Cu , Ag , Cd , and Zn in solutions of their complex $\text{CS}(\text{NH}_2)_2$ salts show that the Cu and Ag complexes are stable, whilst those of Zn and Cd are resolved into their components, especially in dil. solutions. These measurements and observations of chemical deposition show that in such solutions the electrochemical series is: Ni , Ag (Fe , Sn , Pb), Cu , Cd , Zn . The Cu and Zn complex solutions are suitable for the electrolytic deposition of the metals. E. S. H.

Diagram of state for mixtures of any number of constituents. V. FISCHER (Ann. Physik, 1934, [v], 21, 426—432).—A plane orthogonal isobaric diagram is constructed for a mixture of any no. of constituents, and is applied to $\text{N}_2\text{--O}_2\text{--A--CO}$ mixtures. A. J. M.

Two co-existent phases. A. K. VLCEK (Chem. Listy, 1934, 28, 262—268, 282—283).—Theoretical. R. T.

F.p. of mixtures of H_2O and H_2O . Latent heat of fusion of H_2O . V. K. LAMER and W. N. BAKER (J. Amer. Chem. Soc., 1934, 56, 2641—2643).—By extrapolation of the experimental data the f.p. of pure H_2O is 3.802°. The calc. latent heat of fusion of H_2O is 1510 g.-cal., which is estimated to be at least 10 g.-cal. too low. E. S. H.

Absorption of nitrogen on fusion of iron in the arc and the iron-nitrogen diagram. A. PORTEVIN and D. SEFERIAN (Compt. rend., 1934, 199, 1613—1615).—The absorption has been studied in an arc containing at. N , when Fe_3N is formed. An equilibrium diagram for the system $\alpha\text{Fe--Fe}_3\text{N}$ (0—10% Fe_3N) is described, differing from that of Fry (B., 1923, 1074). The Curie point (I) of Fe is lowered by the presence of Fe_3N , the (I) of which is at 480°. H. J. E.

System pyridine-acetic acid. II. M.p. L. E. SWEARINGEN and R. F. ROSS (J. Physical Chem., 1934, 38, 1085—1089).—M.-p. data for mixtures of $\text{C}_5\text{H}_5\text{N}$ and AcOH indicate the presence of the compounds $\text{C}_5\text{H}_5\text{N}\cdot\text{AcOH}$, m.p. —59°, and $\text{C}_5\text{H}_5\text{N}\cdot 4$ or 5AcOH , m.p. approx. —42°. The composition of the second compounds also corresponds with the composition of max. viscosity. M. S. B.

Solid-liquid equilibria in system β -naphthol- β -naphthylamine. K. HRYNAKOWSKI and M. SZMYTÓWNA (Z. physikal. Chem., 1934, 171, 234—238).—The components are miscible in all proportions in the solid state and the liquidus and solidus curves touch at a min.; no compounds are formed (cf. A., 1919, ii, 54). R. C.

Redetermination of thermal dissociation equilibria of inorganic compounds. IV. Deter-

mination of dissociation equilibria of strontium and barium hydroxides with high-temperature vacuum balance. V. Determination of dissociation equilibria of hydrates of strontium and barium hydroxides with high-temperature vacuum balance. S. TAMARU and K. SIOMI (Z. physikal. Chem., 1934, 171, 221—228, 229—233; cf. A., 1932, 1204).—IV. The dissociation pressures, p , of $\text{Ba}(\text{OH})_2$ at 500—750° and $\text{Sr}(\text{OH})_2$ at 390—670° are given by $\log p = -25,100/4.575T + 6.906$ and $\log p = -25,190/4.575T + 8.531$, respectively. $\text{Ba}(\text{OH})_2$ forms liquid and solid solutions with BaO .

V. For $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O} \rightleftharpoons \text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O} + 7\text{H}_2\text{O}$ and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} \rightleftharpoons \text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O} + 7\text{H}_2\text{O}$ $\log p(\text{mm.}) = -13,200/4.575T + 10.80$ and $\log p(\text{mm.}) = -13,600/4.575T + 10.84$, respectively. No evidence could be obtained for the existence of $\text{Sr}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2 \cdot 16\text{H}_2\text{O}$. R. C.

Effect of pressure on the dissociation of a solid. T. E. FIELD (J. Amer. Chem. Soc., 1934, 56, 2535).—The effect of piston pressures up to 105 atm. on the dissociation pressure of $\text{BaCl}_2 \cdot 8\text{NH}_3$ has been determined. The mol. fraction of NH_3 in equilibrium at 31.85° and at various pressures of H_2 up to 150 atm. has been determined by approaching the equilibrium from both sides. At every pressure the product of mol. fraction and total pressure is $>$ the pressure calc. from the Poynting equation, assuming that the inert gas has a pressure effect only on the activities of the solids, and the divergence is the greater the higher is the pressure. E. S. H.

Alkali aluminium silicates. VIII. Validity of Hüttig's equation for permutites. E. GRUNER (Z. anorg. Chem., 1934, 221, 142—148; cf. A., 1933, 579).—V.-p. isotherms for H-, Na-, and Ca-permutite have been determined from 69° to 184°. Hüttig's formula $\log_e p = \log_e p_0 - kn/n'$ is not valid for permutites without H_2O of hydration, but gives vals. which are very high and not const. If n' is diminished by a const. quantity representing those H_2O mols. which exercise a purely chemical function in the mol., the expression becomes valid, and $k=1$.

F. L. U.

Equilibrium relations in system calcium oxide-sulphur dioxide-water (acid region) at pressures below atmospheric. F. H. CONRAD and W. L. BEUSCHLEIN (J. Amer. Chem. Soc., 1934, 56, 2554—2562).—The system has been examined at 15° and 25°, and at pressures up to 1 atm. The solid phase in equilibrium appears to be $2\text{CaSO}_3 \cdot \text{H}_2\text{O}$.

E. S. H.

Phase-rule studies on metallic thiocyanates. III. The systems $\text{Ba}(\text{NCS})_2\text{--NH}_4\text{NCS--H}_2\text{O}$ and $\text{Ba}(\text{NCS})_2\text{--AgNCS--H}_2\text{O}$ at 25°. V. J. OCCLES-SHAW (J.C.S., 1934, 1892—1895; cf. A., 1934, 1091).—The compounds $\text{Ba}(\text{NCS})_2 \cdot \text{NH}_4\text{NCS} \cdot \text{H}_2\text{O}$, $\text{Ba}(\text{NCS})_2 \cdot \text{AgNCS} \cdot 2\text{H}_2\text{O}$, $\text{Ba}(\text{NCS})_2 \cdot 2\text{AgNCS} \cdot 2\text{H}_2\text{O}$, and $\text{Ba}(\text{NCS})_2 \cdot 3\text{AgNCS} \cdot 2\text{H}_2\text{O}$ are recorded and some crystal properties described. The double salts decompose when recrystallised from water. The solubility curves of NH_4NCS and $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ intersect at a metastable invariant point, but the results do not conform with Kuklin's theorem. R. S.

M.-p. diagram of the system $\text{AlCl}_3\text{--NaCl--KCl}$. L. WASILEWSKI, A. KACZOROWSKI, and M. DYNKIN (Przemyśl Chem., 1934, 18, 608—617).—The recorded eutectic data are: AlCl_3 66, NaCl 34, 93°, AlCl_3 71, KCl 29, 114°; AlCl_3 66, NaCl 20, KCl 14, 70°. Transition point data are: AlCl_3 50, NaCl 50, 146°; AlCl_3 50, KCl 50, 241°; AlCl_3 43.5, NaCl 43.5, KCl 13, 123°; AlCl_3 54, NaCl 31, KCl 15, 110°. Composition is expressed in mol.-%.

R. T.

Equilibria in the mutual system $\text{Na}_2\text{SO}_4\text{--NH}_4\text{HCO}_3\text{--H}_2\text{O}$ at 0°. A. P. BELOPOLSKI, S. J. SCHPUNT, and M. T. SEREBRENKOVA (J. Appl. Chem. Russ., 1934, 7, 669—686).—The solid phases are $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (I), $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (II), $(\text{NH}_4)_2\text{SO}_4$ (III), NH_4HCO_3 (IV), and NaHCO_3 (V). At the 3 invariant points the solid phases are (II), (III), and (IV) (0°); (I), (II), and (IV); and (I), (IV), and (V). The cryst. fields of (I) and (V) diminish with fall in temp.

R. T.

Metal displacement equilibria in fused halides, oxides, and pyrophosphates. K. JELLINEK and H. SIEWERS (Z. Elektrochem., 1934, 40, 871—884; cf. A., 1933, 783).—Equilibria in the following reactions have been determined: $\text{Cu} + \text{AgCl}(\text{Br}) \rightleftharpoons \text{Ag} + \text{CuCl}(\text{Br})$, $\text{Zn} + \text{CdCl}_2(\text{Br}_2) \rightleftharpoons \text{Cd} + \text{ZnCl}_2(\text{Br}_2)$, $3\text{Pb} + \text{Bi}_2\text{O}_3 \rightleftharpoons \text{Bi}_2 + 3\text{PbO}$, $\text{Zn} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{ZnCl}_2$, $2\text{Pb} + \text{Ag}_2\text{P}_2\text{O}_7 \rightleftharpoons 2\text{Ag}_2 + \text{Pb}_2\text{P}_2\text{O}_7$. The law of mass action is followed in all but the two last. Differences between the normal potentials of the two metals in their respective compounds are given for each system except the last. Bi is diat. in molten Pb.

F. L. U.

Double decomposition in absence of a solvent. XXVI. Mutual system $\text{Ba}(\text{NO}_3)_2 + 2\text{KCl}$ $\text{BaCl}_2 + 2\text{KNO}_3$. A. P. ROSTKOVSKI (J. Gen. Chem. Russ., 1934, 4, 1010—1020).—The phase diagrams indicate formation of KNO_3 , KCl and $\text{BaCl}_2 \cdot 2\text{KCl}$.

R. T.

System $\text{MgCl}_2\text{--KCl--MgSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ at 100°. A. N. CAMPBELL, K. W. DOWNES, and C. S. SAMIS (J. Amer. Chem. Soc., 1934, 56, 2507—2512).—In the quaternary system the stable double salt is langbeinite. Kainite does not occur. E. S. H.

Heat of formation of ammonia and nitric acid. G. BECKER and W. A. ROTH (Z. Elektrochem., 1934, 40, 836—843).—New determinations give 11.01 ± 0.07 and 14.84 ± 0.08 kg.-cal. per mol. of NH_3 and dil. aq. HNO_3 , respectively, at 20° and const. pressure, the latter substance from N_2 , O_2 , and H_2O .

F. L. U.

Heat of combustion of standard sample benzoic acid. R. S. JESSUP and C. B. GREEN (J. Res. Nat. Bur. Stand., 1934, 13, 469—495).—A brief description of a standard bomb calorimeter and of the method of using it is given, followed by tabulated results for a large no. of tests made on BzOH . The mean val. obtained for the calorific val. of pure BzOH is 26,419 international joules per g. (wt. corr. for air buoyancy) when the sample (I) is burned at 25° in O_2 at 30 atm. abs. in a bomb (II) of const. vol., the mass of (I) and of the H_2O in (II) each being 3 g. per litre of the vol. of (II); this val. is within 0.03% of recent determinations of other workers.

A. R. P.

Thermochemical researches on diazo-derivatives of *p*-chloroaniline and a few other amines. M. WOJTECHOWSKI (Bull. Acad. Polonaise, 1934, A, 280—292).—The mol. heats of diazotisation of NH_2Ph , $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and *H*-acid are 22.74, 21.64, 18.38, and 21.66 kg.-cal. per mol., respectively. Diazotisation is not quant. for the first two unless 20% excess NaNO_2 is present, but with the two last it is quant. The heat of reaction of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$ with NaOH increases with $[\text{NaOH}]$, probably owing to tautomeric change. The heats involved in the change of diazonium hydroxides into their isomerides and their heats of reaction with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ have also been measured. The heat of reaction of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ with HCl is 6.49 kg.-cal. per mol. J. W. S.

Optical method for determination of heats of dissociation of organic molecular compounds of the type AB_2 . G. BRIEGLEB and J. KAMBEITZ (Z. physikal. Chem., 1934, B, 27, 161—175).—The determination of the heat of dissociation of org. mol. compounds in solution from measurements of extinction coeff. is described. The method has been applied to compounds of $\text{C}_6\text{H}_3(\text{NO}_2)_3$ with stilbene, toluene, and dibenzyl. R. C.

Integral heats of dilution, relative partial molal heat contents, and heat capacities of dilute aqueous sodium chloride solutions. E. A. GULBRANSEN and A. L. ROBINSON (J. Amer. Chem. Soc., 1934, 56, 2637—2641).—Data covering the range 0.0001—0.816*M* and 10—25° are recorded. E. S. H.

Osmotic pressure and the thermal effect of chemical reactions from the viewpoint of technical thermodynamics. C. GRABOWSKI (Przemysł Chem., 1934, 18, 385—397).—Theoretical. R. T.

Behaviour of electrolytes in mixed solvents. VI. Electrical conductivities of some salts in water-ethyl alcohol solutions. L. C. CONNELL, R. T. HAMILTON, and J. A. V. BUTLER (Proc. Roy. Soc., 1935, A, 147, 418—433).—Data for LiCl and KI in a series of H_2O — EtOH solutions are recorded. The change of $\Delta_0 \propto$ the fluidity of the solvent up to 20 mols.-% EtOH , but beyond this increasing divergence is found, and this is ascribed to solvation of the ions by EtOH mols. The Kohlrausch equation $\Delta = \Delta_0 -$ is obeyed in all the solvents. From the fact that Onsager's equation applies more exactly in the mixed than in the pure solvents, it is inferred that the former are better ionising media. Measurements for ZnCl_2 suggest that it is completely dissociated, even in conc. solutions, whilst in EtOH it behaves as a weak uni-univalent electrolyte with $\alpha_0 = 4 \times 10^{-8}$. In the mixed solvents the ionisation for each salt concn. seems to be complete up to about 40 mols.-% EtOH ; it then falls to about 1% in pure EtOH . In more conc. solutions ($c = 0.01$ — 0.5) EtOH depresses the ionisation more readily. The extent of complex ion formation in the alcoholic solutions is estimated. L. L. B.

Resistivity of sulphuric acid solutions and its relation to viscosity and temperature. G. W. LINAL and D. N. CRAIG (J. Res. Nat. Bur. Stand.,

1934, 13, 689—697; cf. B., 1933, 752).—Data are recorded from 30° to —40° for 15—45% H_2SO_4 . The composition of solutions of max. resistivity depends on the temp. An empirical relation between resistivity, kinematic viscosity, and abs. temp. is given.

H. J. E.

Electrolytic conduction by proton jumps: transference number of barium hydrogen sulphate in solvent sulphuric acid. L. P. HAMMETT and F. A. LOWENHEIM (J. Amer. Chem. Soc., 1934, 56, 2620—2625).—The apparent transference no. of Ba^{++} in solutions of $\text{Ba}(\text{HSO}_4)_2$ in H_2SO_4 is 0.012. Using $\text{CCl}_3\cdot\text{CO}_2\text{H}$ as reference solute the true transference no. is shown to be about 0.006. Conduction in these solutions does not depend on simple ionic migration, and supports the theory of conduction by intermol. proton jumps. E. S. H.

High-frequency conductivity of an electrolyte in the region of anomalous dipolar absorption of the solvent. M. KUBO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1415—1427).—A method for the measurement of high-frequency conductivities is described and applied to glycerol and aq. glycerol solutions of NaCl between —80° and 80°, where anomalous dispersion is shown by the solvent. J. W. S.

Single electrode potentials and the e.m.f. of a cell. E. HUTOHSSON and A. L. ROBINSON (Physical Rev., 1933, [ii], 44, 323).—The e.m.f. of a cell has been obtained by summing the p.d. at the metal-liquid and metal-metal interfaces (electrolyte at unit activity) calc. by applying a Born-Haber-Fajans cycle. L. S. T.

Applicability of Nernst's electrochemical law to extremely dilute solutions. Normal potentials of bismuth and polonium. M. HAISSINSKY (Compt. rend., 1934, 199, 1397—1399).—The crit. potential (I) for the cathodic deposit from dil. $\text{Bi}(\text{NO}_3)_3$ solutions has been studied with the apparatus of Joliot (A., 1930, 713), using *Ra-E* and *Th-C* as radioactive indicators of Bi deposition. (I) is independent of the material of the cathode (Au or Ag) and is sensibly the same for HNO_3 and AcOH solutions. Initially, Bi deposits on the cathode at much lower potentials than is suggested by theory, but this deposit redissolves slowly and redeposition occurs only when the potential reaches the theoretical val. This phenomenon is especially marked for concns. $< 10^{-3}N$. The normal potential of $\text{Bi}/\text{Bi}^{+++}$ at 18° is $+0.226 \pm 0.015$ volt. The normal potentials calc. for the electrodes $\text{Po}/\text{Po}^{+++}$ and Po/Po^{++} are $+0.775 \pm 0.015$ and $+0.53 \pm 0.03$, respectively. J. W. S.

Electrochemistry of magnesium. II. S. BODFORSS and H. KAJMER (Z. physikal. Chem., 1934, 171, 190—198; cf. A., 1931, 435).—The electrode potential, *E*, of different samples of Mg in buffer solutions has been measured. With decrease in from ~ 7, *E* becomes increasingly negative and passes through a max. Rotating the electrode shifts the *E*-*p_H* curve towards higher *p_H*. The curve also depends on the anion of the buffer, and the effect of NH_4 salts, fluorides, and pyrocatechol has been studied. The rate of evolution of H_2 from Mg in buffer solutions is for each buffer \propto to the amount of acid and prac-

tically independent of the acid/salt ratio, observations which agree fairly well with Kilpatrick and Rushton's results (A., 1934, 605). R. C.

Thermodynamic study of potassium amalgams. M. H. ARMBRUSTER and J. L. CRENSHAW (J. Amer. Chem. Soc., 1934, 56, 2525—2534).—The e.m.f. of the cell $K(c_2)(\text{amalgam})|KCl(aq.)|K(c_1)(\text{amalgam})$ has been measured at 15°, 25°, and 35° over a wide range of concn., using dropping electrodes. Reproducible results are obtained when the amalgams contain 0.01—0.40 g. of K per 100 g. of Hg. The influence of variations in technique is discussed. The calc. standard electrode potential of K is 2.9243 volts at 25°. The solubility of K in Hg has been determined between 0° and 35°. E. S. H.

Glass electrode. III. Statistical explanation of the alkaline solution behaviour. M. DOLE (J. Chem. Physics, 1934, 2, 862—866).—Gurney's quantum-mechanical theory of electrode potential (A., 1932, 26, 669), when applied to the glass electrode, gives the same equation previously obtained by application of the liquid-junction theory (*ibid.*, 126, 1207), but makes unnecessary any assumptions concerning the mobility of H^+ and Na^+ . It also explains other difficulties inherent in the earlier theory. Negative ions have no effect on glass electrode potentials because the form of the glass lattice is such that large repulsive forces for negative ions come into play and these have not sufficiently high energies to reach the glass surface. Gross and Halpern's theory (A., 1934, 601) is criticised. M. S. B.

Influence of sucrose on the p_H of alkaline solutions. K. SMOLENSKI and W. KOZŁOWSKI (Bull. Acad. Polonaise, 1934, A, 160—171).—Sucrose (I) behaves as a polybasic acid and reduces the p_H . The val. of the dissociation equilibrium const. K depends on the ratio $[NaOH]/[sucrose]$. Assuming (I) to be dibasic, $K_1 = 3-4 \times 10^{-13}$ and $K_2 = 0.3 \times 10^{-13}$. R. S.

Platinum electrode potentials in mildly alkaline sugar solutions, the electromotively active reductant present, and the catalytic effect of iron on its oxidation. J. M. ORT and M. H. ROEPKE (J. Physical Chem., 1934, 38, 1061—1074).—Pt electrodes in alkaline sugar solutions do not give exactly reproducible potentials. This is attributed to adsorption of an oxygenated glucose ion, GO' , at the surface of the electrode. Oxidation or reduction appears to remove it. The electromotively active reductant accumulating in such solutions appears to be H_2 . On addition of excess of oxidant H_2 is oxidised, GO' is formed, and finally GO_2' , giving a high oxidation potential. Finely-divided Pt and Fe do not catalyse the rate of formation of the reductant (cf. A., 1932, 345), but they catalyse the oxidation of GO' to GO_2' , and then the oxidation of H_2 by GO_2' giving GO' and H_2O . A formula is given for the relation between time and reduction potential after the reduction of added oxidants. It has been confirmed by the determination of the potential fall after the reduction of $K_2Fe(CN)_6$ in conc. aq. glucose at p_H 10. The results apply qualitatively to other sugars. M. S. B.

Determination of the dissociation constants of weak bases by the silver iodide electrode. B. B. OWEN (J. Amer. Chem. Soc., 1934, 56, 2785—2786).—The possibilities of the AgI electrode are discussed. E. S. H.

Stannous-stannic oxidation-reduction potential. C. S. HUEY and H. V. TARTAR (J. Amer. Chem. Soc., 1934, 56, 2585—2588).—The e.m.f. of cells of the type $Hg|HCl, SnCl_2, SnCl_4|HCl|H_2, Pt$ has been determined at 15°, 25°, and 35°. The normal oxidation-reduction potential of $Sn^{++}-Sn^{+++}$ at 25° is -0.154 volt. The change in heat content for $Sn^{++} \rightarrow Sn^{+++} + 2e$ (in 1.1M-HCl) is 120 g.-cal. E. S. H.

Oxidation-reduction potentials of hypoxanthine, xanthine and xanthine \rightleftharpoons uric acid. S. FILITTI (Nature, 1935, 135, 35).—A reply to criticism (A., 1934, 1257). L. S. T.

Oxidising agents and vat-dyed cotton. H. A. TURNER, G. M. NABAR, and F. SCHOLEFIELD (Nature, 1935, 135, 68).—Evidence of a simple relationship between the e.m.f. of a Pt electrode in a dil. solution of $NaOCl$ and the action of the latter on cellulose fibres dyed with a reduced vat dye has been obtained. L. S. T.

Occurrence and position of the principal inflexion point in certain acid-base titration curves. E. D. EASTMAN (J. Amer. Chem. Soc., 1934, 56, 2646—2648).—Mainly a reply to criticism (A., 1932, 1101). E. S. H.

Electrometric titration of lecithin and kephalin. T. H. JUKES (J. Biol. Chem., 1934, 107, 783—787).—Kephalin (I) in 98% EtOH behaves towards $NaOH$ as a monobasic acid with pK_a' val. of 8.9, very close to that of $+NH_3Et$. Lecithin (II) shows no base-binding power. Both lipins show acid-binding power at very low p_H vals. (I) and (II) form zwitter ions which should be represented as $RO \cdot P(O)_2 \cdot CH_2 \cdot CH \cdot NR'_3$, where $R' = H$ for (I) and Me for (II). A. E. O.

Electrometric titration of zein and iodozein. A. NEUBERGER (Biochem. J., 1934, 28, 1982—1992).—The acid-binding power for different preps. of zein (I) in 90% EtOH varies between 16.6 and 20.1 and the base-binding power between 46.2 and 54.6×10^{-5} mols. per g. of protein. From titrations at different temp. and concn. of EtOH it is shown that the titration curve of (I) is determined by the no. of free CO_2H , phenolic, iminazole, and guanidino-groups. The I of iodozein (II) is found exclusively in the C_6H_5 ring of tyrosine (III). Titration curves of (II) confirm that the base-binding power of (I) is due to the (III) groups. C. G. A.

Titration constants of some amides and dipeptides in relation to alcohol and formaldehyde titrations of amino-N. J. MELVILLE and G. M. RICHARDSON (Biochem. J., 1935, 29, 187—195).—Titration consts. at 25° are given for *d*-glutamine, *d*-isoglutamine, *l*-isoasparagine, *d*-glutaminyglycine, *d*-glutaminy-*d*-glutamic acid, and *d*-alanyl-*l*-proline, and re-determined for *d*-tyrosyl-*d*-arginine and glycyl-*l*-proline. The effect of structure on pK' is discussed. The position of $\cdot CO \cdot NH \cdot$ is the most important factor in determining the magnitude of peptide pK'_{NH} .

hence peptides containing a free $\cdot\text{CO}\cdot\text{NH}_2$ show an abnormally low pK'_{NH_2} , and largely escape determination in CH_2O titration; *e.g.*, peptides of glutamine and asparagine would be 75–90% titrated in the preliminary p_{H} adjustment. No titration method can be safely applied without previous knowledge of the composition of the biological fluid to be tested (cf. A., 1934, 574). The criteria for buffering dipeptidase hydrolyses are discussed, and *isoglutamine* is recommended as the only adequate buffer for the study of peptide scission. A. E. O.

Mutual displacement of metals. N. A. IZGARISCHEV and I. A. MIRKIN (J. Gen. Chem. Russ., 1934, 4, 982–987).—The phenomena of replacement by Zn of Cu, Cd, Pb, Ni, Fe, and Co are ascribed to the overpotential of H_2 in presence of the galvanic couples formed, and to activation of H, by the cations present. R. T.

Dissolution rates of zinc electrodes in acid solutions. H. MOUQUIN and W. A. STEITZ (Trans. Electrochem. Soc., 1935, 67, 35–40).—The velocity of dissolution (v) of rotating Zn anodes under an applied variable p.d. (E) at const. current has been studied in HCl, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, and AcOH at 20° , using H_2O_2 as depolariser. Correction has been made for loss due to electrolysis, the results representing chemical action only. v passes through a min. which is approx. the same for each acid, and $(v_{\text{min.}} - v_0) \propto$ the degree of ionisation of the acid ($v_0 = v$ for $E=0$). The product of current and voltage at the min. is approx. const. It is suggested that v is controlled by electrostatic attraction between anode and solution. R. S. B.

Researches on cathodic polarisation of metal electrodes by means of Heyrovsky and Shikata's polarograph. I. Cathodic polarisation of solid metal electrodes. II. Overpotential phenomenon appearing in electrodeposition of metallic ions. III. Theory of the overpotential of hydrogen. I. ZLOTOWSKI (Bull. Acad. Polonaise, 1934, A, 115–126, 127–142, 143–160).—I. The electrode is renewed continuously by drawing a wire through the cell. An enamelled wire bared at intervals gives periodic renewal. The wire cathode and a Ag plate anode have been used in conjunction with the polarograph (cf. A., 1925, ii, 674).

II. Overpotentials for Cd, Pb, and Zn deposited from 0.1N- CdCl_2 , -Pb(OAc) $_2$, and -Zn(OAc) $_2$ on a non-renewed Cu cathode are -0.046, -0.044, and -0.086 volt, respectively, and for Cd from 0.1N- CdCl_2 on Ag, -0.066 volt. The overpotential (I) is increased by continuous renewal of the cathode surface and by increasing dilution of the metallic ions in accordance with the view that it is associated with the formation of germ crystals.

III. The deposition potential (I) of H_2 on Pt, Cu, Ag, Pb, and Hg cathodes has been studied. Vals. for 0.1N-HCl on non-renewed electrodes are Pt -0.02, Cu -0.420, Ag -0.497, and Hg -0.931 volt. Continuous renewal of the cathode reduces (I) in proportion to the (I) of the non-renewed electrode. (I) for non-renewed electrodes of Cu and Hg in HCl is a min. at

T relation $\tau = a - b \log i$ holds in every case, but b increases with $1/[\text{H}^+]$ and varies with the cathodic metal. (I) is ascribed to the accumulation of H atoms

on the cathode surface and to some physical hindrance possibly related to the interfacial tension.

R. S.

Limiting currents in the anodic polarisation of metals in aqueous solutions. IV. E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1934, 40, 862–870; cf. A., 1933, 785).—Potential-c.d. measurements have been made on anodes of Pb immersed in aq. solutions of inorg. and org. Pb salts. In certain of these, *e.g.*, $\text{Pb}(\text{ClO}_4)_2$, the apparent resistance increases from about 100 ohms to $> 10^6$ ohms, and a polarisation e.m.f. of 60 volts has been observed. The latter can be due only to the anode functioning as a condenser and receiving a capacitative charge. Similar behaviour is shown by Zn in saturated ZnSO_4 , but not by Ni in 0.5M-Ni(ClO_4) $_2$. The results are discussed. F. L. U.

Hydrogen overvoltage and the anodic behaviour of tungsten in aqueous solutions of potassium hydroxide. M. DE K. THOMPSON and C. W. RICE, jun. (Trans. Electrochem. Soc., 1935, 67, 41–48).—W anodes dissolve in KOH with 100% current efficiency even at high polarisation, which is more pronounced at low temp., high c.d., and in dil. solutions; polarisation produces a burnished electrode. After all KOH has been converted into K_2WO_4 electrolysis gives O_2 at the anode, a blue colour due to a small amount of WV , and $\text{K}_{10}\text{W}_{12}\text{O}_{41}$ as a ppt., and the current efficiency falls. The anodic potential-c.d. curves of W in aq. KOH of varying concn. resemble the curves for Mo, but are restricted to a lower c.d. owing to polarisation. The H overvoltage decreases with increasing concn. of KOH, and is least in aq. H_2SO_4 . R. S. B.

Influence of cathodic hydrogen overvoltage on the [tensile] strength of different kinds of steel. T. KRASSÓ (Z. Elektrochem., 1934, 40, 826–829).—Certain kinds of steel become brittle when cathodically polarised in pure 0.1N- H_2SO_4 . The H overvoltage for such is $>$ for steels the tensile strength of which is unaffected. Addition of As or Hg to the electrolyte raised the H overvoltage and induced brittleness in 10 out of the 12 specimens examined. It is inferred that absorption of H by steel depends on a certain overvoltage being attained. The lowering of the overvoltage by H_2S , reported by Alexeiev and Perminov (following abstract), is in conflict with previous work (cf. A., 1930, 1254). F. L. U.

Overvoltage and cathodic brittleness of steel. D. ALEXEIEV and P. PERMINOV (Z. Elektrochem., 1934, 40, 823–826; cf. A., 1934, 356).—The cathodic polarisation of steel in N- H_2SO_4 is lowered by the presence of H_2S but raised by that of As_2O_3 , both of which induce brittleness by promoting the entry of H into the metal. It is inferred that the process is not determined by overvoltage. F. L. U.

Overvoltage. VII. Electrode discharge phenomena studied by means of an electromagnetic interrupter together with an oscillograph. A. L. FERGUSON and G. M. CHEN (J. Physical Chem., 1934, 38, 1117–1125).—With the apparatus described it is possible to superimpose curves for various types of potentials as determined

by the direct method and in each case to break the circuit at the same point on the film. The results give no indication of the existence of a transfer or surface resistance, thus confirming previous conclusions (A., 1932, 701). M. S. B.

Passivity of iron and steel in nitric acid solutions. III, IV. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1446—1500, 1501—1517; cf. A., 1934, 736).—III. HNO_3 containing $\text{CO}(\text{NH}_2)_2$ does not render Fe and steel passive. This is attributed to the removal of HNO_2 , which acts as an O_2 carrier to the surface of the metal. Fe in HNO_3 loses its passivity on addition of $\text{CO}(\text{NH}_2)_2$ in a short time. HNO_3 -resistant stainless steel is attacked severely by HNO_3 containing $\text{CO}(\text{NH}_2)_2$.

IV. The effect of HNO_3 in making Fe passive is increased by addition of NaNO_2 , but the passivity of Fe immersed in HNO_3 is not destroyed by subsequent addition of NaNO_2 . J. W. S.

Photovoltaic cells and photo-electric cells with an irreversible layer. G. ATHANASIU (Compt. rend., 1934, 199, 1604—1607).—A discussion. The assumption of an irreversible layer, as in Cu-Cu₂O photo-electric cells, is shown to be inapplicable to photovoltaic cells in general. H. J. E.

Determination of flame velocities of mixtures of inflammable gases.—See B., 1934, 53.

Equation for hydrogen-oxygen explosion limits. H. H. STORCH and C. W. MONTGOMERY (J. Amer. Chem. Soc., 1934, 56, 2644—2646).—An equation representing the explosion limits as a function of the partial pressures of the reactants is derived. E. S. H.

Spark ignition of methane-oxygen mixtures. G. A. GIMMELMAN and M. B. NEIMAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 35—41).—Capacity and potential producing the spark, pressure, electrode separation, and reaction temp. were varied; the efficiency of the spark varies as CV^2 , and not as CV , in agreement with Semenov's equation. A. B. D. C.

Kinetics of the reaction between gaseous methyl alcohol and nitrous oxide. E. W. R. STEACIE and R. D. McDONALD (J. Physical Chem., 1934, 38, 1031—1043).—The reaction between gaseous MeOH and N_2O has been studied at 500—570°. The velocity is much > that of the thermal decomp. of N_2O and approx. $\propto [\text{N}_2\text{O}]$, but is independent of [MeOH]. The apparent heat of activation is approx. 60,000 g.-cal. Velocity \propto surface area, indicating that the reaction is either heterogeneous or a chain process. The latter alternative is doubtful, since it was not found possible to cause an explosion by raising the temp. The main reaction is probably $\text{MeOH} + \text{N}_2\text{O} = \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{N}_2$, $\text{CH}_2\text{O} = \text{H}_2 + \text{CO}$. M. S. B.

Thermal oxidation of methylamine. L. J. JOLLEY (J.C.S., 1934, 1957—1966).—The slow homogeneous reaction between gaseous NH_2Me and O_2 , examined between 250° and 600°, consists of a series of consecutive reactions giving mainly a mixture of CH_2O , CO , CO_2 , HCN , NH_3 , and H_2O . Since the reaction is retarded by increase in the ratio surface/vol.

of the containing vessel, a chain mechanism is probably involved. The velocity \propto a power of $[\text{NH}_2\text{Me}]$ between 1 and 2 and approx. the first power of $[\text{O}_2]$. Foreign gases have no marked influence. Above a definite limiting pressure, determined by the temp., ignition occurs. It is a thermal process and results in a series of products different from those in the slow reaction. Greatly increased proportions of H_2 , CO , and N_2 are found. There is an initial period of induction. Thermal decomp. of NH_2Me does not become appreciable until 500° is attained. It consists mainly of the two reactions $\text{NH}_2\text{Me} = \text{HCN} + 2\text{H}_2$ and $\text{NH}_2\text{Me} + \text{H}_2 = \text{CH}_4 + \text{NH}_3$. Since oxidation readily takes place at 250° these reactions cannot take part in the oxidation process. M. S. B.

Slow oxidations at high pressures. I. Methane and ethane. II. Methyl alcohol, ethyl alcohol, acetaldehyde, and acetic acid. D. M. NEWITT and P. SZEGO (Proc. Roy. Soc., 1935, A, 147, 555—571).—By using hydrocarbon- O_2 mixtures containing < 5% of O_2 and a flow method in which the gaseous medium is passed rapidly at 50 atm. through a reaction zone maintained at a suitable temp. between 340° and 430°, the proportion of primary product (alcohol) surviving is increased, until with CH_4 it corresponds with 50% and with C_2H_6 with 62.6% of the hydrocarbon burnt: there is no trace of peroxidation. Additional evidence supporting the hydroxylation theory of hydrocarbon combustion is obtained by studying the slow oxidation and thermal decomp. of each of the principal intermediate oxidation products of C_2H_6 (EtOH, MeOH, MeCHO, AcOH) at appropriate temp. and pressures. The oxidation of AcOH in a SiO_2 vessel at 426—486°/200 mm. proceeds uniformly without an induction period, the products consisting of CO , CO_2 , CH_4 , H_2O , and traces of MeOAc and COMe₂.

L. L. B.
Significance of proknocks in hydrocarbon combustion. A. R. UBBELOHDE and A. EGERTON (Nature, 1935, 135, 67).—Org. compounds which can disrupt to give radicals thus: $\text{EtO}-\text{OEt}$, $\text{EtO}-\text{OH}$, $\text{AcO}-\text{OH}$, $\text{EtO}-\text{NO}$, have a pronounced proknocking effect in concns. as low as 10^{-5} — 10^{-6} mol. fraction. Peroxides and NO_2 -compounds which do not disrupt in this manner show no such marked effects. L. S. T.

Thermal decomposition of acetaldehyde. C. N. HINSHELWOOD (Nature, 1935, 135, 67).—New data confirm the homogeneous nature of the reaction under conditions of previous work (cf. A., 1934, 1294, 1312), and show that the pressure increase measures the actual rate of disappearance of MeCHO. L. S. T.

Thermal decomposition of acraldehyde. H. W. THOMPSON and J. J. FREWING (Nature, 1934, 134, 900).—The decomp. of acraldehyde has been studied at 550°. Three independent "bimol." regions occur over the approx. ranges 15—40, 40—200, and 200—600 mm. The energy of activation, which is of the order of 5×10^4 g.-cal., is different in the several regions (cf. A., 1934, 1311). L. S. T.

Vapour-phase hydrolysis. S. YAMASAKI and T. TITANI (Bull. Chem. Soc. Japan, 1934, 9, 501—

504).—There is no detectable hydrolysis of CH_2PhCl vapour when heated for 5 hr. with H_2O vapour at 130° or 200° , or of EtOAc vapour after 150 hr. at the same temp. F. L. U.

Rate of reactions in solution. R. S. BRADLEY (J.C.S., 1934, 1910—1917).—Formulae for uni- and bi-mol. reactions in liquids, which take into account the mol. structure of the liquids and avoid the introduction of viscosity, are calc. Agreement with experimental data is found in a no. of cases. For bimol. reactions the formula applies to reactions between mols. and large ions which are not strongly solvated, as well as to reactions between mols. The same conceptions may be applied to the study of diffusion in solutions. M. S. B.

Kinetics of oxidation of nitrous acid by chloric and bromic acids. W. G. LOWE and D. J. BROWN (Z. anorg. Chem., 1934, 221, 173—176).—The reaction between ClO_3' and HNO_2 is of the second order; $k \propto [\text{H}']$. Alteration of $[\text{Cl}']$ produces no significant change in k . The reaction with BrO_3' is similarly unaffected by changing $[\text{Br}']$, whence it is inferred that oxidation of Br' to Br plays no part. F. L. U.

Kinetics of the reaction between potassium permanganate and oxalic acid. II. H. F. LAUNER and D. M. YOST (J. Amer. Chem. Soc., 1934, 56, 2571—2577; cf. A., 1932, 1002).—Reaction between MnO_4' and $\text{C}_2\text{O}_4''$ is extremely slow, whilst that between Mn^{++++} or Mn^+ and $\text{C}_2\text{O}_4''$ proceeds at a measurable rate. Mn^{++++} is present in equilibrium with MnO_4' , Mn^{+++} , and Mn^{++} ; a solution containing no Mn of low valency reacts slowly or not at all with $\text{H}_2\text{C}_2\text{O}_4$. The mechanism of reaction proposed varies according to the concn. of the reagents; the intermediate formation of CO_2' is assumed. E. S. H.

Velocity of decomposition of diazo-compounds in water. XVI. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 687—690B).—The rate of decomp. of aq. $\alpha\text{-C}_{10}\text{H}_7\cdot\text{N}_2\text{Cl}$ is unaffected by the addition of MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, CaCl_2 , or $\text{Pb}(\text{OAc})_2$; it is slightly increased by CuSO_4 (after an induction period), FeSO_4 , or NaOAc , and greatly increased by NaOH or Na_2CO_3 . A. G.

Kinetics of sucrose inversion by adiabatic temperature measurements. S. S. JOSHI and G. R. PHANSALKER (J. Indian Chem. Soc., 1934, 11, 751—766).—The velocity of the initial stages of the inversion of aq. sucrose (I) (2—30 g. per 100 c.c.) by 0.4—0.9N-HCl has been determined by the rise of temp. measured under adiabatic conditions. The velocity coeff., k , is a function of $[\text{HCl}]$, and with const. $[\text{HCl}]$, k increases with increasing $[(\text{I})]$. The sp. heat of aq. (I) diminishes with increase of $[(\text{I})]$ and the heat of dilution of aq. HCl in H_2O is $>$ in aq. (I), possibly owing to removal of H_2O from the solvent phase by hydration of (I). J. G. A. G.

Variation of the velocity coefficient of the saponification of amides by sodium carbonate in saturated solutions. E. CALVET and (MME.) CALVET (Compt. rend., 1934, 199, 1313—1315).—vals. are recorded for the saponification of NH_2Bz by Na_2CO_3 (0.1—3N) at 17.90° . NH_2Bz behaves

in solution as if it exists in 2 forms in equilibrium, only one being saponifiable. H. J. E.

Kinetic considerations regarding the Riesenfeld test in the investigation of the nature of a peroxy-compound. H. A. LIEBHAFSKY (Z. anorg. Chem., 1934, 221, 25—32).—By using a buffer solution in the Riesenfeld test, i.e., the reaction of peroxy-compounds (I) with KI, a clear distinction may be made between true (I) such as $\text{K}_2\text{S}_2\text{O}_8$ and apparent (I) such as H_2O_2 . In the former case liberation of I progresses continuously and in the latter the liberation of I soon reaches a stationary state and evolution of O_2 takes place at a rate corresponding with the rate of destruction of (I). (I) of an intermediate character behave like mixtures of H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$. M. S. B.

Kinetics of the interactions of sodium hydroxide with penta- and hexa-chloro- and -bromoethane in aqueous and ethyl-alcoholic solutions. W. TAYLOR and A. M. WARD (J.C.S., 1934, 2003—2010).—In aq. EtOH-NaOH at 25° and 35° the halogen compounds, C_2HX_5 ($\text{X}=\text{Cl}$ or Br), lose HX immediately and C_2X_6 lose X_2 very slowly. Both types give C_2X_4 , the latter undergoing a further very slow elimination of X. On the assumption that the reactions are all bimol., ratios of the velocity coeff. k for the compounds $\text{C}_2\text{H}_2\text{X}_4$ and C_2HX_5 have been determined by a competitive method. Elimination of X from C_2X_6 and C_2X_4 is essentially bimol., but complications, varying with the character of X, are caused by oxidation of EtOH by X. The compounds $\text{C}_2\text{H}_{6-n}\text{X}_n$ are classified into two groups, according to whether they undergo slow or immediate elimination of X. Observed vals. of k have been compared with those calc. from crit. increments. M. S. B.

Kinetics of the decomposition of ammonium amalgam. A. J. DEYRUP (J. Amer. Chem. Soc., 1934, 56, 2594—2599).—The decomp. of NH_4 amalgam at -20° and -30° follows the rate law $dx/dt = k_2(a-x)^{1.5}$. Decomp. is mainly heterogeneous, occurring at the surface of bubbles of the reaction product, which consist of spherical shells of liquid NH_3 enclosing gaseous H_2 . The heterogeneous reaction is probably an electrode reaction obeying the laws of overvoltage; it is completely inhibited by $> 0.005M\text{-Li}$. The homogeneous decomp. measured at 0° , 10° , and 20° follows the rate law $dx/dt = k_1(a-x)^2$, which may be explained by effective collisions between two NH_4 ions and two electrons. The energy of activation of the homogeneous reaction is 22,400 g.-cal. E. S. H.

Local element effect in corrosion processes. I. STERN and N. NEKRASOV (Physikal. Z. Soviet-union, 1934, 5, 729—745).—A theoretical relationship between the total potential of a metal surface and the individual local potentials is deduced and applied to the electrochemical changes in the corrosion of Fe. The active area of an Fe surface was calc. as approx. 10% of the total area. CH. ABS. (e)

Increased velocity of formation of silicates in powdered mixtures as a result of the loosening of the metal oxide [lattice] and the crystallo-

graphic transformation of the quartz. J. A. HEDVALL and G. SCHILLER (Z. anorg. Chem., 1934, **221**, 97—102).—The amount of reaction taking place between quartz and ZnO, CuO, NiO, CoO, and Co_3O_4 has been determined. In general there was an increase in reactivity at the $\beta \rightarrow \alpha$ transition, and then, after a halt, a still more pronounced increase in velocity at the temp. of formation of cristobalite. This was especially marked in the case of Co_3O_4 , since the temp. is also that at which, owing to its nearness to the thermal dissociation temp. of Co_3O_4 , there is a strong tendency towards the break-up of the crystal lattice of the latter.

M. S. B.

Mechanism of chlorination of aliphatic acid chlorides. I. Dark reaction. E. HERTEL, G. BECKER, and A. CLEVER (Z. physikal. Chem., 1934, **B**, **27**, 303—315).—The reaction of Cl₂ at concns. of 0.05—0.65 mol. per litre with AcCl , EtCOCl , and PrCOCl at 15—50° is of zero order, and not catalysed by HCl. Dilution of the acid chloride (I) with CCl_4 retards the reaction without altering its order, an effect probably connected with a variation in the physical properties of the medium. These observations are explained by supposing the primary reaction to be transformation of (I) into an active form, probably by keto-enol change. The reactivity of (I) seems to be connected with its Raman spectrum, the dissociation const. of the corresponding acid, and the dipole moment of the corresponding ketone.

R. C.

Velocity of bromination of acetoacetic acid. K. J. PEDERSEN (J. Physical Chem., 1934, **38**, 999—1022).—The velocity of bromination of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ (I) has been determined in the following media: (1) 0.022—0.75*M*·HCl at 0°, (2) aq. (I) and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Na}$, (3) aq. $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, (4) aq. AcOH and NaOAc at 0° and 18°. The results may be explained on the assumption that the rate of bromination is determined by the enolisation of the undissociated (I) and $\text{CHBrAc}\cdot\text{CO}_2\text{H}$ (II) (cf. A., 1933, 910) which is catalysed in each case by bases and not by acids. The unimol. coeffs. for the uncatalysed or H_2O -catalysed reaction have been calc. and also the coeffs. for the catalysis of the enolisation by $\text{CH}_2\text{Ac}\cdot\text{CO}_2'$, AcO' , and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2'$. A comparison is drawn between basic strength and the val. of the catalytic const. The calc. val. for the dissociation const. of (II) is 0.021.

M. S. B.

Catalytic decomposition of hydrogen peroxide by iron salts. F. HABER and J. WEISS (Proc. Roy. Soc., 1934, **A**, **147**, 332—351).—The decomp. of H_2O_2 by both Fe^{II} and Fe^{III} salts is both a chain and a radical reaction involving the radicals OH and H_2O and the anion HO_2' . Varying concns. of the reactants alter the length of the chains and provide alternative methods for terminating them, giving rise to various reaction products. The main stages of the reactions accord with: (1) $\text{Fe}^{\text{III}} + \text{H}_2\text{O}_2 = \text{Fe}^{\text{II}} + \text{OH}' + \text{OH}$; (2) $\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2'$; (3) $\text{HO}_2 + \text{H}_2\text{O}_2 = \text{O}_2 + \text{H}_2\text{O} + \text{OH}$; (4) $\text{OH} + \text{Fe}^{\text{II}} = \text{Fe}^{\text{III}} + \text{OH}'$. By inserting the appropriate reaction velocity coeffs., an equation can be obtained from which the ratio of the consumption of H_2O_2 to Fe^{II} may be

expressed mathematically, and this agrees with the experimental results. The effect of Fe^{III} salts is described and partly explained.

L. L. B.

Decomposition of nitrates and nitrites of metals having various valencies. IV. Vanadyl nitrate. E. VERNAZZA (L'Ind. Chimica, 1934, **9**, 1616—1623).—Aq. $\text{VO}(\text{NO}_3)_2$ decomposes, even at room temp. in an atm. of CO_2 , evolving NO, NO_2 , and N_2O and pptg. hydrated V_2O_5 . At the b.p. the reaction is $6\text{VO}(\text{NO}_3)_2 + 5\text{H}_2\text{O} = 3\text{V}_2\text{O}_5 + 10\text{HNO}_3 + 2\text{NO}$. HNO_3 acts as a catalyst. Consequently the decomp. occurs with acceleration. $\text{VO}(\text{NO}_3)_2$ could not be obtained from the aq. solution, but on evaporating a mixture of VOSO_4 and NaNO_3 in EtOH, greenish-brown prisms, believed to be *vanadyl nitrate*, separate. They decompose rapidly with evolution of nitrous fumes.

D. R. D.

Catalytic action of ammonium salts and ammono-acids on ammonolysis of santonin in liquid ammonia solution. A. I. SCHATTENSTEIN (Z. physikal. Chem., 1934, **171**, 286—288).—The ammonolysis, which gives santonamide, is catalysed by this. The catalytic activity of NH_4 salts does not vary with the anion at low concns. and differs from their thermodynamic activity as judged by v.-p. measurements.

R. C.

Kinetics of the formation of sulphonic acids from dithio-acids. I. Oxidation of cystine to cysteic acid by thallic sulphate. II. Positive and negative catalytic effects of halides on the oxidation of cystine to cysteic acid by thallic sulphate. P. W. PREISLER and D. B. PREISLER (J. Physical Chem., 1934, **38**, 1099—1107, 1109—1115).—I. The amount of $\text{Ti}_2(\text{SO}_4)_3$ reduced was determined at intervals by adding excess of aq. KI and starch and titrating with $\text{Na}_2\text{S}_2\text{O}_3$ until the bright yellow colour only of pptd. TiI remained. The rate-controlling reaction in presence of H_2SO_4 is of the second order. In the complete reaction 1 g.-mol. of cystine is oxidised to cysteic acid, whilst 5 Ti^{III} are reduced. K (bimol.) increases with increase in Ti^{III} up to 0.0005 g.-ion, when K becomes nearly const. K decreases slightly with increase of [cystine], but is nearly const. above 0.002*M*. $[\text{Ti}^{\text{I}}]$, and therefore the oxidation-reduction potential of the system $\text{Ti}^{\text{II}} - \text{Ti}^{\text{I}}$, has no apparent effect on K . K decreases with increase in $[\text{H}_2\text{SO}_4]$. At 30° in $N\text{-H}_2\text{SO}_4$, using 0.0005 g.-atom Ti^{III} and 0.001*M*-cystine, Ti^{III} reduction takes place at the rate of 23.3 g.-atom and cystine oxidation at the rate of 4.7 g.-mol. per min. per litre. By measurements at 15—35° and different acidities the heat of activation 24,000 g.-cal. has been obtained.

II. KI, when present at a very low concn., catalyses the above reaction, and the rate increases with increasing concn. up to a max., after which it diminishes. At a sufficiently high concn. KI has a retarding effect. The rate of catalytic reduction increases as the ratio $\text{KI}/\text{Ti}^{\text{III}}$ increases. [Cystine] or $[\text{Ti}^{\text{I}}]$ does not affect the catalytic reaction rate, but increase in $[\text{H}_2\text{SO}_4]$ increases it. The energy of activation of the catalytic reaction is 21,700 g.-cal. The KI catalysis is a zero order reaction over a wide range of concn. Cl' and Br' have an inhibiting effect

which is complete when the ratio halide/ Ti^{+++} exceeds 2. F' has no effect. Br' and, to a smaller extent, Cl' increase the acceleration in the I' -catalysed reaction. M. S. B.

Reduction of platinum oxide by carbon monoxide and catalysis of the reaction between carbon monoxide and oxygen. P. V. MCKINNEY (J. Amer. Chem. Soc., 1934, 56, 2577—2580).—Dry PtO_2 is reduced by CO at 25° after an induction period, the duration of which is diminished by raising the temp. The process is autocatalytic and exothermic, and may become explosive. When the reagents are moist, reduction occurs at 0° and the induction period is shorter. Small amounts of Fe accelerate the reaction. PtO_2 catalyses the reaction between CO and O_2 at 80° and is not reduced when O_2 is in excess. The combustion of CO in O_2 is also catalysed by Pt-black prepared from PtO_2 and CO. With excess of O_2 , reaction occurs at 184° and is complete at 218° . E. S. H.

Pyrophoric properties of copper methyl alcohol catalysts. V. A. PLOTNIKOV and K. N. IVANOV (J. Gen. Chem. Russ., 1934, 4, 1003—1005).—The pyrophoric properties of $\text{Cu-ZnO-Cr}_2\text{O}_3$, Cu-ZnO , and $\text{Cu-Cr}_2\text{O}_3$ catalysts (I) prepared by simultaneous pptn. of Cu(OH)_2 and Zn(OH)_2 and/or Cr(OH)_3 , and reducing the ppt. with H_2 or CO, are a consequence of the highly disperse state of the Cu, agglutination of the particles of which is prevented by the ZnO or Cr_2O_3 . The (I) are converted chiefly into Cu_2O on free oxidation in air. R. T.

Iron catalysts for ammonia synthesis.—See B., 1935, 20.

Catalytic decomposition of thiophen in presence of hydrogen.—See B., 1935, 12.

Catalytic hydrogenation of unsaturated compounds. III. Selectivity of attack in relation to the nature of the catalyst. E. H. FARMER and L. A. HUGHES (J.C.S., 1934, 1929—1938; cf. A., 1934, 509).—In the 50% hydrogenation of sorbic acid (I) and Na muconate, resulting in a step-wise reduction, the solvents employed, PhMe , EtOAc , H_2O , and EtOH , appear to exert no sp. action apart from the fact that ageing of the catalyst, with resulting modification of the additive mode, may occur in low concn. of solvent. Poisoning of the catalyst decreases the activity, but does not appear to affect the additive mode of (I). The action of the catalyst is sp., but the action of one particular catalyst does not vary greatly with the form or method of application. M. S. B.

Hydrogenation of ethylene with heavy hydrogen. R. KLAR (Z. physikal. Chem., 1934, B, 27, 319—320).—The rate, k , of hydrogenation with H_2 and H_2^3 over an Fe catalyst has been measured at 0 — 175° . For H_2^3 k is a max. at $\sim 150^\circ$ and for H_2 at $\sim 125^\circ$. Up to $\sim 100^\circ$ k for H_2 is $>$ for H_2^3 at the same temp., but above 100° is smaller. The approach of k for H_2^3 to k for H_2 with rise in temp. is temporarily interrupted at 55° . R. C.

Catalytic dissolution of copper in sulphuric acid. M. O. CHARMANDARIAN and G. H. DACHNIK (J. Appl. Chem. Russ., 1934, 7, 736—739).—

Dissolution of Cu in H_2SO_4 is catalysed by Ag and in particular by $\beta\text{-CoS}$, which increases the velocity 3-fold; the CoO is inactivated after 10 operations, but may be re-activated by aq. $(\text{NH}_4)_2\text{S}$. R. T.

Polymerisation of vinyl bromide. A. GUYER and H. SCHÜTZE (Helv. Chim. Acta, 1934, 17, 1544—1548).—The influence of various substances on the polymerisation of $\text{CH}_2=\text{CHBr}$ in the dark has been studied. A classification based on chemical nature is not possible. The largest positive effect observed was with H_2O_2 . In the absence of any added material, a glass containing vessel, especially if Bohemian, accelerates polymerisation, whilst Fe or bronze completely inhibits it. F. L. U.

Active oxides. LXXXIII. Systems zinc oxide-chromic oxide and cupric oxide-chromic oxide as catalysts of the decomposition of methyl alcohol. O. KOSTELITZ (Kolloid-Beih., 1934, 41, 58—72; cf. this vol. 44).—The relative amounts of H_2 , CO, CO_2 , CH_4 , C_2H_4 , HCO_2H , CH_2O , HCO_2Me , and Me_2O resulting from the catalytic decomp. of MeOH at 300° , 320° , and 360° , using the oxide mixtures in different proportions, have been measured. With pure ZnO the main products are CO and H_2 , whilst Cr_2O_3 gives mainly Me_2O . The forces between adjacent ZnO and Cr_2O_3 mols. are discussed in the light of the products obtained by the catalytic action of the mixtures. E. S. H.

Catalytic action of Japanese acid earth. VIII. Relation between catalytic activity and adsorption. K. ISHIMURA (Bull. Chem. Soc. Japan, 1934, 9, 493—501; cf. A., 1934, 850).—Adsorption rates and capacities of different specimens of the earth for H_2O , C_6H_6 , and C_{10}H_8 have been determined and shown to be parallel with the catalytic action on C_{10}H_8 . F. L. U.

Fractionation of the isotopes of hydrogen and oxygen in a commercial electrolyser. E. W. WASHBURN, E. R. SMITH, and F. A. SMITH (J. Res. Nat. Bur. Stand., 1934, 13, 599—608).—Electrolysis of 18% NaOH at 60° in a 16-litre commercial cell (Ni electrodes) gave no further isotopic separation after 160 litres of make-up H_2O (I) had been added. The gases evolved at this stage have the same isotopic composition as (I). The residue was 60 p.p.m. heavier than ordinary H_2O , approx. 50% of the change being due to enrichment of the heavy O isotope. H. J. E.

Cathodic behaviour of organic salts of copper. M. G. KRAVTSOFF (Compt. rend., 1934, 199, 1105—1107).—The proportion of Cu_2O formed in electrolysis increases as the dissociation const. of the org. acid decreases. Addition of a salt with a common anion decreases the Cu_2O yield, except in the case of HCO_2NH_4 and $(\text{HCO}_2)_2\text{Cu}$. H. J. E.

Electrolytic deposition of copper-nickel-iron alloys. H. PAWECK, J. BAUER, and J. DIENBAUER (Z. Elektrochem., 1934, 40, 857—862).—Homogeneous deposits cannot be obtained from solutions of the mixed sulphates, but addition of Na citrate up to 2% gives rise to homogeneous deposits of satisfactory character when the Ni content is $> 42\%$. The influence of c.d. and of the composition of the

electrolyte on the deposit has been determined. The effect of the citrate is to displace the electrode potentials to "baser" vals., the shift being greatest for Cu and least for Fe. F. L. U.

Electrolytic production of lithium. L. WASILEWSKI and J. Z. ZALESKI (*Przemysł Chem.*, 1934, 18, 628—633).—A fused 6:4 mol. mixture of LiCl and KCl is electrolysed at 410° in a special apparatus, using graphite anodes, and hollow, conical cathodes, from which the fused Li, containing $\approx 2\%$ K, is periodically removed. R. T.

Electrodeposition of chromium under pressure.—See B., 1935, 28.

Electrolytic oxidation. VI. Anodic oxidation of acetates: mechanism of the Kolbe and Hofer-Moest reaction in aqueous solution. S. GLASTONE and A. HICKLING (*J.C.S.*, 1934, 1878—1888).—The electrolysis of aq. solutions of acetates and AcOH with smooth and platinised Pt, Au, Ni, and C anodes has been studied under different conditions. Catalysts for the decomp. of H_2O_2 , e.g., Pb^{++} , Ag^+ , Mn^{++} , Cu^{++} , Co^{++} , and Fe^{++} , inhibit the formation of C_2H_6 by the Kolbe synthesis, whilst Na^+ , K^+ , NH_4^+ , Ca^{++} , Sr^{++} , Ba^{++} , Mg^{++} , Zn^{++} , Ni^{++} , and UO_2^{++} , which do not decompose H_2O_2 , allow the formation of C_2H_6 to take place. Poisoning the platinised Pt anode for H_2O_2 decomp. increases the yield of C_2H_6 . Au and Ni anodes become coated with oxides which decompose H_2O_2 and, therefore, do not yield C_2H_6 . The Kolbe synthesis is also inhibited by the anions F^- , ClO_4^- , NO_3^- , PO_4^{--} , Cl^- , SO_4^{--} , or $\text{Fe}(\text{CN})_6^{--}$. The effect \propto the mobility of the ions. The results do not agree with previous theories of the Kolbe reaction. It is suggested that H_2O_2 is formed by the union of discharged OH^+ and reacts with AcO^+ to give C_2H_6 . If the $[\text{H}_2\text{O}_2]$ or $[\text{AcO}^+]$ is kept low, formation of MeOH occurs, probably with AcO_2H as an intermediate product. Alkalinity is not necessary for MeOH formation. Anode potential is merely a secondary indication of the particular reaction taking place, and not a primary factor in determining it. M. S. B.

Electrolytic reduction of acetophenone. S. SWANN, jun., and G. H. NELSON (*Trans. Electrochem. Soc.*, 1935, 67, 49—54).—COPhMe when reduced electrolytically in aq. EtOH- H_2SO_4 with Cd, Sn, Pb, Hg, Al, Zn, C, Ni, Cu, and Fe cathodes, at 65—70° and c.d. 0.054 amp. per sq. cm., gives acetophenonepinacone (I), $(\text{CHPhMe})_2\text{O}$, and a resin of unknown composition. A Pb cathode gives the best yield of (I), but the cathode material has very little influence on the course of the reaction. R. S. B.

Chemical action in the glow discharge. XIV. Ignition of hydrogen-oxygen mixtures. A. K. BREWER and P. D. KUECK (*J. Physical Chem.*, 1934, 38, 1051—1059).—Ignition in the positive column is different from that in the condensed discharge (A., 1931, 44), but there is a distinct analogy between the latter and the reaction in the negative glow. In the positive column there is a hyperbolic relation between power input and pressure. The addition of foreign gases lowers the power input necessary

for ignition in proportion to the ability of these gases to retard the rate of diffusion. 25% H_2 -75% O_2 is the mixture most easily ignited in the positive column. Rise in temp. causes a relatively large increase in ignitability. This is also increased by increasing the length of the positive column, but is decreased by the approach of a surface to the path of the discharge if the distance is \approx about 1 cm. A glass surface has a lowering effect $<$ that of Ag. These results may be interpreted on the basis of the reaction chain hypothesis previously given (this vol., 45). The energy of the gas surrounding the discharge must, for the positive column, be very much $>$ for the condensed discharge. M. S. B.

Electrothermal production of nitric oxide in the light of researches on dissociation. W. DOMINIK (*Przemysł Chem.*, 1934, 18, 367—373).—The formation of NO and NH_3 from their elements at high temp. is ascribed to combination between dissociated mols. of N_2 , O_2 , and H_2 , and not to the greater stability of NO or NH_3 at higher temp. N_2 is calc. to be 0.65% dissociated at 2000°, 3.6% at 3000°, and 8.3% at 4000°. R. T.

Combination of hydrogen and oxygen in direct-current discharges. E. M. GUENAU and R. V. WHEELER (*J.C.S.*, 1934, 1895—1901).—Measurements of the rate of combination of H_2 and O_2 in the d.-c. discharge have confirmed the results of earlier investigators. The temp. at different points in the path of the discharge varies systematically with the conditions of the experiment. In comparative experiments, in which N_2 , A, or He was used as a diluent, the relative rates \propto the temp. produced in the mixture by the discharge, and not \propto the effect each diluent gas would have on the degree of ionisation. The combination of H_2 and O_2 in the d.-c. discharge is not primarily due to its ionising effect, but the chemical reaction as a result of electron excitation is probably considerably augmented by its thermal effect. M. S. B.

Action of an electric discharge on nitric oxide. Production of active nitrogen. C. ZENGHELIS and S. EVANGELIDES (*Compt. rend.*, 1934, 199, 1418—1419).—When an ozonising discharge is passed through NO, the latter is decomposed into N_2 (partly as active N) and O_2 (partly as O_3) as well as into NO_2 . As a second phase oxidation occurs to NO_2 and N_2O_5 ; in the third stage of the action these combine with NO and NO_2 to form N_2O_5 . J. W. S.

Active chlorine. E. J. B. WILLEY and S. G. FOORD (*Proc. Roy. Soc.*, 1934, A, 147, 309—332).—The activation of Cl_2 in the silent discharge is not accompanied by a vol. change. No change in the absorption spectrum of activated Cl_2 could be detected. Experiments were carried out using a spark discharge between C electrodes, and also with the silent discharge. Active Cl_2 reacts with H_2O giving an increased amount of HCl. No difference (from ordinary Cl_2) could be detected in the oxidation of FeCl_2 , but with FeSO_4 the amount of Cl_2 reacting decreased. No difference was observed in the oxidation of $\text{H}_2\text{C}_2\text{O}_4$, but an increase in reaction was found with AcOH in the case of the sparked Cl_2 .

Active Cl_2 reacts with C_6H_6 giving both substitution and additive compounds. The effect of traces of impurities, O_2 , N_2 , and air, and of irradiation of the Cl_2 was investigated. The nature of active Cl_2 is discussed, the balance of evidence suggesting that it is at.

L. L. B.

Heterogeneous chemical reactions in the silent electric discharge. XI. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1934, 9, 505—510; cf. A., 1934, 739).— H_2 reacts with the following solid substances: $\text{KAg}(\text{CN})_2$, KCNS , $\text{Ca}(\text{CNS})_2$, NH_4CNS , $\text{Na}_2\text{S}_2\text{O}_3$, MgS_2O_3 , BaS_2O_3 , $\text{Ba}(\text{ClO}_3)_2$. Details are given.

F. L. U.

Photochemistry. M. BODENSTEIN (Naturwiss., 1935, 23, 10—16).—A lecture.

Decomposition of ozone photosensitised by chlorine. R. G. W. NORRISH and G. H. J. NEVILLE (J.C.S., 1934, 1864—1872).—The decomp. of O_3 , photosensitised by Cl_2 , has been studied using light of $\lambda 365 \text{ m}\mu$ at 25° . It is a chain reaction, and quantum efficiencies, γ , up to 10 may be obtained. The law $\gamma \propto I^{-0.5}$, where I is the light absorbed, is approached when the pressure of O_3 is high and those of Cl_2 and O_2 are low. When the pressure of Cl_2 or O_2 is high, γ is independent of I , the reaction is of zero order with respect to O_3 , and the rate \propto the first power of I . For const. I and increasing pressure of O_2 and Cl_2 γ is depressed towards a limiting val. of 2. Foreign gases have no effect. At high Cl_2 and O_3 pressures a red liquid $(\text{ClO}_3)_2$ is obtained. When this does not separate, the results are uniform and reproducible, and there is no indication of after-effects when irradiation is discontinued. After separation, however, it continues to decompose in the dark, causing an increase of pressure. A reaction mechanism involving the propagation of chains by Cl and ClO is suggested, and applied also to the thermal decomp. of O_3 sensitised by Cl_2 .

M. S. B.

Photochemical reaction between chlorine and formaldehyde. Preparation of formyl chloride. K. B. KRAUSKOPF and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 2542—2548).—The reaction occurs in two steps. The first is an exothermic, long-chain process, involving no pressure change, which is accompanied by a marked Draper effect and under certain conditions may become explosive. One of the products is HCOCl , which decomposes in the second step into CO and HCl . The decomp. takes place by a rapid Cl_2 -sensitised photochemical process if Cl_2 is in excess, and by a slow, heterogeneous, thermal reaction if no Cl_2 is available or if illumination is stopped. HCOCl is prepared by allowing an illuminated mixture of Cl_2 and CH_2O to flow through a liquid-air trap. At room temp. it decomposes rapidly.

E. S. H.

Photochemical carbon monoxide oxidation. JACKSON (J. Amer. Chem. Soc., 1934, 56, 2631—2635).—At room temp. O reacts with CO to form CO_2 at least 150 times as rapidly as with CO to form CO_2 . At high temp. (up to 600°) in absence of O the rate of oxidation is almost independent of temp. and total pressure; in presence of H_2O the

reaction rate varies with pressure and has a large temp. coeff. A mechanism of reaction is suggested.

E. S. H.

Photochemical reactions. Action of phosphorous and hypophosphorous acids on uranyl salts. F. DIENERT and F. VILLEMAINE (Compt. rend., 1934, 199, 1113—1114).—Reduction occurs on illumination in a Pyrex vessel. The product is a U phosphate, its composition varying with the light intensity and the acidity.

H. J. E.

Influence of salts on intermittent photographic exposures. T. H. JAMES, J. M. BLAIR, and F. E. E. GERMANN (J. Physical Chem., 1934, 38, 1023—1030).—Intermittent exposures of a photographic emulsion produce developable densities which are different from, and usually $<$, those produced by equal continuous exposures. The influence of different ions on this intermittent effect is similar to their influence on the Herschel effect (cf. Narbutt, A., 1930, 1385).

M. S. B.

Mechanism of the desensitisation of photographic plates. M. BLAU and H. WAMBACHER (Z. wiss. Phot., 1934, 33, 191—197).—Plates treated with pinakryptol-yellow (I) are more sensitive to α -particles and slow protons; treated plates are also sensitised to high-speed protons, if exposed in vac. or in N_2 . With visible light the desensitisation normally produced by (I) decreases with the degree of vac. obtaining during the exposure, and is almost entirely removed in an atm. of N_2 , CO_2 , or other O_2 -free atm. The effect is not obtained by evacuation after exposure, and only weakly when the plate is kept in vac. until just before exposure. Other desensitisers (pinakryptol, induline-scarlet, phenosafranine, etc.) show the effect, but not pinaflavol. The effect is less with the more strongly dyeing reagents. Desensitisation is hence considered as an oxidation of reduced AgBr , the desensitiser being reduced by photochemical action, but reoxidisable by atm. O_2 to re-form the dye, which can then again oxidise Ag . The presence of H_2O is also necessary.

J. L.

Relation between exposure and photographic blackening on exposure to Röntgen rays. E. HOFER (Z. wiss. Phot., 1934, 33, 198—200).—Mathematical. The formula $S = f(v) \cdot \phi(v) \cdot N a \log e$ is derived, where S is the blackening produced, $f(v)$ is the absorption coeff. of the emulsion layer, $\phi(v)$ is the no. of AgBr grains rendered developable by one X-ray quantum, N is the total no. of quanta to which the emulsion is exposed, and a is the size of a AgBr grain rendered developable by one quantum falling on an area of 1 sq. cm. (Cf. Arens *et al.*, A., 1931, 579; Eggert and Noddack, A., 1929, 124.)

J. L.

Compensational development. W. ROMER (Przemysł Chem., 1934, 18, 533—546).—The part of the $dD/d \log E$ curve for which the slope is $> \gamma/2$ (D optical density, E intensity of illumination, γ coeff. of development) is termed the "useful section" (I), and the corresponding part of the log E axis the "gradation of usefulness" (II). Ordinary developers (III) at first shift (I) in the direction of smaller E , and then in that of greater E ; these effects are ascribed to diffusion of the

(III) and of the products of reaction in the emulsion. (III) adapted to over- (under-)exposed plates exert only the latter (former) effect. The successive use of (III) for over- and under-exposed plates leads to a considerable extension of (II) in both directions (compensational development). R. T.

Autophotographic location of radioactive ions in gelatin. (MILLER.) S. VEIL (Compt. rend., 1934, 199, 1044—1046; cf. A., 1933, 1005; 1934, 961, 1172).—When radioactive ions are concerned in the formation of diffusion figures in gelatin, additional data can be obtained from the pattern obtained on a photographic plate in contact with the gelatin film. The colourless $\text{Th}(\text{NO}_3)_4$ aureole has thus been shown to have distinct diffusion zones. The autophotographic pattern of a gelatin film, impregnated with BaCl_2 solution containing Ra, after electrolysis to almost zero conductivity, shows a distribution of radioactive material corresponding with the relative opacity of the film. J. W. S.

Photo-decomposition of gaseous ethyl iodide and a comparison of the photo-change in the gaseous and condensed states. W. WEST and E. GINSBURG (J. Amer. Chem. Soc., 1934, 56, 2626—2630).—The quantum yield (I) is < 0.01 in the continuous spectrum, about 2600 Å., increases to about 0.1 at 2026 Å. in the band spectrum at about 90 mm. pressure, and is lower in this region at 0.1 mm. In the continuous region, liquid EtI and its solution in hexane have much higher (I) than the gas (about 0.6), whilst at 2026 Å. (I) in the liquid is about 0.24. Rise in temp. by 10° does not appreciably change (I) at 2026 Å. The mechanism is discussed. E. S. H.

Photochemical studies. XX. Photochemical decomposition of acetone in the Schumann region. W. M. MANNING (J. Amer. Chem. Soc., 1934, 56, 2589—2594; cf. A., 1933, 792).—The proportion of CO , H_2 , CH_4 , C_2H_4 , and C_2H_6 produced at different initial pressures has been determined. The products and rate of reaction vary with the pressure. More H_2 is produced by decomp. in the Schumann region than when light in the near ultra-violet is used. E. S. H.

Photochemical changes of *l*-aspartic acid, *l*-asparagine, and chemically related substances by X-rays and ultra-violet light. J. P. BECKER (Strahlenther., 1934, 50, 357—363; Chem. Zentr., 1934, ii, 1422).—*l*-Aspartic acid (I) when irradiated with X-rays and dissolved in 0.1N-NaOH gave an absorption max. at 2650 Å., not observed with *l*-asparagine (II), *l*-malic acid, or cinnamic acid after similar treatment. Irradiation of (II) in solution gave a similar max. at 2750 Å. Ultra-violet illumination of an aq. NaOH solution of (I) gave a max. absorption at 2650 Å. H. J. E.

Photochemical process for measuring ultra-violet radiation. H. SCHREIBER (Meteorolog. Z., 1933, 399—402; Chem. Zentr., 1934, ii, 986).—The COMe_2 method of Friedrich and Bender (Meteorolog. Z., 1930, 285) has been tested and is discussed. H. J. E.

Photo-bromination of α -phenylcinnamic acid. A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1934, 17, 1548—1557).—The speed of this reaction, at 25° and in blue light, is greatly increased if the CCl_4 used as a solvent is first acted on by Cl_2 in the light for 8 hr., treatment which appears to destroy a negative catalyst present in material purified in the usual way. The velocity $\propto I^{0.89}[\text{Br}_2][A]^{0.70}$ for total absorption and $I^{0.77}[\text{Br}_2]^{1.66}[A]^{0.70}$ for weak absorption (I =intensity, A =unsaturated acid), the reaction thus differing from other similar brominations. The difference is attributed to simultaneous reactions leading to the formation of more highly brominated compounds. F. L. Ü.

Combined action of ultra-violet light and platinum on transformation of fumaric and maleic acids and their salts. F. BEREZOVSKAJA, M. KOGON, and E. MOSKALENSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 50—56).—Conductivity measurements show that this combined action does not transform fumaric (I) into maleic (II) acid, but produces decomp. by adsorption at the Pt surface; a similar effect was observed with (II) and the Ba salt of (I), but the Ba salt of (II) showed no decomp. A. B. D. C.

Photochemical decomposition of glycine. Influence of the medium and wave-length. V. HENRI, C. WEIZMANN, and Y. HIRSBERG (Compt. rend., 1934, 199, 1205—1207; cf. A., 1934, 264).—The decomp. rate has a max. at p_{H} 3 and a min. at p_{H} 6. The effective wave-length is < 2478 Å. Extinction coeff. measurements before and after irradiation are recorded. H. J. E.

Photosynthesis of amino-acids. N. R. DHAR and S. K. MUKHERJI (J. Indian Chem. Soc., 1934, 11, 727—735).—Details are given of results already published (A., 1934, 1208). Coloured inorg. salts increase the photosynthesis. Of several NH_4 salts of org. acids, only the lactate affords an NH_4 -acid on illumination in presence of TiO_2 . J. G. A. G.

Kinetics of photosynthesis. E. C. C. BALY (Nature, 1934, 134, 933).—A reply to criticism (A., 1934, 1078). L. S. T.

Mechanism of the action of light on selenium electrolytic photo-cells. R. AUDUBERT and J. ROULLEAU (J. Chim. phys., 1934, 31, 553—558).—A detailed account of work already noted (A., 1934, 584).

Lithium cobaltinitrite. S. KIKUCHI (Compt. rend., 1934, 199, 1414—1416).—On mixing aq. LiNO_3 [prepared from $\text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 82 g., and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, 43 g.] with aq. $\text{Co}(\text{NO}_3)_2$ (28 g.) and acidifying with 50% AcOH (20 c.c.), an orange-yellow solution is obtained which on evaporation under reduced pressure deposits orange-yellow prismatic crystals of *Li cobaltinitrite*, $\text{Li}_3\text{Co}(\text{NO}_2)_6 \cdot 8\text{H}_2\text{O}$, decomp. $< 100^\circ$. It is very hygroscopic and is sol. in EtOH and $\text{EtOH-Et}_2\text{O}$ mixtures, but not in pure Et_2O . On addition of a K salt to its aq. solution a ppt. of $\text{K}_3\text{Co}(\text{NO}_2)_6$ is formed even when the Li:K ratio is 200:1. J. W. S.

Interaction of alkali chlorides with calcium nitrate in liquid ammonia. A. GUYER, A. BIELER,

and E. SCHMID (Helv. Chim. Acta, 1934, 17, 1538—1544; cf. this vol., 26).—The reaction $2\text{NaCl} + \text{Ca}(\text{NO}_3)_2 = 2\text{NaNO}_3 + \text{CaCl}_2$ is nearly quant. at 0° in NH_3 containing $> 15\%$ of H_2O , owing to formation of $\text{CaCl}_2 \cdot 8\text{NH}_3$ which is only slightly sol. in NH_3 . The concn. must be such that NaNO_3 remains dissolved. At lower temp., and with anhyd. NH_3 , the reaction is more rapid in consequence of the greater solubility of NaCl and, below -20° , of $\text{NaCl} \cdot 5\text{NH}_3$. The reaction with KCl is incomplete and much slower. F. L. U.

Preparation of pure sodium fluoride. I. TANANAEV (J. Appl. Chem. Russ., 1934, 7, 729—730).—40—45 g. of impure NaF are dissolved in 1000 c.c. of H_2O , 15—20 g. of KCl added, and the solution is filtered after 2—3 days. The filtrate is free from Na_2SiF_6 if the red colour obtained by adding a drop of 0.1N- NaOH and of phenolphthalein persists after boiling; if not, more KCl should be added. The filtrate is conc. to 100 c.c. in a Pt vessel and the pptd. NaF washed free from Cl^- and dried at 150° . Yield 55—60%. R. T.

Synthesis of sodium cyanamide and sodium cyanide under pressure. I. Sodium cyanamide. K. SAKURAZAWA, M. HANDA, and R. HARA (J. Soc. Chem. Ind. Japan, 1934, 37, 701—702b).—Approx. 100% yields of Na_2CN_2 may be obtained by the reaction $\text{NaCN} + \text{Na} + 0.5\text{N}_2 \rightarrow \text{Na}_2\text{CN}_2$ under suitable conditions, e.g., 620° , 83 atm., 120 min., with Fe as catalyst. The equilibrium pressure rises rapidly with % Na_2CN_2 in the mixture. A. G.

Action of halogen compounds on alkali iodide solutions. A. PERRET and R. PERROT (Bull. Soc. chim., 1934, [v], 1, 1531—1548).—The oxidising powers of the halogen compounds have been investigated by means of the I liberated or determined in the reactions with neutral, acid, and alkaline aq. and COMe_2 solutions of KI or NaI alone, and with excess of $\text{Na}_2\text{S}_2\text{O}_3$, and by means of LiBr in COMe_2 . The reaction $\text{S}_2\text{Cl}_2 + 2\text{KI} \rightarrow 2\text{S} + 2\text{KCl} + \text{I}_2$ proceeds to completion in 2N- HCl and in KI with excess of $\text{Na}_2\text{S}_2\text{O}_3$. In CCl_4 , the reaction is $\text{S}_2\text{Cl}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{S} + 2\text{NaCl}$. With neutral KI , the process $\text{CCl}_4 \cdot \text{SCl} + 2\text{KI} \rightarrow \text{CSCl}_2 + \text{I}_2 + 2\text{KCl}$ is complete in 20 hr., and with a mixture of KI and $\text{Na}_2\text{S}_2\text{O}_3$, 2.4—3.1 Cl atoms of CSCl_4 are available. SOCl_2 and KI afford S , and the quantity of I liberated varies with the acidity. The competing reactions are considered. The I rapidly liberated from alkaline NaI by SO_2Cl_2 oxidises the SO_3^{2-} produced. 81% of the PhSO_2Cl in a mixture of NaI in aq. COMe_2 and excess of $\text{Na}_2\text{S}_2\text{O}_3$ reacts: $\text{PhSO}_2\text{Cl} + 2\text{NaI} \rightarrow \text{PhSO}_2\text{Na} + \text{I}_2 + \text{NaCl}$, and (InSO_3) $_2$ is not formed. With $\text{CCl}_4 \cdot \text{SO}_2\text{Cl}_2$, I is liberated quantitatively from NaI in COMe_2 thus: $\text{CCl}_4 \cdot \text{SO}_2\text{Cl}_2 + 2\text{NaI} \rightarrow \text{CCl}_3 \cdot \text{SO}_2\text{Na} + \text{I}_2 + \text{NaCl}$. By analogy with the action of COCl_2 on NaI , BzCl liberates small quantities of I from NaI in anhyd.

Although I is not liberated by treating aq. $(\text{COCl})_2$, the reaction in anhyd. COMe_2 is $(\text{COCl})_2 + 2\text{NaI} \rightarrow 2\text{NaCl} + \text{I}_2 + 2\text{CO}$. Whereas ICN and BrCN liberate I quantitatively from acid KI , there is a deficiency with ClCN owing to hydrolysis. Ph_3CCl reacts with NaI in anhyd. COMe_2 mainly

thus: $2\text{CPh}_3\text{Cl} + 2\text{NaI} + 2\text{COMe}_2 \rightarrow \text{CPh}_3 \cdot \text{OH} + \text{CHPh}_3 + 2\text{NaCl} + \text{I}_2 + \text{CMe}_2 \cdot \text{CH} \cdot \text{COMe}$. J. G. A. G.

Action of potassium iodide on fairly insoluble compounds. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 1405—1407).—Aq. KI reacts with PbSO_4 , AgCl , TiCl_3 , $\text{Cu}(\text{CNS})_2$, Ag_3AsO_4 , Ag_2CrO_4 , Hg_2CrO_4 , HgCrO_4 , Ti_2CrO_4 , and $\text{Bi}_2(\text{CrO}_4)_3$, but not with BaCrO_4 or PbCrO_4 . F. L. U.

Action of potassamide on sulphur in liquid ammonia. F. W. BERGSTROM (Z. anorg. Chem., 1934, 221, 113—123; cf. A., 1934, 1110).—When S is added gradually to KNH_2 dissolved in liquid NH_3 at -33° in presence of Fe as catalyst, a yellow ppt. is at first formed which dissolves on further addition of S . The reaction at first is $6\text{KNH}_2 + 3\text{S} = 2\text{K}_2\text{S} + \text{S}(\text{NK})_2 + 3\text{NH}_3$, and subsequently $6\text{KNH}_2 + 12\text{S} = 2\text{K}_2\text{S}_4 + \text{S}_4(\text{NK})_2 + 4\text{NH}_3$. If the reaction takes place slowly K_2S_3 is formed. F. L. U.

Compounds of magnesium chloride with organic compounds. I. Compounds with alcohols and acetic acid. L. J. OLMER and (MILE.) M. L. QUINET (Bull. Soc. chim., 1934, [v], 1, 1579—1584).—Optimal conditions for preparing anhyd. MgCl_2 (I) from $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ are defined. By evaporating or by adding Et_2O to solutions of (I) in the appropriate alcohol, the following compounds were obtained: $\text{MgCl}_2 \cdot 6\text{MeOH}$ (II), m.p. $115-120^\circ$, $\text{MgCl}_2 \cdot 6\text{EtOH}$ (III), m.p. $72-77^\circ$, $\text{MgCl}_2 \cdot 6\text{PrOH}$, $\text{MgCl}_2 \cdot 6\text{BuOH}$, m.p. $55-60^\circ$, and a substance containing (I) and $\text{CH}_3\text{Bu}^t\text{OH}$. Et_2O ppts. from a mixture of alcohols the compound containing the alcohol with the lowest mol. wt. In vac., thermal decomp. of (II) and (III) affords variable proportions of HCl , the alkyl chloride, MgCl_2 , MgO , MgCO_3 , and C. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and AcCl or Ac_2O afford $\text{MgCl}_2 \cdot 6\text{AcOH}$ (IV), m.p. $85-90^\circ$, at low temp. and $\text{MgCl}_2 \cdot 4\text{AcOH}$ (V), m.p. 110° , at $> 80^\circ$. At the m.p. (IV) changes into (V), which is decomposed by heat into variable proportions of MgCl_2 , $\text{Mg}(\text{OAc})_2$, HCl , MgCO_3 , and C. J. G. A. G.

Dissociation of magnesium chromate. I. G. RISS and R. G. URITZKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 213—217).—The prep. of pure anhyd. MgCrO_4 is described. Thermal decomp. follows the reactions $2\text{MgCrO}_4 = 2\text{MgO} + \text{Cr}_2\text{O}_3 + 1.5\text{O}_2$; $2\text{MgO} + \text{Cr}_2\text{O}_3 = \text{MgO} + \text{MgO} + \text{Cr}_2\text{O}_3$. H_2 reacts at 300° with inflammation. The dissociation pressure of MgCrO_4 is given by $\log \frac{p}{\text{atm.}} = -16,488/T + 23.271$; the heat of dissociation is 75,370 g.-cal. per mol. of O_2 . E. S. H.

Hydrates of calcium aluminates, sulphatoaluminates, and chloroaluminates. J. LEFOL (Compt. rend., 1934, 199, 1412—1414; cf. A., 1934, 31, 853).— $\text{Al}_2\text{O}_3 \cdot 4\text{CaO} \cdot 12\text{H}_2\text{O}$ passes into $\text{Al}_2\text{O}_3 \cdot 4\text{CaO} \cdot 8\text{H}_2\text{O}$ in a dry atm. The reaction is reversible. $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 6\text{H}_2\text{O}$, cubic, is very stable and does not lose H_2O even at a relatively low H_2O v.p. $\text{Al}_2\text{O}_3 \cdot 2\text{CaO} \cdot 8\text{H}_2\text{O}$ gains or loses H_2O readily according to the H_2O v.p. in the atm. The hydrate $\text{Al}_2\text{O}_3 \cdot 2\text{CaO} \cdot 5\text{H}_2\text{O}$ has been identified, but its formation is not reversible. $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ are stable hydrates which in a dry atm. pass into $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$

and Al_2O_3 , 3CaO , CaCl_2 , $6\text{H}_2\text{O}$, respectively. The change is reversible for the latter compound, but not for the former. J. W. S.

Brick-red zinc oxide. A. KUTZELNIGG (Z. anorg. Chem., 1934, 221, 46—48; cf. A., 1933, 239).—The red ZnO formed by dissolution of white ZnO in fused NH_4NO_3 and explosion is not due to the presence of an unknown N compound, since the N_2O_5 content is 0.25% and the loss in wt. on calcination only 0.28%. Under the microscope the cryst. form is similar to that of ZnO prepared by the decomp. of $\text{Zn}(\text{NO}_3)_2$. The magnetic susceptibility of the red ZnO is -0.20×10^{-6} with 4 amp. and -0.25×10^{-6} with 5 amp. The temp. of formation is $> 300^\circ$. By heating above this temp. up to 540° the colour is gradually destroyed. No similar coloured oxide could be obtained by replacing ZnO by MgO , BeO , SnO_2 , or SiO_2 , or NH_4NO_3 by NH_4ClO_4 . By decomp. at a lower temp. the residue from the evaporation of aq. $\text{Zn}(\text{ClO}_3)_2$ or $\text{Zn}(\text{ClO}_4)_2$ a S-yellow compound is obtained. M. S. B.

Complex [cadmium and zinc] compounds [with pyridine and quinoline].—See this vol., 222.

Preparation of metallic barium and its amalgams. V. D. POLJAKOV (J. Appl. Chem. Russ., 1934, 7, 731—735).—Ba amalgam, prepared by electrolysis saturated aq. BaCl_2 with a Hg cathode (Mo connexion) and a graphite anode (0.28 amp. per sq. cm. of Hg surface for 3 hr.), is vac.-distilled in an Fe apparatus for 6 hr., gradually raising the temp. to 850° , when a product containing 10% Hg remains. This is gradually heated to 1000° in a second still (8 hr.), with a vac. of 10^{-3} mm. The residue, containing 0.02—0.2% Hg, m.p. 650° , is sealed in Cu tubes under A. H_2 combines very energetically with Ba or its amalgam. R. T.

Boron arsenate. W. C. SCHUMB and W. H. HARTFORD (J. Amer. Chem. Soc., 1934, 56, 2646).— BaAsO_4 , prepared by boiling an aq. solution containing H_3AsO_4 and H_3BO_3 , has d 3.40, n_D 1.66. It is readily hydrolysed and is slightly decomposed at red heat without melting. E. S. H.

Preparation of pure gallium. J. I. HOFFMAN (J. Res. Nat. Bur. Stand., 1934, 13, 665—672).—A HCl solution of the specimen is extracted with Et_2O , which dissolves the chlorides of Ga, Mo, Au, Fe, Tl, and traces of other elements. Sb, As, Bi, Cd, Cu, Ge, Au, Hg, Ag, and Sn and most of the Pb, Mo, and Rh are pptd. with H_2S from an acid solution of the Et_2O extract. Fe and Tl are then pptd. with aq. NaOH and filtered off, Ga being deposited electrolytically on Pt from the alkaline filtrate. Final purification from traces of Pb and In is effected by fractional crystallisation. Pure Ga separates first. Recovery of the Ga residues is described. H. J. E.

Preparation of pure europium, gadolinium, and terbium compounds. J. K. MARSH (J.C.S., 1934, 1972—1974).—Pure EuSO_4 can be separated quantitatively from a mixture of earths containing 3% Eu by electrolysis once, or at most twice, with an amalgamated Pb cathode of large area. Gd may be purified by fractionation of double Mg nitrates with

the addition of much $\text{Bi}(\text{NO}_3)_3$. Pure Tb is prepared by preliminary concn. as bromate and fractional crystallisation of the Me_2 phosphates. The possible influence of changes of lattice dimensions during fractionation is discussed. M. S. B.

Double sulphates of the rare-earth and alkali metals. Sulphates of praseodymium and potassium, of praseodymium and rubidium, of praseodymium and caesium, and of samarium and sodium. S. RESTAINO (Atti R. Accad. Lincei, 1934, [vi], 20, 192—200).—Investigation of the systems $\text{M}_2\text{SO}_4\text{—Pr}_2(\text{SO}_4)_3\text{—H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{—Sm}_2(\text{SO}_4)_3\text{—H}_2\text{O}$ at 25° ($\text{M}=\text{K, Rb, Cs}$) shows the formation of the compounds $x\text{Pr}_2(\text{SO}_4)_3 \cdot y\text{K}_2\text{SO}_4 \cdot z\text{H}_2\text{O}$ with $x, y, z=1, 5, 1; 1, 4, 5, 0; 1, 4, 1; 1, 3, 2; 2, 3, 8;$ and $1, 1, 2$, respectively; $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$; $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$; $\text{Sm}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$; and $4\text{Sm}_2(\text{SO}_4)_3 \cdot 5\text{Na}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$. O. J. W.

Reactivity of solids. III. Combustion of carbon. K. FISCHBECK (Z. Elektrochem., 1935, 41, 60—66).—A review.

Carbonyl fluoride COF_2 . O. RUFF and G. MILTSCHITZKY (Z. anorg. Chem., 1934, 221, 154—158).—CO and F_2 combine explosively when sparked at atm. pressure, and COF_2 can be prepared by feeding F_2 into CO through a spark gap. O_2 present in the F_2 forms CO_2 which cannot afterwards be separated from the COF_2 . Pure COF_2 , obtained by passing CO over AgF_2 , has m.p. $-114.0 \pm 0.3^\circ$, b.p. $-83.1 \pm 0.5^\circ$. V.p. is given by $\log p = 7.3231 - 843.05/T$ (mm.) and $d = 1.809 - 0.00420T$. COF_2 is hydrolysed with extreme readiness. Other chemical properties are described. F. L. U.

Action of titanium tetrachloride on organic nitrogen compounds. O. C. DERMER and W. C. FERNELIUS (Z. anorg. Chem., 1934, 221, 83—96).—The following mol. compounds have been obtained by the addition of an org. base to a solution of TiCl_4 in C_6H_6 or CHCl_3 : $\text{TiCl}_4 \cdot \text{NHPH}_2$, $\text{TiCl}_4 \cdot 2\text{NACPh}_2$, $\text{TiCl}_4 \cdot 2(\text{CH}_2\text{CO})_2\text{NH}$, $\text{TiCl}_4 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NH}_2(p)$, $\text{TiCl}_4 \cdot \text{CHPh} \cdot \text{NPh}$, $\text{TiCl}_4 \cdot \text{CPh}_2 \cdot \text{NPh}$, $3\text{TiCl}_4 \cdot 2\text{NPh} \cdot \text{NPh}$, $\text{TiCl}_4 \cdot \text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$, $\text{TiCl}_4 \cdot \text{NPh} \cdot \text{N} \cdot \text{NHPH}$, $3\text{TiCl}_4 \cdot 2\text{PhN} \cdot \text{N} \cdot \text{NPh}_2$, $\text{TiCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$, $\text{TiCl}_4 \cdot 2\text{C}_6\text{H}_5\text{N}$, $\text{TiCl}_4 \cdot 4\text{C}_6\text{H}_7\text{N}$ (γ -picoline), $\text{TiCl}_4 \cdot \text{C}_5\text{H}_{10}\text{N}$. Liquid TiCl_4 and $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ give $\text{Cl}_2\text{Ti}[\text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3]_2$. By the action of $\text{NH}(\text{CH}_2\text{Ph})_2$ and excess of CS_2 on TiCl_4 a compound, $\text{Ti}[\text{S} \cdot \text{CS} \cdot \text{N}(\text{CH}_2\text{Ph})_2]_4$ is obtained. NPh_2K and TiCl_4 give $\text{Ti}[\text{NPh}_2]_4$. The mol. wts. of $\text{CPh}_2 \cdot \text{NPh}$, COPh_2 , and $\text{NPh} \cdot \text{NPh}$ in boiling TiCl_4 have been determined, but owing to the volatility of the solute too high vals. have been obtained for the first two.

M. S. B.

Zirconium and hafnium tetrafluorides. G. VON HEVESY and W. DULLENKOPF (Z. anorg. Chem., 1934, 221, 161—166; cf. A., 1930, 1362).—The crystallographic characters of ZrF_4 and HfF_4 are recorded. The electrical conductivity of solid ZrF_4 has been measured and found to be due almost entirely to F^- ions. HfF_4 can be partly separated from ZrF_4 by fractional sublimation, or by distillation of their solution in fused K_2ZrF_6 . They are conveniently separated from Fe and other impurities by sublimation.

NO₃F, an explosive compound. G. H. CADY (J. Amer. Chem. Soc., 1934, 56, 2635—2637).—Reaction of F₂ with dil. HNO₃ produces a gaseous compound, NO₃F, b.p. —42°, which explodes when heated. NO₃F reacts slowly with H₂O, liberating O₂, and liberates I from aq. KI.

E. S. H.

Nitrogen selenide. W. STRECKER and H. E. SCHWARZKOPF (Z. anorg. Chem., 1934, 221, 193—198).—Pure (NSe)_x can be prepared by the action of dry NH₃ on Et₂SeO₃ or Me₂SeO₃ dissolved in C₆H₆, and removal of the accompanying SeO₂ and Se by 10% KCN. The product is usually orange-red and amorphous, and has been obtained crystalline in monoclinic prisms analogous to N₄S₄ on one occasion only. It is highly explosive. Chlorination yields mainly SeCl₄. Dry HCl gives SeCl₄, NH₄Cl, (NH₄)₂SeO₃, and H₂Se. The Cl₂ and HCl used in these reactions must be greatly diluted with CO₂.

F. L. U.

Absorption of oxygen by phosphorus. C. T. KINGZETT (Analyst, 1934, 59, 816; cf. A., 1934, 1186).—Attention is directed to previous work by the author (J.C.S., 1880, 37, 792).

E. C. S.

Production of pure, finely-divided vanadium. T. DORING and J. GEILER (Z. anorg. Chem., 1934, 221, 56—62).—A method for the prep. of very pure V by the reduction of VCl₃ with pure H₂ at approx. 900° is described.

M. S. B.

Decomposition of arsine by fine fibrous materials. G. LOCKEMANN (Z. anal. Chem., 1934, 99, 178—180).—Polemical against Gangl *et al.* (A., 1934, 1084).

J. S. A.

Preparation of pure oxygen for laboratory use. J. KRUTZSCH and H. KAHLE (Chem. Fabr., 1934, 7, 452—453).—The decomp. of H₂O₂ in a vessel of relatively small vol., leaving little free gas space, is accelerated by the presence of beads. An apparatus suitable for generating 10—50 c.c. per hr. is described.

J. W. S.

Oxygen preparation from sodium peroxide. G. H. CHEESMAN and D. R. DUNCAN (Nature, 1934, 134, 971).—An explosion under conditions similar to those previously described (this vol., 51) is reported.

L. S. T.

Yellow coloration of hydrochloric acid containing selenium. H. DITZ and F. ULLRICH (Z. anorg. Chem., 1934, 221, 33—45).—Although Se is practically insol. in pure conc. HCl, it dissolves in HCl solutions of SeO₂ giving an intense yellow coloration due to the formation of Se₂Cl₂ in solution. The extent of the reaction may be studied quantitatively by titrating solutions of SeO₂ in HCl with SnCl₂ until a faint cloudiness due to the separation of Se appears. The Se formed by reduction of SeO₂ redissolves giving Se₂Cl₂. In approx. 37% HCl the Se₂Cl₂ formed is about 90% of the theoretical quantity. This freshly reduced Se is more sol. than powdered or pptd. Se.

M. S. B.

Tellurium nitride. W. STRECKER and C. MAHR (Z. anorg. Chem., 1934, 221, 199—208; cf. A., 1926, 137).—By the long-continued action of liquid NH₃ on Te a yellow powder is obtained which, after removal of NH₃, explodes on contact with H₂O. The ex property is due to heat of wetting resulting from

its fine state of division. Analysis leads to the formula Te₃N₄ as previously surmised (A., 1926, 137); it is therefore not analogous to the S and Se compounds. The reaction with Br is very incomplete and yields chiefly TeBr₄. When the substance is suspended in Et₂O and treated with Br, the resulting HBr forms (NH₄)₂TeBr₆. Dry HCl reacts with the solid to give (NH₄)₂TeCl₆.

F. L. U.

Hydrolysis of inorganic salts and chemistry of high-molecular hydrolysis products (including iso- and hetero-poly-compounds. I. G. JANDER and K. F. JAHR (Kolloid-Beih., 1934, 41, 1—57).—A summary of published work, especially on the complex oxy-acids of W, Mo, V, Ta, and Si.

E. S. H.

Oxidation of manganous sulphate by hydrogen peroxide in an alkaline medium. P. DUBOIS (Compt. rend., 1934, 199, 1310—1313).—The effect of *p*_H, [H₂O₂], [aq. NH₃], and [KOH] on the composition of the ppt. was studied. With aq. NH₃ or KOH the ppt. is hydrated Mn₂O₃. With excess of KOH the composition varies between MnO_{1.5} and MnO_{1.8}, and the ppt. retains KOH after washing. Excess of H₂O₂ gave the same results.

H. J. E.

Hydrate and allotropic forms of manganese sesquioxide. P. DUBOIS (Compt. rend., 1934, 199, 1416—1418).—Oxidation of MnSO₄ by H₂O₂ in presence of NH₃ yields Mn₂O₃ in a form which appears colloidal, but is crystalline to X-rays. When heated in air this tends to yield MnO₂, but the reaction is never complete. In absence of air, the α-form of Mn₂O₃ is formed, this being oxidised on heating in air. When heated to 600°, however, it passes into the normal β-form of Mn₂O₃, which is not oxidised by heating in air. The X-ray diagram of α-Mn₂O₃ is very similar to that of Mn₃O₄ resulting from the thermal decomp. of β-Mn₂O₃.

J. W. S.

Complex sulphates. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1934, 221, 21—24).—By dialysis of solutions of the sulphates of bi- or trivalent metals containing excess of alkali or NH₄ sulphates it is shown that the following ions exist: [M₂(SO₄)₄]⁴⁻ (M=Mn, Fe, Co, Ni, Cu, Zn, Cd, or Mg) and [Fe₃(SO₄)₆]⁶⁻. The possibility that the effects observed may be due to heavily hydrated metallic ions is excluded by experiments to be described later.

M. S. B.

Frictional oxidation [of metals]. F. ROLL and W. PULEWKA (Z. anorg. Chem., 1934, 221, 177—181).—Oxidation occurring when a metal specimen is pressed against a revolving steel plate has been studied with respect to pressure and speed of rotation. The zones of Fe₂O₃ and Fe₃O₄ formed are related to the temp. produced by the friction, contrary to the statement of Fink and Hoffmann (A., 1933, 241).

F. L. U.

Preparation of [iron-tin] alloys. P. PINGAULT (Compt. rend., 1934, 199, 1223—1225).—The compound FeSn₂ (I) is formed by heating Sn with aq. ZnCl₂ containing 340 g. of FeCl₂ per litre at < 300°. (I) is also formed by the direct action of FeCl₂ on Sn at < 300°.

H. J. E.

Intermediate compounds between ferro-cyanides and ferroammines. A. G. BARBIERI

(Atti R. Accad. Lincei, 1934, [vi], 20, 273—278).—By the action of KCN on $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Br}_2 \cdot 6\text{H}_2\text{O}$ in solution reddish-violet crystals of $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{CN})_2] \cdot 3\text{H}_2\text{O}$ (I) are obtained. Prolonged warming of (I) with conc. aq. KCN gives orange-brown crystals of $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CN})_4]\text{K}_2 \cdot 3\text{H}_2\text{O}$ (II). From a solution of (II) the free acid, $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CN})_4]\text{H}_2 \cdot 2\text{H}_2\text{O}$ is obtained as a yellow ppt. by the addition of a mineral acid. With *o*-phenanthroline instead of dipyrldyl the compounds corresponding with (I) and (II) have been prepared. Magnetic susceptibility measurements for the above compounds are recorded. O. J. W.

Influence of temperature on the formation of additive compounds. G. SCAGLIARINI and M. RAGNO (Atti R. Accad. Lincei, 1934, [vi], 20, 278—282).—From solutions of CoX_2 ($\text{X}=\text{Cl}, \text{Br}$) in $\text{C}_5\text{H}_5\text{N}$ which have been kept at 70—80° for several hr., the compounds $\text{CoX}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ crystallise out, whereas from cold solutions the compounds $\text{CoX}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ are obtained. The transition points for the changes $\text{M}(\text{SCN})_2 \cdot 4\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \rightarrow \text{M}(\text{SCN})_2 \cdot 4\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ ($\text{M}=\text{Co}, \text{Ni}, \text{Fe}$) and $\text{MX}_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \rightarrow \text{MX}_2 \cdot 4\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ ($\text{MX}_2=\text{CoBr}_2, \text{CoCl}_2, \text{or NiCl}_2$) are < 80°. O. J. W.

Influence of substituents in bases and anions on the co-ordination index of a metal. VI. Additive products of benzylamine and phenylhydrazine with the nickel salts of substituted acetic acids. A. ABLOV (Bull. Soc. chim., 1934, [v], 1, 1489—1494; cf. A., 1934, 1083).—The following compounds are described: $\text{Ni}(\text{OAc})_2 \cdot 4\text{CH}_2\text{Ph} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$;
 $(\text{CH}_2\text{Ph} \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{CH}_2\text{Ph} \cdot \text{NH}_2$;
 $(\text{CH}_2\text{Cl} \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{CH}_2\text{Ph} \cdot \text{NH}_2$;
 $(\text{CHCl}_2 \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{CH}_2\text{Ph} \cdot \text{NH}_2$;
 $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{CH}_2\text{Ph} \cdot \text{NH}_2$;
 $(\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{CH}_2\text{Ph} \cdot \text{NH}_2$;
 $\text{Ni}(\text{OAc})_2 \cdot 4\text{NHPh} \cdot \text{NH}_2$;
 $(\text{CH}_2\text{Ph} \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{NHPh} \cdot \text{NH}_2 \cdot 3\text{H}_2\text{O}$;
 $(\text{CH}_2\text{Cl} \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{NHPh} \cdot \text{NH}_2$;
 $(\text{CHCl}_2 \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{NHPh} \cdot \text{NH}_2$;
 $(\text{CCl}_3 \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{NHPh} \cdot \text{NH}_2$;
 $(\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Ni} \cdot 4\text{NHPh} \cdot \text{NH}_2$. These salts probably have the constitution $[\text{Ni}(\text{base})_4]\text{X}_2$, and the constancy of the no. of base mols. co-ordinated (cf. the variable no. of $\text{C}_5\text{H}_5\text{N}$ which co-ordinate; A., 1934, 1084) is attributed to the higher energy of addition of $\text{CH}_2\text{Ph} \cdot \text{NH}_2$ arising from the greater deformability of the $\cdot\text{NH}_2$ group. J. G. A. G.

Constitution of thiosemicarbazide compounds of nickel. See this vol., 202.

Thiosemicarbazide compounds of bivalent palladium and platinum.—See this vol., 202.

Red tetraethylamminoplatinum chloride. H. REIMLEN and E. FLOHR (Ber., 1934, 67, [B], 2010—2017; cf. Hantzsch *et al.*, A., 1930, 440).—Treatment of aq. K_2PtCl_4 with 2 mols. of NH_2Et at 15—20° until the solution becomes colourless and with a further 2 mols. at 65—70° affords tetraethylamminoplatinum chloride (I), $[\text{Pt}(\text{ae})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{ae}=\text{NH}_2\text{Et}$) in 93% yield. (I) is transformed by 3% H_2O_2 and 5*N*-HCl into the red salt (II) $[\text{Pt}(\text{ae})_4]\text{Cl}_2 \cdot [\text{Pt}(\text{ae})_4]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, m.p. 177°, which does not react with dil. HNO_3 , is transformed by HCl into

the compound $[\text{Pt}(\text{ae})_4]\text{Cl}_2$, and in acid solution liberates 1 atom of I per atom of Pt from KI. (II) is converted by Na_2PtCl_6 in cold solution into the compounds, $[\text{Pt}(\text{ae})_4][\text{PtCl}_6]$ and $[\text{Pt}(\text{ae})_4]\text{Cl}_2 \cdot [\text{PtCl}_6]$. With excess of K_2PtCl_6 (II) is completely transformed into the sparingly sol., violet-red compound $[\text{Pt}(\text{ae})_4][\text{PtCl}_4]$. (II) and $\text{Ag}_2\text{C}_2\text{O}_4$ afford the salt $[\text{Pt}(\text{ae})_4]\text{C}_2\text{O}_4$. H. W.

Varying valency of platinum with respect to mercaptanic radicals. VIII. (SIR) P. C. RAY and N. N. GHOSE (J. Indian Chem. Soc., 1934, 11, 737—742; cf. A., 1928, 44, 751).—The product of the interaction in EtOH solution of $(\text{SEt} \cdot \text{CH}_2)_2$ ($=\text{es}$) and H_2PtCl_6 is $\text{Pt}(\text{es})\text{Cl}_3$ (I), m.p. 180—182° (decomp.), which is converted into $\text{Pt}(\text{es})\text{Cl}_2$ (II) by heating with NPhMe_2 and into the compound $\text{Pt}(\text{es})\text{Cl}_4$ (III), m.p. 230° (decomp.), by heating with fuming HCl and $\text{C}_5\text{H}_5\text{N}$ and (I) afford $[\text{Pt}(\text{C}_5\text{H}_5\text{N})]\text{Cl}_2$ (IV) and the substance $\text{Pt}(\text{C}_5\text{H}_5\text{N})\text{Cl}_3$, m.p. 261—265° (decomp.), (II) gives (IV), and (III) yields $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4] \cdot (\text{CH}_2 \cdot \text{NH}_2)_2$ ($=\text{en}$) produces $[\text{Pt}(\text{en})_2]\text{Cl}_2$ with (I), (II), and (III), whilst aq. NH_3 and (III) afford $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$. The results show that (I) is neither a mixture nor a mol. compound of (II) and (III), and (II) and (III) are probably best represented by the formulæ $[\text{esPtCl}_3]$ and $[\text{esPtCl}_4]$, respectively. J. G. A. G.

New indicators and other reagents employed in volumetric analysis. A. D. MITCHELL (Inst. Chem., 1934, 21 pp.).—A lecture.

Polarimetric methods in chemistry. T. M. LOWRY (Nature, 1934, 134, 920—921, 958—960).—An address to the British Association. L. S. T.

Methylal as a solvent in analytical chemistry. L. ESPIEL (Bull. Soc. chim., 1934, [v], 1, 1502—1503).—The purification of technical methylal (I) is described. The range of complete miscibility with H_2O of (I) is of Et_2O (II). (I) extracts AcOH, lactic, succinic, citric, malic, and tartaric acids from aq. solution acidified with H_2SO_4 , and the process is facilitated by saturating with Na_2SO_4 . The advantages of (I) over (II) are emphasised and distribution data are recorded. J. G. A. G.

Determination of small concentrations. VII. Potentiometric acid and alkali determinations. E. V. TEIS and O. R. VAGNER (J. Gen. Chem. Russ., 1934, 4, 927—935).—The potentiometric titration of acids by alkalis (Cu and W electrodes) gives more accurate results than when alkalis are titrated, in particular when carbonates are present. R. T.

Colorimetric determination of p_{H} with the Pulfrich photometer. I. S. HAHNEL (Svensk Kem. Tidskr., 1934, 46, 262—279).—Details of a method for two-colour indicators using two wavelengths are given. With sulphonephthalein indicators the p_{H} can be calc. from the measured absorption vals. by the theoretical equations. With thymol-blue in acid solution and with Me-red empirical equations must be used; this is probably due to the existence of > two forms of the indicator. A series of indicators is given for measurements from p_{H} 1.0 to 10.0. R. P. B.

Potentiometric and conductometric studies. II. Conductometric. J. PIEPER (Z. Elektrochem.,

1934, 40, 844—857).—Graphical methods of determining the equivalence point in conductometric titrations are discussed critically, and it is shown how more satisfactory results may be obtained by calculation. Both methods being empirical, the procedure to be followed in a particular experiment must be established by a preliminary titration with standardised solutions, and as far as possible identical conditions maintained. The neutralisation point in NaOH containing Na_2CO_3 can be determined only with difficulty, and the transition of Na_2CO_3 to NaHCO_3 not at all. The choice of apparatus is also discussed. F. L. U.

Mercurimetric determination of halogens. A. IONESCU-MATIU and S. HERSCOVICI (Bull. Soc. chim., 1934, [v], 1, 1379—1386; cf. A., 1933, 1023).—The authors' method has been applied to the volumetric determination of the halogens, including F. The procedure is described in detail. The degree of precision attained is the same as in the classical methods. F. L. U.

Semi-micro-volumetric determination of halogens. (Sodium-higher alcohol method.) W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 590—591b; cf. A., 1928, 82).—The halogen compound is reduced with Na and a higher alcohol (best $\text{CH}_3\text{Ph}\cdot\text{OH}$). The resulting Na halide is determined volumetrically by Volhard's method. H. N. R.

Influence of higher alcohols and of ether on the titration of halogens by Volhard's method. W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 589—590b).—The influence is negligible. H. N. R.

Accurate quantitative analysis of chlorides in presence of thiocyanates. E. COHEN and K. PREPENBROEK (Z. anal. Chem., 1934, 99, 258—269).—Schulek's iodometric method (A., 1923, ii, 591), and oxidation of CNS' by means of HNO_3 according to Rosanoff and Hill (A., 1907, ii, 984) are satisfactory. Oxidation of CNS' with H_2O_2 in acid solution (cf. A., 1915, ii, 124) gave accurate results only when the amount of acid was reduced to 1 c.c. of $4N\text{-H}_2\text{SO}_4$ in 60 c.c. of liquid. J. S. A.

Determination of perchlorates. C. SMEETS (Natuurwetensch. Tijds., 1934, 16, 262—266).—The best conditions for determining ClO_4' in presence of various interfering ions have been investigated. If only Li, Na, Ni, Co, Zn, Cd, Pb, Al, Cr, and/or Fe are present, a sample containing 0.2—0.3 g. of perchlorate may be dissolved in ≈ 10 c.c. of EtOH ($\approx 96\%$ and preferably abs.) and 5—7 c.c. of cold saturated KOAc in EtOH added. After a short time, the pptd. KClO_4 is collected and dried at 130° . This method cannot be used in presence of Ag, Mg, Ca, Sr, Ba, Cu, or Mn, to the insolubility of their acetates in EtOH, nor in presence of NH_4 or other NH_3 derivatives, owing to the insolubility of their perchlorates. In these cases, g. of the sample is moistened with 0.1 c.c. of distilled H_2O , 0.2—0.3 g. of Na_2CO_3 in 0.2 c.c. of H_2O added, and the mixture is evaporated to dryness. In this way the metals are converted into insol. carbonates and the NH_3 is volatilised. The NaClO_4 formed is then extracted by means of EtOH and the ClO_4' is pptd. as KClO_4 . CO_3'' and SO_4'' do not interfere. If

Cl' or NO_3' is present, the NaClO_4 should be extracted by means of dry COMe_2 , the solution evaporated, the NaClO_4 redissolved in EtOH, and the ClO_4' pptd. as KClO_4 . If ClO_3' is present, it should first be reduced to Cl' . D. R. D.

Detection of chlorine and bromine in air, gas mixtures, and solutions by formation of iris-blue. H. EICHLER (Z. anal. Chem., 1934, 99, 272—275).—Free Br and Cl_2 convert resorufin (I) into non-fluorescent halogenated iris-blue. (I) is used as its 0.1% solution in aq. Na_2CO_3 . An approx. quant. determination of Cl_2 or Br in gases may be made by determining the vol. of gas (e.g., measured roughly with a rubber pinch bulb) necessary to destroy the fluorescence of a measured amount of (I). J. S. A.

Cyanide-formaldehyde reaction, and new volumetric analytical applications. A. MUTSCHIN (Z. anal. Chem., 1934, 99, 335—348).— CH_2O reacts reversibly with KCN, giving $\text{OH}\cdot\text{CH}_2\cdot\text{CN}$ (I) (cf. A., 1925, ii, 1009). A 3-fold excess of CH_2O is necessary to remove CN' quantitatively. Reaction in acid solutions is slow. Hydrolysis of (I) takes place only extremely slowly, and is not accelerated by MgSO_4 (cf. A., 1925, ii, 606). Cl' , Br' , I' , or CNS' in presence of CN' may thus be determined by adding excess of CH_2O to the neutral or alkaline solution, neutralising against Me-red, and titrating with AgNO_3 . CH_2O may be determined by adding excess of KCN, and converting the excess into BrCN by means of $\text{Br}\cdot\text{H}_2\text{O}$. Excess of Br is removed with N_2H_4 , H_2SO_4 , KI added, and the BrCN then determined iodometrically. J. S. A.

Application of cyanogen bromide as universal standardisation material. M. MØLLER (Z. anal. Chem., 1934, 99, 351—354).— BrCN , readily obtained and preserved in analytical purity, may be used for standardisation (a) of $\text{Na}_2\text{S}_2\text{O}_3$, against the I liberated on dissolution in KI, (b) of acids, (c) of AgNO_3 . For (b), BrCN is hydrolysed by KOH to CNO' . The solution is acidified, and CO_2 boiled off. The NH_3 formed is liberated by NaOH and distilled into the acid. The excess of acid is then titrated back. For (c), BrCN is dissolved in NaOH, and the solution neutralised. Br' so formed is titrated with AgNO_3 . J. S. A.

Determination of bromide ion in presence of large quantities of chloride ion. F. P. ZORKIN (J. Appl. Chem. Russ., 1934, 7, 852—856).—Szabo's method (A., 1931, 811) is preferred. R. T.

Sensitivity of the starch-iodine reaction. I. M. KORENMAN (J. Appl. Chem. Russ., 1934, 7, 847—851).—The sensitivity of the reaction is a function of the concns. of KI, I, and acid or alkali in the solution; for a given [I], $N/C = k$, where N is the concn. of acid or alkali, C the [KI], and k a const. for the given acid or alkali. The colour obtained changes from blue to red-dish-violet as the [KI] rises from 1 to 10%. R. T.

Potentiometric determination of minimal quantities of iodine. R. FLATT (Helv. Chim. Acta, 1934, 17, 1494—1513).—The solution containing I' , acidified with HCl, is titrated with KBrO_3 , whereby I' is oxidised first to I (I) and then to ICl (II). A break in the potential curve occurs at the completion of (I) and a sharper one at the completion of (II). A micro-

method by which the I in 1 c.c. of liquid can be determined with a max. error of 5×10^{-3} g. is described. Apart from the high precision attainable, an advantage of the method is the absence of I from the reagents introduced, and the consequent possibility of repeated determinations on the same sample, after reduction of the ICl by CrCl_2 . F. L. U.

Micro-iodometry. J. RENAUDIN and (MME.) J. RENAUDIN (J. Pharm. Chim., 1934, [viii], 30, 516—527).—Conditions and precautions for accurate work with 0.01N solutions are defined. The solutions should be neutral. A. E. O.

Determination of fluorine in phosphorites and apatites.—See B., 1935, 60.

Microchemical colour reaction of elementary sulphur. A. SCHONBERG and W. URBAN (Ber., 1934, 67, [B], 1999—2003).—The finely-powdered material (I) is placed in a m.p. capillary tube, covered with about 10 times its wt. of *benzyliminodi-p-anisylmethane*, m.p. 93° [obtained by the successive action of SOCl_2 and $\text{NH}_2\cdot\text{CH}_2\text{Ph}$ on $\text{CO}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$], and the tube is sealed. The contents are mixed by repeatedly inverting the tube and then heated at about 210° for 5 min. The cold product is dissolved in boiling C_6H_6 , which if free S is present in (I) becomes blue owing to the formation of $\text{CS}(\text{C}_6\text{H}_4\cdot\text{OMe})_n$. The intensity of the colour is diminished by adding a crystal of HgCl_2 , which becomes red superficially. Reaction is not given by Se or by compounds of S.

H. W.

Potentiometric determination of sulphates. I. I. SHUKOV and C. G. RAICHINSCHTEIN (J. Gen. Chem. Russ., 1934, 4, 962—968).—50 c.c. of EtOH, 0.2 c.c. of 0.0025M- $\text{K}_4\text{Fe}(\text{CN})_6$, and 2 c.c. of 0.1M- $\text{K}_3\text{Fe}(\text{CN})_6$ are added to 30 c.c. of aq. Na_2SO_4 (approx. 0.1N), a Pt electrode is introduced, and the system is connected with a HgCl electrode and titrated with 0.1N- $\text{Pb}(\text{NO}_3)_2$; the results differ by $\approx 0.04\%$ from the theoretical. Salts enhancing the solubility of PbSO_4 cause high, and of $\text{Pb}_2\text{Fe}(\text{CN})_6$ low, results to be obtained. R. T.

Detection of hyposulphites and sulphonylates and of nascent hydrogen with resazurin. H. EICHLER (Z. anal. Chem., 1934, 99, 270—272).—Hyposulphites and sulphonylates, also freshly pptd. $\text{Fe}(\text{OH})_2$ and $\text{Sn}(\text{OH})_2$, but not $\text{S}_2\text{O}_3^{''}$ or $\text{SO}_3^{''}$, in alkaline (Na_2CO_3) solution reduce the blue solution of resazurin (I) (fluorescing a weak brownish-red) to non-fluorescent hydroresorufin, which oxidises in contact with air to the vividly yellowish-red fluorescing resorufin. In acid solution, $\text{SO}_3^{''}$, $\text{S}_2\text{O}_3^{''}$, and nascent H also reduce (I). J. S. A.

Analysis of reducing acids of sulphur. E. CHERBULIEZ and A. HERZENSTEIN (Helv. Chim. Acta, 1934, 17, 1582—1587).—In the analysis of mineral waters H_2S can be determined in presence of other I-reducing substances by treatment with suspended CdCO_3 and iodometric titration of the CdS produced. In dil. ($\approx 10^{-4}\text{N}$) solution $\text{S}_2\text{O}_3^{''}$ is determined by means of its catalytic effect on the interaction of NaN_3 and I, for which a simple iodometric method is described. $\text{SO}_3^{''}$ is determined by adding colloidal S at p_H 6, when $\text{S}_2\text{O}_3^{''}$ is formed according to SO_3H^+ +

$\text{S}=\text{S}_2\text{O}_3^{''}+\text{H}^+$, and is itself determined in the manner already described. F. L. U.

Determination of ammonia in water and air. A. KROGH (Biol. Bull., 1934, 67, 126—131).—The H_2O sample is treated with 0.2N-NaOH to 9—11 and then distilled under reduced pressure. NH_3 evolved is absorbed in dil. HBr, the aq. NH_4Br is treated with a definite vol. of standard aq. NaOBr at p_H 8.5—9, and the excess of NaOBr titrated with 0.0005N-naphthyl-red solution, which is decolorised as long as NaOBr remains. $0.05\text{—}2 \times 10^{-6}$ g. of N may be determined. NH_3 in air is determined by first absorbing it in dil. HBr. CH. ABS. (e)

Drop reaction for arsenic with N-ethyl-8-hydroxytetra[hydro]quinoline hydrochloride (kairin). W. REPPMANN (Z. anal. Chem., 1934, 99, 180—182).—A drop of solution containing As^{III} on filter-paper, is moistened with HCl and 0.5% aq. N-ethyl-8-hydroxytetrahydroquinoline hydrochloride. A drop of aq. FeCl_3 is added, and the test paper warmed. In presence of As a reddish-brown coloration results; limit, 6×10^{-10} g. Hg, Pb, and Cu interfere. J. S. A.

Apparatus for the detection and determination of arsenic by the Gutzeit and Beck-Merres methods. R. STEINBRUCK (Pharm. Zentr., 1935, 76, 5—6).—Gnessin's statements (this vol., 53) are criticised. Alteration of the Beck-Merres apparatus is unnecessary and the addition of the substance and the acid all at once is not a fault. The necessity for the evolution of H_2 to be const. and also for the use of 10% HCl is emphasised. The max. of 0.07 g. As is too low. 10^{-6} g. can be detected, but amounts of 1, 2, and 3×10^{-6} g. cannot be easily differentiated.

E. H. S.

Determination of small quantities of arsenic. (Determination of arsenic in iron ore, soot, etc.) L. W. STROCK (Z. anal. Chem., 1934, 99, 321—335).—As is reduced by nascent H to AsH_3 , which is absorbed in 2—6% aq. HgCl_2 . The yellow ppt. formed does not contain the total As, but decomposes to $\text{H}_3\text{AsO}_3 + \text{Hg}_2\text{Cl}_2$. For small amounts of As (0.01—1 mg.), NaHCO_3 is added to the solution + ppt., and exactly neutralised with HCl (Me-orange). $\text{Hg}_2\text{Cl}_2 + \text{H}_3\text{AsO}_3$ are then titrated with 0.01N-I, requiring 8 I per atom of As. With larger amounts of As (1—10 mg.), the ppt. is allowed to decompose completely, Hg_2Cl_2 is removed by filtration, and H_3AsO_3 titrated iodometrically after exact neutralisation, as before. Fe ores etc. are fused with 2 parts of $\text{Na}_2\text{B}_4\text{O}_7 + 4$ parts of Na_2CO_3 , dissolved in H_2SO_4 containing Na_2HPO_4 , and AsH_3 is at once generated from the considerably diluted solution before pptn. of SiO_2 occurs. Metallic Fe and org. material (soot, humus, etc.) are dissolved in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$. J. S. A.

Volumetric determination of arsenates. F. TABOURY and H. AUDIDIER (Bull. Soc. chim., 1934, [v], 1, 1570—1578).—The effects of concn. of reagents and time of boiling on the reduction of $\text{AsO}_4^{''}$ to $\text{AsO}_3^{''}$ by KI in H_2SO_4 solution have been investigated. The reduction is complete when a mixture of 10 c.c. of 0.001—0.0165M- As_2O_5 with 2 c.c. of H_2SO_4 (d 1.8) and 0.8 g. of KI is heated at 100° for 10 min.

The I liberated is exactly titrated with $\text{Na}_2\text{S}_2\text{O}_3$ and, after adding excess of NaHCO_3 , the $\text{AsO}_3^{''}$ is titrated with I. The method is used for analysis of Pb arsenate after pptg. the Pb as PbSO_4 . J. G. A. G.

Rapid determination of silica in water-glass.—See B., 1935, 60.

Determination of dissolved organic carbon and nitrogen in sea-water. A. KROGH and A. KRYS (Biol. Bull., 1934, 67, 132—144).—A sample of the H_2O is evaporated in a Ag tube, which is heated at 500° in a stream of H_2 . The NH_3 evolved is absorbed in dil. HBr , and determined, together with residual NH_3 , by the NaOBr method (cf. this vol., 184). C is determined by acidifying to remove $\text{CO}_3^{''}$, and pptg. most of the Cl' with Ti_2SO_4 . The H_2O is then evaporated to dryness, and heated with conc. H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, Ag_2CrO_4 , and CrO_3 . CO_2 evolved is absorbed in aq. $\text{Ba}(\text{OH})_2$ and excess titrated with HCl . CH. ABS. (e)

Application of perchloric acid to the indirect determination of carbon dioxide in carbonates. F. VOJTA (Chem. Listy, 1934, 28, 299—301).—The non-volatility of HClO_4 and the solubility of its salts render it preferable to HCl for expelling CO_2 from carbonates. R. T.

Determination of carbon dioxide in the atmosphere of a closed system. C. Z. ROSECRANS (Science, 1934, 80, 483—484).—Attention is directed to advantages of the thermal conductivity method of determination (cf. A., 1934, 1190). L. S. T.

Determination of carbon disulphide in air.—See B., 1935, 47.

Sensitiveness of detection of the alkali metals in the arc spectrum. P. URBAIN and M. WADA (Compt. rend., 1934, 199, 1199—1201).—The limits for spectrographic detection of Li, Na, K, Rb, and Cs in the Cu arc were 2, 70, 1200, 2600, and 8000×10^{-6} mg. respectively. H. J. E.

Rapid determination of potassium. K. NOWAK (Przemysł Chem., 1934, 18, 509—510).—5 c.c. of clear, neutral solution, containing about 0.05 g. K_2O , and free from NH_3 , are added to 17 c.c. of reagent (I) in a special centrifuge tube, the bottom of which is drawn out into a capillary, and previously filled with H_2O . The solution is centrifuged for 15 sec. at 21—23 and 1000 r.p.m., and the K content is read directly on a scale on the capillary from the height of the column of ppt. (I) is prepared by dissolving 450 g. of NaNO_3 in 800 c.c. H_2O , adding the solution after 24 hr. to 250 g. of $\text{Co}(\text{OAc})_3$ in 800 c.c. of H_2O , diluting to 2 litres, and adding 65 c.c. of H_2O and 5 c.c. of AcOH to 100 c.c. of the solution so obtained. R. T.

Application of spectrum analysis to determination of alkalis and alkaline earths. IV. Micro-determination of potassium and calcium. W. H. JANSEN, J. HEYES, and C. RICHTER (Z. physikal. Chem., 1934, 171, 268—280).—The method previously described (A., 1934, 745) is used, the sensitivity being increased by utilisation of an improved atomiser which makes it possible to carry out a determination in a c.c. dil. solution. The precision attainable is 8% for K and 10% for Ca. R. C.

Direct colorimetric determination of sodium. O. M. SMITH and H. BLAIR (Proc. Oklahoma Acad. Sci., 1934, 13, 33—35).—Caley and Foulk's method (cf. A., 1929, 900) was tested on 140 H_2O samples, and is accurate to approx. 0.35 mg. Na. CH. ABS. (e)

Rapid spectroscopic determination of metals. I. Lithium. A. P. SNESSAREV (J. pr. Chem., 1934, [ii], 141, 327—330).—The min. concn. (0.0000010728 g. per c.c.) of Li which can be detected spectroscopically is first determined; the unknown solution is then diluted to the same concn. Results are reproducible and compare favourably with those obtained by Gooch's method. H. B.

Use of phosphomolybdic acid in chemical analysis. J. W. ILLINGWORTH and J. A. SANTOS (Nature, 1934, 134, 971).—Phosphomolybdic acid detects 1 part of Cs in 5×10^5 of H_2O and ppts. 1 of K in 10^4 of H_2O . The ppt. of $\text{K}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, where n is ≥ 2 (probably 0), is stable at 120° . L. S. T.

Systematic potentiometric analysis. II. Determination of Ag, Bi, Pb, Cu, Cd. W. HILTNER and W. GITTEL (Z. anal. Chem., 1934, 99, 169—178; cf. this vol., 55).—Ag, Bi, Pb, Cu, and Cd are separated by pptn. as sulphides and dissolved in HNO_3 . Ag is titrated potentiometrically with HCl at room temp. Excess of 0.1N- HCl is added, and the solution boiled and neutralised to Congo-red by 2N- NaOAc , thereby pptg. BiOCl quantitatively. The ppt. is collected, dissolved in HNO_3 , and titrated with AgNO_3 . Pb is pptd. from the filtrate as PbCrO_4 , and this dissolved in HCl . A measured excess of 0.2N- SbCl_3 is added, and titrated back with KMnO_4 . Excess of $\text{CrO}_4^{''}$, and $\text{Cu}^{''}$ in the filtrate are reduced with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, and Cu is pptd. as CuCNS . The ppt. is dissolved in NaOH , and CNS' titrated with AgNO_3 . Cd in the remaining solution is titrated with Na_2S . J. S. A.

Determination of silver by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, 37, 754—756B).—Ag can be titrated photometrically with NaCl , preferably in a coloured beaker and with the addition of starch as a protective colloid; Cu does not interfere. A. G.

Applicability of potentiometric silver titration in determining silver in practice. E. RAUB (Mitt. Forsch.-Inst. Probieramts. Edelmet. Schwab. Gmünd, 1934, 8, 11 pp.; Chem. Zentr., 1934, ii, 1168).—A discussion. The potentiometric method is more accurate. In determining Ag in material insol. in HNO_3 , Cl is first removed, Pb is added to concentrate the Ag, and the Ag determined potentiometrically in the Pb-Ag mixture. In alloys containing Au Cu must be added until Au : other metals is $< 1 : 3$. H. J. E.

Volumetric [micro-]determination of calcium and magnesium in water.—See B., 1935, 48.

Application of photo-elements to the determination of salts in natural waters.—See B., 1935, 48.

Analysis of limestone.—See B., 1935, 60.

Determination of magnesium as magnesium oxide in presence of ammonium salts.—See B., 1935, 21.

Determination of magnesium using 8-hydroxyquinoline. M. JAVILLIER and J. LAVOLLAY (Bull. Soc. Chim. biol., 1934, 16, 1531—1541).—The technique of a method for the determination of Mg by pptn. at p_H 8 of the complex (I) which it forms with 8-hydroxyquinoline (II) is described. Ca may be removed by preliminary pptn. as oxalate, and Fe, Al, Mn, Zn, and Cu, when present in small quantity, may be separated by extraction of (I) with EtOH. Interference of Fe and Al in larger amounts may be avoided by a preliminary pptn. with (II) at p_H 5—6. A. L.

Precipitation of zinc salts by alkali metal chromates in a gelatin medium. Discrimination of zinc and cadmium. (MLLE.) S. VEIL (Bull. Soc. chim., 1934, [v], 1, 1358—1359).—Zn forms a banded ppt. of chromate in gelatin, whilst Cd does not. F. L. U.

Electrolytic determination of cadmium. J. ŠEBOR (Chem. Listy, 1934, 28, 290—291, 297—299).—The well-stirred solution (400 r.p.m.), containing 12 g. of $K_2C_2O_4$, 3 g. of NaOAc, and 3 c.c. of 20% AcOH per 120 c.c., is electrolysed at 70—80°, using 0.1—0.2 amp. and \approx 2.9 volts, when all the Cd is deposited as an adherent, cryst. deposit after 0.5—1 hr. In presence of Zn a current of 0.1 amp. at 2 volts is recommended. R. T.

Fluorescence analysis of minerals. H. HABERLANDT (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 11—13; Chem. Zentr., 1934, ii, 1496).—Certain yellow specimens of topaz show a yellow fluorescence, whilst others, initially colourless, become yellow and fluoresce after irradiation with Ra. Certain scheelite and zircon specimens after heating show fluorescence lines of the rare earths. Some skapolites gave the fluorescence spectrum of U compounds. H. J. E.

Sensitive drop reaction for copper. A. S. KOMAROVSKI and N. S. POLUEKTOV (J. Appl. Chem. Russ., 1934, 7, 844—846).—A drop of saturated solution of hydroxyquinoline (I) in 80% AcOH, a drop of the solution under analysis, and a second drop of (I) are placed on the same spot on filter-paper, followed by a drop of 25% aq. KCN, when a bluish-red coloration indicates $\approx 0.4 \times 10^{-6}$ g. of Cu^{II} . The coloration is due to C_2N_2 , formed from Cu^{II} and CN^+ . Hg^{II} , Pb, Bi, Cd, Sb^{III}, Sn^{II}, MnO_4^- , WO_4^{2-} , VO_3^- , Ni^{II} , and Co^{II} do not interfere. Fe^{II} gives a black spot under the above conditions, and should previously be pptd. as $Fe(OH)_3$. R. T.

Determination of copper in copper sulphate.—See B., 1935, 60.

Detection and determination of copper in pharmaceutical preparations.—See B., 1935, 45.

Determination of copper in organic compounds. N. N. MELNIKOV (Z. anal. Chem., 1934, 99, 182—184).—The compound is completely oxidised by adding $KMnO_4$ to its H_2SO_4 solution at 70—90°. Excess of $KMnO_4$ is removed with H_2O_2 or $H_2C_2O_4$, and Cu determined iodometrically. J. S. A.

Potassium stannochloride in the volumetric determination of copper. E. VOYATZAKIS (Bull.

Soc. chim., 1934, [v], 1, 1356—1357).—A weighed excess of solid K_2SnCl_4 is added to the solution of Cu^{II} deprived of dissolved O_2 and strongly acidified with HCl. $CuCl$ is pptd., and the residual K_2SnCl_4 is titrated with I. F. L. U.

(A) **Determination of mercury applicable to mercury cyanide.** (B) **Application of the mercuric sulphate reagent.** G. DENIGES (Bull. Soc. Pharm. Bordeaux, 1934, 72, 5—13, 13—18; Chem. Zentr., 1934, ii, 1499).—A. To 20 c.c. of the solution (\approx 0.3% Hg^{II}) 20 drops of the $HgI_2, 2KI$ reagent (cf. A., 1932, 355) and 10 drops of HCl are added. HgI_2 is pptd. and is titrated with 0.1N- $Na_2S_2O_3$ at 20° until just redissolved. Non-ionised $Hg(CN)_2$ reacts quantitatively on adding the HCl, and may be determined in presence of Hg^{II} .

B. The reagent (5 g. of red HgO in a mixture of 100 c.c. of H_2O and 20 c.c. of conc. H_2SO_4) can be used for the microchemical detection of halides, halogenates, and cyanuric acid by adding an equal vol. of aq. NH_3 to the reagent instead of using a conc. acid solution. H. J. E.

Determination of aluminium in aqueous aluminium acetate. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1934, 2, 64—68).—5 g. of solution are heated at 100° with 4 c.c. of conc. HCl and 20 c.c. of an aq. suspension of filter-paper pulp, 5—6 drops of 30% H_2O_2 and excess of aq. NH_3 are added, and the suspension is filtered after 1 hr. The residue is washed, dried, ignited, and weighed as Al_2O_3 . R. T.

Titrimetric determination of aluminium sulphate and sulphuric acid present together. G. BURSTEIN and J. KRONMAN (Przemysł Chem., 1934, 18, 317—321).—A series of colour standards matching the colours given by thymol-blue with a scale of concns. of $Al_2(SO_4)_3$ (I) is prepared by mixing 0.5N- $CoCl_2$ and $-FeCl_3$ in various proportions. The solution, the (I) content of which is approx. known, is titrated with 0.27N- $Ba(OH)_2$ to the same shade as the appropriate standard, and the H_2SO_4 content hence calc. The solution is further titrated with 0.5N- $NaOH$ at 100° to a colour change from yellow to blue, and the (I) content hence calc. R. T.

Determination of small quantities of aluminium in complex media. Application to plants. P. MEUNIER (Compt. rend., 1934, 199, 1250—1252).—Conditions for pptn. and colloidal ppt. formation for Al with cupferron (I) (cf. Pinkus and Martin, A., 1927, 406) have been studied. Opacity measurements are described for the determination of 0.01—0.06 mg. of Al per g. of dried plant. The elimination of other metals (e.g., Fe, Cu, or Ti) by pptn. with (I) at controlled p_H is described. H. J. E.

Rapid determination of aluminium in iron ores.—See B., 1935, 63.

Determination of small quantities of aluminium in special iron-containing copper-zinc alloys.—See B., 1935, 64.

Behaviour of aqueous ammonium sulphide towards manganous ions. D. TOTOIIESCU (Z. anorg. Chem., 1934, 221, 182—186).—Aged solutions of $(NH_4)_2S$ often give no ppt. with Mn^{II} in presence of

NH₄ salts or of KCN. The cause is traced to the gradual disappearance of SH' through oxidation.

F. L. U.

Benzoate method for the separation of iron, aluminium, and chromium. Suggested changes for its application to qualitative analysis. L. LEHRMAN and J. KRAMER (J. Amer. Chem. Soc., 1934, 56, 2648—2649).—Modified procedure is recommended (cf. A., 1934, 621).

E. S. H.

Precipitation of aluminium with 8-hydroxyquinoline in presence of iron, nickel, cobalt, copper, chromium, and molybdenum. T. HECZKO (Chem.-Ztg., 1934, 58, 1032—1033).—The alloy is dissolved, tartaric acid and excess of NH₃ are added, and the metals other than Al are converted by adding KCN into complexes from which they are not pptd. by 8-hydroxyquinoline (I). If Fe is present H₂S is also passed. Al is pptd. by adding a solution of (I) in 10% EtOH.

E. S. H.

Application of flotation to qualitative analysis. A. M. BELOUSOV and A. G. BELOUSOVA (J. Appl. Chem. Russ., 1934, 7, 837—838).—The ppt. of Ni dimethylglyoxime is masked by Fe(OH)₂ when Fe^{II} is present; it may be separated by shaking with iso-C₆H₁₁·OH (I), when it undergoes concn. at the H₂O—(I) interface. The mixture of Al(OH)₃ and FeS obtained by adding (NH₄)₂S to aq. salts of Al and Fe is separated by adding alizarin-red (II) and (I), and shaking, when the Al(OH)₃—(II) complex is suspended in the (I) layer. PbS, Sb₂S₃, and As₂S₃ can be separated from S by shaking the suspension with (I), when S remains in the aq. layer.

R. T.

Titration of oximes of nickel and copper. B. TOUGARINOFF (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 314—324).—Ni dimethylglyoxime (I) is pptd. in the usual way, and is then hydrolysed by boiling with dil. H₂SO₄. The NH₂OH liberated is determined by addition of excess of acidified Fe₂(SO₄)₃ and titration of the FeSO₄ formed by 0.1N-KMnO₄. The method is applicable to the determination of Ni in alloys, e.g., German silver, Ni steel, and coinage metal, if (I) is pptd. in presence of tartaric acid. For the determination of Cu, the compound with salicylaldoxime is pptd. and determined in a similar way. The method is directly applicable to Cu alloys.

A. J. M.

Separation of nickel and cobalt by means of alkali phosphates. A. COLANI (Bull. Soc. chim., 1934, [v], 1, 1478—1479; cf. A., 1934, 747).—Polemic and historical. Other methods are more trustworthy.

J. G. A. G.

[Separation of nickel and cobalt by means of alkali phosphates.] H. WUNSCHENDORFF and (MME.) P. VALIER (Bull. Soc. chim., 1934, [v], 1, 1480). A reply (cf. preceding abstract).

J. G. A. G.

Determination of tervalent chromium in chromic acid and in chromium-plating baths. H. WILLARD and P. YOUNG (Trans. Electrochem. Soc., 1935, 67, 55—64).—Cr^{III} in Cr-plating baths in presence of H₂CrO₄ may be determined by adding HNO₃ and excess of 0.1N-Ce(SO₄)₂, heating at 50—55° for 5 min., and titrating with 0.05N-NaNO₂ at 50—55°, the end-point being determined potentiometrically. The Pt electrode must be cleaned in K₂Cr₂O₇—H₂SO₄ to

obtain a sharp end-point, with which Fe and Mn at moderate concns. do not interfere. A similar method is applicable for the determination of Cr₂O₃ in H₂CrO₄.

R. S. B.

Determination of chromium in tungsten steels.—See B., 1935, 63.

Potentiometric determination of chromium, vanadium, and molybdenum present together.—See B., 1935, 63.

Volumetric determination of chromium, manganese, and vanadium in steel.—See B., 1935, 64.

Weighing of molybdenum as silver molybdate. L. W. MCCAY (J. Amer. Chem. Soc., 1934, 56, 2548—2549).—Mo in alkali molybdates can be determined by conversion into Ag₂MoO₄, which is slightly sol. in H₂O, but insol. in H₂O containing AgNO₃.

E. S. H.

Determination of small quantities of vanadium in uranium preparations.—See B., 1935, 60.

Laboratory apparatus for conducting pyrogenesis. J. DOLIŃSKI (Przemysł Chem., 1934, 18, 366).—SiO₂ apparatus is described.

R. T.

Calorimetric apparatus. K. KLING and J. PFANHAUSER (Przemysł Chem., 1934, 18, 420—424).—The calorimeter bomb is enclosed within a Dewar flask (I), and the heat of combustion is calc. from the expansion of the air within the (I). The method involves an error of 50—100 g.-cal., but is suitable for most technical purposes.

R. T.

Autographic thermal expansion apparatus. W. SOUDER, P. HIDNERT, and J. F. FOX (J. Res. Nat. Bur. Stand., 1934, 13, 497—513).—A description is given of an autographic expansion apparatus utilising the optical lever method of recording continuous expansion curves photographically. The results obtained with the apparatus for low-, medium-, and high-expanding materials are compared with those obtained with the previous apparatus of the Bureau of Standards; for steels the error is 6% between 20° and 100° and 3% between 20° and 500°.

A. R. P.

Magnetic method of producing low temperatures. P. DEBYE (Physikal. Z., 1934, 35, 923—928).—A summary of the results of the method using adiabatic demagnetisation of rare-earth salts and Cr alum is given. Consideration of entropy-temp. diagrams shows that 0° abs. is not attainable by this method. Since the nuclear moment is about 10⁻³ × the Bohr magneton, the former will be of great importance in the range 0.001—0.01° abs., and hence direct results on nuclear magnetism may be expected from observations within this range.

A. J. M.

Simple and inexpensive thermoregulator. A. RAIGNIER (Natuurwetensch. Tijds., 1934, 16, 267—268).—The expansion of Et₂O in a closed metal vessel operates a lever controlling a Hg break. An accuracy of ±1° may be obtained.

D. R. D.

Automatic temperature control of thermostats, ovens, etc. by means of an alternating-current valve relay. A. L. DELAUNOIS (Natuurwetensch. Tijds., 1934, 16, 268—270).—A modification of Fonteyne's d.-c. apparatus (A., 1934, 162) is described.

D. R. D.

Determination of the heat of combustion by means of the micro-bomb. J. J. VRIJLING (Chem. Weekblad, 1935, 32, 20—22).—The method is described and data for BzOH and various fuel and lubricating oils, agreeing well with macro-determinations, are recorded.
D. R. D.

Investigation of photographic-photochemical processes with the aid of the electro-optical Kerr effect. A. NARATH (Physikal. Z., 1934, 35, 992—996).—A method for the determination of the intensity and wave-length of actinic light using the electro-optical Kerr effect is described.
A. J. M.

Combined recording microphotometer, densitometer, and comparator. P. A. LEIGHTON, S. SMITH, and F. C. HENSON (Rev. Sci. Instr., 1934, [ii], 5, 431—434).—Full constructional details of an instrument incorporating a radiometer are given.
C. W. G.

Self-registering microphotometer. L. A. WOODWARD and R. G. HORNER (J. Sci. Instr., 1935, 12, 17—22).—The photometer unit moves bodily across a magnified image of the plate under examination, moving uniformly and without vibration under gravity controlled by an oil leak.
C. W. G.

Photometric stage for the study of emission spectra. R. BRECKPOT (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 299—314).—An apparatus in which the spectrum is projected on to a horizontal screen, in the centre of which is an opening over a photo-electric cell, is described.
A. J. M.

Ultra-violet microscope for the examination of opaque objects. B. K. JOHNSON (J. Sci. Instr., 1934, 11, 384—394).—A new form of reflecting microscope utilises a lens-mirror objective in place of an object glass. Opaque objects can be examined without introducing back-reflected light from the lens system. Ultra-violet transmissions and reflecting powers for several substances are recorded.
C. W. G.

Johann's X-ray spectrometer for high vacuum with concave crystal. II. A. SANDSTROM (Z. Physik, 1934, 92, 622—630; cf. A., 1933, 1036).
A. B. D. C.

Source of the Lyman continuum for use with spectrographs of high dispersion. G. COLLINS and W. C. PRICE (Rev. Sci. Instr., 1934, [ii], 5, 423—425).—A Lyman discharge tube is so made that the capillary can easily be replaced when enlarged by use.
C. W. G.

Photo-electric densitometer. E. OBERMER (Chem. and Ind., 1934, 1077).—Colorimetric biochemical analyses of blood, urine, faeces, and food are mentioned.
C. W. G.

Electrical characteristics of barrier-layer photo-cells. P. R. GLEASON (Physical Rev., 1933, [ii], 44, 315).—The resistance of barrier-layer photo-cells has been determined over a wide range of illumination and for currents in the same directions as and opposite to the photo-currents.
L. S. T.

Use of selenium unidirectional layer photo-cells in the measurement and record of very intense illuminations. G. LIANDRAT (Compt. rend., 1934, 199, 1394—1395; cf. A., 1934, 272,

716).—The effect of variation of sensitivity of these cells should be diminished by reducing the thickness of the Se layer and reducing the effect of the external surface of the layer.
J. W. S.

Monochromatic filter. W. H. AUGHEY and W. D. LANSING (Physical Rev., 1933, [ii], 44, 326).—Photographic plates treated with a NaOH solution of β -methylasculetin transmit only λ 4358 Å. from a Hg arc. This filter is only a photographic, and not a visual, monochromat.
L. S. T.

Precision photometry. P. COPEL (J. Phys. Radium, 1934, [vii], 5, 563—567).—Considerations on measurements with an accuracy of 1 mm. are discussed.
N. M. B.

Microphotography and radiation studies with various wave-lengths of monochromatic ultra-violet radiation. A. J. ALLEN, R. FRANKLIN, and E. McDONALD (J. Franklin Inst., 1934, 218, 701—716).—A detailed account of work already noted (this vol., 124).
L. S. T.

Temperature control system for use in the study of the Raman effect of liquids. A. H. LECKIE and W. R. ANGUS (J. Sci. Instr., 1935, 12, 22—23).—Heated H₂O from the jacket circulates by convection through a bath kept at a controlled temp.
C. W. G.

Cuprous oxide rectifiers. W. C. VAN GEEL (Physica, 1934, 1, 1143—1152; cf. Z. Physik, 1931, 69, 765).—Current-voltage characteristics are recorded between 20° and 134°. The mechanism of rectification is discussed.
H. J. E.

Temperature-control box for saturated standard cells. E. F. MUELLER and H. F. STIMSON (J. Res. Nat. Bur. Stand., 1934, 13, 699—704).—The cells are contained in a small Al box, placed inside and thermally insulated from a larger Al box, in the wall of which is a Hg thermoregulator controlling an electrical heater. The temp. was const. to $\pm 0.01^\circ$.
H. J. E.

Life tests of commercial type standard cells. T. T. SMITH (Rev. Sci. Instr., 1934, [ii], 5, 425—427).—No definite time coeff. can be applied. Measurements with a single cell should not be trusted for accurate work.
C. W. G.

Field combinations for velocity- and mass-spectrography. III. W. HENNEBERG (Ann. Physik, 1934, [v], 21, 390—404; cf. A., 1934, 341, 713).—The use of a superposition of a cylindrical electric field, a homogeneous magnetic field, and a magnetic dipole field as a focussing lens for electrons and positive rays is described. By a special arrangement, a non-focussing "prism" may be produced.
A. J. M.

Cataphoresis apparatus. H. THEORELL (Biochem. Z., 1934, 275, 1—10).—A description is given of an apparatus which may be used for accurate determination of ionic mobilities, for the separation of the constituents (I) of mixtures [including those in which (I) move in the same direction], and for other purposes.
W. McC.

Precision recording cosmic-ray meter. A. H. COMPTON, E. O. WOLLAN, and R. D. BENNETT (Rev. Sci. Instr., 1934, [ii], 5, 415—422).—The steel ionis-

ation chamber holds 19.3 litres of A at 50 atm. Balancing current is supplied by ionisation by β -rays from U in an auxiliary chamber. C. W. G.

Amplifying and recording small e.m.f. H. E. MORGAN, L. T. DE VORE, and R. F. BAKER (Physical Rev., 1933, [ii], 44, 324).—The p.d. to be measured is applied to a sensitive galvanometer which causes a beam of light to play across the cathode of a photo-electric cell. L. S. T.

Increased resolving power of the electron-optical immersion objective. E. BRÜCHE and W. KNECHT (Z. Physik, 1934, 92, 462–466).—The electron microscope together with an oil-immersion objective can resolve to 1.5μ . A. B. D. C.

Camera for electron diffraction. J. A. DARBYSHIRE and E. R. COOPER (J. Sci. Instr., 1935, 12, 10–14).—The instrument is suitable for both reflexion and transmission. C. W. G.

Portable Geiger-Müller tube. K. GRANT and M. ILIFFE (J. Sci. Instr., 1935, 12, 6–8).—Full constructional details are given. 1 mg. of Ra can be detected at 50 ft. C. W. G.

Quinhydrone micro-electrode. F. L. VODRET (Rend. Sem. Fac. Sci. Cagliari, 1933, 3, 55–60; Chem. Zentr., 1934, ii, 1165).—A Pt wire fused into a capillary is mounted in an open glass tube constricted at the lower end. The use of the electrode is described. H. J. E.

Apparatus for uninterrupted p_H determination. M. M. MUSCHKATBLAT and I. M. BRUSKIN (J. Appl. Chem. Russ., 1934, 7, 857–863).—Apparatus for the measurement of continually changing p_H (e.g., dissolution of ZnO in aq. H_2SO_4) is described. R. T.

Simple micro-burette. R. FLATT (Helv. Chim. Acta, 1934, 17, 1513–1516).—The burette consists of a U-tube in which one limb (a) is of wide bore, and the other of about 1 mm. bore bent over at the top and drawn to a fine point. There is no tap, the titration liquid being confined between the delivery point and a surface of Hg. Liquid is expelled by admitting Hg to (a) from a dropping funnel. The vol. can be measured to within 0.2 cu. mm. F. L. U.

Apparatus for continuous extraction of aqueous solutions by non-miscible solvents. A. A. POLICARD and R. FAVIER (Bull. Soc. chim., 1934, [v], 1, 1523–1525).—The rod of a stirrer (I) situated axially in the flask (II) is surrounded by a tube down which flows the solvent (III) from a condenser fed by solvent vapour from an auxiliary flask (IV). The (III) flowing into the aq. solution just above the vanes of (I) is broken into fine droplets which rise and flow back to (IV) by way of a side tube in the neck of (II). J. G. A. G.

Microbalance to weigh to 10^{-6} g. M. ZIEGLER-WELLMANN (Chem. Fabr., 1934, 7, 472–473).—A direct-reading null instrument on the torsion principle using spiral hairsprings is described. D. R. D.

Soldering molybdenum to copper. A. MÜLLER and R. E. CLAY (J. Sci. Instr., 1934, 11, 405).—A small chip of Ag is placed on a layer of $NaNO_2$

lying on the Mo. On heating until the Mo and the $NaNO_2$ react, heat is evolved sufficient to melt the Ag, which flows over the surface of the Mo, to which hard and soft solder will then adhere. C. W. G.

Device for water circulation. A. B. BURCH and R. M. EAKIN (Science, 1934, 80, 563–564).—A simple air pump maintaining a continuous circulation of clean aerated H_2O is described. L. S. T.

Determination of the specific gravities of liquids. E. A. BECKER (Farben-Ztg., 1934, 39, 1311–1313).—The vol. of liquid delivered by one complete stroke of certain medicinal syringes is sufficiently reproducible to enable them to replace a pycnometer. It is much easier to avoid air bubbles in this way. G. H. C.

Recording dilatometer of high sensitivity. A. GOETZ, J. W. BUCHTA, and T. L. HO (Rev. Sci. Instr., 1934, [ii], 5, 428–431).—Expansion is amplified by an optical lever and thermocouple, actuating a galvanometer. C. W. G.

Visco-conductimeter. C. L. BABCOCK and J. V. HOFFACKER (Physical Rev., 1933, [ii], 44, 320–321).—The apparatus is suitable for determining of ordinary liquids at room temp. and of silicate glass up to 1400° . L. S. T.

Separation of neon into its isotopic components by means of rectification. W. H. KEESOM, H. VAN DIJK, and J. HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 615, and Physica, 1934, 1, 1109–1114).—A glass rectifying apparatus for the separation of the Ne isotopes in relatively large quantities has been constructed. Fractions of at. wt. 20.091 and 20.574 (normal at. wt. 20.183) have been obtained. The efficiency of the rectifying column is about 50% of theoretical. M. S. B.

New glass apparatus. I. Siphon with attached filter. II. Filter reagent glass. H. BARSCH (Pharm. Zentr., 1935, 76, 20–21, 21).—I. A sintered glass filter forms the siphon inlet. II. A sintered glass filter crucible with a curved rim fits into a rubber ring placed in the top of a filtering tube. E. H. S.

High-vacuum cut-off. G. W. LOBB and J. BELL (J. Sci. Instr., 1935, 12, 14–17).—Na-Bi and Li-Bi amalgams at temp. just $>$ m.p. are suitable for use in cut-off seals; they have Hg v.p. about 10^{-6} mm. C. W. G.

Two demonstration experiments with liquid hydrogen. K. CLUSIUS (Physikal. Z., 1934, 35, 929–930).—An apparatus using liquid and solid H, by means of which a temp. of 9.5° abs. may be reached, and its use for the demonstration of superconductivity in Nb carbide (transition point 10.2° abs.) is described. An apparatus for demonstrating the differences in v.p. and m.p. of H_2^1 and H_2^2 is also described. A. J. M.

Symbol for hydrogen-ion concentration. T. HENNIG (Chem.-Ztg., 1934, 58, 1021).—A question of nomenclature. E. S. H.

Heavy water in chemistry. M. POLANYI (Nature, 1935, 135, 19–26).—A lecture. L. S. T.

Geochemistry.

Analysis of the water of the Boniface spring at Morszyn. S. JURKOWSKI (Arch. Chem. Farm., 1934, 2, 41—61).—The rise in concn. of salts per kg. of H_2O since 1881 is: K 5.7 to 23.9, Na 14.25 to 64.2, Mg 3.8 to 22.9, Cl 17.8 to 131.7, Br 0.004 to 0.075, and SO_4 28 to 75.8 g. R. T.

Fluorine content of French mineral waters. R. CHARONNAT and (Mlle.) S. ROCHE (Compt. rend., 1934, 199, 1325—1328).—Numerous determinations based on de Boer's colorimetric method (A., 1926, 40) are recorded. H. J. E.

Anohaline stratification of the chemical constituents of Lake Osoresanko, Aomori Prefecture, Japan. S. YOSHIMURA (Proc. Imp. Acad. Tokyo, 1934, 10, 475—478).—Temp. and salinity of this acid lake both decrease towards the bottom. C. W. G.

New sulphur constituent of the thermal waters of Pistany (Czechoslovakia). E. CHERBULIEZ and A. HERZENSTEIN (Helv. Chim. Acta, 1934, 17, 1587—1592; cf. this vol., 184).—A residual I-reducing effect observed in these waters after allowing for the H_2S present, not due to $H_2S_2O_3$, is ascribed to an unstable S acid. The chemical behaviour of the substance, which has not been isolated, resembles that of $Na_2S_2O_4$. F. L. U.

Radium in field waters and petroleum of Bibi-Eibat oil-field. B. A. NIKITIN and M. S. MERKULOVA (Trav. inst. état radium, U.S.S.R., 1933, 2, 160—176).—The Ra content was variable, but decreased with depth. The U and Ra contents were not interdependent. The Ra in H_2O is due only to the leaching of minerals. CH. ABS. (e)

Origin of radium in oil-field waters. L. V. KOMLEV (Trav. inst. état radium, U.S.S.R., 1933, 2, 207—223).—Leaching of solid rocks (granodiorite) with distilled H_2O removes about 15% of Ra at slightly elevated temp. and with long contact. Aq. $BaCl_2$ extracts Ra rapidly at room temp. The Ra, Ms-Th, and Th-X in field H_2O arise from the leaching of rocks. CH. ABS. (e)

Radioactivity of waters from the oil-fields of Dagestan, Kuban, and Azerbaidjan. L. V. KOMLEV, P. MYATELKIN, and V. SAVCHENKO (Trav. inst. état radium, U.S.S.R., 1933, 2, 176—207).—Data are recorded. The Rn in the natural gas was > that required by the equilibrium conditions. CH. ABS. (e)

Thorium-X content of water from well No. 1 in Ukhta oil-field. P. L. BOBIN (Trav. inst. état radium, U.S.S.R., 1933, 2, 157—159).—Average contents of Ra and Th-X were 7.58×10^{-9} and 2.86×10^{-2} g. per litre, respectively. CH. ABS. (e)

Sorption by snow. Y. KAUKO and V. MANTERE (Suomen Kem., 1934, 7, B, 97—98).—Snow has considerable adsorptive power for CO_2 . A. G. P.

Occurrence of lithium on the earth. F. HERMANN (Metallbörse, 1934, 24, 535; Chem. Zentr., 1934, ii, 1433).—The mean Li content of the earth's crust is $4 \times 10^{-5}\%$. The occurrence is discussed. H. J. E.

Radioactivity of the geological layers of the Rhine valley. E. ROTHE and F. STOECKEL (Compt. rend., 1934, 199, 1330—1332).—Data are recorded. H. J. E.

New mineral containing metals of the platinum group. O. E. ZVJAGINZEV (Compt. rend. Acad. Sci., U.R.S.S., 1934, 4, 176—179).—"Aurosmirid," a solid solution of Au, Os, and Ru in Ir, has been isolated in the residue remaining after dissolving Pt in aqua regia. The substance is very hard and brittle, and has a cubic lattice. E. S. H.

Molybdenite-quartz veins of Shih-ping-chuan, Tsingtien, Chekiang. H. M. MENG and K. CHANG (Contr. Nat. Res. Inst. Geol., Sinica, 1933, No. 4, 47—58).—Porphyry, lamprophyric apophyses, and veins are described, and the paragenesis and genesis of the latter discussed. CH. ABS. (e)

Ores in middle East Bothnia and the Skellefte area. M. SAKSELA (Suomen Kem., 1934, 7, A, 129—132).—Ores described are principally Fe, Cu, and As pyrites, Pb glance, and Zn blende. Considerable proportions of Au ore occur in some areas. A. G. P.

Zinc-lead lode at Rosebery, Tasmania. F. L. STILLWELL (Proc. Austral. Inst. Min. Met., 1934, No. 94, 43—67).—A description is given of the mode of occurrence and characteristics of the following minerals of the lode: Zn blende, galena, pyrite, chalcopyrite, mispickel, tetrahedrite, bournonite, and native Au. The gangue contains quartz, spessartite, rhodochrosite, sericite, chlorite, barytes, and ilmenite. A. R. P.

Petrography of Sardinia. Characteristic kersantitic vein with prasinitic "facies" from Sarrabus. II. A. CAVINATO (Atti R. Accad. Lincei, 1934, [vi], 20, 205—209).—The mineral (chloritic prasinite, ovoidite; SiO_2 53.90, TiO_2 1.06, Al_2O_3 10.21, Fe_2O_3 9.00, FeO 7.76, CaO 1.59, MgO 7.18, K_2O 1.00, Na_2O 4.40, H_2O 4.90, total 101.00%) is described. O. J. W.

Mindigite, a new [copper] cobalt hydroxide. L. DE LEENHEER (Natuurwetensch. Tijds., 1934, 16, 237—241).—This mineral, found in the Belgian Congo, $9Co_2O_3 \cdot 2CuO \cdot 16H_2O$, d 3.07, hardness 2.5, colour dark brown, is non-magnetic. Its apparently amorphous character is confirmed by X-ray powder diagrams. Curves are given for the loss of H_2O on heating at different temp. At high temp. it loses O_2 , forming Co_3O_4 and CoO . Its optical properties are given. D. R. D.

Composition of titaniferous silicates, especially astrophyllite. B. GOSSNER and E. REINDL (Zentr. Mineral., 1934, A, 161—167; Chem. Zentr., 1934, ii, 747).—Astrophyllite, $\{[Si_2O_7]_2[(Ti,Zr)(OH,F)_2](Fe,Mn)_4(K,Na)_2\}$, is rhombic (a 11.70, b 5.40, c 21.10 Å; 4 mols. in unit cell). H. J. E.

Hornblende synthesis at low pressures. K. H. SCHEUMANN and W. LUDKE (Ber. Verh. sachs. Akad. Wiss. Leipzig, math.-phys. Kl., 1933, 85, 273—278; Chem. Zentr., 1934, ii, 747).—Tremolites identical with the natural products have been prepared by

heating at 900° a mixture of silicofluorides and H carbonates pressed into pastilles with SiO₂ gel.

H. J. E.

Product of [radioactive] transformation of potassium. G. VON HEVESY and W. DULLENKOPF (*Z. anorg. Chem.*, 1934, **221**, 167—172).—The extraction of Ca from a very old Norwegian biotite is described, and explanations are proposed to account for the apparent identity of the specimen so obtained with ordinary Ca (cf. A., 1934, 825).

F. L. U.

Composition and age of crystalline uraninite from Katanga. C. S. HITCHEN and R. VAN AUBEL (*Compt. rend.*, 1934, **199**, 1133—1135).—Spectrographic analytical data are recorded and discussed.

H. J. E.

Exhalation of radon from the soil. P. R. ZUPANCIC (*Terrestr. Mag. and Atm. Elec.*, 1934, **39**, 33—46).—The method of collection and measurement is described. The average amount of Rn exhaled was 23×10^{-18} curie per sq. cm. per sec. The amount increases with rise of soil temp.

CH. ABS. (e)

Iodine contents of the soils in Japan. A. ITANO and Y. TUJI (*Proc. Imp. Acad. Tokyo*, 1934, **10**, 524—527).—The I content of 120 samples of Japanese soils is between 0.49 and 56.53 p.p.m., average 7.41. I contents decrease in the order clay, loam, sand, sandy loam. The higher is the p_H the greater is the I content.

C. W. G.

Italian volcanic soils. L. RIGOTARD (*Ann. Agron.*, 1934, **4**, 770—780).—The composition of deposits of varying age is examined.

A. G. P.

Soils of the lower Charente. Relations between pedology and local designations. H.

VERDIÉ, G. SILORET, and J. F. DE FERRIÈRE (*Ann. Agron.*, 1934, **4**, 732—769).—The formation, analysis, classification, and practical usage of these soils are discussed.

A. G. P.

Soil formation on the coloured clays of Trans-ural. L. N. ALEXANDROVA (*Trans. Dokuchaiev Soil Inst.*, 1934, **10**, No. 3, 23—46).—The clays were formed by the sialitic weathering of massive crystalline rocks during the Tertiary period. The content of bases is low, whilst that of R₂O₃ is high. The HCl-sol. fraction is small in comparison with that of laterites. The present soils are of the podsol type, but are thin and with no great humus accumulation.

A. M.

[Origin of] natural oil. J. M. MACFARLANE (*Science*, 1934, **80**, 478—479).—Polemical (cf. A., 1934, 1198).

L. S. T.

Petrographical investigation of lignite, petroleum, etc. R. POTONIE (*Braunkohle*, 1934, **33**, 209—212; *Chem. Zentr.*, 1934, ii, 1060—1061).—A discussion.

H. J. E.

Radioactivity and the age of meteorites. R. D. EVANS (*Physical Rev.*, 1933, [ii], **44**, 131).

L. S. T.

Relative abundance of the oxygen isotopes O¹⁶:O¹⁸ in stone meteorites. S. H. MANTAN, H. C. UREY, and W. BLEAKNEY (*J. Amer. Chem. Soc.*, 1934, **56**, 2601—2609).—Methods for converting the O of silicate rocks and stone meteorites into CO, by heating with CCl₄ at 1000°, thence by reduction with H₂ to H₂O and by electrolysis to O₂, have been devised. The ratio O¹⁶:O¹⁸ is the same, within the experimental error $\pm 2.5\%$, in the terrestrial and extra-terrestrial specimens.

E. S. H.

Organic Chemistry.

Electron diffraction and its application to the study of organic compounds. J. J. TRILLAT (*Kolloid-Z.*, 1934, **69**, 378—388).—A review of published work, especially on paraffins, fatty acids, cellulose and its derivatives, and caoutchouc.

E. S. H.

Isomerism. I. F. P. A. TELLEGEN (*Chem. Weekblad*, 1935, **32**, 3—5).—A discourse on the three types of isomerism.

S. C.

Catalysis in preparative organic chemistry. K. YOSHIKAWA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **25**, 235—301).—A detailed report on experiments described previously (cf. A., 1931, 693; 1932, 918; 1934, 1102, 1206).

J. W. S.

Thermal decomposition of organic compounds from the viewpoint of free radicals. XII. Decomposition of methane. F. O. RICE and M. D. DOOLEY (*J. Amer. Chem. Soc.*, 1934, **56**, 2747—2749).—The gases formed during thermal decomp. of CH₄ in quartz at low pressures (cf. A., 1932, 1108) are passed over a Te mirror; Te₂Me₂ (but no TeCH₃) is thus obtained, showing the production of Me and the absence of CH₂ (cf. Kassel, A., 1932, 1209). The activation energy of the dissociation into free radicals

is determined (method: A., 1934, 276) to be 100 ± 6 kg.-cal. The first step in the decomp. is probably CH₄ → Me + H; the H then combines on the walls of the vessel or reacts thus: CH₄ + H → Me + H₂.

H. B.

[Preparation of ethylene.] V. N. IPATIEV (*Ber.*, 1934, **67**, [B], 2018; cf. A., 1934, 864).—A reply to Sakmin (*ibid.*, 508, 1198).

H. W.

Combustible liquid obtained from ethylene. K. SMOLEŃSKI and S. KOWALEWSKI (*Bull. Acad. Polonaise*, 1934, **A**, 315—328).—The polymerisation of C₂H₄ was studied by slowly heating it at initial pressures, *P*, of 34, 51, and 90 atm. The variations of pressure with temp. showed that polymerisation begins at 300—340°, according to *P*. The liquid hydrocarbons (yield, 80—97% according to *P*) obtained contain paraffins, olefines, and aromatic compounds: the relative proportions of light and heavy (lubricating oil) fractions depend on *P*. The yield of liquid product is diminished by heating above 420° when depolymerisation occurs, and by heating the products with H₂, which increases the proportion of paraffins in the product. Al₂O₃ has no appreciable catalytic effect.

H. G. M.

Polymerisation of isobutylene with alumina on silica gel as a catalyst, and addition of hydrogen chloride to the reaction products without catalyst. H. I. WATERMAN, J. J. LEENDERTSE, and A. J. DE KOK (Rec. trav. chim., 1934, 53, 1151—1158).—The products (di-, 2 tri-, tetra-, and penta-merides, separated by fractional distillation) obtained by polymerisation of isobutylene in the vapour phase with a SiO_2 gel- Al_2O_3 catalyst (activated at 350°) at $> 40^\circ$ are similar to those obtained with H_2SO_4 (Tongberg *et al.*, A., 1932, 1109) or floridin (Lebedev *et al.*, A., 1930, 316) as catalysts. They are mono-olefinic, those obtained with AlCl_3 being more cyclic. The $(n^2-1)/d(n^2-2)$ vals. for the low-b.p. fractions are $>$ the theoretical vals. for the olefines, as also are those of the saturated paraffins obtained by their reduction with H_2 -Ni at 190° under pressure. The Br vals. (MacIllhiney) for the polymerides are much $<$ the theoretical C_nH_{2n} vals., and are not considered trustworthy as a measure of unsaturation. This discrepancy is possibly due to elimination of HBr, since the *trans*-isobutylene fraction, completely saturated by addition of dry HCl in C_5H_{12} at -78° , readily loses HCl above 0° . J. W. B.

Isomerisation of *n*-butenes. V. N. IPATIEV, H. PINES, and R. E. SCHAAD (J. Amer. Chem. Soc., 1934, 56, 2696—2698).—When Δ^a -butene (I) is passed through 100% H_3PO_4 , isomerisation to Δ^b -butene (II) occurs to the extent of 4% at 26° , 12% at 78° , 34% at 100° , and 60% at 135° . Passage of (I) or BuOH through a mixture of $\text{Al}(\text{OH})_3$ (1 mol.) and H_3PO_4 (1.6 mols.) in a Pyrex tube at 427° gives a mixture of (I) (20–30%) and (II) (70–80%). When (I) is passed under pressure through diatomaceous earth impregnated with H_3PO_4 at 249° , quant. conversion into (II) occurs (36–94% isomerisation is found at 100 – 200°); the catalyst loses its activity when reaction is continued for a long time at 250 – 325° and then causes 70–80% conversion. A second sample of the catalyst gave (probably) an equilibrium mixture [containing 72–79% of (II)], irrespective of the contact time. The amounts of (II) formed when (I) is passed through 70–72% HClO_4 at 21° , aq. 75% PhSO_3H at 76° , and aq. 75% ZnCl_2 at 100° are 21, 13, and 5%, respectively; AcOH , $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, and $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ at 100° do not cause isomerisation. A mixture of 6.6% of (I) and 6% of *cis*- and 87.4% of *trans*-(II) is obtained when *trans*-(II) is passed through 100% H_3PO_4 at 100° . The various mixtures are analysed by Podbielniak's method (A., 1933, 690).

H. B.

Catalytic dehydration of butyl alcohols. V. KOMAREWSKY, W. JOHNSTONE, and P. YODER (J. Amer. Chem. Soc., 1934, 56, 2705—2707).—Dehydration of BuOH over Al_2O_3 - H_3PO_4 at 250° gives a mixture of 45% of Δ^a -(I) and 55% of Δ^b -(II)-butene; *sec*.-BuOH similarly affords (I) (24.1%) and (II) (75.9%), whilst BuOH gives isobutene (III) as the sole product. (I)–(III) are identified by low-temp. distillation (Podbielniak column); (III) is characterised further by addition of HBr in AcOH and hydrolysis (H_2O) of the resulting mixture of BuBr and BuBr (thus removed as BuOH). Analysis of (I)–(III) as dibromides is inaccurate, since Br_3 - and

Br_1 -derivatives (from butene and HBr evolved during reaction) are also formed. Dehydration of BuOH over pumice- H_3PO_4 at 350 – 400° gives (I) (27.5%) and (II) (72.5%), whilst *sec*.-BuOH affords (I) (47.5%) and (II) (52.5%); the results of King (J.C.S., 1919, 115, 1404) and of Young and Lucas (A., 1930, 888) are incorrect. H. B.

Formation of butadiene and acetylene by the action of the high-frequency discharge on ethylene. A. A. BALANDIN, J. T. EIDUS, and N. G. ZALOGIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 132–135).—In a closed system treatment of C_2H_4 with a high-frequency discharge produces H_2 , saturated hydrocarbons, and a thick oil, mol. wt. about 500. In a circulatory system the product contains butadiene (I) and C_2H_2 . The amount of (I) formed is dependent on the velocity of circulation and on the amount of H_2 added to C_2H_4 . A chain mechanism is proposed. H. N. R.

Effect of peroxides and acids on reduction of olefines in alcohol solution with platinum oxide catalyst. G. THOMSON (J. Amer. Chem. Soc., 1934, 56, 2744–2747).—The time required for 91–95% reduction of $\text{CHMe}\cdot\text{CMe}_2$ (I) by H_2 and an Fe-containing PtO_2 -Pt-black catalyst (II) in EtOH-MeOH (95 : 5) is shortened considerably by addition of 0.001 mol. of Bz_2O_2 or furoyl or succinyl peroxide (III) (which are probably reduced to the corresponding acids), 0.002 mol. of BzOH or furoic or succinic acid, or (best) 2 drops of AcOH or conc. HCl. Using a (II) which effected only 27% addition of H_2 to the freshly distilled (over Na) (I), the % reduction can be increased by preliminary shaking of the (I) with air; a peroxide (IV), which decomposes to COMe_2 and MeCHO (oxidised further to AcOH), is probably formed. (IV) may be reduced to $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{OH}$; addition of pinacol or mannitol has only a small accelerating effect. The reduction of amylene and anethole (cf. Kern *et al.*, A., 1925, i, 625) is similarly accelerated by (III) and AcOH, respectively. A mechanism to explain the offset of the poisoning effect of Fe by small amounts of acids is discussed.

H. B.

Polymerisation of olefines formed by the action of sulphuric acid on methylisopropylcarbinol. G. M. KLINE and N. L. DRAKE (J. Res. Nat. Bur. Stand., 1934, 13, 705–712).— $\text{CHMePr}\cdot\text{OH}$ at 80° with 75% H_2SO_4 yields Δ^b - $\gamma\delta\epsilon\epsilon$ -tetramethylhexene and Δ^b - $\gamma\epsilon\epsilon$ -trimethylheptene. Whitmore's theory of olefine polymerisation (A., 1932, 1016) does not explain this result without postulating a complicated rearrangement. A theory is proposed in which the trimethylethylene behaves as if it were activated to $-\text{CH}_3^+\cdot\text{CMe}\cdot\text{CHMe}$. It is applied to explain the formation of di- and tri-isobutylenes from isobutylene. H. J. E.

Preparation and physical properties of aliphatic acetylenes. F. R. MOREHOUSE and O. MAASS (Canad. J. Res., 1934, 11, 637–643).—The m.p., b.p., d , γ , v.p., and the parachor and other consts. derived from these vals. for pure C_2H_2 , C_2HMe , C_2HET , C_2Me_2 , and C_2HPr (prepared by alkylation of the Na derivatives obtained in liquid NH_3) are tabulated and discussed in relation to the vals. of the similar consts.

in the corresponding C_nH_{2n} and C_nH_{2n+2} series. In general the properties of the C_nH_{2n-2} series differ from those of C_nH_{2n} and C_nH_{2n+2} , due, it is suggested, to the polarity of the triple linking. Symmetry in the mol. decreases unsaturation. J. W. B.

Acetylenes. I. Preparation of Δ^a -heptinene by dehalogenation methods. G. B. BACHMAN and A. J. HILL (J. Amer. Chem. Soc., 1934, 56, 2730—2732).—Me *n*-amyl ketone and PCl_5 in C_6H_6 at $<10^\circ$ and then at room temp. give $\beta\beta$ -dichloroheptane (I), b.p. $77^\circ/25$ mm., and β -chloro- Δ^a -heptene (II), b.p. $71^\circ/75$ mm.; with PCl_3Br_2 in C_6H_6 , Me α -bromo-, b.p. $80^\circ/9$ mm., and $\alpha\alpha$ -dibromo-, b.p. 118 — $120^\circ/9$ mm., -*n*-amyl ketones result. $\alpha\beta$ -Dichloroheptane (III), b.p. 68 — $72^\circ/7$ mm., is best prepared from Δ^a -heptene and SO_2Cl_2 . When (III) and $\alpha\alpha$ -dichloro- (IV) and $\alpha\beta$ -dibromo- (V) -heptanes are passed with N_2 over soda-lime at 420° , Δ^a -heptinene (VI) is obtained (cf. A., 1928, 269) in isolable yields of 3, 23, and 3%, respectively. Dehalogenation of the following with powdered KOH in mineral oil at 250° (cf. Guest, *ibid.*, 988) gives (VI) (isolable yield quoted): (III) 33%; (IV) 40%; (V) 64%; α -chloro- 37%, α -bromo- 88%, and $\alpha\alpha$ -dibromo- (VII) 21%, - Δ^a -heptenes; bromoheptene mixture [obtained by dehalogenation of (V)] 65%. (VI) is not similarly obtained from (I) or (II). (VI) polymerises readily at 300° ; the polymeride cracks at 400° , but does not regenerate (VI). (VI) is not rearranged by soda-lime at 200 — 250° (cf. Guest, *loc. cit.*). $\alpha\alpha$ -Dibromoheptane could not be prepared by Bruylants' method (Ber., 1875, 8, 409), by reduction of (VII), or from (I) and NaBr in MeOH-COMe₂ containing I and KI. H. B.

Identification of alkyl halides. N-Alkyl-*p*-bromobenzenesulphon-*p*-anisidides. H. B. GILLESPIE (J. Amer. Chem. Soc., 1934, 56, 2740—2741).—The following *N*-alkyl derivatives of *p*-bromobenzenesulphon-*p*-anisidide, m.p. 142° (from p - $C_6H_4Br \cdot SO_2Cl$ and p -OMe- $C_6H_4 \cdot NH_2$ in C_5H_5N), are obtained with the appropriate alkyl halide (I) in aq. EtOH-KOH: Me, m.p. 96 — 97° , Et, m.p. 113.5° , Pr ^{α} , m.p. 75° , Pr ^{β} , m.p. 107° , Bu ^{α} , m.p. 74.5° , Bu ^{β} , m.p. 78 — 79° , *n*-, m.p. 88.5° , and iso-, m.p. 52.5° , -amyl, *n*-heptyl, m.p. 56° , allyl, m.p. 82° , benzyl, m.p. 167.5° , β -hydroxyethyl, m.p. 92 — 93° , and β -hydroxypropyl, m.p. 92° . These derivatives are useful for the identification of (I). H. B.

Preparation of higher aliphatic bromides. J. R. RUHOFF, R. E. BURNETT, and E. E. REID (J. Amer. Chem. Soc., 1934, 56, 2784).—The alcohol (I) is saturated with dry HBr [simplified prep. (cf. Baxter and Coffin, A., 1909, ii, 397) described] at about 100° and the crude product washed successively with conc. H_2SO_4 [removes unchanged (I)], dil. MeOH-NH₃, and dil. MeOH. cycloHexyl, *n*-heptyl, and do-, tetra-, and octa-decyl bromides are thus prepared in yields of 73, 88, 89, 89, and 90%, respectively. H. B.

Compounds of magnesium chloride with alcohols and acetic acid.—See this vol., 179.

Pyrogenic transformations of ethyl alcohol. SMOLENSKI and S. KOWALEWSKI (Bull. Acad. Polonaise, 1934, A, 304—314).—EtOH, heated in an

autoclave at various temp. and for various times, affords mainly aliphatic substances. The yield of gaseous products is increased at higher temp. The max. yield of oily liquid products is obtained at 450° with an initial concn. of EtOH of 3.5 g.-mol. per litre. An Al_2O_3 catalyst increases the yield of liquid hydrocarbons, which now consist mainly of aromatic and unsaturated compounds. H. G. M.

Reaction of ethylene oxide with acetylenic Grignard reagents. J. P. DANEHY, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 2790; cf. Faucounau, A., 1934, 1199).— $(CH_2)_2O$ and $CR \cdot C \cdot MgX$ give Δ^y -noninen- α -ol (I), δ -phenyl- Δ^y -butinen- α -ol (II), and Δ^y -octinen- α -ol (III), b.p. $97^\circ/15$ mm. (II) is accompanied by an approx. equal amount of the H_2O -sol. 2-phenyl-4:5-dihydrofuran, b.p. $55^\circ/15$ mm.; similar compounds are formed with (I) and (III). H. B.

Action of *Aspergillus niger* on *n*- $\alpha\beta$ -diols. A. WALTJ (J. Amer. Chem. Soc., 1934, 56, 2723—2726).—*dl*-OH-CHR-CH₂-OH (I) (R=Me, Et, Pr) are converted by *A. niger* (II) under sterile conditions into COR-CH₂-OH (III); the recovered $\alpha\beta$ -diols are optically active (— when R=Me and + when R=Et or Pr) and rotate in the same direction as those obtained by reduction of (III) or OH-CHR-CHO with yeast (A., 1932, 143). Infected (II) under non-sterile conditions also converts (I) (R=Et, Pr) into (III); the recovered diols are, however, levorotatory. Hexane- $\alpha\beta$ -diol, b.p. $100^\circ/5$ mm., from (V) (below) and H_2O at 180° (sealed tube), is unaffected by (II). The following are described: 1-propane- $\alpha\beta$ -diol, m.p. 146° , $[\alpha]_D^{25} +9.3^\circ$ in EtOH, d., m.p. 117 — 118° , $[\alpha]_D^{25} +3.7^\circ$ in EtOH, and l., m.p. 118° , $[\alpha]_D^{25} -0.47^\circ$ in EtOH, -butane- $\alpha\beta$ -diol, and d., m.p. 100 — 101° , $[\alpha]_D^{25} +1.2^\circ$ in EtOH, and l., m.p. 102° , $[\alpha]_D^{25} -2.3^\circ$ in EtOH, -pentane- $\alpha\beta$ -diol di(phenylcarbamates); α -hydroxybutan- β -one-2:4-dinitrophenylhydrazone, m.p. 150° ; α -hydroxypentan- β -one-2:4-dinitrophenylhydrazone, m.p. 165° ; $\alpha\beta$ -oxidopentane (IV), b.p. 91 — 92° , from OH-CHPr-CH₂Cl and warm conc. aq. NaOH; $\alpha\beta$ -oxidohexane (V), b.p. 118 — 120° , from OH-CHBu-CH₂Cl and powdered NaOH or KOH in Et₂O. (IV) and H_2O at 90° (sealed tube) give pentane- $\alpha\beta$ -diol, b.p. 96 — $99^\circ/11$ mm., and a little dihydroxydiethyl ether, b.p. 130 — $132^\circ/7$ mm. (IV) and aq. 30% NHMe₂ at about 0° —room temp. afford α -dimethylaminopentan- β -ol, b.p. 165 — $166^\circ/762$ mm. [methiodide (= β -*n*-propylcholine iodide), m.p. 198°]. α -Bromohexan- β -ol, b.p. 89 — $90^\circ/13$ mm., is obtained from (V) and cold 48% HBr. H. B.

Preparation of ethylene glycol from dichloroethane. A. L. KLEBANSKI and I. M. DOLGOPOLSKI (J. Appl. Chem. Russ., 1934, 7, 790—806).— $(\cdot CH_2 \cdot OH)$, (I) is obtained in 87—90% yield from $C_2H_4Cl_2$ by heating for 20—25 min. with a 5% excess of 15% Na₂CO₃ at 185—190°/100 atm.; CH₂:CHCl, a by-product of the reaction, is best absorbed by xylene from the reaction gases. Using aq. -EtOH HCO₂Na in place of Na₂CO₃ 80% yields of (I) are obtained by heating at 160—170°/18 atm. for 5.5 hr. R. T.

Di-tertiary diols derived from diacetone alcohol (β -hydroxy- β -methylpentan- δ -one). R.

JACQUEMAIN (Compt. rend., 1934, **199**, 1315—1317).—Diacetone alcohol with the appropriate Grignard compound gives $\beta\delta$ -dihydroxy- $\beta\delta$ -dimethyl-hexane, b.p. $98^\circ/5$ mm., -heptane, b.p. 107 — $108^\circ/5$ mm., -octane, b.p. 116 — $117^\circ/5$ mm., -nonane, b.p. 123 — $124^\circ/2$ mm., $\beta\delta$ -dihydroxy- $\beta\delta\epsilon$ -trimethylhexane, b.p. 103 — $106^\circ/2$ mm., - $\beta\delta\zeta$ -trimethylheptane, b.p. 105 — $106.5^\circ/2$ mm., and $\beta\delta\eta$ -trimethyloctane, b.p. 119 — $120^\circ/4$ mm., which readily lose H_2O . J. L. D.

Constitution of polyhydroxycyclohexane. I. 1-Tetrahydroxymannocyclitol. Y. HAMAMURA (Proc. Imp. Acad. Tokyo, 1934, **10**, 459—462).— α -, Di-iodo-*d*-mannitol $\beta\gamma\delta\epsilon$ -tetrabenzoate (I) (cf. A., 1932, 928) with Ag in dioxan at 125 — 130° affords a syrup, hydrolysed [5% MeOH-Ba(OH) $_2$] to 1:2:3:4-tetrahydroxycyclohexane (II), m.p. 146 — 147° , $[\alpha]_D^{25}$ -27.7° in H_2O (cf. A., 1932, 834) (Ac_4 derivative, m.p. 79°), which absorbs Br in AcOH, does not reduce Fehling's solution, and with H_2 (Pd-BaSO $_4$) at room temp. gives $\alpha\beta\gamma\delta$ -tetrahydroxy-*n*-hexane, m.p. 123 — 125° (CPh $_3$ ether, m.p. 124 — 125°), the oxidation product (PrOH) of which confirms its structure. (I) with Zn-AcOH at 100° gives a product which is converted into $\beta\gamma\delta\epsilon$ -tetrahydroxy-*n*-hexane (?), m.p. 150° , which does not reduce KMnO $_4$ or absorb Br, and differs from (II). J. L. D.

Mannitol. IV. Acetone- [isopropylidene-] mannitols and mixed esters of mannitol. P. BRIGL and H. GRÜNER (Ber., 1934, **67**, [B], 1969—1973; cf. A., 1934, 1199).—Mannitol is shaken with HBO $_2$ (or H $_3$ BO $_3$) and conc. H $_2$ SO $_4$ in COMe $_2$ until dissolution is complete. The solution is conc. to a syrup, which is repeatedly evaporated with MeOH to remove HBO $_2$. The residue is extracted with ligroin, from which diisopropylidenemannitol separates. Triisopropylidenemannitol (I) is obtained from the mother-liquors, whilst treatment of the material insol. in ligroin with EtOH leads to isopropylidenemannitol. $\alpha\beta\epsilon$ -, Diisopropylidenemannitol is converted by *p*-C $_6$ H $_4$ Me-SO $_2$ Cl in C $_5$ H $_5$ N at 35° into $\alpha\beta\epsilon\zeta$ -diisopropylidenemannitol $\gamma\delta$ -di-*p*-toluenesulphonate, m.p. 120 — 121° , $[\alpha]_D +9.3^\circ$ in CHCl $_3$, which is hydrolysed and then transformed by BzCl in C $_5$ H $_5$ N into mannitol $\alpha\zeta$ -dibenzoate $\gamma\delta$ -di-*p*-toluenesulphonate, m.p. 145 — 146° , $[\alpha]_D +42.2^\circ$ in CHCl $_3$, whence (Ac $_2$ O in C $_5$ H $_5$ N) mannitol $\beta\epsilon$ -diacetate $\alpha\zeta$ -dibenzoate $\gamma\delta$ -di-*p*-toluenesulphonate, m.p. 142° , $[\alpha]_D +55.9^\circ$ in CHCl $_3$. Mannitol $\alpha\zeta$ -dibenzoate is converted by COMe and conc. H $_2$ SO $_4$ into isopropylidenemannitol $\alpha\zeta$ -dibenzoate, which is transformed by *p*-C $_6$ H $_4$ Me-SO $_2$ Cl and C $_5$ H $_5$ N at 15 — 20° into $\gamma\delta$ -isopropylidenemannitol $\alpha\zeta$ -dibenzoate $\beta\epsilon$ -di-*p*-toluenesulphonate, m.p. 96 — 97° , $[\alpha]_D +27.0^\circ$ in CHCl $_3$, hydrolysed to mannitol $\alpha\zeta$ -dibenzoate $\beta\epsilon$ -di-*p*-toluenesulphonate, m.p. 76 — 77° , $[\alpha]_D -27.8^\circ$ in CHCl $_3$, whence mannitol $\gamma\delta$ -diacetate $\alpha\zeta$ -dibenzoate $\beta\epsilon$ -di-*p*-toluenesulphonate, m.p. 121° , $[\alpha]_D +56.4^\circ$ in CHCl $_3$. The compound of Müller *et al.* (A., 1933, 931) is therefore mannitol $\gamma\epsilon$ -diacetate $\alpha\zeta$ -dibenzoate $\beta\delta$ -di-*p*-toluenesulphonate. $\gamma\delta$ -Diisopropylidenemannitol, m.p. 84 — 85° , $[\alpha]_D^{19} +30.4^\circ$ in H_2O , is readily obtained by partial hydrolysis of (I) with AcOH-H $_2O$ at 15 — 20° . H. W.

Preparation and determination of ethylene oxide. W. DOMINIK and J. BARTKIEWICZÓWNA (Przemysł Chem., 1934, **18**, 373—375).—(CH $_2$) $_2$ O is obtained in 90% yield by dropping aq. EtOCl on to CaO in a flask heated on an oil-bath, and fitted with a reflux condenser connected with a manometer. The yield of (CH $_2$) $_2$ O is calc. from the rise in pressure in the flask. Lower yields are obtained when aq. NaOH is substituted for CaO. R. T.

Molecular changes of the α -disubstituted oxides of the aliphatic series, and of normal structure. M. FAVORSKI, M. TOHITCHONKIN, and I. IVANOV (Compt. rend., 1934, **199**, 1229—1230).— α -Methyl- β -ethylethylene oxide (I), b.p. 79 — 82° (prepared through CHMe:CHEt and its monochlorohydrin), with fused ZnCl $_2$ at 315 — 320° gives COMePr. Similarly, α -ethyl- β -propylethylene oxide, b.p. 131 — 132° , is converted into COEtBu. The C atoms nearer the periphery possess the greater affinity for O, so CO is situated as near the end of the chain as possible. J. L. D.

Specificity of phosphatase.—See this vol., 122.

Spontaneous decomposition of lecithin and its bearing on determination of isoelectric point. H. FISCHGOLD and E. CHAIN (Biochem. J., 1934, **28**, 2044—2051).—Lecithin (I) is titrated electrometrically in 99% EtOH, with NaOH, giving a curve similar to that of the solvent alone; back titration with HCl shows slight buffering at p_H 7.5. Back titration after keeping 66 hr. in excess of NaOH shows the formation of a new group, pK 7.5. Fresh and old preps. of (I) are titrated in C $_6$ H $_6$ -EtOH (19:1) with HClO $_4$ and also with NaOEt. On the acid side no significant change in the titration occurs with age, whilst on the alkaline side an increase in the groups titratable by NaOEt occurs. The pK of stearic acid in 90% EtOH at 25.7° is 7.36. After emulsification of (I) in H_2O and subsequent addition of HCl and Fe(OH) $_3$, choline chloride (II) is not present in the supernatant fluid. Fatty acids are present in an EtOH extract of an old prep. of (I) after pptn. with CdCl $_2$, but not of a fresh prep. A solution of (II) in H_2O was neutral. The titration curve of (II) is identical with its blank correction curve. From the p_H of a solution of (II) in 0.1*N*-NaOH a val. of 14 for its pK is obtained, giving a theoretical isoelectric point of (I) at p_H 7.5 approx. H. D.

Isoelectric points of lecithin and sphingomyelin. E. CHAIN and I. KEMP (Biochem. J., 1934, **28**, 2052—2055).—A fresh prep. of lecithin has an isoelectric point (I) at p_H 6.7+0.2 as determined by the min. cataphoretic velocity of dispersions in aq.-EtOH media. (I) is independent of the buffers used and the ionic strengths of the solutions; in 0.05*N*-BaCl $_2$ strong adsorption of Ba $^{++}$ occurs. The (I) of preps. of sphingomyelin increases from a val. <2 to a val. >6 with successive purifications through the Cd salt. H. D.

Mechanism of chlorination of aliphatic acid chlorides. I. Dark reaction.—See this vol., 174.

Oxidation of fatty acids.—See this vol., 114.

Rotatory dispersion curves of α -substituted *n*-carboxylic acids.—See this vol., 14.

Preparation of formyl chloride.—See this vol., 177.

Organic reactions with boron fluoride. VIII. Condensation of propylene with acids. T. B. DORRIS, F. J. SOWA, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 2689—2690).— $\text{Pr}^\beta\text{OAc}$, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Pr}^\beta$, $\text{CHCl}_2\cdot\text{CO}_2\text{Pr}^\beta$, and $\text{CCl}_3\cdot\text{CO}_2\text{Pr}^\beta$ are obtained in yields of 16.8, 38.8, 48.6, and 57.8%, respectively, from the acid, Pr^βOH , and BF_3 (cf. A., 1932, 728); the yields are in the reverse order with HCl as catalyst (Sudborough and Lloyd, J.C.S., 1899, 75, 467). $\text{Pr}^\beta\text{OBz}$ (I) is similarly obtained in 60% yield. The esters are also prepared in yields of 7, 34.2, 39.5, and 48.8%, respectively, from the acid, C_3H_8 , and BF_3 at 60—70°. The solubility of C_3H_8 in the acids and esters increases with the no. of Cl atoms. (I) is obtained in 88% yield from BzOH [in (I)], C_3H_8 , and BF_3 at 20—30°; ring-substitution does not occur (cf. A., 1934, 1349).

H. B.

Hetero-formato-salts of calcium. J. V. DUBSKÝ and J. TRTÍLEK (Publ. Fac. Sci. Univ. Masaryk, 1934, No. 196, 1—6).—The compounds $[\text{Ca}_2\text{R}_2]\text{Cl}_2\cdot 8\text{H}_2\text{O}$, $[\text{Ca}_2\text{R}_2][\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\cdot 4\text{H}_2\text{O}$, m.p. 160°, $[\text{Ca}_2\text{R}_2]\text{CrO}_4\cdot 2\text{H}_2\text{O}$, $\text{CaR}_2\cdot \text{K}_3\text{Fe}(\text{CN})_6$, and $[\text{Ca}_2\text{R}_2](\text{OAc})_2$, in which $\text{R}=\text{HCO}_2$, have been prepared.

R. T.

Olefinic acids. XIII. Δ^7 -*n*-Hexenoic acid and "hydrosorbic" acid. R. A. LETCH and R. P. LINSTEAD. **XIV. Preparation and additive reactions of Δ^8 -*n*-hexenoic acid. Unusual isomeric change in the three-carbon system.** **XV. Effect of peroxides on orientation of addition of hydrogen bromide to vinyl- and allyl-acetic acids.** R. P. LINSTEAD and H. N. RYDON (J.C.S., 1934, 1994—1995, 1995—2001, 2001—2003).—XIII. "Hydrosorbic" acid (A., 1928, 868, 1214) contains Δ^7 (I) and Δ^8 -*n*-hexenoic acids. Hot alkali partly converts the latter into the Δ^8 -isomeride, which may be separated by partial esterification. After two repetitions of the whole process pure (I) remains. The acid thus obtained is identical with that prepared by other methods (A., 1897, i, 13, 590; 1901, i, 63; 1929, 1271). $\gamma\delta$ -Dibromo-*n*-hexoic acid has m.p. 84°.

XIV. Decarboxylation of Δ^7 -*n*-butenylmalonic acid, m.p. 92° [from α -bromo- Δ^7 -*n*-butene (II) (improved prep.) and $\text{CHNa}(\text{CO}_2\text{Et})_2$], gives Δ^8 -*n*-hexenoic acid (III), which after regeneration from the *p*-toluidide, m.p. 58° (cf. A., 1904, i, 547), through the *Et* ester, b.p. 65—66°/15 mm., has m.p. —37°, b.p. 107°/17 mm. With $\text{PBr}_3\text{-C}_6\text{H}_5\text{N}$, Δ^7 -*n*-buten- α -ol gives pure (II), out with $\text{H}_2\text{SO}_4\text{-HBr}$ a mixture of (II), the Δ^8 -isomeride [identified by conversion (A., 1931, 597) into Δ^7 -*n*-pentenoanilide, and Δ^8 -*n*-butenylmalonic from which (I) and its Br_2 -derivative were obtained], and dibromobutane, b.p. 171—176°, is obtained. Lactonisation of (III) (cf. A., 1933, 934) gave some δ -hexolactone (IV) and considerable quantities of side-products. The hydrolysis of (IV) was followed quantitatively. *Et* δ -bromohexoate [from (IV), HBr , and EtOH] has b.p. 121—122°/21°. Addition of HBr to (III), alone or in light eum., gave some α - Br -derivative (characterised by malonation to suberic acid).

XV (cf. A., 1933, 934). The orientation of addition of HBr to vinyl- (V) and allyl- (VI) -acetic acids in hexane is unaffected by anti oxidants [H_2 , $p\text{-C}_6\text{H}_4(\text{OH})_2$, NHPH_2]. Addition to (VI), but not to (V), in the absence of solvent is reversed by admixture of 1% of Bz_2O_2 . Addition to stale samples of (VI) in the absence of solvent occurs in the same direction as to fresh samples. The orienting effect of solvents in the above examples is not considered to be due to variations in the peroxide effect.

H. G. M.

Arachidonic acid and its quantitative determination. W. C. AULT and J. B. BROWN (J. Biol. Chem., 1934, 107, 615—622).—Specimens of Me arachidonate (I) prepared by fractional distillation, by the Li soap-COME₂ method, and by reduction of Me octabromoarachidonate all have the same polybromide no., 86.5. By use of this no. as described by Brown (A., 1928, 208), (I) and arachidonic acid (II) may be determined. (I) has b.p. 200—205°/1—2 mm.; (II) has m.p. —49.5°.

C. G. A.

Unsaturated fatty acids and their derivatives.

X. Constitution of clupanodonic acid. Y. INOUE and H. KATO. **XI. Configuration of eruco- and brassido-dibromobehenic acid.** T. MARUYAMA (Proc. Imp. Acad. Tokyo, 1934, 10, 463—466, 467—469; cf. A., 1932, 252; 1933, 145).—X. Decabromobehenic acid (I) [from clupanodonic acid (II)] with KI in $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ gives the octabromide (III), m.p. 98—98.5°, reconverted into (I) with Br , and with O_3 , followed by hydrolysis, gives hexabromooctadecanedicarboxylic acid (IV), m.p. 65° [Me ester (V), m.p. 52—52.5°, similarly obtained from the Me ester of (I) or Me hexabromoclupanodone (VI)]. (IV) and (V) when debrominated and hydrogenated (Pd-BaSO_4) both give hexadecane- ω -dicarboxylic acid (Pb salt), and ozonisation in each case affords $\text{Pr}^\alpha\text{CO}_2\text{Ag}$. Because both (VI) and (III) give (I), the centres of unsaturation are the same, but (VI) must have a triple and (III) a double linking. (II) with fuming HNO_3 affords an α -diketone, and with conc. H_2SO_4 and H_2O affords monoketotrihydroxybehenic acid, decomp. 128° (oxime, decomp. 150°).

XI. Erucic acid with Br gives eruco-dibromobehenic acid (VII), which with the calc. amount of EtOH-KOH at 80° affords μ -bromo- Δ^7 -behenic acid (VIII), m.p. 33°, the Me ester of which when oxidised gives octoic acid (IX) and α -hydroxydodecane- ω -dicarboxylic acid, m.p. 108°. (VII) with excess of EtOH-KOH at 80° gives behenolic acid and the acid, $\text{CH}_3\cdot[\text{CH}_2]_6\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}_2\cdot\text{CO}_2\text{H}$ (X), m.p. 63°, the Me ester of which is oxidised to $\text{H}_2\text{C}_2\text{O}_4$ (IX), and decane- ω -dicarboxylic acid. (X) with EtOH-KOH at 150° gives behenolic acid. Brassido-dibromobehenic acid with EtOH-KOH at 80° gives μ (or ν)-bromo- Δ^8 -behenic acid (XI), m.p. 41°, the Me ester of which is oxidised to nonoic acid and brassylic acid. HBr is difficult to remove from (XI), but not from (VIII); which indicates a *cis*-structure for (VIII) and *trans*- for (XI).

J. L. D.

Hydrogenation of unsaturated α -keto-acids, aldehydes, and alcohols by fermenting yeast.—See this vol., 123.

Hetero-compounds of glycollic acid. J. V. DUBSKÝ and D. VINOGRADOVA (Publ. Fac. Sci. Univ. Masaryk, 1934, No. 196, 7—16).—The salts CuR_2 , NiR_2 , $\text{MgR}_2 \cdot 2\text{H}_2\text{O}$, BaR_2 , $\text{ZnR}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdR}_2 \cdot 2\text{H}_2\text{O}$, PbR_2 , $\text{MnR}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoR}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuR}_2 \cdot 2\text{NH}_3$, $[\text{Cu}_2\text{R}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, $[\text{Mg}_2\text{R}_2]\text{Cl}_2 \cdot 3$, m.p. 282° , and $4\text{H}_2\text{O}$, $[\text{Ca}_2\text{R}_2]\text{Cl}_2 \cdot 5$, m.p. 188° , and $6\text{H}_2\text{O}$, m.p. 128° , $[\text{Ba}_2\text{R}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, m.p. $275\text{--}280^\circ$, $[\text{Hg}_2\text{R}_2]\text{Cl}_2$, $[\text{Pb}_2\text{R}_2]\text{Cl}_2$, $[\text{Mn}_2\text{R}_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, m.p. $162\text{--}164^\circ$, $[\text{Ni}_2\text{R}_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, m.p. $126\text{--}128^\circ$, $\text{CoCl}_2 \cdot \text{CoClR} \cdot 10\text{H}_2\text{O}$, m.p. 52° , $[\text{Co}_2\text{R}_2]\text{Cl}_2 \cdot 5 \cdot 5\text{H}_2\text{O}$, m.p. $86\text{--}90^\circ$, $[\text{Ca}_2\text{R}_2](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, m.p. 174° , $[\text{Zn}_2\text{R}_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, m.p. 119° , $[\text{Pb}_2\text{R}_2](\text{NO}_3)_2$, decomp. at 160° , $[\text{Cu}_2\text{R}_2]\text{R}'\text{R}'$, $[\text{Cu}_2\text{R}_2]\text{R}'\text{H}_2\text{O}$, $3\text{ZnR}_2 \cdot 2\text{ZnR}'_2 \cdot 11\text{H}_2\text{O}$, m.p. 230° , $[\text{Ba}_2\text{R}'_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $[\text{Ba}_2\text{R}'_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and $[\text{Pb}_2\text{R}'_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, m.p. $182\text{--}187^\circ$, have been prepared ($\text{R}=\text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2$; $\text{R}'=\text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2$; $\text{R}''=\text{HCO}_2$). R. T.

Hydroxy-acids obtained by the atmospheric oxidation of paraffin. II. P. P. SCHORIGIN and A. P. KRESCHKOV (J. Gen. Chem. Russ., 1934, 4, 988—994).—The product of oxidation of paraffin by atm. O_2 consists of a mixture of OH-acids (I), their anhydrides, lactones, and lactides, carboxylic acids, and unidentified, unsaponifiable substances. The (I) were converted into Me esters with Me_2SO_4 , the mixture of esters fractionally distilled, the fractions hydrolysed with aq. KOH, the individual (I) fractionally pptd. as Cd salts, and the acids $\text{OH} \cdot \text{C}_9\text{H}_{18} \cdot \text{CO}_2\text{H}$, $\text{OH} \cdot \text{C}_{11-17}\text{H}_{22-34} \cdot \text{CO}_2\text{H}$, $\text{OH} \cdot \text{C}_{20}\text{H}_{40} \cdot \text{CO}_2\text{H}$ (2 isomerides), $\text{OH} \cdot \text{C}_{21}\text{H}_{42} \cdot \text{CO}_2\text{H}$, $\text{OH} \cdot \text{C}_{28}\text{H}_{52} \cdot \text{CO}_2\text{H}$, and $\text{OH} \cdot \text{C}_{31}\text{H}_{62} \cdot \text{CO}_2\text{H}$ isolated; OH is chiefly, but not exclusively, in the β -position, and the C chain is probably branched in every case. R. T.

Combined action of ultra-violet light and platinum on transformation of fumaric and maleic acids and their salts.—See this vol., 178.

Preparation of pimelic acid. A. MÜLLER (Monatsh., 1934, 65, 18—20).—Pimelic acid is obtained in 50% yield by treating $o\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ with Na in boiling amyl alcohol. H. W.

Muconic and hydromuconic acids. VI. *cis*- and *trans*- Δ^2 -Dihydromuconic acids. E. H. FARMER and L. A. HUGHES (J.C.S., 1934, 1938—1940; cf. *ibid.*, 1923, 123, 2531).—The mixture obtained by heating Δ^2 -dihydromuconic acid (I) with hot aq. NaOH contains unchanged (I) and *trans*- Δ^2 -dihydromuconic acid (II), m.p. 191° (Me_2 ester, b.p. $127^\circ/14$ mm), also formed (32—57%) in the 50% hydrogenation (Pd or Ni) of muconic acid (as Na salt in H_2O). In both cases pure (II) was isolated by partial esterification (MeOH-HCl) and hydrolysis of the resulting *Me H* ester (III), m.p. 60° . (III) is oxidised almost quantitatively to $\text{H}_2\text{C}_2\text{O}_4$ and $(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$. The bromide of (III) is hydrolysed to $\alpha\beta$ -dibromoadipic acid, m.p. $171\text{--}173^\circ$, reconverted (Zn-COMe_2) into 50% hydrogenation of *Me cis-cis*-muconate (*ibid.*, 2531) gives a product from which *cis*- Δ^2 -dihydromuconic acid, m.p. 81° , some (I) (*trans*-form), and adipic acid were isolated. H. G. M.

Methylation of trihydroxyglutaric acid and tartaric acid with diazomethane. O. T. SCHMIDT and H. ZEISER (Ber., 1934, 67, [B], 2120—2127).—

Treatment of *l*-(arabo)-trihydroxyglutaric acid with excess of CH_3N_2 in Et_2O gives a product containing 45.4% OMe, transformed by Ag_2O and MeI into *Me*, *l*-(arabo)-trimethoxyglutarate, b.p. $74\text{--}76^\circ/0.005$ mm., $[\alpha]_D^{25} +32.2^\circ$ in MeOH [*l*-(arabo)-trimethoxyglutardimethylamide, m.p. $173\text{--}174^\circ$, $[\alpha]_D^{25} +59.4^\circ \pm 0.9^\circ$ in H_2O], in 60% yield. With excess of CH_3N_2 (xylo)-trihydroxyglutaric acid affords essentially *Me*, hydroxydimethoxyglutarate, b.p. $97\text{--}99^\circ/0.003$ mm., hydrolysed to a mixture of an acid and the monolactone of α -hydroxy- α' - β -dimethoxyglutaric acid, m.p. $109.5\text{--}110.5^\circ$. *d*-Tartaric acid is converted by an excess of CH_3N_2 into *Me*, *d*-dimethoxysuccinate, b.p. $130\text{--}132^\circ/12$ mm., in 95% yield; the same substance is produced by vigorous action, but in somewhat lower yield, from *Me*, *d*-tartrate. Mucic acid, probably by reason of its sparing solubility, reacts so slowly with CH_3N_2 in Et_2O that complete esterification is not attained. *d*-Saccharic acid reacts vigorously, acquiring about 4Me, but apparently undergoing complex change. H. W.

Identification reactions for *l*-ascorbic acid (vitamin-C).—See this vol., 130.

Types of lactones formed from monobasic sugar acids under varying conditions. J. M. BRACKENBURY and F. W. UPSON (J. Amer. Chem. Soc., 1934, 56, 2659—2662; cf. A., 1933, 808).—The rate of lactone formation by various acids in (usually) AcOH, 0.5N- H_2SO_4 , and H_2O at 25° is studied polarimetrically. *d*-Mannonic acid is converted more slowly but to a greater extent into the δ -lactone in AcOH than in H_2O , and gradual conversion of the δ - into the γ -lactone (isolable from the equilibrium mixture; the change is also established independently) occurs; *l*-rhammonic acid shows a similar behaviour. *d*-Gluconic acid lactonises to a greater extent in AcOH than in H_2O ; the main constituent of the equilibrium mixture is (probably) the δ -lactone (which is isolable). α -*d*-Glucosheptonic acid (I) is also converted more slowly but to a greater extent into the δ -lactone (II) in AcOH than in H_2O or dil. acid; reaction is slower at 0° and gives an equilibrium mixture of (I) and (II). α -*l*-Rhamnosheptonic acid resembles (I); its δ -lactone has a α -rotation in accordance with Hudson's lactone rule (A., 1910, i, 220). δ -Lactone formation by arabonic, talonic, and galactonic acid is not much > in AcOH than in H_2O . H. B.

Reduction of galacturonic acid and of methyl methylgalacturonate. K. SMOLEŃSKI and A. ZŁOTNIK (Bull. Acad. Polonaise, 1934, A, 293—303).—*d*-Galacturonic acid (I) (from peptic materials from sugar-beet) is reduced to *l*-galactonic acid (*a*) by Na-Hg and (*b*) by Ca, the solution being maintained faintly alkaline. This establishes the *d*-configuration for (I). *Me* α -methylgalacturonate [obtained from (I); A., 1933, 53] is reduced in acid solution (p_H 2—3) by Na-Hg to α -methyl-*d*-galactoside (yield about 10%), hydrolysed to *d*-galactose. H. G. M.

Sugars with branched carbon chains. III. Configuration of the two fructosheptonic acids and hamamelose. IV. Optical behaviour of aldonic acids in presence of sodium molybdate. O. T. SCHMIDT and C. C. WEBER-MOLSTER. V.

Synthesis of hamamelonic acid. O. T. SCHMIDT and K. HEINTZ (Annalen, 1934, 515, 43—64, 65—76, 77—96; cf. A., 1930, 197; 1931, 70).—III. A mixture of α -fructoheptonic acid (I), $[\alpha]_D^{18} -20.26 \pm 0.5^\circ$ in H_2O , $-11.58 \pm 0.4^\circ$ (as Na salt in H_2O) {brucine salt (II), m.p. 162° (Kiliani, A., 1928, 47); phenylhydrazide, m.p. 164° , $[\alpha]_D^{18} +9.6 \pm 0.5^\circ$ in H_2O (Kiliani and Düll, A., 1890, 596); amide, m.p. $175-176^\circ$, $[\alpha]_D^{18} -9.3^\circ$ in H_2O ; anilide, m.p. $164-165^\circ$, $[\alpha]_D^{18} +22.5 \pm 0.5^\circ$ in H_2O ; lactone, $[\alpha]_D^{18} +82.15^\circ$ in H_2O }, and β -fructoheptonic acid (III), $[\alpha]_D^{18} +1.4 \pm 0.4^\circ$ in H_2O , $+2.1 \pm 0.3^\circ$ (as Na salt in H_2O) {brucine salt ($+2.5H_2O$), m.p. (anhyd.) $143-145^\circ$ (not sharp); phenylhydrazide (IV), m.p. $190-191^\circ$, $[\alpha]_D^{18} -30.75 \pm 0.5^\circ$ in H_2O (cf. Kiliani, A., 1922, i, 1111)}, is obtained from fructose and HCN by Kiliani's method (*loc. cit.*); (I) is separated from the mixture as (II), and (III) is then isolated from the filtrate as (IV). (III), obtained as a syrup, is converted by repeated evaporation with aq. HCl into an anhydrolactone, $C_7H_{10}O_6$, m.p. $189-190^\circ$, $[\alpha]_D^{18} +100.7^\circ$ in H_2O (free acid, $[\alpha]_D^{18} +8.4 \pm 0.4^\circ$); the anhydride ring does not undergo fission with acid or alkali. (I) does not give an analogous compound. Interconversion of (I) and (III) could not be effected by boiling C_5H_5N or quinoline. The nitrile, m.p. 105° , of Kiliani and Düll (*loc. cit.*) (the m.p. of different preps. is found to be $95-117^\circ$) is hydrolysed to (I). Comparison of the $[M]_D$ of (I), (III), gluconic, mannonic, arabonic, ribonic, and hamamelonic (V) acids and their derivatives shows that (I) and (III) are α -hydroxymethyl-gluconic and -mannonic acid, respectively. (V) (cf. Part V) shows the same optical behaviour as (I).

IV. Lutz and Jirginson's method (A., 1932, 720) of determining the configuration of α -OH-acids fails with aldonic acids. Investigation of the optical rotatory changes occurring when the following acids (as Na salts) are mixed with varying amounts of Na_2MoO_4 (I) and the solutions then treated with acid or alkali, shows that trustworthy results are obtained only when the mol. ratio Na aldinate : (I) is 2 : 1: gluconic, galactonic, talonic, mannonic, rhamnonic, α - (II) and β - (III) -fructoheptonic, 4-methylmannonic, arabonic, lyxonic, ribonic, and hamamelonic (IV). The results for (II), (III), and (IV) confirm the constitutions assigned from rotation measurements.

V. *d*-Xyloketose (I) (A., 1934, 173), aq. HCN, and a little aq. NH_3 at 0° —room temp. for 3 days give [after hydrolysis with $Ba(OH)_2$] α -hydroxymethyl-*d*-lyxonic acid (II) (phenylhydrazide, m.p. $155-156^\circ$, $[\alpha]_D^{18} -32.7 \pm 0.7^\circ$ in H_2O) and galactonic acid [which arises from *d*-lyxose, formed by the action of the NH_3 on (I)], purified through the Ca salts and separated as the phenylhydrazides. In the absence of NH_3 , (I) similarly affords (II) and α -hydroxymethyl-*d*-xyloonic acid (Ca salt; phenylhydrazide, m.p. $194-195^\circ$, $[\alpha]_D^{18} +56 \pm 7^\circ$ in H_2O). *l*-Arabinose (III) is boiled with anhyd. C_5H_5N and the resulting mixture is crystallised from $EtOH + Et_2O$, whereby the bulk of unchanged (III) is removed; treatment of the residue with $CH_3Ph \cdot NPh \cdot NH_2$ gives some (III)-phenylbenzyl-nyrazone. Subsequent treatment of the residual product with $PhCHO$ in H_2O and extraction with Et_2O affords an aq. solution of *l*-araboketose, $[\alpha]_D^{18} +12.7^\circ$. This and HCN give α -hydroxymethyl-*l*-

arabonic acid (phenylhydrazide, m.p. $194-195^\circ$, $[\alpha]_D^{18} +83 \pm 5^\circ$ in H_2O) and α -hydroxymethyl-*l*-ribonic acid (phenylhydrazide, m.p. 204° , $[\alpha]_D^{18} -33 \pm 4^\circ$ in H_2O). *d*-Araboketose, $[\alpha]_D^{18} -12.4^\circ$, similarly prepared from *d*-arabinose, and HCN afford α -hydroxymethyl-*d*-arabonic acid (phenylhydrazide, m.p. $194-195^\circ$) and hamamelonic (α -hydroxymethyl-*d*-ribonic) acid (phenylhydrazide, m.p. $202-203^\circ$, $[\alpha]_D^{18} +34 \pm 4^\circ$ in H_2O). Hamamelose is, therefore, an α -hydroxymethyl-*d*-ribose (IV).

Further investigation of the action of C_5H_5N on *d*-xylose (V) [3:5-dinitrobenzoylhydrazone (VI), m.p. 194° , $[\alpha]_D^{18} +35.4^\circ$ (final val.) in C_5H_5N] shows that (I) is accompanied by a little lyxose; the initial reaction product can be freed from (V) with 3 : 5-(NO_2)₂ $C_6H_3 \cdot CO \cdot NH \cdot NH_2$ [thus giving (VI); ketoses do not react], and (after treatment with $PhCHO$) (I) can then be isolated as the *p*-bromophenylhydrazone (*loc. cit.*). The production of (I) from (V) is contrary to the results of Levene and Hill (A., 1933, 1278). The composition of mixtures of aldo- and keto-pentoses cannot be determined by titration with I in alkaline solution (cf. Levene and Hill, *loc. cit.*). (V) undergoes quant. oxidation with I in aq. $KHCO_3$ after 12 hr.; (I) similarly consumes I = 65% of aldose. H. B.

Thiodiisobutyric acids. E. LARSSON (Ber., 1934, 67, [B], 2109—2111; cf. A., 1934, 870).—Et β -bromoisobutyrate (I) and $SH \cdot CMe_2 \cdot CO_2H$ are converted by $NaOEt-EtOH$ and subsequent hydrolysis into thio- $\alpha\beta'$ -diisobutyric acid, m.p. 151° . Et α -bromoisobutyrate and Na_2S in $EtOH-C_6H_6$ afford thio- $\alpha\alpha'$ -diisobutyric acid, m.p. 142° , whilst similar treatment of (I) yields thio- $\beta\beta'$ -diisobutyric acid, m.p. 115° . The assigned constitutions (*loc. cit.*) are thus confirmed. H. W.

Application of Raman spectrography to the study of the allylic transformation and of *cis-trans* isomerism of crotonyl derivatives. (MLLE.) B. GREDY and L. PIAUX (Bull. Soc. chim., 1934, [v], 1, 1481—1489).—Raman spectra prove the following: $CH_3 \cdot CH \cdot CH_2 \cdot CHO$ and Charon's $CH_3 \cdot CH \cdot CH_2 \cdot CH_2 \cdot OH$ (I) contain only a little *cis*-compound. Acetylation of (I) and of $CH_3 \cdot CH \cdot CHMe \cdot OH$ (II) is completely "normal." (I) with HBr and (II) with PBr_3 give the same mixture of *trans*- $CH_3 \cdot CH \cdot CH_2 \cdot CH_2 \cdot Br$ (80%) and 10% each of the other two ingredients, which with $NaOAc$ in $AcOH$ gives a mixture of about equal amounts of the acetates of (I) and (II), hydrolysed "normally" by alkali to a corresponding mixture of (I) and (II). R. S. C.

[Aldehyde of violet leaves.] E. SPATH and F. KESZTLER (Ber., 1934, 67, [B], 2099—2100).—A reply to Walbaum *et al.* (this vol., 66). H. W.

Allyl change. Studies by the Raman effect. A. KIRRMANN (Compt. rend., 1934, 199, 1228—1229).—Crotonaldehyde with PCl_5 gives a mixture (I) of Cl-compounds which cannot be separated by fractional distillation. (I) with $NaOEt$ affords α -chloro- γ -ethoxy- Δ^2 -butene, the spectrum of which shows only one double linking. (I) gives two fractions, b.p. $120-123^\circ$ and $124-125^\circ$, each of which shows

the same lines (1666 and 1620 cm^{-1}) but of different intensities. (I) is mainly the *trans*-compound; very little of the *cis*-isomeride is formed. J. L. D.

Polymerisation of dihydroxyacetone. H. H. STRAIN and W. H. DORE (J. Amer. Chem. Soc., 1934, **56**, 2649—2650).—Unimol. $\text{CO}(\text{CH}_2\text{OH})_2$ (I), m.p. 72° , polymerises completely to the bimol. form, m.p. 78 – 81° , during 25–30 days at room temp.; the rate of polymerisation is determined by X-ray diffraction patterns (II) and is independent of the radiation. Polymerides, m.p. 130 – 133° , 230 – 260° (decomp.), and 230 – 250° (decomp.), obtained when (I) is kept for many months, show definite (II). H. B.

Preparation of $\alpha\gamma$ -diketones by the Claisen reaction. J. M. SPRAGUE, L. J. BECKHAM, and H. ADKINS (J. Amer. Chem. Soc., 1934, **56**, 2665—2668).—The following $\text{COR}\cdot\text{CH}_2\cdot\text{COR}'$ are prepared (in 50–70% yield) from COMeR , $\text{R}'\text{CO}_2\text{Et}$, and (usually) NaOEt (prepared in Et_2O or xylene) in Pr^sO or PhMe (except when large excess of ester is used), and purified by fractional distillation (Widmer column): $\text{CH}_2\text{Ac}\cdot\text{COPr}^s$; $\text{CH}_2\text{Ac}\cdot\text{COBu}^r$ (I); $\text{CH}_2\text{Ac}\cdot\text{COBu}^s$; $\text{CH}_2\text{Ac}\cdot\text{COEt}$; $\text{CH}_2\text{Ac}\cdot\text{COPr}^a$; $\text{CH}_2\text{Ac}\cdot\text{COBu}^a$; $\text{CH}_2\text{Ac}\cdot\text{COBu}(\text{sec.})$; hexahydrobenzoylacetylmethane; furoylacetylmethane; tetrahydrofuroylacetylmethane, b.p. 95 – $97^\circ/8$ mm. (from COMe_2 and Et tetrahydrofuroate); CH_2BzAc ; 2:4:6-trimethylbenzoylacetylmethane, m.p. 46 – 47° ; benzoylfuroylmethane, m.p. 68° ; *p*-phenylbenzoylacetylmethane, m.p. 156 – 157° (from EtOAc and *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COMe}$). CH_2Ac_2 is best prepared by using Na as condensing agent. $\text{COMe}\cdot\text{CHNa}\cdot\text{COR}$ and $\text{R}'\text{Hal}$ in (usually) COMe_2 or dioxan (cf. Weygand, A., 1928, 643) give $\text{COMe}\cdot\text{CHR}\cdot\text{COR}$; the following are new: α -benzoyl- α -acetyl-pentane, b.p. 156 – $160^\circ/10$ mm., and -octane, b.p. 178 – $183^\circ/8$ mm.; α -acetyl- α -trimethylacetyl-propane, b.p. 77 – $78^\circ/17$ mm., and -pentane, b.p. 113 – $117^\circ/11$ mm.; α -acetyl- α -trimethylacetyl- β -phenylethane (II), b.p. 155 – $163^\circ/10$ mm. [from (I) and CH_2PhCl]; β -acetyl- β -trimethylacetyl- $\alpha\gamma$ -diphenylpropane, b.p. 165 – $174^\circ/1$ mm. [from (II) and CH_2PhCl]. $\text{COMe}_3\cdot\text{CO}_2\text{Et}$ and Et valerate could not be condensed (NaOEt) with COMeBu^r or COMeBu^a ; similarly, Et hexahydrobenzoate, phenylacetate, and β -phenylpropionate do not react with COMe_2 . H. B.

Alcoholysis of $\alpha\gamma$ -diketones. L. J. BECKHAM and H. ADKINS (J. Amer. Chem. Soc., 1934, **56**, 2676—2679; cf. A., 1932, 1020).—The alcoholysis of various $\alpha\gamma$ -diketones by EtOH (twice dried over CaO) in a brass reaction vessel at 150 – $250^\circ/100$ atm. of H_2 , is investigated by the method previously used (*loc. cit.*). For $\text{COMe}\cdot\text{CH}_2\cdot\text{COR}$ (I), the % of Ac cleavage (A) is $\text{R}=\text{Ph}$ 80, Bu^r 75, *sec.*- Bu 63, Bu^s 59, Bu^a 54, Pr^a 52, Et 51, Me 50, Pr^s 38. For $\text{COMe}\cdot\text{CHR}\cdot\text{COBu}^r$, (A) is $\text{R}=\text{Bu}^a$ 82, CH_2Ph 80, and Et 75%, whilst for $\text{COMe}\cdot\text{CHR}\cdot\text{COPh}$, (A) is $\text{R}=\eta$ -heptyl 43, Bu^a 34, Et 34, and CH_2Ph 16%. β -Acetyl- β -trimethylacetyl- $\alpha\gamma$ -diphenylpropane undergoes 43% (A). The % (A) for various (I) using EtOH dried over $\text{Al}(\text{OEt})_3$ is $>$ with EtOH containing 0.1–0.2% H_2O ; addition of 1–2% of $\text{Al}(\text{OEt})_3$ to the reaction mixture diminishes (A) considerably. With the following reaction vessels, the % (A) diminishes thus: glass $>$

$\text{Cu} >$ steel or brass. The rate (k) of alcoholysis of various $\text{COMe}\cdot\text{CHR}\cdot\text{COR}'$ is measured by interrupting the reaction before completion and determining the amounts and ratio of the products formed; reactions are carried out in glass (in which k is $<$ in brass vessels). The effects of R and R' on k and (A) are discussed. Some of the results are correlated with the polar effects of the substituent groups and the mechanism previously given (A., 1934, 759). H. B.

Hydrogenation and hydrogenolysis of $\alpha\gamma$ -diketones. J. M. SPRAGUE and H. ADKINS (J. Amer. Chem. Soc., 1934, **56**, 2669—2675).—Reduction [H_2 (usually 1.6–1.9 mols.) at 150 – 200 atm.; Raney Ni ; Et_2O] of $\text{COR}\cdot\text{CH}_2\cdot\text{COR}'$ (A) at 125° and $\text{COR}\cdot\text{CHAlk}\cdot\text{COR}'$ (B) at 50 – 60° usually gives a good yield of the corresponding glycols. In several cases fission (hydrogenolysis) of $\text{C}\cdot\text{C}$ (leading to, e.g., $\text{RCHO} + \text{COR}'\cdot\text{CH}_2\text{Alk}$ and/or their reduction products) and $\text{C}\cdot\text{O}$ (giving e.g., $\text{COR}\cdot\text{CH}_2\cdot\text{CH}_2\text{R}'$ and/or $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CH}_2\text{R}'$) occurs. Definite conclusions could not be reached regarding $\text{C}\cdot\text{C}$ fission and the enol content of (A) and (B). The order of facilitation (as determined by temp. required) of $\text{C}\cdot\text{C}$ fission by various groups is: $\text{Me} > \text{Et} > \text{Pr}^s > \text{Bu}^r > \text{Ph}$, 2-furyl $>$ $\text{OH} > \text{O} > \text{CH}_2\cdot\text{OH} > \cdot\text{CHR}\cdot\text{OH} > \cdot\text{COR}$. The relative labilities of the 2 $\text{C}\cdot\text{C}$ linkings in (A) appear to be the same in alcoholysis, hydrolysis, or hydrogenolysis.

CH_2Ac_2 is thus reduced to pentane- $\beta\delta$ -diol (80%) and $\text{EtOH} + \text{Pr}^s\text{OH}$; $\text{CH}_2\text{Ac}\cdot\text{COPr}^s$ gives (at 25°) EtOH , β -methylhexane- $\gamma\epsilon$ -diol (I) (73%), b.p. 123 – $124^\circ/24$ mm., and (probably) β -methyl- Δ^8 -hexen- γ -one (9.6%), b.p. 135 – 139° [semicarbazone, m.p. 180 – 190° (decomp.)], whilst at 125° , (I) (60%) and COPr^aPr^s (30%) result; $\text{CH}_2\text{Ac}\cdot\text{COBu}^r$ affords (at 60°) EtOH , COMeBu^r (5.4–6.7%), $\beta\beta$ -dimethyl- Δ^8 -hexen- γ -one (16.3–62%), b.p. 153 – 155° [oxidised (KMnO_4) to $\text{CMe}_3\cdot\text{CO}_2\text{H}$; dibromide, b.p. 102 – $104^\circ/10$ mm., m.p. 31 – 32°], $\beta\beta$ -dimethylhexan- ϵ -ol- γ -one (15–68%), b.p. 89 – $90^\circ/22$ mm., and $\beta\beta$ -dimethylhexane- $\gamma\epsilon$ -diol (17–52%), b.p. 108 – $109^\circ/11$ mm., m.p. 61 – 62° according to H_2 absorbed (1–1.6 mols.); acetylisovaleryl-methane yields 77% of β -methylheptane- $\delta\epsilon$ -diol (II), b.p. 114 – $116^\circ/9$ mm., at 85° and (II) (44%) and COPr^aBu^s (42%) at 125° ; hexahydrobenzoylacetylmethane furnishes cyclohexyl Pr ketone (38%) and α -cyclohexylbutane- $\alpha\gamma$ -diol (47%), b.p. 163 – $167^\circ/21$ mm.; furoyl- and tetrahydrofuroyl-acetylmethane give 73 and 92%, respectively, of α -tetrahydrofurylbutane- $\alpha\gamma$ -diol, b.p. 160 – $163^\circ/24$ mm.; *p*-phenylbenzoylacetylmethane affords 57% of α -*p*-cyclohexylphenylbutan- γ -ol, b.p. 140 – $144^\circ/2$ mm. [oxidised to *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$]; 2:4:6-trimethylbenzoylacetylmethane yields *n*-butyrylmesitylene (79%), b.p. 132 – $136^\circ/10$ mm., and α -2:4:6-trimethylphenylbutane- $\alpha\gamma$ -diol (12%), b.p. 177 – $179^\circ/7$ mm.; CH_2BzAc furnishes PhBu^a (3.7%), $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ (40%), and α -phenylbutane- $\alpha\gamma$ -diol (50%); CHEtBzAc gives PhCHO (25%), COMePr (43.7%), COPhPr (11.3%), and α -phenyl- β -ethylbutane- $\alpha\gamma$ -diol (32.3%), b.p. 170 – $173^\circ/12$ mm.; α -benzoyl- α -acetylpentane affords PhCHO (25%), Me (35%) and Ph (18%) *n*-amyl ketones, and α -phenyl- β -*n*-butylbutane- $\alpha\gamma$ -diol (40.5%), b.p. 186 – $191^\circ/14$ mm.; α -benzoyl- α -acetyloctane

yields PhCHO (18%), Me (20%) and Ph (20%) *n*-octyl ketones, and α -phenyl- β -*n*-heptylbutane- α - γ -diol (50%), b.p. 197—202°/8 mm.; α -benzoyl- α -acetyl- β -phenylethane furnishes PhCHO (24%). CH₂Ph·CH₂·COMe (III) (48%), CH₂Ph·CH₂·COPh (20·5%), and α -phenyl- β -benzylbutane- α - γ -diol (30·5%), b.p. 182—187°/2 mm.; α -diacetyl- β -phenylethane gives (III) (40%) and γ -benzylpentane- β - δ -diol (46%), b.p. 140—143°/2·5 mm.; CH₂EtAc₂ affords EtOH, COMePr (10%), unsaturated material (9%), b.p. 154—157°, and γ -ethylpentane- β - δ -diol (64%), b.p. 205—210°; CH₂EtBz₂ yields PhCHO (14%), COPhPr (15%), and α - γ -diphenyl- β -ethylpropane- α - γ -diol (80%), b.p. 190—196°/3 mm.; benzoyl-2 : 4 : 6-trimethylbenzoylmethane furnishes PhCHO, acetylmesitylene (25%), and β -phenylpropionylmesitylene (70·8%), b.p. 168—172°/1·5 mm.; benzoylfuroylmethane gives CH₂Ph·OH and 28 and 30%, respectively, of γ -phenyl- α -tetrahydrofurylpropan- α -ol, b.p. 128—130°/1 mm., and α - γ -diol, b.p. 170—171°/2 mm.; methone (5 : 5-dimethyldihydroresorcinol) affords 3 : 3-dimethylcyclohexanol (3·8%) (phenylcarbamate, m.p. 90—91°) and 80% of two stereoisomeric 5 : 5-dimethylcyclohexane-1 : 3-diols, m.p. 102—104° and 146°; CH₂Bz₂ yields COPhMe, CH₂(CH₂Ph)₂ (11%), and α - γ -diphenylpropan- α -ol (20%) and α - γ -diol (51%). α -Tetrahydrofurylbutan- γ -ol has b.p. 120·5—123°/22 mm., 221—223°/740 mm.

H. B.

Purification of α -D-xylose and its mutarotation. H. S. ISBELL (J. Res. Nat. Bur. Stand., 1934, 13, 515—517).—The dark-coloured xylose syrup obtained from cottonseed hulls may be purified by treatment with decolorising C (I) and basic Pb acetate in slight excess with kieselguhr to collect the ppt. The filtrate is treated with H₃PO₄ to remove most of the excess of Pb, then with H₂S to ppt. the remainder; after another treatment with (I) the nearly colourless solution obtained yields crystals of pure α -D-xylose (II) on evaporation and slow rotation over-night. (II) has $[\alpha]_D^{20} + 94·8^\circ$ (initial; extrapolated), $+ 78·7^\circ$ (after 5 min.), $+ 18·3^\circ$ (after 24 hr.). The mutarotation coeff. is $>$ the accepted val. of 0·0207 during the first 5 min., but remains const. at this val. thereafter.

A. R. P.

Mechanism of Walden inversion in sugars. Inversion of rhamnose *p*-toluenesulphonates. I. E. MUSKAT (J. Amer. Chem. Soc., 1934, 56, 2653—2656).—Walden inversion is most likely to occur in reactions involving removal of one of the groups (attached to the asymmetric C) with the bonding electron pair, e.g., alkaline hydrolysis of *p*-toluenesulphonates. The occurrence of inversion during hydrolysis of, e.g., 5 : 6-anhydro-1 : 2-isopropylidene-glucofuranose is probably due to fission at C₅·O, thus leaving C₅ positively charged; subsequent addition of H₂O gives the normal or inverted (according to steric effects and experimental conditions) sugar. Hydrolysis (aq. MeOH-KOH at 74°) of 2 : 3-isopropylidenemethylrhamnopyranoside 5-*p*-toluenesulphonate (A, 1934, 1207) gives a little (II) (below) and (mainly) 2 : 3-isopropylidenemethyl-6-deoxy-D-gulofuranoside, b.p. 100°/1 mm., $[\alpha]_D^{25} - 16·9^\circ$ in MeOH (*p*-toluenesulphonate, m.p. 60°, $[\alpha]_D^{25} + 22·3^\circ$ in MeOH), which is hydrolysed (1% H₂SO₄) to 6-deoxy-D-gulose,

P

m.p. about 65°, $[\alpha]_D^{25}$ (in H₂O) $+ 14^\circ \rightarrow -14^\circ$ [*p*-bromophenylhydrazone, m.p. 162°, $[\alpha]_D^{25}$ (in EtOH) $-6·1^\circ \rightarrow +13^\circ$]. (I) and aq. MeOH-KOH at 100° (bath) afford (probably) 2 : 3-isopropylidenemethyl-1 : 5 : 6-mannofuranoside (II), b.p. 80°/3 mm., $[\alpha]_D^{25} + 14^\circ$ in MeOH. 2 : 3-isoPropylidenemethyl-6-deoxy-1-talopyranoside, b.p. 90°/0·8 mm., $[\alpha]_D - 15·5^\circ$ in MeOH (*p*-toluenesulphonate, m.p. 76·5°, $[\alpha]_D + 3·1^\circ$ in MeOH), is similarly obtained by hydrolysis of 2 : 3-isopropylidenemethylrhamnopyranoside *p*-toluenesulphonate, m.p. 57°, $[\alpha]_D + 14^\circ$ in MeOH. H. B.

Vacciniin and other monobenzoylglucoses. P. BRIGL and W. ZERRWECK (Z. physiol. Chem., 1934, 229, 117—124).—Elimination of mercaptan by HgCl₂ in aq. EtOH in presence of BaCO₃ from glucose Et₂ mercaptal 6-benzoate affords glucose 6-benzoate (I) (phenylhydrazone, m.p. 136°; -osazone, m.p. 141°). (I) is identical with vacciniin isolated from cranberries (Griebel, A., 1910, ii, 440). (I) yields a β -Ac₄ derivative, m.p. 133°, converted by ZnCl₂-Ac₂O into α -glucose 6-benzoate 1 : 2 : 3 : 4-tetra-acetate, m.p. 136°. 4 : 6-Benzylideneglucose with BzCl in C₅H₅N gives a mixture of its 1-benzoate, β -2-benzoate (II), m.p. 200—201°, $[\alpha]_D - 8·4^\circ$ in COMe₂ ($+43^\circ$ in presence of NH₃) [1 : 3-Ac₂ derivative, m.p. 204°, $[\alpha]_D + 14·6^\circ$ in CHCl₃ (β -form, $[\alpha]_D - 80·4^\circ$ in CHCl₃), 3-benzoate (III), m.p. 177°, $[\alpha]_D - 5·3^\circ \rightarrow 27·7^\circ$ (mutarotation) in COMe₂. (II) on catalytic hydrogenation (Pd) yields glucose 2-benzoate, m.p. 182°, $[\alpha]_D + 62·9^\circ$ in H₂O (Ac₄- α -derivative, m.p. 186°, $[\alpha]_D + 5·18^\circ$ in CHCl₃). Similarly (III) affords β -glucose 3-benzoate (Ac₄- β -, m.p. 156°, $[\alpha]_D + 13·1^\circ$ in CHCl₃, and - α , m.p. 118°, $[\alpha]_D + 66·7^\circ$ in CHCl₃, derivatives), also obtainable from diisopropylideneglucose 3-benzoate. β -Glucose 1 : 2 : 3 : 6-tetra-acetate with BzCl in C₅H₅N affords the β -4-benzoate, m.p. 177°, $[\alpha]_D - 31·0^\circ$ in CHCl₃, yielding the α -form, m.p. 93°, $[\alpha]_D + 41·9^\circ$ in CHCl₃.

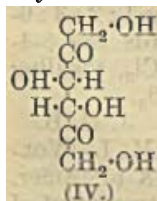
J. H. B.

Tritylation of sugar mercaptals. M. L. WOLFROM, J. L. QUINN, and C. C. CHRISTMAN (J. Amer. Chem. Soc., 1934, 56, 2789).—Successive treatment of *D*-glucose Et mercaptal with CPh₃Cl and BzCl in C₅H₅N gives 6-triphenylmethylglucose Et mercaptal tetrabenzoate, m.p. 161—162°, $[\alpha]_D + 49^\circ$ (all rotations are in U.S.P. CHCl₃), converted (HBr) into the 6-Br-derivative, m.p. 169—170°, $[\alpha]_D + 39^\circ$ [also prepared by benzoylation of 6-bromoglucose Et mercaptal (Fischer *et al.*, A., 1920, i, 529)], and thence (NaI in COMe₂) into the 6-I-derivative, m.p. 165—166°, $[\alpha]_D + 39^\circ$. Successive treatment of this with AgNO₃ (in dil. COMe₂) and HgCl₂+CdCO₃ (in moist COMe₂) affords the glucopyranose tetrabenzoate of Fischer and Noth (A., 1918, i, 225); migration of Bz has, therefore, occurred. 6-Triphenylmethylgalactose Et mercaptal tetra-acetate, m.p. 123—124°, $[\alpha]_D - 22·5^\circ$ (the tetrabenzoate has m.p. 138—139°, $[\alpha]_D - 22·5^\circ$) (cf. Micheel and Spruck, A., 1934, 1338), is converted (HBr) into the 6-OH-derivative, m.p. 96—97°, $[\alpha]_D - 7^\circ$ (removal of SEt groups from which gives the galactose 2 : 3 : 4 : 5-tetra-acetate hydrate of Micheel and Suckfull (A., 1933, 596)], or the 6-Br-derivative, m.p. 110—111°, according to the con-

ditions used. 6-Triphenylmethylgalactose tetra-acetate (+EtOH) has m.p. 153°, $[\alpha]_D -28^\circ$. Triphenylmethyl-L-arabinose and -D-xylose Et mercaptal triacetates have m.p. 101–102°, $[\alpha]_D -24^\circ$ and m.p. 149–150°, $[\alpha]_D -20.5^\circ$, respectively. H. B.

Application of the principle of optical superposition in ketose series. Preparation of the true α -fructose (2:6)penta-acetate. E. PACSU (J. Amer. Chem. Soc., 1934, 56, 2788).—Partial Walden inversion occurs at C₂ during replacement of the Cl in β -chlorofructose (2:6)tetra-acetate by OAc (using NaOAc in boiling Ac₂O); a mixture of α -fructose (2:6)penta-acetate, m.p. 122–123°, $[\alpha]_D +47.4^\circ$ in CHCl₃, and the β -isomeride is obtained. The sp. rotations of the α -derivatives can now be calc. (cf. Hudson, A., 1924, i, 372). The calc. and observed vals. for α -methylfructoside tetra-acetate (Schlubach and Schröter, A., 1928, 873) are in close agreement, thus supporting the validity of the principle of optical superposition in the ketose series. H. B.

A fermentable diketose, 5-ketofructose (5-fructonose). F. MICHEEL and K. HORN (Annalen, 1934, 515, 1–10).— β - γ -Di(methylenedioxy)- $\Delta^{\alpha\alpha}$ -hexadiene (I), $[\alpha]_D^{25} +280.3^\circ$ in CHCl₃ (A., 1932, 834), and BzO₂H (≈ 2.04 O) in CHCl₃ at about 0° give a non-cryst. mixture (A) of the α -mono- and α -di-benzoates of $\alpha\alpha$ -tetrahydroxy- β - γ -di(methylenedioxy)hexane; hydrolysis (5% H₂SO₄) of (A) affords some 5-fructonose 1:6-dibenzoate (II), m.p. 155°, $[\alpha]_D^{25} -99.3^\circ$ in EtOH. Hydrolysis (H₂O) of the product from (I) and Pb(OAc)₄ in C₆H₆ gives 5-fructonose 1:6-diacetate dihydrate, m.p. 75° (sinters at 65°), $[\alpha]_D^{25} +79.4^\circ$ in EtOAc, and (mainly) a syrup (III). Hydrolysis (MeOH-NaOMe in CHCl₃ at 20°) of (III) affords the amorphous 5-fructonose (IV), $[\alpha]_D -29.7^\circ$ in H₂O [bisphenylosaz-



one, m.p. 198° (decomp.), $[\alpha]_D^{25}$ (in C₅H₅N) $+20.8^\circ \rightarrow -9.3^\circ$; bis-*p*-nitrophenylhydrazone, m.p. 220° (decomp.), also isolable (less satisfactorily) from the hydrolysis products accompanying (II). (IV) reduces Fehling's solution in the cold. (IV) is fermented by yeast in phosphate buffer (p_H 6.64) with the production of 1 mol. of CO₂; the rate is about $\frac{1}{3}$ that of glucose. Oxidation (O₃ in AcOH) of (I) and subsequent hydrolysis (H₂O) gives *l*-tartaric acid. γ -Dihydroxy- $\beta\epsilon$ -diketohexane (*loc. cit.*) (bis-*p*-nitrophenylhydrazone, m.p. 208°, $[\alpha]_D^{25} -1101^\circ$ in C₅H₅N; di-*p*-nitrobenzoate, m.p. 155°, $[\alpha]_D^{25} +137.9^\circ$ in CHCl₃) has m.p. 77°, $[\alpha]_D^{25} +106^\circ$ in H₂O. H. B.

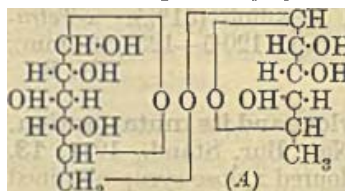
Configuration of digitalose. O. T. SCHMIDT and H. ZEISER (Ber., 1934, 67, [B], 2127–2131).—Successive treatment of the dicarboxylic acid, obtained by the oxidation of digitalose, with CH₂N₂ and MeI-Ag₂O leads to Me₂ 1-(arabo)-trimethoxyglutarate, b.p. 69–69.5°/0.003 mm., $[\alpha]_D^{25} +29.6^\circ$ in MeOH [corresponding di(methylamide), m.p. 173–174°, $[\alpha]_D^{25} +59.4^\circ$ in H₂O]. The bearing of this result on the configuration of digitalose is discussed. H. W.

Methylation of sorbose and of its acetyl derivatives by Fischer's method. G. ARRAGON (Compt. rend., 1934, 199, 1231–1233).—Sorbose with MeOH-0.5% HCl at 0°, 20°, or 37° affords methyl-

sorboside (I); the yield decreases at higher temp., when a hygroscopic syrup is a by-product (cf. A., 1895, i, 437). Sorbose tetra- or penta-acetate as above gives (I), but methylsorboside tetra-acetate is not de-acetylated under these conditions, or in presence of more HCl. * J. L. D.

β -Glucoseptose and its mutarotation. H. S. ISBELL (J. Amer. Chem. Soc., 1934, 56, 2789–2790).— β -Glucoseptose, m.p. 121°, $[\alpha]_D^{25}$ (in H₂O) -1.4° (1.3 min.) $\rightarrow -5.93^\circ$ (18 min.) $\rightarrow -0.13^\circ$ (24 hr.), prepared by reduction (Na-Hg) of β -glucoseheptono- γ -lactone, is obtained cryst. The mutarotation resembles that of ribose (A., 1934, 494). H. B.

Action of mercury salts on acetohalogenosugars. IX. Synthesis of derivatives of β -1-l-rhamnosido-6-d-glucose. G. ZEMPLÉN and A. GERECs. X. Synthesis of derivatives of the presumed β -1-d-glucosido-2(or 3)-d-glucose. G. ZEMPLÉN and Z. CSÜROS (Ber., 1934, 67, [B], 2049–2051, 2051–2053; cf. A., 1931, 1400).— α -Acetobromo-L-rhamnose, $[\alpha]_D^{20} -165.0^\circ$ in CHCl₃ (from rhamnose tetra-acetate and TiBr₄ in CHCl₃), is transformed by 1-chloroglucose 2:3:4-triacetate and Hg(OAc)₂ in C₆H₆ at 50° into chloro- β -1-l-rhamnosido-6-d-glucose hexa-acetate, m.p. 142–143° after softening at 133°, $[\alpha]_D^{24} +70.86^\circ$ in CHCl₃, converted by AgOAc and Ac₂O into the corresponding hepta-



acetate (cf. A), m.p. 168–169°, $[\alpha]_D^{24} -29.66^\circ$ in CHCl₃, which does not give a cryst. product when hydrolysed by NaOMe.

X. 6-Bromo-1- β -methylglucose, acetodibromoglucose, and Hg(OAc)₂ in C₆H₆ yield 6:6'-dibromo-1- β -methyl-1-d-glucosido-d-glucoside penta-acetate (I), m.p. 237° with subsequent darkening and decomp., $[\alpha]_D^{25} -18.1^\circ$ in CHCl₃, in very small amount. (I) is transformed by NaI in COMe₂ at 100° into 6:6'-di-iodo-1'- β -methyl-1-d-glucosido-d-glucoside penta-acetate, m.p. 222° (slow decomp.), $[\alpha]_D^{25} -6.7^\circ$ in CHCl₃, which is not identical with Helferich's 6:6'-di-iodo-1- β -methylcellobiose penta-acetate. (I) is therefore regarded as derived from β -1-d-glucosido-2(or 3)-d-glucose. H. W.

Physico-chemical properties of lactose. II. Factors influencing the crystalline habit of lactose. IV. Influence of salts and acids on the mutarotation velocity of lactose. B. L. HERRINGTON (J. Dairy Sci., 1934, 17, 533–542, 659–670; cf. A., 1934, 1168, 1174).—II. The form and growth of lactose (I) crystals is largely influenced by the ratio of the concn. of the solution to the solubility. The effect of sucrose is not sp., but results from its pptg. action on (I). Both the α -hydrate and β -anhydride form needle crystals if crystallisation is very rapid.

IV. The accelerated mutarotation (*M*) of lactose by ions other than H⁺ and OH⁻ is attributable to general acid and base catalysis, in which the influence of weak acids is much > that of weak bases. The catalytic effect of lactate ions is small in concns. <

0.1*N*, but increases rapidly above this. An empirical relationship between the velocity of *M* and *p_H* is established.

A. G. P.

Preparation and enzymic fission of basic glycosides. II. B. HELFERICH and F. PHILIPP (Annalen, 1934, 514, 228—233).—*m*-Cresol- β -*D*-glucoside tetra-acetate (I), m.p. 137—139° (corr.), $[\alpha]_D^{20}$ -19.61° in CHCl_3 , obtained by the method previously described (A., 1933, 379) from *m*-cresol, glucose penta-acetate, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ at 100°, is brominated (method: A., 1934, 282) to ω -bromo-*m*-cresol- β -*D*-glucoside tetra-acetate, m.p. 122—124° (corr.), $[\alpha]_D^{20}$ -20.4° in CHCl_3 , which is converted (aq. $\text{EtOH}\cdot\text{NH}_3$; cf. *loc. cit.*) into *m*-aminomethylphenol- β -*D*-glucoside (II), m.p. 196.5—199° (corr.), $[\alpha]_D^{20}$ -68.52° in aq. AcOH (1 mol.). The *Ac*₂ derivative, m.p. 96—97° (corr.), $[\alpha]_D^{25}$ -19.95° in CHCl_3 , of (II) is hydrolysed (*N*- NaOH in COMe_2) to *m*-acetamidomethylphenol- β -*D*-glucoside (III), m.p. 176—177° (corr.), $[\alpha]_D^{25}$ -62.6° in H_2O , whilst (I) is hydrolysed [$\text{MeOH}\cdot\text{NaOMe}$ (trace)] to *m*-cresol- β -*D*-glucoside (IV), m.p. 183—184° (corr.), $[\alpha]_D^{25}$ -69.7° in H_2O . *m*-Cresol- β -*D*-galactoside (V), m.p. 166—168°, $[\alpha]_D^{18}$ -44.3° in H_2O , and its tetra-acetate, m.p. 81—83°, $[\alpha]_D^{25}$ +2.7° in CHCl_3 , are similarly prepared. (III) is hydrolysed (emulsin) much more rapidly than the *o*- and *p*-isomerides (A., 1934, 282) and (II) (and its *o*- and *p*-isomerides); (IV) is hydrolysed more rapidly than (V) but less rapidly than its *o*-isomeride (*loc. cit.*). H. B.

Polysaccharides. XVIII. **Constitution of xylan.** W. N. HAWORTH, E. L. HIRST, and E. OLIVER (J.C.S., 1934, 1917—1923; cf. A., 1932, 44).—Xylan (I) (from esparto celluloses of different origin) on hydrolysis gives arabinose; on methylation and subsequent hydrolysis it gives 2 : 3-dimethylxylopyranose (90%), 2 : 3 : 5-*l*-arabofuranose (about 6%), and a monomethylxylose (II). (I) therefore contains an *l*-arabofuranose unit (*A*) as a terminal group attached to a chain of xylopyranose units (*B*) (one of *A* is associated with 18—20 of *B*). The nature of the other terminal group, which is not CO_2H (cf. A., 1932, 934), is discussed with regard to the facts that the above cleavage products contain (II) but no trimethylxylose, and that (I) is non-reducing.

H. G. M.

Crystalline erythrodextrin.—See this vol., 133.

Reaction of starches with proteins.—See this vol., 165.

Determination of the carboxyl groups of cellulose by conductometric titration. E. SCHMIDT, M. HECKER, W. JANDEBEUR, and M. ATTERER [with W. SIMSON and R. SCHNEGG] (Ber., 1934, 67, [B], 2037—2049).—Cellulose is treated with an excess of NaOH in presence of Humectol and conductometrically titrated with 0.1*N*-acid. The graph consists of 3 sections, the first representing the neutralisation of the excess of NaOH , the second depicting the liberation of the cellulose acid from its Na salt, and the third being due to the further addition of HCl . The validity of the process is established by comparative experiments with lauric, palmitic, cholic, and anthraquinone-2-carboxylic acids and with pentaerythritol, β -glucosan, mannitol, α -methyl-

glucoside, sucrose, raffinose, and lævulan. Native cellulose (I) contains 0.282% of CO_2H ($\pm 1.4\%$). The possibility that (I) adsorbs NaOH is excluded by the observations that (1) the results are independent of the temp. between 0° and 25°; at $> 25^\circ$ the data are influenced by evaporation of the H_2O ; (2) identical results are obtained in presence or absence of Humectol *CA*; (3) identical results are obtained with (I) from cotton wool in fibrous form or as powder after pptn. from $\text{CuO}\cdot\text{NH}_3$ or from cellulose *B* crushed or as powder. Since the vals. obtained by the titration of (I) with *N*/44- NaOH in presence of thymolphthalein accord with those obtained conductometrically, the hypothesis that the Na salt of (I) is decomp. by excess of NaOH into celluloses containing less CO_2H cannot be maintained. In the direct titration only ash-free cellulose can be used. The electro-dialysis of cellulose is described; the products contain 0—0.6% of ash which does not influence the conductometric process. H. W.

Osmometric investigation of dilute solutions of polymeric carbohydrates. VI. Mol. wt. of crystalline cellulose acetates. II. K. HESS and M. ULMANN (Ber., 1934, 67, [B], 2131—2145; cf. A., 1934, 841).—Limit dextrin acetate I (I) is as resistant to fractionation as the corresponding II (II) derivative (*loc. cit.*), which it resembles very closely in composition and röntgenographic behaviour, whilst differing somewhat in optical activity. Osmometric measurements establish a step-wise degradation of (I) from even multiples of $(\text{C}_6)_2$ to $(\text{C}_6)_2$ dependent on the concn., but the simpler forms persist at a higher concn. in the case of (I) than of (II). The stepwise transitions of (I) occur with measurable rapidity which is greater than with (II). A further difference is found in the occurrence of the $(\text{C}_6)_4$ stage in the case of (I), whereas with (II) $(\text{C}_6)_2$ appears to pass immediately and reversibly into $(\text{C}_6)_8$. In contrast to (II), the electrolytic conductivity of (I) increases with dilution at concn. $> 0.1\%$ and in this region solutions of (I) do not follow van 't Hoff's law; it is considered that at this dilution a complex of (I) and solvent dissociates into ions. In this respect (I) resembles cellobiose acetate. The behaviour of an early fraction obtained in the purification of (II) is less clearly defined than that of (II) over the whole region of concn. in consequence of adherent impurities. H. W.

Acetylation of cellulose. D. KRUGER, M. LUDTKE, and F. OBERLIES (Angew. Chem., 1934, 47, 806—810).—When lower acetates of cellulose (I) ($< 3\text{Ac}$ per $\text{C}_6\text{H}_{10}\text{O}_5$) are prepared using feebly catalysed acetylating mixtures, all the chain mols. of (I) are equally acetylated. When a strongly catalysed mixture is used, the rate of reaction is fast compared with the rate of diffusion into micelles, and the exposed chain mols. are preferentially acetylated; if the process is interrupted before equilibrium is reached the material is micro-heterogeneous. A. G.

Cellulose diacetate. I. SAKURADA and T. KITABATAKE (J. Soc. Chem. Ind. Japan, 1934, 37, 604—605B).—Cellulose 2 : 3-diacetate was prepared by protecting the primary OH with $\cdot\text{CPh}_3$ from acetylation. Treatment with CPh_3Cl showed that $\frac{1}{3}$ of the free OH

groups in commercial COMe_2 -sol. cellulose diacetate were primary, and hence that Ac was equally easily eliminated from each of three positions 2, 3, and 6.

A. G.

Thioanhydrides of cellulosexanthic acid. S. N. DANILOV and D. S. BROCHINA (J. Gen. Chem. Russ., 1934, 4, 995—1002).— BzCl and Na cellulosexanthate (I) in aq. Na_2CO_3 or C_6H_6 afford the *thioanhydride* of (I), which eliminates H_2S in acid, and regenerates (I) in alkaline solutions.

R. T.

Asymmetric nitrogen atom. LX. Optical activity of ammonium salts as a means of detection of double decomposition in non-ionising solvents. E. WEDEKIND (Ber., 1934, 67, [B], 2007—2009).—The optical activity of $\text{I-NPhMcPr}^+(\text{CH}_3\text{Ph})\cdot\text{NO}_3$ in CHCl_3 (in which it is optically stable when alone) gradually diminishes after addition of an inactive NH_4 halide. The rate of decay of the optical activity of the corresponding inherently unstable halides is retarded by the addition of nitrate to a labile limiting val. The occurrence of an equilibrium active nitrate (optically stable) + halide

active halide (optically unstable) + nitrate is supported by the concurrence of fall in $[\alpha]$ with diminution of halogen titre. Similar results are obtained with active phenylbenzylmethylallyl-ammonium nitrate (I) and inactive NPhMe_2EtI . The optical activity of (I) in CHCl_3 is not affected by EtI .

H. W.

Action of secondary amines on epichlorohydrin. N. S. DROZDOV and O. M. TSCHERNTZOV (J. Gen. Chem. Russ., 1934, 4, 969—974).—Epichlorohydrin (I) and aq. NHEt_2 at $28-30^\circ$ give *diethyl-aminoepihydrin* (65% yield), b.p. $55-60^\circ/15$ mm., which when heated at 100° for 30 min. with $\text{MeOH}\cdot\text{NH}_3$ gives 70% yields of $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NEt}_2$, b.p. $118-123^\circ/15$ mm. (I) and aq. NHMe_2 at 30° afford a *polymeride*, charring at 210° , of dimethyl-aminoepihydrin, whilst piperidine and (I) give *piperidinoepihydrin* (70% yield), b.p. $86.5-88^\circ/15$ mm., from which γ -amino- α -N-piperidino- β -hydroxypropane, b.p. 133° , is obtained as above.

R. T.

Glutathione. Its reaction with alkali and some N- and S-derivatives. B. C. SAUNDERS (Biochem. J., 1934, 28, 1977—1981).—The abnormal reaction of glutathione (I) and CH_2PhCl in presence of NaOH is due to oxidation of (I) and dismutation of the product to give (I) and higher oxidation products together with H_2S and S. (I) with $1:2:4\text{-C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ in alkaline solution gives cryst. *S-2:4-dinitrophenyl-glutathione* (II), m.p. 211° , which with $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_2\text{Cl}$ gives *N-naphthalene-2-sulphonyl-S-2:4-dinitrophenyl-glutathione*, m.p. 158° . *S-2:4-Dinitrophenylcysteine*, m.p. $148-154^\circ$, is similarly prepared.

C. G. A.

Esters of ethylene- $\alpha\beta$ -dioxamic acid and its derivatives. J. VAN ALPHEN and (in part) H. DEN OTTER (Rec. trav. chim., 1934, 53, 1159—1166).—Dropwise addition of $(\cdot\text{CH}_2\cdot\text{NH}_2)_2$ hydrate to $\text{R}_2\text{C}_2\text{O}_4$ ($\text{R}=\text{Me}$ or Et) in abs. EtOH affords a starch-like substance (not ethyleneoxamide) and Me_2 (I), m.p. 168° , or Et_2 (II), m.p. 129° , *ethylene- $\alpha\beta$ -dioxamate* ($\text{CO}_2\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot$), converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling EtOH into the *dihydrazide*, m.p. 295° (decomp.

with resolidification) (block), which with the appropriate aldehyde gives its *dibenzylidene*, decomp. $>360^\circ$, *difurfurylidene*, m.p. $>360^\circ$, and *disopropylidene*, decomp. 330° (block), derivatives. With 1 mol. of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (II) gives its *monohydrazide*, m.p. 179° (decomp. with resolidification), from which the *mono-benzylidene*, m.p. 229° , *-anisylidene*, m.p. 229° , *-piperonylidene*, m.p. 254° , and *-furfurylidene*, m.p. 247° , derivatives are obtained. (I) similarly affords its *monohydrazide*, decomp. 220° . With the appropriate NH_2R in boiling aq. EtOH (II) gives a *monoamide*, m.p. 211° , and *monomethylamide*, m.p. 207.5° [*hydrazide*, m.p. 305° (*benzylidene* derivative, m.p. 335°)].

J. W. B.

Reaction of aliphatic diazo-compounds with mercury salts. A. N. NESMEJANOV and G. S. POVCH (J. Gen. Chem. Russ., 1934, 4, 958—961).— Et diazoacetate and HgCl_2 yield $\text{CH}_3\text{Cl}\cdot\text{CO}_2\text{Et}$, N_2 , and $\text{Hg}[\cdot\text{CCl}(\text{HgCl})\cdot\text{CO}_2\text{Et}]_2$.

R. T.

Constitution of thiosemicarbazide compounds of nickel. K. A. JENSEN (Z. anorg. Chem., 1934, 221, 11—17).—The compounds $\text{Ni}(\text{COSN}_2\text{H}_3)_2$, $\text{Ni}(\text{CS}_2\text{N}_2\text{H}_3)_2$, and $[\text{Ni}(\text{OEt}\cdot\text{CS}\cdot\text{N}_2\text{H}_3)](\text{NO}_3)$. (I) have been prepared from $\text{SH}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$, $\text{SH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, and $\text{OEt}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$, respectively. The similarity of these to thiosemicarbazide compounds previously obtained confirms the formula in which the metal is bound to S and the N_2H_4 group. The aq. solution of (I) gives with NH_3 the compound $\text{Ni}(\text{OEt}\cdot\text{CS}\cdot\text{N}_2\text{H}_3)_2$. $[\text{Ni}(\text{SCN}_3\text{H}_5)_2]\text{SO}_4$ has been obtained in two different modifications which may be *cis*- and *trans*-isomerides.

M. S. B.

Thiosemicarbazide compounds of bivalent palladium and platinum. K. A. JENSEN (Z. anorg. Chem., 1934, 221, 6—10).—The following compounds have been prepared: ($\text{M}=\text{Pd}$ or Pt ; $\text{T}=\text{CSN}_3\text{H}_5$), $[\text{MTCl}_2]$, $[\text{MT}_2]\text{Cl}_2$, $[\text{MT}_2]\text{SO}_4$, and $\text{M}(\text{CSN}_3\text{H}_5)_2$. $[\text{PdT}_2]\text{Cl}_2$ and $\text{Pd}(\text{CSN}_3\text{H}_5)_2$ have differently coloured *cis*- and *trans*-modifications.

M. S. B.

Varying valency of platinum with respect to mercaptanic radicals. VIII.—See this vol., 182.

Mercury alkyl derivatives. M. C. HART and H. P. ANDERSEN (J. Amer. Chem. Soc., 1934, 56, 2752—2753).—The following are prepared from $\text{HgAlk}\cdot\text{OH}$ and the acid or phenol in EtOH : HgEt salts of *o*-, m.p. $75-76^\circ$, and *p*-, m.p. $177-178^\circ$, $\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, PhOH , m.p. $115-116^\circ$, $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, m.p. $78-79^\circ$, *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$, m.p. $54.5-55.5^\circ$, *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, m.p. $191-192^\circ$ (also formed from *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$), *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, m.p. $72-73^\circ$, *p*-hydroxy-, m.p. $139-140^\circ$, and $4:4'$ -dihydroxy-, m.p. $201-203^\circ$, *p*-diphenyl, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ (?), m.p. $85.5-86.5^\circ$, $\text{C}_6\text{H}_5\text{I}_3\cdot\text{OH}$, m.p. $169-170^\circ$, $\text{C}_6\text{H}_5\text{Br}_3\cdot\text{OH}$, m.p. 107° , $\text{C}_6\text{H}_5\text{Cl}_3\cdot\text{OH}$, m.p. $60-61^\circ$, *o*- and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$, both m.p. $98-99^\circ$, chlorocyclohexylphenol, m.p. $79.5-80.5^\circ$, 5-chloro-2-hydroxydiphenyl, m.p. $101-102^\circ$, vanillin, m.p. $100-101^\circ$, 3-nitro-*p*-cresol, m.p. $89-90^\circ$, *o*-, m.p. $76-77^\circ$, and *p*-, m.p. $122-123^\circ$, $\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, chlorothymol, m.p. $81-82^\circ$, *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. $81-82^\circ$, *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, 6-chloro-*m*-cresol, m.p. $77.5-78.5^\circ$, *o*-, m.p. $83-84^\circ$, and *p*-, m.p. 108° , $\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, phenolphthalein, m.p. $198-199^\circ$, *o*-cresolsulphone-

phthalcin, m.p. 128—131°, phenolsulphonophthalein, m.p. 118—121°, and thymolsulphonophthalein, m.p. 145—155°; *HgMe* salts of $m\text{-C}_6\text{H}_4(\text{OH})_2$, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 119—120°, and *m*-cresol m.p. 84—86°; *HgPr* salts of $m\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 161—162°, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 75°, and *m*-cresol, m.p. 61—62°; *HgBu* salts of $m\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 148°, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 51—52°, and *m*-cresol; *Hg amyl* salts of $m\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 132.5—133.5°, and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 46—47°; *Hg hexyl* salt of $m\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 128—129°. Few of the salts are bactericidal (towards *S. aureus*); the bacteriostatic properties are quite high (variation of R and R' in $\text{HgR}\cdot\text{OR}'$ has a very limited influence).
H. B.

Conversion of open-chain molecules into cyclic compounds. E. PUXEDDU (Rend. Seminar Fac. Sci. Cagliari, 1933, 3, 61—63; Chem. Zentr., 1934, ii, 1437).—Theoretical.
H. N. R.

Ring closure and radical formation. VI. 1:1:2:2-Tetraphenylcyclopropane. G. WITTING and B. OBERMANN (Ber., 1934, 67, [B], 2053—2060; cf. A., 1933, 944).— $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\text{Bz}$ is converted by MgPhBr into COPh_2 and COPhMe (whence $\text{CPh}_2\cdot\text{OH}$ and $\text{CPh}_2\text{Me}\cdot\text{OH}$, respectively). The mol. is ruptured by LiPh at 15—20°, whereas at −80° $\alpha\gamma\gamma$ -tetraphenylpropane- $\alpha\gamma$ -diol (I), m.p. 112—113.5°, is produced. (I) is transformed by $\text{MeOH}\cdot\text{HCl}$ at room temp. into $\alpha\gamma$ -dimethoxy- $\alpha\gamma\gamma$ -tetraphenylpropane, m.p. 174—175°, converted by $\text{K}\cdot\text{Na}$ in dioxan into $\alpha\gamma$ -dipotassium- $\alpha\gamma\gamma$ -tetraphenylpropane, which yields $\alpha\gamma\gamma$ -tetraphenylpropane, m.p. 135—136°, with MeOH and 1:1:2:2-tetraphenylcyclopropane (II), m.p. 165.5°, with $\text{C}_2\text{Me}_4\text{Br}_2$. (II) can be distilled in vac., its solutions are stable to air, and it is not decomposed by boiling with AcOH or $\text{Br}\cdot\text{CCl}_4$.

Me_2 glutarate is transformed by LiPh in Et_2O into $\alpha\alpha\epsilon\epsilon$ -tetraphenylpentane- $\alpha\epsilon$ -diol, m.p. 111—112°, whence $\alpha\epsilon$ -dimethoxy- $\alpha\alpha\epsilon\epsilon$ -tetraphenylpentane, m.p. 127.5—129.5°, converted by $\text{K}\cdot\text{Na}$ into $\alpha\epsilon$ -dipotassium- $\alpha\alpha\epsilon\epsilon$ -tetraphenylpentane, which gives $\alpha\alpha\epsilon\epsilon$ -tetraphenylpentane, m.p. 79—80°, with MeOH and ill-defined polymeric hydrocarbons with $\text{C}_2\text{Me}_4\text{Br}_2$ in dioxan or Et_2O . Similar results are obtained with the corresponding Na_2 and Li_2 derivatives and $\text{CH}_3(\text{CH}_2\text{Br})_2$. Me_2 $\beta\beta$ -dimethylglutarate and LiPh in Et_2O give $\alpha\alpha\epsilon\epsilon$ -tetraphenyl- $\gamma\gamma$ -dimethylpentane- $\alpha\epsilon$ -diol, m.p. 156—157°, converted by $\text{HCl}\cdot\text{MeOH}$ into tetraphenyldimethylpentanemethylene oxide, m.p. 149—150.5°, and by KPr^6 and MeI into $\alpha\epsilon$ -dimethoxy- $\alpha\alpha\epsilon\epsilon$ -tetraphenyl- $\gamma\gamma$ -dimethylpentane, m.p. 115—116°, whence $\alpha\alpha\epsilon\epsilon$ -tetraphenyl- $\gamma\gamma$ -dimethylpentane, m.p. 88—89°. Attempts to prepare 1:1:2:2-tetraphenyl-4:4-dimethylcyclopentane resulted in resins.
H. W.

Thermal polymerisation of cyclopentadiene. K. ALDER and G. STEIN (Angew. Chem., 1934, 47, 837—842).—A lecture.
H. W.

Many-membered carbon rings. L. RUZICKA (Chem. and Ind., 1934, 2—8).—A lecture.

Raman spectra of cyclopentene derivatives.
Synthesis of Δ^1 -benzylcyclopentene.—See this vol., 146.

Fulvenes in ionone series. E. P. KOHLER and J. KABLE (J. Amer. Chem. Soc., 1934, 56, 2756—2757).—*cyclopentadiene* (I) and β -ionone in $\text{MeOH}\cdot\text{NaOMe}$ give 2-(γ -cyclopentadienylidene- Δ^1 -butenyl)-1:3:3-trimethyl- Δ^1 -cyclohexene (II), b.p. 111—113°/0.5 mm. (cf. Willstaedt, A., 1934, 641), which absorbs 10 H on complete reduction (H_2 , PtO_2 , EtOH) and is oxidised (O_3 in CCl_4) to geronic acid. α -Ionone and (I) similarly afford 6-(γ -cyclopentadienylidene- Δ^1 -butenyl)-1:5:5-trimethyl- Δ^1 -cyclohexene (III), b.p. 107—109°/5 mm., which also absorbs 10 H. (II) and (III), which are orange-coloured oils, are regenerated when piperidine solutions of their colourless H_2 -derivatives are shaken with air. ϕ -Ionone and (I) give the red κ -cyclopentadienylidene- $\beta\zeta$ -dimethyl- Δ^6 -undecatriene (IV), b.p. 139—141°/0.5 mm., which also affords a colourless dihydro-derivative and absorbs 12 H on complete reduction. (II)—(IV) give blue colours with SbCl_3 and undergo ready autoxidation; cryst. adducts could not be obtained with maleic anhydride.
H. B.

Internal energy relationships among carbocyclic compounds. II. Stability and reactivity of cyclic polyolefines. O. SCHMIDT (Ber., 1934, 67, [B], 2078—2080; cf. this vol., 73).—On the basis of the Heitler-London theory it is shown that C_6H_6 is the first cyclic olefine $[\text{CH}\cdot\text{CH}]_n$ capable of existence and also the most stable, since the electron ring has the greatest possible distance from the outer C ring.
H. W.

Synthesis of benzene hydrocarbons. A. KIRRMANN and M. GRAVES (Bull. Soc. chim., 1934, [v], 1, 1494—1498).—The condensation of C_6H_6 and alcohols by conc. H_2SO_4 is modified. Preps. of the following are described: PhPr^6 ; $p\text{-C}_6\text{H}_4\text{Pr}^6$, b.p. 85—86°/14 mm., 210° (corr.)/760 mm.; 1:3:4- $\text{C}_6\text{H}_3\text{Pr}^6$ (I), b.p. 113—114°/14 mm., 244° (corr.)/760 mm. [SO_3H derivative, $+\text{H}_2\text{O}$, m.p. 149° (rapid heating) (*Ba* salt, $+2\text{H}_2\text{O}$)]; 1:2:4:5- $\text{C}_6\text{H}_2\text{Pr}^6$, m.p. 118°, b.p. 133°/17 mm., 169°/70 mm. [resistant to CrO_3 and KMnO_4 ; with Br gives a derivative of (I), $\text{C}_{15}\text{H}_{22}\text{Br}_2$, m.p. 84°]; PhMe gives *p*-cymene and $\text{C}_6\text{H}_5\text{MePr}^6$. Alkyl sulphates are sparingly sol. in conc. H_2SO_4 , by which they are slowly hydrolysed.
R. S. C.

Preparation of cymene. E. RAYMOND (Bull. Soc. chim., 1934, [v], 1, 1470—1478).—*p*-Cymene (I) is best (50%) prepared from pinene by bromination at −18° to −15° and dehalogenation of the fraction, b.p. < 195°, of the product by heating with 2% of I (35% yield without I). Chlorination leads to poor yields of (I).
R. S. C.

Selenium and tellurium as carriers in bromination of benzene. A. A. O'KELLY (J. Amer. Chem. Soc., 1934, 56, 2783).— C_6H_6 (70.3 g.) and Br (80% excess) in presence of 2 g. of Fe , Se , Te , and $\text{Te}\cdot\text{Fe}$ for 12 hr. (no heat) and then for 7 hr. (slight heating) give 46.2, 25.4, 30.7, and 46.2%, respectively, of PhBr and 4.6, 3.2, 6.9, and 4.6%, respectively, of $\text{C}_6\text{H}_4\text{Br}_2$.
H. B.

Action of fluorine on aromatic organic compounds. II. Fluorination of hexachlorobenzene. L. A. BIGELOW and J. H. PEARSON (J. Amer. Chem. Soc., 1934, 56, 2773—2774; cf. A., 1934, 62).—

C_6Cl_6 (I) is treated with F_2 in CCl_4 in a glass apparatus (*loc. cit.*) first at 0° and then at room temp., the product is freed (vac. distillation) from (I), then treated with F_2 (no solvent) in a Cu vessel (*loc. cit.*) at 0° , and finally fractionated. When emulsions of the fractions, b.p. $135-160^\circ/1$ mm. and $100-115^\circ/7$ mm., with H_2O are kept in the cold, *hexachlorotetrafluorocyclohexene*, m.p. $113-114^\circ$, and *hexachlorohexafluorocyclohexane*, m.p. $94-96^\circ$, respectively, are obtained.

H. B.

Vapour-phase hydrolysis.—See this vol., 172.

Nitration of alkylbenzenes. III. Orientation of dinitro-*p*-tert.-butyltoluene. O. L. BRADY and J. K. LAHRI (J.C.S., 1934, 1954—1957; cf. A., 1934, 286).—The orientation of 2:6-dinitro-4-tert.-butyltoluene (I) [obtained by nitration of *p*-tert.-butyltoluene (cf. A., 1897, i, 514; 1899, i, 424; 1917, i, 34)] is established by the following reactions. (I) is reduced by $(NH_4)_2S$ in boiling EtOH to 6-nitro-2-amino-4-tert.-butyltoluene [hydrochloride (II), m.p. 210° (decomp.); Ac derivative, m.p. $138-139^\circ$]. (II), by the diazo-reaction, gives 2-nitro-4-tert.-butyltoluene (III) (A., 1924, i, 1176) [reduced (Sn-HCl) to 2-amino-4-tert.-butyltoluene] and 6-nitro-2-hydroxy-4-tert.-butyltoluene, m.p. 128° . (III) is oxidised (AcOH-Ac₂O- H_2SO_4 -CrO₃) below 10° to an aldehyde diacetate, hydrolysed to 2-nitro-4-tert.-butylbenzaldehyde (2:4-dinitrophenylhydrazones, m.p. 228°), obtained as a semi-solid mass which gave the Baeyer-Drewson indigo reaction. (II) is converted (Sandmeyer) into 6-nitro-2-cyano-4-tert.-butyltoluene, m.p. 83° , hydrolysed to 6-nitro-4-tert.-butyltoluene-2-carboxylic acid, m.p. 219° , oxidised [HNO_3 (3 c.c., *d* 1.5)- H_2O (12 c.c.) at 200° during 8 hr.] to 5-nitro-tert.-butylbenzene-3:4-dicarboxylic acid, m.p. 365° (decomp.), which forms an anhydride, m.p. $147-149^\circ$, insol. in cold $2N-Na_2CO_3$.

H. G. M.

Dichloro-*o*-xylenes. II. L. E. HINKEL, E. E. AYLING, and T. M. WALTERS (J.C.S., 1934, 1946—1948).—3:6-Dichloro-*o*-xylene (I), m.p. 29° , b.p. $234^\circ/760$ mm. [from 6-chloro-*o*-3-xylidine (A., 1934, 644)], is not identical with the compound, m.p. 68° , obtained from the chlorination of *o*-xylene (A., 1928, 995, 1238). Chlorination of (I) gives 3:4:5:6-tetrachloro-*o*-xylene, m.p. 226° . 3:6-Dichloro-4-nitro-*o*-xylene, m.p. 84° [from (I); also from 6-chloro-4-nitro-*o*-3-xylidine (A., 1934, 644)], is reduced to the corresponding amine (Ac derivative, m.p. 146°). 3:6-Dichloro-4:5-dinitro-*o*-xylene, m.p. 174° , is prepared from (I) and HNO_3 , and is reduced to the corresponding diamine (phenazine derivative, m.p. above 250°). (I) with Br gives 3:6-dichloro-4:5-dibromo-*o*-xylene, m.p. 238° . 4:5-Dichloro-*o*-xylene (II), m.p. 76° (cf. A., 1928, 995), is synthesised from 1:2:5:4- $C_6H_3Me_2Cl \cdot NH_2$ (A., 1934, 644) and affords 4:5-dichloro-3:6-dibromo-*o*-xylene, m.p. 232° . 4:5-Dichloro-*o*-3-xylidine (A., 1934, 644) gives 4:5-dichloro-3-bromo-*o*-xylene, m.p. 111° (lit. 90°). Chlorination of 3-chloro-*o*-xylene (from *o*-xylidine) gives 3:4-dichloro-*o*-xylene (III) [cf. A., 1928, 995; also obtained from 3-chloro-*o*-4-xylidine (A., 1934, 644)]. Chlorination of 4-chloro-*o*-xylene (IV), f.p. -6.25° , b.p. $194^\circ/755$ mm. [lit. 191.5° (corr.) and 195°] (from *o*-4-xylidine), gives (II). (IV) with HNO_3 ,

d 1.5, gives 4-chloro-5-nitro-*o*-xylene (A., 1891, 921; 1934, 644) and a solid, m.p. 111° . Nitration of (III) gives 3:4-dichloro-5:6-dinitro-*o*-xylene, m.p. 172° .

H. G. M.

Highly-arylated aromatic compounds. IV. Tetraphenylbenzenes. W. DILTHEY and G. HURTING (Ber., 1934, 67, [B], 2004—2007; cf. A., 1934, 641; this vol., 213).—4:5-Diphenylcyclopentenolone is converted by toluene at 275° into a greatly resinified mass from which 1:2:4:5-tetraphenylbenzene, m.p. $262-263^\circ$, is isolated in small amount. It is also obtained from 2:3:5-triphenylcyclopentadienone and CH·CPh and is identical with the "hexaphenylbenzene" of Durand *et al.* (A., 1931, 207). COMe·CH₂Ph and benzil in MeOH-KOH afford 2:3:4-triphenylcyclopentenolone (I), m.p. 165° , transformed by CH·CPh into 1:2:3:4-tetraphenylbenzene, m.p. $190-191^\circ$, obtained also from (I) and CPh₂·C·CO₂H. (I) and toluene at 280° afford C_6HPh_5 , m.p. 251° (corr.). Tetraphenylcyclopentadienone and toluene at $225-315^\circ$ give C_6Ph_6 , m.p. 426° , which can readily be halogenated, sulphonated, and hexanitrated. The corresponding hexa-amine can be diazotised.

H. W.

Phenomena of isomerisation in the cracking of decahydronaphthalene with aluminium chloride. N. D. ZELINSKI and M. B. TUROVA-POLJAK (J. Appl. Chem. Russ., 1934, 7, 753—756).—On heating with $AlCl_3$ at $175-210^\circ$ *cis*-decahydronaphthalene is transformed into the *trans*-isomeride, and this into dimethyldicyclopentane; at the same time cyclopentane and -hexane hydrocarbons are formed.

R. T.

Nitration of 2-bromonaphthalene. J. SALKIND and F. FILINOV (J. Gen. Chem. Russ., 1934, 4, 979—981).—2-Bromo-7-nitro-, m.p. $110-111^\circ$, and -1-nitronaphthalene are obtained by nitrating 2- $C_{10}H_7$ -Br.

R. T.

Fractionation and purification of organic substances by chromatographic adsorption. IV. Polycyclic aromatic hydrocarbons. A. WINTERSTEIN and K. SCHÖN. V. Anthracene, chrysene, and pyrene. A. WINTERSTEIN, K. SCHÖN, and H. VETTER. VI. 1:2-Benzpyrene. A. WINTERSTEIN and H. VETTER (Z. physiol. Chem., 1934, 230, 146—158, 158—169, 169—174).—IV. The following pairs of hydrocarbons are separable using Al_2O_3 (activated) as adsorbent: anthracene (I)- $C_{10}H_8$ (not adsorbed); (I)-chrysene (II); (I)-phenanthrene (III); (I)-pyrene (IV); (III)-(IV); (II)-(IV); (II)-1:2-benzpyrene (V); perylene-(V). Mixtures of $C_{10}H_8$, (I), and 2:3-benzanthracene, and of 1:2:5:6-dibenz- (VI), 1:2-benz-5:6:2':3'-naphth- [prepared (cf. Cook, A., 1931, 612) from anthracene-2-carboxyl chloride and 2- $C_{10}H_7Me$ (Friedel-Crafts), pyrolysis of the resulting ketone, and adsorption on Al_2O_3], and 1:2:5:6-di-2':3'-naphth-anthracenes are similarly separable. Inspection of the chromatograms in ultra-violet light shows (usually) varying coloured zones. The deeply coloured hydrocarbons are most readily adsorbed; thus, the yellow 1:2:6:7-dibenzanthracene (VII) is adsorbed more readily than the colourless (VI). The mixture of (VII) and 1:2:3:4-dibenz- and 1:2:1':2'-naphth-anthracene obtained from phenanthrene and

o-C₆H₄Me·COCl with subsequent pyrolysis (Clar, A., 1929, 922), is readily separable; so is the mixture of (VII) and 1:2:2':3'-naphthanthracene, m.p. 255—257° (lit. 265°), formed by the method of Clar *et al.* (*ibid.*, 689) from *p*-C₆H₄(COCl)₂ and *o*-C₆H₄Me·MgBr. 1:2-Benz-5:6:2':3'- and -6:7-1':2'-naphthanthracenes could not be separated, but the closely related anthrodianthrene and *antidiperidibenzcoronene* are separable.

V (cf. A., 1934, 643). Adsorption of a "benzine" solution of technical anthracene (I) on activated Al₂O₃ gives 3 well-defined zones (visible only in ultra-violet light), from which by extraction with Et₂O and repetition of the process pure (I), m.p. 219° (corr.; Berl), naphthacene (2:3-benzanthracene) (II), m.p. 337° (corr.), and carbazole are isolated; the filtrate contains varying amounts [according to purity of (I)] of paraffin and C₁₀H₈ derivatives. The blue fluorescence of pure (I) is almost inhibited by 0.00001% and prevented by 0.000033% of (II). Small amounts of (II), 1:2-benzcarbazole, and a S-compound are similarly separated from chrysene (III); pure (III), m.p. 255—256° (corr.; Berl), is obtained in only 10—20% yield. Pyrene is shown to contain (II), 1:2:6:7-dibenzanthracene, 2:3-1':2'-naphthanthracene (IV), and dibenzcoumarone (2:3-benzdiphenylene oxide). Crude picene contains (II), (IV), and (probably) 1:2-benzpyrene and 1:2-benz-6:7-1':2'-naphthanthracene.

VI. 1:2-Benzpyrene (I), m.p. 177° (corr.; Berl) [quinone, m.p. 292—293° (corr.; Berl) (cf. Cook *et al.*, A., 1933, 601)], is prepared by dehydrogenation (Se at 320—340°) of 4'-keto-1':2':3':4'-tetrahydro-1:2-benzpyrene, and purified by adsorption on Al₂O₃+Al₂O₃-C (whereby a little 4'-hydroxy-1:2-benzpyrene, m.p. 180°, is separated). (I) is carcinogenic. Addition of (I) (in CMe₂) to hot aq. 20% Na deoxycholate gives a solution containing 2 mg. of (I) per c.c. Absorption curves for (I) in various solvents are given.

H. B.

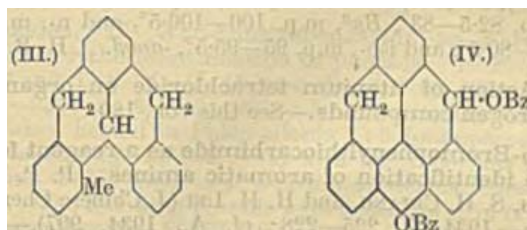
Synthesis of alkylphenanthrenes. VIII. Attempted synthesis of 4:5-dimethylphenanthrene. R. D. HAWORTH and G. SHELDRICK (J.C.S., 1934, 1950—1952).—8-Methyl-2-naphthyl CH₂Br ketone [from the Me ketone (I) and Br in CHCl₃] and CHNa(CO₂Et)₂ in C₆H₆ give, after hydrolysis with MeOH-KOH and decomp. of the resulting acid at 180°, β-(8-methyl-2-naphthyl)propionic acid, m.p. 113—115° (Me ester, m.p. 87—88°, b.p. 185—190°/0.5 mm.), which is reduced (Clemmensen) to γ-(8-methyl-2-naphthyl)butyric acid (Me ester, b.p. 170—175°/0.3 mm.). This is cyclised to a product, b.p. 180—190°/0.5 mm., considered to be impure 1-keto-5-methyl-1:2:3:4-tetrahydroanthracene (II), which on treatment with MgMeI followed by dehydration and dehydrogenation (Se at 280—300°) gives 1:5-dimethylanthracene, m.p. 139—140° [picrate, m.p. 166—167°; quinone, m.p. 190°, which does not react with *o*-C₆H₄(NH₂)₂]. The formation of (II), instead of a prenanthrene derivative, is explained on steric grounds. (I) was prepared by Clemmensen reduction of β-*p*-anisoylpropionic acid, followed by cyclisation and dehydrogenation to 7-methoxy-1-methylnaphthalene; the OMe group then successively converted into NH₂, CN, and COMe.

H. G. M.

[Di-radical formula of rubene and constitution of its dissociable peroxide.] C. DUFRASSE (Ber., 1934, 67, [B], 2018; cf. A., 1934, 882).—A question of priority (cf. Schonberg, *ibid.*, 997).

H. W.

Triphenylmethanes with linked benzene rings. VIII. Reduction products of trimethylenetriphenylmethane triketone. R. WEISS and F. MÜLLER (Monatsh., 1934, 65, 129—136).—The blue triketone C₂₂H₁₀O₃ (I) (A., 1925, i, 560) exists in its anthranol form, since with *p*-C₆H₄Me·SO₂Cl and boiling C₅H₅N it gives a *p*-toluenesulphonyl derivative, decomp. 220° [hydrolysed by KOH-EtOH to (I)]. Reduction of (I) with red P-HI (*d* 1.7) affords a brown, KOH-sol. (OH)₃-derivative, C₂₂H₁₂(OH)₃O₃ + AcOH and + MeOH (II) (Ac₃ derivative, turns blue at 285°), and the hydrocarbon (III), m.p. 182°. With



Zn dust-*N*-KOH (O₂ excluded) and subsequent benzylation (II) affords a Bz₂ derivative (IV), C₃₆H₂₂O₄, decomp. 200°. In the prep. of di-*o*-tolylphthalide (*loc. cit.*) is obtained a second modification, m.p. 176°, also reduced to CO₂H·C₆H₄·CH(C₆H₄Me)₂, identical with a specimen obtained by similar reduction of the form, m.p. 128°.

J. W. B.

Action of sodiomalonic ester on diphenylthiocarbamide and carbodiphenylimide. V. E. TISCHTSCHENKO and N. V. KOSCHKIN (J. Gen. Chem. Russ., 1934, 4, 1021—1026).—CS(NHPh)₂ (I) or C(NPh)₂ (II) and CHNa(CO₂Et)₂ (III) in C₆H₆ yield the substance (IV) NPh:C(NHPh)·CH(CO₂Et)₂, m.p. 166—167°, giving on hydrolysis with NaOH-EtOH diphenylacetamide, NPh:CMc·NHPh, m.p. 131—132°. The reaction is probably (I) → (II) + H₂S; (II) + (III) → (IV).

R. T.

Reactions of unsaturated compounds. III. Addition of arylamines to butadiene. W. J. HICKINBOTTOM (J.C.S., 1934, 1981—1984; cf. A., 1932, 1242; 1934, 644).—Butadiene (I) with excess of NH₂Ph and NH₂Ph·HCl (or HBr) at 220—260° during 4—25 hr. affords mainly α-*p*-aminophenyl-Δ³-butene (II), b.p. 135—136°/24 mm. (hydrochloride; sulphate), the Ac derivative of which, m.p. 98—99°, is converted by Br in CHCl₃ into β-γ-dibromo-α-*p*-acetamidophenylbutane, m.p. 127—128°, reduced (H₂-Pd) to *p*-C₆H₄Bu^α·NHAc (which indicates that aryl is attached to the terminal C of the butenyl group), and oxidised (KMnO₄) to MeCHO (which indicates a βγ double linking) and *p*-NH₂·C₆H₄·CO₂H. The diazonium derivative of (II) with β-C₁₀H₇·OH gives an azo-derivative, m.p. 100—101°, and α-anilino-Δ³-butene (III), purified through its nitrosoamine. The Ac derivative, b.p. 165—168°/28 mm., of (III) reacts slowly with Br and H₂ and is oxidised (KMnO₄) to MeCHO. NHPh₂ and 2:3-dimethylindole are also isolated. (I) with excess of *p*-C₆H₄Me·NH and

p - $C_6H_4Me \cdot NH_2 \cdot HCl$ (or HBr) affords α - p -toluidino- Δ^{β} -butene, b.p. $135^{\circ}/33$ mm. [platinichloride, m.p. 200 — 201° (decomp.); nitrosoamine], and 4-butenylamino-3-butenyltoluene, b.p. $185^{\circ}/30$ mm. (nitrosoamine), and a small amount of di- p -tolylamine and 2:3:5-trimethylindole (picrate, m.p. 188 — 189°). The reactions described are distinct from those of the Diels-Adler diene syntheses because a catalyst is necessary to bring about reaction. The formation of indoles may be due to a $\beta\gamma$ -reaction of (I). J. L. D.

Preparation of nitrogen-substituted sulphon- o -toluidides. G. H. YOUNG (J. Amer. Chem. Soc., 1934, 56, 2783—2784).—The following N -alkyl derivatives of p -toluenesulphon- o -toluidide are described (cf. A., 1934, 1342): Me, m.p. 87 — 87.5° (lit. 119 — 120°), Pr^{α} , m.p. 72 — 72.5° , Pr^{β} , m.p. 92 — 92.5° , Bu^{α} , m.p. 82.5 — 83° , Bu^{β} , m.p. 106 — 106.5° , and n-, m.p. 80 — 80.5° , and iso-, m.p. 95 — 95.5° , -amyl. H. B.

Action of titanium tetrachloride on organic nitrogen compounds.—See this vol., 180.

p -Bromophenylthiocarbimide as a reagent for the identification of aromatic amines. P. P. T. SAH, S. H. CHIANG, and H. H. LEI (J. Chinese Chem. Soc., 1934, 2, 225—228; cf. A., 1934, 997).— p - $C_6H_4Br \cdot NH_2$ with boiling CS_2 -EtOH during 3—4 hr. gives dibromodiphenylthiocarbimide, decomposed by boiling Ac_2O to p -bromophenylthiocarbimide (I), which gives sharply melting derivatives with many amines. The p -bromophenylthiocarbimides from the following amines are described: NH_2Ph , m.p. 150 — 151° ; p -bromo-, m.p. 186 — 187° , p -chloro-, m.p. 189 — 190° , o -, m.p. 60 — 61° , m -, m.p. 163 — 164° , and p -nitro-aniline, m.p. 164 — 165° ; o -, m.p. 147 — 148° , m -, m.p. 147 — 148° , and p - $C_6H_4Me \cdot NH_2$, m.p. 174 — 175° ; m -bromo- p -toluidine, m.p. 158 — 159° ; α -, m.p. 165 — 166° , and β - $C_{10}H_7 \cdot NH_2$, m.p. 175 — 176° ; o -, m.p. 131 — 132° , and ν -aminophenol, m.p. 163 — 164° . J. L. D.

Identification of metanilic acid and sulphanilic acid. R. B. FORSTER (J.S.C.I., 1934, 53, 358T).—These acids can be identified by conversion into the corresponding chlorobenzenesulphonic acid (diazo-reaction), arylamine salts of which have sharp m.p. m - $C_6H_4Cl \cdot SO_3Na$ with $NH_2Ph \cdot HCl$ in H_2O gives the aniline salt, m.p. 206 — 207° . Similarly prepared, the p -toluidine, p -chloroaniline, m -xylidine, α -naphthylamine, and benzidine salts have m.p. 199 — 200° , 195 — 196° , 151 — 152° , 207 — 208° , and $> 320^{\circ}$ (decomp.), respectively. NH_2Ph , m.p. 222 — 223° , p - $C_6H_4Me \cdot NH_2$, m.p. 207 — 209° , p - $C_6H_4Cl \cdot NH_2$, m.p. 210 — 211° , and benzidine salts, m.p. $> 320^{\circ}$ (decomp.), of p - $C_6H_4Cl \cdot SO_3H$ are described. J. L. D.

m -Toluidine-6-sulphonic acid. M. S. SHAH, C. T. BHATT, and D. D. KANGA (J.C.S., 1934, 2010—2011).— m - $C_6H_4Me \cdot NH_2$ with oleum at 125° gives only m -toluidine-6-sulphonic acid, the diazonium derivative of which with boiling H_2O gives m -cresol-6-sulphonic acid (cf. A., 1888, 280), identified by several derivatives (A., 1933, 1292). J. L. D.

Additive products of benzylamine and phenylhydrazine with the nickel salts of substituted acetic acids.—See this vol., 182.

Monoethyl- o -toluidine and rhodamines obtained therefrom. H. E. FIERZ-DAVID and J. P. RUFENER (Helv. Chim. Acta, 1934, 17, 1452—1459).— o - $C_6H_4Me \cdot NH_2$ (I) (380 g.), EtOH (195 g. = 20% excess), and conc. H_2SO_4 (57 g.) are heated for 12 hr. at 200° . The bases are liberated by NaOH and distilled through a Frey column, whereby o - $C_6H_4Me \cdot NH_2$ (II), b.p. $95.5^{\circ}/10$ mm., is obtained in 66% yield. The preliminary fractions contain (I) and (II) whereas o - $C_6H_4Me \cdot NEt_2$ (III) is not produced. d of mixtures of (I) and (II) in varied proportion has been determined. The separation of (II) from (III) is not readily effected through the hydrochlorides, the sulphonic acids, or their salts. The solubilities of the sulphonic acids and their Na and K salts is recorded for 2:1:4- $R \cdot C_6H_3Me \cdot SO_3H$, where $R = NH_2$, $NHMe$, NMe_2 , NH_2Et , NEt_2 . Rhodamine-B, -G, and -GP have been transformed into their Me, Et, Pr^{α} , Pr^{β} , Bu^{α} , Bu^{β} , amyl, hexyl, octyl, benzyl, and cyclohexyl esters. H. W.

Addition of methyl alcohol to methyl o -nitro-styrylcarbamate with formation of methyl α (?)methoxy- β - o -nitrophenylethylcarbamate. F. SCHENCK (Ber., 1934, 67, [B], 2035—2036).—The protracted action of NaOCl on o -nitrophenylcinnamide in $MeOH-H_2O$ leads to the formation of Me α (?)methoxy- β - o -nitrophenylethylcarbamate, m.p. 121° , converted by dil. H_2SO_4 into o -nitrophenylacetaldehyde. The ester is considered to react in its tautomeric form, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH \cdot N \cdot CO_2Et$. H. W.

Preparation of arylcarbimides. D. V. N. HARDY (J.C.S., 1934, 2011).— p -Xenylamine (I) in boiling $PhMe$ with $COCl_2$ affords (cf. A., 1931, 834) p -xenylcarbimide (II) and s -di- p -xenylcarbamide [by interaction of (I) and (II)], but the hydrochloride of (I) with $COCl_2$ gives only (II). Similarly, $NH_2Ph \cdot HCl$ affords only $PhNCO$. J. L. D.

Manufacture of derivatives of diazo-compounds.—See B., 1935, 14.

Action of chlorine, bromine, and iodine monochloride on aryl azoacetates and related compounds. F. D. CHATTAWAY and R. D. ASHWORTH (J.C.S., 1934, 1985—1988).—The following are described (cf. A., 1933, 705; 1934, 182): Et 2:4-dinitrobenzeneazoacetate (I), m.p. 108° , 2:4-dinitrobenzeneazo-benzoyl- (II), m.p. 203° , and -acetylacetone (III), m.p. 176° , Et α -bromo- (IV), m.p. 122° , and α -amino-glyoxylate-2:4-dinitrophenylhydrazone, m.p. 169° . (I) with Br in $AcOH-NaOAc$ at room temp. gives (IV), but in boiling $AcOH$ it affords Et 2:4-dinitrobenzeneazo- γ -bromoacetate, m.p. 141° . Cl_2 is without action on (I) in cold or boiling $AcOH$ or $CHCl_3$, but in cold $AcOH-NaOAc$, Cl_2 gives Et α -chloroglyoxylate-2:4-dinitrophenylhydrazone, m.p. 120° , and in dry $CHCl_3$ it affords Et 2:4-dinitrobenzeneazo- γ -chloroacetate (V), m.p. 143° . Similarly, (II) and (III) with Cl_2 in cold $AcOH-NaOAc$ give ω -chlorophenylglyoxal-, m.p. 177° , and ω -chloro- α -ketopropaldehyde-2:4-dinitrophenylhydrazone, m.p. 159° , respectively. The action of ICl depends partly on the nature of the substituents in the Ph nucleus. Et 2:4:6-tribromo-, 2:4-dibromo-, p -bromo-, p -nitro-, or o -nitro-benzeneazoacetate (which are not

easily acetylated) with ICl in AcOH afford *Et* 2:4:6-tribromo-, m.p. 104°, 2:4-dibromo-, m.p. 127°, *p*-bromo-, m.p. 114°, *p*-nitro-, m.p. 154°, and *o*-nitrobenzeneazo- γ -iodoacetoacetate, m.p. 128°, respectively, which also result when the corresponding γ -Cl- or -Br-compounds react with KI. The γ -I-compounds with KOAc afford pyrazoles (cf. A., 1932, 1125; 1933, 1156). (I) with ICl in cold AcOH gives (V), which is unchanged by excess of ICl. *Et* benzeneazoacetoacetate with ICl in AcOH gives *Et* α -chloroglyoxylate-*p*-iodophenylhydrazone, m.p. 176°, which is reduced (Sn-HCl) to *p*-C₆H₄I-NH₂. *Et* *p*-chlorobenzeneazoacetoacetate similarly affords *Et* α -chloroglyoxylate-*p*-chlorophenylhydrazone (cf. A., 1932, 1125). α -Ketopropaldehyde-*o*-nitrophenylhydrazone with ICl in AcOH at 40° gives β -iodo- α -ketopropaldehyde-*o*-nitrophenylhydrazone, m.p. 174°. Similarly, the 2:4:6-tribromophenylhydrazone gives ω -chloro- α -ketopropaldehyde-2:4:6-tribromophenylhydrazone (cf. A., 1934, 998). The arylazo-acetyl- and -benzoyl-acetones do not react with ICl. ω -Bromo- α -ketopropaldehyde-*o*-nitrophenylhydrazone with KI in boiling EtOH gives the ω -I-compound, m.p. 189°. Similarly prepared are ω -iodo- α -ketopropaldehyde-2:4-dibromo-, m.p. 169°, and 2:4:6-tribromo-phenylhydrazone (VI), m.p. 150°. $\beta\omega$ -Tribromo- α -ketopropaldehyde-2:4:6-tribromophenylhydrazone with KI in AcOH at 100° gives (VI), which is similarly obtained from the $\beta\gamma$ -dibromo-analogue, m.p. 134° (prepared by brominating α -ketopropaldehyde-2:4:6-tribromophenylhydrazone). The *N*-acetates of *Et* 2:4:6-tribromo- (VII) and 2:4:6-trichloro-benzeneazoacetoacetate (VIII) (cf. A., 1932, 377) with excess of Br in boiling AcOH give *Et* 2:4:6-tribromo-, m.p. 178°, and 2:4:6-trichloro-benzeneazo- $\gamma\gamma$ -dibromoacetoacetate-*N*-acetate, m.p. 141°, respectively, identical with the Ac derivatives of *Et* 2:4:6-tribromo- and 2:4:6-trichloro-benzeneazo- $\gamma\gamma$ -dibromoacetoacetate. *N*-Acetylation of (VII) and (VIII) prevents the replacement of Ac by Br (see above). J. L. D.

The azochromophore. VI. J. S. P. BLUMBERGER (Chem. Weekblad, 1935, 32, 6—8).—Absorption spectra of *peri*-hydroxyazo-dyes (I) of the type 1:8-aminonaphthol- \rightarrow - α -C₁₀H₇-NH₂ in neutral and alkaline solutions, in which a bathochromic colour change (chromophore inversion) takes place, show that the OH and N:N groups in (I) form a conjugated system similar to that present in *o*-hydroxyazo-dyes (A., 1933, 946). Absorption curves are given for the following dyes: 1:8-aminonaphthol-3:6-disulphonic acid (II) \rightarrow - α -C₁₀H₇-NH₂, (II) \rightarrow 1:6-NH₂-C₁₀H₆-SO₃H (III), 1:8-aminonaphthol-3:5-disulphonic acid \rightarrow (III), 1:5- and 2:5-aminonaphthol-7-sulphonic acid \rightarrow (III), 1:7-aminonaphthol-4-sulphonic acid \rightarrow (III), 2:8-aminonaphthol-6-sulphonic acid \rightarrow (III), *p*-C₆H₄(NH₂)₂ (IV) 1- and 2-naphthol-3:6-disulphonic acid, (IV) \rightarrow 1:4-OH-C₁₀H₆-SO₃H. S. C.

Amphoteric aromatic substitution. II. Reactions of benzoyl peroxide and benzeneazotriphenylmethane. D. H. HEY (J.C.S., 1934, 1966—cf. A., 1926, 286, 612).—Bz₂O₂ with PhCl at 100° gives CO₂, BzOH, and 4-chlorodiphenyl. Similarly Bz₂O₂ with PhNO₂ gives CO₂, 4- and 2-nitrodiphenyl [which indicates that the substituting agent

functions as an anionoid reagent (cf. A., 1929, 1313)], and with EtOBz it affords CO₂, Et diphenyl-4- (I) and -3-carboxylate, which accords with the less definite distinction between the *o*- and *p*-directive influence of CO₂Et, as compared with the almost exclusively *m*-directing NO₂. Na benzenediazoate with EtOBz gives mainly (I), but also smaller amounts of the 3- and 2-CO₂Et-compounds (cf. A., 1924, i, 1295). Benzeneazotriphenylmethane (II) with boiling C₆H₆ gives CHPh₃, Ph₂, and CPh₄; and again (II) with PhCl gives CPh₄, CHPh₃, and 4-chlorodiphenyl, which indicates that decomp. of (II) involves the formation of free Ph radicals (cf. A., 1922, i, 772) which can react with a neutral aromatic compound (this vol., 78). (II) with PhNO₂ at 100° gives some CHPh₃, a phenol, and a substance, m.p. 240—241°. J. L. D.

Azides. II. 3:5-Dinitrobenzazide as a reagent for the identification of phenols. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1934, 2, 229—233; cf. A., 1934, 997).—3:5-Dinitrobenzazide (I) when heated in PhMe affords 3:5-dinitrophenylcarbimide, m.p. 92—93°. (I) with many phenols in boiling PhMe gives aryl 3:5-dinitrophenylurethanes (II). The following phenols were tested [m.p. of (II) in parentheses]: PhOH (192—193°); *o*- (140—142°), *m*- (188—189°), and *p*-nitro- (200—201°), *o*- (182—183°) and *p*-chloro- (197—198°), *o*- (253—254°) and *p*-amino-phenol (266—267°); *o*- (205—206°), *m*- (209—210°), and *p*-cresol (184—185°); thymol (154—155°); α - (228—229°) and β -C₁₀H₇-OH (238—239°); *p*-cresol-*o*-aldehyde (227—228°); Me (180—181°), Et (145—147°), and benzyl salicylate (172—173°). J. L. D.

Bromination of benzoates of phenolic compounds. L. C. RAIFORD and J. E. MILBERRY (J. Amer. Chem. Soc., 1934, 56, 2727—2729).—During bromination of ArOBz [Ar=Ph, C₆H₄Me, *p*-CHO-C₆H₄, 2:4-(OMe)(CHO)C₆H₃], Br enters the *p*-position (if available) of Ar; *o*-substitution occurs less readily, whilst *m*-substitution was not found (cf. Claus and Hirsch, A., 1889, 389). In many cases, the HBr evolved caused hydrolysis to BzOH and ArOH (subsequently brominated); PhOBz thus gives *p*-C₆H₄Br-OBz, *s*-C₆H₄Br₃-OH, and BzOH. The methods of bromination used are: (i) a modification of Kauschke's (A., 1895, i, 280) using I as catalyst at < 60° in open vessels; (ii) Br in AcOH containing NaOAc and I at about 40° for 48 hr.; (iii) Br in hot AcOH containing NaOAc, I, and the catalyst described by Fierz-David (A., 1929, 273). The bromoaryl benzoates are also synthesised. 4-Bromo-2-methyl-, m.p. 67—68°, 2- and 3-bromo-4-methyl-, m.p. 71—72° and 75—76°, respectively, 2-bromo-4-nitro- (I), m.p. 131—132°, and *p*-bromomethyl- (II), m.p. 109—110°, -phenyl benzoates are new. A 1:1-mixture, m.p. 113—117°, of (I) and *p*-NO₂-C₆H₄-OBz (III) is obtained by repeated crystallisation of the bromination product from (III). (II), obtained in 14% yield from *p*-C₆H₄Me-OBz by method (iii), is converted into *p*-benzoyloxybenzylpyridinium bromide (+H₂O), m.p. (anhyd.) 174—175°. *O*-Benzoylvanillin (IV) gives [method (ii) for 6 days] the 6-Br-derivative, m.p. 117—118° (hydrolysed to 6-bromovanillin), whilst nitration affords 70% of the 2- and 4% of the 6-NO₂-derivative. (IV) and PBr₅ at about 100° give 4-benz-

oxyloxy-3-methoxybenzylidene bromide, m.p. 108.5—109.5°. *p*-Benzoyloxybenzaldehyde, m.p. 90° (lit. 72°) [*p*-bromophenylhydrazone, m.p. 179—180° (decomp.)], could not be brominated [method (ii); in contact with air *p*-OBz·C₆H₄·CO₂H results], indicating that in (IV) the active directing group is OMe, and the activity of OH is suppressed by acylation. Similarly, 4-*o*-, m.p. 103—104°, -*m*-, m.p. 95—96°, and -*p*-, m.p. 117—118°, -*chloro*-, 4-*m*-bromo-, m.p. 114—115°, and 4-*p*-nitro-, m.p. 199—200°, -benzoyloxybenzaldehydes could not be brominated; 4-*o*-, m.p. 215—216°, -*m*-, m.p. 217—218°, and -*p*-, m.p. 239—240°, -*chloro*- and 4-*m*-bromo-, m.p. 211—212°, -benzoyloxybenzoic acids are described. H. B.

Stereochemistry of dicyclic ring systems. X. Stereochemistry of hydrindane and its derivatives. II. Derivatives of *cis*-hydrindane with substituents in the six-membered ring. W. HUCKEL and E. GOTH (Ber., 1934, 67, [B], 2104—2107; cf. Linstead *et al.*, A., 1934, 1002).—Catalytic hydrogenation of 5-hydroxyhydrindene (Pt sponge-AcOH; PtO₂-AcOH; colloidal Pt-H₂O) in all cases yields a similar mixture of isomerides in which *cis*-5-hydroxyhydrindane (I), m.p. 41° (*H* succinate, m.p. 81.5°; normal succinate, m.p. 90°; phenylurethane, m.p. 125°), greatly predominates and is accompanied by *as*-5-hydroxyhydrindane (II) (phenylurethane, m.p. 74°). Oxidation of (I) with CrO₃ in AcOH gives the corresponding ketone (III), b.p. 103°/17 mm. (semicarbazone, m.p. 208°), and *cis*-cyclopentane-1:2-diacetic acid, m.p. 173°, also obtained in very small yield when (III) is oxidised with KMnO₄ or, together with an acid, m.p. about 100°, when (I) is dehydrated with KHSO₄ and the unsaturated hydrocarbon, b.p. 165—170°/730 mm., is oxidised with KMnO₄. Hydrogenation of 5-acetamidohydrindene (IV) (Skita) gives a mixture of products from which, after hydrolysis, *Bz* derivatives, m.p. 165° (V), 145°, and 143°, respectively, are isolated. (V) is hydrolysed to an amine (VI), b.p. 86°/12 mm., the *Ac* derivative, m.p. 107—108°, of which is obtained by the Willstätter hydrogenation of (IV). Treatment of (VI) with HNO₂ affords (II). Hydrogenation of 4-hydroxyhydrindene (Skita) does not give a homogeneous hydrindanol. Oxidation of 4-hydroxyhydrindane with CrO₃ in AcOH gives imperfectly homogeneous *cis*-hydrindan-4-one (VII), b.p. 100°/17 mm. (semicarbazone, m.p. 193°); the corresponding, non-cryst. oxime yields two *Bz* derivatives, m.p. 114° (*cis*-compound), and m.p. 92° (? *trans*-compound). Oxidation of (VII) with HNO₃ yields only (·CH₂·CO₂H)₂. H. W.

4-Iodopyrocatechol. E. FOURNEAU and J. DRUEY (Compt. rend., 1934, 199, 870—872).—Iodopyrocatechol diacetate (I), b.p. 148—150°/0.8 mm., is prepared by diazotisation of 4-aminopyrocatechol diacetate and treatment with KI. Hydrolysis of (I) with HCl in MeOH yields 4-iodopyrocatechol, m.p. 92° and 50° (dimorphous), which gives a green coloration with FeCl₃, becoming red with Na₂CO₃ and reddish-violet with NaHCO₃. A. G. P.

Hydroxytriphenylmethanes. Condensation of aromatic aldehydes and phenols with phosphoric acid. I. TANASESCU and T. SIMONESCU (J. pr. Chem., 1934, [ii], 141, 311—326).—PhCHO, PhOH (I), and

cryst. H₃PO₄ at 100° (bath) give 4:4'-dihydroxytriphenylmethane (leucobenzaurin), m.p. 161°; *p*-OH·C₆H₄·CHO and (I) similarly afford 17% of tri-*p*-hydroxyphenylmethane (leucoaurin), m.p. 240°, and 35% of a phenolic substance; *o*-C₆H₄(CHO)₂ yields *α*-*p*-hydroxyphenylphthalide, m.p. 148°; *o*-NO₂·C₆H₄·CHO furnishes 2-nitro-4':4''-dihydroxytriphenylmethane (about 70%), amorphous, m.p. about 92° [also prepared by diazotisation of the 4':4''-(NH₂)₂-derivative] [*Ac*₂ and *Bz*₂, m.p. 155° (not sharp), derivatives; *Me*₂ ether], reduced (Zn dust, aq. EtOH, little CaCl₂) to the amphoteric 2-amino-4':4''-dihydroxytriphenylmethane, m.p. 195° (not sharp) (*Bz*₃ derivative, m.p. 110°); *m*-NO₂·C₆H₄·CHO gives (cf. De Varda and Zenoni, A., 1891, 1346) about 50% of 3-nitro-4':4''-dihydroxytriphenylmethane, m.p. 90—91° (*Bz*₂ derivative, m.p. about 89°; *Me*₂ ether, m.p. 70°), similarly reduced to 3-amino-4':4''-dihydroxytriphenylmethane (+EtOH), m.p. 114° (decomp.) (*Bz*₃ derivative); *p*-NO₂·C₆H₄·CHO affords 4-nitro-4':4''-dihydroxytriphenylmethane (II), m.p. 130° (previous sintering) (cf. Danckwortt, A., 1909, i, 938; King and Lowy, A., 1924, i, 646) (*Bz*₂ derivative; *Me*₂ ether), reduced to 4-amino-4':4''-dihydroxytriphenylmethane (III), m.p. 110° (*Bz*₃ derivative). When a solution of (II) in 25% KOH is kept for 24 hr. and then acidified (HCl), 4-nitro-4'-hydroxyfuchson (+H₂O), carmine-red with green reflex (*Bz* derivative) [reduced (as above) to (III)], is obtained. Nearly all the above compounds are amorphous. H. B.

Apiole. H. WINDISCH (Mercks Jahresber., 1934, 47, 56—57; Chem. Zentr., 1934, ii, 1171).—A method for the isolation of apiole and myristicin as their Br additive compounds, m.p. 118—120° and 126—129°, respectively, is described. H. N. R.

cis- and *trans*-Chlorohydrins of 1-methyl-Δ¹-cyclopentene. P. D. BARTLETT and R. V. WHITE (J. Amer. Chem. Soc., 1934, 56, 2785; cf. A., 1934, 1221).—2-Chlorocyclopentanone and MgMeBr give 2-chloro-1-methylcyclopentan-1-ol (I), b.p. 50—57°/8 mm., whilst 1-methyl-Δ¹-cyclopentene and HOCl afford an isomeride (II), b.p. 61—64°/7 mm., m.p. 35—37°, and Cl-containing material (which does not react with EtOH-alkali) (cf. Chavanne and de Vogel, A., 1928, 745). (I) is converted by KOH in Et₂O or aq. 33% NaOH into 2-methylcyclopentanone; (II) similarly gives 1:2-oxido-1-methylcyclopentane. H. B.

Preparation of cyclohexanol. N. A. ORLOV, M. F. SCHOSTAKOVSKI, and V. V. SCHABAROV (J. Appl. Chem. Russ., 1934, 7, 760—763).—cyclohexanol is obtained in 96% yield by heating PhOH and H₂ at 265°/100 atm. for 7 hr. in presence of 4—6% of Ni₂O₃. R. T.

Esters of hydrogenated phenols. J. S. SAL-KIND and M. G. GERCHIKOV (Plast. Massi, 1934, No. 3, 37—40).—The esterification of cyclohexanol with AcOH, HCO₂H (85—90% yield with 95% acid in cold without catalyst for 1 day), and H₂C₂O₄, and of methylcyclohexanol with AcOH, is described. CH. ABS. (7)

Reaction of magnesium dimethyl and diethyl with cyclohexene oxide. P. D. BARTLETT and C. M. BERRY (J. Amer. Chem. Soc., 1934, 56, 2683—

2685).—The residue after removal of Et_2O from cyclohexene oxide and $\text{Et}_2\text{O-MgEt}_2$ (Noller and Hilmer, A., 1932, 837) is heated at 100° (bath) and then hydrolysed (dil. HCl); *trans*-2-ethylcyclohexanol (I) (contaminated with some impurity) is thus obtained in 42% yield. Slightly impure *trans*-2-methylcyclohexanol is similarly prepared using MgMe_2 . (I) is oxidised to 2-ethylcyclohexanone. No rearrangement occurs in the above reactions. H. B.

Preparation of amino-alcohols. I. J. T. ABRAMS and F. S. KIPPING (J.C.S., 1934, 1988—1991).— $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$, Et α -benzoyl-propionate, -butyrate, and -isobutyrate (I) are prepared by Claisen's method [cf. J.C.S., 1909, 95, 2042; criticisms (A., 1930, 212 and 1932, 944) are unfounded] and give [except (I)] with conc. aq. NH_3 the corresponding amides, m.p. $112\text{--}113^\circ$, 153° (lit. $145\text{--}146^\circ$), 155° (lit., $148\text{--}149^\circ$), respectively, which with Al-Hg in $\text{H}_2\text{O-EtOH}$ give, respectively, β -hydroxy- β -phenyl-propionamide (II), m.p. $118\text{--}119^\circ$, and its α -Me (III), m.p. $134\text{--}135^\circ$, and α -Et, m.p. $134\text{--}135^\circ$, derivatives [and a diastereoisomeride (?), m.p. $128\text{--}131^\circ$, of the last]. (II) and (III) are converted by NaOBr below 0° into β -amino- α -phenyl-ethyl (cf. A., 1914, i, 677) and -propyl alcohol (IV) [also some bromoamide (?), m.p. $116\text{--}117^\circ$, which is converted by NaOH into (IV)], isolated as the hydrochlorides. J. L. D.

Ephedrine. II. New benzyl homologues. S. D. WILSON and L. H. SUN (J. Chinese Chem. Soc., 1934, 2, 243—256).— $\text{CH}_2\text{Ph}\cdot\text{CHBr}\cdot\text{COPh}$ with excess of NH_2Me in C_6H_6 at room temp. during many hr. gives *Ph* α -methylamino- β -phenylethyl ketone hydrochloride, m.p. $225\text{--}226^\circ$, reduced (H_2 -Pt-Pt oxide) in EtOH at $40\text{--}50^\circ$ to dl- β -methylamino- α -diphenyl-propanol, an oil (hydrochloride, m.p. $204\text{--}205^\circ$; sulphate, m.p. $184\text{--}185^\circ$; picrate, m.p. $172\text{--}173^\circ$), which is resolved (tartaric acid) into the d-, $[\alpha]_D^{25} +10.9^\circ$ in 2% EtOH (hydrochloride, m.p. $194\text{--}195^\circ$; d-tartrate, m.p. $202\text{--}204^\circ$), and the l-form, $[\alpha]_D^{25} -11.0^\circ$ (hydrochloride, m.p. $192\text{--}193^\circ$; d-tartrate, m.p. $175\text{--}176^\circ$). Similarly prepared, *Ph* α -benzylamino- β -phenylethyl ketone hydrochloride has m.p. $206\text{--}207^\circ$, and is reduced to dl- β -benzylamino- α -diphenyl-propanol (hydrochloride, m.p. 220° ; sulphate, m.p. $207\text{--}208^\circ$; picrate, m.p. $150\text{--}151^\circ$), which is resolved into the d-, $[\alpha]_D^{25} +9.2^\circ$ in 2% EtOH (hydrochloride, m.p. $229\text{--}230^\circ$), and l-form, $[\alpha]_D^{25} -10.0^\circ$ (l-mandelate, m.p. $156\text{--}157^\circ$), with l-mandelic acid. $\text{CHMeBr}\cdot\text{COPh}$ with $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ (2 mols.) as above gives *Ph* α -benzyl-aminoethyl ketone hydrochloride, m.p. $189\text{--}190^\circ$, reduced to β -benzylamino- α -phenylpropanol, m.p. $72\text{--}73^\circ$ (hydrochloride, m.p. $188\text{--}189^\circ$; sulphate, m.p. $184\text{--}186^\circ$; oxalate, m.p. $213\text{--}215^\circ$; picrate, m.p. $174\text{--}175^\circ$). J. L. D.

Vinylene homologues of "Michler's hydrol-blue." W. KONG and K. SEIFERT (Ber., 1934, 67, —2120).— β -Ethoxyacraldehyde Et_2 acetal, NPi ZnCl_2 yield 1-tri-*p*-dimethylaminodiphenylstyrylmethane (I) $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, m.p. 187° (C₂₇H₃₃N₃), $\text{ZnCl}_2\cdot 8\text{HCl}\cdot 4\text{H}_2\text{O}$, converted by HCl-AcOH into tetramethylbenzidine and *pp'*-tetramethyldiaminophenylstyrylmethane (II); perchlorate, decomp. 165° ; dichloro-

picrate, decomp. 195° . (II) is transformed by NH_3 into the substance (?)

$\text{NH}[\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2]_2$, m.p. 193° .

(II) shows an absorption max. at $689\text{ m}\mu$, that of Michler's hydrol in AcOH being at $609\text{ m}\mu$. When (I) is heated in AcOH from which all trace of oxidising agent has been removed, a small amount of (II) (as acetate) is formed, together with some tetramethylbenzidine. Leuco-crystal-violet undergoes a similar change in AcOH , forming Michler's hydrol acetate. H. W.

Resolution of some cyclanediols. M. GODCHOT, M. MOUSSERON, and R. RICHAUD (Compt. rend., 1934, 199, 1233—1235).—*trans*-cyclopentane-1:2-diol with H_2SO_4 at -15° affords the di-sulphuric ester, the strychnine salt of which when fractionally crystallised, followed by hydrolysis, gives the optical isomerides, $[\alpha]_D^{25} \pm 33.60^\circ$. Similarly, *cis*-1-methylcyclohexane-3:4-diol (A., 1923, i, 1082) gives d- and l-compounds, $[\alpha]_D^{25} \pm 18.10^\circ$, and the *trans*-diol (A., 1923, i, 101), isomerides, $[\alpha]_D^{25} \pm 19.40^\circ$. J. L. D.

p-Fluorophenacyl alcohol and some of its esters. R. M. HANN and J. P. WETHERILL (J. Washington Acad. Sci., 1934, 24, 526—528).—Condensation of $\text{CH}_3\text{Cl}\cdot\text{COCl}$ with PhF and AlCl_3 in CS_2 affords *p*-fluorophenacyl chloride (I), m.p. 48° , converted by fused $\text{NaOAc-AcOH-aq. EtOH}$ into the acetate, m.p. $48.5\text{--}49^\circ$, hydrolysed by $\text{BaCO}_3\text{-H}_2\text{O}$ at 100° to *p*-fluorophenacyl alcohol, m.p. 114° [o-, m.p. 74.5° , m-, m.p. 105° , and *p*-nitrobenzoate, m.p. 134° , from the $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{CO}_2\text{H}$ and (I) in *N*- NaOH]. J. W. B.

Structure of cholesterol. R. ROBINSON (Chem. and Ind., 1934, 1062—1063).—The suggestion (this vol., 81) that the Me group of cholesterol (I) now usually placed at C_{10} is better placed at C_9 was made by the author (A., 1932, 1245), but is not in accord with chemical evidence. The accepted C skeleton of (I) can be constructed without rearrangement from difarnesyl (tail to tail; 2:6:10:15:19:23-hexamethyltetracosane) by elimination of the C_{10} , C_{15} , and C_{23} side-chains and junction of C_7 and C_{10} to C_{23} , of C_{11} to C_{20} , and of C_{14} to C_{19} . Elimination of the C attached to C_{15} may occur as CO_2 from a β -keto-acid, the CO being C_{15} , which carries the OH of cholesterol and cestrin. R. S. C.

Condensation of aromatic amines with cholesterol chloroformate. A. VERDINO and E. SCHADENDORFF (Monatsh., 1934, 65, 141—152).—By condensation (sometimes in COMe_2) of cholesterol chloroformate with the appropriate aromatic NH_2 -compound are obtained the cholesterol esters of phenyl-, m.p. 168° , o-, m.p. 160° , m-, m.p. 157° , and *p*-tolyl-, m.p. 182° ; o-, m.p. 168° , m-, m.p. 185° , and *p*-nitrophenyl-, m.p. $202\text{--}208^\circ$; o-, m.p. $170\text{--}171^\circ$, m-, m.p. $126\text{--}127^\circ$, and *p*-bromophenyl-, m.p. $182\text{--}186^\circ$; o-carboxyphenyl-, m.p. 208° (Et ester, m.p. $191\text{--}194^\circ$); benzyl-, m.p. 148° , *p*-anisyl-, m.p. 137° , o-, m.p. 132° , and *p*-ethoxyphenyl-, m.p. 140° (clears at 180°); 3:4-dimethylphenyl-, m.p. 152° , *p*-hydroxyphenyl-, m.p. 211° to liquid crystals, sinters 178° ; α -naphthyl-, m.p. 166° (decomp.), 5-nitronaphthyl-, m.p. $216\text{--}217^\circ$; β -anthraquinonyl-, m.p. 290° (decomp.), diphenyl, m.p. 193° , anilino-, m.p. 157° ,

p-azobenzene, m.p. 226°, and 2:3'-dimethylazobenzene-4', m.p. 183°, -carbamic acid; and phenyl-*o*-, m.p. 205°, and diphenyl-4:4', m.p. 270° (decomp.), -dicarbamic acid. J. W. B.

Cholesteryl salicylate.—See this vol., 152.

isoCholesterol. V. HUMNICKI (Bull. Soc. chim., 1934, [v], 1, 1560—1563).—*iso*Cholesterol (from lanoline), m.p. 138—139°, $[\alpha]_D^{25} +59.1^\circ$ [*chloride*, m.p. 93—94°; *cinnamate*, m.p. 150° after sintering from 135° (*tetrabromide*, m.p. 127—128°); *benzoate*, m.p. 175—177°; 6 colour reactions described], has the formula, $C_{26}H_{44}O$. It has a blue fluorescence in ultra-violet light. R. S. C.

Bombicesterol.—See this vol., 105.

Position of the hydroxyl group in ergosterol and stigmasterol. E. FERNHOLZ and P. N. CHAKRAVORTY (Ber., 1934, 67, [B], 2021—2026).—Dihydrocholesteryl acetate is oxidised with CrO_3 and the product is hydrolysed to β -3-hydroxyallocholanolic acid, m.p. 218°, the *Me* ester, m.p. 151°, of which is transformed by the successive action of $MgPhBr$, Ac_2O , and CrO_3 into β -3-hydroxynorallocholanolic acid (I), m.p. 226° (*Me* ester, m.p. 156°, and its *acetate*, m.p. 163°; *Na* salt). (I) is also obtained from ergostanyl acetate and from stigmastanyl acetate, which in addition yields an *acid*, m.p. 221°, in small amount. The position and steric arrangement of OH in ergosterol and stigmasterol are thus established and their relationships to cholesterol assured. H. W.

α - and β -Spinastanol. D. LARSEN and F. W. HEYL (J. Amer. Chem. Soc., 1934, 56, 2663—2665).—Reduction (H_2 , PtO_2 , $AcOH$) of α -spinasteryl acetate (A., 1932, 381), m.p. 187°, $[\alpha] -5.8^\circ$ (all rotations are in $CHCl_3$ at $20 \pm 1^\circ$ and $\lambda=5461$) [ozonolysis (method: Guiteras *et al.*, A., 1932, 611) of which shows the presence of a saturated side-chain; the 2 double linkings present are, therefore, in the nucleus], gives the *acetate* (I), m.p. 119°, $[\alpha] +11.6^\circ$, of α -spinastanol, m.p. 110°, $[\alpha] +24.2^\circ$ (*p*-nitrobenzoate, m.p. 192°, $[\alpha] +6.6^\circ$), which contains 1 double linking (BzO_2H). Treatment of (I) with dry HCl in $CHCl_3$ at 0° and subsequent hydrolysis (5% $EtOH$ - KOH) affords β -spinastanol, m.p. 127.5°, $[\alpha] +36.5^\circ$ [*acetate* (II), m.p. 86.5°, $[\alpha] +24.3^\circ$], purified through its *p*-nitrobenzoate, m.p. 183°, $[\alpha] +37.3^\circ$. (II) is reduced (H_2 , PtO_2 , $AcOH$) to the *acetate*, m.p. 132°, $[\alpha] +16.3^\circ$, of the saturated spinastanol, m.p. 137°, $[\alpha] +27.8^\circ$ (*p*-nitrobenzoate, m.p. 213.5°, $[\alpha] +24.4^\circ$; *phenylcarbamate*, m.p. 172°, $[\alpha] +16.4^\circ$). The above changes are analogous to those in the ergosterol series. α -Spinasteryl *p*-nitrobenzoate, m.p. 220°, $[\alpha] +5.2^\circ$, and *phenylcarbamate*, m.p. 177°, $[\alpha] -3.3^\circ$, appear to be new. H. B.

alloPregnandiol, a new alcohol from urine of pregnancy. M. HARTMANN and F. LOCHER (Naturwiss., 1934, 22, 856).—The mother-liquors from pregnandiol diacetate, m.p. 182—183° (corr.), $[\alpha]_D^{25} +35.3^\circ$ in C_6H_6 , obtained from urine of pregnancy, yield *allopregnandiol diacetate*, m.p. 141—142.5° (corr.), $[\alpha]_D^{25} +18.8^\circ$ in C_6H_6 , which gives the free *diol*, m.p. 248—248.5° (corr.), oxidised by CrO_2 in 90% $AcOH$ to *allopregnandione*, m.p. 202—204° (corr.). R. S. C.

Preparation of inositol from inositol phosphates. S. OTOLSKI (Arch. Chem. Farm., 1934, 2, 61—64).—Inositolphosphoric acid (I) is heated with 3 vols. of H_2O for 5 hr. at 190° , 850 g. of CaO in 5 litres of H_2O are added, and the suspension is filtered. The residue of $Ca_3(PO_4)_2$ is washed with hot H_2O , the filtrate + washings are conc. to 1 litre, 7 litres of 85% $EtOH$ added, the ppt. of inositol (II) is allowed to settle, the supernatant liquid decanted off, 500 c.c. of H_2O are added, and the solution is boiled with adsorbent C and filtered. 1 litre of 96% $EtOH$ is added to the filtrate, the ppt. of crude (II) collected, washed with 20% $EtOH$, and dried at 110 — 120° . The product, containing 5% of mineral impurities, is recrystallised from 32% $EtOH$ to yield pure (II) [237 g. per kg. of (I)]. R. T.

Synthesis of 1-cyano-1-methylcyclopropane from diazomethane and α -methylacrylonitrile. D. GOTKIS and J. B. CLOKE (J. Amer. Chem. Soc., 1934, 56, 2710—2712).— $OH \cdot CMe_2 \cdot CN$ is dehydrated [P_2O_5 at 10 — 15° (bath)] to $CH_2 \cdot CMe \cdot CN$, b.p. 89 — 91° , which with $Et_2O \cdot CH_2N_2$ affords (probably) 5-cyano- α -methyl- Δ^1 -pyrazoline. This is decomposed thermally to 1-cyano-1-methylcyclopropane (I), b.p. 127 — 127.5° (corr.)/761.5 mm., and a little unsaturated material (removed by oxidation with cold alkaline $KMnO_4$). (I) is hydrolysed [conc. H_2SO_4 or McMaster and Langreck's method (A., 1917, i, 334)] to 1-methylcyclopropane-1-carboxylamide, m.p. 143 — 145° (corr.); with 100% H_3PO_4 at 140 — 155° , tiglic acid results. The additive compound from (I) and $MgPhBr$ with liquid NH_3 gives Ph 1-methylcyclopropyl ketimine, the hydrochloride, m.p. 103 — 106° , of which rearranges (cf. A., 1929, 703) to a pyrroline [picrate, m.p. 150 — 151° (decomp.); *platinichloride*]. (I) could not be prepared by methylation of cyanocyclopropane, from $EtCN$ and $(\cdot CH_2Hal)_2$, or from $CH_2Hal \cdot CH_2 \cdot CHMe \cdot CN$. H. B.

Sulphonation of benzoic acid. J. S. REESE (Textile Res., 1934, 4, 183—188).—The velocities of reaction of $BzOH$ with conc. H_2SO_4 at 150° , 175° , and 200° , and with fuming H_2SO_4 at room temp., are recorded. CH. ABS. (?)

Preparation of cinnamic acid and *o*-phenylphenol derivatives. R. H. CLARK, R. G. D. MOORE, and M. MCARTHUR (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 97—102).—*m*-Iodocinnamic acid, m.p. 191.5° [improved prep.; lit., 182 — 183° (decomp.)] (*Et* ester, m.p. 36 — 37°), is converted through the *chloride*, m.p. 35.3° , and warm $CH_2Ph \cdot OH$ into *benzyl m*-iodocinnamate, m.p. 50° . Cinnamyl chloride (I) with warm *m*- $C_6H_4I \cdot CH_2 \cdot OH$ (prep. from *m*- $C_6H_4I \cdot CHO$ described) gives *m*-iodobenzyl cinnamate, m.p. 35° . (I) when heated with $CO(NH_2)_2$ gives *monocinnamylcarbamide*, m.p. 197° . Similarly obtained, *m*-iodocinnamylcarbamide has m.p. 207.5° . 5-Benzeneazo-2-hydroxydiphenyl with Zn in boiling $AcOH$ - $EtOH$ gives 5-amino-2-hydroxydiphenyl (cf. A., 1917, i, 390), which is converted with difficulty through the diazonium compound into the 5-I-compound. α -Hydroxydiphenyl with ICl in $AcOH$ at 100° gives *o*-iodo-2-hydroxydiphenyl, b.p. 190 — $200^\circ/10$ mm. (*Ac* derivative, m.p. 82°). J. L. D.

Acetyldiphenylchloroacethydrazide. H. ASPELUND and A. M. AUGUSTSON (Acta Acad. Aboensis math. phys., 1933, 7, No. 10, 1—7; Chem. Zentr., 1934, ii, 1455).—Benzilic acid hydrazide and Ac_2O yield *acetylbenzilhydrazide*, m.p. (+ $2\text{H}_2\text{O}$) 190—191°; this, with $\text{CPh}_2\text{Cl}\cdot\text{COCl}$, affords *acetyldiphenylchloroacethydrazide*, m.p. 94°, which with EtOH yields *acetyldiphenylethoxyacethydrazide*, m.p. 154°. EtOAc and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 130° for 4 hr. give a good yield of 4-amino-3 : 5-dimethyl-1 : 2 : 4-triazole, m.p. 196°.

H. N. R.

Preparation of β -benzylidene- α -o-nitrobenzylidene- and α -benzylidene- β -o-nitrobenzylidene-propionic acid. F. SCHENCK (J. pr. Chem., 1934, [ii], 141, 299—300).— $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and Ac_2O at 125—130° (bath) give γ -phenyl- α -o-nitrobenzylidene- Δ^8 -butenoic (β -benzylidene- α -o-nitrobenzylidenepropionic) acid, m.p. 180—181°. γ -o-Nitrophenyl- Δ^8 -butenoic acid, m.p. 112—113° [from $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHO}$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ at 100° (bath) and finally at 110°], and PhCHO similarly afford γ -o-nitrophenyl- α -benzylidene- Δ^8 -butenoic (α -benzylidene- β -o-nitrobenzylidenepropionic) acid, m.p. 167—168°.

H. B.

o-Phenyldiphenyls and "synchronised rotation." A. M. SADLER and G. POWELL (J. Amer. Chem. Soc., 1934, 56, 2650—2653).—o-Iododiphenyl, $\text{o-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{Et}$ (I), and Cu-bronze at 270—275° give 2 : 2'-didiphenyl, b.p. 193—195°/1 mm., m.p. 117—119°, and a product, b.p. 169—175°/1 mm., which when hydrolysed (KOH in 5% EtOH) affords 2-phenyldiphenyl-2'-carboxylic acid (II), m.p. 143—144.5° (strychnine, m.p. 215°, [α]_D²⁵ 42 to -43° in CHCl_3 , and phenylethylamine, m.p. 115—116°, [α]_D²⁵ -4.1° in EtOH , salts). $\text{o-C}_6\text{H}_4\text{Ph}_2$ is obtained when the Ag salt of (II) is heated. (II) could not be resolved; a model of (II) has a plane of symmetry when the plane of the 2-Ph group is perpendicular to the plane of the Ph_2 groups. 2-Iodo-2'-methylidiphenyl (III) [prepared by Mascarelli and Gatti's method (A., 1932, 607)] and (I) similarly afford 2-o-tolyldiphenyl-2'-carboxylic acid (IV), m.p. 130.5—131.5° [strychnine (+ EtOH), m.p. 210° (shrinks at 85°), [α]_D²⁵ -46.5° in CHCl_3 , and phenylethylamine, m.p. 123—126°, [α]_D²⁵ -3.5° in CHCl_3 , salts], which could not be resolved. (IV) possesses no mirror element of symmetry; non-resolution may be due to "synchronised rotation" (Maclean and Adams, A., 1934, 63). 2 : 2'-Di-(o-tolyl)diphenyl, m.p. 113—114°, is prepared from (III) and Cu at 265—285°. 2-Nitro-2'-methylidiphenyl (from $\text{o-C}_6\text{H}_4\text{I}\cdot\text{Me}$ and $\text{o-C}_6\text{H}_4\text{I}\cdot\text{NO}_2$) has m.p. 64—57—58°. 6-Nitro-2-methylidiphenyl, b.p. 130/3 mm., m.p. 105—106° (from 2-bromo-3-nitro-toluene and PhI), is reduced (SnCl_2 , EtOH -conc. HCl) to the 6-NH₂-derivative, b.p. 144—145°/2 mm., m.p. (hydrochloride), convertible (Sandmeyer) into o-tolao-2-methylidiphenyl, b.p. 135°/1 mm., m.p. 29—(I), $\text{o-C}_6\text{H}_4\text{I}\cdot\text{NO}_2$ and Cu at 250—285° give (after hydrolysis) 2-nitrodiphenyl-2'-carboxylic acid, 165—166.5°; Me 2-bromo-3-nitrobenzoate and PhI similarly afford 2-nitrodiphenyl-6-carboxylic acid, m.p. 187—188°.

H. B.

Geometrical inversion of the acids derived from coumarins. B. B. DEY, R. H. R. RAO, and

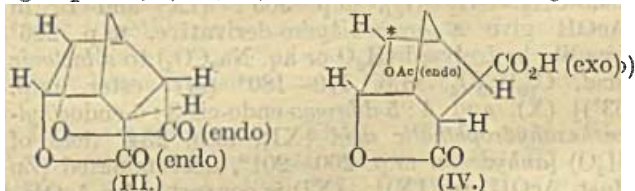
T. R. SESHADRI (J. Indian Chem. Soc., 1934, 11, 743—749).—o-Coumaric acid (I) and its 5- NO_2 - (II) and 4-OMe- (III) -derivatives (modified preps.), when heated, give the styrene and CO_2 , but the Me and Et esters undergo ring-closure rapidly. Both acids and esters give the coumarin in light, the ease of reaction being (II) > (I) > (III). The following are described: Me, m.p. 137°, and Et o-coumarate, m.p. 86°; Et 5-nitrocoumarate, m.p. 170—172°; 7-methoxycoumarin, m.p. 117—118° [from umbelliferone (modified prep.) or malic acid and m-OMe- $\text{C}_6\text{H}_4\cdot\text{OH}$]; Me, m.p. 138°, and Et 4-methoxycoumarate, m.p. 109°.

R. S. C.

cyclopentane-1 : 2-diacetic acid. W. HUCKEL, E. GOTH, and G. DEMMLER (Ber., 1934, 67, [B], 2102—2103; cf. Linstead *et al.*, A., 1934, 1002).—Treatment of Et cyclopentanoneacetate with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn in C_6H_6 gives a mixture of OH-ester, unsaturated ester, oily acids, and other products. Fractionation and hydrolysis of the ester mixture leads to cyclopentene-1 : 2-diacetic acid (I), m.p. 182—183°. Hydrogenation (Pt sponge in AcOH or Et_2O ; PtO_2 -MeOH) leads mainly to cis-cyclopentane-1 : 2-diacetic acid, m.p. 172—173° (monoanilide, m.p. 129—131°; dianilide, m.p. 225—226°), whereas treatment in presence of Pd-C-EtOH or (as Na salt) with Pd-C- H_2O yields essentially trans-cyclopentane-1 : 2-diacetic acid, m.p. 132—133.5° (monoanilide, m.p. 144—146°; dianilide, m.p. 236—237°).

H. W.

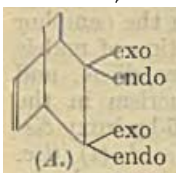
Steric course of addition and substitution reactions. I. Stereochemistry of diene synthesis. K. ALDER and G. STEIN [with F. VON BUDDENBROCK, W. ECKARDT, W. FRERCKS, and S. SCHNEIDER] (Annalen, 1934, 514, 1—33).—The investigation (A., 1933, 941) on the steric configurations of the dicyclopentadienes is being extended to the determination of, e.g., configurations in the camphor group. Preliminary work on the addition of maleic anhydride to cyclopentadiene and -hexadiene, and the occurrence of exo- and endo-isomerism in the adducts, is now reported. 4-Bromo-5-hydroxy-cis-3 : 6-endomethylenhexahydrophthalic acid (I) (loc. cit.) is converted by Zn-Cu and AcOH into endo-cis-3 : 6-endomethylene- Δ^4 -tetrahydrophthalic acid (II), and by 25% MeOH-KOH followed by Ac_2O into the dilactone (III), m.p. 266°, of 4 : 5-dihydroxy-cis-3 : 6-endomethylenhexahydrophthalic acid. These results prove the endo-configuration (cf. III) of the CO_2H groups of (II). (III) can be distilled unchanged and



is unaffected by hot conc. HNO_3 . (III) is rearranged by 25% MeOH-KOH to the trans-lactonic acid, m.p. 200° {Ac derivative (IV), m.p. 200° [Me ester, m.p. 83°, which differs from the trans-acetyl-lactonic ester (IV with H and OAc at C* interchanged) previously described (loc. cit.)]}. The anhydride of (II) and cold 50% H_2SO_4 give the 2 : 4-lactone (V), m.p. 203°, of 4-hydroxy-cis-3 : 6-endomethylenhexahydrophth-

alic acid; *trans*-3:6-*endomethylene*- Δ^4 -tetrahydrophthalic acid similarly affords the 2:4-lactone (VI), m.p. 134°, of the 4-hydroxy-*trans*-acid, whilst β (*exo*)-*cis*-3:6-*endomethylene*- Δ^4 -tetrahydrophthalic anhydride (*loc. cit.*) yields 4-hydroxy-*exo*-*cis*-3:6-*endomethylenehexahydrophthalic acid* (VII), m.p. 203° (decomp.) (*Ac* derivative anhydride, m.p. 112°), (V), and oily products. The *Me* ester, m.p. 85°, of (V) is converted by MeOH-NaOMe into (VI). (V) and (III) are obtained by debromination (method: Busch and Stove, A., 1916, ii, 534) of the lactone of (I); the *trans*-bromolactone (*loc. cit.*) similarly gives (VI). (VII) undergoes the Wagner rearrangement when treated with 50% H₂SO₄ at 150° yielding (V) and (VI) [similarly produced from (V)]. *Mé cyclopentadiene-1-carboxylate* [obtained by slow vac. distillation of its dimeride (Thiele, A., 1901, i, 182)] and maleic anhydride in C₆H₆ give *endo*-*cis*-3:6-*endocarbomethoxymethylene*- Δ^4 -tetrahydrophthalic anhydride, m.p. 151—152°, which with Br in H₂O affords two *bromohydroxy*-*endo*-*cis*-3:6-*endocarbomethoxymethylenehexahydrophthalic acid lactones*, m.p. 155—157° and 197°; these are both converted by 20% MeOH-KOH into the 1:5-lactone, m.p. 263° (loss of H₂O), of (*cis*)-4:5-dihydroxy-*endo*-*cis*-3:6-*endocarbomethoxymethylenehexahydrophthalic acid*, which is dehydrated (Ac₂O) to the *dilactonic acid* [(III) with *endo*-CH₂=CH·CO₂H], m.p. 263° (*Me* ester, m.p. 170°).

2:5-*endo*Ethylenecyclohexanone (A., 1930, 472) is reduced (Wolff-Kishner; using semicarbazone) to 2:2:2-dicyclooctane (VIII), m.p. 169—170°, which undergoes ready autoxidation. (VIII) possesses a higher degree of symmetry than 1:2:2-dicycloheptane (Komppa and Beckmann, A., 1934, 1105) and gives only one type of monosubstitution derivative. The dicyclooctene, like the dicycloheptene (cf. A.,



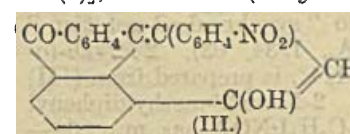
1933, 941), can give rise to *endo*- and *exo*-derivatives (cf. A). Distillation of *trans*-3:6-*endo*ethylenhexahydrophthalic acid gives the *cis*-anhydride only. *endo*-*cis*-3:6-*endo*Ethylen- Δ^4 -tetrahydrophthalic anhydride (IX) (A., 1928, 1018) and Br in H₂O give

4-bromo-5-hydroxy-*endo*-*cis*-3:6-*endo*ethylenhexahydrophthalic acid (X), m.p. 119° [1:5-lactone, m.p. 165—166° (*Me* ester, m.p. 137—138°)], converted by MeOH-KOH into the corresponding *hydroxylactonic acid*, m.p. 257° (decomp.) (*Me* ester, m.p. 172°), which is dehydrated (Ac₂O) to the *dilactone* [(III) with *endo*-CH₂=CH₂·CH₂], m.p. 305°. (IX) and Br in AcOH give a *bromodihydro*-derivative, m.p. 206° [readily hydrolysed (H₂O or aq. Na₂CO₃) to a *lactonic acid*, C₁₀H₁₀O₄, m.p. 179—180° (*Me*₁ ester, m.p. 63°)] (X), and 4:5-*di*bromo-*endo*-*cis*-3:6-*endo*ethylenhexahydrophthalic acid (XI), m.p. 234° (loss of H₂O) [*anhydride*, m.p. 200—201°, debrominated (Zn dust, AcOH) to (IX)]. (XI) is converted by AcOH-HBr at 170° into the *trans*-*isomeride* (XII), m.p. 236—237°, and the *exo*-*cis*-anhydride (XIII), m.p. 223—224°. (XII) is debrominated (Zn dust, AcOH) to *trans*-3:6-*endo*ethylene- Δ^4 -tetrahydrophthalic acid, m.p. 211° [also obtained from (IX) and MeOH-NaOMe]; (XIII) similarly gives *exo*-*cis*-3:6-*endo*ethylene- Δ^4 -tetrahydrophthalic anhydride (XIV), m.p. 157—158° [not depressed by (IX), m.p. 147°]. (XIV)

and Br in AcOH give [cf. (IX) (above)] a quant. yield of (XIII); (IX) and (XIV) are both reduced (H₂, Pt-black, AcOH) to the same dihydro-derivative (A., 1930, 472). H. B.

Formation of glycidamides [$\alpha\beta$ -oxidopropionamides] by the action of hydrogen peroxide on $\alpha\beta$ -ethylenic nitriles. J. V. MURRAY and J. B. CLOKE (J. Amer. Chem. Soc., 1934, 56, 2749—2751).—The compound previously obtained from α -phenylcrotononitrile and alkaline H₂O₂ is not α -phenylacetoacetamide (A., 1932, 739), since it differs from the known forms (Ogata and Ito, A., 1916, i, 654), and gives no colour with FeCl₃; it is probably $\alpha\beta$ -oxido- α -phenylbutyramide. This view is supported by the formation of $\alpha\beta$ -oxido- $\alpha\beta$ -diphenylpropionamide (Köhler and Brown, A., 1933, 1297) from α -phenylcinchonitrile, 10% H₂O₂, and 10% Na₂CO₃ in COMe, (general procedure). Similarly treated, *o*-C₆H₄Me·CN gives *o*-C₆H₄Me·CO·NH₂; CHPh·CH·CN affords CHPh·CH·CO·NH₂; α -phenyl- Δ^4 -hexenonitrile, b.p. 118—118.5° (corr.)/3.5 mm. [obtained by prolonged interaction of CH₂Ph·CN and PrCHO in cold EtOH-NaOEt; hydrolysed (conc. H₂SO₄) to α -phenyl- Δ^4 -hexenoamide (I), m.p. 139—140° (corr.)], yields a compound, C₁₂H₁₅O₂N, m.p. 145—146° (corr.); CH₂·CH·CH₂·CN furnishes CH₂·CH·CH₂·CO·NH₂. α -Phenylcrotonamide and (I) are unaffected. The oxido-amides are probably formed by a 1:4-addition to the system >C:C:C:N. H. B.

β -9-Anthranyl- β -*m*-nitrophenylpropionic acid and its derivatives. A. VACHON, P. E. GAGNON, and J. KANE (Canad. J. Res., 1934, 11, 644—651; cf. A., 1933, 949).—*Me*₂ *m*-nitrobenzylidenemalonate, m.p. 99—100° (*Et*₂ ester, m.p. 75—76°), with anthrone and piperidine in MeOH gives *Me*₂ β -9-anthranyl- β -*m*-nitrophenylethane- $\alpha\alpha$ -dicarboxylate, m.p. 188—189° (*Et*₂ ester, m.p. 135—137°), hydrolysed by 30% H₂SO₄-AcOH at 120—125° to β -anthranyl- β -*m*-nitrophenylpropionic acid (I), m.p. 206—207° (chloride, m.p. 147°; *Et* ester, m.p. 107—109°), oxidised by conc. H₂SO₄ at 140—150° to the lactone (II), m.p. 267—268°, of β -9-(9-hydroxyanthranyl)- β -*m*-nitrophenylpropionic acid + H₂O, m.p. 120° [isolated by treatment with EtOH-KOH, or obtained by KMnO₄-KOH oxidation of (I)], and 1:9-(1'-hydroxy-3'-*m*-nitrophenyl)benz-



anthrone (III), m.p. about 305°. Oxidation of (I) with KMnO₄-KOH gives *m*-NO₂-C₆H₄·CO₂H and anthraquinone, which is not obtained by similar oxidation of (III). J. W. B.

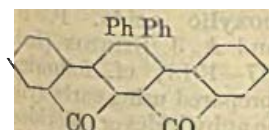
Derivatives of substituted succinic acids. I. Action of alkaline sodium hypobromite on *s*-diphenylsuccinamide and 3:4-diphenylsuccinimide. J. A. McRAE and A. S. TOWNSEND (Canad. J. Res., 1934, 11, 628—636).—With alkaline NaOBr at -10°, raised to 75—80°, (·CHPh·CO·NH₂)₂ (I) gives NH₃, PhCHO (II), and CHPh₂·CO₂H (III); no similar Ph migration occurs with NaOH alone. Reduction of α -(·CPh·N·OH)₂ with Na-EtOH gives both the *dl*- and *i*-forms of (·CHPh·NH₂)₂, affording NH₃ and (II) with NaOBr. In attempts to prepare

substituted derivatives of (I) the following have been obtained: condensation of $\text{CH}_2\text{Ph}\cdot\text{CN}$ with $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ gives α -phenyl-o-chlorocinnamionitrile (IV), m.p. 107° , converted in poor yield by aq. $\text{EtOH}\cdot\text{KCN}\cdot\text{AcOH}$ into the crude dinitrile, hydrolysed by 80% H_2SO_4 to s-o-chlorophenylphenylsuccinic acid, m.p. 217° , and its diamide, m.p. 280° . With hot aq. $\text{EtOH}\cdot\text{KCN}$ (IV) gives (?) the nitrile-acid $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHPh}\cdot\text{CN}$, m.p. 135° . With HNO_3 -90% H_2SO_4 at room temp. $(\cdot\text{CHPh}\cdot\text{CN})_2$ gives pp'-dinitrodiphenylsuccinamide, m.p. 294° (decomp.), converted by NaOBr into NH_3 and a little of the succinamic acid. By similar methods are obtained s-p-anisylphenylsuccinonitrile, m.p. 204° (acid, m.p. 227° , and its Et_2 , m.p. 102° , and Et H , m.p. 154° , esters; imide, m.p. 178° ; anhydride, m.p. 114°).

With NaOBr $\begin{array}{c} \text{CHPh}\cdot\text{CO} \\ \text{CHPh}\cdot\text{CO} \end{array} > \text{NH}$ affords the succinamic acid, m.p. 218° (decomp.), and diphenylmaleic anhydride. $(\cdot\text{CHPh}\cdot\text{CO}_2\text{H})_2$ with PCl_5 gives the i-chloride, m.p. 190° . J. W. B.

Dissociable organic oxides. Ethyl 1:1'-diphenylrubene-3:3'-dicarboxylate; its dissociable oxide. C. DUFRAISSE and M. LOURY (Compt. rend., 1934, 199, 957-959).—*Et* 1:1'-diphenylrubene-3:3'-dicarboxylate (I) (prep. described) has m.p. 270° , and exhibits three absorption bands $200\text{ }\mu$. further towards the ultra-violet than those of the 1:1':3:3'- Ph_4 compound. (I) with O_2 in light easily gives an oxide, m.p. 250° , which loses a little O_2 , but much CO_2 , at 190° . J. L. D.

Highly arylated aromatic compounds. III. Highly phenylated benzenecarboxylic acids and the products of their transformation. W. DILTHEY, I. THEWALT, and O. TRÖSKEN (Ber., 1934, 67, [B], 1959-1964; cf. A., 1934, 62, 641).—Addition of tetraphenylcyclopentadienone (I) to maleic anhydride in boiling C_6H_6 leads to endocarbonyltetraphenylidihydrophthalic anhydride (II), m.p. 223° , whereas in boiling PhCl tetraphenylidihydrophthalic anhydride (III), m.p. 243° , is produced. (II) passes into (III) in boiling PhCl . Treatment of (II) or (III) with boiling PhNO_2 or of (III) with S at 250 – 300° to tetraphenylphthalic anhydride (IV), m.p. 296° converted by $\text{KOH}\cdot\text{EtOH}$ into tetraphenylphthalic acid (V), m.p. 286° (K salt). Accumulation of Ph groups greatly hinders the reactivity of CO_2H in (V) which does not dissolve in aq. NH_3 and is not esterified in the usual manner with EtOH . The Me_2 , m.p. 258° , and Et_2 , m.p. 205 – 206° , esters are obtained from (V) and CH_2N_2 in MeOH or from (I) and $(\cdot\text{C}\cdot\text{CO}_2\text{Me})_2$ or from (I) and $(\cdot\text{C}\cdot\text{CO}_2\text{Et})_2$, respectively cannot be hydrolysed. (IV) and C_6H_6 in presence of AlCl_3 afford triphenylfluorenone-carboxylic acid, m.p. 322° (K salt, oxime, m.p. 300°), or, under more drastic conditions, diphenyldifluorenone (VI), m.p. 396° (di-oxime), also obtained from (IV) and molten ZnCl_2 . (I) and *Me* phenylpropiolate



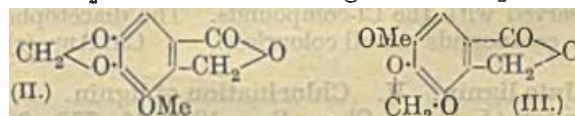
(VI.)

conc. H_2SO_4 or PCl_5 at 170 – 175° yield *Me* pentaphenylbenzoate (VI),

m.p. 342° . The corresponding acid (VII) is obtained from (I) and phenylpropionic acid at 190° and is converted into (VI) by CH_2N_2 . (VII) and PCl_5 in POCl_3 at 100° afford tetraphenylfluorenone, m.p. 298° . *Et* tetraphenyl-o-toluate, m.p. 205° , is derived from (I) and *Et* tetrolate at 200° ; the corresponding acid has m.p. 302° . H. W.

Bile acids. XLIV. M. SCHENCK (Z. physiol. Chem., 1934, 230, 199-206).—The previously described (A., 1934, 1103) dioximinohydroxamic acid, $\text{C}_{24}\text{H}_{37}\text{O}_8\text{N}_3$ (Ia, decomp. about 270°), is now prepared (Ib, decomp. about 257°) by reduction (Zn dust, aq. NH_3) of the nitroketohydroxamic acid (cf. A., 1929, 1070) and subsequent treatment with an excess of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in aq. $\text{EtOH}\cdot\text{NaOH}$ [whereby the NH_2OH salt (II), decomp. 263° (not sharp), of (Ib) results]. (Ib) [as (II)] undergoes the same rearrangement (*loc. cit.*) as (Ia). The NH_2OH salt of (Ia) and (II), but not (Ia) and (Ib), are converted by HNO_3 (d 1.4) into the blue NO-compound, $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}$ (A., 1928, 1007). The diketohydroxamic acid, $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}$ (modified prep.; cf. A., 1929, 1070), and HNO_3 (d 1.4) give bilianic acid, whilst the nitrolactamhydroxamic acid, $\text{C}_{24}\text{H}_{35}\text{O}_9\text{N}_3$ (A., 1934, 653), is similarly decomposed very slowly (definite products not isolable). The hydroxamic acid group is generally stable (towards HNO_3) in compounds containing the 7-C- NO_2 -group; such NO_2 -hydroxamic acids probably contain the structure (A). H. B.

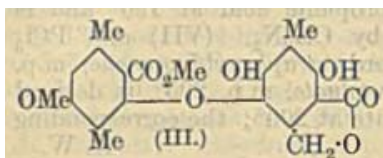
Constitution and synthesis of cotarnic acid and synthesis of 5-methoxy-3:4-methylenedioxyphthalic acid (isocotarnic acid). E. SPATH, L. SCHMID, and H. STERNBERG (Ber., 1934, 67, [B], 2095-2099).—Cotarnineanil is transformed by the successive action of MeI and NaOH into norcotarnone, m.p. 88 – 89° , hydrogenated (Pd-C) to dihydronorcotarnone, m.p. 50.5 – 51.5° , which is transformed by C-methylphloroglucinol into cotarnic acid (I), m.p. 242° (vac.; decomp.). Myristic acid is condensed with CH_2O in AcOH containing HCl to the phthalides



(II), m.p. 150 – 151° , and (III), m.p. 179 – 181° . (II) is smoothly oxidised by KMnO_4 to (I), whereas (III) yields 5-methoxy-3:4-methylenedioxyphthalic (isocotarnic) acid (anhydride, m.p. 196 – 197°). H. W.

Lichen substances. XLVI. Stictic acid. II. Y. ASAHINA and M. YANAGITA (Ber., 1934, 67, [B], 1965-1969; cf. A., 1933, 823).—Treatment of stictic acid (I) with boiling AcOH gives the compound $\text{C}_{19}\text{H}_{14}\text{O}_9$, AcOH , m.p. about 265° , not an *Ac* derivative as previously indicated. *Me* stictate has m.p. about 270° (decomp.) after becoming discoloured at about 240° [not m.p. 167 – 168° (*loc. cit.*)]. Catalytic hydrogenation of (I) leads to hypostictic acid, converted by CH_2N_2 in COMe_2 into *Me* hypostictate (*Me* hyposalazate *Me* ether), m.p. 254° (decomp.) after

becoming discoloured at about 240°, which is hydrogenated (Pd-C in EtOAc) to *hyposticolid* (II), m.p. 265°, transformed by CH_2N_2 into *hyposalazolid* Me_2 ether, m.p. 283°. MeOH-KOH trans-



forms (II) into the substance (III), m.p. 208°, methylated by CH_2N_2 to the substance $\text{C}_{18}\text{H}_{12}\text{O}_4(\text{OMe})_4$, m.p. 111°, obtained from salazic acid. *Hæmatommic acid* Me_1 ether (IV), m.p. 195° (decomp.), is an intermediate product in the conversion of (I) into atranol by NaOH; when heated above its m.p. it loses CO_2 and passes into atranol Me_1 ether, m.p. 78°. (IV) and NH_2Ph in MeOH give the corresponding anil $\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}$, m.p. 220–221° after becoming red at about 205°. Catalytic hydrogenation of (IV) leads to rhizonic acid, m.p. 208–209°. (I), suspended in COMe_2 , is transformed by NH_2Ph into *distictanilide* $\text{C}_{44}\text{H}_{31}\text{O}_{16}\text{N}$, m.p. 251–252° (decomp.) [hydrolysed by cold, dil. AcOH to (I)] and *stictanil* (V), $\text{C}_{25}\text{H}_{19}\text{O}_8\text{N}$, m.p. 163–164° (decomp.) after softening and becoming discoloured at 135°. The dianil (*loc. cit.*) does not appear homogeneous. Treatment of (V) with MeI and subsequently with HCl gives norstictic acid. H. W.

Oxidation of cinnamaldehyde. A. W. POUND and J. R. POUND (J. Physical Chem., 1934, 38, 1045–1049).—In the oxidation of cinnamaldehyde at room temp., in addition to the oxidation to cinnamic acid which is the main reaction, there are also side reactions resulting in the formation of BzOH , HCO_2H , AcOH , CO_2 , and possibly small quantities of other products. M. S. B.

Condensation of vanillin substitution products with acetophenone. G. V. GUNDY and L. C. RAIFORD (Proc. Iowa Acad. Sci., 1932, 39, 175).—The Br- and Cl-substitution products of vanillin (A., 1931, 90) condense with COPhMe to give mono- and diacetophenone derivatives. 3-Bromo- and 2:6- and 5:6-dibromo-vanillylideneacetophenones are yellow, whilst the corresponding 2:5-Br₂- and 2:5:6-Br₃-compounds are colourless. Similar differences are observed with the Cl-compounds. The diacetophenone compounds are all colourless. CH. ABS. (v)

Jute lignin. V. Chlorination of lignin. P. B. SARKAR (J. Indian Chem. Soc., 1934, 11, 777–785; cf. A., 1934, 1355).—Purified jute (I) or HCl-lignin (II) (assumed mol. wt. 816; contains 2 OMe) in CCl_4 , CHCl_3 , or AcOH with wet or dry Cl_2 gives octachlorolignin (III) (Cl 25.8%; mol. wt. in PhOH, 1080). Treatment with KOH greatly increases the rate of chlorination, probably by enlarging the pores. In H_2O (II) gives a more degraded Cl-compound. (III) is sol. in dil. alkali, yields no furfuraldehyde, evolves HCl at 135–140°, gives CH_2O when distilled with 12% HCl or 28% H_2SO_4 , reduces Fehling's solution, gives CO_2 with hot 12% HCl (as also does fructose, but not glucose), and on rechlorination affords a Cl_{11} -derivative (Cl 32.7%). Chlorination causes loss of some CH_2O_2 and OMe; it occurs by direct substitution only (Cl:HCl ratio), indicating that the side-chain of (II) is saturated. In presence of cata-

lysts or at 60° (II) gives a compound with 17.7% of Cl and a similar substance is formed from (III) by hot or cold, dil. NaOH. R. S. C.

Lignin. IX. Lignin from barley straw. M. PHILLIPS and M. J. GOSS (J. Amer. Chem. Soc., 1934, 56, 2707–2710).—The straw is extracted first with 2% aq. EtOH-NaOH at room temp. and then with 4% aq. NaOH at 100°. The lignin (I) (*penta-acetate*) from the aq. EtOH extract has the composition $\text{C}_{36}\text{H}_{31}\text{O}_6(\text{OH})_5(\text{OMe})_4$, and is methylated by $\text{Et}_2\text{O-CH}_2\text{N}_2$ to the Me_3 derivative, $\text{C}_{36}\text{H}_{31}\text{O}_6(\text{OH})_2(\text{OMe})_7$, and by Me_2SO_4 and aq. NaOH to the Me_5 derivative. Chlorination (method: A., 1927, 961) of (I) gives a product, $\text{C}_{36}\text{H}_{24}\text{O}_{11}\text{Cl}_{12}(\text{OMe})_4$. The lignin (II) (*tetra-acetate*) from the aq. extract has the composition $\text{C}_{36}\text{H}_{26}\text{O}_8(\text{OH})_4(\text{OMe})_4$, and is methylated ($\text{Et}_2\text{O-CH}_2\text{N}_2$) to the Me_3 derivative, $\text{C}_{36}\text{H}_{26}\text{O}_8(\text{OH})(\text{OMe})_7$. Distillation of (I) and (II) with 12% HCl gives CH_2O (cf. A., 1932, 1032), the formation of which is considered not to prove the presence of a CH_2O_2 group (cf. Freudenberg *et al.*, A., 1928, 1227). H. B.

Alkaline oxidation of lignin. A. W. WALDE and R. M. HIXON (J. Amer. Chem. Soc., 1934, 56, 2656–2659).—Ammonia-lignin (I) from oat-hulls (prep. described) is oxidised completely (in 35–40 min.) by I in dil. NaOH (not in acid) at room temp.; 1 g. of (I) consumes 150–190 c.c. of 0.1N-I (according to prep.) and CHI_3 is produced. Oxidation of (I) with the calc. amount of 0.2N-I in N-NaOH gives [after acidification ($\text{N-H}_2\text{SO}_4$)] “iodocarboxylignin” (II) (OMe 7.4, N 3, and I 13.3%) (also obtained directly from oat-hulls after HCl hydrolysis) which is sol. in aq. Na_2CO_3 . Methylation (Me_2SO_4) of (I) gives a methyl-lignin (OMe 26%), which is not oxidised to any appreciable extent by I in alkali; (II) similarly affords a product (OMe 22.2, I 10.2%), which is insol. in cold 10% NaOH, but is hydrolysed at 80–90° to a CO_2H -containing product (OMe 17.4, I 10.48%), mol. wt. about 1200 (assuming 1 atom of I is present). The amount of I consumed by lignins varies considerably according to the method of prep. (I) appears to contain $\cdot\text{CHMe}\cdot\text{OH}$ (cf. Harris *et al.*, A., 1934, 653) (which gives rise to CHI_3) and CHO (or other easily oxidised group) [since oxidation of (I) with Fehling's solution and subsequent treatment with NaOI still gives CHI_3]. Oxidation of (I) proceeds to a greater extent with alkaline NaOBr than with NaOI and gives CBr_4 and an alkali-sol. Br-containing product, decomp. < 100°; (II) is also oxidised further by NaOBr. Sol. products and much CO_2 are obtained from (I) and alkaline NaOCl. H. B.

Electrolytic reduction of acetophenone.—See this vol., 176.

Condensation of carboxylic acids. P. H. GROGGINS, R. H. NAGEL, and A. J. STIRTON (Ind. Eng. Chem., 1934, 26, 1317–1318; cf. following abstract).—Ketones can be prepared using carboxylic acids with AlCl_3 instead of the anhydrides or chlorides. AcOH with AlCl_3 (2.5 mols.) and C_6H_6 gives COPhMe in good yield, which is increased by SOCl_2 and PCl_3 . Similar results are obtained from AcOH and PhMe or Ph₂, BzOH and PhCl, and EtCO_2H and PhMe.

HCO₂H and PhCl give a 2% yield of *p*-C₆H₄Cl·CHO; a resin is the main product.

J. L. D.

Friedel-Crafts reaction. Preparation of ketones and keto-acids. P. H. GROGGINS and R. H. NAGEL (Ind. Eng. Chem., 1934, **26**, 1313—1316).—Interaction of Ac₂O with C₆H₆ containing AlCl₃ is not facilitated by Fe or Al, whereas KClO₃ and SOCl₂ markedly retard the reaction, which probably proceeds through the formation of AcCl from AcOH and AlCl₃; the second AcOH residue (from Ac₂O) is also partly available for reaction. 3 mols. of AlCl₃ are employed which probably (a) form AcCl and AlCl₂·OAc by double decomp., the latter of which with AlCl₃ gives AcCl and AlOCl; (b) AcCl and AlCl₃ form a salt which is the active acylating agent. AcCl affords less pure products than Ac₂O, but in as good yield, and SOCl₂, KClO₃, and Fe have no effect on the reaction. AcCl and PhMe give impure products with > 1 mol. of AlCl₃, but with Ac₂O the use of 3·3 mols. results in but little side-chain chlorination. Oxyhalogen compounds decrease the yields of 4'-methyl-(or chloro)-2-benzoylbenzoic acids. Cast iron vessels have no deleterious effect on the reaction or reaction product.

J. L. D.

α-Hydrinden-4-one from δ-ketosebacic acid. W. HUCKEL and R. SCHLUTER (Ber., 1934, **67**, [B], 2107—2109).—Oxidation of 1-ketodecahydronaphthalene with KMnO₄ at 100° gives δ-ketosebacic acid, m.p. 116°, converted by distillation with Ac₂O into α-hydrinden-4-one (I) (*semicarbazone*, m.p. 255°; *oxime*, m.p. 136°). (I) is hydrogenated (Pd-C-EtOH) to *cis*-α-hydrindan-4-one (Bz derivative of oxime, m.p. 112°).

H. W.

Acyl derivatives of phenylcyclohexane. D. Y. CHANG (J. Chinese Chem. Soc., 1934, **2**, 216—220).—Phenylcyclohexane (I) with Ac₂O in boiling CS₂ containing AlCl₃ during 1 hr. affords *p*-acetylphenylcyclohexane (cf. A., 1929, 550). Similarly, (I) with (EtCO)₂O and (PrⁿCO)₂O gives, respectively, *p*-propionyl-, b.p. 191—196°/20 mm. (*oxime*, m.p. 106°; *phenylhydrazone*, an oil), and *p*-butyryl-phenylcyclohexane, b.p. 208—214°/20 mm. [*oxime*, m.p. 112—113°; *phenylhydrazone*, m.p. 85° (decomp.)].

J. L. D.

Formation of benzanthrone from anthraquinone and glycerol. J. S. TURSKI (Przemysł Chem., 1934, **18**, 605—607).—The view that benzanthrone is formed by condensation of aldehyde with anthrahydroquinone is advanced.

R. T.

Chlorobenzophenoneoximes. C. W. PORTER and H. B. WILCOX (J. Amer. Chem. Soc., 1934, **56**, 2688—2689).—Oximation of *o*-C₆H₄Cl·COPh gives two oximes, m.p. 131° (I) and 96—97°, re-solidifying with m.p. 130—131° (II) (in pre-heated bath), separable by fractional crystallisation from aq. MeOH. When (II) is heated it changes rapidly into (I). Beckmann rearrangement of (I) and (II) gives *o*-C₆H₄Cl·CO·NHPh and *o*-C₆H₄Cl·NHBz, respectively. (I) and (II) are unaffected by 30% NaOH at room temp., but in the not both afford the same indoxazen; *cis-trans* isomerisation may precede elimination of HCl. Indoxazen formation is no guide to the structure of the oxime (cf. Meisenheimer and Meis, A., 1924, i, 433).

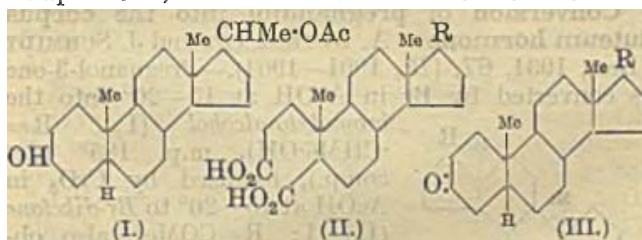
H. B.

Michael condensation. II. Reactivity of the addendum. R. CONNOR and D. B. ANDREWS (J. Amer. Chem. Soc., 1934, **56**, 2713—2716; cf. A., 1934, 72).—Three types of products formed in the Michael condensation are recognised: (1) normal product, *e.g.*, (CO₂Et)₂CMc·CHMc·CH₂·CO₂Et from CHMe(CO₂Et)₂ (I) and CHMe·CH·CO₂Et (II) in presence of a little NaOEt or piperidine (cf. Michael and Ross, A., 1931, 67); (2) rearrangement product, *e.g.*, (CO₂Et)₂CH·CHMc·CHMc·CO₂Et from (I) and (II) in presence of 1 equiv. of NaOEt (cf. Michael and Ross, *loc. cit.*; Holden and Lapworth, *ibid.*, 1272); (3) rearrangement-retrogression products, *e.g.*, CH₂Bz·CO₂Et and CHPh·CMc·CO₂Et, formed by a reversed Michael condensation from CO₂Et·CHMc·CHPh·CHBz·CO₂Et [the rearrangement product (cf. 2) from (I) and CHPh·CH·COPh (III)]. The addition of various com-

pounds containing an active CH₂ to (III) under conditions (1) and (3) is studied; the reactivity of the addendum cannot be correlated with the no. of activating groups attached to C* or from the amount of enolisation. The reactivity of any given structure is decreased by introduction of substituents on C*; the effect of Me is much < that of higher alkyl groups. The original must be consulted for details. *Et α-dibenzoyl-β-phenylbutyrate*, m.p. 135—135·5° [from CH₂Bz·CO₂Et and (III)], and *Et 3:5-diphenyl-6-ethyl-Δ²-cyclohexenone-6-carboxylate*, m.p. 135—135·5° [from CHEtAc·CO₂Et and (III) or Et γ-benzoyl-α-acetyl-β-phenylbutyrate and EtI in EtOH-NaOEt; in both cases intramol. dehydration is involved], appear to be new.

H. B.

Pregnan-20-ol-3-one. A. BUTENANDT and J. SCHMIDT (Ber., 1934, **67**, [B], 1893—1896).—Partial hydrolysis of pregnan-3:20-diol diacetate by MeOH-KOH at 15—20° leads to the (20-)monoacetate (I), m.p. 170·5°, the constitution of which follows from

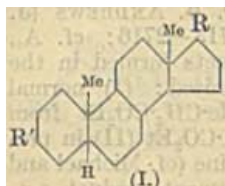


its energetic oxidation by CrO₃ to the *acetoxydicarboxylic acid*, m.p. 272° (II; R=CHMe·OAc), hydrolysed to the *OH-acid*, m.p. 346° (II; R=CHMe·OH), which is transformed by gentle oxidation into the keto-acid, m.p. 271° (II; R=Ac) obtained previously from pregnandiol. Cautious oxidation of (I) affords the *keto-acetate* (III; R=CHMe·OAc), m.p. 142—142·5°, hydrolysed to *pregnan-20-ol-3-one* (III; R=CHMe·OH), m.p. 152° (*semicarbazone*, m.p. 203—204°). The last-named compound is not identical with the similarly composed material from the corpus luteum.

H. W.

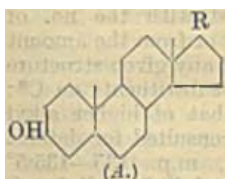
alloPregnan-3-ol-20-one, a companion of the corpus luteum hormone. A. BUTENANDT and L. MAMOLI (Ber., 1934, **67**, [B], 1897—1901).—3-Hydroxybisanorcholeonic acid is hydrogenated (Pt in AcOH) to 3-hydroxybisanallocholanolic acid, m.p.

170°, the

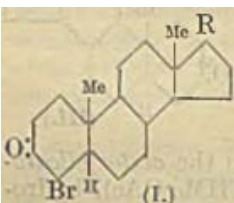


Me ester, m.p. 152.5°, of which is transformed by MgPhBr in Et_2O into the *carbinol* (I; $\text{R} = \cdot\text{CHMe}\cdot\text{CPh}_2\cdot\text{OH}$; $\text{R}' = \text{OH}$), dehydrogenated and acetylated by boiling AcOH to the unsaturated *acetate* (II) ($\text{R} = \cdot\text{CMe}\cdot\text{CPh}_2$; $\text{R}' = \text{OAc}$), m.p. 238.5° [corresponding *alcohol*, m.p. 163.5°, re-acetylated to (II)]. Ozonisation of (II) affords COPh_2 and *allopregnan-3-ol-20-one acetate*, m.p. 144.5°, hydrolysed to *allopregnan-3-ol-2-one* (I; $\text{R} = \text{COMe}$; $\text{R}' = \text{OH}$), m.p. 194.5° (oxime, m.p. 224°), identical with the product derived from the corpus luteum (see following abstract). H. W.

Constitution of the hydroxyketone, $\text{C}_{21}\text{H}_{34}\text{O}_2$, from corpus luteum. E. FERNHOLZ (Z. physiol. Chem., 1934, 230, 185—189).—*Me* acetoxybisnor-allochohanate (A., 1933, 1290) and MgPhBr give the *carbinol* (I) (A., $\text{R} = \cdot\text{CHMe}\cdot\text{CPh}_2\cdot\text{OH}$), m.p. 207° (monoacetate, m.p. 197°). Distillation of crude (I) at about 1 mm. affords the compound (A., $\text{R} = \cdot\text{CMe}\cdot\text{CPh}_2$), m.p. 168° {chloride, m.p. 199°; acetate (II), m.p. 246° [oxide (III), m.p. 225°, from (II) and BzO_2H in CHCl_3]}. Dehydration of (I) with AcOH , Ac_2O , or AcOH-HCl gives (II), an isomeric acetate, m.p. 263°, and resin. Oxidation (O_3 in CHCl_3) of (II) affords (III) (trace) and the acetate, m.p. 145° (semicarbazone, m.p. 273°), of 3-hydroxyalloethiochyl *Me* ketone (IV) (A., $\text{R} = \text{COMe}$), m.p. 195° [oxime, m.p. 227°; semicarbazone, m.p. 253° (decomp.)]. (IV) is probably identical with the hydroxyketone, $\text{C}_{21}\text{H}_{34}\text{O}_2$, isolated by Butenandt *et al.* (A., 1934, 1039, 1268) from corpus luteum (see preceding abstract). H. B.



Conversion of pregnandiol into the corpus luteum hormone. A. BUTENANDT and J. SCHMIDT (Ber., 1934, 67, [B], 1901—1904).—Pregnanol-3-one is converted by Br in AcOH at 15—20° into the bromoketo-alcohol (I; $\text{R} = \cdot\text{CHMe}\cdot\text{OH}$), m.p. 185° (decomp.), oxidised by CrO_3 in AcOH at 15—20° to *Br-diketone* (II) (I; $\text{R} = \text{COMe}$), also obtained by cautious oxidation of pregnandione. (II) in boiling $\text{C}_5\text{H}_5\text{N}$ passes into the corpus luteum hormone, m.p. 121° or 128.5° [oxime, m.p. 244° (decomp.)]. H. W.



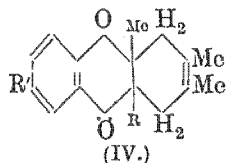
Corpus luteum hormones.—See this vol., 127, 128.

Heteropolarity. XXIV. Colour and halochromism of deeply coloured aromatic five-ring ketones. W. DILTNEY, O. TROSKEN, K. PLUM, and W. SCHOMMER (J. pr. Chem., 1934, [ii], 141, 331—349).—2 : 5-Diphenyl-3 : 4-di-*p*-tolyl, m.p. 218—219°; 3 : 4-di-*p*-isopropylphenyl-, m.p. 214°, 3 : 4-di-*p*-diphenyl-, m.p. 258—259°, 3 : 4-dianisyl-, m.p. 222—223°, 3 : 4-di-*p*-ethoxyphenyl-, m.p. 198—199°, 3 : 4-di-*p*-phenoxyphenyl-, m.p. 219—220°, 3 : 4-di-*p*-phenylthiolphenyl-, m.p. 199°, 3 : 4-di-*n*-bromophenyl-, m.p. 244—245°, and 3-*p*-chlorophenyl-4-*p*-

dimethylaminophenyl-, m.p. 230—231°, and 2 : 3 : 5-triphenyl-4-*p*-diphenyl-, m.p. 215°, -4-anisyl-, m.p. 213—214°, and 4-*p*-dimethylaminophenyl-, m.p. 220—221°, -cyclopentadienones are prepared from $\text{CO}(\text{CH}_2\text{Ph})_2$, the appropriate benzil, and NaOMe in boiling EtOH . The colours of these ketones and tetraphenylcyclopentadienone (I) (A., 1931, 91) and their solutions in C_6H_6 and conc. H_2SO_4 are given. Introduction of positive groups into the *p*-positions of the 3- and 4-Ph groups is accompanied by a hypsochromic effect (which increases with the positivity of the auxochromes and is a max. for SPh). An analogous hypsochromic effect is observed by introduction of *p*-OMe or 4 : 4'-(OEt)₂ into benzil; the results parallel those with stilbenes (A., 1928, 627). Ph and SPh exert a bathochromic action on the halochromism, whilst Alk, OAlk, and NMe_2 cause a hypsochromic effect; these results are not similar to those shown by the substituted benzyis or distyryl ketones. Since 3 : 4 : 5-triphenyl-2-anisylcyclopentadienone (II), m.p. 189—190°, dissolves in conc. H_2SO_4 to a greenish-blue solution, whilst (I) affords a violet-blue solution, C_2 is considered to be positive (see A.); the OMe in (II) thus exerts a bathochromic effect. Alternative structures for salts are discussed. Deoxybenzoin, Ph *p*-methoxystyryl ketone, and MeOH-NaOMe give $\alpha\epsilon$ -diketo- $\alpha\beta\epsilon$ -triphenyl- γ -anisylpentane (III), m.p. 155°, and (probably) $\alpha\beta$ -dibenzoyl- β -phenyl- γ -anisylpropane, m.p. 143—144° (oxime, m.p. 218°). (III) is reduced (Zn dust, AcOH) to 1 : 2 : 3-triphenyl-4-anisylcyclopentane-1 : 2-diol, m.p. 126—127°, dehydrated (HCl in MeOH) to 3 : 4 : 5-triphenyl-2-anisylcyclopentadiene, m.p. 125—126°. This and *p*-NO₂-C₆H₄-NMe₂ with piperidine in $\text{C}_5\text{H}_5\text{N-EtOH}$ give the *p*-dimethylaminoanil, m.p. 204—205°, of (II). 4 : 4'-Diphenylthiolbenzil, m.p. 104—105°, is prepared from Ph_2S , ($\cdot\text{COCl}$)₂, and AlCl_3 in CS_2 . 4-Chloro-4'-dimethylamino-benzil, m.p. 143—144°, is obtained (cf. Jenkins, A., 1931, 1158) by oxidation (Fehling's solution) of the -benzoin. H. B.

Additive reactions of alkylated naphthaquinones. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1934, 56, 2690—2696).—3 : 7-Dimethyl-1 : 2-naphthaquinone (I) (improved prep.; cf. Weissgerber and Kruber, A., 1919, i, 315) and $\text{NH}_2\text{OH}\cdot\text{AcOH}$ in aq. MeOH give the 2-oxime, m.p. 222° (decomp.), since reduction (alkaline $\text{Na}_2\text{S}_2\text{O}_4$) does not afford 1-amino-3 : 7-dimethyl- β -naphthol (*N-Ac* derivative, m.p. 107.5°, obtained from the hydrochloride and Ac_2O in aq. NaOAc), but yields an unstable amine [Ac_3 derivative, m.p. 245° (not sharp)]. Successive treatment of (I) with aq. NaHSO_3 , dil. H_2SO_4 (boiling), aq. $\text{K}_2\text{Cr}_2\text{O}_7$, and aq. KCl gives *K* 3 : 7-dimethyl-1 : 2-naphthaquinone-4-sulphonate (+ H_2O), whilst (I) and Ac_2O -conc. H_2SO_4 at 10° and finally at 60° afford 1 : 3 : 4-triacetoxy-2 : 6-dimethylnaphthalene, m.p. 161°, converted (aq. EtOH-NaOH) into 3-hydroxy-2 : 6-dimethyl-1 : 4-naphthaquinone, m.p. 194° (acetate, m.p. 75—76°; *Me* ether, m.p. 108°). (I) also reacts readily with $\text{EtOH-NH}_2\text{Ph}$ and *p*-C₆H₄Me- SO_2H , but not with CH_3N_2 . 2 : 6-Dimethyl-1 : 4-naphthaquinone (II) (*loc. cit.*) undergoes little or no reaction with Ac_2O -conc. H_2SO_4 , NaHSO_3 , NH_2Ph , or ArSO_2H ;

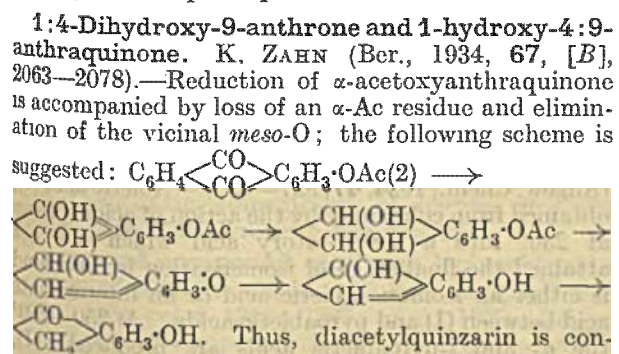
with $\text{Et}_2\text{O}-\text{CH}_2\text{N}_2$ in C_6H_6 at 100° (sealed flask), 3 : 7 : 3' : 7' - tetramethyl-2 : 2' - dinaphthylmethane-1 : 4 : 1' : 4' - diquinone, m.p. 300° , results in 40% yield. 3 : 7-Dimethyl- β -naphthyl acetate is oxidised (CrO_3 , AcOH) to 7-acetoxy-2 : 6-dimethyl-1 : 4-naphthaquinone, m.p. 171° , which with Zn dust and Ac_2O followed by NaOAc (if this is present throughout the reaction an unidentified substance, m.p. $149-150^\circ$, results) gives 1 : 4 : 7-triacetoxy-2 : 6-dimethylnaphthalene, m.p. 139° .



γ -Dimethylbutadiene (III) and (II) in EtOH at $100-105^\circ$ (sealed tube) give the tetramethyltetrahydroanthraquinone (IV) ($\text{R}=\text{H}$, $\text{R}'=\text{Me}$), m.p. $75-77^\circ$ (semicarbazone, m.p. 263°), reduced (Clemmensen) to the tetramethylhexahydroanthracene [(IV) with $\text{R}=\text{H}$, $\text{R}'=\text{Me}$, and both $\text{O}=\text{H}_2$], and dehydrogenated (S) to 2 : 3 : 6-trimethylantraquinone, m.p. 232° [lit. 240° (corr.)]. (I) and (III) similarly afford a tetramethyltetrahydrophenanthraquinone (?), m.p. 106° , which undergoes deep-seated decomp. on attempted dehydrogenation. 2 : 3-Dimethyl-1 : 4-naphthaquinone and (III) give the tetramethyltetrahydroanthraquinone (IV) ($\text{R}=\text{Me}$, $\text{R}'=\text{H}$), an oil; 2-methyl-1 : 4-naphthaquinone affords an adduct, an oil, dehydrogenated to 2 : 3-dimethylantraquinone, whilst thymoquinone yields 6 : 7 : 9-trimethyl-3-isopropyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone (?), an oil. H. B.

Alkannin. III. H. RAUDNITZ and E. STEIN (Ber., 1934, 67, [B], 1955—1959; cf. A., 1932, 396; Dieterle *et al.*, A., 1931, 1297; Betrabet *et al.*, A., 1933, 1165, 1217).—Technical alkannin dissolved in warm EtOH is treated with $\text{Ni}(\text{OAc})_2$. The Ni salt is extracted successively with boiling EtOH and C_6H_6 to remove wax and decomposed with the necessary amount of 1% $\text{HCl}-\text{MeOH}$, whereby alkannin (I), $\text{C}_{17}\text{H}_{18}\text{O}_5$, is obtained as crystals, m.p. 109° . Since (I) is a derivative of naphthazarin (*loc. cit.*), 10 C are involved. A further C is present in OMe , the remaining 6 in a side-chain which contains a double linking, since (I) absorbs 7H_2 in presence of Pt. Ozonolysis (I) in AcOH leads to the formation of 0.7 mol. of COMe_2 . Reductive acetylation of (I) gives dihydroalkannin tetra-acetate, m.p. $133-134^\circ$. (I) is therefore 5 : 8-dihydroxy-3(?) -methoxy-2- δ -methyl- Δ^7 -pentenyl-1 : 4-naphthaquinone. H. W.

1 : 4-Dihydroxy-9-anthrone and 1-hydroxy-4 : 9-anthraquinone. K. ZAHN (Ber., 1934, 67, [B], 2063—2078).—Reduction of α -acetoxyanthraquinone is accompanied by loss of an α -Ac residue and elimination of the vicinal *meso*-O; the following scheme is suggested: $\text{C}_6\text{H}_4-\text{CO}-\text{C}_6\text{H}_3\cdot\text{OAc}(2) \rightarrow$



converted by H_2 at $85-90^\circ/40$ atm. in presence of Ni or by $\text{Na}_2\text{S}_2\text{O}_4$ in $\text{H}_2\text{O}-\text{AcOH}$ at 65° into 4-hydroxy-1-acetoxy-9-anthrone (I), m.p. about 208° (decomp.),

hydrolysed to 1 : 4-dihydroxy-9-anthrone (II), m.p. 227° (decomp.). (I) or (II) is converted by hot Ac_2O in presence of NaOAc or $\text{C}_5\text{H}_5\text{N}$ into 1 : 4 : 9-triacetoxyanthracene, m.p. $211-212^\circ$. (I) and BzCl in warm $\text{C}_5\text{H}_5\text{N}$ afford 1-acetoxy-4 : 9-dibenzoyloxyanthracene, m.p. $240-241^\circ$, oxidised by CrO_3 in AcOH to 1-acetoxy-4-benzoyloxyanthraquinone, m.p. $195-196^\circ$. 5 : 8-Dichlorodiacetylquinizarin is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to 5 : 8-dichloro-4-hydroxy-1-acetoxy-9-anthrone, m.p. $222-223^\circ$ after softening, whence 5 : 8-dichloro-1 : 4 : 9-triacetoxyanthracene, m.p. about 228° . Diacetylchrysazin yields 5-hydroxy-4-acetoxy-9-anthrone, m.p. $247-248^\circ$, whence 4 : 5-dihydroxy-9-anthrone, m.p. $292-293^\circ$, and 4 : 5 : 9-triacetoxyanthracene, m.p. $221-222^\circ$. Diacetylalizarin gives 4-hydroxy-3-acetoxy-9-anthrone ($-\text{H}_2\text{O}$), m.p. $187-189^\circ$, whence 3 : 4-dihydroxy-9-anthrone and 3 : 4 : 9-triacetoxyanthracene, m.p. 193° . 4-Hydroxy-3-methoxy-9-anthrone, m.p. $203-205^\circ$, results from acetylalizarin 2-Me ether; 3-methoxy-4 : 9-diacetoxyanthracene has m.p. $189-191^\circ$. 1-Acetoxyanthraquinone is transformed into 4-hydroxy-9-anthrone, m.p. $239-240^\circ$ (decomp.), converted by 1 or 2 mols. of $p\text{-C}_6\text{H}_4\text{Me}-\text{SO}_2\text{Me}$ in $\text{C}_6\text{H}_4\text{Cl}_2$ containing NaHCO_3 into 4-methoxy-9-anthrone, m.p. $132-133^\circ$, and 4 : 9-dimethoxyanthracene, m.p. $86-87^\circ$, respectively. (I) is easily transformed by boiling MeOH -conc. HCl into 1-hydroxy-4-methoxy-9-anthrone (III), m.p. $156-157^\circ$, which gives 4-methoxy-1 : 9-diacetoxyanthracene, m.p. 178° , with Ac_2O and $\text{C}_5\text{H}_5\text{N}$. 1-Hydroxy-4-ethoxy-9-anthrone, m.p. $146-147^\circ$, and 4-ethoxy-1 : 9-diacetoxyanthracene, m.p. $160-161^\circ$, are described. (III) and 5-chloroisatin-2- p -chloroanil in $\text{C}_5\text{H}_5\text{N}$ at 100° afford 2-[4-methoxy-9-anthrone]-2'-[5'-chloroindole]-indigotin. Oxidation of (II) or, preferably, of (I) with FeCl_3 leads to 1-hydroxy-4 : 9-anthraquinone (IV), decomp. about 200° after softening. 5 : 8-Dichloro-1-hydroxy-4 : 9-anthraquinone (V) has m.p. 257° . 1-Acetoxy-4 : 9-anthraquinone (VI), decomp. about 200° , is obtained from (I) by FeCl_3 and HCl in EtOH or from (IV), Ac_2O , and $\text{C}_5\text{H}_5\text{N}$.

Bromoanthrone is readily prepared from acetyl-(VII) or phenylacetyl-, m.p. $102-103^\circ$, -anthranol by the action of Br in hot AcOH . 10-Chloro-9-anthrone, decomp. 233° , is obtained from Cl_2 and (VII) in cold AcOH , whereas benzoylanthranol and Br in AcOH afford 10-bromo-9-benzoylanthranol, m.p. $214-215^\circ$. 10-Bromo-1 : 4-diacetoxy-9-anthrone (VIII), decomp. 183° after becoming discoloured, is transformed by boiling $\text{COMe}_2-\text{H}_2\text{O}$ into 10-hydroxy-1 : 4-diacetoxy-9-anthrone, m.p. 140° in a pre-heated bath. (VI) is converted by Ac_2O containing conc. H_2SO_4 or ZnCl_2 into 1 : 4 : 10-triacetoxy-9-anthrone, m.p. 179° , also obtained from (VIII) and KOAc in boiling AcOH , and transformed by boiling Ac_2O containing KOAc or $\text{C}_5\text{H}_5\text{N}$ into 1 : 4 : 9 : 10-tetra-acetoxyanthracene, m.p. $240-242^\circ$. 10-Chloro-1-acetoxy-4 : 9-anthraquinone, m.p. $196-197^\circ$, is described.

(VI) and butadiene in EtOH at $75-80^\circ$ yield the adduct $\text{C}_{20}\text{H}_{16}\text{O}_4$, m.p. $181-182^\circ$, transformed by air in alkaline solution into 9-hydroxynaphthacenequinone and by boiling Ac_2O and KOAc into 9 : 11 : 12-triacetoxy-1 : 4-dihydronaphthacene, m.p. $225-227^\circ$. (VI) is transformed by boiling $\Delta^{1:3}$ -cyclohexadiene into the substance $\text{C}_{20}\text{H}_{16}\text{O}_3$, m.p. $160-161^\circ$, whence

hydroxy-1 : 4-endoethylene-1 : 4-dihydronaphthacene-quinone, which loses C_2H_4 when heated and yields 9-hydroxyanthracenequinone.

(IV) is converted by Br in warm AcOH into 2 : 3-dibromo-1-hydroxy-2 : 3-dihydro-4 : 9-anthraquinone, decomp. about 157°, transformed by Ac_2O -conc. H_2SO_4 into the *Ac* derivative $C_{16}H_{10}O_4Br_2$, m.p. about 197° (decomp.), also obtained from (VI) and converted by KOAc in boiling AcOH- H_2O into 2(3)-bromo-1-acetoxy-4 : 9-anthraquinone (IX), m.p. 230°. The position of Br in (IX) follows from its reduction by HI and AcOH and subsequent acetylation by Ac_2O - C_5H_5N to a bromotriacetoxyanthracene, m.p. 203—204°, oxidised by CrO_3 and then hydrolysed by conc. H_2SO_4 to 2-bromoquinizarin, m.p. 232—233°. 2(3)-Bromo-1-hydroxy-4 : 9-anthraquinone has been prepared. 2 : 3 : 10-Trichloro-1-hydroxy-2 : 3-dihydro-4 : 9-anthraquinone (X), m.p. 178—179° (decomp.), and its *Ac* derivative, m.p. 146—148°, are described. 2(3) : 10-Dichloro-1-hydroxy-4 : 9-anthraquinone (XI), m.p. about 190°, from (X) and KOAc in boiling AcOH or in boiling PhCl, readily passes into 2-chloroquinizarin, is converted by Ac_2O in C_5H_5N into the *Ac* derivative, m.p. 230°, and by Ac_2O - H_2SO_4 into 2-chloroquinizarin diacetate. (XI) and boiling NH_2Ph afford 2(3) : 10-dianilino-1-hydroxy-4 : 9-anthraquinone, slow decomp. > 220°.

Quinizarin is transformed by $SOCl_2$ at 135—140° into 10-chloro-1-hydroxy-4 : 9-anthraquinone, converted by Ac_2O in C_5H_5N into the *Ac* derivative, m.p. 174—175°, hydrolysed by warm, conc. H_2SO_4 to 2 : 4-dichloro-1-hydroxyanthraquinone, m.p. 241—242°.

H. W.

Constitution of tannins. IV. Absorption spectra of natural phlobatannins and synthetic flavpinacols. A. RUSSELL, J. TODD, and C. L. WILSON (J.C.S., 1934, 1940—1945).—The absorption spectra of synthetic flavpinacols are entirely similar to those of typical natural phlobatannins, consisting of 2 sharply defined bands at λ 2700 and λ 2800—2900. The parent chalcones also show 2 bands in approx. the same positions, but have in addition a broad characteristic band in the violet region, differentiating the spectra very sharply from those of the flavpinacols.

F. R. S.

Structure of the cardiac aglucones. W. A. JACOBS and R. C. ELDERFIELD (Science, 1934, 80, 533—534).—The Me and Et esters of the acid obtained by the degradation of digitoxigenin (this vol., 88) are identical with those of aëtiocholanolic acid. These results and those of Tschesche (A., 1934, 1354) show that the cardiac aglucones possess the sterol ring system. Revised partial formulæ for strophanthidin and related aglucones are given.

L. S. T.

Uzargenin. G. A. R. KON (Chem. and Ind., 1934, 1008).—If the identity of the acid obtained by Tschesche (A., 1934, 1354) from uzargenin (I) with alloaëtiocholanolic acid is finally established, it follows that the lactone ring of the cardiac aglucones is directly attached to the 5-membered ring IV in position C_{17} , and that, apart from the lactone ring, their C skeleton is identical with that of the sterols and bile acids. Tschesche's work confirms that of Bernal *et al.* (*ibid.*) and confirms the position of the

CHO of strophanthidin which replaces a Me of (I) and must occupy C_{10} . The position of the OH groups in ring I follows naturally.

H. W.

Saxatilis acid. G. KOLLER and A. KLEIN (Monatsh., 1934, 65, 91—92).—Comparison of the Ac_3 and Ac_6 derivatives establishes the identity of saxatilis and salazic acids.

H. W.

Constituents of red sandal-wood. Pterocarpin. H. LEONHARDT and K. FAY (Arch. Pharm., 1935, 273, 53—60).—Pterocarpin (I) (modified prep.), $C_{14}H_9O_2(OMe)(O_2CH_2)$ (lit. $C_{14}H_{12}O_4$), dimorphic, m.p. 165° and 156—157° [*Br*-derivative, m.p. 165° (decomp.)]; 2 : 4-dinitrophenylhydrazones, decomp. about 305°, contains no OH, but, when hydrogenated (Pd-C) in EtOAc, affords, by opening of an O-ring, dihydropterocarpin, $C_{17}H_{16}O_5$, m.p. 141—142° [*Ac*, m.p. 96—97°, and *Bz* derivative, m.p. 128.5°; *Me ether*, m.p. 107—108° (*Br* derivative, m.p. 136—137.5°)]. KOH fusion of (I) gives *m*- $C_6H_4(OH)_2$, and O_3 affords an ozonide decomposed by H_2O . Homopterocarpin gives a 2 : 4-dinitrophenylhydrazone. R. S. C.

Artemisic and dihydroartemisic acids from desmotroposantonin. P. P. BERTELO (Atti Congr. naz. Chim., 1933, 4, 396—401; Chem. Zentr., 1934, ii, 951—952).—The Et ester of dihydroartemisic acid (I) (*Ba* salt) yields an *Et*₁ ether, m.p. 68—70°, and a monoacetate, m.p. 72°. Both (I) and artemisic acid (II) yield 1 : 4-dimethyl-7-ethyl- β -naphthol on fusion with KOH; it is thus not possible to ascertain whether the acid obtained from desmotroposantonin is (I) or (II).

H. N. R.

Constitution of resin phenols and their biogenetic relationships. I. Pinoresinol. H. ERDTMAN (Svensk Kem. Tidskr., 1934, 46, 229—233).—Pinoresinol, $C_{20}H_{22}O_6$ (I) (not $C_{19}H_{20}O_6$, Zinke *et al.*, A., 1924, i, 1088), is best purified by the action of Ac_2O - C_5H_5N on its K salt to give an *Ac*₂ derivative (II), m.p. 165.5—167.5°, [α]_D 55.8°, hydrolysed and benzoylated to the *Bz*₂ derivative, m.p. 162—164° (*loc. cit.*, 159°), [α]_D +42.8° [*Br*₂-derivative, $C_{20}H_{18}O_4Br_2(OBz)_2$, [α]_D +37.1°]. Hydrolysis and methylation of (II) affords a *Me*₂ ether, m.p. 98—99°, [α]_D +66.0°, of (I), affording a 1-*Br*₂-derivative, m.p. 171—172°, and (with HNO_3 -AcOH) a (*NO*)₂-derivative, m.p. 210—212°, and oxidised by $KMnO_4$ to veratric acid, and by HNO_3 to trimethylveratrol (50% yield). The biogenetic relationships of (I) and other compounds of the coniferyl type as derivatives containing two guaicol residues are discussed, (I) being represented by the partial formula ($>CR \cdot O \cdot$)₂(C_6H_5) [$R=4 : 3-C_6H_3(OH)(OMe)$], the two O atoms having ether linkings. All [α]_D vals. are in $COMe_2$.

J. W. B.

Pyro- and hydro-abietic acids. A. GRETH (Angew. Chem., 1934, 47, 827—830).—Abietic acid (I), obtained from colophony by the action of acids, passes at 230° into a laevorotatory acid which has not attained the final stage of isomerisation by heat and is either an isomeric abietic acid or an intermediate acid between (I) and pyroabietic acids. At 250—260° the *d*- and *l*-pyroabietic acids are produced. (I), whether obtained by heat or by acid isomerisation, is hydrogenated (Pt-sponge) to tetrahydroabietic acid (II), m.p. 174—175°, [α]_D +15°. Pyroabietic acid affords

dihydropyroabietic acid, m.p. 170—171°, $[\alpha]_D^{25} +45^\circ$ or $+34.5^\circ$, and a H_1 -acid, m.p. 170—171°, $[\alpha]_D^{25} +37.5^\circ$ or $+28^\circ$, provisionally regarded as identical with (II). The same acid appears to be isolable from the products of the hydrogenation of colophony at 300°/200 atm. The course of pyrogenation is discussed. H. W.

Constituents of ammoniacum resin. I. K. KUNZ, H. WEIDLE, and K. FISCHER (J. pr. Chem., 1934, [ii], 141, 350—356; cf. Luz, A., 1896, i, 249; Casparis *et al.*, Pharm. Acta Helv., 1928, 3, 25, 41).—The resin is extracted with Et_2O and the solution then extracted with 5% Na_2CO_3 ; the material obtained by acidification (HCl) of the alkaline extract is acetylated (Ac_2O) to *diacetylammoresinol* (I), $C_{28}H_{34}O_6$, m.p. 102°. (I) is hydrolysed by 2*N*- Na_2CO_3 in MeOH to the NaOH-sol. *acetylammoresinol*, m.p. 129—130°, and by 6% EtOH-KOH to *ammoresinol*, m.p. 109° [Bz_2 (II), m.p. 75°, and *di-p-chlorobenzoyl*, m.p. 93.5°, derivatives]. Reduction (H_2 , PtO_2 or Pd-BaSO₄, AcOH) of (I) gives a *hexahydro*-derivative, m.p. 64°. (I) and (II) consume approx. 10 Br (6 for addition; 4 for substitution) in AcOH. (I) is OMe-free. Oxidation (H_2O_2 , AcOH) of (I) affords γ -resorcylic acid (III); NaOH-KOH-fusion gives β -resorcylic acid (IV). Ozonolysis of (I) gives an aldehyde, $C_{14}H_{12}O_7$, degraded (no details) to (III) and (IV). H. B.

Poisonous substance in croton oil. II. Constitution of *crotophorbolone*. B. FLASCHEN-TRÄGER and F. F. VON FALKENHAUSEN (Annalen, 1934, 514, 252—260; cf. this vol., 64).—*Crotophorbolone* (I) (previously designated anhydrophorbol), $C_{20}H_{28}O_5$, m.p. 228°, $[\alpha]_D^{25} +172^\circ$ in MeOH [*Ac* (II), m.p. 116.5—117.2°, *Bz*, m.p. 172—173°, and *p-nitrobenzoyl*, m.p. 208.5—209°, derivatives], a little of an *isomeride*, m.p. 217° (decomp.), $[\alpha]_D^{25} -12.7^\circ$ in MeOH, and small amounts of $COMe_2$ and CO_2 are obtained from phorbol (III) and very dil. H_2SO_4 in N_2 at 100° (bath). (I) reduces Fehling's solution, contains 3 OH (Zerevitinov) (2 are probably *tert.*, since they are not esterified), a CO (method: this vol., 228) (cryst. derivatives could not be prepared), 2 or 3 double linkings, and 3 or 4 rings. (I) is reduced (H_2 , Pd-BaSO₄, AcOH) to a *hexahydro*-derivative, m.p. 239—241°, $[\alpha]_D^{25} +196^\circ$ in MeOH, which does not reduce Fehling's solution, $KMnO_4$, or Br. The formation of (I) from (III) may involve a pinacol-pinacolin change. Crystallographic data [by STEINMETZ] for (I) and (II) and absorption spectra curves for (I) and (III) are given. H. B.

Teramus labialis.—See this vol., 132.

Crystalline principles from *Artemisia*.—See this vol., 268.

Constituents of *Buellia canescens*.—See this vol., 133.

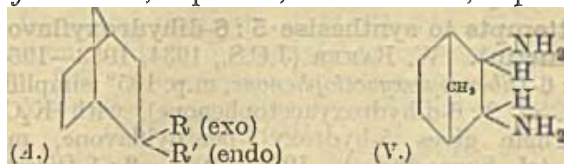
Anthelmintic constituent of leaves of *Calycopteris floribunda*.—See this vol., 246.

Grignard compound of pinene hydrochloride. Action of ethylene oxide. R. BOUSSET (Bull. Soc. chim., 1934, [v], 1, 1305—1307; cf. A., 1930, 1591).—The Grignard compound (I) of pinene hydrochloride reacts with $(CH_2)_2O$ in Et_2O at -10° , the temp. being gradually raised and Et_2O replaced by Bu_2O , to give β -camphanylethyl alcohol, b.p. 135—136°/17

mm., m.p. 25°, $[\alpha]_{5460}^{25} -35.6^\circ$ in C_6H_6 , isolated as its *H phthalate*, m.p. 155°, $[\alpha]_{5460}^{25} -16.8^\circ$ in C_6H_6 , from which it is obtained by hydrolysis with aq. NaOH. (I) has almost no action on $EtOAc$, only traces of camphane, dibornyl, bornylene, and a substance, b.p. 120—130°/13 mm. [giving a substance, m.p. 249—250° (corr.), with $NH_2 \cdot NH \cdot CO \cdot NH_2$], being isolated.

J. W. B.

Steric course of addition and substitution reactions. III. *endo-exo*-Isomerism [of *norbornyl* compounds]. I. K. ALDER and G. STEIN [with E. ROLLAND and G. SCHULZE] (Annalen, 1934, 514, 211—227).—The Me ester of 2:5-*endomethylenehexahydrobenzoic acid* (*endo*) (I) (this vol., 211) is converted (to the extent of 70—80%) by conc. MeOH-NaOMe into 2:5-*endomethylenehexahydrobenzoic acid* (*exo*) (II) (A , $R=CO_2H$, $R'=H$), m.p. 48° (*amide*, m.p. 187—188°; *anilide*, m.p. 130°); the change occurs through an intermediate enolic form (cf. Hückel and Goth, A., 1925, i, 402). The chloride of (I) with activated NaN_3 (Nelles, A., 1932, 1118) in C_6H_6 followed by hydrolysis (conc. HCl) gives *endonorbornylamine* (III) (A , $R=H$, $R'=NH_2$) (*hydrochloride*, m.p. 295°; *Ac* derivative, m.p. 124°)



(cf. Komppa and Beckmann, A., 1934, 1105); *endo*-norbornylcarbamide has m.p. 191°. The chloride, b.p. 83—84°/12 mm., of (II) is similarly converted into *exonorbornylamine* (IV) (A , $R-NH_2$, $R'=H$) (*hydrochloride*, m.p. $>345^\circ$; *Ac* derivative, m.p. 139°); *exonorbornylcarbamide* has m.p. 186°. (III) and (IV) are both converted by HNO_3 into *exonorborneol* (A , $R=OH$, $R'=H$), m.p. 127° [the β -norborneol of Komppa and Beckmann (*loc. cit.*)]. The α -norborneol of Komppa and Beckmann is *endonorborneol*. In agreement with these authors and Brecht (cf. A., 1929, 571), and contrary to Vavon and Peignier (A., 1926, 1042) and Hückel *et al.* (A., 1930, 206), borneol and isoborneol are considered to have *exo*- and *endo*-OH, respectively. *trans*-3:6-*endo*-Methylenehexahydrophthaloyl chloride and NaN_3 (as above) give 1:2-*diamino*-[1,2,2]-*dicycloheptane* (V), b.p. 212°/767 mm. (*dihydrochloride*, m.p. $>350^\circ$; Ac_2 derivative, m.p. 272°). H. B.

Synthesis of thiocamphor and other cyclic thioketones. P. C. RAY (Nature, 1934, 134, 1010).—Camphor in abs. EtOH yields *thiocamphor*, m.p. 145°, when treated simultaneously at 0° with dry H_2S and dry HCl. Thiocyclohexanone and its tripolymeride have been synthesised by a similar method. L. S. T.

p-(or 2:5-)Diketocamphanecarboxylic acid and related acids.—See B., 1935, 46.

Nuclear condensations of furan. H. GILMAN, B. L. WOOLEY, and R. J. VANDERWAL (Proc. Iowa Acad. Sci., 1932, 39, 176).—Furan and its derivatives have been condensed with CH_2N_2 , aryldiazonium compounds, and $CHN_2 \cdot CO_2Et$. The condensations are sometimes preceded by 1:2 and 1:4 additions.

CH. ABS. (7)

Preparation and properties of furyl phenyl ketimine. J. B. CULBERTSON and B. DAVIS (Proc. Iowa Acad. Sci., 1932, **39**, 177).—*Furyl phenyl ketimine* (I) is prepared from furonitrile and MgPhBr. The *hydrochloride* is rapidly hydrolysed to furyl Ph ketone; the velocity of this hydrolysis and the basic strength of (I) are recorded. CH. Abs. (r)

Hydropyran nucleus. II. Bromo-derivatives of tetrahydropyran. R. PAUL (Bull. Soc. chim., 1934, [v], **1**, 1397—1405; cf. A., 1934, 1225).—With dry Br in Et₂O at -17° dihydropyran (I) affords 2:3-dibromotetrahydro- (II), b.p. 96—98°/9 mm. [contaminated with (III)], converted by distillation at 25 mm., or better by NPhEt₂, into 3-bromo-5:6-dihydro-pyran (III), b.p. 65°/25 mm. With HBr (I) gives 2-bromotetrahydropyran, b.p. 61°/16 mm. (resinifies in air). With NaOH in presence of Pb(NO₃)₂ (II) affords 3-bromo-2-hydroxytetrahydropyran (IV), m.p. 79—80° (reduces Fehling's solution or NH₃-AgNO₃), but with H₂O at room temp. is obtained the ether (CH₂<CH₂·CHBr>CH·O), m.p. 110° (block) (no reducing properties), also obtained by interaction of equimol. quantities of (II) and (IV). J. W. B.

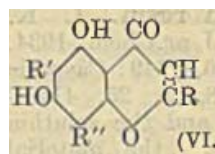
Attempts to synthesise 5:6-dihydroxyflavone (primetin). W. BAKER (J.C.S., 1934, 1953—1954).—2:6-Dibenzoyloxyacetophenone, m.p. 105° (simplified prep. of 2:6-dihydroxyacetophenone), with K₂CO₃ in PhMe gives 5-hydroxy-3-benzoylflavone, m.p. 177° (cf. Sugawara, A., 1934, 1107). 2:4-Diacetylresorcinol dibenzoate, m.p. 123°, with KOAc-EtOH yields a small amount of 5-hydroxy-6-acetylflavone (I), m.p. 201°, also obtained from 5-acetoxyflavone and AlCl₃ in PhNO₂. Quinacetophenone and NaOAc-Ac₂O form 5-O-acetylquinacetophenone. (I) cannot be oxidised with H₂O₂ or BzO₂ to primetin. F. R. S.

Constitution of fukugetin. II. M. MURAKAMI and T. IRIE (Proc. Imp. Acad. Tokyo, 1934, **10**, 568—571; cf. A., 1933, 398).—Fukugetin (I) (H sulphate), C₂₄H₁₆O₉ (loc. cit., C₂₂H₁₆O₈), with 50% KOH gives fukugenetin, garcinol (II), and 3:4-C₆H₃Ac(OMe)₂. (II), C₁₅H₁₀O₅ (lit., C₁₆H₁₂O₅) (derivatives give depressions of the m.p., when mixed with those of 5:7-dihydroxy-3-p-hydroxyphenylcoumarin), readily gives a H₂-derivative (catalytic reduction) and with Me₂SO₄-KOH affords, by opening of the lactone ring, "pentamethylgarcinol hydrate" (III), m.p. 142—143°, which is synthesised. p-OMe·C₆H₄·CHO and ω-chloro-2:4:6-trimethoxyacetophenone give the substance, O<CH·C₆H₄·OMe>CH·CO·C₆H₃(OMe)₃, m.p. 115—116°,

which yields successively β-p-anisyl-α-2:4:6-trimethoxyphenyl-lactic acid, amorphous, the anhydride, OMe·C₆H₄·CH·C(CO₂Ac)·C₆H₂(OMe)₃, m.p. 100—103°, and α-carboxy-2:4:6:6'-tetramethoxystilbene, m.p. 188—188.5°, the Me ester of which is (III). (II) is, therefore, 2-p-hydroxybenzylidene-4:6-isocoumarone.

(I) affords by Ac₂O-NaOAc the Ac. derivative, m.p. 273—274°, and by Me₂SO₄ the Me₃ ether, m.p. 252—254°, of anhydrofukugetin, C₂₄H₁₀O₄(OH)₄. Since also (I) is sol. in KOH

and pptd. therefrom by CO₂, it does not contain a CO₂H or lactone ring. By CH₃N₃ or Me₂SO₄ (I) gives the Me₃ ether (IV), m.p. 203° (oxime), which with hot 5% KOH-EtOH rapidly yields an iso-derivative (V), m.p. 136° (dioxime; Ac derivative, m.p. 158°), previously called (IV). With Me₂SO₄ (V) gives

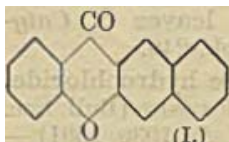


isofukugetin Me₃ ether, m.p. 188°, stable to KOH, but giving with HCl (IV); the isomerisation of (IV) to (V) is due to change of O<CH· to ·CO·C(OH)·CH.

KOH fusion of (I) gives phloroglucinol, protocatechuic acid, and AcOH. (I) is, therefore, (VI) [R=3:4-C₆H₃(OH)₂; R' and R''=H and O<CH·C₆H₄·OH(p) respectively, or vice versa]. Garcinin is impure (I). R. S. C.

Constitution of hydroxy-derivatives of diphenylene oxide. K. TATEMATSU and B. KUBOTA (Bull. Chem. Soc. Japan, 1934, **9**, 448—457).—The compound obtained by heating resorcinol with W₃O₈ (A., 1925, i, 809) is 2-hydroxydiphenylene oxide (I), m.p. 138—138.5° [Ac derivative, m.p. 111—111.5°; Me ether, m.p. 97—97.5°; (NO₂)₂ derivative, m.p. 216—217° (decomp.)], obtained by diazo-reaction from 2-aminodiphenylene oxide (II), m.p. 99—99.5° (lit., m.p. 94°; cf. Cullman, A., 1931, 96) [Ac derivative (III), m.p. 176.5—177°]. Bromination of (I) affords 3-bromo-2-hydroxydiphenylene oxide (IV), m.p. 113—113.5° (Me ether, m.p. 147—148°). Bromination of (III) affords 3-bromo-2-acetamidodiphenylene oxide, m.p. 195—195.5°, hydrolysed to the corresponding amine (V), m.p. 129—130°, which gives (IV) by diazo-reaction. Replacement of NH₂ in (V) by H gives 3-bromodiphenylene oxide (Mayer et al., A., 1922, i, 746). (V) affords (Sandmeyer) 2:3-dibromodiphenylene oxide (VI), m.p. 150—150.5°. 3-Nitro-2-aminodiphenylene oxide (VII) (A., 1924, i, 161) affords (diazo-reaction) 2-bromo-3-nitrodiphenylene oxide, m.p. 171—172°, reduced to 2-bromo-3-aminodiphenylene oxide, m.p. 172—172.5°, which gives (VI) (Sandmeyer). The constitutions of (IV) and (VII) were thus established [cf. Cullman, loc. cit., who supposes the NO₂ in (VII) to be in the 1-position]. H. G. M.

Pyrenium compounds. XXIV. 2:3-Benzoxanthone and 9-phenyl-2:3-benzoxanthanol. W. DILTHEY and F. QUINT (J. pr. Chem., 1934, [ii], **141**, 306—310; cf. A., 1934, 1227).—3-Phenoxy-β-naphthoic acid, m.p. 183—184° (obtained together with an acid, m.p. 132—133°, from NaOPh, 3:2-C₁₀H₆I·CO₂K, and Cu-bronze), is converted by PCl₅ in C₆H₆ into 2:3-benzoxanthone (I), m.p. 201—202°, which is more yellow than the 1:2- and 3:4-isomerides. (I) and MgPhBr in EtO·C₆H₅ give 9-phenyl-2:3-benzoxanthanol (II), m.p. 157.5—158.5° [corresponding perchlorate, m.p. 271—272° (decomp.)], which

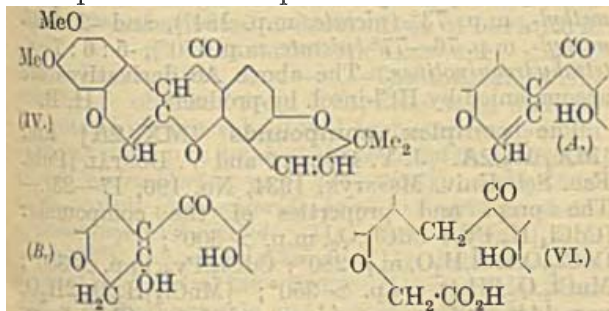


affords green salts. The 2:3-benzo-group has a bathochromic action (cf. Dutta, A., 1934, 1013). (II) is reduced (Zn dust, AcOH) to 9-phenyl-2:3-

benzoxanthen (Kaufmann and Egner, A., 1914, i, 39). The compound described as (II) by Gomberg and Schoepfle (A., 1917, i, 551) is 9-phenyl-1:2-benzoxanthenol. H. B.

Varying valency of platinum with respect to mercaptanic radicals.—See this vol., 182.

Poisonous constituents of the seeds of *Tephrosia vogelii*. K. W. MERZ and G. SCHMIDT (Arch. Pharm., 1935, 273, 1—21; cf. A., 1932, 888).—These seeds, freed from protein (39%) and oil (10.5%) by ligroin, yield to COMe_2 a mixture containing dehydrodeguelin (I), allotephrosin (II), $\text{C}_{23}\text{H}_{22}\text{O}_7$, m.p. 194—195°, and isodeguelin (III), $\text{C}_{23}\text{H}_{22}\text{O}_6$, m.p. 167—168°. The Ac derivative, m.p. 119.5—120.5°, of (II) loses AcOH at 180° to yield isodehydrodeguelin (IV), m.p. 235—236°, colourless; with $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ it gives (I) and with 0.03N-KOH-aq. EtOH gives isoallotephrosin (V), $\text{C}_{23}\text{H}_{22}\text{O}_7$, m.p. 202°. Hydrogenation (PtO_2) of (II) in AcOH gives impure dihydroallotephrosin, the Ac derivative, m.p. 266°, of which with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ affords dihydrodehydrodeguelin. (II) with $\text{KMnO}_4\text{-COMe}_2$ gives allotephrosindicarboxylic acid, $\text{C}_{23}\text{H}_{22}\text{O}_{11}$, m.p. (+ ? H_2O) 122—124°, (anhyd.) 171°, hygroscopic, isomerised by $\text{H}_2\text{O}_2\text{-KOH}$ to an acid, m.p. 210—211° (decomp.). With $\text{H}_2\text{SO}_4\text{-AcOH}$ (1:2) at 60—65° (II) yields (I), but with boiling $\text{Ac}_2\text{O-NaOAc}$ (IV), which with KOH-Zn dust affords deguelic acid (VI) [*Me* ester, m.p. 125—126°; oxime, m.p. 168—169° (decomp.)]. (II) and cold $\text{NH}_3\text{-EtOH}$ give (V), the Ac derivative of which, when heated above the m.p., 193—194° (decomp.), gives AcOH and (IV). Hydrogenation of (V) gives *acetyl*dihydroisoallotephrosin, m.p. 193—194°, and dehydration by $\text{H}_2\text{SO}_4\text{-AcOH}$ gives (IV). (III), α 0° (oxime, m.p. 233—234°), gives by hydrogenation dihydrodeoxydeguelin, $\text{C}_{23}\text{H}_{26}\text{O}_5$, m.p. 153—154°, by $\text{K}_3\text{Fe}(\text{CN})_6$ (IV), and by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ (I). Aerial oxidation of (III) in NaOH- COMe_2 affords (V), whilst in $\text{Et}_2\text{O-aq. NaOH}$ a mixture is rapidly formed, wherefore it is concluded that (II) may be formed from (III) during isolation from the plant. The formula given is assigned to (IV) and it is considered that tephrosin and isotephrosin are *cis*- and *trans*-7-



and (II) and (V) *cis*- and *trans*-8-hydroxydeguelins, and that deguelin and (III) are *cis-trans*-ring isomerides. The change of (IV) into (VI) is assumed to proceed by way of (A) and (B). R. S. C.

Ketonic acids with pyrrole nucleus. F. INGRAFFIA (Gazzetta, 1934, 64, 778—784).—The Mg derivative (I) of 2:4-dimethylpyrrole reacts with $\text{COCl}\cdot\text{CO}_2\text{Et}$ to give Et 2:4-dimethylpyrrole-5-glyoxylate, of which the acid (II) gives on decomp.

2:4-dimethylpyrrole-5-aldehyde. (I) with $\text{COCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ yields Et 3:5-dimethyl-2-pyrrolylacetate (III), m.p. 95° (semicarbazone, decomp. about 170°); from (III), 5-acetyl-2:4-dimethylpyrrole, 3:5-dimethyl-2-pyrrolylphenylpyrazolone, m.p. 141°, and, using NH_2Me , 3:5-dimethyl-2-pyrrolylmethylacetamide, m.p. 156°, are prepared. E. W. W.

Mixed functional derivatives of 2:4-dimethylpyrrole. F. INGRAFFIA (Gazzetta, 1934, 64, 784—792).—(I) (preceding abstract) with $\text{CH}_2\text{Cl}\cdot\text{COCl}$ yields 5-chloroacetyl-2:4-dimethylpyrrole, which gives the following products: with KOH, 3:5-dimethyl-2-pyrrolylcarbinol, m.p. 208° (Ac derivative, m.p. 108°), oxidised (KMnO_4) to (II); with KCN, 3:5-dimethyl-2-pyrrolylacetonitrile, m.p. 195°; with aq. NH_3 and NH_2Me at 100°, 5-aminoacetyl-, m.p. 203° [hydrochloride; picrate, m.p. about 195° (decomp.)], and 5-methylaminoacetyl-2:4-dimethylpyrrole, decomp. 260° (hydrochloride), respectively. (I) and BzCl yield 5-benzoyl-2:4-dimethylpyrrole (A., 1915, i, 990) (picrate, m.p. 92°; iodate, m.p. 109°). E. W. W.

Reaction between phthalic anhydride and the magnesium derivative of 2:4-dimethylpyrrole. F. INGRAFFIA (Gazzetta, 1934, 64, 714—718).—This reaction yields 3:5-dimethyl-2-pyrrolylphthalide (I), m.p. 207° (4-benzeneazo-derivative, m.p. 76°), and 3:5-dimethyl-2-pyrrolylphenylcarbinol-o-carboxylic acid (II), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{C}(\text{Me})_2$, m.p. 198° (Ag salt); (I) with KOH gives (II). E. W. W.

Pyrrole derivatives. I. I. J. RINKES (Rec. trav. chim., 1934, 53, 1167—1174).—2-Acetylpyrrole with $\text{Ac}_2\text{O-HNO}_3$ (*d* 1.51) at -10° to -15° gives a mixture of its 4- (I), m.p. 197°, and 5- NO_2 - (II), m.p. 156°, -derivatives (cf. Ciamician *et al.*, A., 1886, 718). *Me* pyrrole-2-carboxylate with 1.5 mols. of HNO_3 also gives its 4- (III), m.p. 197°, and 5- NO_2 -, m.p. 181—182° (*lit.* 178°), -derivatives, also obtained (after esterification) together with 2-nitropyrrole (IV), m.p. 55°, by $\text{Ac}_2\text{O-HNO}_3$ (1.25 mol.) on the corresponding acid. Nitration of pyrrole with $\text{Ac}_2\text{O-HNO}_3$ (1.25 mols.) at -10° gives (IV) (21% yield), but with 2 mols. of HNO_3 , 2:4- (V), m.p. 149—150°, and 2:5-(NO_2)₂-, m.p. 173°, -derivatives [also by similar nitration of (IV)] are obtained. With HNO_3 (*d* 1.51) at -10° (III) gives (V). When heated with 25% HNO_3 (I) and (II) are converted, respectively, into 4:4', m.p. 219°, and 5:5', m.p. 176°, -dinitro-2:2'-dipyrrolyl-dinitrosacyl (cf. Holleman, A., 1892, 971), hydrolysed by hot aq. NaOH, respectively, to 4-, m.p. 217°, and 5-, m.p. 160—161°, -nitropyrrole-2-carboxylic acid. J. W. B.

Thiopyrrolecarboxylic acids. K. NEISSER (Ber., 1934, 67, [B], 2080—2083).—Et 2:4-dimethylpyrrole-3-carboxylate is transformed by $\text{Cu}(\text{CNS})_2$ in boiling MeOH into Et 5-thiocyano-2:4-dimethylpyrrole-3-carboxylate, converted by cautious hydrolysis into Et 5-thiol-2:4-dimethylpyrrole-3-carboxylate, m.p. 107—108°, which loses H_2S and NH_3 under the action of aq. KOH. The product obtained by the action of CO_2 on the pyrrole-Grignard compound is pyrrole-2-carboxylic acid (I), m.p. 207°, and a dimorphous modification (II), m.p. 161°, incorrectly regarded as

pyrrole-3-carboxylic acid, since (I) and (II) do not give a depression in mixed m.p., and yield identical Me esters (III), m.p. 72.5–73°, and Me Br₃-esters, m.p. 208–210°; hydrolysis of the ester from (II) gives (I), and (I) is obtained when the solution of (II) in H₂O is seeded with (I). Cautious bromination of (III) gives *Me dibromopyrrole-2-carboxylate*, m.p. 164–165°. (III) is transformed by Cu(CNS)₂ in boiling MeOH into *Me 2-thiocyanopyrrole-5-carboxylate*, m.p. 107°, converted by cautious hydrolysis into *2-thiopyrrole-5-carboxylic acid*, m.p. 173° (decomp.) [*Me ester*, m.p. 83–84°], not identical with the product obtained by Windaus *et al.* (A., 1934, 1415) from vitamin-B₁.
H. W.

Fission of pyridine. H. FREYTAG (Ber., 1934, 67, [B], 1995–1998).—Addition of BzCl to C₅H₅N-H₂O followed by acidification of the solution leads to BzOH and glutacondialdehyde (I) [identified by the "fluorescence test" (II), which consists in adding *p*-NH₂-C₆H₄-CO₂Et and HCl to the solution and extraction with amyl alcohol, thus giving a solution with green fluorescence]. The presence of (I) in C₅H₅N which has been exposed to moist air but not in freshly distilled C₅H₅N and also in the products of the action of NaOH and CHCl₃ on C₅H₅N is established by (II).
H. W.

Influence of temperature on the formation of additive compounds.—See this vol., 182.

Indoleacetic acids. F. E. KING and P. L'ECUYER (J.C.S., 1934, 1901–1905).—2-Carboxyindole-3-acetic acid, obtained by hydrolysing the Et ester, gives at its m.p. skatole, but in quinoline at 195° loses 1 mol. of CO₂ to give indole-3-acetic acid in small yield. NHPh-NHMe (I) and α-ketoglutaric acid afford 2-carboxy-1-methylindole-3-acetic acid, m.p. 234°, decarboxylated in quinoline to 1-methylindole-3-acetic acid (II). *Et 2-carboxy-1-methylindole-3-acetate*, m.p. 184°, at 190–200° gives *Et 1-methylindole-3-acetate*, b.p. 165°/1 mm., hydrolysed to (II) [best method of prep. for (II)]. (I) and acetonedicarboxylic ester form (HCl) *Et 3-carbethoxy-1-methylindole-2-acetate*, m.p. 90°, hydrolysed to 3-carboxy-1-methylindole-2-acetic acid, m.p. 262°, or to 3-carbethoxy-1-methylindole-2-acetic acid, m.p. 170°. The half-ester at 180–190° gives *Et 1:2-dimethylindole-3-carboxylate*, further hydrolysed to the acid.
F. R. S.

Condensation of isatin and 1:3-indanedione. W. M. FISCHER and A. CIRULIS (Annalen, 1934, 514, 261–267).—Isatin (I) (1 pt.) and 1:3-indanedione (II) (2 pts.) in MeOH at room temp. for 5 days give a little of a blue compound, m.p. 263° (insol. in aq. NaOH), and (mainly) the NaOH-sol. 2-keto-3:3-di-(1':3'-diketo-2'-indanyl)-2:3-dihydroindole,

$$\text{NH} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \text{CO} \end{array} \text{C} \begin{array}{c} \diagup \text{CH} \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{CO} \end{array}, \text{ m.p. } 240\text{--}241^\circ \text{ (decomp.) } [\text{Na}_2 \text{ (anhyd. and } +5\text{H}_2\text{O) and Ag}_2 \text{ salts; } 1:2':2'\text{-Br}_3\text{-derivative, m.p. } 175^\circ \text{ (decomp.)}; \text{ } p\text{-phenylhydrazone, m.p. } 252^\circ \text{ (decomp.)}; \text{ } N\text{-Ac derivative, m.p. } 222^\circ \text{ (decomp.)}], \text{ similarly prepared from } N\text{-acetyl isatin and (II)], \text{ which is phototropic and dissolves in cold C}_5\text{H}_5\text{N to a yellow solution which turns red when heated. } N\text{-Benzoyl isatin and (II) in boiling AcOH give the same quinolyne phenylene}$$

ketonocarboxylic acid (III) as is obtained (Noelting and Herzbaum, A., 1911, i, 917) from (I) and (II) in alkali. Di-indone and (I) in boiling *N*-NaOH also afford (III); in AcOH, a substance, m.p. 310° (Cu block), results.
H. B.

Synthesis of Bz-tetrahydroquinolines. II. U. BASU (Annalen, 1934, 514, 292–298; cf. A., 1934, 1111).—6-Methyl-2-hydroxymethylenecyclohexanone and *Et β*-aminocrotonate at 100° give *Et 2:8-dimethyl-5:6:7:8-tetrahydroquinoline-3-carboxylate*, b.p. 166°/11 mm. (*picrate*, m.p. 127°); the free acid, m.p. 214° (decomp.), distilled with soda-lime in a vac. affords 2:8-dimethyl-5:6:7:8-tetrahydroquinoline, b.p. 227–228°/754 mm. (*picrate*, m.p. 118°; *platinichloride*, m.p. 182–183°; *mercurichloride*, m.p. 136°). 2:6-Dimethyl-5:6:7:8-tetrahydroquinoline-3-carboxylic acid [*Et ester*, b.p. 170–171°/9 mm. (cf. *loc. cit.*)] similarly affords 2:6-dimethyl-5:6:7:8-tetrahydroquinoline, b.p. 235–236°/752 mm. (cf. von Braun *et al.*, A., 1924, i, 553) (*picrate*, m.p. 146°; *platinichloride*, m.p. 185°); the 2:7-Me₂ derivative (*loc. cit.*) gives a *mercurichloride*, m.p. 151°, and a *hydrochloride*, m.p. 168–169°. 4:5-Dimethyl-2-hydroxymethylenecyclohexanone similarly affords *Et 2:6:7-trimethyl-5:6:7:8-tetrahydroquinoline-3-carboxylate*, b.p. 172°/13 mm. [*free acid*, m.p. 135–136° (decomp.)]; 2:6:7-trimethyl-5:6:7:8-tetrahydroquinoline (*picrate*, m.p. 105°; *platinichloride*, m.p. 187°) has b.p. 239–240°/752 mm. 2-Hydroxymethylenecyclohexanone (I) and β-aminocrotononitrile at 100° give 3-cyano-2-methyl-5:6:7:8-tetrahydroquinoline (II), m.p. 107–108° (*picrate*, m.p. 160–161°), and a substance, m.p. 235°; (II) is hydrolysed (75% H₂SO₄) to the 3-carboxylic acid (*loc. cit.*) (*platinichloride*, m.p. 120–121°). (I) and acetylacetoneimine at 100° afford 3-acetyl-2-methyl-5:6:7:8-tetrahydroquinoline, m.p. 55° (*picrate*, m.p. 155°; *semicarbazone*, m.p. 195°); 3-acetyl-2:6, b.p. 165°/15 mm., m.p. 65° (*picrate*, m.p. 168°; *semicarbazone*, m.p. 215°), and -2:7-dimethyl-5:6:7:8-tetrahydroquinoline, b.p. 169–170°/16 mm. (*picrate*, m.p. 169°; *semicarbazone*, m.p. 214°), are similarly prepared. Benzoylacetoneimine and the appropriate hydroxymethylenecyclohexanone give 3-benzoyl-2-methyl-, m.p. 73° (*picrate*, m.p. 184°), and -2:6-dimethyl-, m.p. 76–77° (*picrate*, m.p. 170°), -5:6:7:8-tetrahydroquinolines. The above Ac derivatives are accompanied by HCl-insol. by-products.
H. B.

The complex compounds [MX₂,2A] and [MX₃,H₂,2A]. J. V. DUBSKÝ and V. DOSTAL (Publ. Fac. Sci. Univ. Masaryk, 1934, No. 196, 17–23).—The prep. and properties of the compounds: [CdCl₂], H₂, Py₂; CdCl₂, Q₂, m.p. > 300°; CdCl₂, Q, HCl, H₂O, m.p. 280°; CdCl₂, Py₂, m.p. > 350°; MnCl₂, Q₂, 3H₂O, m.p. > 350°; [MnCl₄], H₂, Q₂, 2H₂O, m.p. 144°, and its isomeride, m.p. 105°; CoCl₂, Q₂, m.p. 248°; [CoCl₄], H₂, Q₂, 2H₂O, m.p. 125°; ZnCl₂, Q₂, m.p. 235°; [ZnCl₄], H₂, Q₂, 2H₂O, m.p. 124°; ZnBr₂, Q₂, m.p. 244°; [ZnBr₄], H₂, Q₂, 2H₂O, m.p. 106–112°, are described (Py=C₅H₅N; Q=quinoline).
R. T.

Preparation of quinoline derivatives. V. K. DZIEWONSKI, J. MOSZEW, J. MAKSYMOWICZ, and P. TRZESINSKI (Bull. Acad. Polonaise, 1934, A, 190–195).—The structure of 4-m-toluidino-2-phenyl-5-methylquinoline, m.p. 134–135° [*hydrochloride*, m.p.

173—175° (decomp.); *picrate*, m.p. 245—246°; *Ac*, m.p. 149—150°, and *NO*-, m.p. 144°, derivatives], obtained by heating *COPhMe* with *m*-C₆H₄Me·NH·CS·NHPH at 180—205° and finally at 300°, is proved by its hydrolysis with KOH-EtOH at 200° to 4-hydroxy-2-phenyl-5-methylquinoline, m.p. 281°, different from the known -7-Me isomeride, m.p. 270°. Condensation of CH₂Ph·COPh with CS(NHPH)₂ at 190—220° and then at 280° affords 4-anilino-2:3-diphenylquinoline, m.p. 196—197° [hydrochloride, m.p. 279°; *nitrate*, m.p. 185° (decomp.); *picrate*, m.p. 259—260°; and *NO*-derivative, m.p. 153—154° (decomp.)], similarly hydrolysed to 4-hydroxy-2:3-diphenylquinoline. J. W. B.

Direct introduction of amino-groups into aromatic and heterocyclic nucleus. II. Reaction of isoquinoline with alkali and alkaline-earth amides in liquid ammonia. F. W. BERGSTROM (Annalen, 1934, 515, 34—42; cf. A., 1934, 1110).—1-Aminoisoquinoline (I), m.p. 122—123°, is obtained in 60—75% yield from isoquinoline (II) and an excess of KNH₂ (III) in liquid NH₃ at room temp.; the reaction mixture is freed from NH₃ and then treated with C₆H₆ and H₂O. NaNH₂ similarly gives 20—30% of (I) and resin. Little reaction occurs between (II) and LiNH₂, Ca(NH₂)₂, or Mg(NH₂)₂. Ba(NH₂)₂ reacts rapidly but somewhat less readily than (III); reaction is accelerated by Ba(CNS)₂. Of the complex ammonio-salts investigated, only BaKN₂NH₃ and K₂NaN₂NH₃ react with (II) to give (I); dissociation probably occurs to some extent. H. B.

Preparation of 3:6-dicarboxybenzoyl-N-ethylcarbazole. V. A. IGNATIUK-MAJSTRENKO and N. S. TICHONOV (Anilinokras. Prom., 1934, 4, 473—475).—AlCl₃ is added to a 1:4:20 mol. mixture of *N*-ethylcarbazole, *o*-C₆H₄(CO)₂O, and PhCl, the mixture heated at 50—70°, poured on ice, made acid with HCl, and PhCl removed by steam-distillation. The residue is dissolved in aq. NaOH, the solution filtered, 3-mono- (I) and 3:6-di-carboxybenzoyl-9-ethylcarbazole are pptd. by HCl, and separated by C₆H₆, which dissolves only (I). R. T.

New *N*-substituted *C*-derivatives of barbituric acid. E. GRYSZKIEWICZ-TROCHIMOWSKI (Arch. Chem. Farm., 1934, 2, 1—8).—The following compounds are obtained from NEt₂·CH₂·CH₂Cl and the Na salts of various substituted barbituric acids (I) in EtOH at the b.p.: 3-β-diethylaminoethyl-5:5-diethyl-, an oil (hydrochloride, m.p. 225—226°); -5-ethyl-5-n-butyl-, an oil (hydrochloride, m.p. 212—213°); -5-Δ¹-cyclohexenyl-1:5-diethyl- (II) (hydrochloride, m.p. 150—151°); -5-phenyl-5-ethyl- (III) -barbituric acid (hydrochloride, m.p. 245—246°). (II) and (III) have only a feeble analgesic and narcotic action as compared with the corresponding (I), but greatly depress blood pressure. R. T.

Degradations of allantoin. H. BILTZ and L. LOEWE (J. pr. Chem., 1934, [ii], 141, 284—298).—3-Methylallantoin (I) and Ac₂O-conc. H₂SO₄ give (probably) the 1:6-*Ac*₂ derivative,

$\begin{array}{c} \text{NMe} \cdot \text{CO} \\ \text{CO} \cdot \text{NAC} \end{array} > \text{CH} \cdot \text{NAC} \cdot \text{CO} \cdot \text{NH}_2$, m.p. 230° (uncorr.); allantoin (II) similarly affords the 1:3-*Ac*₂ derivative,

m.p. 247° (decomp.), hydrolysed (conc. aq. NH₃) to the 1-*Ac* derivative, m.p. 236° (decomp.), and thence to (II). (I) and boiling Ac₂O-C₅H₅N or Ac₂O at 160—170° (bomb) give 5-acetamido- (III) (A., 1926, 414) and a little 5-diacetamido-, m.p. 100° (uncorr.), -1-acetyl-3-methylhydantoin. (III) is converted by aq. basic Pb acetate at 100° into 5-acetamido-3-methylhydantoin (IV), re-acetylated (Ac₂O-conc. H₂SO₄) to (III). (III) or (IV) and conc. aq. NH₃ give NH₄ α-acetamido-ω-methylhydantoate, m.p. 178—180° (decomp), converted by basic Pb acetate into (IV) and by Ac₂O into (III). 1:8-Dimethylallantoin (V) or its Ac₂ derivative and boiling Ac₂O afford 5-acetyl-methylamino-1-acetyl-3-methylhydantoin, m.p. 128—130°, whilst the 6-*Ac* derivative of (V) similarly gives 4-ethoxy-3:6-diacetyl-1:8-dimethylacetylenediureine, CO< $\begin{array}{c} \text{NAC} \cdot \text{CH} \text{---} \text{NMe} \\ \text{NMe} \cdot \text{C}(\text{OEt}) \cdot \text{NAC} \end{array}$ >CO, m.p. 155—156°, hydrolysed (EtOH-NH₃) to the 6-*Ac* derivative, m.p. 185° (decomp.); the OEt is probably introduced during crystallisation of the reaction product from EtOH. All m.p. are corr. unless stated otherwise. H. B.

Constitution of porphyrindine; magnetic proof of an organic bi-radical. R. KUHN, H. KATZ, and W. FRANKE (Naturwiss., 1934, 22, 808—809).—Porphyrindine is paramagnetic and is a true bi-radical (cf. A., 1934, 718). This is in agreement with the constitution given by Piloty (A., 1903, i, 523). H. G. M.

Amidations with sodium and potassium amides in the alkaloid series. II. α- and α'-Aminoanabasine. M. I. KABATSCHEV and M. M. KATZNELSON (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 47—50; cf. A., 1934, 538).—Anabasine and NaNH₂ in NHMe₂ at 135—145° afford 2-(2'-amino-3'-pyridyl)-, m.p. 109° (cf. A., 1934, 422), and 2-(2'-amino-5'-pyridyl)-piperidine, m.p. 85.5—90°, the diazonium compounds of which are converted into the 2'-Cl-compounds, m.p. 99.5—100° and 58.5—59.5°, respectively. These are oxidised (KMnO₄) to 2-chloropyridine-3- and -5-carboxylic acid, respectively. J. L. D.

Complex salts of 2:2'-dipyridyl with bivalent copper.—See this vol., 167.

Intermediate compounds between ferrocyanides and ferroammines.—See this vol., 181.

Cyanine dyes. VII. Synthesis of pentamethinecyanines. T. OGATA (Proc. Imp. Acad. Tokyo, 1934, 10, 572—574).—In a new method of preparing 1:3:3:1':3':3'-hexamethylindodicarbo-cyanine iodide, the product obtained by condensing 1 mol. of diphenylformamidine with 1 mol. of 2:3:3-trimethylindolenine methiodide is heated with Ac₂O, together with CH(OEt)₃ or the K salt of a carboxylic acid. Similar preps. of 2:2'-diethylthiadicarbo-cyanine iodide are described. The course of the reaction is not clear. F. M. H.

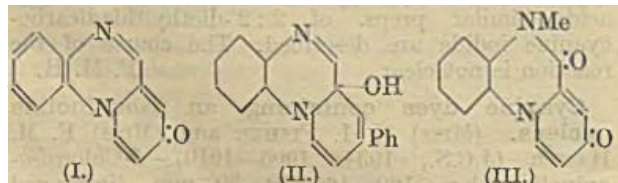
Cyanine dyes containing an isoquinoline nucleus. (Miss) N. I. FISHER and (Miss) F. M. HAMER (J.C.S., 1934, 1905—1910).—1-Chloroisoquinoline, b.p. 160—165°/20—30 mm. (improved prep.) and MeI under pressure give 1-iodoisoquinoline methiodide (I), m.p. 228°; the ethiodide, m.p. 188—

189°, is similarly prepared. The ethiodide with NH_3 forms 1-amino-, m.p. 194°, and with NH_4Ph 1-anilino-isoquinoline ethiodide, m.p. 192—193°. 1-Bromoisoquinoline ethobromide, m.p. 128°, and 1-iodoisoquinoline n-propiodide, m.p. 116—117°, are similarly obtained. Quinaldine methiodide (I) and Na in EtOH give 1:2'-dimethyl-2:1'-cyanine iodide, m.p. 234°, and by use of the appropriate reagents 2'-methyl-1-ethyl-, m.p. 250°, 1:2'-diethyl-, m.p. 258°, 6:2'-dimethyl-1-ethyl-, m.p. 234°, and 2'-methyl-1-ethyl-5:6-benz-2:1'-cyanine iodide, m.p. 250°; 2'-methyl-1-ethyl-4:1'-cyanine iodide, m.p. 210° [from lepidine ethiodide and (I)], and 2:2'-diethylthia-, m.p. 246° (from 1-methylbenzthiazole ethiodide and 1-iodoisoquinoline ethiodide), 2-ethyl-2'-n-propylthia-, m.p. 237°, 2'-methyl-2-ethyl-3:4-benzthia-, m.p. 235° [from 2-methyl- β -naphthathiazole ethiodide and (I)], 2'-methyl-2-ethyl-5:6-benzthia-, m.p. 233°, and 2'-methyl-2-ethylseleno-, m.p. 238° [from 1-methylbenzselenazole ethiodide and (I)], and 4:2'-dimethyl-3-ethylthiazolo-1-cyanine iodide, m.p. 235° [from 2:4-dimethylthiazole ethiodide and (I)], are obtained. The cyanines containing an isoquinoline nucleus are, in general, definitely weaker as photographic sensitizers than those containing a quinoline nucleus. M.p. are also decomp. points. F. R. S.

New phenazine synthesis. Phenazhydrins. I. G. R. CLEMO and H. McILWAIN (J.C.S., 1934, 1991—1993).—cycloHexane-1:2-dione and o- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ condense (AcOH - NaOAc) to 1:2:3:4-tetrahydrophenazine, m.p. 92.5°, dehydrogenated with I in AcOH to phenazine. 1-Methyl-1:2:3:4-tetrahydrophenazine (I), b.p. 160—165°/20 mm., m.p. 37°, similarly prepared, is dehydrogenated to 1-methylphenazine, m.p. 108°, which is oxidised by H_2CrO_4 to phenazine-1-carboxylic acid. Oxidation (H_2CrO_4) of (I) yields an acid, $\text{C}_{11}\text{H}_{10}\text{N}_2(\text{CO}_2\text{H})_2\cdot\text{H}_2\text{O}$, m.p. 114—117°, subliming at 1 mm. to a dehydrated acid, m.p. 187°. Phenazhydrins between the phenazines and dihydrophenazines are obtained by heating with H_2 and platinised asbestos at 325°: phenazhydrin, $\text{C}_{13}\text{H}_{10}\text{N}_2\cdot\text{C}_{13}\text{H}_{12}\text{N}_2$, between methylphenazine and its H_2 -derivative, m.p. 116°, between phenazine and dihydrophenazine, m.p. 209° (decomp.), and between phenazine and methyl-dihydrophenazine, m.p. 157—160°. The constitution of the compounds is discussed.

F. R. S.

Synthesis of heterocyclic compounds from o-diamines and sugars. K. MAURER and B. SCHIEDT (Ber., 1934, 67, [B], 1980—1985).—Condensation of o- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ with glucose, fructose, or, preferably, sucrose in boiling H_2O - AcOH gives 2- $\alpha\beta\gamma\delta$ -tetrahydroxybutylquinoxaline, m.p. 188°, converted by H_2SO_4 at 100° into a substance $\text{C}_{12}\text{H}_8\text{O}_2\text{N}_2$, m.p. 159°, and a compound (I), m.p. 104°. (I) is



optically inactive, does not reduce Fehling's solution, rapidly decolorises KMnO_4 , yields a hydrochloride,

m.p. 184°, and does not react with Ac_2O , BzCl , or ketonic reagents. The constitution (I) is supported by its transformation by MgPhBr into the compound (II), m.p. 149° [hydrochloride, m.p. 130° after softening at 122°; picrate, m.p. 139° (decomp.); methiodide, m.p. about 96° (decomp.); Ac derivative, m.p. 176°]. Similarly (I) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ give the substance $\text{C}_{19}\text{H}_{16}\text{ON}_2$, m.p. 132° [picrate, m.p. 128° (decomp.); Ac derivative, m.p. 139°]. (II) gives a methiodide, m.p. 213° (decomp.) [corresponding perchlorate, m.p. 208° (decomp.), and picrate, m.p. 200°], oxidised by $\text{K}_3\text{FeC}_6\text{N}_6$ in alkaline solution to the compound (III), m.p. 181°, which is converted by MgPhBr into a substance, m.p. 264°, and a compound [picrate, m.p. 170° (decomp.)]. 3-Hydroxy-2-tetrahydroxybutylquinoxaline is transformed by dehydrating agents into a substance, m.p. 255°.

H. W.

Photochemical formation of 6:7-dimethylalloxazine from lactoflavin. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1936—1939).—The formation of 6:7-dimethylalloxazine by irradiation of lactoflavin in neutral or weakly acidic solution is established by treatment of the product with CH_2N_2 , whereby 1:3:6:7-tetramethylalloxazine, m.p. 250° (corr.), is produced.

H. W.

Synthetic compounds of the lactoflavin group. R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 1939—1941).—Halogeno-o-nitro-benzenes and -xylenes are condensed in presence of *tert.*-bases ($\text{C}_5\text{H}_5\text{N}$) with the amines $\text{NH}_2\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{OH}$ obtained by reduction of the oximes of *l*-arabinose and *d*-xylose, and the products are reduced (SnCl_2) in presence of a large excess of alloxan, whereby leucoflavins are produced which are oxidised by air to the flavins. These behave similarly to lactoflavin with respect to solubility, formation of lumilactoflavin by irradiation in alkaline solution, absorption spectrum, dependence of fluorescence on p_{H} , and formation of a red radical when reduced in mineral acid solution.

H. W.

Synthesis of tetrahydroharman derivatives under physiological conditions. I. G. HAHN and H. LUDEWIG (Ber., 1934, 67, [B], 2031—2035).—Tetrahydroharman is obtained in almost quant. yield from tryptamine (I) and MeCHO at 25° and p_{H} 5.2, 6.2, or 7.0. Similarly (I) and $\text{CH}_2\text{Ph}\cdot\text{CHO}$ afford 3-benzyl-3:4:5:6-tetrahydronorharman [hydrochloride (II), m.p. 278° (decomp.)]. (I) and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ afford tryptamine phenylacetate, m.p. 178° (decomp.), which passes at 180—190° into phenylacet-tryptamide (III), m.p. 144°. (III) with POCl_3 in boiling C_6H_6 gives 3-benzyl-5:6-dihydronorharman [picrate, m.p. 225° (decomp.)], from which (II) is obtained by reduction with Na and EtOH and addition of HCl.

H. W.

γ -Triazines. XXV. Property of o- and p-nitrophenyliminoketotriazidines (o- and p-nitrobenzylideneguanylcaramide) of giving platinum-octachloride besides the normal platinum-hexachloride. First two complexes of quadrivalent platinum with co-ordination number eight. A. OSTROGOVICH and V. BENA MEDIAN. XXVI. Dihydroxytriazinylformaldoxime and its salts. A. OSTROGOVICH and V. CRASU. XXVII. Syn-

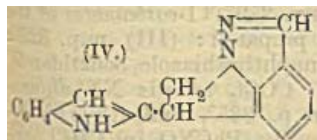
thesis of phenacetylbiuret and its transformation into dihydroxybenzyltriazine. A. OSTROGOVICH and I. TANISLAU (Gazzetta, 1934, 64, 792—800, 800—824, 824—832).—XXV. Iminoketo-*o*-nitrophenyltriazidine, $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}) \text{---} \text{NH} \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ (M), in *N*-HCl gives a normal *platinichloride*, $[\text{PtCl}_6](\text{H} \cdot \text{M})_2$, m.p. 249—250°, which in 2*N*-HCl gives the abnormal $[\text{PtCl}_6](\text{H} \cdot \text{M})_4$, new m.p. 229—230° (cf. A., 1929, 827). The *p*-isomeride similarly gives the normal, new m.p. 244—245° (cf. *loc. cit.*), and the abnormal *platinichloride*. Λ_v of the compounds is determined.

XXVI. N_2O_3 converts dihydroxymethyltriazine into dihydroxytriazinylformaldoxime,

$\text{N} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{---} \text{NH} \end{array} \text{C} \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$ (I) [*H* sulphate, hydrochloride; Na (+ H_2O), Na_2 (+ $2\text{H}_2\text{O}$), Na_3 (+ H_2O), K (+ H_2O), NH_4 , and Ag (+ H_2O) salts; Ba salt, $(\text{C}_4\text{H}_3\text{O}_3\text{N}_4)_2\text{Ba}$ (+ $2\text{H}_2\text{O}$ or + $3\text{H}_2\text{O}$) (II); Fe salt, $(\text{C}_4\text{H}_3\text{O}_3\text{N}_4)_2\text{Fe}$ (+ $2\text{H}_2\text{O}$); Cu salts, $\text{C}_4\text{H}_3\text{O}_3\text{N}_4\text{Cu}$ (+ H_2O), and $(\text{C}_4\text{H}_3\text{O}_3\text{N}_4)_2\text{Cu}_2$ (+ $4\text{H}_2\text{O}$)]. Crystallographic data for (I) and (II) are determined.

XXVII. $\text{CH}_2\text{Ph} \cdot \text{COCl}$ and biuret give phenylacetylbiuret, m.p. 199—200° (decomp.), converted by KOH into dihydroxybenzyltriazine, m.p. 251—252° (decomp.) [hydrochloride, m.p. 258—259° (decomp.); Na, m.p. 236—237°, Ag, m.p. 264—265°, and Ba, m.p. 254—256°, salts (all decomp.)]. E. W. W.

Constitution of dimeric indoles. O. SCHMITZ-DUMONT (Annalen, 1934, 514, 267—279).—Nitrosodi-3- (I) and -7- (II) -methylindoles are shown to be *N*- and not *C*-NO-derivatives by the methods of Lehmann (A., 1927, 1062) and Clauser (A., 1903, ii, 180), and by the formation of NO (with small amounts of N_2O and/or N_2) when (I) and (II) are warmed with AcOH. (I) is reduced (Zn dust, EtOH-conc. HCl) to di-3-methylindole (III) [Ac derivative, m.p. 178—179°, readily hydrolysed (aq. EtOH-KOH) (cf. Oddo, A., 1934, 419) to (III), thus indicating the presence of *N*- and not *C*-Ac]. (II) is converted by EtOH-KOH or -NaOEt in N_2 into a compound, $\text{C}_{18}\text{H}_{15}\text{N}_3$ [probably (IV)], m.p. 200°; with EtOH-NaOEt in air, a compound, m.p. 237—238°, results. The formation of oximino-2:3-di-7-methylindole (A., 1933,



958) is not observed in any experiment. Nitrosodiindole and EtOH-KOH or -NaOEt in N_2 give a compound analogous to (IV) and a substance, m.p. 227—230° (decomp.). Indole and 3- but not 2-methylindole are polymerised [to tri-indole and (III), respectively] when solutions in aq. EtOH-HCl are kept at 30°. The above results support the constitution previously assigned (A., 1933, 958) to di-indole, but not that of Oddo (*loc. cit.*). H. B.

Acetylation and ethylation of 1:9-dimethylspirodihydantoin and related experiments. H. BILTZ and L. LOEWE (J. pr. Chem., 1934, [ii], 141, 245).—1:9-Dimethylspirodihydantoin (I) (simplified prep.; cf. A., 1917, i, 290) and boiling Ac_2O give the 3-Ac, m.p. 176°, and then the 3:7-Ac₂, m.p.

136°, derivatives; 1:3:9-trimethylspirodihydantoin similarly affords the 7-Ac derivative, m.p. 110—120° (decomp.) (all m.p. except this are corr.), whilst 3:7-dimethylspirodihydantoin (II) gives only a Ac₂ derivative, m.p. 178° (cf. A., 1926, 962). (I) is ethylated (CHMeN_2) to the 3:7-Et₂ derivative, m.p. 123°, whilst spirodihydantoin similarly gives a Et₄ derivative, b.p. 120—140°/0.02 mm.; cryst. products could not be obtained from (II) and 1-acetyl-3-methyl- and 3-methylspirodihydantoin. 3:7-Dimethylcaffolide (isoapocaffeine) similarly affords the 1-Et derivative m.p. 110°. H. B.

Action of acetic anhydride on uric acid glycols and their ethers. II. 9-Methyluric acid [glycol]. III. 3:9-Dimethyluric acid [glycol]. H. BILTZ and L. LOEWE (J. pr. Chem., 1934, [ii], 141, 246—267, 268—283; cf. this vol., 96).—II. 9-Methyluric acid glycol is converted by short treatment with boiling Ac_2O into 1-acetyl-3-methylspirodihydantoin (I), decomp. 195°, and a trace of 1-acetyl-3-methylallantoin (II), m.p. 255° (decomp.) (all m.p. are corr. unless stated otherwise). (I) is acetylated further to the 1:9-Ac₂ derivative (III), m.p. 170°, and is methylated ($\text{Et}_2\text{O} \cdot \text{MeOH} \cdot \text{CH}_2\text{N}_2$) to tetramethylspirodihydantoin (IV). (I) and pure CH_2N_2 (cf. A., 1931, 853) give 9-acetyl-1:3:7-trimethylspirodihydantoin, m.p. 185—186°. (II), obtained also from (I) and H_2O at 60—100°, is hydrolysed (conc. HCl) to, and prepared by acetylation of, 3-methylallantoin (V). (II) is reduced (HI) to 3-methylhydantoin. (I) is converted by boiling MeOH into Me 1-acetyl-3-methylallantoin-5-carboxylate (VI), m.p. 223—225° (decomp.), hydrolysed (conc. HCl or MeOH-HCl) to (V) and a little (VIII) (below); (I) is unaffected by boiling EtOH. (III) is hydrolysed (piperidine in Et_2O) to a little (I) and is ethylated (CHMeN_2) to a mixture of 3-methyltriethyl-, m.p. 110—115°, and 1:9-diacetyl-3-methyl-7-ethyl-, m.p. 105—110°, spirodihydantoin. Impure 3-methyl-7-ethylspirodihydantoin has m.p. 115° (uncorr.). (I) is converted by EtOH- NH_3 , dil. aq. NH_3 , or aq. NH_4HCO_3 into 1-acetyl-3-methylallantoin-5-carboxylamide (VII) (+ H_2O), m.p. 220° (decomp.), m.p. (anhyd.) 240—245° (decomp.), also prepared from (VI) and dil. aq. NH_3 ; (III) similarly gives 1:6-diacetyl-3-methylallantoincarboxylamide, m.p. 245°. The Ac group in (VI) and (VII) is removed only with difficulty; hydrolysis (aq. HCl) of (VII) affords (V) and (VIII). (III) is hydrolysed (conc. HCl at 100° or conc. aq. NH_3 at room temp.) to 3-methylspirodihydantoin (VIII) (+ $0.5\text{H}_2\text{O}$), m.p. 155° (loss of H_2O), re-solidifying with m.p. 180—190°, m.p. (anhyd.) 210° (decomp.) (sinters at 200°), which is acetylated to (III), methylated (CH_2N_2) to (IV), and converted by aq. basic Pb acetate at 100° into (V). The Ag salt, m.p. about 265° (decomp.; uncorr.), of (VIII) and MeI give 3:7-dimethylspirodihydantoin (IX), m.p. 297° (cf. A., 1917, i, 290), also methylated to (IV). 1:7-Dimethyl- and 1:3:9-trimethylspirodihydantoin and (VIII) titrate as monobasic acids; spirodihydantoin and its 1:9-Me₂ and 1:9-Ac₂ derivatives act as dibasic acids, whilst its 1:3:7-Me₃ derivative and (IX) have practically no acidic properties.

III. 3 : 9-Dimethyluric acid glycol Me₂ ether (4 : 5-dimethoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid) is acetylated (boiling Ac₂O) slowly to the 7-Ac derivative, m.p. 223°, whilst the 5-Me₁ ether gives 4-acetoxy-5-methoxy-, m.p. 187—189°, and 4-acetoxy-5-methoxy-7-acetyl-, m.p. 145—148°, -3 : 9-dimethyl-4 : 5-dihydrouric acid and 5-methoxy-1 : 7-diacetyl-3-methylhydantamide (I), $\begin{matrix} \text{CO-NHAc} \\ \text{NMe-CO} \end{matrix} > \text{C(OMe)·CO·NHAc}$, m.p. 170—173°, according to the time of reaction. (I) is hydrolysed by EtOH-NH₃ to 5-methoxy-3-methylhydantamide (A., 1921, i, 614), and is accompanied by a little 5-methoxy-7-acetyl-3-methylhydantamide (?), m.p. 212° (sinters at 205°). 3 : 9-Dimethyluric acid glycol [4 : 5-Ac₂ derivative, m.p. 158—160° (decomp.), prepared using cold Ac₂O-conc. H₂SO₄] and boiling Ac₂O give 3 : 9-diacetyl-1 : 7-dimethylspirodihydantoin (II), m.p. 137°, hydrolysed (EtOH-NH₃) to, and prepared also by acetylation of, 1 : 7-dimethylspirodihydantoin (III) (modified prep.; cf. loc. cit.). (II) is hydrolysed (boiling H₂O) to the 9-Ac derivative, m.p. 232—234° (decomp.), and a mixture of 6-acetyl- (IV), m.p. 197—200° (decomp.), and 3 : 6-diacetyl- (V), m.p. 180—185° (decomp.), -1 : 8-dimethylallantoin; the amounts of (IV) and (V) [hydrolysed (EtOH-NH₃) to (IV)] are diminished when hydrolysis is effected with 50% AcOH. (IV) and basic Pb acetate give 1 : 8-dimethylallantoin [also prepared similarly (cf. A., 1921, i, 893) from (III)], which is reduced (HI) to 1-methylhydantoin. The spirodihydantoin ring system is very stable towards acids, but is readily converted into an allantoin by alkali. H. B.

Syntheses of drugs. VIII. [Use of] complex compounds in the synthesis of drugs. I. Calcium theobromide-calcium nitrite. H. P. KAUFMANN [with KUCHLER] (Arch. Pharm., 1935, 273, 22—31).—The salt, Ca⁺⁺[T₂Ca(H₂O)₂(NO₂)₂]⁺⁺ (T=theobromine), is prepared and its homogeneity demonstrated. The absorbability of drugs is changed by administration as complex compounds. R. S. C.

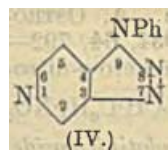
Compound of theophylline and di(hydroxyethyl)amine.—See B., 1935, 46.

Graebe-Ullmann carbazole synthesis and its application to N-substituted pyridinotriazoles. O. BREMER (Annalen, 1934, 514, 279—291).—4-Bromo-4'-nitro-2'-aminodiphenylamine and NaNO₂ in EtOH-HCl give 5-nitro-, m.p. 222°, reduced (SnCl₂, AcOH-HCl) to 5-amino-, m.p. 171°, -1-p-bromophenyl-1 : 2 : 3-benzotriazole. 4'-Nitro-2'-amino-4-methoxydiphenylamine, m.p. 144—145° [prepared (cf. Gallas and Alonso, A., 1930, 1571) by reduction (EtOH-NaHS) of the 2' : 4'-(NO₂)₂-derivative], similarly affords 5-nitro-, m.p. 244—245°, and 5-amino-, m.p. 157°, -1-anisyl-1 : 2 : 3-benzotriazole. -5-Nitro-, m.p. 171°, and 5-amino- (I), m.p. 117°, -1-p-tolyl-1 : 2 : 3-benzotriazole are prepared. (I) heated in paraffin oil at 320—350° gives a good yield of 3-amino-6-methylcarbazole, m.p. 252°; 5 : 4'-diamino-1-phenyl-1 : 2 : 3-benzotriazole similarly affords a trace of 3 : 6-diaminocarbazole, whilst the other NH₂-triazoles undergo decomp. 4-Chloro-3-nitropyrindine (II) (Koenigs and Freter, A., 1924, i, 990) and NH₂Ph at 130° give 3-nitro-4-anilinopyridine (III), m.p. 118°, reduced (Na₂S₂O₄ in aq. COMe₂) to the 3-NH₂-

derivative, m.p. 170°, converted by HNO₂ into 9-phenyl-3 : 4-pyridino-7 : 8 : 9-triazole (IV), m.p. 110°. The product obtained from (III) and SnCl₂-conc. HCl gives, with HNO₂, (IV) and its 6-Cl-derivative, m.p. 164—165°. (IV) and HNO₂ (d 1.4) in conc. H₂SO₄ at 50° afford the 4'-NO₂-, m.p. 222—223°, reduced (SnCl₂, conc. HCl) to the 4'-NH₂-derivative (V), m.p. 206—207°. The Ac derivative, m.p. 235—236°, of 3-nitro-4-p-aminoanilinopyridine, m.p. 163° [from (II) and p-C₆H₄(NH₂)₂ in EtOH-KOAc], is reduced (aq. EtOH-Na₂S₂O₄) to 3-amino-4-p-acetamidoanilinopyridine, m.p. 159°, converted (HNO₂) into 9-p-acetamidophenyl-3 : 4-pyridino-7 : 8 : 9-triazole, m.p. > 295°, which is hydrolysed (EtOH-conc. HCl) to (V). 3-Nitro-4-2'-pyridylaminopyridine, m.p. 131—132° [from (II) and 2-aminopyridine], is reduced (aq. Na₂S₂O₄) to the 3-NH₂-derivative, m.p. 148—149°, convertible into 9-2'-pyridyl-3 : 4-pyridino-7 : 8 : 9-triazole, m.p. 194°. 3-Nitro-4-(6'-methoxy-8'-quinolyl-amino)pyridine, m.p. 203° [from (II) and 8-amino-6-methoxyquinoline], which, like (III), does not give a N-NO-derivative, is reduced (Na₂S₂O₄, aq. COMe₂) to the 3-NH₂-derivative, m.p. 163—164° (darkening) (p-dimethylaminobenzylidene derivative, m.p. 234—235°). (IV) heated in paraffin oil at 320—350° affords 5-carboline, m.p. 231—232° (picrate, m.p. 250°) (Robinson and Thornley, A., 1924, i, 1349), in nearly quant. yield; the other pyridinotriazoles undergo resinification. H. B.

Syntheses of drugs. IX. Benzthiazolecarbamides. H. P. KAUFMANN [with P. SCHULTZ and (in part) WURL] (Arch. Pharm., 1935, 273, 31—52).—p-NH₂·C₆H₄·NHAc and (SCN)₂ (from NH₄SCN and Br) in AcOH give 1-amino-5-acetamidobenzthiazole (I), m.p. 239°, hydrolysed (dil. H₂SO₄) to the 1 : 5-(NH₂)₂-compound (II), m.p. 207°, which (diazo-reactions) affords 5-chloro-1-aminobenzthiazole (III), m.p. 198°, and 5-p-aminobenzeneazo-1-aminobenzthiazole, m.p. 245° [reduced by Sn-HCl to (II)]. 1-Amino-5-ethoxybenzthiazole (IV) and HCNO in CHCl₃ give the 1-carbamate, m.p. 289°; 1-carbamates of the following are similarly prepared : (III), m.p. 325°; (II), m.p. about 315°; α-naphthathiazole, benzthiazole, and (I), m.p. > 300°. COCl₂ affords NN'-di(benzthiazolyl-1)-carbamide, m.p. 325°, and its 5 : 5-Cl₂-derivative, m.p. 241°. By PhCNO in CHCl₃ are obtained N-phenyl-N'-benzthiazolyl-, sublimes > 200°. -5-ethoxy-, m.p. about 243°, -5-chloro-, m.p. > 325°, and -6-nitro-benzthiazolyl-1-carbamide, m.p. > 300°. and -α-naphthathiazolyl-1-carbamide, m.p. > 325°. Allyl thiocyanate yields N-5-ethoxybenzthiazolyl-1-N'-allyl-carbamide, m.p. 185°. PhCNS gives N-phenyl-N'-benzthiazolyl-1-thiocarbamide, m.p. 207°, and its 5-Cl-derivative, m.p. 174°. The carbamides have very slight anaesthetic action, but (IV) is intermediate between cocaine and novocaine. R. S. C.

Cactus alkaloids. XII. Constitution of anhalamine. E. SPATH and F. BECKE (Ber., 1934, 67, [B], 2100—2102).—Anhalamine (I) is treated with EtI and NaOEt and the product is acted on successively with Ag₂O and KMnO₄, whereby 4 : 5-dimethoxy-3-ethoxy-o-phthalic anhydride, m.p. 106—



107° after softening, is produced. (I) is therefore 8-hydroxy-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline. H. W.

Alkaloids of *Anabasis aphylla*. XI. Hofmann degradation of aphyllidine. A. OREKHOV and S. NORKINA [with T. MAXIMOVA] (Ber., 1934, 67, [B], 1974—1979; cf. A., 1932, 405).—Aphyllidine (I) is transformed by MeI in MeOH into the methiodide, m.p. 223—225°, $[\alpha]_D^{25} + 9.8^\circ$ in H₂O, converted by boiling KOH-MeOH into de-*N*-methylaphyllidine (II), m.p. 120—121°, $[\alpha]_D^{25} - 18.1^\circ$ in MeOH, the methiodide, m.p. 224—225°, of which passes when treated with KOH-MeOH into a mixture of bases (III), b.p. 230—238°/5 mm. Dissolution of (III) in HCl and treatment with NaClO₄ gives the sparingly sol. perchlorate, m.p. 180—182°, of the optically inactive de-*N*-dimethylaphyllidine (IV), b.p. 240—242°/5 mm. The corresponding methiodide, m.p. 121—122°, passes when treated with AgOH and then distilled into NMe₃ and hemiaphyllidene. Although a double linking has been shown to occur in (I), catalytic hydrogenation (PtO₂) of (II) leads only to dihydrode-*N*-methylaphyllidine, m.p. 118—120°, the methiodide, m.p. 234—235° (decomp.), of which is degraded to an oil of indefinite b.p., from which dihydrode-*N*-dimethylaphyllidine, b.p. 218—220°/5 mm., is obtained through the perchlorate, m.p. 209—210° [methiodide (V), m.p. 194—195°]; it is not hydrogenated (PtO₂) at 15—20°. It can also be obtained by hydrogenation (PtO₂) of (IV). Treatment of (V) with AgOH and subsequent distillation yields NMe₃ and dihydrohemiaphyllidine, b.p. 206—207°/8 mm., hydrogenated to hexahydrohemiaphyllidine, b.p. 206—207°/8 mm. (I) and CNBr in anhyd. C₆H₆ afford the compound C₁₆H₂₂ON₂Br, m.p. 116—117°, readily transformed (Zn dust-AcOH or H₂-Pd-CaCO₃) into the corresponding cyanoamide, hydrolysed with difficulty by 70% H₂SO₄ at 165—170° to a substance, m.p. 260—265°. H. W.

Composition of amorphous quinine iodobismuthates. G. VITA and L. BRACALONI (J. Pharm. Chim., 1934, [viii], 20, 512—516; cf. B., 1932, 622).—The composition of quinine iodobismuthate prepared by the method of François and Seguin (A., 1925, i, 1084) varies with the ratio Bi/quinine in the reactants. The products corresponding with ratios 2.05 and 0.78 have the following % compositions: Bi, 25.8 and 21.01; quinine, 14.12 and 22.42; I, 57.4 and 56.2; H₂O, 0.19 and 1.30, respectively. A. E. O.

Modified cinchona alkaloids. I. apoQuinine and apoquinidine. T. A. HENRY and W. SOLOMON (J.C.S., 1934, 1923—1929).—Quinine is demethylated by AlCl₃ (cf. Oberlin, A., 1927, 681) to crude "apo-quinine," m.p. 175° $[\alpha]_D^{25} - 177^\circ$ in MeOH, which is an equimol. mixture of C₁₉H₂₂O₂N₂ and C₁₉H₂₂O₂N₂Cl, preserved in a dihydrochloride, m.p. 225°, $[\alpha]_D^{25} + 204.1^\circ$ in H₂O, and a zincchloride, m.p. 242°. From the mixture by crystallisation from MeOH-chlorodihydroapoquinine (*H* sulphate, m.p. 205°, $[\alpha]_D^{25} - 206.7^\circ$ in H₂O) is obtained, and by crystallisation of the dianisoyl-*d*-tartrate, impure apo-quinine acid dianisoyltartrate may be prepared. Pure quinine and 60% H₂SO₄ yield apoquinine, froths at 84°, $[\alpha]_D^{25} - 281^\circ$ in 0.1*N*-H₂SO₄, or -214.8° in EtOH, isolated as the hydrochloride, m.p. 265° $[\alpha]_D^{25} - 154.5^\circ$

in H₂O (cf. Jarzynski *et al.*, A., 1933, 1312), and a second component, possibly a stereoisomeride. The salts of apoquinine are dihydrochloride, m.p. 261°, $[\alpha]_D^{25} - 224.4^\circ$ in H₂O, hydrobromide, m.p. 284°, dihydrobromide, m.p. 255°, $[\alpha]_D^{25} - 180.9^\circ$ in H₂O, *H* sulphate, soft platelets, sinters 90° or 170—190°, and hard plates, m.p. 203—208°, $[\alpha]_D^{25} - 193.6^\circ$ in H₂O, and acid dianisoyl-*d*-tartrate, m.p. 235.5°. apoQuinine Me ether, m.p. 183—185° (no decomp.), $[\alpha]_D^{25} - 201.2^\circ$ in EtOH, forms a hydrochloride, m.p. 249—251°, $[\alpha]_D^{25} - 196^\circ$ in H₂O, and the Et ether, m.p. 195—197° (no decomp.), $[\alpha]_D^{25} - 199.7^\circ$ in EtOH, gives a hydrochloride, m.p. 247—250°, $[\alpha]_D^{25} - 191.7^\circ$ in H₂O.

Quinidine (99.5% pure) and 60% H₂SO₄ form dextrorotatory apoquinidine (70%) and isoapoquinidine, m.p. 245° (no decomp.), $[\alpha]_D^{25} + 25.6^\circ$ in 0.1*N*-H₂SO₄ or -12.6° in EtOH (hydrochloride, m.p. 255°, $[\alpha]_D^{25} - 40.2^\circ$ in H₂O; dihydrobromide, m.p. 280° $[\alpha]_D^{25} + 18.6^\circ$ in H₂O; and *H* sulphate, decomp. 235—240°, $[\alpha]_D^{25} + 17.6^\circ$ in H₂O), and not cupreidine as stated by Ludwiczakowna (A., 1933, 1312). M.p. are also decomp. points except where stated. F. R. S.

Eserine. III. Synthesis of *d*- and *l*-eserethole methiodide. T. HOSHINO and T. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1934, 10, 564—567; cf. A., 1934, 667).—The substance, m.p. 79—80° [picrate, m.p. 150—151° (lit., 139—140°, 140—141°)], previously called *dl*-eserethole (A., 1934, 1236, 667), is C₁₆H₂₄ON₂ (macro-analyses are faulty), *dl*-methyleserethole. The following corrected data are given: *H* *d*-tartrates of *l*-, m.p. 166—167°, $[\alpha]_D^{25} - 73.9^\circ$, and *d*-dinoreserethole, m.p. 164—165°, $[\alpha]_D^{25} + 235.1^\circ$, and of *l*- (I), m.p. 190—191°, $[\alpha]_D^{25} - 53.3^\circ$, and *d*-noreserethole (II), m.p. 188—189°, $[\alpha]_D^{25} + 202.1^\circ$. (I) and (II) with MeI in cold Et₂O give *l*- (III) and *d*-eserethole (IV) methiodide, m.p. 168—169°, respectively (mixed m.p. about 155°). The methopicates of (III) and (IV) have m.p. 189° (mixed m.p. about 173°), the corresponding *dl*-derivative (V) having m.p. 190—191°. The picrate, m.p. 184—185° (*loc. cit.* and *ibid.*, 89), is *dl*-noreserethole picrate, the other product, m.p. 192—193°, being (V). The criticisms of Robinson *et al.* (*loc. cit.*) are refuted. R. S. C.

Organic arsenic compounds. XVII. Polymeric phenylarsenoxide and reactions of *m*-phenylenediarsinic acid. W. STEINKOPF, S. SCHMIDT, and H. PENZ (J. pr. Chem., 1934, [ii], 141, 301—305).—Reduction (SO₂) of PhAsO₃H₂ in dil. H₂SO₄ gives PhAsO, m.p. 142—145° (lit. 119—120° to 145—147°), and (probably) the dimeride,

AsPh<O>AsPh, m.p. 210—220° (converted by conc.

HCl into PhAsCl₂). *m*-C₆H₄(AsO₃H₂)₂ is converted (usual method) into *m*-phenylenedi(dichloroarsine), m.p. 43.5° (previous sintering), which with MgMeBr gives *m*-phenylenedi(dimethylarsine), b.p. 140—141°/12 mm. This and CNBr in Et₂O afford *m*-phenylenedi(dimethylarsine hydroxybromide), *m*-C₆H₄(AsMe₂Br·OH)₂, m.p. 161—162°. H. B.

Arsenical derivatives of organic sulphides. S. M. SCHERLIN and A. J. JAKUBOVITSCH and (in part) L. EXEMPLARSKY (Bull. Soc. chim., 1934, [v], 1, 1367—1373).—AsCl₃ reacts with diazotised *p*-NH₂·C₆H₄·SEt to give *p*-ethylthiolphenylarsinic acid (I), not melting

at 200°, reduced by $\text{SO}_2\text{-HCl}$ to *p*-ethylthiolphenyldichloroarsine, m.p. 39.5–40°, re-oxidised by $\text{CCl}_3\cdot\text{NO}_2$ in EtOH-NaOH to (I). Oxidation of (I) with warm 30% H_2O_2 , or with $\text{KMnO}_4\text{-AcOH}$, affords *p*-ethylsulphonylphenylarsinic acid, not melting at 280°, converted by SO_2 -reduction into the corresponding dichloroarsine, m.p. 116–118.5°. With aq. H_3PO_2 the Na salt of (I) affords pp'-diethylthiolarsenobenzene. Similar diazotisation of *p*- $\text{NH}_2\text{-C}_6\text{H}_4\text{-SCN}$ in presence of AsCl_3 in $\text{MeOH-H}_2\text{SO}_4$ gives a 50% yield of *p*-thiocyanophenylarsinic acid, reduced by $\text{SO}_2\text{-HCl}$ to *p*-thiocyanophenyldichloroarsine, b.p. 193–195°/7–8 mm., m.p. 55–56°; and with AsPhCl_2 in place of AsCl_3 , phenyl-*p*-thiocyanophenylarsinic acid, m.p. 138–139° (decomp.), is obtained, but reduction of this affords only AsPhCl . (oxidised to PhAsO_2H).

J. W. B.

Furan arsenicals. H. GILMAN and W. H. KIRKPATRICK (Proc. Iowa Acad. Sci., 1932, 39, 176).—Furan arsenicals may be prepared from furan mercurials and AsCl_3 , and from furan Grignard reagents and As halides.

CH. ABS. (r)

Methyl ester of phenylphosphorous acid. A. E. ARBUZOV (J. Gen. Chem. Russ., 1934, 4, 898–900).— PPhCl_2 and NaOMe yield a mixture of PPh(OMe)_2 , b.p. 101–102°/15 mm. (CuBr salt, m.p. 139.5–140°), and PPhMe-OMe , b.p. 139–140°/15 mm. R. T.

Diphenyl- and di-*o*-tolyl-guanidinium polyselenides. R. L. McCLEARY and W. C. FERNELIUS (J. Amer. Chem. Soc., 1934, 56, 2499).—Treatment of the solution from diphenylguanidine and H_2Se in air-free EtOH with Se (excess) gives di(diphenylguanidinium) tetraselenide, $\text{C}_{26}\text{H}_{28}\text{N}_6\text{Se}_4$, decomp. 152–156°; di(di-*o*-tolylguanidinium) tetraselenide, $\text{C}_{30}\text{H}_{36}\text{N}_6\text{Se}_4$, decomp. 170–174°, is similarly prepared. These are readily decomposed by dil. acids to H_2Se and amorphous black Se.

H. B.

Lecithins of egg-yolk. Y. YOKOYAMA (Proc. Imp. Acad. Tokyo, 1934, 10, 582–585).—The prep. of α - (I) and β -lecithin (II) from egg-yolk is described. (I) yields oleic (III) (72), clupanodonic (2), and isopalmitic (IV) (m.p. 57–57.5°; 26%) acids. (II) gives (III) and (IV) only. With Br (I) affords the diisopalmite, cryst., dioleate tetrabromide (3HgCl_2 -derivative, cryst.), and oleate clupanodonate dodecaboromide, m.p. 180° (decomp.). (II) gives similarly the oleate isopalmite dibromide (3HgCl_2 -derivative, cryst.) and dioleate tetrabromide, m.p. about 2°. Photomicrographs are given.

R. S. C.

Kephalin of egg-yolk. U. NISHIMOTO (Proc. Imp. Acad. Tokyo, 1934, 10, 578–585).—Details are given for the purification of kephalins from egg-yolk and the prep. therefrom of palmitodibromostearo- ($3\text{X} : 2\text{HgCl}_2$ -derivative, m.p. 138–139°) and -octabromoarachido- α -kephalin, m.p. 173–175°, hygroscopic, and palmitodibromostearo- ($3\text{X} : 2\text{HgCl}_2$ -derivative, m.p. 132–133°), palmito-octabromoarachido-, m.p. 174–176.5°, and diocetabromoarachido- β -kephalin, m.p. 191–193°. Photomicrographs are given.

R. S. C.

Hydrolysis of blood-albumin.—See this vol., 230.

Determination of copper in organic compounds.—See this vol., 186.

Colorimetric test for compounds containing CH , CH_2 , or CH_3 contiguous to negative groups. M. GOSWAMI, A. SHAHA, and B. MUKERJEE (J. Indian Chem. Soc., 1934, 11, 773–775).—28 compounds containing CH , CH_2 , or CH_3 adjacent to a negative group (usually CO) give red or brown colours with slightly alkaline, alcoholic picric acid. CH_2O , PhCHO , etc. give no colour. Bitto's reagents give similar colours.

R. S. C.

Cyanide-formaldehyde reaction, and new volumetric analytical applications.—See this vol., 183.

Detection of diazonium salts and of primary amines with resorufin. H. EICHLER (Z. anal. Chem., 1934, 99, 348–350).—Slightly acid solutions of diazonium salts give with the brightly fluorescent resorufin (I) brown insol. products not fluorescing when made alkaline. Aromatic NH_2 groups may be detected by diazotising and then testing the solutions with (I). Free HNO_2 in diazo-solutions may be detected with Magdala-red (cf. A., 1934, 269). Fluorescein behaves like (I), but with certain diazonium salts only.

J. S. A.

Micro-determination of carbonyl groups. F. VON FALKENHAUSEN (Z. anal. Chem., 1934, 99, 241–257).—5–15 mg. of substance are allowed to react quantitatively at 100° with a weighed excess of $\text{NHPh-NH}_2\cdot\text{HCl}$ in 67% aq. $\text{C}_2\text{H}_5\text{N}$; excess of NHPh-NH_2 (I) is then decomposed by mixing with Fehling's solution + C_6H_6 at 100°, and the vol. of N_2 so evolved is measured in a micro-gas burette. An empirical correction for spontaneous decomp. of (I) must be introduced. The method fails with certain ketones.

J. S. A.

Sensitive and specific reaction for ergosterol. J. BRUCKNER (Biochem. Z., 1934, 274, 465).—An addendum (A., 1934, 910). This reaction is obtained only when "acetone puriss. Merck," and not when "acetone pro analysi Merck" is used, and must depend on the presence of some impurity in the former solvent.

P. W. C.

Acidimetric method for determining salicylic acid and its salts. C. N. THOMAS (Praktika, 1933, 8, 281–286; Chem. Zentr., 1934, ii, 811).—The free acid is extracted from acidified solutions of salts with Et_2O , and after removal of solvent is dissolved in H_2O and titrated with NaOH , using thymol-blue, until the pure yellow colour changes to bright green.

A. G. P.

Exact analysis and characterisation of saponins. F. ÜLZER and W. HAAS (Pharmaz. Mh., 1934, 15, 95–97; Chem. Zentr., 1934, ii, 1171).—Saponins may be characterised by the reducing power of the sugar obtained on hydrolysis with HCl . Other useful characteristics are the OH content, sap. val., and acidity.

H. N. R.

Oxidation of rotenone by copper in an alkaline medium. R. M. WHITTAKER and I. GLICKMAN (Rec. trav. chim., 1934, 53, 1145–1150).—Application of the method used by Gnadinger *et al.* (B., 1929, 996) for pyrethrin to determine small amounts (0.01–0.02 g.) of rotenone (I) (x mg.) in 95% EtOH [free from other reducing substances (II), CHCl_3 , or CCl_4]

is described. The (I) solution is treated as in a modified Folin's determination (A., 1926, 648) for glucose (III), and the solution compared colorimetrically with a similarly treated standard (III) solution (y mg.); then $y = 0.6195 - 0.006858x + 0.008371x^2$. The accuracy is 0.2%. Owing to the presence of (II) the method is not applicable to the determination of the (I) content of derris root. J. W. B.

Argentometric determination of 2-thiolbenzthiazole. M. I. USCHAKOV and A. S. GALANOV (Z. anal. Chem., 1934, 99, 185—195).—The 2-thiolbenzthiazole (I) is dissolved in aq. NH_3 , and excess of AgNO_3 added. Aq. NH_3 is added to dissolve other Ag salts, and the Ag salt of (I) then filtered off, dried at room temp., and weighed. Volumetrically, an excess of 0.1N- AgNO_3 is added to (I) in EtOH-NH_3 solution, followed by an equal vol. of Et_2O .

Excess of AgNO_3 is titrated back with NH_4CNS . Alternatively, (I) may be titrated directly with AgNO_3 , using dichlorofluorescein as adsorption indicator. J. S. A.

Detection of scopolamine and atropine in the presence of phenol. O. FREY (Wiss. Mitt. österr. Heilmittelstelle, 1934, 12, 3—4; Chem. Zentr., 1934, ii, 1500).—The alkaloids are first extracted with Et_2O from alkaline solution. H. N. R.

Electrometric titration of lecithin and cephalin.—See this vol., 170.

Electrometric titration of zein and iodozein.—See this vol., 170.

Titration constants of some amides and dipeptides in relation to alcohol and formaldehyde titrations of amino-nitrogen.—See this vol., 170.

Biochemistry.

Carbon dioxide balance between maternal and foetal bloods in goats. A. B. KEYS (J. Physiol., 1934, 80, 491—501).—Foetal blood has a greater CO_2 capacity, alkali reserve, and CO_2 content, but is less acid than maternal blood.

CH. ABS. (p)

Solubility of oxygen in red blood-corpuscles. E. F. YANG (Chinese J. Physiol., 1934, 8, 365—382).—The solubility of O_2 in blood-cells, after conversion of haemoglobin into cyanohaemoglobin (I) by NO_2' and CN' , follows Henry's law and is not affected by the p_{H} . The coeff. of O_2 absorption for horse-, sheep-, dog-, and cow-cells are 0.0228, 0.0259, 0.0272, and 0.0298, respectively. Since the val. for (I) solution is only slightly < that of H_2O , the high coeff. for the cells must be due to the presence of lipins. H. G. R.

Solubility of nitrogen in corpuscles. E. F. YANG (Chinese J. Physiol., 1934, 8, 383—397).—The coeff. of the absorption of N_2 for the cells of horse, dog, and sheep are 0.0100, 0.0151, and 0.0120, respectively. Some dialysable substance in blood (I) gives a high and variable val. for the coeff. in whole (I) and in serum. H. G. R.

Haemoglobin and blood-cell relations as determined by iron and oxygen capacity methods. O. BROWN and A. P. BRIGGS (J. Lab. Clin. Med., 1934, 19, 886—892).—Average vals. for men and women, are, respectively, haemoglobin 16.6, 14.0 g. per 100 c.c.; cell vol. 46.57, 40.3%. CH. ABS.

Osmotic behaviour of red cells. I, II. E. PONDER (Cold Spring Harbor Symp. Quant. Biol., 1933, 1, 170—177, 178—183).—I. The erythrocyte is unchanged in an isotonic solution of NaCl , or glucose. In a hypertonic solution they shrink and in a hypotonic solution they swell <, cal

II. Erythrocytes from different animals have different crit. vols. Human or rabbit cells are more resistant to distension than ox or sheep cells. The cell membrane is regarded as a fluid or semi-fluid permeability of which is governed by a few layers of mols. CH. ABS.

Osmotic properties of the erythrocyte. V. Rate of haemolysis in hypotonic solutions of electrolytes. M. H. JACOBS and A. K. PARPART (Biol. Bull., 1932, 63, 224—234).—Within certain limits the rate of haemolysis (I) of ox-blood and the concn. of the solution are related by simple osmotic laws. The permeability const. for H_2O in these limits is $\frac{1}{2}$ — $\frac{1}{3}$ of that for non-electrolytes. Retardation of (I) by dil. solutions of electrolytes increases rapidly with the valency of the cations present.

CH. ABS. (p)

Osmotic pressure and mol. wt. of the haemoerythrin of Sipunculus. A. ROCHE and J. ROCHE (Compt. rend., 1934, 199, 1678—1680).—Determination of the mol. wt. of the haemoerythrin by the method of Adair (A., 1925, ii, 965) ($M = 10RT/\pi_0$; π_0 = val. of the osmotic pressure/concn. extrapolated to infinite dilution) is approx. 66,000, i.e., of the same order as that of the haemoglobins. Dialysis of the cryst. pigment at 0° increases the mol. wt., probably due to aggregation. J. W. B.

Prosthetic group of Limulus haemocyanin. J. B. CONANT, F. DERSCH, and W. E. MYDANS (J. Biol. Chem., 1934, 107, 755—766).—The prosthetic group (I) formed by decomp. of the haemocyanin by alkali, followed by purification by dissolution in AcOH , is a black substance containing 14% Cu and 6% S. (I) with aq. NH_3 yields a Cu-free, colourless, amorphous polypeptide (II) from which tyrosine and *l*-leucine were isolated. (II) is probably composed of 3 mols. of serine + 1 each of leucine and tyrosine. (I) is the Cu salt of (II) (viz., $\text{C}_{24}\text{H}_{35}\text{O}_{10}\text{N}_5\text{Cu}$) united to a S-containing substance, probably $\text{C}_7\text{H}_{15}\text{O}_5\text{N}_2\text{S}_2$. The same kind of (I) is also present in octopus haemocyanin (cf. A., 1931, 497, 753). A. E. O.

Ammonia formation and respiration in the erythrocytes of birds. A. A. BAEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 69—73).—Pigeon erythrocytes in Ringer's solution containing glucose liberate 40×10^{-6} g. of $\text{NH}_3\text{-N}$ per c.c. of cells per hr. when respiration is restricted by small amounts of HCN , CO , and phenylurethane, or a N_2 atm., the

normal rate being $0.25-2 \times 10^{-6}$ g. per hr. The restriction has a similar effect on dephosphorylation. Most of the NH_3 is formed in the first hr. The $\text{N}:\text{H}_3\text{PO}_4$ ratio is variable (0.5—0.25). J. L. D.

Influence of bone-marrow extract of normal and splenectomised animals on the synthesis of hæmoglobin. V. BAENA (Biochem. Z., 1934, 274, 358—361).—The view that bone-marrow extract (I) contains a factor which accelerates the synthesis of hæmoglobin *in vitro* is confirmed, and it is shown that (I) of splenectomised has a greater effect than (I) of normal animals. This confirms the view that the spleen exerts an inhibitory action of the function of the marrow. P. W. C.

Detection of true nucleal substance in thrombocytes. K. VOIT and H. KEMPA (Z. Biol., 1934, 95, 635—638).—Thymonucleic acid is detectable in the blood-platelets of men and horses by Feulgen's nucleal reaction (A., 1924, i, 905). F. O. H.

Blood-proteins of children. Distribution of total nitrogen in whole blood, red blood-cells, and serum-proteins from the same specimen. A. BERNHARD, J. S. LEOPOLD, and I. J. DREKTER (Amer. J. Dis. Children, 1934, 47, 1256—1260).—The N contents of whole blood (I), red cells (II), and serum (III) are recorded. Vals. for (I) and (II) are < and for (III) > in adults. CH. ABS. (p)

Refractometric determination of serum-proteins. M. PAÍÓ and V. DEUTSCH (Compt. rend., 1934, 199, 1306—1308).—A modification of Reiss' method is described. Changes in n with temp. of serum are substantially the same as those for H_2O . A. G. P.

p_H of heat-inactivated serum. P. L. DU NOUY and V. HAMON (Compt. rend. Soc. Biol., 1934, 117, 337—338).—When heated above 56° the p_H falls to a min., usually at 60° , after which it fluctuates feebly, in some cases rising again. The mean initial fall is 0.05. R. N. C.

Hydrolysis of blood-albumin by autoclaving in 2% potassium carbonate solution. V. S. SADIKOV, V. ROZANOVA, and G. NOVOSELOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 217—221).—Hydrolysis for 2 hr. at 180° with 2% K_2CO_3 yields a small proportion of free NH_2 -acids, with a predominance of heterocyclic and cyclopeptide material, the latter being removed by extraction with Et_2O and CHCl_3 . 24.14% of the total N was lost as NH_3 and amines. H. G. R.

Clearing agent for blood. Application to determination of blood-sugar. M. PAGET and DUPONT (Compt. rend. Soc. Biol., 1934, 117, 881—882).—Blood is deproteinised by a mixture of suitable concns. of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{Zn}(\text{OAc})_2$. The clear solution contains the sugar, which reduces Baudouin's solution. R. N.

Indirect bilirubin of serum and its extraction by chloroform. Techniques proposed by de Castro, and by Kerpola and Leikola. B. VARELA-FUENTES, C. VIANA, and P. RECARTE (Compt. rend. 1934, 117, 903—908).—Extraction with CHCl_3 of the indirect bilirubin of both normal and icteric sera is incomplete, even when continued to

exhaustion. It becomes completely extractable if Na_2SO_4 solution is added to the serum. There are no definite grounds for postulating two different indirect bilirubins. R. N. C.

Micro-determination of cholesterol in whole blood, serum, and plasma. J. KAMLET (J. Lab. Clin. Med., 1934, 19, 883—884).—0.2 c.c. is dried on filter-paper at $35-40^\circ$ for 20—30 min., and extracted for 2 hr. at room temp. with CHCl_3 (10 c.c.). The Liebermann-Burchard procedure is then used. CH. ABS.

Control of blood-cholesterol by the kidney. H. MIYAZAKI (J. Chosen Med. Assoc., 1934, 24, 263—277).—Injection of 2 c.c. per kg. of renal venous blood-serum of a normal rabbit into another rabbit causes a fall in blood-cholesterol; arterial blood or auricular venous blood-serum causes no change. The action is due to a hormone secreted from the epithelium of the kidney tubules. The hormone reduces hypercholesterolaemia in experimental nephritis or nephrectomy. CH. ABS.

Determination of uric acid in human, bovine, and avian blood. G. H. PRITHAM and A. K. ANDERSON (J. Lab. Clin. Med., 1934, 19, 892—896).—Any method involving isolation of uric acid is satisfactory for human or avian blood. Benedict's direct method and Folin's method for unaltered blood are satisfactory; for bovine blood Folin's direct method is preferred. CH. ABS.

Electrodialysis as method of separation and determination of bases in biological fluids. II. Determination of total bases in blood, serum, and erythrocytes. N. P. MESCHKOVA and S. E. SEVERIN (Z. physiol. Chem., 1934, 230, 114—121).—The cathode fluid obtained from protein-free (using a limited amount of $\text{CCl}_3\text{CO}_2\text{H}$) blood (2 c.c.), erythrocytes (2 c.c.), and serum or plasma (1 c.c.) is treated with 0.01N- H_2SO_4 (excess of which is then determined iodometrically). The error is $\pm 2\%$. H. B.

Electrolytes in the serum of the rat. P. K. SMITH and A. H. SMITH (J. Biol. Chem., 1934, 107, 673—680).—Vals. are recorded for the concn. of CO_2 , Cl, inorg. PO_4''' , Ca, Mg, K, Na, and protein in the serum of albino rats. The Ca, Mg, and PO_4''' are > and the Na, HCO_3' , and protein < in man. C. G. A.

Physical chemistry of the blood. D. D. VAN SLYKE (Cold Spring Harbor Symp. Quant. Biol., 1933, 1, 184—189).—Plasma and lymph contain about 18 times as much Na^+ as K^+ ; cellular tissues have a relative excess of K^+ . $\text{Na}^+ + \text{K}^+$ (I) in blood and tissue cells is a little > in blood-plasma. 0.33 0.75 of (I) in the cell is neutralised by complex acids which are buffered and indiffusible colloids. The ratio cell : serum-Cl' is < 1 by an amount which α the amount of base as hæmoglobinate in the cells. CH. ABS.

Blood-calcium and -magnesium of the cow in health and disease. W. M. ALLCROFT and H. H. GREEN (Biochem. J., 1934, 28, 2220—2228).—The normal range of serum-Ca and -Mg in 139 clinically healthy cows is 8.65—11.65 mg. and 1.85—3.17 mg. per 100 ml., respectively. No marked change occurs

in cases of *Brucella abortus* infection, but in advanced generalised tuberculosis hypomagnesaemia (I) occurs. (I) is associated with lactation tetany (II) and hypocalcaemia with milk fever. The Ca/Mg ratio is not the determining factor of (II). C. G. A.

Relation between the ossification of the skeleton and the state of the blood-calcium of fish. M. FONTAINE (Compt. rend., 1934, 199, 1452—1454).—The proportion of blood-Ca which is adsorbable on BaSO₄ is greater for fish with much ossified cartilage than for those with little, and within the latter class greater for those with much cartilage than for those with little. R. S. C.

Blood-iodine. II. Normal iodine content of human blood. C. B. DAVIS, G. M. CURTIS, and V. V. COLE (J. Lab. Clin. Med., 1934, 19, 818—830).—I is a const. constituent of human blood (normally 12×10^{-6} g. per 100 c.c.). Vals. in summer are > in winter. CH. ABS.

Blood-iodine content of normal and thyrotoxic individuals. Iodine-tolerance test. H. J. PERKIN, B. R. BROWN, and J. LANG (Canad. Med. Assoc. J., 1934, 31, 365—368).—Blood is heated with K₂CO₃ in a Ni crucible at 260° for 5 hr. The ash is extracted with EtOH, filtered, and the filtrate evaporated to dryness. The residue is dissolved in H₂O, I⁻ is oxidised to IO₃⁻, and the latter determined by treatment with KI and titration with Na₂S₂O₃. CH. ABS. (p)

Is thrombin a calcium compound? O. KASTL (Biochem. Z., 1934, 274, 452—460).—The view of Loucks and Scott (A., 1930, 802) that thrombin (I) is a "Ca-tissue-juice" compound, inactivatable by decalcification with H₂C₂O₄, is not confirmed. Moreover, the method employed by these authors is now known not to lead to complete decalcification. (I) preps. obtained from sera rigorously decalcified by the more recent techniques of Kramer-Tisdall and of Schimmelpfeng have the same activity as (I) from Ca-containing serum. P. W. C.

Effect of hydrogen ions and thrombase on the coagulation of fibrinogen.—See this vol., 165.

Opacification reaction in the serum of sensitised rabbits. P. VALLERY-RADOT, G. MAURIC, and A. HUGO (Compt. rend. Soc. Biol., 1934, 117, 1091—1093).—The opacifying power (I) of rabbits' serum is affected to different degrees in different animals by sensitising with horse-serum. There is no connexion between (I) and the appearance or non-appearance of anaphylactic shock. R. N. C.

Opacification reaction and precipitins in the sensitised rabbit. P. VALLERY-RADOT, G. MAURIC, and A. HUGO (Compt. rend. Soc. Biol., 1934, 117, 1093—1095).—There is no parallelism between the sensitised state and the appearance of precipitins. R. N. C.

Reversibility of certain metalloprotein precipitations by the action of sodium thiosulphate. Serological behaviour of the complexes from hæmolytic and syphilitic sera. H. DIACONO (Compt. rend., 1934, 199, 1686—1687).—The pptd. metalloprotein complexes formed by addition of 0.1% HgCl₂ or CuSO₄ to hæmolytic and syphilitic

sera contain the antibodies (only the alexin being destroyed), and are completely sol. in 10% Na₂S₂O₃, the solution so obtained exhibiting the same biological properties as the original serum. J. W. B.

Excretion of antibody through the urine. O. SUZUKI (Sci-i-Kwai Med. J., 1933, 52, No. 9, 31—40, 41—62).—Excretion through the urine and intestinal fluid is the main cause of loss of antibody from the serum. CH. ABS.

Inactivation of the third component of alexin by yeast. O. BIER (Compt. rend. Soc. Biol., 1934, 117, 720—722).—Guinea-pig serum (I) peptonised with physiological salt solution and treated with a yeast suspension at 37° lost the third component of the alexin. Under the same conditions (I) peptonised with KI remained active. A. L.

Magnetic properties of animal fibrous tissues. H. G. CLAMANN (Z. Biol., 1934, 95, 639—640).—Whilst celluloid and cocoon-fibres are paramagnetic, wood, aq. and dry gelatin, neck-fibres, tendons, liver, bone, spleen, hair, fibrin, muscle, and powdered fibrinogen are diamagnetic. F. O. H.

X-Ray spectrographic structure investigations on biological objects and human tissues. E. SAUPE (Kolloid-Z., 1934, 69, 357—363).—A lecture. E. S. H.

X-Ray diffraction studies on nerve. F. O. SCHMITT, G. L. CLARK, and J. N. MEGUDICH (Science, 1934, 80, 567—568).—X-Ray photographs indicate a fundamental similarity between the fine structure of the axis cylinder of nerve and other fibres such as hair, tendon, and muscle. Details of the patterns are discussed in relation to their possible chemical significance. L. S. T.

Cyto-chemistry of incinerated nerve-cells. J. KRUSZYNSKI (Bull. Acad. Polonaise, 1934, B, 105—116).—Paraffin sections (> 3 μ) of nerve-tissue (fixed with 85—90% EtOH) are mounted in the usual manner, and the slide is heated to give the ash-picture ("spodogram") of the cell-structure formed by its mineral constituents. Subsequent treatment with 2% H₂SO₄, 10% H₂PtCl₆, Na₂HPO₄, or NH₄SCN indicates the distribution of Ca, K, Mg, and Fe, respectively. F. O. H.

Chromosome behaviour in terms of protein pattern. D. M. WRINCH (Nature, 1934, 134, 978—979).—An attempt to correlate the properties of chromosomes and the facts of genetics with protein structure. L. S. T.

New fixing-mixtures revealing the morphology of chromosomes. G. A. LEVITSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 143—144).—A no. of new CH₃O fixing-mixtures are described. H. N. R.

Approximate determination of proteins of muscle. E. C. SMITH (J.S.C.I., 1934, 53, 351—364T).—The minced muscle is extracted 6 times at 0° with 10% aq. NH₄Cl. Myosin (I) is determined by pptn. from the extract by dilution with 19 parts of H₂O, a correction being applied for the amount of (I) remaining in solution [12% of the total (I)]. Collagen in the residue after extraction is converted

into gelatin (II) by autoclaving at 121° for 2 hr. (II) is extracted with boiling H₂O, and the residue is digested with trypsin to remove and determine residual intracellular protein. The final residue consists of elastin (cf. B., 1927, 264). Typical analyses of rabbit- and ox-muscle are given. E. C. S.

Determination of lactic acid in muscle. C. P. STEWART, J. P. DICKSON, and R. GADDIE (Biochem. J., 1934, 28, 1945—1948).—AcCHO should be removed by distillation prior to treatment with CuSO₄+CaO for removal of sugar, otherwise the lactic acid content found by oxidation with KMnO₄ to MeCHO will be too high. CuSO₄+CaO convert AcCHO into a substance oxidised by KMnO₄ to MeCHO (2:4-dinitrophenylhydrazone, m.p. 161°; not 148° as in lit.) and other substances which combine with NaHSO₃. A. E. O.

Combined or free potassium in muscle. E. ERNST and J. FRICKER (Pflüger's Archiv, 1934, 234, 360—368).—An aq. COMe, extract of a frog's gastrocnemius (I), rendered rigid by heat or electrically stimulated, contains a proportion of the muscle-K > that extracted from a similar (I) frozen immediately after excision, suggesting that muscle-K is converted into a more diffusible form by heat-rigor (II) or fatigue (III). The increases in diffusible K correspond with 0.10% of total alkali calc. as NaCl in (II), and 0.05% in (III). R. N. C.

Pentose polynucleotide of the pancreas. E. JORPES (Biochem. J., 1934, 28, 2102—2108).—The substance has a pentanucleotide structure containing 3 mols. of purine pentose nucleotides and 2 mols. of pyrimidine nucleotides. It contains 2 mols. of guanylic acid (I) per mol. of adenylic acid. The titration curve of pancreas nucleic acid (II) is similar to that of thymus (II), showing that the substance is not a mixture of (I) with yeast (II). H. G. R.

Determination of adenine in the presence of guanine. E. JORPES (Biochem. J., 1934, 28, 2097—2101).—Guanine is oxidised by KMnO₄ in acid solution, determinations of purine-N being made before and after the reaction by pptn. with Cu H sulphite reagent. H. G. R.

Vitreous body. I. W. S. DUKE-ELDER, E. B. ROBERTSON, and H. DAVSON (Biochem. J., 1935, 29, 72—75).—The vitreous body (I) does not show uptake of H₂O at 8, nor does swelling occur in presence of 1% Na oleate or Na laurate. This does not eliminate swelling of (I) as the cause of intra-ocular pressure in glaucoma simplex, as the behaviour of (I) is different *in vivo* and *in vitro*. C. G. A.

Polysaccharide of the vitreous humour. K. MEYER and J. W. PALMER (J. Biol. Chem., 1934, 107, 629—634).—A polysaccharide of high mol. wt. has been obtained from the vitreous humour of cattle eyes by pptn. with COMe, and fractionation from acid EtOH. It has an acid equiv. approx. 450 and a dissociation const. 4.58×10^{-5} at 32°. It contains a uronic acid, an NH₂-sugar, and a pentose. Galactose is absent. C. G. A.

Determination of copper in the aqueous humour. I. I. NITZESCU and I. GEORGESCU (Compt. rend. Soc. Biol., 1934, 117, 1135—1137).—

Cu is determined either by the C₅H₅N-thiocyanate (I) or the chromotropic method (II). In (I), the liquid, after centrifuging, is incinerated (wet) with HNO₃ and H₂SO₄, and the clear neutral solution treated with NH₄CNS and C₅H₅N. The green Cu(C₅H₅N)₂(CNS)₂ complex is extracted with CHCl₃ and determined colorimetrically. In (II) the Cu is titrated with nitroschromotropic acid, a colorimeter being employed to determine the end-point. Aq. humour contains 0.14—0.18 mg. Cu per litre. R. N. C.

Antiscorbutic action of the eye lens and its reductone and thiol content. H. VON EULER and M. MALMBERG (Z. physiol. Chem., 1934, 230, 225—230; cf. A., 1933, 1090).—The no. of mg. of ascorbic acid (I), determined by titration with 2:6-dichlorophenol-indophenol at 2.5 [at p_H 5.5—6.5, (I)+SH-compound is found], in 1 g. (unless stated otherwise) of lens (II) from the following are: human, 0.2; human (cataract), 0—0.5 per (II); ox (III), 1 per (II); *Salmo salar*, 1.04; *Gadus minutus*, 0.53; *G. callarius*, 0.48; *G. merlangus*, 0.45; *Labrus exoletus*, 0.32. The presence of (I) in (III) is confirmed by biological tests. (III) appear to contain a substance which is toxic to guinea-pigs. Administration of C₁₀H₈ and 2:4-(NO₂)₂C₆H₃-OH to rabbits does not affect the (I) content of the (II). H. B.

Variations in glycogen and accompanying substance of active and hibernating snails. L. SEMICHON (Compt. rend. Soc. Biol., 1934, 117, 774—775).—The glycogen (I) content of the vesicular cells of conjunctive tissue of snails approaches zero during hibernation, whilst the hyaline substance accompanying (I) remains more const. F. O. H.

Galactogen. VII. Galactogen and glycogen contents of starved snails. VIII. Detection of galactogen in animals and man. F. MAY (Z. Biol., 1934, 95, 606—613, 614—634).—VII. During starvation of vineyard snails, galactogen (I) is converted into glycogen (cf. A., 1933, 380).

VIII. (I) occurs in the eggs [36% of the total polysaccharides (II)] of snails (*Limacidae*), in the sexual glands (51.8%) of fresh-H₂O mussels (*Anodonta*), in carp's roe (1.2, 9.84%), in adult (but not young) rabbits (7%) after removal of ovaries, uterus, brain, mammary glands, and liver [all of which are free from (I)], and in human placenta (approx. 1%). Traces of (I) occur in the carp before maturation of the ova; organs other than the ovaries are approx. free from (I). The nature and function of (II) in the organism are discussed. F. O. H.

Liver-glycogen. Blood-sugar level. M. C. HRUBETZ and L. B. DOTTI (J. Biol. Chem., 1934, 107, 731—733).—Correlation coeffs. are calc. for liver-glycogen, liver-wt., and body-wt. Blood obtained by decapitation has a sugar content significantly > blood obtained by venesection. A. E. O.

Spreading of complex proteins.—See this vol., 161.

Substance resembling acetylcholine in adrenals and other organs. F. PLATTNER (Pflüger's Archiv, 1934, 234, 258—263; Chem. Zentr., 1934, ii,

1149).—Repeated evaporation of solutions does not cause loss of acetylcholine (I). The (I) of a cat adrenals is not increased by stimulation of the splanchnic nerve. The brain, pituitary, and lachrymal glands contained $1-4 \times 10^{-6}$ g. of the substance per g. Smaller amounts occur in spleen and liver.

A. G. P.

Choline or acetylcholine content of human placenta. E. STRACK, H. GEISSENDORFER, and E. NEUBAUER (Z. physiol. Chem., 1934, 229, 25—36).—Only a small amount of choline is present in the placenta before parturition, but this is considerably increased on interruption of the blood-flow, and the choline content becomes greater the longer the placenta remains in the uterus.

J. H. B.

Hydrocarbon in basking shark. I. M. TSUJIMOTO (J. Chem. Soc. Japan, 1934, 55, 702—741).—Isolation is described of an unsaturated hydrocarbon, "zamene," $C_{18}H_{36}$, 0.8006, n_D^{20} 1.4500, I val. 78.4.

CH. ABS. (p)

Hydrocarbons of pig liver. H. J. CHANNON, J. DEVINE, and J. V. LOACH (Biochem. J., 1934, 28, 2012—2025).—The unsaponifiable matter from 63 kg. of pig liver yielded 52 g. of a sterol-free oil which was fractionated by Et_2O and MeOH into an insol. fraction (I) of I val. 266 and a sol. fraction (II) of I val. 140. (I) yielded 70% of an unsaturated hydrocarbon (29 mg. per 100 g. of liver), $C_{45}H_{76}$ or $C_{50}H_{84}$, from which the bromide and hydrochloride were prepared. 10% of (I) consists of a saturated hydrocarbon not yet obtained pure and a further 10% of a compound containing O. (II) contains a third hydrocarbon with one double linking reacting with I.

C. G. A.

Body-fats of the pig. IV. Progressive hydrogenation as an aid in the study of glyceride structure. T. P. HILDITCH and W. J. STAINSBY (Biochem. J., 1935, 29, 90—99).—The increase of fully saturated glycerides in pig, ox, and sheep depot-fats and cow milk-fats, in which the total content of saturated fats progressively increases, is very similar to that displayed by pig back-fat (I) artificially hydrogenated to varying stages of saturation. (I) contains about 15% of tri- C_{18} -glycerides, other than tristearin, which is absent, probably consisting mainly of steardioleins. The monopalmito-compounds are largely, or solely, β -palmitoglycerides. Palmito-unsaturated compounds (chiefly palmitodiolein) constitute 42—57% of the fat, and palmitostearo-oleins 21—38%.

C. G. A.

Abdominal fat of the Western range horse. H. A. SCHUETTE, T. M. GARVIN, and E. J. SCHWOGGLER (J. Biol. Chem., 1934, 107, 635—639).—The acids of the glycerides of the abdominal fat contain the following: palmitic 26.28%, stearic 4.50%, oleic 46.86%, linoleic 11.88%, and linolenic 4.48%. No heptadecic acid was present.

C. G. A.

Toxic components of fish liver-oils. K. KAWA and I. YAMAMOTO (Bull. Inst. Phys. Chem. Res., Tokyo, 1934, 13, 86—88).—Liver-oil toxins are of three kinds, A, B, and C. A occurs in the saponifiable fraction and causes nutritive disturbances. B and C occur in the unsaponifiable fraction. B causes cramp in rats, when injected subcutaneously; it is obtained

in highly conc. form, b.p. 120—140°/5 mm. (C 75.45, H 10.65%), free from vitamin-A, and unaffected by fuming HNO_3 at 130°. The B contents of 14 oils are given. The toxic action of A is destroyed by hydrogenation (I), but that of B is unaffected by (I), oxidation, or saponification. C is narcotic. *Paralithodes camtschatica* liver-oil contains C and possibly A; the body-fat of sardines contains only A. Cod-liver oil contains A, B, and C.

R. S. C.

Fatty acids of the phosphatides of ox adrenals. W. C. AULT and J. B. BROWN (J. Biol. Chem., 1934, 107, 607—614).—The fatty acids of the phospholipins of ox adrenal have been fractionated by way of the Me esters, and pure palmitic, stearic, and arachidic acids isolated. Some myristic acid may be present. The principal unsaturated acids are oleic and arachidonic, the latter being present to the extent of 22%.

C. G. A.

Lecithin and kephalin of egg-yolk.—See this vol., 228.

Flavin content of animal tissues under different conditions. A. J. CHARIT and N. W. KHAUSTOV (Biochem. J., 1935, 29, 34—37).—The tissue is washed with H_2O , extracted with aq. MeOH (1:3), and the solution extracted with $CHCl_3$. The MeOH solution is compared colorimetrically with a standard K_2CrO_4 solution. The method is not applicable to blood and tissues containing yellow pigments. The distribution of flavin in the tissues of the rabbit and cat is determined, and agrees with the results of Euler and Adler (A., 1934, 544). A small decrease occurs in the liver-flavin (I) of rats deficient in vitamin-A; neither avitaminosis-C nor a rich protein diet influences the (I) of rats.

H. D.

Constitution of pectenoxanthin. E. LEDERER (Compt. rend. Soc. Biol., 1934, 117, 411—413).—The cryst. material, $C_{40}H_{54(\pm 2)}O_3$, has the properties of a xanthophyll; it contains 11 double linkings and 2 OH. It is very similar to β -carotene, but does not act as provitamin-A.

H. G. R.

Carotenoids of three Ascidiae (*Halocynthia papillosa*, *Dendrodoa grossularia*, *Botryllus Schlosseri*). E. LEDERER (Compt. rend. Soc. Biol., 1934, 117, 1086—1088).—*H. papillosa* contains a hypophasic ester of astacene (I), m.p. 228—230° (large band at 500 $m\mu$ in C_5H_5N), and a xanthophyll, *cynthiaxanthin*, m.p. 188—190° (bands at 517, 483, 452 $m\mu$ in CS_2), which resembles zeaxanthin closely, but differs in adsorbability. *D. grossularia* contains an epiphasic ester of (I), m.p. 230° (large band at 500 $m\mu$ in C_5H_5N). *B. Schlosseri* contains capsorubin, capsanthin, and pectenoxanthin. Carotenes are present only in traces in all three species.

R. N. C.

Yellow pigment of the thalamo-subthalamal region. G. ROUSSY and M. MOSINGER (Compt. rend. Soc. Biol., 1934, 117, 1054—1056).—A yellow pigment of the lipochrome type is present in varying quantities in certain parts of the thalamus and hypothalamus in adult man.

R. N. C.

Origin of the colours in the plumage of birds. C. V. RAMAN (Proc. Indian Acad. Sci., 1934, 1, A, 1—7).—Observations on the feathers of a jay, *Coracias indica*, show that the tints may range over the whole

spectrum; a simple Tyndall effect explanation is thus insufficient. Possible explanations are discussed.

N. M. B.

Micro-chemistry of the pigmentation of the ear-lobes of the cock. R. LOUVIER (Compt. rend. Soc. Biol., 1934, **117**, 328—330).—The situation and staining reactions of the typical granular pigmentation (due to purine bases) are described. F. O. H.

Occurrence of iron in the milk glands of the rat and the mouse. A. SCHULTZ (Arch. Gynakol., 1934, **155**, 479—489; Chem. Zentr., 1934, ii, 977).—Microscopical examination shows the presence in the milk glands of rats and mice of Fe, which disappears during pregnancy and lactation. R. N. C.

Chemical constitution of bone salts of healthy and rachitic animals. (A) R. KLEMENT. (B) J. MAREK, O. WELLMANN, and L. URBANYI (Z. physiol. Chem., 1934, **229**, 22—24, 24).—(A) Polemical against Marek *et al.* (A., 1934, 1133).

(B) A reply.

J. H. B.

Chemical composition of teeth. I. Determination of fluorine: fluorine content of normal teeth. J. H. BOWES and M. M. MURRAY (Biochem. J., 1935, **29**, 102—107).—F as determined by the Zr-alizarin method constitutes 0.02% of the human enamel in the London area. The teeth of rats fed on a diet not designed to be F-free contained 0.02—0.03% of F. C. G. A.

Copper content of teeth. E. TIEDE and H. CHOMSE (Ber., 1934, **67**, [B], 1992—1995).—The supposition that the discoloration observed in the residue (I) obtained by strongly igniting teeth in air is due to the presence of minute amounts of Cu is supported by the prep. of similar materials from hydroxyapatite containing Cu (100,000:1). Further, addition of (I) to pure ZnS leads to ZnS-Cu phosphors. Electrolysis of a solution of (I) in 7% HNO₃ gives Cu, 1.2×10^{-5} g. of which is obtained from 1 g. of ox tooth. H. W.

Luminescence of teeth. E. TIEDE and H. CHOMSE (Ber., 1934, **67**, [B], 1987—1992).—Addition of traces of activating metals to hydroxyapatite (I), Ca₁₀(OH)₂(PO₄)₆, followed by ignition of the products at 430° or 710° does not lead to preps. with luminescent properties comparable with those of natural teeth (II). Addition of small amounts of glycine, tyrosine, hippuric acid, leucine, gelatin, or collagen from teeth to (I) gives materials the luminescence of which is greatly increased by heating at 430° and then very closely resembles that of (II). The colour depends less on the added substance than on the temp. and experimental conditions. Extraction of (II) with alkaline glycerol does not remove org. matter sufficiently to inhibit luminescence; this effect is produced by H₂O₂-NH₃. Treatment of (II) with 8% HCl removes inorg. matter, leaving collagen, which fluoresces and phosphoresces even when dried. Fatty matter in (II) is not concerned with luminescence. H. W.

Bromine in tissues. T. F. DIXON (Biochem. J., 1934, **29**, 86—89).—The Br content of blood and pituitary is variable and is thought to be dependent on food intake. There is no evidence of a Br-con-

taining pituitary hormone, nor that Br metabolism is a factor in mental disease. C. G. A.

Deterioration of shells when stored in oak cabinets. J. R. NICHOLLS (Chem. and Ind., 1934, 1077—1078).—Traces of AcOH emitted from oak attack shells on which they are absorbed by moisture collected on hygroscopic sea-salt. C. W. G.

Composition of amniotic fluid. A. R. TANKARD, D. J. T. BAGNALL, and F. MORRIS (Analyst, 1934, **59**, 806—808).—The *d*, acidity, *p_H*, and f.p., and the % of total solids, ash, Cl, albumin, and urea, are given. E. C. S.

Modes of stimulation of gastric secretion. B. P. BABKIN (Nature, 1934, **134**, 1005).—A summary. L. S. T.

Influence of temperature on the conductivity of milk. E. MESSNER (Compt. rend. Soc. Biol., 1934, **117**, 897—899).—Empirical equations are given for calculating the sp. conductivity at 25° from that observed at any different temp. R. N. C.

Combination curves, hydrogen-ion regulating powers, and equivalents of lactalbumin and its non-identity with serum-albumin. S. E. WOONS (Biochem. J., 1934, **28**, 2034—2038).—Titration curves show that lactalbumin (I) is not identical with serum-albumin (II). (I) requires less acid to bring it to a given *p_H* than either (II) or ovalbumin. Above *p_H* 10.5 the buffering power of (I) is > that of (II). C. G. A.

Extraction from urine of a substance possessing the biological properties of Oriel's "substance P." H. THIERS (Compt. rend. Soc. Biol., 1934, **117**, 940—943).—Oriel's method is modified. Urine is acidified, shaken with $\frac{1}{3}$ — $\frac{1}{2}$ its vol. of Et₂O, and left for $\frac{1}{2}$ hr. The Et₂O is evaporated at 50° and coagulated mucus removed by centrifuge. The liquid is treated with 5 vols. of EtOH, and then with Na₂CO₃ until alkaline to phenolphthalein. The ppt. is separated by filtration after 10 min., washed with EtOH, dried at 37°, dissolved in H₂O with a drop of NaOH, and the insol. residue is removed. The solution is pptd. at alkaline *p_H* with 5—6 vols. of EtOH, and the ppt. washed with EtOH and dried. R. N. C.

Extraction from bile of a substance possessing the biological properties of Oriel's "substance P." H. THIERS (Compt. rend. Soc. Biol., 1934, **117**, 943—944).—Bile is treated with 4 vols. of 95% EtOH and 1 vol. of 20% CCl₃·CO₂H, and the ppt. removed. The clear liquid is made alkaline to phenolphthalein with Na₂CO₃, and the ppt. washed with EtOH, dried, dissolved in 0.1N-NaOH, and the insol. residue removed by centrifuge. The solution is pptd. with 5 vols. of 95% EtOH. The ppt. is sol. in H₂O or artificial serum, and has the biological properties of Oriel's "substance P." R. N. C.

Determination of bile-salts in body-fluids based on bile-salt hæmolysis. S. S. LICHTMAN (J. Biol. Chem., 1934, **107**, 717—730).—The hæmolytic activity of bile-salts (I) on a standard suspension of sheep's red cells previously stabilised by treatment with PO₄''' buffer is determined in presence of citrate, which enhances hæmolysis by (I), but inhibits

the hæmolytic activity of soaps, thus rendering possible the determination of the (I) content of body-fluids. The order of activity of (I) is Na deoxycholate (II) (the standard) > taurocholate > glycocholate > cholate. The activity of mixtures of (I) is strictly additive. Vals. are given for the (I) content of normal blood, urine, and bile and for cadaver gall-bladder bile. The first two fluids contain 0.5—4.0 mg. of (II) (or its equiv.) per 100 c.c.

A. E. O.

Colloidal solution of acid bilirubin. Preparation and properties. B. VARELA-FUENTES and P. RECARTE (Compt. rend. Soc. Biol., 1934, 117, 900—902).—A colloidal solution of bilirubin (I) is obtained from a filtered, saturated COMe₂ solution by a process of repeated dilution and vac. evaporation. It is stable in the dark, and contains only traces of COMe₂, removal of which ppts. the (I). Various properties are recorded. Small quantities of alkali convert (I) into H₂O-sol. bilirubate. R. N. C.

Bilirubin excretion of the liver. T. OKADA (Trans. Japan. Path. Soc., 1933, 23, 567—571).—The bile of the newborn infant consists chiefly of bilirubin I, and that of the adult of bilirubin I and II.

CH. ABS.

Clinical tests for bilirubin in urine. E. G. GODFRIED (Biochem. J., 1934, 28, 2056—2060).—Hunter's test (A., 1931, 863) for bilirubin is modified. To the urine acidified with AcOH are added BaCl₂ and (NH₄)₂SO₄ and the ppt. is washed with H₂O. Abs. EtOH, saturated aq. (NH₄)₂SO₄, 6% Na₂HPO₄, and diazo-reagent are added. When the colour has developed CHCl₃ is added. The lower layer contains the azobilirubin, and is compared with a standard Co solution. H. D.

Action of light on lyochromes. W. KOSCHARA (Z. physiol. Chem., 1934, 229, 103—111).—Aquoflavin (I) may be isolated from the lyochrome concentrate of urine by chromatographic analysis. It is eluted by H₂O or aq. NaOAc. Irradiation of (I) in alkaline solution with ultra-violet light (II) gives aquolumiflavin (III) insol. in CHCl₃. (III) is eluted by 5% aq. C₂H₅N. Irradiation of uroflavin in alkaline solution gives, as by-product, a CHCl₃-insol. pigment resembling (III). Neither visible light nor (II) acts on the leuco-form of lactoflavin in alkaline solution. Irradiation of the pigments in aq. Na₂CO₃ in air yields products resembling deuteroflavin. In aq. NaOH the pigments are irreversibly bleached. H₂SO₃, inactive in the dark, reduces uroflavin in the light to the leuco-compound. Other H₂-donators are also effective. J. H. B.

Chromogen of melanuria. L. LINNELL and H. S. RAPER (Biochem. J., 1935, 29, 76—85).—The chromogen (I) of human melanuria can be separated from urine by pptn. with Pb or Hg acetate. Administration of 5:6-dihydroxyindole (II) to rabbits causes excretion of a melanogen in the urine the properties of which suggest identity with (I). 5:6-dihydroxyindole-2-carboxylic acid does not produce melanuria. (I) appears to be a simple derivative of (II), possibly a sulphate or glycuronate. The synthesis of the A, disulphate of (II) is described.

C. G. A.

Composition of glomerular urine. XII. Concentration of chloride in glomerular urine of frogs and *Necturi*. B. B. WESTFALL, T. FINDLEY, and A. N. RICHARDS (J. Biol. Chem., 1934, 107, 661—672).—The sensitivity of Isaac's colorimetric method for Cl⁻ is sufficiently increased by use of *s*-diphenylcarbazine to enable determination to be made of 0.001 mg. of NaCl with an accuracy of 3% in urine or plasma. The [Cl⁻] of the glomerular urine and blood-plasma is approx. equal in both frogs and *Necturi*. C. G. A.

Excretion of copper in urine and faeces and its relation to the copper content of the diet. S. L. TOMPSETT (Biochem. J., 1934, 28, 2088—2091).—The average daily intake of Cu is 2.0—2.5 mg., which is balanced by the total excretion. Human urine contains 0.08—0.48 mg. of Cu per litre. H. G. R.

Routine determination of fat in faeces. E. C. WOOD and T. W. SIMPSON (Analyst, 1934, 59, 817—818).—The material is acidified with HCl, dried with Na₂SO₄, and extracted with light petroleum. Fatty acids and neutral fats are determined consecutively in the extract. Free fatty acids and soaps may be differentiated by repeating the determination on a new sample, omitting the addition of HCl. Specimen analyses are given. E. C. S.

Application of emission spectrum analytical methods to problems of social medicine. WALTER GERLACH and WERNER GERLACH (Angew. Chem., 1934, 47, 825—827).—A lecture. H. W.

Energy requirement of an acromegalic giant. A. W. ROWE (Science, 1934, 80, 482—483).—Respiratory data demonstrate an established level of hypofunction. L. S. T.

Cholesterolaemia in experimental infectious anaemia in the horse. G. GUILLOT and J. GUILHON (Compt. rend. Soc. Biol., 1934, 117, 320—321).—In colts inoculated with infectious anaemia the blood-cholesterol remained normal until the onset of fever, when it increased steadily until death. R. N. C.

Respiration of red blood-corpuscles of normal subjects and in various forms of anaemia. W. DEUTSCH (Biochem. J., 1934, 28, 2002—2011).—Since no formation of methaemoglobin (I) is observed when red blood-cells (II) are mixed with liver extract and examined spectroscopically or by respiration of (II), the (I) test cannot replace the clinical determination of hæmopoietic potency. Saline extracts of fresh rat-liver produce a slight and limited loss of O capacity when mixed with hæmoglobin (III), without production of (I). The stimulating effect (IV) of the "respiratory supplement" on the respiration of (II) in pernicious and secondary anaemias is highest at the time of reticulocyte crisis, and then falls to the val. for normal blood. (IV) is independent of the (III) content of (II). C. G. A.

Effect of inorganic iron with and without ultra-violet irradiation on prevention and cure of nutritional anaemia. E. J. ANDES and H. D. BEARD (Amer. J. Physiol., 1934, 108, 91—98).—Irradiation (I) accelerated the curative action of low

but not of high dosages of Fe. (I) affects the erythrocyte rather than haemoglobin regeneration.

CH. ABS. (p)

Active principle of liver extract in recovery from anaemia due to bleeding. T. ASAO (Aichi Ig. Zasshi, 1933, 40, 313, 863).—The third fraction of the Et₂O extract of liver (Levene, Sueyoshi) was the most effective in curing anaemia in rabbits. An extract of erythrocytes was similarly active. Brain extract was inactive. The active substance was absent from fish-liver.

CH. ABS. (p)

Italian work on liver therapy. H. I. GOLDSTEIN (Science, 1934, 80, 561).—Concerning priority.

L. S. T.

Bence-Jones protein in serum. D. M. KYDD (J. Biol. Chem., 1934, 107, 747—753).—Bence-Jones protein (I) begins to be pptd. when [PO₄''''] reaches 1.98M, whereas globulin is pptd. at 1.48M. The various sections of the discontinuous solubility curve are extrapolated logarithmically to zero and the various individual serum-protein contents determined (cf. A., 1933, 293). (I) from urine is identical with (I) from serum. (I) exists in the serum of myelomatous individuals and may or may not appear in the urine.

A. E. O.

Hormones in cancer. IX. Resistance factor in normal urine affecting carcinoma 256. F. BISCHOFF and L. C. MAXWELL (J. Pharm. Exp. Ther., 1934, 52, 378—382).—Injection of crude callicrein preps. (I) increased the no. of takes of carcinoma 256 in rats and the rate of tumour growth. Purified preps. of (I) failed to produce these effects. H. D.

Influence of vitamin-A and -D on the frequency of tumours in mice. E. HARDE and N. KOBOZIEFF (Compt. rend. Soc. Biol., 1934, 116, 848—849).—Increased dietary Ca and vitamin-A and -D decreased the appearance of tumours.

CH. ABS. (p)

Action of ascorbic acid on tumour metabolism. D. L. WOODHOUSE (Biochem. J., 1934, 28, 1974—1976).—Injection of ascorbic acid, although having no effect on the induction period for the production of tar warts in mice, exerted a stimulating effect on the proliferation of the tumours.

A. E. O.

Blood changes following snake-venom treatment of cancer. J. VELLARD and M. MIGUELOTE-VIANNA (Compt. rend., 1935, 200, 98—100).—The lethal dose of *Lachesis atrox* venom for the normal rat is 4 mg. and for the cancerous rat 1.5 mg. In man repeated small injections (0.1—1 mg.) cause intense lysis of red blood-cells and leucocytes, decrease of fibrinogen and complement, and increase of the coagulating power of the serum. Hepatic and renal troubles may also occur.

C. G. A.

Stabilisation and purification of specific anti-cancer bodies. T. LUMSDEN and T. F. MACRAE (Biochem. J., 1934, 28, 1968—1973).—Anti-cancer sera can be highly conc. by fractional pptn. of the euglobulin (J. Path. Bact., 1932, 35, 441) and subsequent adsorption on Al(OH)₃ and elution at p_H 7.5, when 40—50% of the antibodies (I) are eluted. (I) are pptd. in solutions containing 12% EtOH, but CMe₂ is ineffective as a precipitant. Antibody

preps. are stabilised (for many months) by rapid drying and subsequent storage, both at low temp.

A. E. O.

Influence of potassium and calcium chlorides and sodium, potassium, and calcium acetates on the flocculation of hydrosols (organ extracts) by human serum. M. L. CHEVREL-BODIN and M. CORMIER (Compt. rend. Soc. Biol., 1934, 117, 764—765).—With normal and cancer sera as controls, the flocculation of syphilitic sera when mixed with an (EtOH) extract of ox-heart at p_H 6.8 is sp. in presence of Na⁺ or K⁺, but not of Ca⁺⁺.

F. O. H.

Fat-soluble vitamins and dental caries in children. C. D. M. DAY and H. J. SEDGWICK (J. Nutrition, 1934, 8, 309—328).—Feeding of vitamin-A and -D had no influence on the progress of caries.

A. G. P.

Effect of diet on the course of experimental coccidiosis in chickens. E. E. JONES (J. Amer. Vet. Med. Assoc., 1934, 38, 193—206).—Vitamin-A in the diet did not affect the course of infection of *E. tenella*. Infected chickens maintained live wts. nearer to those of controls when fed a high-protein than when fed a low-protein (I) diet. Immunity to reinfection developed more rapidly in chickens receiving (I).

A. G. P.

Therapeutic effect of total ablation of normal thyroid on congestive heart failure and angina pectoris. VIII. Relationship between serum-cholesterol values, basal metabolic rate, and clinical aspects of hypothyroidism. D. R. GILLIGAN, M. C. VOLK, D. DAVIS, and H. L. BLUMGART (Arch. Int. Med., 1934, 54, 746—757).—After removal of the thyroid, serum-cholesterol (I) increases to 300 mg. per 100 c.c. as the basal metabolic rate decreases. (I) is significantly decreased by thyroid medication and may be used as an index of hypothyroidism.

H. G. R.

Fur dermatitis. S. A. WOODHEAD (Analyst, 1934, 59, 815).—A fur, suspected of causing dermatitis, contained no dye, but contained 0.78% of H₂SO₄ and 12.43% of solids sol. in boiling H₂O, of which 4.89% was NaCl.

E. C. S.

Blood-potassium in different forms of diabetes mellitus. F. RATHERY and J. BERTOLIATTI (Compt. rend. Soc. Biol., 1934, 117, 875—878).—Plasma-K (I) and total blood-K (II) were normal in simple diabetes (III). (I) was raised in cases of (III) with foot-gangrene or hepatic lithiasis, but not with cervical abscess. Insulin had scarcely any effect on (II), even after several months. In some cases of diabetic coma (IV) results were too variable to indicate a definite relation between (II) and (IV). In bronzed (III), (II) was normal.

R. N. C.

Lumbar and sub-occipital cerebrospinal fluids in experimental poliomyelitis in monkeys. P. MOLLARET and B. ERBER (Compt. rend. Soc. Biol., 1934, 117, 1098—1100).—Fatal forms of poliomyelitis (I) in monkeys produce increases in albumin (II) and leucocytes (III) in the cerebrospinal fluid (IV); Cl remains normal, and the pptn. curve for colloidal benjoin (V) broadens. The modifications begin 48 hr. before the appearance of symptoms, at

which point they attain their max., and remain thus until death. In curable (I), the modifications are similar. The increased (II) persists longer than (III), and suboccipital (IV) becomes normal again before lumbar (IV). The same modifications appear in abortive (I). Anti-(I) vaccination produces a broadened (V). R. N. C.

Lumbar and sub-occipital cerebrospinal fluid in experimental yellow fever in *Macacus rhesus*. P. MOLLARET and G. J. STEFANOPOULO (Compt. rend. Soc. Biol., 1934, 117, 1101—1103).—Animals with yellow fever (I) show an increased lymphocyte reaction of the cerebrospinal fluid, but albumin and the colloidal benjoin pptn. curve are scarcely changed. The same modifications appear in animals with nervous (I), and immunised animals inoculated with either form. R. N. C.

Protein exchange in relation to hepatic function. R. MESSINA (Arch. Farm. sperim., 1934, 58, 280—302).—Persons with normal liver function (I) show a serum-albumin (II) > -globulin (III). In cases of atrophic cirrhosis (IV) and luetic hepatitis (V), (II) falls and (III) rises until the (II)/(III) ratio is inverted. The change is more marked in (V) than in (IV), and increases with (I) deficiency, but the inverted (II)/(III) ratio always remains near unity. Total serum-protein is diminished in (IV). The blood-sugar curve is higher and more prolonged in (I) deficiency. R. N. C.

Metabolism in hepatic diseases. VI. Blood-sugar. Y. KIN (J. Chosen Med. Assoc., 1934, 24, 208—220).—Of 37 hepatic patients, 15 had blood-sugar (I) > 0.12% and 5 < 0.07%, the former being associated with jaundice or liver abscess. In coma (I) rises, but cerebrospinal fluid-sugar fluctuates. CH. ABS.

Lipin antigens of organs in sero-diagnosis. New antigen of seroflocculation in leprosy. M. C. RUBINO (Compt. rend. Soc. Biol., 1934, 117, 894—897).—Aq. EtOH extracts of spinal marrow, liver, and CH₂O-treated corpuscles, suspended in 0.9% NaCl solution after evaporation of EtOH, exhibit a sp. flocculating effect with leprosy sera (I). If diluted without evaporating the EtOH, the specificity of the effect for (I) disappears or is diminished, showing that (I) flocculates a sp. group of lipins. The group is absent from kidney extracts; brain extracts show a diminished effect, due probably to the presence in large quantities of stabilising lipins. R. N. C.

Adrenal cortex and electrolyte metabolism. R. L. ZWEMER (Endocrinol., 1934, 18, 161—169).—Oral administration of Na salts prolongs the life of adrenalectomised cats. CH. ABS.

Blood chemistry of adrenal insufficiency in cats. R. L. ZWEMER and R. C. SULLIVAN (Endocrinol., 1934, 18, 97—106).—Adrenalectomy is followed by early loss of Na, lowered CO₂ capacity, and increase in K and non-protein-N. Before death, blood-sugar and -Cl are lowered; -P and -Mg are raised. Injection of extract of adrenal cortex into adrenalectomised animals reverses the chemical changes occurring in adrenal insufficiency. CH. ABS.

Nitrogen and sulphur metabolism in Bright's disease. V. Metabolic study of a patient with oedema of unknown origin. G. P. GRABFIELD, M. DRISCOLL, and M. G. GRAY (Arch. Int. Med., 1934, 54, 764—769).—Non-nephritic, non-cardiac oedema was accompanied by a negative S balance together with some retention of N. The diuresis produced by urea comes from within the cells. H. G. R.

Glycogen. I. Nasal polypus. S. HORIE (Sei-ikwai Med. J., 1933, 52, No. 9, 1—30).—The distribution of glycogen in the various cells has been investigated. CH. ABS.

Phosphoric acid exchange in the blood of the pregnant woman. E. MOMIGLIANO (Arch. Ist. Biochim. Ital., 1934, 6, 351—408).—The inorg. (I), total acid-sol. (II), and total PO₄''' (III) in the blood are increased in pregnancy (IV), but the increase is not always \propto the stage of (IV); P₂O₇''' (V) is unchanged. Reducing hexose phosphoric esters are present in the placental tissues, indicating enzymic control of sugars and PO₄''' in their trans-placental passage. (I), (II), and (III) are all increased during the expulsive period of parturition (VI), but the increases are independent of uterine contraction. In several cases where caesarian section was carried out, no difference was found in uterine arterial and venous P. During puerperium, (I) only is increased, the other fractions oscillating irregularly and variably. (I), (II), and (V) in the foetal blood are considerably increased, particularly in the umbilical artery, but lipin-PO₄''' is decreased, whilst (III) is the same for foetus and mother. R. N. C.

Diagnosis of pregnancy from the urine. W. HOFFMANN (Deut. med. Woch., 1934, 60, 822—824; Chem. Zentr., 1934, ii, 1148).—The growth of wheat or barley (I) is accelerated by urine (II) of pregnant women, and retarded or prevented by (II) of non-pregnant women. Flowering is not affected; in summer-(I) the H₂O-treated controls flower earlier. The effects are not destroyed by boiling the (II), nor by removing the nutritional salts by dialysis. R. N. C.

Influencing of the antidiuretic and chlorine-releasing action of the posterior pituitary hormone by the blood-serum of pregnant and non-pregnant women. (Posterior pituitary theory of pregnancy toxæmia.) W. BICKENBACH and H. RUPP (Arch. Gynakol., 1934, 155, 572—584; Chem. Zentr., 1934, ii, 792—793).—Mixtures of pituitrin (I) with sera of pregnant or non-pregnant women generally weaken or suppress the antidiuretic and Cl-releasing actions of (I), the pregnancy sera showing the greater effect. Sera of pre-eclampsia show the same property. R. N. C.

Experimental renal insufficiency produced by partial nephrectomy. III. Diets containing whole dried liver, liver residue, and liver extract. A. CHANUTIN (Arch. Int. Med., 1934, 54, 720—745).—A low-protein diet causes albuminuria and polyuria, with little retention of N and a delay of hypertension, whereas a high-protein diet causes an increased excretion of dil. urine (I). The amount of protein excreted has no relation to the vol. of (I). H. G. R.

Examination of urine in renal disorders. H. GIBBONS III (Arch. Int. Med., 1934, 54, 758—763).—The method shows the rate at which cells and casts are excreted in the urine (I). Tables are given showing the cells, casts, and protein in normal and pathological (I). H. G. R.

Colorimetric test for renal function using intravenous iodine preparations. R. H. HERBST and G. O. BAUMRUCKER (J. Urol., 1934, 32, 131—140).—After injection of Neoskiodan, I in urine is determined colorimetrically by oxidation with KNO_3 - H_2SO_4 and extraction with CHCl_3 . The method is applicable to any substance of the uroselectan group. CH. ABS. (p)

Effect of rickets on the structural characteristics of bone. G. L. CLARK and J. N. MRGUDICH (Amer. J. Physiol., 1934, 108, 74—79).—The X-ray diffraction pattern of rat humerus shows crystals oriented lengthwise in normal animals. In rachitic animals the collagen is broken down and no longer holds crystals in this position. CH. ABS. (p)

Comparison of the antirachitic action of methyl phosphates, glycerophosphates, and lecithin. R. LECOQ and M. L. BARBAN (Compt. rend. Soc. Biol., 1934, 117, 671—673).—The PO_4''' in Ca Me phosphate has an antirachitic activity (I) < that in Ca glycerophosphates, but with Mg the reverse is the case. The fatty acids and choline do not decrease the (I) of the glycerophosphate in egg-lecithin. A. L.

Antirachitic action of glycerophosphates. M. L. BARBAN (Compt. rend. Soc. Biol., 1934, 117, 999—1001).—The glycerophosphates of Na and Mg have a similar antirachitic activity, but that of the Ca salt is less. Their activities, however, are < that of the corresponding Me phosphates. A. L.

Chlorine and phosphorus contents of the brains of normal and starved guinea-pigs and of those suffering from chronic and acute scurvy. Magnesium content of striated muscle. A. MICHAUX (Compt. rend., 1934, 199, 1460—1462).—The Cl and P contents of the brain of normal and starved guinea-pigs (I) are the same, but increase during serious attacks of chronic or acute scurvy; the P content is affected only in prolonged cases. The Mg content of striated muscle of (I) does not decrease during scurvy, unless the muscle is very hæmorrhagic. R. S. C.

Blood-lipase and other conditions in tuberculosis. S. RYU (J. Chosen Med. Assoc., 1934, 24, 305—313).—In severe tuberculosis blood-lipase is reduced. CH. ABS.

Calcium, potassium, ultrafilterable calcium content, and the ratio of calcium to potassium in the blood in pulmonary tuberculosis. A. DE M. SARMIENTO and M. J. B. DA COSTA (Compt. rend. Soc. Biol., 1934, 117, 741—744).—Fibrous tuberculosis is associated with reduced vals. for ultrafilterable serum-Ca (I). Ultrafilterable serum-K (II) and (I) increase in amount as the disease progresses. Pulmonary tuberculosis, on the other hand, is associated with increased vals. for (I), (II), and ultrafilterable (I), the last decreasing, and the ratio (I)/(II) increasing

as conditions improve. As exudative tuberculosis develops, ultrafilterable (I) vals. increase. A. L.

Apparatus for measuring the gaseous metabolism of dogs. F. FOLDES (Biochem. Z., 1934, 275, 66—73).—A simple valveless apparatus for use under physiological conditions is described. The error is ± 3 to $\pm 4\%$. W. McC.

Metabolism of ducks (*Anas platythyncha*, L.). II. Gas metabolism and respiratory quotient. T. C. SHEN and S. M. LING. III. Carbohydrate metabolism. S. M. LING and T. C. SHEN (Chinese J. Physiol., 1934, 8, 307—333, 335—349).—II. After feeding, O_2 consumption and CO_2 production increase due to a conversion of carbohydrate into fat: R.Q. increases, reaching a max. in about 5 hr.

III. Liver-glycogen runs parallel with the R.Q. and a linear relationship was found between the glycogen (I) and the wt. of the liver (II). Of the total carbohydrate ingested, 54% is utilised for energy production, 24% for fat, and 22% is stored as (I), whilst 12% of the last amount is temporarily accumulated in (II). H. G. R.

Ability of fresh-water fish to extract oxygen at different hydrogen-ion concentrations. A. H. WIEBE, A. M. MCGAVOCK, A. C. FULLER, and H. C. MARKUS (Physiol. Zool., 1934, 7, 435—448).—In normal ranges of the initial O_2 content of the H_2O did not influence the O_2 content at death. Beyond normal p_{H} ranges O_2 concn. at death increased with the initial O_2 . CH. ABS. (p)

Effect of oxygen tension on oxygen consumption of a developing egg (*Orthoptera*). J. H. BODINE (Physiol. Zool., 1934, 7, 459—463).—With O_2 tensions (I) of 25—160 mm. Hg, O_2 consumption (II) of *M. differentialis* is independent of (I). With (I) < 25 mm., (II) declines rapidly. Eggs in diapause are stimulated to higher (II) by 380—760 mm. (I). CH. ABS. (p)

Iron content and oxidation rates of a developing egg (*Orthoptera*). J. H. BODINE and J. E. WOLKIN (Physiol. Zool., 1934, 7, 464—469).—The total Fe in eggs of *M. differentialis* is unchanged during development, but embryo-Fe (I) increases at the expense of yolk-Fe. During diapause O_2 consumption (II) is low and (I) is const. On resumed growth (I) increases with (II). The degree of saturation of the Fe is less in diapause than in active growth. CH. ABS. (p)

Calculation of the permeability of the cell surface to oxygen. N. RASHEVSKY (Physical Rev., 1933, [ii], 44, 322).—An attempt to calculate the permeability of the [living?] cell surface to O_2 from O_2 -pressure- O_2 -consumption curves at low pressures has been made. L. S. T.

Micro-determination of calorific value of foods. V. S. IVLEV (Biochem. Z., 1934, 275, 49—55).—The food is oxidised with excess of 0.1N- $\text{K}_2\text{Cr}_2\text{O}_7$ (3 vols.) and 0.1N- $\text{Ag}_2\text{Cr}_2\text{O}_7$ (1 vol.) in H_2SO_4 and the excess of $\text{H}_2\text{Cr}_2\text{O}_7$ is determined. Since protein (I) is not completely oxidised, a correction must be applied. Since the amount of heat produced on consumption of 1 g. of O_2 varies little when the proportions of food constituents [fat, carbohydrate, (I)] change, a

general "cal. coeff." is used to calculate the calorific val., but where the (I) content is unknown a N determination (micro-Kjeldahl) is made. W. McC.

Balanced diets, net energy values, and specific dynamic effects. H. H. MITCHELL (*Science*, 1934, 80, 558—561).—A discussion. L. S. T.

Permeability and ion concentration in muscle excitation. E. ERNST and J. FRICKER (*Pflüger's Archiv*, 1934, 234, 399—405).—Perfusion of a Laewen-Trendelenburg frog prep. with Ringer's solution with indirect stimulation of one gastrocnemius (I) does not alter muscle-K. With a solution with increased K:Ca ratio, which raises the permeability (II), muscles give off K on stimulation. In a KCl-rich perfusion solution, the stimulated (I) always contains less K than the unstimulated (I). Stimulation does not increase muscle-(II). R. N. C.

Permeability of frog's muscle under the influence of different substances involved in muscle metabolism. F. BECKMANN (*Pflüger's Archiv*, 1934, 234, 469—475).—The permeability (I) of the frog's abdominal muscle is steadily and reversibly increased by lactic acid, fructose, and Na fructose diphosphate, malonate, glycerophosphate, propionate, and citrate (II). The increase in (I) or the increased output of AcCO_2H (III) from breakdown in the muscle of all these substances except (II). (III) also increases (I). R. N. C.

Seasonal variations of the permeability and metabolism of the muscle of the cold-blooded animal. (Effect of creatine on the frog's muscle.) B. KATZ (*Pflüger's Archiv*, 1934, 234, 492—509).—The effect of creatine (I) on the muscle (II) is dependent on the season, and on the general metabolic condition of the (II) cells. In normal frogs, (I) is either ineffective or produces a passing relaxation of (II), and a marked increase in resting respiration, whilst in frogs with low carbohydrate reserve after hibernation, or in normal animals treated with toxic doses of insulin, (I) produces a contraction of (II), probably accompanied by an increased synthesis of creatinephosphoric acid. R. N. C.

Action of monophosphate on the blood and the circulation in physical work. A. KRESTOVNIKOV, A. KORJAKINA, E. KOSSOVSKAJA, P. RETELSKAJA, and S. SCHIROBOKOV (*Arbeitsphysiol.*, 1934, 13—19).—Administration of small doses of NaH_2PO_4 immediately prior to physical work causes a smaller rise of blood-lactic acid (I). Inorg. PO_4''' shows only an insignificant increase compared with controls (II); P is not raised by small doses. Blood-sugar shows no increase over that of (II). The alkali reserve is also unaffected. NaH_2PO_4 decreases production of leucocytes, but increases that of lymphocytes; there is no parallelism between the changes due to NaH_2PO_4 and the white-cell and chemical composition of the blood. NaH_2PO_4 accelerates resynthesis of (I) after work. R. N. C.

Influence of phosphate on the distribution of water and salts in muscular work. A. DANILOV, A. KORJAKINA, E. KOSSOVSKAJA, A. KRESTOVNIKOV, and A. FOMICHOV (*Arbeitsphysiol.*, 1934, 8, 1—

12).—Oral administration of NaH_2PO_4 increases the O_2 consumption in muscular work. The average losses of body-wt. and of H_2O through sweating are diminished. Diuresis is reduced more by small doses than by large doses. Blood-haemoglobin in most cases decreases. Blood-Cl is unaffected, but sweat-Cl falls, whilst urinary Cl rises. Large doses of NaH_2PO_4 administered 9—10 hr. before the work period have no effect. R. N. C.

Chemical reactions in muscle. J. K. PARNAS, P. OSTERN, and T. MANN (*Biochem. Z.*, 1934, 275, 74—86; cf. A., 1934, 1027, 1394).—Inorg. phosphate undergoes esterification in the absence of adenosinetriphosphoric acid in frog-muscle pulp poisoned with $\text{CH}_2\text{I}-\text{CO}_2\text{H}$. In such pulp phosphocreatine is synthesised from added phosphoglyceric acid (I), but not from added phosphate, and added creatine is phosphorylated. From (I) AcCO_2H is produced. A frog heart, poisoned with $\text{CH}_2\text{I}-\text{CO}_2\text{H}$, is kept beating by addition of (I). Many of the chemical changes which occur in muscle are depicted in a scheme which is in harmony with the views of Embden, Meyerhof, Lohmann, and the authors. The interacting substances frequently behave as sp. phosphate donors and acceptors. W. McC.

Mechanism of poisoning [of muscle] with iodoacetic acid. P. OSTERN (*Biochem. Z.*, 1934, 275, 87—89; cf. A., 1934, 1394).—In muscle pulp $\text{CH}_2\text{I}-\text{CO}_2\text{H}$ affects neither the production of hexose diphosphate and adenylic acid (I) from adenosinetriphosphoric acid (II) and glycogen nor the resynthesis of (II) from (I) and phosphocreatine, but it prevents the production of phosphoglyceric acid from fructose-diphosphoric acid. W. McC.

Decrease of glycolysis and increase of readily hydrolysable acid-soluble phosphorus in blood after prolonged fatiguing work. Z. DISCHE and K. SACHS (*Biochem. Z.*, 1934, 274, 346—357).—The glycolytic power of the blood of an adult dog after exhaustive work decreases, but of a growing dog may increase or decrease considerably. The concn. of readily hydrolysable acid-sol. P always increases, but not in amount corresponding with the decrease of glycolysis. The relationship of phosphorylation (I) of sugar, dephosphorylation of and subsequent (I) to adenosinetriphosphoric acid, and the velocity of glycolysis is discussed. P. W. C.

Influence of cortical hormone and ascorbic acid on the chemistry of active muscle. V. BAENA (*Biochem. Z.*, 1934, 274, 362—366).—The time required for complete exhaustion of rats in a treadmill under standard conditions (cf. A., 1934, 332) is greater when the animals receive both adrenal-cortex hormone (I) and ascorbic acid (II) and the decrease of glycogen at exhaustion is < when they receive (I) alone. The increase of residual N in fatigued muscle is almost completely inhibited by administration of (I)+(II). P. W. C.

Blood-lactic acid and oxygen consumption during and after muscular work in man. O. BANG (*Arbeitsphysiol.*, 1934, 7, 544—554).—The O_2 supply (I) during hard work of short duration, and at first during more prolonged work, is insufficient.

The greater part of the accumulated lactic acid (II) in the muscles is removed as soon as cessation of work increases (I), (II) being partly oxidised and partly reconverted into glycogen. A small part of (II) diffuses into the blood, from which it is afterwards taken up by the resting muscle or oxidised and resynthesised in the liver. This quantity of (II) is not always large enough to alter the O_2 consumption (III). The increased (III) during and after work depends chiefly on oxidation in the working and recovering muscles, and has no immediate quantitative relation with blood-(II). R. N. C.

Formation of pyruvic acid from lactic acid in muscle. E. AUBEL and E. SIMON (Compt. rend. Soc. Biol., 1934, 117, 658—659).—Chopped muscle in presence or absence of O_2 is capable of converting lactic acid into $AcCO_2H$. A. L.

First type of formation of lactic acid in the tissues in oxido-dynamic metabolism of hexoses: glucose and maltose. M. WIERZUCHOWSKI and F. SEKURACKI (Compt. rend. Soc. Biol., 1934, 117, 915—918).—Continuous intravenous injection of glucose or maltose results in an increase in the lactic acid (I) of the afferent and efferent blood-vessels of the liver, muscles, intestines, and head-tissues, the (I) being produced in all these except the liver, which retains it. Galactose does not produce this effect. This type of (I) formation is termed "hepatopetal." R. N. C.

Second type of formation of lactic acid in the organism during the combustion of hexoses, accompanied by specific dynamic action: fructose. M. WIERZUCHOWSKI and F. SEKURACKI (Compt. rend. Soc. Biol., 1934, 117, 919—922).—Continuous intravenous injection of 0.9% NaCl, inositol, Na lactate, or MeCHO does not alter the "hepatopetal" cycle of lactic acid (I) circulation. Fructose causes a formation of (I) which occurs chiefly in the liver, and is hence termed "hepatofugal." R. N. C.

Cellulose in the diet of rats and mice. C. M. MCKAY [with C. C. KU, J. C. WOODWARD, and B. S. SEHGAL] (J. Nutrition, 1934, 8, 435—447).—Rats receiving a diet containing 10—20% of cellulose (I) produced normal growth. The digestibility of crude fibre from beet pulp, bran, and regenerated (I) was 40, 20, 20%, respectively. Feeding of (I) increases faecal dry matter to an extent > can be ascribed to the amount ingested. A. G. P.

Exogenous melituria in man. B. G. EDWARDS and M. R. EVERETT (J. Nutrition, 1934, 8, 253—267).—Ingestion of toast results in urinary excretion of an unknown product which is neither dextrin (I) nor anhydro-sugar (II). After ingestion of glucose syrups (III) urine contains an unknown non-fermentable, reducing saccharide of low mol. wt., which occurs in the "isomaltose fraction" of (III). (I) and (II) have no relation to the hydrolysable sugar of normal urine. Uroketose is probably a product of intermediate metabolism. A. G. P.

Nutritive value of lactose. A. E. KOEHLER and S. E. ALLEN (J. Nutrition, 1934, 8, 377—383).—The gain in wt. of rats receiving a lactose diet was,

for a short time, slightly >, and subsequently definitely <, that with a glucose or sucrose diet. A loss of 40—50% of ingested lactose may occur in so far as wt. or energy relationships are concerned.

A. G. P.

Quantitative changes of glycogen in the liver of the foetus and of the new-born infant. S. MITANI (Trans. Japan. Path. Soc., 1933, 23, 245—247). CH. ABS.

Available carbohydrate of fruits. Determination of glucose, fructose, sucrose, and starch. E. M. WIDDOWSON and R. A. McCANCE (Biochem. J., 1935, 29, 151—156).—The glucose (I), fructose (II), sucrose (III), and starch (IV) contents of 41 varieties of fresh fruit have been determined. All fruits (except bananas) contain negligible amounts of (IV). Most fruits contain approx. equal amounts of (I) and (II). Cherries, grapes, figs, tomatoes, pomegranates, and mulberries contain no (III), whilst (III) is the chief sugar present in apricots and peaches. (II), but not (I), is partly destroyed by boiling 5% HCl. A. E. O.

(A) **Absorption by intact organs of glucose, maltose, and galactose injected at constant rate into the blood-stream.** (B) **Assimilation by the organs of fructose introduced into the blood-stream at constant rate.** M. WIERZUCHOWSKI and H. FISZEL (Compt. rend. Soc. Biol., 1934, 117, 1019—1022, 1022—1025).—(A) A comparison is made of the carbohydrate content of the femoral blood-vessels, the portal and hepatic veins, and the carotid artery and jugular vein of dogs during fasting (I) and during the continuous separate injection of glucose (II), maltose (III), and galactose (IV) at const. rate. During (I) the liver produces considerable quantities of (II), whilst the other organs, particularly the head, absorb it. In the head 13%, and in the muscles 48%, of (II) taken up is converted into lactic acid. Whereas during injection of (II) and (III) the muscles absorb the greatest amount of (II) and the intestine least, during (IV) the absorption in the head is greatest and that in the intestine least.

(B) The (II) balance of the blood-vessels of fasting dogs is unaffected by the introduction of physiological salt solution, Na lactate, MeCHO, and inositol into the blood-stream. When fructose (V) is injected, the organs arranged in order of decreasing absorption of (V) are the liver, the muscles, the intestine, and the head. The liver produces (II) at its normal rate, and whilst the head absorbs (II) it does not stop the circulation of (V). A. L.

Balance of water in the organs during the injection of carbohydrates and related substances. M. WIERZUCHOWSKI and H. FISZEL (Compt. rend. Soc. Biol., 1934, 117, 1025—1028).—A comparison is made of the haemoglobin content of the blood-vessels of the liver (I), muscles (II), intestine (III), and head (IV) of dogs during fasting (V) and during the separate continuous injection (under amytaesthesia) of 2 g. per kg. per hr. of physiological salt solution, Na lactate, MeCHO, inositol, glucose, maltose, and galactose (VI). During (V) and with all the injections except (VI) the haemoglobin content of the blood from (I), (II), and (III) is

increased; that from (IV) is almost unchanged. In general the increase is < that during (V). No relationship could be established between the actual vals. obtained and the amount of assimilation or the lactic acid production of the organs. A. L.

Specific dynamic action and oxidation of hexoses introduced into the circulation of amytal-anæsthetised dogs. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1934, 117, 909—912).—The sp. dynamic actions, mol. heats of oxidation, and R.Q. for glucose, fructose, and maltose in dogs are of the same order, and are not altered in amytal anæsthesia.

R. N. C.

Intravenous assimilation of hexoses in narcosis provoked by amytal. M. WIERZUCHOWSKI and H. FISZEL (Compt. rend. Soc. Biol., 1934, 117, 913—915).—Narcosis (I) raises slightly the % of glucose (II) and maltose (III) assimilated from the blood, the non-assimilated (III) being excreted partly as (II). With fructose (IV), the % assimilated is reduced by (I). Exposure of the blood-vessels and withdrawal of samples of blood during (I) reduces the % assimilation considerably for (II) and (III), but only slightly for (IV). Galactose is assimilated only moderately, (I) showing the same effects as for (II) and (III), whilst inositol is not assimilated.

R. N. C.

Carbohydrate metabolism of the liver. IV. Sugar output in amytalised cats. C. TSAI and C. L. YI (Chinese J. Physiol., 1934, 8, 399—409).—The concn. of hepatic sugar (I) was > that of the portal (I) and of the arterial (I). During amytalisation the (I) output does not materially increase, and the fall in liver-glycogen is due to inhibition of glycogen formation.

H. G. R.

Carbohydrate metabolism at high altitudes. II. Action of adrenaline (and content of K and Ca in the blood). V. F. MADON and E. SAPEGNO (Atti R. Accad. Lincei, 1934, [vi], 20, 119—125; cf. A., 1932, 885).—With individuals acclimatised on high mountains, the rapidity of action of adrenaline on the equilibrium conditions of the carbohydrates is increased, as is that of the reaction of the organism to the consequent hyperglycæmia. No definite modification in the concns. of K⁺ and Ca⁺⁺ in the serum is detectable.

T. H. P.

Biological oxidation of inositol. B. C. GUHA and N. DAS (Current Sci., 1934, 3, 157—158).—Oxidation of inositol *in vitro* at p_H 7.4 and 37.3° is effected by brain, heart muscle, kidney, and (more slowly) liver tissue of adult albino rats fed on a standard mixed diet.

J. W. B.

Control of carbohydrate metabolism by the kidney. H. MIYAZAKI (J. Chosen Med. Assoc., 1934, 24, 1—22).—The epithelial cells of the urinary tubes secrete a hormone, of the nature of sterol, which controls carbohydrate metabolism by increasing the combustion of glucose by the tissue. CH. ABS.

Significance of coupled reactions of lower aliphatic compounds for carbohydrate and fat degradation. R. MEIER and K. BALLOWITZ (Z. physiol. Chem., 1934, 230, 122—138).—Oxidation (O₂) of glyceraldehyde (I) to CO₂ in phosphate buffer

(II) (p_H 7.4) in absence or presence of Cu (cf. Wind, A., 1925, ii, 1174) proceeds with a R.Q. of 0.2—0.3. The rate of oxidation of (I) in (II) + 0.0004M-CuSO₄ is increased by addition of (CHO)₂ (III) and is max. with 20 mols. (30—40 mols. cause almost complete inhibition); the R.Q. is 0.37 and 1.14 with 1 mol. and 16 mols., respectively, of added (III). (III) alone is not oxidised in (II). The amount of CO₂ produced is not \propto added (III). Similar increased oxidation occurs when CHO·CO₂H (IV) or AcCO₂H (V) is added to (I). (III) or (IV) also causes increased oxidation of CO(CH₂·OH)₂. Oxidation of (I) is retarded by EtCO₂H, PrCO₂H, OH·CHMe·CH₂·CO₂H (VI), or valeric acid. Glyceric, crotonic, and glycollic (VII) acids, (·CH₂·OH)₂ (VIII), glycerol (IX), and crotonaldehyde have no effect. Oxidation of (I)+(III) is unaffected by added EtOH or (IX), but oxidation of (I)+(V) is retarded by (IX) (not by EtOH). Oxidation of AcCHO is increased by (V) and retarded slightly by (VII), (VIII), or (VI). Oxidation of fructose is greatly retarded by (III), (IV), or (V). Biological oxidations of carbohydrates are undoubtedly influenced by the formation of trioses as intermediate products.

H. B.

Effect of a high-fat meal on the respiratory quotient and heat production of normal and obese individuals. B. D. BOWEN, F. R. GRIFFITH, jun., and G. E. SLX (J. Nutrition, 1934, 8, 421—434).—The post-absorptive R.Q. was in obese < in normal subjects. The sp. dynamic action of the fat was similar in both cases, but was greater in obese diabetic individuals.

A. G. P.

Seasonal variation in butter-fat. II. Seasonal spectroscopic variation in the fatty acid fraction. R. G. BOOTH, S. K. KON, W. J. DANN, and T. MOORE (Biochem. J., 1935, 29, 133—137).—Fatty acids (I) from summer butter-fat (II) always show an absorption at 230 m μ > twice as intense as that of (I) from winter (II) (cf. A., 1933, 1087). This increase \propto increased inhibiting power (III) of the fat in the SbCl₃ reaction for vitamin-A, but the substances responsible for (III) are much more sensitive to oxidation and irradiation than those responsible for increased absorption.

A. E. O.

New spectroscopic phenomenon in fatty acid metabolism. Conversion of "pro-absorptive" into "absorptive" acids in the cow. W. J. DANN, T. MOORE, R. G. BOOTH, J. GOLDING, and S. K. KON (Biochem. J., 1935, 29, 138—146).—When cod-liver, sardine, rape, or linseed oil is fed to cows in the winter, the resulting butter-fat (I), although somewhat less in relative amount, shows absorption at 230 m μ much > in summer. *In-vivo* conversion of "pro-absorptive" into "absorptive" fatty acids has taken place, not accompanied by a fall in the I val., i.e., not caused by oxidation of unsaturated "pro-absorptive" acids (II). Prolonged boiling of (II) from these oils with EtOH-KOH also results in a similar increase in absorption, but similar treatment shows that "absorptive" winter (I) contains no "pro-absorptive" acids. Ingested foreign fats are very rapidly secreted in the milk.

A. E. O.

Fat metabolism. V. Degradation of unsaturated fatty acids in man. P. E. VERKADE and J. VAN DER LEE (*Z. physiol. Chem.*, 1934, **230**, 207—215).—After ingestion of tri- Δ^4 -undecenoïn (which may cause mild nephritis) together with adequate carbohydrate, sebaceous acid is excreted in the urine; direct oxidation at the double linking thus occurs. Definite decomp. products were not isolated after ingestion of olive and rape oils. H. B.

Fat metabolism in fishes. IV. Mobilisation of depot-fat in the salmon. V. Fat of the salmon in its young fresh-water stages. J. A. LOVERN (*Biochem. J.*, 1934, **28**, 1955—1960, 1961—1963).—IV. Compared with other fish-fats, salmon body-fats exhibit low palmitoleic acid (I) content and high content of C_{22} acids, and low degree of unsaturation of C_{20} acids. Mobilisation of the depot-fat (II) is almost non-selective in the females, but in the males acids of low mol. wt. are preferentially mobilised and the (I) content falls steadily. Ova-fat is more unsaturated than (II), and a high degree of selectivity is displayed in its formation.

V. In the parr stage, the fat of the young salmon is of the fresh-water type (III), but the fat of the smolt appears to be at a transitional stage between (III) and the special fat of the adult salmon. A. E. O.

Variation in nutritive properties of skimmed milk with habituation to milk-assimilation. P. MAZE, P. J. MAZE, jun., and R. ANXIONNAZ (*Compt. rend. Soc. Biol.*, 1934, **117**, 751—752).—Rats fed for a long period on a complete diet including normal or skimmed milk (I) are able to synthesise the vitamins (II) necessary for fertility when fed on diets containing (I) but deficient in (II), which apparently occur as precursors in (I). Oxidation (CI) or ultra-violet irradiation partly corrects the deficiency of (I). F. O. H.

Assimilation of albumin by normal dogs and dogs with Eck fistulæ. S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (*Compt. rend. Soc. Biol.*, 1934, **117**, 1088—1090).—Dogs with Eck fistulæ show increases in total non-protein-, urea-, NH_2 -acid-, and NH_3 -N (I) after ingestion of ovalbumin. Normal dogs show only a slight increase of (I). R. N. C.

Effect of feeding carrot on rat serum-protein. A. L. BLOOMFIELD (*J. Exp. Med.*, 1934, **59**, 687—698).—On exclusively fresh carrot diet serum-protein falls; a similar effect is produced by carrot powder only after addition of H_2O and agar. CH. ABS.

Synthesis of creatinine and creatine during protein starvation. G. MOUROT (*Compt. rend.*, 1934, **199**, 1341—1343).—Examination of creatinine (I) excretion during protein starvation confirms the synthesis of considerable amounts of (I) under these conditions. Creatine disappearing from the organism (rat) appears as (I) in the urine. A. G. P.

Measurement of creatinine clearance. R. F. HANZAL and J. M. HAYMAN, jun. (*Proc. Soc. Exp. Biol. Med.*, 1934, **31**, 730—733).—After administration of creatinine, dil. urine and blood-plasma are treated with picric acid and centrifuged. The clear liquids are mixed with NaOH and compared colorimetrically. CH. ABS. (p)

Metabolism of *l*- and *dl*-cystine in growing dogs maintained on diets of various protein content. J. A. STEKOL (*J. Biol. Chem.*, 1934, **107**, 641—648).—*l*-Cystine-S is practically completely oxidised and excreted as inorg. $SO_4^{''}$ in the urine of pups maintained on Cowgill's diet. Much of the S is retained by pups on other diets. *dl*-Cystine fed to pups on low-protein diets is not so well retained, much of the S appearing in the urine as neutral S. *l*-Cystine may be used as an indicator of the min. protein requirement for growth and maintenance of dogs. C. G. A.

Effect of fasting, refeeding, and variations in the cystine content of the diet on the composition of the tissue-proteins of the white rat. W. C. LEE and H. B. LEWIS (*J. Biol. Chem.*, 1934, **107**, 649—659).—Neither fasting nor subsequent refeeding results in significant change of the composition of the muscle or kidney of growing or adult rats, or the proteins of these tissues. The N and S of the livers increased after fasting, but the change is not due to alteration of the composition of the liver-proteins. The S of all tissues is higher in young rats receiving adequate cystine (I) than in those receiving a deficiency of (I), although the composition of the proteins is the same in each group, the excess being due to non-protein-S. C. G. A.

Urea formation in the liver. H. A. KREBS (*Z. physiol. Chem.*, 1934, **230**, 278—279; cf. A., 1932, 1059).—The conclusions of London *et al.* (A., 1934, 1392) are not in agreement with their results. H. B.

[Urea formation in the liver.] E. S. LONDON (*Z. physiol. Chem.*, 1934, **230**, 279).—A reply to Krebs (preceding abstract). H. B.

Factors in cellular multiplication. P. JOYET-LOVERGNE (*Compt. rend.*, 1934, **199**, 1339—1341).—The function of glutathione and vitamin-A in the growth, reproduction, regeneration, and proliferation of cellular tissue is discussed. A. G. P.

Effect of variations in the diet on absorption of food in absence of pancreatic digestion. M. B. HANDELSMAN, L. A. GOLDEN, and J. H. PRATT (*J. Nutrition*, 1934, **8**, 479—495).—After exclusion of pancreatic juice from the intestine dogs absorbed large proportions of ingested foods including fats, although faecal N and fat were abnormally high. Gains in body-wt. resulting from increased diets are influenced by factors other than the amounts of ingested fat, carbohydrate, and protein. A. G. P.

Action of prolonged administration of food grown with and without artificial manuring. A. SCHEUNERT, M. SACHSSE, and R. SPECHT (*Biochem. Z.*, 1934, **274**, 372—396).—Rats fed on a diet of which the materials had received artificial manuring during growth were superior in fertility and length of life to others receiving food grown without such fertilisers. P. W. C.

Method of partial regression in analysis of comparative feeding trial data. II. E. W. CRAMPTON and J. W. HOPKINS (*J. Nutrition*, 1934, **8**, 329—339).—Interpretation of statistical analyses is discussed. A. G. P.

Inorganic salts in nutrition. X. Electrolyte balance in the serum of rats receiving a diet deficient in inorganic constituents. A. H. SMITH and P. K. SMITH. **XI. Changes in composition of the whole animal induced by a diet poor in salts.** A. E. LIGHT, P. K. SMITH, A. H. SMITH, and W. E. ANDERSON (*J. Biol. Chem.*, 1934, **107**, 681—688, 689—695).—X. Animals receiving only 0.32 milliequiv. of base per day maintain a normal electrolyte balance in the serum, but cease to gain wt., take in less food, and excrete NH_3 in the urine instead of fixed base.

XI. In rats on salt-poor diets (I) there is loss of fat, little or no change of ash content, slight increase of protein, and slight loss of Ca, Mg, and P. There is no appreciable loss of Na or Cl. Compared with animals of the same age on an adequate diet rats on (I) have lower Ca, P, and Ca : P ratio. C. G. A.

Significance of phosphatase determinations in the adult fowl. D. W. AUOHINACHIE and A. R. G. Emslie (*Biochem. J.*, 1934, **28**, 1993—2001).—It is suggested that the plasma-phosphatase activity of normal hens may be little affected by egg-laying, but that marked changes may be expected in cases of vitamin-D or Ca deficiency. Anomalies are discussed.

C. G. A.

Results of ingestion of cod-liver oil and yeast on calcium and phosphorus metabolism of women. H. A. HUNSCHER, E. DONELSON, B. N. ERICKSON, and I. G. MACY (*J. Nutrition*, 1934, **8**, 341—346).—Retention of Ca and P was not consistently affected by feeding cod-liver oil or yeast.

A. G. P.

Salivary glands and calcium metabolism. T. MATSUO (*Trans. Japan. Path. Soc.*, 1933, **23**, 254—257).—Serum-Ca was increased by extirpation of the parotid gland, and decreased by injection of parotid venous blood-serum.

CH. ABS.

Calcium metabolism of the foetus. T. MATSUO (*Trans. Japan. Path. Soc.*, 1933, **23**, 257—261).—Foetal blood is higher in Ca than the blood of the mother or of the umbilical cord.

CH. ABS.

Calcium in the foetal liver of the calf in embryonic development. G. ROUSSEL and Z. GRUZEWSKA (*Compt. rend. Soc. Biol.*, 1934, **117**, 863—864).—Liver-Ca rises to max. in the 4th and 8th months of gestation, afterwards falling to normal.

R. N. C.

Iron metabolism. III. T. KOSUZI, K. UMEDA, E. LEE, S. TACHIBANA, and C. LEE (*Trans. Japan. Path. Soc.*, 1933, **23**, 203—205).—Oral administration of Fe compounds accelerates the metabolism through the entero-hepatic circulation.

CH. ABS.

Relation between salts and acidosis. G. SUZUKI (*Aichi Ig. Zasshi*, 1933, **40**, 1152).—No relationship was apparent between acidosis (I) alkalosis, and serum-Cl'. Production of (I) by lowered NaCl consumption results from smaller intake of Na rather than of Cl'. In the Gerson and other treatments (I) is due to the low carbohydrate and high fat contents of diet and not to absence of NaCl.

CH. ABS. (p)

Effect of feeding raw rock phosphate on the fluorine content of the organs and tissues of

dairy cows. C. Y. CHANG, P. H. PHILLIPS, and E. B. HART (*J. Dairy Sci.*, 1934, **17**, 695—700).—All tissues examined contained F, max. proportions occurring in bones (I) and teeth (II). Ingestion of F (in rock phosphate) increased the storage of F in (I) and (II) (16—25 times normal) and in internal organs, tendons, and hair (twice normal).

A. G. P.

Iodine metabolism. III. T. YUZURIHA (*Trans. Japan. Path. Soc.*, 1933, **23**, 96—100).—In the control of I metabolism the reticulo-endothelial system and the thyroid are synergetic; the former is the more important.

CH. ABS.

Heavy water in the animal body. E. J. McDOUGALL, F. VERZAR, H. ERLÉNMEYER, and H. GAERTNER (*Nature*, 1934, **134**, 1006—1007).—Using H_2O as indicator, it has been shown that H_2O injected into fasting rats is distributed throughout the body in 1 hr.

L. S. T.

Dosage above the pharmacopoeial maximum. A. F. HURST (*Lancet*, 1934, **227**, 1379—1383).—A lecture.

L. S. T.

Hypoglycæmic action of yeast extracts, especially the relation of yeast extracts to true hormones. I. Influence of yeast extract on normal and adrenaline blood-sugar balance. II. Relation between the effect produced on blood-sugar by yeast extract and insulin : influence of the thyroid. K. MAEHARA (*Folia Endocrinol. Japon.*, 1934, **9**, 34—35, 36).—I. Aq. and acid (0.5% HCl) EtOH extracts of yeast lower the blood-sugar level. Adrenaline hyperglycæmia is retarded.

II. Insulin hypoglycæmia is increased by injection of extracts. Hypoglycæmia resulting from injection of extracts is checked by feeding thyroid and increased by thyroidectomy.

CH. ABS. (p)

Blood-sugar variations in rabbits poisoned by ingestion of carbon tetrachloride. P. M. DERVILLE and R. CASTAGNOU (*Compt. rend. Soc. Biol.*, 1934, **117**, 365—367).—Ingestion of CCl_4 produced considerable hypoglycæmia during the first day, followed by slow recovery if the animal survived.

R. N. C.

Modifications of blood-sugar and liver-glycogen in splenectomised animals. D. ZORZI (*Arch. Farm. sperim.*, 1934, **58**, 253—269).—Blood-sugar in rabbits rises irregularly to a max. at the end of the 1st month after splenectomy (I), thence falling very gradually to normal at the end of the 5th month. The alimentary glycæmic curve (II) is normal 5 days after (I); at 20 days from (I) it falls to a min. at the 2nd hr. after feeding, afterwards rising to its original val. At 30 days from (I) the fall is still greater and is preceded by a slight rise, which is more pronounced at 60 days, (II) afterwards tending to return to normal. (II) provoked by injection of adrenaline or glucose is not altered by (I). Liver-glycogen falls in the first few days from (I), afterwards rising to > normal.

R. N. C.

Effect of hepatic denervation on the stability of liver-glycogen. P. DEMANT (*Compt. rend. Soc. Biol.*, 1934, **117**, 323—326).—Hepatic denervation reduces liver-glycogen (I) and the hyperglycæmia (II)

provoked by ingestion of glucose. Splanchnic section reduces (I) but raises (II); (I) disappears entirely if the adrenal nerve supply is interfered with. Glycosuria does not occur. R. N. C.

Influence of hepatic stimulation on exogenous and endogenous hypercholesterolaemia in the rabbit. M. ECK and J. DESBORDES (Compt. rend. Soc. Biol., 1934, 117, 681—683).—Hypercholesterolaemia (I) induced in rabbits by administration of a lipin-rich diet was increased by injection of the extract of *Cynara scolymus* (II). (I) induced endogenously by adrenaline injection was reduced by (II). A. L.

Choline and the "cholesterol" fatty liver. H. J. CHANNON and H. WILKINSON (Biochem. J., 1934, 28, 2026—2033).—Feeding choline (I) does not cure the "cholesterol" fatty liver of rats previously fed on a diet containing fat and 2% of cholesterol. (I) has no obvious effect in causing a decrease of any of the lipid constituents except the glyceride fraction. C. G. A.

Lecithin, kephalin, and duration of hæmorrhage. J. ROSKAM and S. COMHAIRE (Compt. rend. Soc. Biol., 1934, 117, 802—804).—Injection of lecithin, free from kephalin (I) and allied substances, into rabbits increases the duration of bleeding by 30—50%, whilst injection of (I) decreases it by approx. 30% (cf. A., 1922, i, 697). F. O. H.

Influence of hydrogen- and hydroxyl-ion concentration on intestinal tonus. M. TIFFENEAU and D. BROWN (Compt. rend. Soc. Biol., 1934, 117, 1002—1004).—The inhibiting action of adrenaline and atropine on the isolated guinea-pig intestine increases as decreases, and inversely. On the other hand, the accelerating effect of acetylcholine, pilocarpine, histamine, anterior pituitary extract, and BaCl_2 decreases as p_{H} decreases, and inversely. A. L.

Chemical transmitter at synapses in a sympathetic ganglion. W. FELDBERG and J. H. GADDUM (J. Physiol., 1934, 81, 305—319).—The superior cervical ganglion of a cat, perfused with Locke solution containing eserine, liberated acetylcholine (I) on stimulation of the cervical sympathetic. Liberation of (I) forms the mechanism by which nerve impulses pass the synapse. CH. ABS. (p)

Chemical transmitter of vagus effects to the stomach. H. H. DALE and W. FELDBERG (J. Physiol., 1934, 81, 320—334).—Acetylcholine (I) acts as the chemical transmitter of vagus effects to the stomach. Following injection of eserine and stimulation of the vagi to cause contractions of the stomach wall (II) the (I) content of venous blood from (II) increases by 400%. CH. ABS. (p)

Appearance of an acetylcholine-like substance in the portal blood of the cat. I. DONOMAE (Pflüger's Archiv, 1934, 234, 318—324).—On injection of eserine (I) or prostigmine, an acetylcholine-like action in the portal blood can be demonstrated by contraction of leech muscle in Ringer's solution, or by its depressor effect, inhibited by atropine. Larger quantities of (I) produce the same effect to a small extent in the vena iliaca. R. N. C.

Appearance of an acetylcholine-like substance in the perfusion-liquid from perfusion of the isolated small intestine of the cat. W. FELDBERG and H. KWIATKOWSKI (Pflüger's Archiv, 1934, 234, 333—341).—Perfusion of the isolated intestine with physiological NaCl solution gives no result, but if eserine (I) is added an acetylcholine (II)-like substance, destroyed by alkali but not by acid, and possibly (II) itself, can be detected in the emergent liquid. On re-perfusion with NaCl the effect decreases after 20—25 min. (II) added to the perfusing solution without (I) is destroyed in the intestine, so that the action of (I) is to inhibit the tissue-esterase without causing (II) production. Nicotine has no effect on (II) production. R. N. C.

Substance sensitising muscle to acetylcholine formed in the vagus nerve by electrical excitation. L. BINET and B. MINZ (Compt. rend. Soc. Biol., 1934, 117, 1029—1031).—Electrical excitation of a piece of the vagus nerve isolated from a dog causes the liberation of a thermostable and oxidisable substance which sensitises the dorsal muscle of the leech to the action of acetylcholine. A. L.

Biological significance of the linkings in adenosinetriphosphoric acid. J. H. GILLESPIE (J. Physiol., 1934, 80, 345—359).—The action of the acid on heart and uterus of guinea-pigs is > that of any of its derivatives. Removal of PO_4''' from the mol. affects its activity < deamination. Scission of pentose from the purine base destroys biological activity. CH. ABS. (p)

Micro-determination of ethyl alcohol in organs. O. MOLLESTAD (Biochem. Z., 1935, 275, 136—146).—By using a special flask in which solid matter is finely ground the procedure of Widmark (A., 1922, ii, 789) is made applicable to the determination of EtOH in organs. W. McC.

Alcohol. II. Concentration in blood. M. SCHMIDT (J. Ind. Hyg., 1934, 16, 355—365).—Typical curves of the changes in blood-EtOH (I) after ingestion of EtOH (0.6 c.c. per kg. body-wt.) by habitual users (II) and abstainers (III) are given. Max. vals. (0.04—0.08%) of (I) are attained more rapidly with (II) than with (III) (average times of approx. 36 and 48 min., respectively), whilst a return to normal levels generally occurs within 4—5 hr. for both (II) and (III). The psychological effects of EtOH are related to (I). F. O. H.

Concentrations of ethyl alcohol in the blood and its rate of oxidation in the organism. E. LE BRETON (Compt. rend. Soc. Biol., 1934, 117, 707—709).—The equations of Widmark for determining the quantity of EtOH oxidised by man can be applied to the rat, but not to the rabbit. Vals. of β (decrease in $[\text{EtOH}]$ per min.) and r (total $[\text{EtOH}]/[\text{EtOH}]$ in blood) are const. for the individual animal and the species, respectively. A. L.

Rate of diffusion of ethyl alcohol in the organism. E. LE BRETON (Compt. rend. Soc. Biol., 1934, 117, 704—707).—Determinations are made of the decrease (I) with time in $[\text{EtOH}]$ after injection of animals with EtOH, and when (I) becomes const. for unit time equilibrium (II) is assumed to be

attained. The time taken for (II) to be reached is used as a basis for the comparison of the rates of diffusion of EtOH in rats, mice, and rabbits according to the method of administration. The order of decreasing [EtOH] in the organs is always the same, namely, blood, brain, carcase, liver. A. L.

Influence of diet on the rate of oxidation of ethyl alcohol. E. LE BRETON (Compt. rend. Soc. Biol., 1934, 117, 709—712).—Rabbits receiving EtOH after ingestion of Witte peptone or alanine oxidise more EtOH per kg. of body-wt. than fasting animals or those having received glucose. A. L.

Barbiturates. II. Methods of barbital research. T. KOPANYI, J. M. DILLE, W. S. MURPHY, and S. KROP (J. Amer. Pharm. Assoc., 1934, 23, 1074—1079).—Improved methods of extraction from urine, blood, and tissues are described. Colorimetric methods of determination using $\text{Co}(\text{OAc})_2$ and LiOH , $\text{Ba}(\text{OH})_2$, or NH_2Pr^s are equally sp., the only other CHCl_3 -sol. substances showing positive tests being theobromine, theophylline, thymine, and lecithin. The micro-test (using LiOH) can be performed only in CHCl_3 solution. A. E. O.

Hæmatological changes produced by poisoning with barbiturates. R. E. CARRATALA (Semana méd., 1934, II, 402—405).—Chemical changes include decreased Ca, Mg, and P and increased NaHCO_3 in the blood. CH. ABS. (p)

(A) **Prolongation of narcosis by piperidino-methylbenzdioxan and related derivatives.** D. BOVET and A. SIMON. (B) **Central analgesic and sedative action of the aminomethylbenzdioxans, aminocoumarans, and phenoxyethylamines.** D. BOVET, A. SIMON, and F. DEPIERRE (Compt. rend. Soc. Biol., 1934, 117, 958—960, 961—963).—(A) Preliminary injection of piperidino- (I) and diethylamino-methylbenzdioxan (II) prolong the narcosis in rabbits produced by paraldehyde and Na 5-cyclohexyl-1-methylbarbiturate. The duration of anæsthesia produced by Na tetrathylbarbiturate in sticklebacks is increased by (II) and particularly by allyaminomethylbenzdioxan (III). The aminocoumarans are also active in this respect, especially the O-OMe-derivatives; $\text{NEt}_2\text{CH}_2\text{CH}_2\text{OPh}$ is inactive, although $\text{NEt}_2\text{CH}_2\text{CH}_2\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ is active.

(B) (I) and its related derivatives, particularly the coumarans, possess comparable analgesic properties; diethylaminophenetole is, however, inactive. (I) diminishes the emetic action of apomorphine and digitalis. (I) and (III) injected into rabbits at the base of the fourth ventricle cause a pronounced narcosis indicating that their action is of central origin. A. L.

"Adrenolytic" action of a dioxan derivative (933F). Z. M. BACQ and H. FREDERICQ (Compt. rend. Soc. Biol., 1934, 117, 806—808).—The typical reactions of adrenaline in the organism are inhibited by administration of 933F (2-piperidylmethylbenzdioxan hydrochloride), the action of which is better described as "adrenolytic" than as sympathicolytic." F. O. H.

Phenolsulphonates in the urine of dogs. Y. VARREAU (Compt. rend. Soc. Biol., 1934, 117, 683—

685).—Examination of the urine of dogs, injected with PhOH, for phenolsulphonates gave negative results. A. L.

Denervated kidney. II. Action of sodium salicylate on uric acid, allantoin, sodium chloride, and total nitrogen excretion in dogs. M. G. GRAY and G. P. GRABFIELD (J. Pharm. Exp. Ther., 1934, 52, 383—389; cf. A., 1934, 324).—Section of the renal nerves (I) depresses the increased excretion of N, has no effect on the allantoin output, and decreases the uric acid output produced by Na salicylate (II). (I) has no effect on the changed vol. : [Cl⁻] relationship produced by (II). H. D.

Action of various hyperthermic agents on the respiration of cells of starfish tissues. P. CREAC'H (Compt. rend. Soc. Biol., 1934, 117, 367—368).—Respiration is increased by basic vital stains (I) of $rH > 8$, and decreased by (I) of $rH < 8$, and acid indigo stains. It is scarcely affected by 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$ (II), but increased by reduced (II), whilst Me-blue reduces it. R. N. C.

Action of vital stains and nitrophenols on the respiration of oyster-tissues and blood-cells of Sipunculus. M. CHAPHEAU (Compt. rend. Soc. Biol., 1934, 117, 370—371).—Vital stains of $rH > 8$ increase the respiration, whilst those of $rH < 8$ have no effect. 2:5- (I) and 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$ (II), when reduced, increase the respiration of the blood-cells of *Sipunculus*; unreduced (I) is ineffective, and unreduced (II) acts only very slowly. Oyster-tissues are not affected by (I) or (II), either normal or reduced. R. N. C.

Elimination of theobromine and caffeine from the circulation. R. A. HATCHER and N. T. KWIT (J. Pharm. Exp. Ther., 1934, 52, 430—436).—Immediately after the injection of caffeine (I) or theobromine (II) the concns. of (I) and (II) in the blood fall rapidly and more slowly after 5 min. The concns. of (I) and (II) 30 min. after administration are the same whether given intravenously or orally. H. D.

Action of certain alkaloids on the physiological polarity of infusoria. A. SERFATY (Compt. rend. Soc. Biol., 1934, 117, 1077—1079).—The polarity is reversed by choline, pilocarpine, and atropine in decreasing order of potency. R. N. C.

Curarising poisons and muscular fatigue. O. DEHENNOT (Compt. rend. Soc. Biol., 1934, 117, 318—320).—Curaro has no effect on the fatigue of frogs' muscles, sparteine raises the fatiguability (I) in doses < the min. curarising dose (II), whilst KCl does not affect it in doses < (II). Eserine in (II) increases (I) in respect to indirect excitation (III); with direct (III) variable results are obtained. Results are compatible with the hypothesis of acetylcholine formation by nervous (III). R. N. C.

[Pharmacology of] morphine, codeine, and derivatives. VII. **Dihydromorphine (paramorphin), dihydromorphinone (dilaudid), and dihydrocodeinone (dicodide).** N. B. EDDY and J. G. REID (J. Pharm. Exp. Ther., 1934, 52, 468—493).—The effects of hydrogenation and methylation of the phenolic OH, and of the introduction of the keto-CO in morphine and codeine are in accordance

with the rules which hold for the other alkaloids studied (A., 1934, 805). H. D.

Morphine acidosis. N. RAKIETEN, H. E. HIMWICH, and D. DUBOIS (J. Pharm. Exp. Ther., 1934, 52, 437—444).—Dogs given 25 mg. per kg. body-wt. of morphine sulphate showed a decrease of blood- p_H of approx. 0.2 unit accompanied by an increased serum- CO_2 , - d , and -total solids, and a decreased alkaline reserve. No changes were produced in the lactic acid, total base, or $[Cl^-]$ of the blood. H. D.

Changes in the physical and chemical characteristics of the blood-sera of opium addicts. R. N. CHOPRA and S. N. MUKHERJI (Current Sci., 1934, 3, 201—202).—In opium addicts, the p_H of blood-serum is near the lower limit of normal Indian adults and the buffer action is lowered. η is diminished and σ is increased. The albumin fraction and euglobulin content are increased, whilst pseudoglobulin and total proteins are < normal. L. S. T.

Blood-sugar of opium addicts. S. CHO (Folia Pharmacol. Japon., 1934, 17, No. 2, 230—242).—Vals. are normal, but rise slightly during abstinence. Adrenaline produces greater hyperglycaemia in addicts during abstinence. Pilocarpine has the usual effect; atropine sometimes lowers and again slightly raises blood-sugar. CH. ABS.

Effects of intravenous injections of colloids. I. Deposition of acacia in the liver and other organs and its excretion in urine and bile. M. ANDERSCH and R. B. GIBSON (J. Pharm. Exp. Ther., 1934, 52, 390—407).—In rabbits 50% of the total acacia (I) injected intravenously was recovered in the livers; in dogs about 30%. (I) is removed from the liver very slowly. Injection of (I) into the gall-bladder decreases the excretion of bile acids and bilirubin (II) and (II) is replaced by a yellow pigment. H. D.

Poisonous constituents of the seeds of *Tephrosia vogelii*.—See this vol., 221.

Toxic principle of poison ivy. G. A. HILL, V. MATTACOTTI, and W. D. GRAHAM (J. Amer. Chem. Soc., 1934, 56, 2736—2738).—The bark (I) of *Rhus toxicodendron* is extracted with boiling 95% EtOH for 4 days; slow cooling of the conc. extract ppts. wax and gum (removed by filtration). Saturation of the residual extract with NaCl and extraction with xylene gives urushiol (II), b.p. 210°/0.5 mm. (Majima, A., 1922, i, 262). (I) gathered in winter is practically free from (II). The Me_2 ethers of (II) and dihydrourushiol are non-toxic (cf. *ibid.*, 263). H. B.

Toxic properties of greasewood. Physiological action of oxalic acid and its soluble salts. V. A. WILLSON (J. Amer. Vet. Med. Assoc., 1934, 38, 76—81).—Toxicity is due to Na and K oxalates (Na : K = 4 : 1). CH. ABS. (p)

Chemotherapeutic testing of nitro-derivatives. V. FISCHL (Z. Immunität., 1934, 82, 146—153).—Of 60 NO_2 -compounds tested for chemotherapeutic effect on trypanosomes in mice, 2 : 5- $C_6H_3(NO_2)_2 \cdot OH$. Victoria-yellow, picric (I), picramic (II), and picrolonic (III) acids, and sun-yellow showed very weak effects on *T. recurrentes*. (II) was also slightly effective

against *T. nagana*. (I) and (III) were the only effective compounds on staphylococci and *B. coli*. These compounds all contained two NO_2 -groups (IV) and a phenolic OH, the 2 : 5-positions for (IV) being specially favourable for activity. R. N. C.

Chemical nature and biological activity of methylphenarsazine dihydroxide and its derivatives. V. M. KARASIK and M. M. LICHATSOEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 161—163).—Methylphenarsazine dihydroxide (I) (the Ac derivative of which has no trypanocidal action) causes augmented reflex action and convulsions in white mice and frogs. Replacement of Me by Et and, especially, by Pr increases the effect. Dimethylphenarsazine hydroxide (II) is much more toxic than (I) and exerts a central paralytic action. The nitrate of (II) is less toxic than (II), but more rapid in its action. H. N. R.

Comparative toxicity of sodium and diethylamine derivatives of 3-acetamido-4-hydroxyphenylarsinic acid. R. POTTIER and F. VAN DEN BRANDEN (Compt. rend. Soc. Biol., 1934, 117, 830—832).—The ratio of the toxicities to rabbits of intravenously administered Na salt and $NHEt_2$ derivative of stovarsol is 1 : 1.25. F. O. H.

Anthelmintics. I. Effect of hydrogen peroxide and some oxygenated terpene hydrocarbons on *Ascaris lumbricoides*. L. W. BUTZ and W. A. LALANDE, jun. (J. Amer. Pharm. Assoc., 1934, 23, 1088—1094).— H_2O_2 and the products obtained by the oxygenation of α -pinene, turpentine, and *d*-limonene are very toxic to *A. lumbricoides*. The active constituents of the oxygenated hydrocarbons are probably not peroxides or ketones. A. E. O.

Anthelmintic constituent of leaves of *Calycopteris floribunda*. A. N. RATNAGIRISWARAN, K. B. SEHRA, and K. VENKATARAMAN (Biochem. J., 1934, 28, 1964—1967).—A yellow flavone, *calycopterin*, $C_{18}H_{18}O_8$ (I), with anthelmintic properties was isolated in 0.1% yield by $COMe_2$ extraction of the dried leaves of *C. floribunda*, Lamk. (I) contains 4 OMe and 2 OH, and yields Ac_2 , m.p. 129°, Bz_2 , m.p. 165°, and Me_2 derivatives, m.p. 131° (sintering at 127°). Demethylation with HI yields the parent hexahydroxyflavone, *calycopteretin*, $C_{15}H_{10}O_8$, m.p. 310° (sintering at 294°) [Ac_6 derivative, m.p. 212° (sintering at 207°)], not identical with gossypetin, myricetin, or quercetagenin. Boiling aq. KOH on (I) in H_2 yields $p-OH \cdot C_6H_4 \cdot CO \cdot H$; hence (I) must be represented as $OH \cdot (OMe)_3 C_6 < \begin{matrix} C \\ CO \cdot C \cdot OMe \end{matrix} H_4$. A. E. O.

Elimination of water from the human body. G. VON HEVESY and E. HOFER (Nature, 1934, 134, 879).—The *d* of H_2O prepared from urine after the intake of dil. H_2O has been determined after different intervals of time have elapsed. Using H_2O as indicator, it is found that 30 min. after the beginning of the intake of H_2O , some of it (approx. 0.2%) is found in the urine. Most of the H_2O , however, leaves the body slowly. Approx. 9 days elapse before half is eliminated. The average time a mol. of H_2O spends in the human body is 13 ± 1.5 days, and this

is explained by assuming that most of the H_2O taken becomes completely mixed with the total H_2O of the body.
L. S. T.

Fibrillation in the chicken embryo heart *in vitro*. I. Effects of excess potassium, calcium, magnesium, and sodium, and of high and low osmotic pressures. II. Character and mechanism of the fibrillation. P. D. F. MURRAY (Proc. Soc., 1935, B, 116, 434—451, 452—478).

Control of cyanide action: cyanohydrin equilibria *in vivo* and *in vitro*. E. K. MARSHALL, jun., and M. ROSENFELD (J. Pharm. Exp. Ther., 1934, 52, 445—461).—The protective val. of aldehydes and ketones against CN^- poisoning varies directly with their rate of cyanohydrin formation (I) and inversely with the magnitude of their cyanohydrin equilibrium const. (II). Initial respiratory stimulation (III) varies directly with (II) and inversely with (I). Prolonged (III) is produced by cyanohydrins with small (II). $AcCO_2H$ is particularly effective in (III).
H. D.

Antitoxic effect of glutathione in cyanide poisoning. M. T. RÉGNIER (J. Pharm. Chim., 1934, [viii], 20, 501—512).—In the guinea-pig, the injection of glutathione (0.5 mol.) has a direct and immediate effect in arresting asphyxia due to HCN (1 mol.). The effect is not due to formation of SCN^- .
A. E. O.

Nitrite-thiosulphate combination as a remedy for cyanide poisoning in sheep. H. BUNYEA, J. F. COUCH, and A. B. CLAWSON (J. Washington Acad. Sci., 1934, 24, 528—532).—Prompt intraperitoneal injection of $NaNO_2-Na_2S_2O_3$ is generally an effective antidote for sheep poisoned by administration (*per os*) of $2.75 \times$ min. lethal dose of KCN . The safest therapeutic dose is 1 g. of $NaNO_2$ for 35—40 kg. body-wt.; doses of 0.095 g. per kg. body-wt. may themselves prove fatal, and 0.05 g. per kg. doses are dangerous. Increase of the $Na_2S_2O_3$ (1—3 g.) is possibly advantageous, and is not itself toxic.
J. W. B.

Bibliography of the more important heavy metals occurring in food and biological material, 1921—1933 (Soc. Public Analysts, 1934, 30 pp.).—Very brief abstracts are included in many cases under each of the 13 metals.

Determination of traces of lead in biological materials, with special reference to bone. G. R. LYNCH, R. H. SLATER, and T. G. OSLER (Analyst, 1934, 59, 787—806).—After wet oxidation, the Pb is extracted with diphenylthiocarbazone, and determined colorimetrically as PbS . Special precautions must be taken to exclude Bi, if present. The Pb content of 20 normal bones was 14.5—146.0 p.p.m. of fresh tissue, that of the teeth of 5 normal persons 2.5—247.5 p.p.m. The method has been applied to marrow, organs, blood, urine, and faeces.
E. C. S.

Absorption and distribution of mercury in animals. A. STOCK and F. CUCUEL (Angew. Chem., 1934, 47, 801—806; cf. A., 1934, 862, 1257).—The traces of Hg present in various tissues of normal guinea-pigs (I) are increased by exposure for 10—24

hr. to Hg-saturated (6—7 mg. per cu.m.) air. A high content ($21-88 \times 10^{-6}$ g. per g.) of Hg subsequently occurs in the lungs (II) and kidneys (III), whilst that of the liver (IV), heart, spleen, brain, etc. is generally $<$ the blood level ($5.7-20.0 \times 10^{-6}$ g. per g.); relatively small amounts occur in the urine. Curves are given for the accumulation of Hg in (II), (III), and the remainder (V) of (I) and also for the diminution in Hg content after cessation of administration. The retention of Hg by (III) persists for several weeks. The blood-N indicates a toxic action of Hg on (III). Absorption of Hg through the alimentary tract is $<$ that through (II) and produces a rapid rise in the Hg content of (III), those of (IV) and (V) increasing slightly and remaining approx. const., respectively.
F. O. H.

Detection of mercury in bullet wounds. G. GUARESCHI (Deut. Z. ges. gerichtl. Med., 1934, 23, 89—96; Chem. Zentr., 1934, ii, 102).—Material cut from around the wound is treated with HNO_3 , diluted with H_2O , filtered, and tested for Hg with $SnCl_2$. A microscopical method of detection is also applicable.
H. J. E.

Amino-aciduria and ammoniuria in the course of acute uranium nephritis in the dog, rabbit, and rat. R. DEVÈZE (Compt. rend. Soc. Biol., 1934, 117, 1111—1112).— $UO_2(NO_3)_2$ nephritis produces in all species an increased NH_2 -acid excretion. NH_3 excretion varies with the species, being scarcely affected in the rat, increased in the rabbit, and decreased in the dog.
R. N. C.

Organic-aciduria in the course of acute uranium nephritis in the dog, rabbit, and rat. R. DEVÈZE (Compt. rend. Soc. Biol., 1934, 117, 1113—1114).—Excretion of org. acids is increased in all three species in $UO_2(NO_3)_2$ nephritis, the increase being largely due to lactic acid. Hippuric acid excretion is diminished.
R. N. C.

Renal origin of albuminuria in nephritis produced by uranium nitrate. R. WEEKERS (Compt. rend. Soc. Biol., 1934, 117, 817—818).—Perfusion of nephritic kidneys with normal or nephritic blood produces the same degree of albuminuria (I). Hence the blood plays no part in (I) due to $UO_2(NO_3)_2$.
F. O. H.

Variations in blood-gases after Röntgen irradiation of the spleen. I. Variations after irradiation of various regions of the body with small and large doses. T. ABE (Tohoku J. Exp. Med., 1934, 23, 394—414).—Changes in blood- O_2 and $-CO_2$ depend on the site and size of the dose.
CH. ABS. (p)

Blood-sugar modifications in hyperthermal and radioactive media. M. SENDRAIL, R. MOLINERY, and J. AVERSENQ (Compt. rend. Soc. Biol., 1934, 117, 322—323).—Hypoglycæmia (I) is widespread among miners in galleries in volcanic rocks, where the air is affected by deep mineral hot springs charged with H_2S and Rn. The greatest (I) was shown by diabetics.
R. N. C.

Possible action of cosmic rays on living organisms. R. B. ENGELSTAD and N. H. MOXNES (Nature, 1934, 134, 898).—The only detectable differ-

ence in mice is a greater mean wt. of animals shielded from cosmic rays. L. S. T.

Enzyme reactions from the viewpoint of heterogeneous catalysis. W. FRANKENBURGER (Ergebn. Enzymforsch., 1934, 3, 1—22; Chem. Zentr., 1934, ii, 952—955).—A theoretical discussion. A parallel is drawn between the heterogeneous catalysis of gas reactions and enzyme reactions.

H. N. R.

Enzymic histochemistry. K. LINDERSTRÖM-LANG and H. HOLTER (Ergebn. Enzymforsch., 1934, 3, 309—334; Chem. Zentr., 1934, ii, 1144).—Distribution of proteinase, peptidase, carbohyrase, deamidase, and esterase among various organs and tissues is examined.

A. G. P.

Proportionality studies on catalase. G. W. MARKS (J. Biol. Chem., 1934, 107, 623—627).— p_H curves are given for the catalases (I) from *Amphiroa aspergillum forma nana*, *Corallina officinalis* (II), and *Pikea californica*. For (I) from (II) the quantities of H_2O_2 decomposed \propto (I) concn. and are independent of H_2O_2 concn. over a p_H range 4.5—10.0. Sharp changes occur in the slopes of some of the curves.

C. G. A.

Inhibitors of catalase reaction. D. KEILIN and E. F. HARTREE (Nature, 1934, 134, 933—934; cf. A., 1934, 1136).— NaN_3 is a strong inhibitor of catalase. 0.018*M*-Dimethylglyoxime treated by the method of Sevag and Maiweg gives approx. 0.024*M*- NH_2OH , which is a known catalase inhibitor.

L. S. T.

Peroxidase specificity. M. DIXON (Biochem. J., 1934, 28, 2061—2064).—Pyrocatechol, guaiacol (I), guaiacum, and pyrogallol are readily oxidised by $S_2O_8^{2-}$ in the presence of milk-peroxidase (II) but not when (II) is replaced by horseradish-peroxidase (III) or haematin. Bz_2O_2 oxidises all the usual peroxidase reagents with (II) or (III) except (I). H. D.

Peroxidase. A. K. BALLS and W. S. HALE (J. Biol. Chem., 1934, 107, 767—782).—A method of determining peroxidase (I) based on iodometric titration of residual H_2O_2 is described. The increase in (I) content during dialysis of sliced horseradish roots (cf. A., 1929, 1106) depends on the absence of air in the H_2O used. p_H optima for various substrates were determined. In the enzymic oxidation of pyrogallol (II), aerated (II) may replace H_2O_2 , hence it is possible to determine (I) in presence of catalase if (II) is also present. (I) is able to combine with almost any amine or phenol, but successful oxidation takes place only when the substrate may yield a quinone at a min. oxidation-reduction potential rather > that necessary to reduce *o*-chlorophenol-indophenol at p_H 7, i.e., the substrate must be an *o*- or *p*-disubstituted C_6H_4 derivative, with either one substituent OH, or both NH_2 . In presence of H_2O_2 , (I) is either destroyed or irreversibly bound in the attempt to oxidise an unfavourable substrate. The possibility of "oxidative synthesis" by the action of (I) is mentioned.

A. E. O.

Biological oxidation-reduction potential. Potential determinations in the system alcohol-dehydrogenase-acetaldehyde. J. LEHMANN (Bio-

chem. Z., 1934, 274, 321—328).—The reversibility of the oxido-reduction process in the system EtOH-dehydrogenase (prep. from washed dried yeast)-MeCHO is demonstrated in a series of potential (I) determinations at 30°. The equimol. (I) at p_H 7.45 amounts with the normal H_2 electrode (II) to E'_0 —0.090 volt, or with a (II) of the p_H of the enzymic system to $E=0.356$ volt.

P. W. C.

Xanthine-oxidase. XII. Oxidation of nucleosides. M. DIXON and R. LEMBERG (Biochem. J., 1934, 28, 2065—2079).—Xanthine-oxidase oxidises inosine (I), inosinic acid (II), adenosine (III), muscle adenylic acid (IV), and cozymase, due to the liberation of hypoxanthine (V) by other enzymes. Oxidation of (I) is brought about by a nucleosidase, sp. towards the purine part of the mol., which liberates free (V). The action on (III) is shown to be deamination by a third enzyme to form (I) with subsequent formation of (V). Since (II) and (IV) behave like (I) and (III), respectively, the presence of a phosphatase is indicated.

H. G. R.

Effect of X- and γ -rays on indophenol-oxidase. R. E. HAVARD (Brit. J. Radiol., 1934, 7, 296—304).—Indophenol-oxidase was not affected by irradiation under the conditions examined. CH. Abs. (p)

[Nature of] the respiratory co-enzyme of red blood-cells. H. THEORELL (Biochem. Z., 1934, 275, 11—18; cf. A., 1934, 1136; Warburg *et al.*, *ibid.*, 109).—Cataphoresis cannot be used to purify the co-enzyme (I), but it indicates that (I) is an acid (probably a phosphoric acid) which dissociates in two stages. (I) contains no conjugated OH groups.

W. McC.

Acid groups of the respiratory co-enzyme. H. THEORELL (Biochem. Z., 1934, 275, 19—29).—Measurements in the cataphoresis apparatus show that the co-enzyme is a tetrabasic acid, probably a diposphoric ester, 2 H being liberated at each stage of dissociation.

W. McC.

[Nature of] mixtures of respiratory enzymes with substrates. H. THEORELL (Biochem. Z., 1934, 275, 30—36).—At p_H 7.4 the intermediate respiratory enzyme (I) and the co-enzyme (II) react with the substrate (III) (hexosemonophosphoric acid), but (I) does not react with (II). All the components of the system [yellow enzyme, (I), (II), (III)], and hence (presumably) all combinations of them are negatively charged.

W. McC.

Active group of the yellow enzyme. H. THEORELL (Biochem. Z., 1934, 275, 37; cf. A., 1934, 1136).—No yellow enzyme (I) is produced when lactoflavin is added to the inactive constituent of (I). The constituents of (I) are separated by adding 3 vols. of MeOH to aq. (I), the protein constituent, which contains no P, being pptd. 1 mol. of the active yellow constituent contains 1 P. The active group of (I) is probably a monophosphoric ester, a nucleotide in which the purine base is replaced by dimethylall-oxazine (Karrer, *et al.*, A., 1934, 1233).

W. McC.

Reduction of nitric oxide by oxidising enzymes. O. MEYERHOF and W. SCHULZ (Biochem. Z., 1934, 275, 147—161).—Yeast maceration juice (I) in presence of oxidisable substrates (II) (especially

hexose phosphates) and the yellow respiratory enzyme (III) in presence of hexose monophosphate reduce NO to N_2O , (II) being oxidised at the same or at a greater rate than by atm. O_2 . With (I) CO_2 is produced and the R.Q. is the same as when atm. O_2 is the oxidising agent, but the O_2 uptake is $1\frac{1}{2}$ times as great with NO as with O_2 . Reduction of NO occurs only with such (II) as are enzymically oxidised with O_2 . The extent of reduction varies considerably with the (II) used. W. McC.

Reduction of glutathione by the Warburg-Christian system. N. U. MELDRUM and H. L. A. TARR (Biochem. J., 1935, 29, 108—115).—Glutathione (I) is reduced both aerobically and anaerobically by the Warburg-Christian enzyme-co-enzyme system (II), derived from brewer's top yeast, baker's yeast, or rat's blood, in presence of hexosemonophosphoric acid (III), less readily with phosphohexonic acid and fructosediphosphoric acid, and not by diphosphoglyceric acid, glucose, or fructose. (I) acts as O carrier when (III) is oxidised by (II) in presence of O_2 ; the velocity of oxidation \propto the amount of (I), the limiting factor being the rate of reoxidation of (I). Cystine (IV) also acts as O carrier in the same system, the rate being independent of (IV) concn. as the limiting factor here is the rate of reduction of (IV). C. G. A.

Salts of base from co-enzyme preparations. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1934, 275, 112—113; cf. this vol., 121).—The base (I), m.p. 125° , yields a *picrolonate*, m.p. 220° (decomp.), a *hydrochloride* (II), m.p. 224° , and a *platinichloride*, m.p. $> 300^\circ$ (decomp.). 1 mol. of (II) reduced with $Pd+H_2$ takes up 3 H_2 . (I) is obtained from (II) by shaking with Ag_2CO_3 ; it has mol. wt. about 120 (Rast's method gives 154). 100 litres of horse blood yield 10—20 mg. of (I). W. McC.

Michaelis constant for fumarase. F. B. PEREIRA and A. DA CRUZ (Compt. rend. Soc. Biol., 1934, 117, 723—726).—Results of determinations of fumarase activity at 37° , 22° , and 5° indicate that there is no change with temp. in the val. for the substrate concn. below which diminution in enzyme activity takes place. The dissociation const. of the fumarase-fumarate complex is only slightly affected by change of temp. (0.0017 at 22° and 0.0035 at 37° and 5°). A. L.

Temperature coefficient of fumarase. K. P. JACOBSON and A. DA CRUZ (Compt. rend. Soc. Biol., 1934, 117, 726—728).—The Arrhenius const. for the hydration of fumaric acid by fumarase is the same as that for the reverse reaction, viz., 10,000. A. L.

Amylosynthase. XXIV. Reaction velocity. III. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 550—553).—Dextrin is polymerised with difficulty by yeast extract, but relatively easily if amylose is previously removed from the extract. Amylosynthase, purified by pptn. with $(NH_4)_2SO_4$, polymerises α - and β -dextrins (from starch by taka-amylase and various amylases) with equal facility. CH. ABS. (p)

Amylase of batate (*Ipomoea batatas*). K. V. (Biochem. Z., 1934, 275, 106—111; cf. A., 1934,

1136).—The amylase (I) is purified at about 0° by dialysis of extracts of batate and adsorption of (I) on $Al(OH)_3$. The degree of adsorption is independent of the concn. of (I), but increases with increasing purity of (I). The optimum pH for adsorption is 3.7—4.2. (I) contains carbohydrate but no protein.

W. McC.

Development of amylase during germination of barley. H. LUERS and W. RUMMLER (Woch. Brau., 1935, 52, 9—12).—Using barley extract, with or without papain digestion, liquefying and dextrinising action could not be demonstrated, and the appearance of an amylokinase during germination could not be confirmed. Destruction of saccharogen-amylase (S) by heating extracts to 70° had little effect on liquefying power, but decreased dextrinisation markedly, suggesting that the two reactions are due to different factors. Investigation of S activity, in normal and papain-digested extracts, suggested that 3 factors are active during germination, and not S and dextrinogen-amylase only. I. A. P.

Biochemical micro-methods. VI. Photometric determination of amylase and maltase. B. J. KRIJGSMAN (Z. physiol. Chem., 1934, 230, 190—198).—The amylase content of saliva is determined by an adapted Rona and van Eweyk's method (A., 1925, i, 1264); the max. error is 2.5%. The method previously described (A., 1933, 845) for determination of blood-sugar is adapted for the maltase activity of yeast and pancreas extracts using maltose as substrate; the max. error is 2.8%. H. B.

Degradation of glycogen in muscle. II. Effect of muscle compounds on the activity of amylase. III. Action of amylase in presence of myosin. S. J. VON PRZYŁECKI and B. FILIPOWICZ (Biochem. Z., 1934, 275, 56—61, 62—65; cf. A., 1932, 193).—II. The degradation of starch or glycogen (I) by amylase (II) is only slightly or not at all affected by addition of nucleic acid, nucleotides (guanylic, adenylic, xanthylic acids), or muscle extract (rabbit). Hence the reactions which lead to great and rapid increase in degradation of (I) are not the cause of the increased activity of (II), which results rather from spatial changes (III). (III) bring (I) and (II) into direct contact or separate them.

III. The degree of activation of ptyalin (IV) by myosin (V) is slight at the isoelectric point (VI), but increases with the distance from (VI). (V) does not adsorb (IV). Polysaccharoproteins (VII) are degraded with much greater difficulty than are free polysaccharides (VIII). Hence hydrolysis of (VIII) decreases following production of (VII) at physiological pH and salt concn. W. McC.

Presence of a kinase of amylase in trypsin preparations. T. CHRZĄSZCZ and J. JANICKI (Biochem. J., 1934, 28, 1949—1954).—Trypsin (I) increases both the saccharifying and dextrinising functions of barley, the effect on the latter being very marked. Inactivated (I) partly protects the amylase against inactivation by shaking. A. E. O.

Influence of aeration on the diastatic activity of barley during steeping. R. H. R. RAO and V. SUBRAHMANYAN (Proc. Indian Acad. Sci., 1934, 1, B,

1—9).—Steeping of barley diminishes the diastatic activity (I) (due to anaërobiosis) for approx. 24 hr., whilst continuous steeping for 2—4 days in presence or absence of air increases (I). The development of (I) is independent of the capacity for germination.

F. O. H.

Dilatometric studies in the enzymic hydrolysis of polysaccharides. I. **Inulin.** M. SREENIVASAYA, H. B. SREERANGACHAR, and N. K. IYENGAR. II. **Hydrolysis of starch by malt diastase.** H. B. SREERANGACHAR and M. SREENIVASAYA (Proc. Indian Acad. Sci., 1934, 1, B, 43—47, 101—105).—I. For equal substrate concns., hydrolysis of inulin (I) [determined by dilatometer (A., 1932, 880) or by the rate of liberation of fructose (II)] at 30° and p_H 3.8 in citrate buffer by inulinase (*Penicillium* extract) is > that of starch (A., 1934, 109). Liberation of (II) is accompanied by a relatively high contraction in vol., viz., 7.9 cu.mm. per millimol. of (II), a val. independent of the concn. of (I).

II. The hydrolysis of sol. starch (0.05—2.0%) by malt diastase at 30° and p_H 5.3 in $PO_4^{'''}$ buffer gives a dilatometric contraction which \propto the amount of maltose liberated (3.9 cu.mm. per millimol.) and also \propto the diminution in α (6.8 cu.mm. per 1°).

F. O. H.

Lucerne emulsin. K. HILL (Ber. Verh. sachs. Akad. Wiss. Leipzig, Math.-Phys. Kl., 1934, 86, 115—128; Chem. Zentr., 1934, ii, 1142—1143).—Prep. of the emulsin is described and its specificity examined in respect of mannose, α - and β -galactose. Comparison is made with almond emulsin. A. G. P.

Emulsin. XVII. Action of ozone on almond-emulsin. B. HELFERICH, S. WINKLER, E. SCHMITZ-HILLEBRECHT, and H. BACH (Z. physiol. Chem., 1934, 229, 112—116; cf. A., 1934, 1402).—When emulsin is progressively inactivated by O_3 , its tryptophan is destroyed at about the same rate. The activity towards β -*d*-glucoside, -isorhamnoside, and -galactoside is lowered to about the same extent in a treated prep, but the activity towards α -*d*-mannoside (I) to a greater degree, indicating that a different enzyme is responsible for (I) hydrolysis, as previously shown.

J. H. B.

Relation between the re-synthesis of adenosinetriphosphoric acid and the reaction of pyruvic acid and dihydroxyacetonephosphoric esters. Z. DISCHE (Naturwiss., 1934, 22, 855).—Theoretical.

R. S. C.

Phosphorylated intermediate product of carbohydrate fission and its enzymic equilibrium. O. MEYERHOF and W. KIESSLING (Naturwiss., 1934, 22, 838).—*d*- α -(2-)Phosphorylglyceric acid (I) (*Ba* salt, $[\alpha]_D^{+24.3^\circ}$), is isolated from the crude β -(3-)acid (II), prepared enzymically. and *dl*-(II) are obtained from glycerol- β - and - α -phosphoric acids, respectively, and *Br*. With dialysed muscle extract the biologically inactive *d*-(I) and *l*-(II) are unaffected, whereas the active *l*-(I) and *d*-(II) enter into equilibrium with each other, *k* for *l*-(II)/*d*-(II) being 3.0 at 28° [75% of (II)].

R. S. C.

Relation between phosphorylation and oxidation-reduction in fermentation and glycolysis. A.

SCHAFFNER and E. BAUER (Naturwiss., 1934, 22, 855—856).—The co-enzyme of horse's blood-cells can be replaced by that of yeast for phosphorylation (I). (I) is connected with a dehydrogenation, since Warburg's intermediate enzyme is necessary for it to occur.

R. S. C.

Production of an optically active phosphoglyceric acid by glycolysis in muscle. G. EMBDEN, H. J. DEUTICKE, and G. KRAFT (Z. physiol. Chem., 1934, 230, 12—28).—Treatment of minced rabbit muscle (I) with 0.5*M*-*Na dl*-lactate containing 0.4% of wheat-starch and 2% of $NaHCO_3$ at 11—13° gives (—)- β -phosphoglyceric acid (II), $[\alpha]_D -11.91^\circ$ in H_2O , $+11.39^\circ$ (as *Na* salt), isolated as the *cryst. Ba* salt ($+H_2O$). (II) is hydrolysed (dil. H_2SO_4) with difficulty to *d*-(—)-glyceric acid (*Ba* salt) and H_3PO_4 . (II) is also produced from (I) and $Na_2C_2O_4$ or NaF ; the amount is much increased by addition of *Na* hexose diphosphate [which is probably an intermediate in the above production of (II)]. H. B.

Significance of phosphoglyceric acid for glycolysis in muscle. G. EMBDEN and H. J. DEUTICKE (Z. physiol. Chem., 1934, 230, 29—49).—Phosphoglyceric acid (I) (as *Na* salt) is converted by minced rabbit muscle (II) into H_3PO_4 and $AcCO_2H$ (III). Little lactic acid (IV) is formed when glycerophosphoric acid (V) (as *Na* salt) is added to (II), but addition of (I)+(V) produces much; (V) is the *H*-donator in the change (III) \rightarrow (IV). (II) does not effect the change (III) \rightarrow (IV); subsequent addition of (V) accelerates reaction. $AcCHO$ is not considered to be an intermediate. The following scheme for the production of (IV) is given: (i) hexosediphosphoric acid is synthesised from polysaccharide, hexose, or hexosemonophosphoric acid and H_3PO_4 ; (ii) $PO_3H_2 \cdot O \cdot CH_2 \cdot CO \cdot [CH(OH)]_3 \cdot CH_2 \cdot O \cdot PO_3H_2 \rightarrow OH \cdot CH_2 \cdot CO \cdot CH_2 \cdot O \cdot PO_3H_2$ (VI) + $CHO \cdot CH(OH) \cdot CH_2 \cdot O \cdot PO_3H_2$ (VII); (iii) dismutation of (VI) and (VII) to (I) and (V); (iv) $CO_2H \cdot CH(OH) \cdot CH_2 \cdot O \cdot PO_3H_2 \rightarrow AcCO_2H + H_3PO_4$; (v) $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot PO_3H_2 + AcCO_2H \rightarrow OH \cdot CHMe \cdot CO_2H + (VII)$.

H. B.

Action of fluoride and bromoacetic acid on intermediary processes in glycolysis in muscle. G. EMBDEN and H. J. DEUTICKE (Z. physiol. Chem., 1934, 230, 50—62; see preceding abstracts).—Minced rabbit muscle (I) treated with NaF and $NaHCO_3$ converts added hexose diphosphate (II) into phosphoglyceric acid (III), but specifically inhibits the conversion of (III) into $AcCO_2H$ (IV) and H_3PO_4 ; reduction of (IV) by glycerophosphoric acid (V) to lactic acid is similarly unaffected, but less "hydrolysis" of (V) occurs [than with normal (I)]. (I) treated with $CH_2Br \cdot CO_2Na$ does not convert (II) into triosephosphoric acids and also retards the above reduction of (IV); conversion of (III) into (IV) occurs.

H. B.

Isolation of glycerophosphoric acid from fluoride-poisoned muscle. G. EMBDEN and T. ICKES (Z. physiol. Chem., 1934, 230, 63—68).—Glycerophosphoric and phosphoglyceric acids (see above) are formed from minced rabbit muscle, $NaF + NaHCO_3$, and *Na* hexose diphosphate; separ-

ation is effected through the differing solubilities of the Ba salts.

H. B.

Intermediate stages in glycolysis in striped muscle. G. EMBDEN and H. JOST (Z. physiol. Chem., 1934, 230, 69—89).—Minced rabbit muscle (vertebral and leg) with *dl*- β -phosphoglyceraldehyde (I) (Fischer and Baer, A., 1932, 364) in 2% NaHCO_3 saturated with CO_2 at 37° gives a preponderance of (+)-lactic acid (II) after a short reaction time. More prolonged reaction leads to an excess of (—)-lactic acid (III), probably owing to hydrolysis of unreacted (I) to AcCHO , which is then converted (as is shown experimentally) into (III). These results are contrary to those of Barrenscheen and Beneschovsky (A., 1933, 1202); they also show that *d*-(I) is an intermediate in glycolysis in muscle. (II) is similarly produced from AcCO_2H +glycerophosphoric acid (IV) or phosphoglyceric acid+(IV); *dl*-glyceraldehyde affords (III). Dihydroxyacetonephosphoric acid (Langheld, A., 1912, i, 415) and $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ are not converted into lactic acid (V) even in presence of (I). The above results support the scheme suggested above for the production of (V) from carbohydrates.

H. B.

Action of fluoride on intermediary processes in glycolysis in yeast. E. LEHNARTZ (Z. physiol. Chem., 1934, 230, 90—95; cf. Neuberg and Kobel, A., 1933, 982; Meycrhof and Kiessling, A., 1934, 328).—Phosphoglyceric acid, $[\alpha]_D^{20} -11.3^\circ$ in H_2O [Ba salt (+1.5 H_2O)], identical with that isolated from muscle (see above), is obtained during fermentation of glucose with dry brewer's yeast in presence of phosphate, Na hexose diphosphate, NaF, and MeCHO (absence of this leads to a diminished yield).

H. B.

Anaerobic glycolysis in kidney. H. JOST (Z. physiol. Chem., 1934, 230, 96—108).—(+)-Lactic acid is formed from minced ox kidney (I) and the following substances in 2% NaHCO_3 saturated with CO_2 at 37° : *dl*- β -phosphoglyceraldehyde (provided a small concn. is used), phosphoglyceric acid (II), glycerophosphoric acid (III)+(II), AcCO_2H (IV), (III)+(IV). (—)-Lactic acid is similarly obtained from AcCHO and glyceraldehyde. (I), unlike muscle, contains a substance [probably (III)] capable of acting as a H-donor to (IV). The production of lactic acid (V) from carbohydrate (VI) in the kidney is considered to involve the same changes as in muscle (Embden and Jost, above). (V) is not similarly produced from $\text{CO}(\text{CH}_2\cdot\text{OH})_2$. Preliminary work on the possibility of the production of (V) from (VI) by way of non-phosphorylated compounds [e.g., (IV)] is discussed.

H. B.

Effect of potassium on the glycolysis of brain tissue with reference to the Pasteur effect. C. A. ASHFORD and K. C. DIXON (Biochem. J., 1935, 29, 157—168).—Addition of K salts (but not Na salts) reversibly increases aerobic glycolysis (I) and O_2 uptake, and irreversibly inhibits anaerobic (I) by brain slices. *dl*-Glyceraldehyde inhibits the raised (I) occurring in the presence of 0.1N-KCl, whilst pyruvate does not modify the action of K^+ . The oxidative removal of lactic acid (II) is not affected by K. The mechanisms of (II) production in O_2 and

N_2 are probably different; the former is activated and the latter inhibited by K^+ .

A. E. O.

Phosphatases. II. Liberation of phospho-esterases from liver. E. BAMANN, E. RIEDEL, and K. DIEDERICH (Z. physiol. Chem., 1934, 230, 175—184).—Of the methods studied, natural autolysis of fresh liver (I) gives an autolysate containing max. amounts of the phosphoesterases [(II) (max. activity at p_H 5.5) and (III) (max. activity at p_H 9.5)]; liberation of (II) and especially (III) is incomplete. Dehydration of (I) with COMe_2 causes loss of enzymes. Neutral solutions of (II) and (III) do not lose their activity when kept at 6° ; (II) is stable in 0.025N-AcOH, whilst (III) is stable in 0.025N- NH_3 . Lyo- and desmo-complexes in (III) are characterised.

H. B.

Phosphatases. III. Separation of the two isodynamic phosphoesterases of animal organs by a selective inactivating process. E. BAMANN and K. DIEDERICH (Ber., 1934, 67, [B], 2019—2021).—The alkaline phosphoesterase of pig's liver is stable only in neutral or weakly alkaline solution and becomes inactivated in the presence of acid. The reverse is true of acid phosphoesterase. The difference in behaviour is so pronounced that it is possible to obtain the individual enzymes from mixtures of them by selective inactivation.

H. W.

Composition and properties of esterases. H. KRAUT and W. VON PANTSCHENKO-JUREWICZ (Biochem. Z., 1934, 275, 114—135; cf. A., 1928, 671; Willstätter, *et al.*, A., 1934, 913).—Liver-esterase (I) is purified by adsorption on $\text{Pb}_3(\text{PO}_4)_2$ (which first adsorbs impurities) and elution with dil. AcOH. (I) and other enzymes are "symplexes" (II) consisting of an active constituent "agon" (III) and a carrier "pheron" (IV). (II), (III), and (IV) are subject to the law of mass action; in the case of (I) large excess of (IV) must be present to maintain (III) in (II) and removal of free (IV) destroys the activity by disturbing the equilibrium. Free (III) changes into an inactive "anagon" incapable of re-forming (II), but other enzymes may have agons which are also active when free. Free (IV) [in (I) at least] is not a true protein. New (I) is produced when (I) rich in (IV) is added to pancreatic lipase (V) rich in (III), and new (V) is produced when (I) rich in (III) is added to (V) rich in (IV). Hence (I) and (V) have the same (III) but different (IV). Differences in specificity amongst esterases are a function of (IV). Activation of (V) with albumin is due to synthesis of a new (II) with excess of (III). In the same manner explanations are provided for many properties of enzymes and (possibly) for those of vitamins and hormones.

W. McC.

Fixation of enzymes by cells. I. Proto-plasmic fixation of liver-esterase. E. BAMANN and J. N. MUKHERJEE. II. Isolation of esterase from liver. E. BAMANN, J. N. MUKHERJEE, and L. VOGEL (Z. physiol. Chem., 1934, 229, 1—14, 15—21).—I. Only about 1% of liver-esterase (I) is immediately sol. in glycerol (II). Extraction of (I) by H_2O -(II) mixtures from the fresh organ progresses slowly and ceases when 30—40% of (I) is dissolved. The rest, bound to high-mol. carriers, is liberated by

autolysis at alkaline reaction. Solutions of (I) are more readily obtained from COMe₂-dried preps. H₂O or (II)-H₂O dissolve 45–65% of the (I) present, the rest being liberated by acid or alkali without autolysis. Distilled H₂O containing CO₂ is less efficient than CO₂-free H₂O.

II. A rapid quant. isolation is attained by subjecting the fresh minced organ to autolysis in alkaline medium for 3–4 days (which renders 50–60% of the esterase sol.), and subsequent treatment with dil. AcOH. The enzyme may be purified by dialysis.

J. H. B.

(A) Reversible inactivation of papain and cathepsin. (B) Activation phenomena of papain and cathepsin. A. PURR (Biochem. J., 1935, 29, 5–12, 13–20).—(A) The proteinase activity of papain (I) extracts is completely inactivated by alloxan (II), AcCHO (III), milk xanthine-oxidase+hypoxanthine+milk peroxidase in the presence of O₂, and by H₂O₂. Cathepsin (IV), from rats' livers, is inactivated by (II), (III), and CH₃I·CO₂H (V); reactivation by cysteine or H₂S is not obtained after inactivation by (V); in this case EtOH reactivates. A parallelism exists between the disappearance of ·SH from (I) or (IV) and inactivation except with (V). Large quantities of inactive (IV) are prepared by extraction of liver with COMe₂ and Et₂O, and extraction of the residue with 85% glycerol.

(B) Vitamin-C+Fe⁺⁺ (VI) fails to activate purified preps. of (I), whilst both (VI) and AcCO₂H+Fe⁺⁺ (VII) activate an impure (I). Pure (I) is activated by fixed ·SH+·S·S· proteins (VIII) (A., 1923, i, 167), (VI), (VII), and succinic acid+Fe⁺⁺ in the presence of (VIII). The activation by (VI) and (VII) results from the reduction of ·S·S· to ·SH. ·S·S· glutathione activates (I) in presence of (VI). The activation phenomena of (IV) are similar except that (VIII)+(VII) does not increase activity.

H. D.

Absorption of ultra-violet radiation by crystalline pepsin. F. L. GATES (J. Gen. Physiol., 1934, 18, 265–278).—Pure cryst. pepsin (I) in 0.1N-NaOAc buffer at p_H 5 gives progressive changes in the ultra-violet absorption curve (II), especially in higher λ, on irradiation for increasing periods. Increasing the λ of the radiation has similar effects. There is no significant difference between the (II) of active and heat-inactivated (I). The log. % of (I)-activity as determined by the Anson-Mirsky method (A., 1932, 1166) ∝ time of exposure. An essential agreement obtains between the determined activity and that deduced on the assumption of a one-quantum relationship, and the destruction curve (III) coincides with (II). However, considerably more energy must be absorbed at 250.9 and 271.9 mμ to produce 50% inactivation than at 235.7 mμ. The (III) of (I) is similar to that of urease.

H. D.

Temperature coefficient of inactivation of crystalline pepsin by ultra-violet radiation. F. L. GATES (J. Gen. Physiol., 1934, 18, 279–282).—The temp. coeff. of inactivation of pepsin by ultra-violet radiation at 253.7 mμ is 1.02.

H. D.

Isolation of crystalline trypsinogen and its conversion into crystalline trypsin. M. KUNITZ and J. H. NORTHROP (Science, 1934, 80, 505–506).—

Details are given of the isolation of cryst. trypsinogen (I) from the mother-liquor obtained from the chymo-trypsinogen crystallisation (A., 1934, 1260) and its conversion into cryst. trypsin by treatment with conc. aq. MgSO₄ at p_H 7.0–8.0. (I) is a protein with no proteolytic activity. The activation reaction is autocatalytic.

L. S. T.

Development of rennin-like and proteolytic activity of trypsin-kinase. M. GUILLAUME (Compt. rend. Soc. Biol., 1934, 117, 354–357).—The rennin-like activity (I) of trypsin-kinase develops at a faster rate than the proteolytic activity (II), the rate for (I) depending on the quantity of enterokinase (III) present. The max. (I) attained is independent of the quantity of (III), and when attained it is unaltered by the addition of sufficient (III) to bring (II) to its max.

R. N. C.

Activity of extracts of the pancreas of *Scyllium catulus* with added enterokinase. M. GUILLAUME (Compt. rend. Soc. Biol., 1934, 117, 747–750).—The proteolytic action (I) of extracts of the pancreas of dogfish (II) is increased by addition of enterokinase (III) preps. from dogs, rabbits, or (II). With low concns. of (III), (I) ∝ (III) concn. Following attainment of max. activity, the milk-curdling action diminishes more rapidly than (I).

F. O. H.

Enzymic liberation of arginine from proteins. F. LIEBEN and H. LIEBER (Biochem. Z., 1934, 275, 38–48).—Arginine (I) liberated from proteins (caseinogen, gelatin, serum-albumin) by enzymes (pepsin, trypsin, papain) is best determined by pptn. with flavianic acid or, colorimetrically, by a modification of the method of Lang (A., 1932, 834). By means of sulphosalicylic acid (II), (I) is separated into a fraction of high mol. wt. pptd. by (II) and another (III) which contains free (I) and peptides of low mol. wt. The arginase method determines free but not combined (I). Sources of error in other methods of determination are indicated and figures are given for the amounts of (I) obtained. The vals. decrease if alkaline digestion is prolonged, possibly because resynthesis and racemisation then occur.

W. McC.

Behaviour of animal proteolytic enzymes with plant proteins. V. S. ŠADIKOV and V. N. MENSCHIKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 138–142).—The process of isolation of proteins changes their behaviour towards enzymes; the native proteins of many seed meals are unattacked by animal proteolytic enzymes. The results cannot be ascribed to the presence of oil, since completely defatted soya-bean meal behaves similarly. The action of dil. HCl and Na₂CO₃ on the meals under different conditions is described.

H. N. R.

Relative actions of pancreatin on caseinogen and gelatin. P. EFENDI (J. Physiol. U.S.S.R., 1934, 17, 45–51).—Caseinogen ("acid protein") is digested better by 0.5% pancreatin than is gelatin ("basic protein").

CH. ABS. (p)

Ultrafiltration of urease using membranes of graded porosity. P. GRABAR and A. RIEGERT (Compt. rend. Soc. Biol., 1934, 117, 712–714).—

Urease is completely retained by a membrane having pores of 30 m μ diam. A. L.

Sugar fermentation. C. NEUBERG and M. KOBEL (J. Bact., 1934, 28, 461—471).—The mechanism of the enzymic changes is discussed. A. G. P.

Influence of p_H on the rate of yeast growth in a synthetic medium containing asparagine. C. TAXNER (J. Inst. Brew., 1935, 41, 27—30).—To a basal mineral-salt medium (without N) an extract of malt rootlets was added to supply "bios," and p_H was adjusted to the required val. with NaOH and lactic acid, the p_H changes during the periods investigated being relatively small. Glucose was added daily to maintain a concn. of 2%, and asparagine was added whenever N fell below 0.005% in the medium. The initial p_H (I) was of greater effect on the yeast growth than that reached later. The optimum (I) for growth was 3.57—3.87, there being here a lag, however, compared with growth at more alkaline vals., the increased growth being shown later. The cultures were continuously aerated.

I. A. P.

Assimilation of nitrogen by brewers' yeast. R. H. HOPKINS (J. Inst. Brew., 1935, 41, 30—33).—The yeast growth obtained by Taxner (preceding abstract) was somewhat > that obtained in brewers' wort (I), and enormously > that usually given in synthetic media. This is only partly due to the conditions of p_H , aeration, and sugar concn. employed, and to the presence of "bios." The low [N] maintained is also effective in increasing growth. It appears necessary to distinguish between "potentially assimilable N" (II) and "immediately assimilable N" (III). For max. growth, it seems that (III) should be maintained at a low val. With excessive (III), growth is rapid at first, but later declines. In (I), (II) reaches a relatively high val., but, in effect, steadily supplies (III) only in small quantities.

I. A. P.

Dehydrase system of yeast. R. SONDERHOFF (Ergebn. Enzymforsch., 1934, 3, 163—184; Chem. Zentr., 1934, ii, 1141—1142).—Dehydrase activity of yeast is discussed. A. G. P.

Role of ferrous and ferric ions in the fermentation and oxidation processes of yeasts. A. MALKOW (Zentr. Bakt. Par., 1934, 91, II, 161—163).—Addition of Fe⁺⁺⁺ to cultures resulted in formation of greater dry-wt. of yeast and less EtOH than when an equal wt. of Fe⁺⁺ was used. Fermentation in presence of Fe⁺⁺⁺ is independent of aeration.

A. G. P.

Effect of liver extract on fermentation by yeast. K. ZIPF and K. RATHERT (Biochem. Z., 1934, 275, 90—96).—In liver extracts anti-anæmic activity (I) \propto power (II) to stimulate fermentation by yeast. The substances responsible for (I) and (II) seem to be identical or closely related, since they very often occur together and have similar properties [stable to heat and to mild acid hydrolysis, not pptd. by Pb(OAc)₂, pptd. by 70% aq. EtOH, not adsorbed by animal C].

W. McC.

Action of dinitrophenols on respiration of yeasts and lactic bacilli. L. GENEVOIS and R.

SARIC (Compt. rend. Soc. Biol., 1934, 117, 368—369).—Dinitrophenols produce no increase of respiration of either yeasts or *B. Delbrücki*. R. N. C.

Results of irradiating *Saccharomyces* with monochromatic ultra-violet light. II. Influence of modifying factors. III. Absorption of ultra-violet energy by yeast. R. H. OSTER (J. Gen. Physiol., 1934, 18, 243—250, 251—254; cf. A., 1934, 1262).—II. Old yeast-cells (I) are more resistant to ultra-violet irradiation (II) than young proliferating cells; the temp. coeff. of the rate of destruction is 1.1. No toxic substances are liberated by cells killed or damaged by (II) nor is any effect on the subsequent growth of (I) produced by the (II) of the malt-agar medium.

III. An approximation to the ultra-violet absorption curve (III) of the absorbing substance responsible for the death of (I) is obtained by plotting the incident energies required to cause the death of 50% of (I) against λ . A min. energy requirement between 260 and 270 m μ and one below 230 m μ are found. The curves obtained resemble the (III) of cytosine and uracil.

H. D.

Extraction of zymoflavin by methylal. L. GENEVOIS and L. ESPIL (Bull. Soc. chim., 1934, [v], 1, 1498—1502).—Fresh yeast is shaken with methylal (I) for 30 min. and the liquid decanted. The paste is extracted with H₂O [saturated with (I)] and filtered. The (I) is removed by evaporation at 30°. Sugars are removed from the resulting aq. solution by yeast. The solution is then conc. in vac. and some NH₄-acids (II) are pptd. by Pb(OAc)₂. The product contains zymoflavin (III) and some (II) and other impurities. (III) is not affected by substitution of the NH₂ or SH of (II). The fluorescence of (III) is const. between p_H 3 and 10; it is destroyed by Na₂S₂O₄, by which (III) can thus be determined.

R. S. C.

Potentiometric determination of oxido-reduction processes in fermenting yeast extract. F. LIPMANN (Biochem. Z., 1934, 274, 329—340).—The author's earlier work (A., 1934, 451) on potentiometric determinations in Lebedev's maceration extract is extended, vals. for oxido-reduction potential being given using Pt electrodes in a vac., in air, and in pure O₂ in presence of traces of a series of indicators, and the results being discussed in reference to the fermenting system.

P. W. C.

Potentiometric experiments on the formation of reducing substances during fermentation. F. LIPMANN (Biochem. Z., 1934, 274, 412—422).—The potential (I) during fermentation is measured with polished Pt electrodes, a const. air stream being passed and a trace of thionine or methylene-blue being added. (I) decreases slowly in slow fermentations (glucose alone), quickly in rapid fermentations (glucose+hexose diphosphate), to a min. of +0.03 to 0.04 volt (p_H 6.4). (I) decreases most quickly on adding glucose+phosphoglyceric acid whilst with glucose+AcCO₂H it falls but only after a latent period, and with glyceric acid phosphate (concn. 0.0015M) the fermentation begins with almost max. velocity. After complete utilisation of the PO₄^{'''} (I) increases and the whole process may be repeated.

By addition of AsO_4''' , (I) falls and does not again increase as long as glucose is present. In presence of F' , (I) falls on addition of substrate at the same rate and to the same level as under normal conditions whilst in presence of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ the addition of substrate is almost without action on (I). P. W. C.

Chloric acid: only a limited plant poison. H. KUNZ-KRAUSE (Pharm. Zentr., 1935, 76, 3—4).—The growth of *S. glutinus*, Fresenius, on 5% KClO_3 solution is instanced. E. H. S.

Oxytrophs and nutrition of flagellated leucophytes. A. Lvov and H. Dusi (Ann. Inst. Pasteur, 1934, 53, 641—653).—The nutrition of *Polytoma uvella*, *Euglena gracilis*, *Astasia Chattoni*, and *Chilomonas paramecium* indicates that the necessity for fatty acids (I) having $< \text{C}_7$ (A., 1933, 536, 647) is related to the presence of plastids and the absence of chlorophyll. (I) can be replaced by starch.

F. O. H.

Relation of certain amino-acids to carbon dioxide and mycelium production of *Fusarium oxysporum*. A. K. ANDERSON and K. ENMART (Plant Physiol., 1934, 9, 823—829).—Glycine (I), leucine (II), tyrosine (III), and aspartic acid (IV) failed to increase the CO_2 production of the fungus. (I) and (IV) were utilised for CO_2 production, which was retarded by (II) and (III). (I), (III), and, notably, (IV) were more effective than glucose for mycelium production. A. G. P.

Carotenoids of some fungi. E. LEDERER (Compt. rend. Soc. Biol., 1934, 117, 1083—1185; cf. A., 1934, 220).—Torulene (I), m.p. 183—185° (blue colour with SbCl_3 with a strong band at 657 $\text{m}\mu$ and a weaker one at 435 $\text{m}\mu$), is present in red *Torula* (II), and also in *Sporobolomyces* (III) and *Lycogala epidendron*; β -carotene (IV) is present in all these except (III). The acid pigment (V) of (II) shows faint bands at 583, 543, and 500 $\text{m}\mu$ in CS_2 , and at 530, 494, and 460 $\text{m}\mu$ in light petroleum and MeOH ; it is present in (II) and (III), and also in *Puccinia coronifera*, together with the three carotenes. *Tremella mesenterica* contains (IV) alone, whilst *Coleosporium senecionis* contains the three carotenes without (V). The absorption curve of (I) in C_6H_6 is given.

R. N. C.

Decomposition of polyuronides by fungi and bacteria. II. Decomposition of alginic acid by bacteria and formation of the enzyme alginase. S. A. WAKSMAN and M. C. ALLEN (J. Amer. Chem. Soc., 1934, 56, 2701—2705; cf. A., 1933, 1082).—Alginic (=polymannuronic) acid (I) (from *Fucus vesiculosus*) is not decomposed to any appreciable extent by *Aspergillus*, *Trichoderma*, or *Fusarium* (cf. loc. cit.). (I) is hydrolysed by sp. bacteria (II) (from soil and sea-water) to simpler groups of uronic acids (III) (not pptd. by Ca), which are then decomposed further or oxidised to CO_2 ; simple (III) are not formed to any appreciable extent. (II) grown on liquid media (containing NaNO_3) produce enzymes which hydrolyse (I), starch, and other polysaccharides; the alginase (max. action at p_{H} 7 and 40° in presence of 2% NaCl) converts (I) into (III). The hydrolysable and non-hydrolysable fractions of (I) are both attacked (the former somewhat more readily)

by (II). Crude algin contains (I) and a lignin-like complex [pptd. in the culture medium as a humus-like complex during the action of (II)]. H. B.

Maintenance of vigorous mould stock cultures. H. C. GREENE and E. B. FRED (Ind. Eng. Chem., 1934, 26, 1297—1299).—The maintenance of morphological and physiological characters of 10 moulds on malt-agar, potato-agar, sterilised bread, and sterilised soil (I) media has been studied. Little variation was observed except with *Aspergillus sydowi*, in which the wt. of dried mycelium produced under standard conditions varied by 34%. Cultures on (I) showed reasonable constancy. The prep. of stock soil cultures is described. E. C. S.

Conversion of guanidine into urea by moulds. T. CHRZASZCZ and M. ZAKOMORNY (Biochem. Z., 1934, 275, 97—105; cf. A., 1934, 1263; Ivanov *et al.*, A., 1931, 524).—Guanidine (I) is degraded by many different species (II) of mould with production of urea and NH_3 , the amounts of urea varying greatly according to (II) and to the kind of nutrient medium. In some cases the urea produced is rapidly degraded further. Although the degradations often proceed concurrently they are entirely separate functions of the moulds. Low concn. (0.1%) of glucose accelerates the degradation of (I) leading to greater accumulation of urea, but higher concn., EtOH , and $\text{Ca}(\text{OAc})_2$ restrict urea accumulation. In the production of urea from peptone by moulds (I) is probably an intermediate. Possibly in the production of urea from arginine the precursor of urea is (I). W. McC.

Respiration and metabolism of moulds. S. MICHAEL (Biochem. Z., 1934, 274, 397—407).—An apparatus is described for following the acid formation (I), O_2 utilisation, and CO_2 elimination of a mould (*A. niger*) during growth. In a medium maintained neutral with CaCO_3 , the $\text{CO}_2 : \text{O}_2$ ratio is approx. 1. In the early period only 3% of the glucose used is utilised for respiratory purposes, the chief reaction being an oxidation to gluconic acid. The ratio of respired CO_2 to CO_2 set free from CaCO_3 is therefore very small, but increases considerably as citric and oxalic acids are formed. In a non-neutral medium the R.Q. falls during (I) to about 0.7, but returns to 1 as (I) slackens. P. W. C.

Growth and nitrogen assimilation of *Aspergillus niger* under the influence of growth regulators and of vitamin-B. E. BUNNING (Ber. deut. bot. Ges., 1934, 52, 423—444).—Dry-matter production (I) by *A. niger* is accelerated by growth-substance-B (synthesised by the fungus) but not by -A. Both substances accelerate the degeneration of mycelium, favour the resorption of NO_3' , and restrict that of NH_4' . In NH_4NO_3 media the latter effect results in increased p_{H} in the nutrient and a more rapid formation of conidia (III). Vitamin-B₁ affects the growth of *A. niger* only in initially neutral media, in which a small beneficial action is recorded. Vitamin-B₂ causes a 30—40% increase in (I). Both vitamins influence N assimilation, the reaction of media, and (III) formation in the same manner as the growth-substances. A. G. P.

Mould tissue. VI. Factors influencing amount and nature of fat produced by *Aspergillus fischeri*. E. A. PRILL, P. R. WENCK, and W. H. PETERSON (Biochem. J., 1935, 29, 21—33).—Different strains of *A. fischeri*, incubated with an inorg. salt medium + glucose for 10 days, showed variations in the fat content (I), sterols (II), lipin-P (III), and the I val. of the fatty acids (IV). A given strain shows an increase in the fat content by increasing the glucose in the medium, and a decrease in (II) and (IV). Increasing the $[\text{NH}_4\text{NO}_3]$ decreases the yield of mould per g. of glucose utilised, (II), and (IV). Increasing the p_{H} of the medium from 2 to 8 increases growth, % of fat, and (II). Raising the temp. decreases the % of fat, whilst aeration increases the mould growth. Continued incubation of the mould after all the glucose has been utilised decreases the % of fat and (III), but (IV) is unchanged. H. D.

Influence of a buffer on the activity of *Aspergillus*. V. BOLCATO (Giorn. Chim. Ind. Appl., 1934, 16, 552—555).—Fe and N compounds inhibit the formation of citric acid by *Aspergillus*, $\text{H}_2\text{C}_2\text{O}_4$ and CO_2 being formed instead. Addition of Na citrate destroys this inhibitive action. D. R. D.

Influence of calcium on the development of *Aspergillus niger* in a medium deficient in potassium. C. PONTILLON (Compt. rend. Soc. Biol., 1934, 117, 647—650).—The presence of Ca activates the utilisation of carbohydrate by *A. niger* grown on a medium deficient in K. A. L.

Influence of anti-oxidants, of methylene-blue, and of 2:4-dinitrophenol on the growth and energy output of *Aspergillus niger*. R. BONNET and R. JACQUOT (Compt. rend., 1934, 199, 1334—1336).—The growth and composition of the organism were not affected by various agents influencing the O_2 exchange. A. G. P.

Classification of acetic acid bacteria and oxidising bacteria isolated from fruits. Method of classifying oxidising bacteria. I. T. ASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 621—629).—Cell membranes of oxidising organisms give no blue colour with neutral or acidified solutions of I in KI. CH. ABS. (p)

Physiological characteristics of propionic acid bacteria. E. R. HITCHNER (J. Bact., 1934, 28, 473—479).—The catalase activity of these organisms is < is usually supposed. Succinic acid (I) as a sole source of C is not utilised by any of the species, but volatile acids may be produced from (I) by some strains in media containing fermentable carbohydrates, e.g., glucose. A. G. P.

***Lactobacillus bifidus*.** J. E. WEISS and L. F. RETTGER (J. Bact., 1934, 28, 501—521).—*L. bifidus* may constitute 90—95% of the intestinal flora of breast-fed infants. Growth conditions, sugar-fermenting ability, and tolerance to indole and PhOH of the organisms are examined. A. G. P.

Activator of lactic acid fermentation. A. K. SAVIN (Mikrobiologiya, 1933, 2, 266—276).—Extracts of French beans contain a H_2O -sol., dialysable, heat-

resistant substance which stimulates the production of lactic acid by *L. caucasicus* in milk-serum.

CH. ABS. (p)

***B. xylinum* cultures in lactic acid.** M. COZZO (Compt. rend. Soc. Biol., 1934, 117, 371—372).—The lactic acid (I) is oxidised to AcCO_2H (II). The anaerobic equilibrium potential (III) between (I) and (II) with *B. xylinum* is equal to (III) between glycerol and dihydroxyacetone, and to the Wurmser-Mayer-Reich (III) between (I) and (II) with lactic bacteria (cf. A., 1933, 850). R. N. C.

Comparative dissimilation of xylose and glucose by *Escherichia coli* and *Citrobacter anindolicum*. O. L. OSBURN and C. H. WERKMAN (Proc. Iowa Acad. Sci., 1932, 39, 134—135).—Differences in the proportions of the end-products (H_2 , CO_2 , AcOH , HCO_2H , lactic and succinic acids) of the fermentation of the two sugars are recorded. No evidence was obtained of the formation of AcCO_2H at any stage of the dissimilation. The xylose mol. splits into fractions other than those containing 2 and 3 C. CH. ABS. (p)

Dehydrogenase activity of *B. coli communis* on higher aliphatic acids. II. F. P. MAZZA and A. CEMMINO (Atti R. Accad. Lincei, 1934, [vi], 20, 113—118; cf. A., 1934, 221).—Methylene-blue (I) may act as H-acceptor in this dehydrogenation, but the process is then far slower than the aerobic process. If the concn. of (I) is > 0.001 mol., dehydrogenation of stearic acid is inhibited, owing to adsorption of (I) on the surface of the bacteria and consequent prevention of contact with the substrate. The dehydrogenase (II) is inactivated by heating sooner than the enzymes effecting the normal oxidations of *B. coli*, and probably requires no oxygenase to catalyse its action. (II) resembles the dehydrogenases of succinic, lactic, and acetic fermentations, but is more sensitive to the action of CO ; in its resistance to PhMe (II) resembles Quastel and Woolbridge's formic (II) (A., 1925, i, 1217). T. H. P.

Toxin of *Bacillus proteus*. H. RANDOLPH (J. Lab. Clin. Med., 1934, 19, 870—875).—Broth filtrates contain a sol. exotoxin capable of producing an antitoxin in rabbits. CH. ABS.

Biological oxidation of carbohydrates. IV. Phosphorus requirements of percolating filters. S. H. JENKINS (Biochem. J., 1935, 29, 116—132).—The amount of PO_4''' required to ensure rapid oxidation of a sugar solution depends on the size and shape of the filter medium, sufficient being required (together with adequate N supply) to establish a continuous film of the organism, but not enough to cause choking. When the film is established less PO_4''' and N are necessary. Excess of PO_4''' passes the filter unchanged, no org. P compounds being produced. The org. P compounds in beet press-water are only slowly available to the filter organisms. Unless adequate available N is present the full effect of PO_4''' is not evident. The increase of acidity of the effluent with increase of PO_4''' is due to removal of NH_3 from NH_4Cl with production of HCl , and not to org. acids. C. G. A.

Flavin transformation by bacteria. L. B. PETT (Nature, 1935, 135, 36).—A bacterial species

which changes the green fluorescence (I) of a lacto-flavin solution to blue has been isolated. The green (I) is restored by shaking in air. The EtOH extract of the dried bacteria gives only a blue (I). The blue fluorescent material can be extracted from CHCl_3 by alkaline H_2O and the blue (I) disappears at $p_{\text{H}} < 5$. Brewers' yeast, *Clostridium acetobutylicum*, and *Mycoderma cerevisiae* do not effect a similar change in flavin solutions. L. S. T.

Histo-chemistry of pigments of organisms producing septicæmia. I. *Bacillus perfringens*. E. DALOUS, J. FABRE, H. PONS, and BOULICAUD (Compt. rend. Soc. Biol., 1934, 117, 765—767).—The histochemical reactions of the brown pigment produced by *B. perfringens* indicate a melanin- and thioamino-type containing only traces of Fe. F. O. H.

Origin of the pigment in *Azotobacter chroococcum*. E. UNGERER (Z. Pflanz. Dün., 1934, A, 36, 287—290).—Tyrosine occurs in the bacterial cell. Pigmentation is associated with the appearance of NH_3 and increased p_{H} in the medium. A. G. P.

Nitro-effect. O. ACKLIN (Wasser u. Gas, 1934, 24, 323—333; Chem. Zentr., 1934, ii, 1176).—Chiefly theoretical. The connexion between nitro-reduction and other biological processes is discussed. The determination of the nitro-effect is described. H. N. R.

Comparative toxicity of sulphuric and acetic acids for *R* and *S* varieties of mammalian tubercle bacilli. A. SAENZ, M. SADETTIN, and L. COSTIL (Compt. rend. Soc. Biol., 1934, 117, 308—311).—Cultures of *B. tuberculosis R* and *S* of human, bovine, or BCG origin were all killed by 5% AcOH, but tolerated H_2SO_4 in concns. < 20%. R. N. C.

Comparative toxicity of sulphuric and acetic acid solutions to the *R* and *S* varieties of avian tubercle bacilli. A. SAENZ, M. SADETTIN, and L. COSTIL (Compt. rend. Soc. Biol., 1934, 117, 1072—1075).— H_2SO_4 is practically non-toxic, but AcOH destroys both strains in concns. > 5%. R. N. C.

Activation of the filterable form of tubercle bacilli by acetone extracts of Koch's bacilli. H. D. BOER (Compt. rend. Soc. Biol., 1934, 117, 772—774).—The results of Nègre *et al.* (A., 1933, 1334) are confirmed. F. O. H.

Antigenic fixatives of tubercle bacilli. I. In lipin-containing extracts of heat-killed bacilli. M. A. MACHEBŒUF and G. LÉVY [with M. CHAMBAZ] (Ann. Inst. Pasteur, 1934, 53, 591—597).—Amongst the various lipin fractions from heat-killed tubercle bacilli (A., 1934, 564, 929), only two (one sol. in hot or cold EtOH, the other only in hot EtOH) fix complement in presence of tubercular sera to a marked extent. Further fractionation by solvents indicates that the fixation is due to a substance (containing approx. 5% P but no glycerol) sol. in Et_2O and CHCl_3 but insol. in COMe_2 , common to both. F. O. H.

Endotoxin of typhus bacilli prepared by repeated freezing. (A) Preparation. B. ZABLOCKI and J. MORZYCKI. (B) Physico-chemical and antigenic properties. J. MORZYCKI and B. ZA-

BLOCKI (Compt. rend. Soc. Biol., 1934, 117, 789—791, 792—794).—(A) Cultures of typhus bacilli are repeatedly kept at -10° for 18 hr. and then at 37° for 6 hr., the final product being centrifuged and filtered through a Chamberland candle. Small doses (0.1—0.5 c.c.) of the filtrate produce marked toxic reactions in men, guinea-pigs, rabbits, and mice.

(B) The preps. are fairly thermostable and contain no protein or cholesterol and only traces of N; their immuno-properties and the ability to produce antibodies (agglutinins and precipitins) are, however, well marked. The residue from filtration contains living but morphologically changed bacilli. F. O. H.

Antigenic power and properties of staphylococcus anatoxin. J. TRAVASSOS (Compt. rend. Soc. Biol., 1934, 117, 717—719).—Staphylococcus toxin modified by CH_2O is grouped with the Ramon anatoxins. A. L.

Preparation of diphtheria anatoxin. M. ISABOLINSKI, I. LEVZOV, and V. BATANOV (Z. Immunität exp. Ther., 1934, 82, 16—25; Chem. Zentr., 1934, ii, 789).—Treatment of the toxin with 0.5—3% aq. SO_2 or HCl in aq. NaCl at 40° for 15—30 days produces an anatoxin having 7.8—8.2. A. G. P.

Chemistry of anti-bodies and serum-proteins.

I. Nitrogen distribution and amino-acids. II. Protein-carbohydrate groups. L. F. HEWITT (Biochem. J., 1934, 28, 2080—2087).—I. No marked difference was observed in the Hausmann no., or in the cystine, tyrosine, or tryptophan content of cryst. albumin, the globulin fractions, and diphtheria toxin-antitoxin floccules.

II. It was not possible to distinguish between serum-globulin (I) and diphtheria or streptococcus antitoxin by determination of carbohydrate (II) groups. Both (I) and serum-albumin can be fractionated into portions of different (II) content, that of the more sol. fractions being greater. H. G. R.

Synthesis of a growth factor by a micro-organism. W. SCHOPFER (Compt. rend., 1934, 199, 1656—1658).—Although the growth of *Phycomyces blakesleeanus* (I) on a synthetic medium (glucose, asparagine, MgSO_4 , KH_2PO_4) is inhibited by the complete absence of vitamin- B_1 (II), growth readily occurs if a small amount of culture of (I), grown on a medium containing (II), is added, a similar effect being produced by similarly grown cultures of other fungi of the same species. (I) can thus synthesise a growth factor which is not (II), since it can also accelerate the growth of *Saccharomyces cerevisiae* which is not sensitive to (II), vitamin- B_2 , or lactoflavin. J. W. B.

Enzymes of bacteria and bacterial metabolism. A. I. VIRTANEN (J. Bact., 1934, 28, 447—460).—A review. A. G. P.

Action of carbon dioxide on putrefactive micro-organisms. F. M. CHISTYAKOV (Mikrobiologiya, 1933, 2, 192—210).—Of 35 species of putrefactive bacteria examined, only 5 were not adversely influenced by CO_2 . CH. ABS. (p)

Influence of cations on bacterial viability. C. E. A. WINSLOW (Quart. Rev. Biol., 1934, 9, 259—274).—Stimulation by low and inhibition by

high concns. of cations results from influence on diffusion, the effects being paralleled by the position of the cation in the electromotive series (Na, K, low). The action of anions is mainly exerted through their effects on p_H . CH. ABS. (p)

Tropical soil microbiology. II. Bacterial numbers in the soil of the Malay peninsula. A. S. CORBET (Soil Sci., 1934, 38, 407—416; cf. A., 1934, 453).—Bacterial counts indicate that the no. of soil organisms is controlled by temp. and H_2O content. Decomp. of org. matter in these soils is mainly fungal. A. G. P.

Preservation of stock cultures of micro-organisms. A. C. THAYSEN (J. Inst. Brew., 1934, 40, 469—471).—Cultures of a no. of micro-organisms, prepared by methods previously described (B., 1924, 485), have remained in a viable condition for 12 years. I. A. P.

Determination of reducing sugars in bacteriological media. E. J. MCCREARY and H. G. SMITH (Proc. Iowa Acad. Sci., 1932, 39, 171—173).—The work of Magee and Smith (A., 1930, 643) is confirmed. Use of Lloyd's reagent for clarification causes less variation in results than that of basic Pb acetate or $Zn(OH)_2$. Discrepancies are reduced by dilution of the solution prior to clarification. Clarifying agents affect results by absorption of glucose and also by removal of interfering substances. $CuSO_4$ removes all non-sugar reducing agents from blood filtrates, but not from beef broth. CH. ABS. (p)

Agglutination of various bacteria by lemon juice. P. LASSEUR and M. A. RENAUX (Compt. rend., 1934, 199, 1454—1456).—This is shown to be due to the low p_H of the juice. R. S. C.

Catalase of filtrates of bacterial cultures after lysis by bacteriophage. I. LOMINSKI (Compt. rend. Soc. Biol., 1934, 116, 839—841).—Catalase content of filtrates through Chamberland L3 candles of cultures of *Staphylococcus* after lysis \propto initial nos. of bacteria. CH. ABS. (p)

Preparation of graded collodion membranes and their use in study of filterable viruses. J. H. BAUER and T. P. HUGHES (J. Gen. Physiol., 1934, 18, 143—162).—Collodion membranes (I) were prepared using as a stock collodion a solution of Parlodion shreds in $EtOH$, Et_2O , $COMe_2$, and C_2H_5OH . The pore size (II) was varied by addition of H_2O or glacial $AcOH$. Average (II) were calc. by application of Poiseuille's law. In the filtration of yellow-fever virus (III) adsorption of proteins was eliminated by passing a hormone broth at p_H 8 first. Suspensions (III) passed through (I) of (II) equal to 70, 55, and 50 μ showed clearly decreasing infective powers. The min. (II) for the filtration of sheep and monkey oxyhaemoglobin (IV) and ovalbumin (V) were 8 and 2 μ , respectively. Using Svedberg's vals. for the mo. sizes, a pore : particle ratio of 1.5 : 1 for both (IV) and (V) was obtained. H. D.

Action of antiseptics on the poliomyelitic virus in vivo and in vitro. G. HORNUS and P. (Compt. rend. Soc. Biol., 1934, 117, 656—657).—Poliomyelitic virus is very resistant to antiseptics. Among several substances examined,

"solganal," "uclarsyl," and isamine-blue proved active. A. L.

Gram staining method. P. LASSEUR and M. BENOIT (Compt. rend., 1934, 199, 1680—1682).—The no. of plastids (*B. mesentericus* and *B. subtilis*) stained by the Gram method decreases from p_H 2 to p_H 12 when the p_H in the pretreatment is varied using MacIlvaine's buffer, and from p_H 8 to p_H 12 when Na_2CO_3 buffers are used. With a Davis buffer (citric acid + alkali citrate) the no. stained increases slightly from p_H 2.2 to p_H 6.5, the increase being more marked with H_2SO_4 (12% at p_H 1.7 to 82% at p_H 5.3). Uniform staining occurs if the dimensions are 0—2 μ ; very old plastids (2.5—3 μ) are not coloured, but the cytoplasm, after rupture of the membrane, is stained. J. W. B.

Bacterial staining with potassium permanganate; spore staining. F. SANDER (Z. Hyg., 1934, 116, 334—336).—Use of H_2SO_4 - $KMnO_4$ for staining is described. A. G. P.

Detection of gold in spirochaetes and trypanosomes. V. FISCHL, J. KOTRBA, and E. SINGER (Z. Hyg., 1934, 116, 69—71).—A spectrographic method is described. A. G. P.

Use of drugs in vitro. E. SINGER and V. FISCHL (Z. Hyg., 1934, 116, 356—360).—The intake of As from atoxyl solutions by spirochaetes, trypanosomes, and other micro-organisms is increased by previous digestion of the solution with liver extract. Digestion with glutathione produces much greater activation. Ascorbic acid-thiourea mixtures are lethal to spirochaetes. A. G. P.

Antiseptic properties of esters of rhodamine-G. Role of surface tension and phenomena of photosensitisation. D. BOVER (Helv. Chim. Acta, 1934, 17, 1460—1465).—The absorption spectra of a series of esters of rhodamine-GP, -G (I), and -B [prep. (Fierz-David) not yet described] are recorded. The antiseptic action of esters of (I) towards staphylococci increases progressively from the Me to the heptyl ester and then declines markedly. The effect is parallel to that exerted by the substances on the surface tension. The simpler esters have a marked photosensitising action (II) and are more active in the light than in the dark; this phenomenon is not presented by the higher members. The (II) of two substances which are very similarly constituted and have almost identical absorption spectra may differ widely. H. W.

Bactericidal action of colloidal solutions. M. PRICA (Z. Hyg., 1934, 116, 385—396).—Colloidal solutions of SiO_2 , such as may be obtained in H_2O left in contact with fine sand for some months are toxic to *B. coli*, *B. paratyphosus*, and *S. pyogenes aureus*. Colloidal $Fe(OH)_3$ and $Al(OH)_3$ have a similar action. The natural purification of H_2O is discussed from this aspect. A. G. P.

Callicrein. IX. Detection and occurrence of callicrein in urine. H. KRAUT, E. K. FREY, E. WERLE, and F. SCHULTZ (Z. physiol. Chem., 1934, 230, 259—277; cf. A., 1930, 1069, 1624; 1932, 547).—Dialysis of human urine (I) through Cellophane against H_2O removes heat-stable depressor substances

from the callicrein (II), which is then assayed using dogs [the (I) of which contains much (II)] (cf. Weese, A., 1933, 1335). Purified (II) is inactivated by short heating at 60°; human (I) does not lose all its (II)-activity even after 30 min. at 90–95°, probably owing to the presence of thermo-stabilisers (removable by dialysis). The (II) in dialysed human (I) is inactivated much more readily by serum (III) (different types of which contain varying amounts of inactivator) or extracts of the lymph (IV) or parotid glands of the ox. The (I) of dogs is not inactivated by (IV) or pancreas (dog); (III) largely inactivates the undialysed (I). Dialysed (I) of cats is inactivated by (III) but not (IV). The amount of (II) in the (I) of adults varies from 0.04 to 0.6 unit per c.c. (mean val. 0.22); 56–550 units are excreted daily. Much less (II) is excreted by infants, children, and old people. The horse excretes little (II). H. B.

Villikinin content of different parts of the intestine. G. DE LUDANY (Compt. rend. Soc. Biol., 1934, 117, 974–975).—Villikinin (I) previously isolated from the duodenum is present also, but in smaller amount, in the mucosa of the large intestine, the ileum, and the stomach. (I) is not destroyed by trypsin or pepsin; it diffuses easily, and is not adsorbed by animal C. A. L.

Renal activity. VII. Effect of adrenal cortex. Y. MIZUNE (Sei-i-kwai Med. J., 1933, 52, No. 9, 63–79).—Acceleration of renal activity is demonstrated by determining urinary: blood-urea-N in rabbits fed with urea with or without injection of interrenin, and by a renal function test with phenol-sulphonephthalein. CH. ABS.

Ovarian stimulation by adrenal extracts. L. E. CASIDA and A. A. HELLBAUM (Endocrinol., 1934, 18, 249–253).—Adrenal (but not blood, serum, liver, or ovary) extracts (I) from non-pregnant mares and geldings, and (I) from pregnant mares caused the formation of large follicles or corpora lutea in rats. CH. ABS.

Variation in blood-calcium fractions caused by adrenaline. C. Rosso (Clin. pediatri., 1934, 16, No. 3).—Intravenous injection of adrenaline causes transition of colloidal Ca into an ultrafilterable form. CH. ABS. (p)

Antagonism of potassium and magnesium ions in adrenaline secretion. R. HAZARD and L. WURMSER (Compt. rend. Soc. Biol., 1934, 117, 864–866).—KCl injected intravenously excites the adrenal glands to secrete; MgCl₂ inhibits the effect. R. N. C.

Muscle-phosphorus compounds in adrenal insufficiency. E. LUNDGAARD and A. T. WILSON (J. Physiol., 1934, 80, 29–30p).—Inorg. PO₄^{'''}, phosphagen, pyrophosphate, and hexose phosphate in muscles of adrenalectomised cats were substantially normal. CH. ABS. (p)

Variations in blood-calcium fraction caused by parathyroid hormone. A. CABITTO (Clin. pediatri., 1934, 16, No. 3).—The total Ca (I) is increased except when the initial level is high. Ultrafilterable Ca varies with (I). Changes in colloidal Ca are independent of (I). CH. ABS. (p)

Action of parathormone. H. K. GOADBY and R. S. STACEY (Biochem. J., 1934, 28, 2092–2096).—Parathormone increases excretion of P in urine independently of the concn. of inorg. P in the plasma. H. G. R.

Oral and duodenal administration of single large doses of pure thyroxine. Comparison of calorigenic effects with those of monosodium thyroxine and thyroxine in alkaline solution. W. O. THOMPSON, P. K. THOMPSON, S. G. TAYLOR III, and L. F. N. DICKIE (Arch. Int. Med., 1934, 54, 818–828).—Oral and duodenal administration of thyroxine has no effect on the basal metabolic rate (I) in myxoedema, 10 mg. of the Na₁ salt increase the (I) 7, 20, and 32 points when administered orally, orally in alkaline solution, and intravenously in alkaline solution, respectively. H. G. R.

Biological demonstration of the thyroid hormone in the blood of pregnancy. Limitation of the activity of the thyrotropic hormone of the anterior pituitary, according to investigations on thyroid-deficient animals. P. THIESSEN (Arch. Gynakol., 1934, 156, 454–458; Chem. Zentr., 1934, ii, 963).—The increase in metabolism produced in rats by injection of pregnancy serum is not due to the thyrotropic hormone in the serum, as it occurs in thyroidectomised animals. R. N. C.

Effect of the epithelial cell and colloidal substance of the thyroid gland on excretion of iodine in urine. G. TANAKA (Folia Endocrinol. Japon., 1933, 9, 32–33).—Normal excretion of I was increased by injection of KI. The effect was accentuated by injection of aq. extracts of epithelial cells and restricted by extracts of colloidal substance. CH. ABS. (p)

Effects of extracts of thyroid gland obtained by treatment with acid alcohol on iodine excretion in urine. G. TANAKA (Folia Endocrinol. Japon., 1933, 9, 33–34).—I excretion was retarded and decreased by small doses and frequently unaffected by larger doses of the extract. CH. ABS. (p)

Effect of the thyrotropic hormone on the ketonic substances in the blood. F. SILBERSTEIN, F. GOTTDENKER, and E. HOHENBERG (Klin. Woch., 1934, 13, 595–596; Chem. Zentr., 1934, ii, 793).—Injection of 1000 units of the thyrotropic hormone (I) in cats produces a rise in blood-ketones (II), lasting several hr. Injection of 500 units causes a rise, followed by a fall below normal. (II) is similarly but not uniformly influenced by (I) after administration of oil. R. N. C.

Endocrine glands and calcium metabolism. H. ZWARENSTEIN (Biol. Rev. Cambridge Phil. Soc., 1934, 9, 299–331).—Thyroidectomy, hyper- and hypo-thyroidism, administration of thyroid gland or thyroxine did not affect the serum-Ca (I) level. Adrenaline had no const. action. The adrenal cortex, pituitary, thymus, and possibly ovaries are concerned in Ca metabolism (II). Administration of insulin with or without glucose increased (I). Pancreatotomy had no consistent effect on (II). CH. ABS. (p)

Inactivation of growth hormone. I. Inadequate refrigeration. II. Exposure to air. H. S. RUBINSTEIN (J. Lab. Clin. Med., 1933, 19, 63—66, 404—405).—The potency of anterior pituitary extracts is lowered by inadequate refrigeration or atm. oxidation. CH. ABS.

Iodine metabolism. VII. Effect of the mid-brain and the pituitary on iodine metabolism. A. STURM (Z. ges. exp. Med., 1934, 93, 490—501; Chem. Zentr., 1934, ii, 792).—Cessation of the functions of the tuber cinereum, lower hypothalamus region, infundibulum, and posterior pituitary produced no change in total I metabolism. Destruction or removal of the anterior pituitary (I) produced hyperiodæmia and hyperioduria for a week, followed by a slowly progressing hypoidæmic phase due to stoppage of the activity of the thyroid following the interruption of the thyrotropic effect of (I).

R. N. C.

Effect of pituitary extracts on the viscosity of blood, and its antagonistic effect on insulin. K. A. TZONI (Praktika, 1933, 8, 249—252; Chem. Zentr., 1934, ii, 1148).—Simultaneous injection of pituitary extract and insulin in rabbits produced an antagonistic effect of the two hormones on the viscosity of the blood.

R. N. C.

Lactic acid content of the muscle of hypophysectomised toads. A. D. MARENZI (Compt. rend. Soc. Biol., 1934, 117, 1035—1036).—The lactic acid content (I) of the gastrocnemius of normal toads (II), of those deprived of the posterior (III), and of those deprived of the anterior pituitary gland (IV) was 10.24, 11.06, and 10.35 mg. per 100 g. of muscle, respectively. (I) after 2 min. electrical excitation of the sciatic nerve was in (II), (III), and (IV), 129, 88, and 53 mg. per 100 g., respectively. After implantation of both glands and (III) alone, (I) increased to 126 and 106 mg., respectively.

A. L.

Melanophore hormone. IV. Isolation of the hormone. F. G. DIETEL (Klin. Woch., 1934, 13, 796—797; Chem. Zentr., 1934, ii, 792).—The hormone is stable to $\text{Ba}(\text{OH})_2$, which destroys oxytocin and vasopressin. To obtain a highly-purified prep. posterior pituitary powder is extracted at room temp. with 50 times its wt. of aq. $\text{Ba}(\text{OH})_2$, insol. material removed, and the solution acidified with H_2SO_4 and filtered after 2 hr. The filtrate is boiled down to $\frac{1}{4}$ vol. at neutral reaction, any ppt. removed, and 5 vols. of COMe_2 are added; the ppt. containing the hormone is collected after 24 hr., dried, taken up in H_2O , and evaporated to dryness. The residue is extracted thrice with boiling EtOH and the extract conc. The amorphous residue is sol. in H_2O ; the solution is not pptd. by $\text{CCl}_2\text{CO}_2\text{H}$ or $o\text{-SH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and the Pauly reaction is negative. The anterior lobe appears to contain inhibiting or sensitising substances.

R. N. C.

Effect of the posterior pituitary hormone on the water and chlorine excretion of the pregnant organism with reference to the hormonal theory of the origin of eclampsia. H. RUPP and W. BICKENBACH (Arch. Gynakol., 1934, 156, 420—427; Chem. Zentr., 1934, ii, 963).—Injection of posterior pituitary extract reduces Cl excretion, which is

increased in eclampsia. Pituitrin can be used to produce a lasting H_2O and Cl retention in pregnancy.

R. N. C.

Synergism between œstrin and pituitrin. E. MØLLER-CHRISTENSEN (Lancet, 1934, 227, 1388—1389).—The injection of œstrin into infantile guinea-pigs gives rise to increased sensibility of the uterus to pituitrin *in vitro*.

L. S. T.

Biological assay of folliculin. H. HINGLAIS and M. HINGLAIS (Compt. rend. Soc. Biol., 1934, 117, 1005—1008).—Using the technique of Allen and Doisy 0.1×10^{-6} g. of folliculin is equiv. to of the Allen and Doisy rat unit and not $\frac{1}{2}$ as has been previously thought. A change of the international unit is suggested.

A. L.

Folliculin content of normal and ectopic testicles. R. COURRIER (Compt. rend. Soc. Biol., 1934, 117, 1117—1120).—The folliculin content (I) of horse-testicles is $>$ that of ox., but $<$ that of hog-testicles (II). Normal and ectopic (II) show similar (I).

R. N. C.

Absorption and excretion ratios of folliculin in man. T. KEMP and K. PEDERSEN-BJERGAARD (Endokrinol., 1934, 13, 156—167; Chem. Zentr., 1934, ii, 1147).—Normal growing persons excrete daily < 10 mouse units per litre of folliculin (I) in the urine, and 30—70 units in the faeces, which probably originates from food. After peroral administration about 6% is eliminated in the urine, and after subcutaneous injection about 3%. Blood-(I) at the end of pregnancy is 5.6—7.6% of that of the urine, (I) being distributed equally between corpuscles and plasma.

R. N. C.

Metaplasia of uterine epithelium produced by chronic œstrin administration. H. SELYE, D. L. THOMSON, and J. B. COLLIP (Nature, 1935, 135, 65—66).—The effect has been observed in castrated female rats injected with oil solutions of œstrone.

L. S. T.

Regeneration of testes degenerated by menformone, spontaneously and by use of the gonadotropic hormone. S. E. DE JONGH and E. LAQUEUR (Nederl. Tijdschr. Geneesk., 1934, 78, 3030—3035; Chem. Zentr., 1934, ii, 1147).—Young rats' testes (I), the hormone production of which is stimulated by the gonadotropic hormone of pregnancy urine (II), are not or very little $>$ those of untreated animals. Menformone (III) causes shrinkage of (I), recovery of wt. being more rapid under administration of (II). (II) has a more marked effect on the Leydig cells (IV) than on (I). Prolonged treatment with (III) causes a temporary decrease in the no. of (IV).

R. N. C.

Constituents in normal urine producing the hyperglycæmia previously attributed to prolan. B. L. DAVIS, jun., J. C. HINSEY, and J. E. MARKEE (Endocrinol., 1934, 18, 382—386).—Hyperglycæmia in rabbits following injection of urine extracts is due to urinary constituents other than prolan.

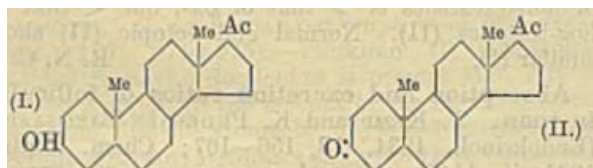
CH. ABS.

Emmenin. J. B. COLLIP, J. S. L. BROWNE, and D. L. THOMSON (Endocrinol., 1934, 18, 71—74).—Emmenin is a hydrolysable complex containing

trihydroxyœstrin. It does not appear to be ovary-stimulating, and its active principle may be converted into a more potent form in presence of ovarian tissue. CH. ABS.

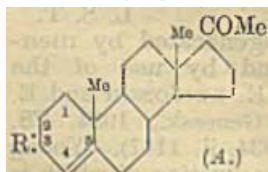
Hormonal function of the unfertilised egg. A. WESTMAN (Arch. Gynakol., 1934, 156, 550—565; Chem. Zentr., 1934, ii, 962).—Luteinisation of granulosa cells of rabbit follicles is not dependent on a hormonal action of unfertilised eggs. A. G. P.

Preparation of the corpus luteum hormone from stigmasterol. E. FERNHOLZ (Ber., 1934, 67, [B], 2027—2031).—3-Hydroxybismorcholenic acid is degraded to the OH-ketone (I), the dibromide of which is oxidised and debrominated to the diketone (ii), m.p. 129°, $[\alpha]_D^{20} + 200^\circ$ in CHCl_3 (dioxime, m.p. 246—248° when rapidly heated), identical with the corpus luteum hormone. Dehydrogenation of (I) to (II) by CuO at 310° is described. (II) is converted



into the variety, m.p. 121°, $[\alpha]_D^{20} + 200^\circ$ in CHCl_3 , when air is aspirated through its solution in H_2O - EtOH - Et_2O . The reverse transformation is effected by crystallisation from MeOH . H. W.

Preparation of the corpus luteum hormone from stigmasterol; constitution of the corpus luteum hormone. A. BUTENANDT and U. WESTPHAL (Ber., 1934, 67, [B], 2085—2087; cf. A., 1934, 1268).—The OH-ketone (I) (*loc. cit.*) is cautiously treated with Br in AcOH and the product is directly oxidised with CrO_3 ; mild treatment of the oily substance (II) thus obtained with AcOH and Zn dust yields Δ^4 -pregnene-3 : 20-dione (III) (A ; $R=O$) identical



natural corpus luteum hormone and with that obtained from pregnandiol. The Δ^4 position of the double linking follows from the optical behaviour of (III) and from the oxidation of (I) to a diketone. More drastic treatment of (II) with Zn and AcOH leads to the *deoxy-hormone*, $\text{C}_{27}\text{H}_{48}\text{O}$ [(?) A ; $R=\text{H}_2$], m.p. 105°, $[\alpha]_D + 96.4^\circ$, which is physiologically inactive. H. W.

Polymorphous modifications of the corpus luteum hormone. A. BUTENANDT and J. SCHMIDT (Ber., 1934, 67, [B], 2088—2091).—It is considered that there is only one corpus luteum hormone, $\text{C}_{27}\text{H}_{48}\text{O}_2$, which exists in several polymorphous forms. Whether the modification (I), m.p. 121°, or the form (II), m.p. 128.5°, is obtained from the gland, from stigmasterol, or from pregnandiol is a matter of accident. (I) and (II) can be interconverted by crystallisation from suitable solvents, they have identical analytical composition, absorption spectra, and optical activity, yield identical derivatives, and, according to the Clauberg test, have the same physiological activity, identical with that of the natural hormone. H. W.

Pregnan-20-ol-3-one. *allo*Pregnan-3-ol-20-one, a companion of the corpus luteum hormone. Conversion of pregnandiol into the corpus luteum hormone.—See this vol., 215, 216.

Male hormone as obtained from urine. T. F. GALLAGHER and F. C. KOCH (Endocrinol., 1934, 18, 107—112).—Testicular hormone (I) in urine extracts is purified by removal of acids and phenols and by distillation at $> 150^\circ$. The residue is fractionated with aq. EtOH , light petroleum, and CCl_4 , and then again distilled at 150—200°. The distillate (10,000 units per g.) differs chemically, but not biologically, from (I) from ox testis. CH. ABS.

Vitamins of olive oil. F. S. GÉRONA (Bull. Mat. Grasses, 1934, 18, 281—286).—The characteristic absorption from the red, blue, indigo, and violet regions of the normal spectrum indicates that the vitamin contents of dark cod-liver oil (I) and olive oil (II) are $>$ that of clear cod-liver oil and that (II), unlike (I), contains vitamin-B. Normal residue oil and (II) heated to 150° contain no vitamin-A, -B, or -D. F. O. H.

Production of vitamins by a pure culture of *Chlorococcum* grown in darkness on a synthetic medium. M. F. GUNDERSON and C. E. SKINNER (Plant Physiol., 1934, 9, 807—815).—Vitamin-A, or the provitamin, was produced in considerable amounts on a mineral salt-glucose medium. Smaller amounts of -B₁ and -B₂ but no -C were formed. A. G. P.

Purification of biosterol (vitamin-A) and a crystalline derivative thereof. S. HAMANO (Bull. Inst. Phys. Chem. Res., Tokyo, 1934, 13, 89).—*Theragra chalcogramma* liver-oil yields vitamin-A (C.L.O.U. 8300); the maleic anhydride adduct, $\text{C}_{30}\text{H}_{36}\text{O}_8$, of the Ac derivative thereof has m.p. 261—262°. R. S. C.

Vitamin-A. I. M. HEILBRON (Chem. and Ind., 1934, 1063).—A correction (A., 1934, 1269). R. S. C.

Vitamin-A content of herring. A. SCHEUNERT and M. SCHIEBLICH (Z. Unters. Lebensm., 1934, 68, 409—411).—Herring roe contains vitamin-A, the hard roe $>$ the soft. The -A content is not diminished by smoking. E. C. S.

Relative biological efficiencies of the vitamin-A and carotene of butter. R. G. BOOTH, S. K. KON, and A. E. GILLAM (Biochem. J., 1934, 28, 2169—2174).—The carotene (I) and vitamin-A (II) contents of the butters of Shorthorn and Guernsey cows have been determined spectrophotometrically and the (II) activities biologically. Although the total biological activity is the same for butters of both breeds, the contributions from (I) and (II) vary considerably with the breed, from which it is calc. that (II) is 6 times as potent as (I). C. G. A.

Fat-soluble vitamins. XLI. Carotene and vitamin-A content of colostrum. J. SEMB, C. A. BAUMANN, and H. STEENBOCK. XLII. Absorption and storage of vitamin-A in the rat. C. A. BAUMANN, B. M. RIISING, and H. STEENBOCK (J. Biol. Chem., 1934, 107, 697—703, 705—715).—The carotene (I) and vitamin-A (II) content of fat

prepared from colostrum is much higher than that of fat from ordinary milk, but decreases rapidly during the first week of milk secretion. The blood-stream may function as a significant storage reserve for (I).

XLII. The (II) content of new-born rats is very low but is increased slightly by raising the (II) intake of the mothers during pregnancy, and markedly by raising their (II) intake during lactation. 95% of the total (II) in the rat is stored in the liver, and (II) storage is greater when (II) is fed to normal animals than when it is fed to (II)-depleted rats. The min. daily dose of (II) necessary to produce storage is 25–50 blue units. Absorption and storage mostly take place within 6 hr. after ingestion. Loss of (II) due to destruction in the digestive tract is large, but faecal elimination of (II) is small. A. E. O.

Vitamin-A and carotene. XII. Elimination of vitamin-A from the livers of rats previously given massive doses of vitamin-A concentrate. A. W. DAVIES and T. MOORE (Biochem. J., 1935, 29, 147–150).—Rats with sufficient vitamin-A (I) stored in their livers to last theoretically for 100 years lose the greater part of their stored (I) in 12 weeks when restricted to a (I)-free diet. A stable storage level of 400 B.U. per g. is then reached. Carotene (in vegetables) is an efficient substitute for preformed (I) in diets suitable for the building up of a large (I) store in the rat's liver. A. E. O.

Influence of vitamin-A on the metabolism of rats and guinea-pigs. A. CHEVALIER and H. BAERT (Compt. rend. Soc. Biol., 1934, 116, 1037–1039).—Absence of vitamin-A from diet increases basal metabolism especially in young animals. CH. ABS. (p)

Carotene and vitamin-A requirements of white Leghorn chicks. W. O. FROHRING, and J. WYENO (J. Nutrition, 1934, 8, 463–477).—The min. requirement of chicks approx. 8 weeks old was 65 units per day. Vitamin-A deficiency did not induce "slipped-tendon." A. G. P.

Vitamins. XIX. Assimilation of carotene and vitamin-A in presence of mineral oil. R. A. DUTCHER, P. L. HARRIS, E. R. HARTZLER, and N. B. GUERRANT (J. Nutrition, 1934, 8, 269–283).—The vitamin-A potency of butter-fat is depressed in the presence of mineral oil (I), the effect varying with the proportion of (I) used. The potency of cod-liver oil was not affected by (I). Faecal excretion of carotene is relatively high when (I) is fed. A. G. P.

Determination of vitamin-A values by a method of single feeding. H. C. SHERMAN and E. N. TODHUNTER (J. Nutrition, 1934, 8, 347–356).—Rats depleted of stored vitamin-A receive a single feeding of test material. Subsequent wt. curves are compared with those obtained by feeding carotene. The area of growth curves for males was > that for females. Fresh kale contained 200 units per g. A. G. P.

Fate of the antirachitic factor in the chicken. Effective levels and distribution of the factor from cod-liver oil and from irradiated ergosterol in certain tissues of the chicken.

W. C. RUSSELL, M. W. TAYLOR, and D. E. WILCOX (J. Biol. Chem., 1934, 107, 735–746).—To produce normal bone ash and body-wt. in chickens at 8 weeks of age, < 144 times as much vitamin-D (I) must be fed in the form of irradiated ergosterol (II) as in the form of cod-liver oil (III). Storage of (I) in the liver is the same for each source of (I). The (I) content of the blood and long bones of cockerels is the same whether (I) is supplied as (III) (1% of the ration) or as (II) equiv. to 24% of (III). Pullets fed with (II) did not show the persistence in laying exhibited by birds receiving (III) under identical conditions. The antirachitic potency of the egg-yolk from birds receiving (III) was much < that from birds receiving (II). As regards body-wt., feathering, and general appearance, 1% of (III) is equiv. to the (I) content of 24% of (III) supplied as (II). (I) from either source is not lost by excretion in the bile. A. E. O.

Relative efficiencies of irradiated ergosterol and irradiated yeast for the production of vitamin-D milk. W. E. KRAUSS, R. M. BETHKE, and W. WILDER (J. Dairy Sci., 1934, 17, 685–693).—The transference of vitamin-D from ingested irradiated ergosterol to milk was approx. two thirds of that from irradiated yeast. A. G. P.

Relation between vitamin-E and sex hormones. G. SPAGNOL (Rev. sud-amer. endocrinol. immunol. quimioterap., 1934, 17, 553–565).—Hormone production is independent of vitamin-E (I), but (I) is necessary for physiological processes produced by hormones. CH. ABS. (p)

Utilisation of energy-producing nutriment and protein as affected by individual nutrient deficiencies. II. Effects of vitamin-B deficiency. F. J. McCLURE, L. VORIS, and E. B. FORBES (J. Nutrition, 1934, 8, 295–308).—Deficiency of vitamin-B resulted in depressed appetite but no change in wt.-increase per unit of food, decreased fat and energy gains, lower body temp., slightly increased digestibility of protein but not of energy foods, lowered efficiency of utilisation of metabolisable energy, increased energy out-go in heat and urine, increased C:N ratio in urine, and depression of oxidative processes of the organism. A. G. P.

Alimentary unbalance caused by Senegal gum. R. LECOQ (Compt. rend. Soc. Biol., 1934, 117, 994–996).—Pigeons fed on an adequate diet relatively high in vitamin-B developed polyneuritis when Senegal gum (I) was added to the diet. The galactose in (I) was probably responsible. A. L.

Optical investigation of the antineuritic vitamin-(B₁). A. SMAKULA (Z. physiol. Chem., 1934, 230, 231–239).—The absorption spectrum (I) of vitamin-B₁ (II) shows max. at 260 and 245 mμ (cf. Windaus *et al.*, A., 1932, 310; Peters and Philpot, A., 1933, 645). The (I) of the fission product C₇H₁₁O₅N₃ (III) (Windaus *et al.*, A., 1934, 1415) has max. at 261 and 225 mμ and is identical with that of 6-hydroxy-2-methylpyrimidine. The (I) of the fission product C₆H₇O₂NS (IV) (*loc. cit.*) has max. at 257 and 198 mμ; (IV) probably contains a pyrrole ring. Superposition of the (I) of (III) and (IV) gives a curve similar to that of (II); (II) contains

2 chromophores separated by a saturated hydrocarbon group. The (I) of the following are also given: hydrolysis product (probably $C_{12}H_{15}O_2N_3S$) of (II); Me pyrrole-2-carboxylate; 2-thiopyrrolidone; Me 4-thiol-3 5-dimethylpyrrole-2-carboxylate; glyoxaline; 2-methylglyoxaline-4-carboxylic acid; Et glyoxaline-4-acetate; pyrrole; 6-hydroxy-4-ethoxy-2-methylpyrimidine; 4:6-dihydroxy-2-methylpyrimidine; C_5H_5N ; thiophen. H. B.

Brain respiration, a chain of reactions as revealed by experiments on catatorulin effect. R. A. PETERS, H. RYDIN, and R. H. S. THOMPSON (Biochem. J., 1935, 29, 53—62).—Minced brain tissue of pigeons (I) prepared while kept warm showed a rate of oxidation in Ringer's solution+lactate or $AcCO_2H$ > when prepared in the cold. Addition of glutathione to the cooled (I) was without influence. Vitamin- B_1 (II) had its greatest effect on warm (I). Avitaminous (I) was incubated for 2½ hr. in Ringer solution+ $P_2O_7^{4-}$ (II). Addition of lactate produced an increased O_2 uptake only when (II) was present.

H. D.

Relation of pyruvic acid in brain to certain tissue poisons. R. A. PETERS, H. RYDIN, and R. H. S. THOMPSON (Biochem. J., 1935, 29, 63—71).—Fluoride (I) and iodoacetate (II) reduce O_2 uptake equally. Each largely reduces the catatorulin effect [extra O_2 uptake in presence of added vitamin- B_1 (III)], both together eliminating it. (I) decreases the pyruvate (IV) accumulation by avitaminous brain and (II) increases it. Glutathione produces only partial restoration of the vitamin effect in presence of (II). Disappearance of (IV) in presence of (III) results from some other change, the poisons influencing a preparatory stage for oxidation.

C. G. A.

Effects of the composition of the diet on the vitamin- B_1 and - B_2 requirements of the growing rat. N. B. GUERRANT and R. A. DUTCHER (J. Nutrition, 1934, 8, 397—420).—Addition of fats to the ration slightly retarded the depletion of vitamin- B_1 in rats, but did not affect that of - B_2 . The - B_2 requirement increased with the amount of mineral salts ingested. Addition of fibre to the diet economised the utilisation of - B_1 and - B_2 . Sucrose increased and dextrin lowered the - B_1 and - B_2 requirements. The latter were not influenced by the level of dietary protein.

A. G. P.

Synthetic vitamin- B_{12} . R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 2084—2085).—The compound $C_{17}H_{20}O_6N_4$, obtained from *l*-arabinose as Ac_4 derivative, has the same growth-promoting action as natural vitamin- B_{12} , whereas the substance $C_{15}H_{16}O_6N_4$ is inactive (cf. this vol., 94). H. W.

Non-identity of vitamin- B_2 and flavins. C. A. ELVEHJEM and C. J. KOEHN, jun. (Nature, 1934, 134, 1007—1008).—Vitamin- B_2 and flavins are not identical.

L. S. T.

Photochemical formation of 6:7-dimethylalloxazine from lactoflavin.—See this vol., 224.

Synthetic compounds of the lactoflavin group.—See this vol., 224.

Inanition as a factor in vitamin- B_{12} deficiency. D. G. REMPE and F. C. BING (J. Nutrition, 1934, 8,

457—462).—Mice receiving a vitamin- B_{12} -deficient diet consumed approx. 60% of the normal caloric intake. The body-wt. remained unchanged, neutral fats disappeared from the body, but phospholipins were unaffected. Bones developed subnormally, nos. of red blood-cells declined, and the concn. of haemoglobin and of serum-protein was < normal. - B_1 and - B_2 are necessary to maintain normal appetite.

A. G. P.

Colour test for vitamin-C. J. H. ROE (Science, 1934, 80, 561).—When ascorbic acid is boiled with HCl furfuraldehyde (I) is formed and CO_2 is liberated. The pink colour produced with (I) and NH_2Ph can then be used for its determination. Pentoses, pentosans, hexoses, and hexosans interfere. L. S. T.

Ascorbic acid and thiosulphate in urine. M. VAN EEKELN (Nature, 1935, 135, 37).— $S_2O_3^{2-}$ is present in the urine (I) of diabetics and of cats and, to a smaller extent, in that of dogs and normal persons. Its interference with the determination of ascorbic acid in (I) by the 2:6-dichlorophenol-indophenol method can be prevented by its removal with $Hg(OAc)_2$ or Ba salts.

L. S. T.

Ascorbic acid content of the intestine of the guinea-pig. S. S. ZILVA (Biochem. J., 1935, 29, 100—101).—Ascorbic acid injected into the jugular vein or given *per os* (as a mixed diet) to scorbutic guinea-pigs is selectively absorbed by the tissues of the intestinal tract, particularly in the small intestine.

C. G. A.

Vitamin-C in Indian food-stuffs. B. C. GUHA and A. R. GHOSH (Current Sci., 1934, 3, 210).—The guava, the mango (I) (langra variety), and the lichi are the richest sources of vitamin-C (II); they contain 1.04, 0.69, and 0.48 mg. of (II) per g., respectively. Different varieties of (I) differ in their (II) contents. The (II) of *kancha-mung* (*Phaseolus mungo*) is increased 7.8 times by germination. The process of development of these fruits appears to involve progressive reduction in (II) content.

L. S. T.

Chinese citrus fruit. VI. Vitamin-C content of Tsun Chü and Chao Kan. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1934, 2, 257—259; cf. A., 1933, 755; 1934, 1042).—Tsun Chü is > twice as rich as Chao Kan in vitamin-C, and is equal in antiscorbutic activity with Fu Chü and Hsiu Mi Chü.

J. L. D.

Vitamin-C content of Peiping summer fruit and vegetables. P. P. T. SAH, T. S. MA, and H. C. CHANG (J. Chinese Chem. Soc., 1934, 2, 260—265; cf. A., 1934, 1042).—The vitamin-C (I) content of many summer fruits and vegetables is recorded. Prolonged boiling of vegetables rich in (I) results in a large loss in nutritional properties.

J. L. D.

Isolation of vitamin-C from Chinese iris. Y. F. CHI and B. E. READ (J. Chinese Chem. Soc., 1934, 2, 271—273).—The yield (isolation described) is small, although titrimetric determinations indicate a high vitamin-C content.

J. L. D.

Vitamin-C and the adrenal gland in dogs. H. M. VARS and J. J. PFIFFNER (Proc. Soc. Exp. Biol. Med., 1934, 31, 839—841).—Adrenalectomised dogs receiving cortical hormone survived 15—33

months without developing scurvy on a diet which was scorbutic to guinea-pigs. Feeding of large amounts of vitamin-C (I) did not affect the requirement of cortical hormone. The adrenal gland is not concerned with the synthesis or metabolism of (I).

CH. ABS. (p)

Is the ascorbic acid content of adrenals and liver under control of nervous system? A. B. L. BEZNAK and Z. HARISS (Biochem. J., 1934, 28, 2039—2043).—No significant change (*i.e.*, within $\pm 15\%$) is produced in the ascorbic acid content of the adrenals (I) and liver (II) on stimulation or degeneration of the splanchnic nerve of the cat or by perfusion of (I) and (II) with solutions of adrenaline or acetylcholine.

H. D.

Effect of ascorbic acid on the thyroid and adrenals of guinea-pigs. D. MARINE, E. J. BAUMANN, and S. H. ROSEN (Proc. Soc. Exp. Biol. Med., 1934, 31, 870—873).—Oral administration of ascorbic acid produced smaller thyroid glands in guinea-pigs receiving a goitrogenic diet and anterior pituitary extract than in control animals.

CH. ABS. (p)

Enzymic reduction of dehydroascorbic acid. E. PFANKUCH (Naturwiss., 1934, 22, 821).—In juice expressed from potato (I), the vitamin is in the form of dehydroascorbic acid (II), owing to the activity of oxidases. If cysteine (III) (about 0.3%) is added to (I), (II) is reduced to ascorbic acid (IV). The reduction is enzymic. In the presence of much (III), (IV) must be titrated in presence of a citrate buffer of p_H 5.3—5.5, after addition of $HgCl_2$ and KCl .

A. J. M.

Biological genesis of vitamin-C. J. MOSONYI (Z. physiol. Chem., 1934, 230, 240—244).—The increase in the ascorbic acid (I) content of the adrenals of rats after administration of γ -hydroxyhexane- β -edione (II) (Henze *et al.*, A., 1933, 88, 377) is approx. the same as when the same amount of (I) is given. (II) is considered to be an intermediate in the biological synthesis of (I).

H. B.

Proportions of chloroplast numbers and chlorophyll concentration in *Elodea densa*. H. VON EULER, B. BERGMAN, and H. HELSTROM (Ber. deut. bot. Ges., 1934, 52, 458—462).—The chlorophyll (I) content per chloroplast (II) and the no. of (II) per cell are practically const.

A. G. P.

Development of chlorophyll and carotenoid pigments in etiolated plants. R. J. NORRIS (Bull. Basic Sci. Res., 1933, 5, 23—32).—Exposure of etiolated plants to artificial light resulted in formation of chlorophyll (I) and xanthophyll (II) in const. proportions. Carotene (III) decreased at first, but after 4—5 hr. increased more rapidly than (I) and (II). With increasing O_2 in the atm. (III) developed still more rapidly, but formation of (I) and (II) reached a max. with 20% O_2 . The proportion of all pigments increased with rising $[CO_2]$ in the atm. p to 3—5%, but subsequently declined.

CH. ABS. (p)

Chlorophyll fluorescence and assimilation of carbonic acid. I. Fluorescence behaviour of green plants. H. KAUTSKY and A. HIRSCH. II. Apparatus for comparative measurement of

changes of fluorescence of living leaves. Influence of temperature on the fluorescence curve. H. KAUTSKY and H. SPOHN (Biochem. Z., 1934, 274, 423—434, 435—451).—I. Change of intensity of chlorophyll fluorescence on irradiation is a general characteristic of green leaves of many plants and is probably related to assimilation of CO_2 by the leaves.

II. A detailed description of the apparatus is given. The velocity of increase of fluorescence on irradiation is probably determined by the intensity of the irradiating light, and is not altered by change of temp., whereas the velocity with which fluorescence falls away after irradiation varies greatly with the temp.

P. W. C.

Chlorophyll spectrum.—See this vol., 145.

Colloid chemistry of chlorophyll.—See this vol., 165.

Biochemistry of chlorophyll-defective barley mutants. H. VON EULER and R. WEICHERT (Svensk Kem. Tidskr., 1934, 46, 301—306; cf. A., 1932, 550).—Three new mutants (I) [normal (II) and chlorophyll-defective (III)] contain the base $C_{11}H_{14}N_2$ (A., 1933, 877) not found in ordinary barley or other green plants. For two (I) the catalase content (IV) of (II) considerably exceeds that of (III) in samples grown in light, but there is less difference in etiolated samples. For the third, (IV) in (III) is $>$ in (II). The dehydrase content (V) of barley seedlings on the 4th day is $>$ on the 6th—9th days. In a mutant irradiated with X-rays (V) in (III) is 100% $>$ in (II). W. McC.

Respiratory rate and enzyme activity as related to the hardened condition of plants. S. T. DEXTER (Plant Physiol., 1934, 9, 831—837).—Respiratory rates of wheat and cabbage seedlings decrease continuously during storage (I) at 2° , irrespective of their sugar content or condition of hardness. Oxidase activity was unchanged. In cabbage, catalase activity (II) was not affected by (I) for 5 days, although plants hardened and had increased proportions of sugar. In wheat (II) decreased in lighted and increased in darkened conditions.

A. G. P.

Temperature characteristics for metabolism of *Chlorella*. II. Rate of respiration of cultures of *C. pyrenoidosa* as function of time and temperature. C. S. FRENCH, H. I. KOHN, and P. S. TANG. III. Catalytic decomposition of hydrogen peroxide by *C. pyrenoidosa*. C. S. FRENCH (J. Gen. Physiol., 1934, 18, 193—207, 209—213; cf. A., 1934, 1262).—II. The O_2 consumption (I) of *C. pyrenoidosa* in Knop's solution in the dark decreases with time; the R.Q. also falls from an initial val. of 0.95 to a const. val. 0.65; hence it is concluded that two substances, A and B, are responsible for (I). The plot of rate of (I) against (I) is linear in the initial stages only; a similar curve for CO_2 consumption (II) runs parallel to this; curves of (I) and (II), corr. for the oxidation of A only, coincide, indicating an R.Q. equal to 1 for this component. The R.Q. of B is 0.65. The Arrhenius const. of (I) of A is 3500 g.-cal. above 11.5° and 19,500 g.-cal. below, whilst that of B is 5600 with no critical temp.

III. The decomp. of H_2O_2 by *C. pyrenoidosa* at p_{H} 6.72 is unimol. only in the initial stages. The plot of $\log. \text{initial } d[\text{H}_2\text{O}_2]/dt$ against $1/t$ is linear, giving an Arrhenius const. of 10,500 g.-cal. H. D.

Respiration of conjugating *Spirogyra* with special reference to fat metabolism. N. L. PAL (New Phytol., 1934, 33, 241—273).—During conjugation CO_2 evolution and the R.Q. decline. The O_2 intake rises in the early stages, but decreases later. Oil globules appear only in conjugating filaments. Starch is present at all times except the final stage of zygote formation, when it is converted into fats and oils. Light energy is essential to the latter process, which is reversed in darkness. A. G. P.

Metabolism of plant and insect waxes. A. C. CHIBNALL and S. H. PIPER (Biochem. J., 1934, 28, 2209—2219).—A general scheme for the metabolism of waxes is based on the hypotheses (1) that the primary alcohols are formed by the reduction of the corresponding acids, and the paraffins, sec.-alcohols, and ketones by indirect decarboxylation of the corresponding $n+1$ acid, and (2) that the saturated, keto-, and OH-acids are formed from unsaturated acids synthesised from shorter products. C. G. A.

Physiology of sugar accumulation in sugar-beet. I. Transformation of sugars in leaf scions. II. Influence of different sugars on photosynthetic energy. A. L. KURSANOV and M. N. KAZAKOVA (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R., 1933, No. 12, 3—13, 13—26).—I. A 3% solution of glucose (I) filtered through leaf scions is partly converted into fructose (II). Some synthesis of sucrose (III) occurs. A 3% solution of (II) is partly transformed into (I) under these conditions and (III) is also formed. Solutions of (III) (8%) were not affected by this treatment.

II. The action of sugar solutions on photosynthetic activity indicates that in beet sugars are translocated in the simple forms, and sugar storage is limited by insufficiently rapid photosynthesis. CH. ABS. (p)

Seasonal cycle of nitrogenous and carbohydrate materials in fruit trees. II. Cycles of alcohol-soluble materials and of carbohydrate fractions and lignin in wood, bark, leaves, and portions of terminal shoots of apple trees under two cultural systems—grass plus annual spring nitrate, and arable without nitrogenous fertiliser. E. S. SMITH (J. Pomology, 1934, 12, 249—292).—Seasonal variations in all constituents are recorded, those for bark (I) and wood being similar. Grassland trees receiving NaNO_3 had higher proportions of reducing sugars in spring and summer and, in general, higher carbohydrate:N ratios. Other constituents were not appreciably affected by differences in cultural treatment. Carbohydrates are translocated principally through (I). Sucrose in shoots acts as a primary reserve (II) rather than a medium of translocation. Complete disappearance of starch in winter does not occur. Hemicellulose is probably not a (II), but has a structural function.

A. G. P.

Variations in enzymic content of different varieties of sugar-beet at the germination period.

S. R. RISKINA (Trans. Central Sci. Res. Inst. Sugar Ind. U.S.S.R., 1933, No. 12, 36—43).—The increase in enzyme content of germinating seed (1—8 days) is irregular, but characteristic of seed type. Variations in forage-beet are less irregular than in sugar-beet.

CH. ABS. (p)

Substance in fleshy fruits inhibitory to germination. A. KOCKEMANN (Ber. deut. bot. Ges., 1934, 52, 523—526).—The Et_2O -extract of apples, pears, tomatoes, etc. contains a H_2O -sol., heat-resistant substance ("blastokolin"), which is decomposed by hot NaOH and by H_2O_2 , and inhibits the germination of seeds.

A. G. P.

Metabolic changes in geotropically stimulated seedlings. P. METZNER (Ber. deut. bot. Ges., 1934, 52, 506—522).—The hypocotyls of *Helianthus* seedlings, after keeping horizontal for some time, exhibited changes in the composition of expressed saps. Sap from the under side had higher d , osmotic pressure, $[\text{H}^+]$, and reducing sugar content than that of the upper side.

A. G. P.

Action of salts of beryllium, zirconium, and palladium on the geotropic sensitivity of roots. V. BAMBACIONI-MEZZETTI (Atti R. Accad. Lincei, 1934, [vi], 20, 125—128).—0.1% PdCl_2 solutions (in tap- H_2O) completely paralyse the geotropic sensitivity of roots of *Vicia sativa*; some roots resume growth subsequently and then show irregular curvature. 0.1% ZrCl_4 solutions inhibit geotropic curvature for 8 hr.; most of the roots dry without the plants dying, but some, after 24—48 hr., show geotropic and ageotropic curves. 0.1% BeCl_2 solutions have less effect. Apparently geotropic curvature depends less on the faculty of growth than on unequal distribution of the growth hormones.

T. H. P.

Absorptive function of roots and concentration of culture media. P. MAZE, P. J. MAZE, jun., and R. ANXIONNAZ (Compt. rend. Soc. Biol., 1934, 117, 753—754).—Maize plant roots immersed in aq. KI , KCl , or NaCl absorb these salts to an extent \propto their concn. in the media. Hence the absorptive power of roots varies with the properties and composition of the protoplasm (cf. B., 1933, 1027).

F. O. H.

Factors in elongation and expansion [of plants] under reduced light intensity. F. E. CLEMENTS and F. L. LONG (Plant Physiol., 1934, 9, 767—781).—The supply of H_2O is the dominant factor in stem elongation, and that of light in dry-matter production.

Variations in composition of protein of ripening wheat grains. A. KIESEL and M. KASTRUBEN (Z. physiol. Chem., 1934, 230, 216—224).—The total, protein, and H_2O -sol. N, gliadin (I), globulin, glutenin, and H_2O -sol. protein (II) of the dry, and the H_2O content of the fresh, grains are determined at various intervals during growth. The composition of (I) and (II) obtained at the various stages varies. EtOH -sol. and -insol. (I) appear to have the same chemical composition.

H. B.

Root stock effects with cherries. Seed and phyton propagation. M. B. CUMMINGS, E. W. JENKINS, and R. G. DUNNING (Vermont Agric. Exp.

Sta. Bull., 1933, No. 352, 36 pp.).—Effects of the stock on the development of tree and fruit and on the sugar and acid contents and pH of fruit are examined.

A. G. P.

Production of ethylene by some ripening fruits. R. GANE (Nature, 1934, 134, 1008).—The gas given off by ripe apples contains small amounts of C_2H_4 . In the absence of O_2 its production ceases or is much diminished.

L. S. T.

Carbohydrate-nitrogen ratios with respect to the sexual expression of hemp. P. J. TALLEY (Plant Physiol., 1934, 9, 731—748).—Staminate plants have higher % of total carbohydrates, polysaccharides, sugars, and reducing sugars, but lower N, than pistillate plants.

A. G. P.

Phytohormones. H. VON EULER, D. BURSTRÖM, and G. GÜNTHER (Svenk Kem. Tidskr., 1934, 46, 250—256).—The retarding action of egg-yolk and malt extracts and of urine on the root-growth of barley mutants grown in saline solution is as pronounced with chlorophyll-defective mutants (albina 1) as with those (I) of normal chlorophyll content. No retardation is caused by ovalbumin, pollen extract, methylene-blue, flavin, or the base $C_{11}H_{14}N_2$ present in (I). No differentiation is observed in the effect of factor-Z (yeast extract) on the growth of large or small plants of *Antirrhinum atardata* (Stubbe). Extraction of factor-Z from Stockholm brewer's yeast (cf. Borchardt *et al.*, A., 1934, 1035) and from barley embryos (best source) is described.

J. W. B.

Electrical behaviour of large plant cells. W. J. V. OSTERHOUT (Cold Spring Harbor Symp. Quant. Biol., 1933, 1, 125—130).—Phase-boundary potentials and potentials in living tissues due to Donnan constraints are usually small. Oxidation-reduction potentials do not account for the electrical behaviour of cells. Diffusion potentials have been studied for multi-nucleate cells. The non-aq. surface appears to be a mixture of substances, some of which may be removed and still leave a non-aq. layer. Anaesthesia may be produced by removing certain substances from the cell.

CH. ABS.

Osmotic pressure in relation to permeability in large plant cells and in models. W. J. V. OSTERHOUT (Cold Spring Harbor Symp. Quant. Biol., 1933, 1, 166—169).—The plant cell maintains a higher osmotic pressure inside by manufacture of sugar or sol. salts, and by accumulation of inorg. such as KCl.

CH. ABS.

Permeability of protoplasm to alcohols. H. ZEHETNER (Jahrb. wiss. Bot., 1934, 80, 505—560).—Comparison is made of the penetration of EtOH and CH_3OH into cells and the mechanism of the process is discussed.

A. G. P.

Balance of ionic sodium and calcium and cell-omès (Compt. rend. Soc. Biol., 1934, 117, 796—797).—Aq. NaCl or $CaCl_2$ penetrates sections of turnip root to an extent such as he is the same with both salts. With aq. $NaCl+CaCl_2$ in varying proportions, max. penetration of Cl^- and min. toxicity (as indicated by the survival period of the tissue) occur with $Na^+ : Ca^{++} =$ approx. 19 : 1.

F. O. H.

Influence of humic acid on the absorption of mineral salts by plants. A. V. BLAGOVEST-SCHENSKI and A. A. PROSOROVSKAJA (Biochem. Z., 1934, 274, 341—345).—Humic acid preps. from peat stimulate the growth of flax seedlings in H_2O culture, increasing considerably the dry wt. and % of N, but decreasing the % of P (increase of protoplasm but not of nuclear material). Tables show the N, P, and K contents of stalks and roots as a % of the dry wt. with varying nutrition.

P. W. C.

Phosphorus metabolism in the leaves of mistletoe. E. MICHEL-DURAND (Compt. rend., 1934, 99, 1653—1655).—Determination of P in the ignited residue of the EtOH- and Et₂O-sol. [lipin-P (I)], and the EtOH-sol. Et₂O-insol. [residual sol. P (II)] fractions of the dried leaves of mistletoe, and of the 10% $CCl_3 \cdot CO_2H$ extract (III) [total sol. P (IV)], the phytin pptd. by $Ca(OAc)_2$ from (III) [phytin-P (V)], and in the Mg phosphates from the (III) filtrate [mineral P (VI)] of the fat-freed leaves, gives an approx. measure of the relative types of P present at different periods between May and September (results tabulated), sol. org. P (VII) being given by (IV)–(V)–(VI), and the residue from (III) giving residual insol. P (VIII). During this period (I) diminishes slightly during leaf fall, (I)+(II) shows a slight increase, (IV) a slight continuous decrease, (VIII) remains const., (V) and (VI) exhibit a parallel and marked decrease, whereas (VII) undergoes a corresponding increase, (V), (VI), and (VII) being the most affected by the fall of the leaves.

J. W. B.

Forms of nitrogen in infusions of maize, timothy, red clover, tobacco, and red top. W. S. EISENMENGER (J. Agric. Res., 1934, 49, 375—378).—Analytical data show the N partition in the various infusions. In all cases NH_3 -, protein-, and proteose-N were present.

A. G. P.

Chemical composition of certain aquatic plants. H. J. HARPER and H. A. DANIEL (Bot. Gaz., 1934, 96, 186—189).—The N, P, and Ca contents of a no. of species are recorded. The influence of algæ on the classification of natural waters is discussed.

A. G. P.

Seasonal variation of hydrocyanic acid in *Molinia caerulea*, Moench. A. JUILLET and R. ZITTI (Compt. rend., 1934, 199, 1150—1152).—Details are recorded of the distribution of HCN in the various parts of the plants and of its variation with the course of the season. Desiccation and preservation cause marked diminution of the cyanogenetic complex. The quantity of HCN disengaged by an organ is not modified by addition of emulsin to the macerated mass, whereas contusion, previous to maceration which precedes distillation, does not permit the action of the enzyme on all the glucoside.

H. W.

Drift of the potassium and calcium content with age in plants. A. H. K. PETRIE (Austral. J. Exp. Biol., 1934, 12, 99—110).—The total K in *Lolium perenne* rises to a max. at maturity or during senescence and then declines, whilst Ca rises until late senescence without appreciable subsequent decline. The relative amount of K declines during the life-cycle; that of Ca declines during adolescence,

subsequently remaining const. or slightly rising. The mechanisms involved in the drifts of K and Ca are discussed. W. O. K.

Significance of manganese in plants. N. C. NAG (Trans. Bose Res. Inst., 1932—1933, 8, 179—194).—The Mn content of the leaves of various species of Coniferae increases markedly during female flower production; the cones also have a high Mn content. In *Abies balsamia* the Mn content rises from 155.0 p.p.m. in October to 430.5 during female inflorescence. The Mn content of chlorotic leaves is < that of normal green leaves. P. G. M.

Symptoms of malnutrition manifested by sugar cane grown in culture solutions from which certain essential elements are omitted. J. P. MARTIN (Hawaiian Planters' Rec., 1934, 38, 3—31).—The effects of deficiencies of N, P, K, Fe, Mn, Mg, and Ca on the development of the various plant organs and on chlorosis are recorded. *Pythium* root rot was severe in plants deprived of P and of S, but very slight where N was omitted. CH. ABS. (p)

Boron deficiency in sugar cane. J. P. MARTIN (Hawaiian Planters' Rec., 1934, 38, 95—107).—Normal growth occurred in the presence of 0.22 p.p.m. of B (as H_3BO_3) in media. Depressed growth with distorted and chlorotic leaves due to B deficiency resemble symptoms of "pokkah boeng" disease. CH. ABS. (p)

Effect of boron on development of sugar-beet in water cultures. M. A. BELOVSOV (Trans. Centr. Sci. Res. Inst. Sugar Ind. U.S.S.R., 1932, No. 8, 50—59).—The presence of H_3BO_3 (0.5—10.0 mg. per litre) favourably affects the growth of beet. Absence of B prevents growth. Concns. > 25 mg. per litre are injurious. The injurious action of heavy metals is counteracted by addition of H_3BO_3 to the medium. CH. ABS. (p)

[Report on] botany research [sugar-cane]. H. EVANS (Mauritius Rept. Agric. Sugar Cane Res. Sta., 3rd Ann. Rep., 1932, 29—46).—Cane arrows, cut and placed in H_2O , wilt in 12 hr. because the vessels are blocked with reddish-brown substance produced by oxidase and peroxidase. Reducing agents ($H_2C_2O_4$ or SO_2), also H_3PO_4 and H_2SO_4 , prolong life, but are toxic later. Invert sugar is less effective. Germination of cane cuttings is increased by soaking in aq. $Ca(OH)_2$ (I) for 8—12 hr. Cane borer larvæ in cuttings are killed by (I) alone or containing $MgSO_4$. CH. ABS. (p)

Pathological effects of deficiency or excess of certain ions on citrus leaves. J. DUFRENOY and H. S. REED (Ann. Agron., 1934, 4, 637—653).—Salts of Zn and Fe have a sp. effect on the assimilatory function of leaves. Cytological examination of leaves of Zn-deficient trees is recorded and discussed in relation to mosaic disease. A. G. P.

Biology of halophytes. I. Physiology of germination. E. SCHRATZ (Jahrb. wiss. Bot., 1934, 80, 112—142).—Retarded germination caused by NaCl solutions and sea- H_2O is due to the high concn. of salts rather than to any sp. action of NaCl. A. G. P.

Reversal of direction of translocation of solutes in stems. P. W. ZIMMERMANN and M. H. CON-

NARD (Contr. Boyce Thompson Inst., 1934, 6, 297—302).—By a system of in-arch grafting and pruning, salts and elaborated foods may be made to move both upwards and downwards in stems. A. G. P.

Chemotropic sensitivity of dicotyledonous seedlings. J. KISSER and I. BEER (Jahrb. wiss. Bot., 1934, 80, 301—335).—Deviation of seedling stems following the application of salt solution to an incision on one side of the stem depends on the concn. of the solution used and the period of treatment. High concns. caused a positive curvature (I) in all cases as a result of mechanical and osmotic effects. With small concns. negative (I) observed is due to unequal growth following chemotropic response. The latter was most marked with LiCl, NH_4Cl , and $MnCl_2$, less with NaCl and KCl, and did not occur with $CaCl_2$, $SrCl_2$, $BaCl_2$, or $MgCl_2$. A. G. P.

Salt concentration and reversibility of ice formation as related to the hardness of winter wheat. S. T. DEXTER (Plant Physiol., 1934, 9, 601—618).—Withdrawal of H_2O by ice formation in wheat crowns is not a fully reversible process, but reversibility increases as hardness (I) develops. The proportion of H_2O remaining unfrozen (II) decreases with the freezing temp. Increasing (I) of plants with the advancing season is associated with a decline in sol. salt content of the tissues and a marked decrease in the salt concn. of (II). A. G. P.

Accumulation of electrolytes. VII. Organic electrolytes. I. A. G. JACQUES (J. Gen. Physiol., 1934, 18, 235—242; cf. A., 1934, 1049).—The cation:anion ratio of the inorg. constituents of the saps of *Rheum rhaponticum*, *Rumex acetosella*, and *Oxalis corniculata* varied between 1.8 and 5.3. H. D.

Elementary composition of some cultivated plants. G. BERTRAND and V. GHITESCU (Compt. rend., 1934, 199, 1269—1273).—Complete analyses are recorded of rape, lucerne, buckwheat, and oats. A. G. P.

Relationships of soils to manganese deficiency of plants. G. W. LEEPER (Nature, 1934, 134, 972—973).—A method for determining the available Mn is described and a mechanism for absorption by plants suggested. Healthy soils contain > 100 p.p.m. Mn deficiency diseases occur with < 15 p.p.m. L. S. T.

Determination of small quantities of aluminium in plants.—See this vol., 186.

"Stony" concretions in the trunk of *Clorophora excelsa*, Bth. L. ADRIAENS (Bull. Agric. Congo Belge, 1934, 25, 86—90).—Brown concretions in the cavity and trunk wood contain Mn and 94% of $CaCO_3$. CH.

Composition of juice of oranges from girdled and normal trees. C. G. CHURCH (Calif. Citrograph, 1933, 18, 348—349).—Juice of fruit from girdled trees had higher proportions of sol. solids, total and reducing sugars. Sucrose and citric acid contents were normal. CH. ABS. (p)

Bog-moss. I. Chemical composition of *Sphagnum fimbriatum*, Wils. (Himemizugoke). M. SHIKATA and M. WATANABE (Proc. Imp. Acad.

Tokyo, 1934, 10 470—471).—The composition is compared with that of wood-pulp. J. L. D.

Amanita toxin. J. RENZ (Z. physiol. Chem., 1934, 230, 245—258).—The most active prep. of the toxin (I) is obtained by adsorption of inactive substances from the MeOH extract (of *Amanita phalloides*, Fr.) on SiO_2 gel and $\text{Al}(\text{OH})_3$, subsequent pptn. with phosphotungstic acid (II), fractional decomp. of the ppt. with basic Pb carbonate in H_2O , and final dialysis. (I), thus obtained, gives no ppt. with (II) or $\text{Hg}(\text{OAc})_2$ (cf. Raab, A., 1932, 785) except in presence of KCl, NaCl, or NH_4Cl , but is pptd. by Ba or K Bi iodide. (I) gives Pauli's diazo-reaction, reduces KMnO_4 (not Fehling's solution), could not be reduced (H_2 , PtO_2 , MeOH), does not react with CH_2N_2 , and gives no colour with ninhydrin. Appropriate acylation of (I) in $\text{C}_2\text{H}_5\text{N}$ affords the Bz, M about 800 (hydrolysed with difficulty), anisoyl, m.p. about 175° [readily hydrolysed (EtOH - NaOEt or $-\text{KOH}$) without much loss of activity], and (probably) the ON-Ac, derivative (III), m.p. 190—195° (decomp.; sinters at 158°) [not hydrolysed by 2N - H_2SO_4 at 30°; hydrolysis with conc. acid or MeOH-KOH gives an inactive product]; these are amorphous H_2O -insol. [except (III)] powders. (III) and conc. KOH in N_2 at 130° give NHMe_2 and NH_3 . H. B.

Differentiation of the toxin ricin and of an allergen in castor-oil seeds. Preparation of ricinallergen. P. GRABAR and A. KOUTSEFF (Compt. rend. Soc. Biol., 1934, 117, 700—701, 702—704).—Seeds of *Ricinus zanzibariensis* contain the toxin ricin (I) and the allergen ricinallergen (II), whilst the rind of the seeds contains only (II). (I) is destroyed by heating to 60° and by EtOH, (II) remaining unaffected. (I) and (II) may be separated from one another and from the dried and oil-free seeds by ultrafiltration or pptn. with $(\text{NH}_4)_2\text{SO}_4$. A method for separating a non-toxic prep. of (II) is described. A. L.

Pharmacologically valuable constituents of Bixa orellana. L. F. W. FREISE (Pharm. Zentr., 1935, 76, 4—5).—Proximate analyses of the fruit, husk, and seeds are given and also the medical application of preps. of the fruit pulp, whole seeds, seed husk, unripe fruits and their husks, and of the fresh leaves. E. H. S.

Entandrophragma palustris, Staner. L. THON (Bull. Agric. Congo Belge, 1934, 25, 21—25).—The bark contains resin, fluorescent material sol. in HCl, pyrocatechol, an alkaloid, a tannin (catechuic), and certain phlobaphens. CH. ABS. (p)

[Constituents of] Ceanothus velutinus. L. W. RICHARDS and E. V. LYNN (J. Amer. Pharm. Assoc., 1934, 23, 332—336).—The leaves of *C. velutinus* present microscopically a peculiar structure, not found in other species, which may be related to the characteristic balsamic coating. They furnish 0.14—0.21% of an oil which consists chiefly of Et and cinnamyl cinnamates, with smaller amounts of salicylaldehyde, terpenes, and esters of an unidentified alcohol (*di-n-butylurethane*, m.p. 56°; *phthalate*, m.p. 204—205°) with cinnamic and probably valeric acids. The root

bark furnishes 0.1% of an alkaloid, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$, m.p. 270° (decomp.), which yields an unstable hydrochloride, completely decomposed at 240°. The symptoms of a dermatitis caused by the leaves are described. A. E. O.

Pigment of "Adsuki bean." C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1934, 10, 472—474).—A purple-coloured material, decomp. at 235° (Pb salt), and substances, m.p. 157° and decomp. at 235°, which are found in the testa (isolation described) give, with alkali, $s\text{-C}_6\text{H}_3(\text{OH})_3$ and protocatechuic acid. A phlobatannin-like substance, decomposed by alkali to $s\text{-C}_6\text{H}_3(\text{OH})_3$ and gallic acid, is also isolated. J. L. D.

Anthocyanin plant colours and yield in maize. R. A. BRINK (J. Amer. Soc. Agron., 1934, 26, 697—703).—Relationships between inheritable yielding capacity and the presence of plant pigments are examined. A. G. P.

Indian acorn oils. S. V. PUNTAMBEKAR and S. KRISHNA (J. Indian Chem. Soc., 1934, 11, 721—726).—The oil from the acorn kernels of *Quercus incana*, Roxb., yields palmitic (17.1), oleic (and isomeric) (82), and (?) lignoceric (0.9%) acids, and contains a small amount of (?) sitosterol, m.p. 126—128°. R. S. C.

Chinese citrus fruit. VII. Isolation of essential oils from Fu Chü and Chao Kan. P. P. T. SAH and H. Y. FANG (J. Chinese Chem. Soc., 1934, 2, 266—270; cf. A., 1933, 755).— C_6H_8 containing some CHCl_3 extracts an essential oil and a substance, m.p. 60° (which contains no N), from Fu Chü (I) and Chao Kan (II). The oil from (I) contains *d*-limonene (III), and has a high sap. val. and N content, whereas that from (II) is about 94% (III). J. L. D.

Essential oil in the ripe Fu Chü [tangerine] fruit. W. S. TAO and C. M. CHU (J. Chinese Chem. Soc., 1934, 2, 282—287).—Light petroleum or Et_2O extracts from the skins an essential oil (3.8—4.9%) which contains mainly *d*-limonene and some aldehyde. J. L. D.

Constitution of the primary alcohols, fatty acids, and paraffins present in plant and insect waxes. A. C. CHIBNALL, S. H. PIPER, A. POLLARD, E. F. WILLIAMS, and P. N. SAHAI (Biochem. J., 1934, 28, 2189—2208).—Analysis by use of the data given previously (this vol., 264) of many plant and insect waxes shows that the alcohols are mixtures of the even-no. members from C_{24} to C_{36} , the acids mixtures of even-no. *n*-fatty acids from C_{24} to C_{34} , and the paraffins mixtures of the odd-no. members from C_{25} to C_{37} . Even-no. paraffins do not occur. The approx. composition of the various waxes is indicated. C. G. A.

Odorous principles of green tea. III. Acids of raw tea oil. S. TAKEI, Y. SAKATO, and M. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1161—1168; cf. A., 1934, 571).—The oil from fresh tea-leaves contains AcOH, EtCO_2H , PrCO_2H , valeric, *n*-hexoic (I), and palmitic (II) acids. The oil from manufactured green tea contains only (I), (II), and heptioic acid, and *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$. R. S. C.

Crystalline principles from Indian species of *Artemisia*. ANON. (Pharm. J., 1935, 134, 3—5).—From various species of *Artemisia* were isolated santonin, β -santonin (A., 1934, 1225), and ψ -santonin, m.p. 184—186°, $[\alpha]^{20}_{\text{D}} -172.5^\circ$ in CHCl_3 .

F. O. H.

Marrubiin content of some *Labiatae*. J. BALANSARD (Compt. rend. Soc. Biol., 1934, 117, 1014—1015).—Marrubiin (I) is present in a large no. of indigenous *Labiatae*. The active principle, m.p. 188—189°, of *Tenerium scordium* is, however, not (I).

A. L.

Heteroside of *Primula acaulis*, Jacq. A. GORIS and H. CANAL (Compt. rend., 1934, 199, 1675—1677).—The isolation of pure *primulaveroside* (I), $\text{C}_{18}\text{H}_{22}\text{O}_{11}(\text{OMe})_2 + \text{H}_2\text{O}$ and anhyd., m.p. 179.5—180° (corr.), $[\alpha]^{20}_{\text{D}} -57.74^\circ$ in H_2O , from the rhizomes of *P. acaulis*, and its separation from the volemitol present, are described. Enzymolysis of (I) with the sepal powder of *P. officinalis*, L. (II), affords primeverose and Me 2-hydroxy-5-methoxybenzoate (structure confirmed by synthesis). (I) is accompanied by traces of a ketonic substance [2:4-dinitrophenylhydrazone, m.p. 230° (decomp.)]. (I) occurs with primeveroside in (II).

J. W. B.

Glucoside and a hydrolysing enzyme in the bark of *Periploca græca*, L. T. SOLACOLU and HERRMANN (Compt. rend. Soc. Biol., 1934, 117, 1138—1140).—*Periplocymarin* (I), m.p. 149—152°, occurs in the bark (II) with periplocin (III), from which it is formed by loss of 1 mol. of glucose. The ratio (I):(III) in (II) is approx. 0.02%. (II) also contains an enzyme which hydrolyses (III) to (I).

R. N. C.

Polysaccharides of *Iridaea laminarioides*. T. TADOKORO and K. YOSHIMURA (J. Chem. Soc. Japan, 1934, 55, 617—621).—Hydrolytic products of a 35% EtOH extract included pentose, methylpentose, and arabinose. A hot- H_2O extract contained in addition galactose, glucose, and fucose.

CH. ABS. (p)

Spruce holocellulose and composition of its easily hydrolysable fraction. E. F. KURTH and G. J. RITTER (J. Amer. Chem. Soc., 1934, 56, 2720—2723).—The holocellulose (I), isolated from the sawdust by a slight modification of the method previously described (B., 1934, 12), contains all the Ac (cf. Hägglund, A., 1934, 819), all CO_2 -forming material, about 12% of the OMe, and nearly all the pentosans of the extracted ($\text{EtOH}-\text{C}_6\text{H}_6$ and hot H_2O) wood (II). Hydrolysis (2.5% H_2SO_4) of (I) or (II) gives HCO_2H [0.56% based on (I)] and AcOH (about 1.95%). Hydrolysis (1% H_2SO_4) of (I) removes a fraction (hemicellulose) [=10.3% of (II)] of the following composition: mannose (17.7%), glucose (8%), galactose (7.8%), arabinose (12.5%), and xylose (20.9%) anhydrides; OMe (3.2%); uronic anhydride (14.6%); volatile acids (8%). The residue [=61% of (II)] from the hydrolysis appears to be identical with the Cross and Bevan cellulose.

H. B.

Substitution staining with free dye-acids and -bases. R. C. MCLEAN (New Phytol., 1934, 33, 316—317).—Solutions in xylene of the free acids of

eosin and erythrosin are utilised for staining cellulose in plant sections. Liquefied tissue, cork, and pith cells are unstained. The free base of methylene-blue is similarly used for staining liquefied membranes.

A. G. P.

Chemical composition of ripe Huang Yen Chü [*Citrus species*]. W. S. TAO, S. Y. YAO, and C. T. LIU (J. Chinese Chem. Soc., 1934, 2, 274—281; cf. A., 1934, 818).—In Chu Hung Chü the acid, reducing sugar, pentosan, and cellulose contents are > in the variety Shih Chü.

J. L. D.

Structure of proteins. M. A. LISITZUIN (Bull. Appl. Bot. Genetics, Plant Breeding U.S.S.R., 1934, A, No. 9, 5—16).—Globulins of peas, beans, and soya beans are examined and classified as "proto-acids."

CH. ABS. (p)

Protein. XIII. Proteins of soya bean. T. HIBINO (J. Chem. Soc. Japan, 1934, 55, 655—692).—The isolation of albumin, glycinin (I), and glutelin is described. The hydrolysis of (I) at different temp. and p_{H} yields varying proportions of sol. protein, proteose, and peptone and of insol. substances. Min. amounts of sol. matter are obtained at 120° at the isoelectric point. The reaction at 150° is reversible.

CH. ABS. (p)

Protein content of barleys at different stages of maturity. K. G. SCHULZ and G. KUNISCH (Woch. Brau., 1934, 51, 321—323).—The protein content (I) of barley is influenced by the rainfall during the principal period of development of the plant, by the nature of the previous crop, and by the soil. In most of the samples examined, a low proportion of available H_2O (judged from soil and rainfall statistics) gave high (I), and *vice versa*.

I. A. P.

Chemical properties of proteins of *Iridaea laminarioides*. T. TADOKORO and K. YOSHIMURA (J. Chem. Soc. Japan, 1934, 55, 525—527).—Two proteins are examined, (i) a chromoprotein, sol. in salt solutions and 30—35% EtOH, with N-containing products of hydrolysis unlike those of phycoerythrin, (ii) sol. in hot H_2O and 2% NaOH, similar to prolamine.

CH. ABS. (p)

Proteins of the seeds of the tobacco plant. G. ILJIN (Biochem. Z., 1934, 273, 350—353).—The fat-free seed (I) contains 7.8% of albumin, 8.5% of globulin (II), and 2.75% of glutenin. The N content of (I) is > that of (II) from other plants. The P contents of the separate proteins differ considerably, whilst the S contents are similar.

W. McC.

Phosphorus in vegetable proteins. I. Globulins of *Lathyrus sativus* and *Vicia sativa*, var. *augustifolia*. Y. V. S. RAU (Proc. Indian Acad. Sci., 1934, 1, B, 73—79).—Data are given for the N, P, and S contents and the N distribution in the globulin and albumin of *L. sativus* (khesari) and in the globulin of *V. sativa* (akta). The latter contains no P, a small fraction [separated by $(\text{NH}_4)_2\text{SO}_4$] containing approx. 10% P being probably an albumin.

F. O. H.

Preparation of white zein from yellow corn. I. D. MASON and L. S. PALMER (J. Biol. Chem., 1934, 107, 131—132).—Fat and pigments are extracted with $\text{C}_2\text{H}_4\text{Cl}_2$ from 95% EtOH solution. H. G. R.

Feulgen's nucleal reaction. A. EICHORN and R. FRANQUET (Compt. rend. Soc. Biol., 1934, 117, 326—328).—The results of staining cell nuclei, chromosomes, etc. of various plant tissues are discussed (cf. A., 1933, 105). No interaction between nucleolus and chromosomes during mitosis is evident.

F. O. H.

Distribution of non-protein-nitrogen in the Alaska pea. S. L. JODIDI (J. Franklin Inst., 1934, 218, 581—591).—The acid-amide-N (7.58—8.13%) of Alaska pea seeds grown on untreated soil is increased to 9.02 and 10.89—11.43% by fertilising with $\text{NaNO}_3 + (\text{NH}_4)_2\text{SO}_4$ and KCl, respectively; the NH_2 - and peptide-N vals. are 8.43—8.59, 9.72, 6.04—7.92, and 39.08—41.83, 33.28, 36.06—37.64%, respectively. The bearing of the data on the vals. of nutritive non-protein-N is discussed (cf. A., 1932, 312).

F. O. H.

Occurrence of organic bases, especially of cadaverine in potato tubers. K. YOSHIMURA (Biochem. Z., 1934, 274, 408—411).—From 20 kg. of fresh materials the following bases were isolated: adenine (as picrate) 0.2 g.; trigonelline (as chloride) 0.2 g.; cadaverine (as chloride) 0.1 g.; choline as aurichloride 0.5 g. Histidine and arginine were also present.

P. W. C.

Preparation of aqueous extracts of soluble nitrogen from plant tissues. O. W. DAVIDSON, H. E. CLARK, and J. W. SHIVE (Plant Physiol., 1934, 9, 817—822).—Boiling the material with H_2O for 20 min. followed by washing on a filter cloth was as effective as cold- H_2O extraction after grinding with sand. Loss of N from cyanogenetic material in peach was minimised by the boiling method.

A. G. P.

Variations of the quantity of tannin during the development of the gall-nuts of the oak. H. GROSSU-HERRMANN (Compt. rend. Soc. Biol., 1934, 117, 1127—1131).—Tannin in *Dryophanta folii* gall-nuts rises to a max. in midsummer, falling to a min. in early autumn. In *Cynips hungarica* the tannin reaches its max. in late summer. In both species the max. occurs simultaneously with max. morphological development.

R. N. C.

Quantity of oil in linseed and hemp seed during different periods of maturation and germination as well as in birch and lime trees during different phases of winter. J. DMOCHOWSKI (Polish Agric. Forest. Ann., 1934, 32, 35—77).—During normal maturation the oil (I) of linseed and hemp increases to a max. as the seeds dry. No increase occurs during drying of shelled seed under germinating conditions. (I) declines and disappears in 24 hr. H_2O is for transformation of oil. In birch and trees changes in (I) and H_2O content during winter and spring are inversely related.

CH. ABS. (p)

Nature of rust-resistance in wheat. VI. Effect of hydrogen-ion concentration, phenolic compounds, and host extracts on germination of urediniospores of *Puccinia graminis tritici*, 21. J. A. ANDERSON (Canad. J. Res., 1934, 1, 661—686).—The optimum p_{H} for spore germination (G) was 5.8—6.5. Among a no. of compounds

examined the min. concn. inhibiting G was lowest in buffered solutions of quinol, followed in increasing order by o-cresol, anisic and benzoic acids, pyrocatechol, guaiacol, and PhOH. In unbuffered solutions the influence of p_{H} accentuates the effects. Expressed juices from wheats exhibited inhibitory effects which showed varietal differences. No relationship was apparent between the inhibitory action of the juice and the resistance of the variety to rust infection.

A. G. P.

Effect of mildew and rust infection on dry weight and respiration of excised clover leaflets. C. E. YARWOOD (J. Agric. Res., 1934, 49, 549—558).—Infection decreased the dry wt. and markedly increased respiration (I) in clover leaflets. Dusting with S increased the (I) of healthy and infected leaflets.

A. G. P.

Chemistry of vegetable tumours. IV. Peroxidase in the tumours. G. KLEIN and W. ZIESE (Biochem. Z., 1933, 267, 22—25; cf. A., 1933, 315).—The peroxidase content (I) of tumours (II) in horse-radish roots (III) is much (up to 100%) > that of roots of the healthy plant and the (I) of the thick upper parts of (III) is > that of the small branches of the roots. Young (II) have lower (I) than old.

W. McC.

Nature of injury to forage legumes by the potato-leaf hopper. H. W. JOHNSON (J. Agric. Res., 1934, 49, 379—406).—Yellow and reddened leaves of lucerne and clover caused by leaf hopper injury have higher contents of dry matter, reducing sugars, sucrose, starch, total hydrolysable matter, and EtOH-sol. N, but lower total N, than normal green leaves. Also the osmotic pressure of the sap is increased. Similar changes are produced artificially by girdling the stems. Coloration of leaves of infested plants is due to excessive accumulation of carbohydrates in areas in which vascular tissues are injured by the insects.

A. G. P.

Photodynamic action of methylene-blue on the virus of a plant disease. H. H. STOREY (Ann. Appl. Biol., 1934, 21, 588—589).—The virus of streak disease in maize is inactivated by exposure to light in the presence of methylene-blue and O_2 .

A. G. P.

Fungi associated with blight diseases of certain cultivated leguminous plants. A. SATTAR (Trans. Brit. Mycol. Soc., 1934, 18, 276—301).—Growth of *Ascochyta pinodella*, *A. pisi*, *Mycosphaerella pinoides*, and *Phyllosticta rabieri* was fairly rapid in the p_{H} range 4.0—8.8 (optimum, 7.0), declined rapidly between 4.0 and 3.0, and ceased between 3.0 and 2.4.

CH. ABS. (p)

Virus causing foliar necrosis of the potato. F. C. BAWDON (Proc. Roy. Soc., 1934, B, 116, 375—395).—A new potato virus "D" (I) is described. In some species this causes foliar necrosis and in others top-necrosis. (I) confers a resistance to further infection with virus "X" and *vice versa*, the extent of which depends on the species of the host.

H. G. R.

Photodynamic action of methylene-blue on plant viruses. J. M. BIRKELAND (Science, 1934, 80, 357—358).—In general, plant viruses such as tobacco virus and streak virus are more resistant to

the photodynamic action of methylene-blue (I) than are animal viruses or bacteriophage. Ringspot virus, however, in presence of (I) is quickly inactivated by exposure to electric light. L. S. T.

Serum reaction as an aid in the study of filterable viruses of plants. H. P. BEALE (Contr. Boyce Thompson Inst., 1934, 6, 407—435).—Serological reactions of tobacco mosaic virus are examined and a method is described for determining the antigenic content of saline extracts of virus. A. G. P.

Action of high-frequency sound waves on tobacco mosaic virus. W. M. STANLEY (Science, 1934, 80, 339—341).—The data given indicate that the inactivation of the virus by supersonic radiation (A., 1934, 822) is associated with expulsion of dissolved gas and with the presence of extraneous matter in the untreated juice. Intense high-frequency sound waves have practically no effect on virus purified under a high vac. L. S. T.

Spreading in a unimolecular film. Method for biological problems. E. GORTER (Amer. J. Dis. Children, 1934, 47, 945—957).—Technique of du Nouy and Langmuir is applied to determinations of lipase activity, fat, and lipins in blood, and protein in solutions. CH. ABS. (p).

Accurate, adjustable gas-mixing apparatus for measurements of biological liquids. H. SCHADE and H. VON PEIN (Z. ges. exp. Med., 1934, 76, 540—548; Chem. Zentr., 1934, i, 1530). L. S. T.

Determination of the p_H of normal and malignant tissues with the glass electrode and vacuum tube null indicator. H. M. PARTRIDGE, J. A. C. BOWLES, and A. GOLDFEDER (J. Lab. Clin. Med., 1934, 19, 1100—1105). CH. ABS. (p)

Electrical method for checking physiological salt solution. J. H. GRAHAM (Amer. J. Pharm., 1934, 106, 325—327).—The concn. of physiological NaCl solution (0.85%) is best checked by determination of its sp. conductivity. J. W. B.

Determination of iron in biological materials. T. G. KLUMPF (J. Biol. Chem., 1934, 107, 213—223).—Knecht and Hibbert's $TiCl_3$ method (A., 1903, ii, 217, 509) is modified and adapted to determination of Fe in blood, food, faeces, and urine. C. G. A.

Micro-detection of insoluble calcium salts in tissues. G. GOMORI (Virchow's Archiv, 286, 682—689; Chem. Zentr., 1934, i, 3500).—The solubilities of Ag_3PO_4 and Ag_2CO_3 are < those of the corresponding Ca salts. Immersion of tissue in 1.5% aq. $AgNO_3$ for 6—10 days results in transformation of Ca into Ag salts the presence of which is detectable by the hypophosphite test. The prep. is fixed in aq. $Na_2S_2O_3$ and Ca is removed by sulphosalicylic acid. A. G. P.

Identification of glass splinters. N. A. MARRIS (Analyst, 1934, 59, 686—687).—The probable identity of two samples of glass, one of which was in the form of minute splinters, was established by determination

of n and d , and by observation of the fluorescence in ultra-violet light. E. C. S.

Blood-iodine. III. Reservoir burette. F. J. PHILLIPS and G. M. CURTIS (J. Lab. Clin. Med., 1934, 19, 896—898).—A 0.2-c.c. Kahn pipette, graduated in 0.001 c.c., is attached to the reservoir tube of a Koch burette by means of a 3-way stopcock. CH. ABS.

Iodometric determination of sugar in presence of thiocyanate. D. KRUGER and E. TSCHIRCH (Biochem. Z., 1934, 274, 34—41).—The influence of p_H and concn. of KI, Cu, and CNS' on the titration of Cu is investigated and the most suitable composition of the required solutions is outlined. P. W. C.

Galactosuria test of Fiessinger. Application of the method of Fleury and Marque to the determination of galactose in urine. R. HAZARD, M. HERBAIN, and C. VAILLE (J. Pharm. Chim., 1935, [viii], 21, 61—71).—The KI-HgI₂ method of Fleury and Marque (A., 1929, 292) may be used for the determination of galactose in urine. W. O. K.

Determination of phenol. G. BARAC (Compt. rend. Soc. Biol., 1934, 117, 259—261).—A modification of the method of Theis and Benedict (A., 1924, ii, 708) is used for the determination of PhOH in blood or urine. A. L.

Colorimetric micro-determination of cholesterol. S. GORTZ (Biochem. Z., 1934, 273, 396—412).—By combining the advantages of the methods of Rappaport and Engelberg (Klin. Woch., 1931, 700) and Milbradt (A., 1933, 624) a simple procedure for determining cholesterol in biological fluids, e.g., 0.1 c.c. of blood, is obtained. $AcCl$ is used to produce the strong, very persistent colour. The average error is about 2%. W. McC.

Biochemical gravimetric methods. IV. Micro-determination of cholesterol by the torsion balance. L. JENDRASSIK and A. BOKRÉTAS (Biochem. Z., 1934, 274, 367—371).—A simplified method is described in which the pptn. is carried out at room temp. with dil. EtOH solutions of digitonin (I) and the ppt. collected on a Seitz asbestos filter and weighed. The method gives accurate vals. for blood-serum. By heating cholesterol a substance arises which is no longer precipitable by (I), but is still detected colorimetrically. P. W. C.

Determination of lactic acid by the method of Mendel and Goldscheider. R. NORDBO (Biochem. Z., 1934, 275, 162).—In the process described in A., 1934, 1050, the colour comparison is made after keeping the solution for 60 min. in ice- H_2O .

Nephelometric investigation of protein solutions. II. E. M. MYSTKOWSKI (Biochem. Z., 1934, 274, 461—464; cf. A., 1934, 1306).—A table summarises the varying degrees of turbidity, determined nephelometrically, of an electro-dialysed solution of ovalbumin as compared with a commercial prep. at varying p_H and in presence of NaCl, $CaCl_2$, $MgCl_2$, $MgSO_4$, and Na_2SO_4 . P. W. C.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1935.

General, Physical, and Inorganic Chemistry.

Spectrum of ordinary hydrogen (H_2). O. W. RICHARDSON (Nature, 1935, 135, 99—100).—The electronic configurations of new bands in the spectrum of H_2 are discussed. L. S. T.

Fine structure of H_a . F. H. SPEDDING, C. D. SHANE, and N. S. GRACE (Physical Rev., 1935, [ii], 47, 38—44).—Separation of the patterns of H^1_a and H^2_a was obtained. Analysis of the spectrograms showed three components of the same relative intensities for each line. The divergence between observed and calc. intensities is discussed. The fine structure const. gave $1/\alpha = 137.4 \pm 0.2$. N. M. B.

Excitation potential of the nitrogen second positive bands. N. THOMPSON and S. E. WILLIAMS (Proc. Roy. Soc., 1935, A, 147, 583—593).—The energy of the $C^3\Pi$ level of N_2 is 13.16 ± 0.05 volts. There are indications of a possible fine structure of the excitation function near the excitation potential. L. L. B.

Structure of the second positive nitrogen group and the predissociation of the N_2 molecule. G. BUTTENBENDER and G. HERZBERG (Ann. Physik, 1935, [v], 21, 577—610).—The fine structure of eight bands of the second positive N_2 group has been analysed. The discontinuance of the rotation structure in consequence of predissociation is discussed. The dissociation heat of N_2 in the ground state is 169.47 ± 0.11 kg.-cal. per g.-mol. A. J. M.

Excitation of the nebular line 4267 (C) in oxygen. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1934, 10, 554—556).—This line is enhanced in an atm. of O_2 when a minute amount of C is present. H. J. E.

Oxygen afterglow. E. M. STODDART (Proc. Roy. Soc., 1935, A, 147, 454—467).—Pure O_2 excited electrodelessly is glowless in "clean" and "poisoned" vessels, even in presence of N_2 ; it is also glowless in discharge tubes with degassed electrodes, but the glow is restored by addition of N_2 . From the facts that NO is synthesised when an electrode discharge is passed through O_2 - N_2 mixtures, but not in electrodeless tubes, and that the addition of NO to an electrodeless discharge through O_2 causes the appearance of an afterglow, it is concluded that the O_2 afterglow is the same phenomenon as the NO- O_3 chemiluminescence. The afterglow spectrum consists of weak diffuse bands from 4200 to 6700 Å. L. L. B.

Influence of temperature on absorption in neon gas. O. MASAKI and T. OKATOME (J. Sci. Hiroshima Univ., 1934, 5, 51—56).—The

absorption of the unstable state 2^3P_1 of Ne decreases very slightly from 20° to 220° , that of the metastable state 2^3P_2 decreases slowly, whereas that of the metastable state 2^3P_0 decreases rapidly with rising temp. R. S. B.

Vacuum spark spectra of sodium, magnesium, aluminium, and silicon. J. SODERQVIST (Nov. Acta Reg. Soc. Sci. Upsali., 1934, [iv], 9, No. 7, 120 pp.; Chem. Zentr., 1934, ii, 1735). H. J. E.

Absorption series of argon, xenon, and krypton to terms between the ionisation limits $2^1P^0_{3/2}$ and $2^1P^0_{1/2}$. H. BEUTLER (Z. Physik, 1935, 93, 177—196). A. B. D. C.

Transition probabilities in the potassium series in flames. E. F. M. VAN DER HELD and J. H. HEIERMAN (Physica, 1935, 2, 71—74).—From the intensities of the $d-p$ and $s-p$ lines of K in an C_2H_2 -air flame, and the temp. calc. by the reversal method, the transition probabilities of these changes are calc. (cf. this vol., I). J. W. S.

Persistence of intercombination lines. A. T. WILLIAMS (Compt. rend., 1935, 200, 230—231).—It is shown that as the ratio of the terms decreases, the intensity and persistence of the lines increases; e.g., for the configuration d^2 the term ratios 1D_2 - 3F_2 / 3F_2 - 3F_4 are Sc II 33.4, Y II 9.2, and La II 5.1. R. S. B.

Hyperfine structure of the zinc resonance line 3076 Å. W. BILLETER (Helv. phys. Acta, 1934, 7, 413—426; Chem. Zentr., 1934, ii, 1096).—Measurements by absorption are recorded. H. J. E.

Zeeman effect of the spectra of arsenic. J. B. GREEN and W. M. BARROWS, jun. (Physical Rev., 1935, [ii], 47, 131—135).—Wave-lengths, classifications, and Zeeman patterns are tabulated for 11 lines of As I, 64 lines of As II, and 2 lines of As III; resulting g vals. agree with perturbation theory. 22 unclassified lines of As II are listed. N. M. B.

Zeeman effect in bromine and iodine. P. LACROUTE (Ann. Physique, 1935, [xi], 3, 5—96).—Under improved conditions data are obtained, classified in orders of excitation, for 180 lines of Br and 400 lines of I, in the Schumann region. Zeeman effects are tabulated for 26 lines of Br I, 182 of Br II, and 244 of I II. Classifications of the arc spectrum of Br are revised; for Br II 26 lines are classified and g vals. for 20 terms are given; certain observed Paschen-Back effects are analysed. The no. of classified lines of I II is extended from 26 to 209, and the no. of terms from 12 to 54, with g vals. for 39 terms. Fundamental terms are identified; the

ionisation potential of I is 19.4 volts, and nuclear moment is $5/2$. N. M. B.

Induced predissociation of the Te_2 molecule. V. KONDRATEEV and A. LAURIS (Z. Physik, 1934, 92, 741—746).— N_2 induces dissociation in excited Te_2 mols. A. B. D. C.

Spark spectrum of iodine. P. N. KALIA (Indian J. Physics, 1934, 9, 179—188).—Data are tabulated for 123 new lines in the range 1275—2376 Å., excited by electrodeless discharge in tubes of I vapour at < 0.05 mm. pressure. N. M. B.

Ultra-violet absorption of iodine vapour. D. T. WARREN (Physical Rev., 1935, [ii], 47, 1—6).—The dependence of absorption on temp. and pressure was investigated. A general survey and explanation of the system 1900—3413 Å. are given. N. M. B.

Magnetic moment of the nucleus of caesium. D. A. JACKSON (Proc. Roy. Soc., 1935, A, 147, 500—513).—The hyperfine structure of 5 terms in the arc spectrum of Cs has been investigated. Applying the formulæ of Goudsmit (A., 1933, 552) and of Fermi and Segré (*ibid.*, 759), all 5 terms yield the same val. ($2.75/1838$ Bohr magneton) for the nuclear magnetic moment. L. L. B.

Temperature change of the mercury arc by the addition of cadmium. W. ELENBAAS (Physica, 1935, 2, 45—54; cf. A., 1934, 936).—Addition of Cd increases the potential gradient of a high-pressure Hg discharge, although the ionisation potential of Cd (8.95 volts) is $<$ that of Hg (10.38 volts). The corresponding temp. variation, calc. from the intensity variation of the Hg lines, leads to a calc. val. of the potential gradient in accord with the measured val. J. W. S.

Zeeman effect of mercury and perturbations. P. JACQUINOT (Compt. rend., 1934, 199, 1603—1604).—Green and Loring's observations were confirmed (cf. Physical Rev., 1934, [ii], 46, 888). H. J. E.

Character of the ^3S terms in the mercury spectrum. I. WALTERSTEIN (Proc. Indiana Acad. Sci., 1934, 43, 190—191).—Shenstone and Russell's data (A., 1932, 439) have been revised. CH. ABS. (e)

Effect of hydrogen on the self-reversal of the resonance line of mercury. O. MASAKI and K. KOBAYAKAWA (J. Sci. Hiroshima Univ., 1934, 5, 47—50).—In presence of H_2 the resonance line of Hg is more intense at 20° , and less intense at $> 40^\circ$, than the neighbouring line 2537.77 Å. R. S. B.

First spark spectrum of lead: Pb II. L. T. EARLS and R. A. SAWYER (Physical Rev., 1935, [ii], 47, 115—122).—Data with classifications are tabulated for 247 lines in the range 800—10,000 Å., locating 89 levels for which term vals. and quantum nos. are given. N. M. B.

Hyperfine structure of singly ionised lead. J. L. ROSE (Physical Rev., 1935, [ii], 47, 122—128; cf. preceding abstract).—Wave-lengths and classifications of about 130 lines of Pb II and isotope shifts between Pb^{208} and Pb^{206} , and also hyperfine structure separations of Pb^{207} are tabulated and discussed. N. M. B.

Radiation of the night sky between 5000 and 8000 Å. J. CABANNES (J. Phys. Radium, 1934, [vii], 5, 601—613; cf. A., 1934, 824; this vol., 3, 59).—The spectrum consists of a discontinuous region of atm. origin, identical with that of the aurora, with strong lines 5577 (attributed to O I) and 6314 Å., and consisting of the first positive system of N_2 , the terrestrial O_2 bands, and the vibration spectrum of H_2O . N. M. B.

Oscillographic test measurements with moving layers of the positive column of rare gases. W. PUPP (Physikal. Z., 1935, 36, 61—66). A. J. M.

Continuous spectra of flames and arcs. W. FINKELNBURG (Z. Physik, 1935, 93, 201—205).—Part of the continuous emission is electron radiation varying with the pressure and degree of ionisation of the gas. A. B. D. C.

Arcs in air between metallic electrodes. H. DZIEWULSKI (Acta Phys. Polon., 1933, 2, 51—58).—The force opposed to the e.m.f. for arcs between W, Ta, Mo, Cu, Ni, and Fe electrodes (I) in air is localised in the layer adhering to (I). CH. ABS. (e)

High-frequency discharge in gases and vapours as a source of light. V. I. ROMANOV (J. Tech. Phys. U.S.S.R., 1934, 4, 512—522).—Pure Zn and Cd vapours and their mixtures with Hg were studied. With oxide electrodes an easily regulated discharge is obtained. CH. ABS. (e)

Ultimate lines and excitation potentials. A. T. WILLIAMS (Rev. Soc. cient. Argentina, 1932, 5—6, 261—272).—Complete data are tabulated. CH. ABS. (e)

X-Ray crystal scale, the absolute scale, and the electronic charge. E. BACKLIN (Nature, 1935, 135, 32—33).—The val. of e calc. from the difference between wave-lengths of Al $K\alpha_{1,2}$ determined by the grating method and by crystal diffraction is 4.805×10^{-10} e.s.u. L. S. T.

Absolute value of the X-unit. M. SODERMAN (Nature, 1935, 135, 67).—Vals. obtained are Al $K\alpha_{1,2}$ 8.340 ± 0.001 Å.; $1000X = (1.00225 \pm 0.0001) \times 10^{-3}$ cm.; and e $(4.806 \pm 0.003) \times 10^{-10}$ e.s.u. L. S. T.

True and apparent absorption coefficient of inhomogeneous X-rays (intensity and dose absorption coefficients). R. JAEGER (Physikal. Z., 1935, 36, 41—44).—An expression previously derived (this vol., 284) may be used in the calculation of the true absorption coeff. (μ) from the apparent μ . The process is illustrated by the calculation of the true μ for air and Cellophane (I) from the apparent μ of (I). A. J. M.

Atomic scattering power of palladium for copper K-radiation. E. NAHRING (Z. Physik, 1935, 93, 197—200). A. B. D. C.

Fine structure of L-edges in the X-ray absorption spectra of the elements tantalum, tungsten, platinum, and gold. J. VELDKAMP (Physica, 1935, 2, 25—34).—The L_{II} and L_{III} absorption edges of Ta and W, which have a body-centred cubic structure, show a strong absorption line near to the edge,

corresponding with a $2p-5d$ transition. No similar line occurs in the L_I absorption edge. Comparison of the fine structures of the L_{III} edge of W and the K edge of Fe indicates that the wave function of the lower state of the electron has an influence on the fine structure near the edges. J. W. S.

X-Ray levels of radioactive elements with applications to β - and γ -ray spectra. A. E. RUARK and F. A. MAXFIELD (Physical Rev., 1935, [ii], 47, 107—114).—Calc. K , L , M , N , O , P series X-ray levels are tabulated for the elements Tl 81—U 92. Data are given for the energies of certain γ -rays of Th- B - C , Th- C'' - D , Ra- C - C' , Ac- B C , and Ac- C - C'' , for the energies of Auger lines of Rd-Ac, Ac-X, and Ms-Th₂, for the β -ray spectrum of Rd-Th, and for the β - and γ -ray spectra of U-X, and U-X₂. N. M. B.

New type of Auger effect and its influence on the X-ray spectrum. D. COSTER and R. DE L. KRONIG (Physica, 1935, 2, 13—24).—The radiationless transition L_I-L_{III} with ejection of an outer electron is responsible for the abnormal weakening of emission lines with L_I as initial level, the great intensity of the L_{III} satellite lines within certain ranges of at. no. both for cathode-ray and fluorescent excitation, and for the diffuseness of L_I emission lines as compared with the L_{II} , L_{III} emission lines. J. W. S.

Auger effect in argon. L. H. MARTIN, J. C. BOWER, and T. H. LABY (Proc. Roy. Soc., 1935, A, 148, 40—46).—The K yield of A, measured with a Wilson expansion chamber, the atom being ionised in turn by the K series characteristic radiations of Cu, Mo, and W, is 0.077. The probability of internal conversion is independent of the frequency of the exciting radiation. L. L. B.

New absolute determinations of the energy consumption in the ionisation of argon by X-rays. O. GAERTNER (Ann. Physik, 1935, [v], 21, 564—572).—The new val. for A is 28.4 ± 0.5 volts per ion-pair, which gives for air 35.2 or 37.5 volts according as the results of Gaertner or of Crowther are used for the relative ionisation of air and A. The deviation from the val. accepted at present (32.2 ± 0.5 volts) is discussed from the point of view of heat theory. A. J. M.

Thermionic emission and catalytic activity. II. Thoria-coated surfaces. Theory of Welsbach gas mantle. B. S. SRIKANTAN (J. Indian Chem. Soc., 1934, 11, 805—810; cf. A., 1931, 576).—The thermionic emission from a Pt wire coated with Ce_2O_3 - ThO_2 mixtures has been determined. The temp. at which emission is perceptible is a min. for 98.97% ThO_2 + 1.03% Ce_2O_3 (temp. = 948°) and this mixture gives max. emission at the same temp. attributed to electron emission. Previous theories of the emissivity of the Welsbach gas mantle are discussed. R. S. B.

Thermionic emission and catalytic activity. Mechanism of activation of gases at hot metallic surfaces. B. S. SRIKANTAN (Indian J. Physics, 1934, 9, 161—166; cf. A., 1931, 576).—On analogy between thermionic emission and catalysis

it is suggested that in a hot metallic catalyst activation is mainly due to the collision of the adsorbed mol. with the freely moving electrons, and an expression is derived, connecting velocity coeff. and temp. coeff., which agrees with available data for thermal decomp. of NH_3 by a W filament and of N_2O by Pt. N. M. B.

Electron emission of tungsten-molybdenum alloys. H. FREITAG and F. KRÜGER (Ann. Physik, 1935, [v], 21, 697—742).—The emission work, b_0 , and the const. A of the Richardson-Dushman equation for the emission of electrons from a heated metal, $I_s = AT^2 e^{-b_0/2T}$ (I_s is saturation current), have been determined for W, Mo, and alloys of these metals containing 10, 40, 60, and 90% W. The curve between b_0 and composition of alloy decreases from 100% W to 90% W—10% Mo, and then increases almost linearly to 100% Mo. The vals. of A for the alloys, calc. from b_0 , are considerably below theoretical except for 60% W—40% Mo. A. J. M.

Surface ionisation of potassium on molybdenum. R. C. EVANS (Proc. Camb. Phil. Soc., 1933, 29, 522—527).—Investigations on the efficiency of ionisation of K at a hot Mo surface show that the degree of ionisation (nearly 100%) is consistent with the most recent val. (4.4 volts approx.) for the electron work function of Mo. N. M. B.

Critical potentials of helium, neon, and argon by the Lenard opposing potential method. H. LÖHNER (Ann. Physik, 1935, [v], 22, 81—91).—Suggested improvements (A., 1930, 1231; 1931, 1107) are incorporated into one apparatus. The following crit. potentials have been determined: He, 19.75, 20.5, 20.8, and 21.1 volts; Ne, 16.6, 17.1, 17.75, 18.5, 19.7 volts; A, 11.55, 11.75, 12.8, 13.2, 14.05, and 14.7 volts. A. J. M.

Spectral selective photo-electric effect. C. ZENER (Physical Rev., 1935, [ii], 47, 15—16).—Mechanisms in which alkali metal electrons directly absorb light cannot give high efficiencies. If alkali atoms outside a unimol. gas layer absorb light, their excitation energy being transferred to the metal electrons, efficiencies comparable with observed results can be obtained. N. M. B.

Action of β - and γ -rays on rock-salt crystals. P. W. BURBIDGE (Proc. Camb. Phil. Soc., 1934, 30, 62—69).—The relation between a weak primary activation and the "inner" photo-electric effect, when the crystal was illuminated with blue light, was investigated. The photo-current decreased exponentially with time, and the crystal returned to its original condition after the total photo-electric charge had been collected. This charge increased with the applied field, and varies largely for different specimens. For a given field and activation dosage the charge rose, at a rate increasing with the intensity of illumination, to a const. max. Explanations in terms of quantum-mechanical crystal theory are discussed. N. M. B.

Direct determination of electron affinities. Electron affinity of iodine. P. P. SUTTON and J. E. MAYER (J. Chem. Physics, 1935, 3, 20—28).—The relative nos. of electrons and negative ions leaving unit area of a hot (2000° abs.) W filament in unit time

when the latter is in I vapour at 10^{-3} mm. pressure have been measured in terms of the ionic and electronic currents flowing when equilibrium is established. The results lead to 72.4 ± 1.5 kg.-cal. as the electron affinity of I atoms. F. L. U.

Emission velocity of electrons in the "spray" discharge. H. FRICKE (Z. Physik, 1934, 92, 728—740).—The "spray" discharge is the cathode fall free discharge. Velocities of emission of electrons from the cathode, and properties of its oxide layer, have been studied. A. B. D. C.

Scattering of electrons by nitrogen molecules. H. S. W. MASSEY and E. C. BULLARD (Proc. Camb. Phil. Soc., 1933, 29, 511—521).—An approx. theory of scattering is developed for cases when the wave-length of the electron is small compared with the internuclear distance. Calc. and observed angular distribution curves are given for 30, 60, 83, 205, 410, and 780 volt electrons scattered by N_2 . N. M. B.

Effect of exchange on the polarisation of electrons by double scattering. R. A. SMITH (Proc. Camb. Phil. Soc., 1934, 30, 520—523).—The discrepancy between the observed and calc. polarisation of beams of electrons scattered twice is investigated from the exchange between the incident electron and the electrons of an atom with which collision took place. Exchange will take place only in *K* and *L* shells, and its magnitude is derived using Schrodinger's electrons in preference to a relativistic treatment. The val. obtained is too small to influence polarisation appreciably. W. R. A.

Influence of screening on the creation and stopping of electrons. J. A. BETHE (Proc. Camb. Phil. Soc., 1934, 30, 524—539).—Theoretical. Cross-sections for the emission of radiation by very fast electrons and for the production of pairs of positive and negative electrons by very hard γ -rays are calc., considering the screening of the at. field in which the processes occur. W. R. A.

Artificially excited positrons. E. RUPP (Z. Physik, 1935, 93, 278).—Previous work is not free from criticism (cf. this vol., 139). A. B. D. C.

Production of electron-positron pairs. E. J. WILLIAMS (Nature, 1935, 135, 66). L. S. T.

Mean lives of excited hydrogen atoms. J. H. E. GRIFFITHS (Proc. Roy. Soc., 1935, A, 147, 547—555).—The average lives of the excited states of H_2 have been measured. The experimental vals. are $1.75 \pm 0.3 \times 10^{-8}$ sec. for H_α and $3.1 \pm 0.5 \times 10^{-8}$ sec. for H_β , corresponding theoretical vals. being 1.52 and 3.13×10^{-8} sec., respectively. From the decrease of life with increasing pressure, the effective collision radius for quenching collisions between excited H atoms and H_2O mols. is calc. to be 6.57 and 9.5×10^{-8} cm. for H_α and H_β , respectively, in agreement with the kinetic theory collision distance. L. L. B.

Positive and neutral rays. I. Neutralisation of positive rays. II. Liberation of electrons from metallic surfaces. A. ROSTAGNI (Nuovo Cimento, 1934, [ii], 11, 34—47, 99—113; Chem. Zentr., 1934, ii, 1094).—I. The production of positive ions is described. The collision diameter of A, Ne, He,

and H_2 for impact with the corresponding ions is independent of the velocity of the latter between 6 and 400 e.v. Ionisation of A and Ne by collision with A^+ begins between 50 and 100 e.v.

II. The coeff. of electron liberation from a metal surface by A^+ , Ne^+ , He^+ , H_2^+ , A, Ne, and He has been studied. H. J. E.

Molecular rays. M. VON LAUE (Chem.-Ztg., 1934, 59, 87—88).—A brief review.

Capture of electrons by positive ions from neutral gas atoms. R. A. SMITH (Proc. Camb. Phil. Soc., 1934, 30, 514—519).—An apparatus for the production of an intense narrow beam of the He^+ ions of uniform velocity is described. Capture cross-sections for He^+ in He and for H^+ in H_2 and He are recorded and discussed. W. R. A.

Collisions of the second kind between magnesium and neon. J. H. MANLEY and O. S. DUFFENDACK (Physical Rev., 1935, [ii], 47, 56—61).—Data on the cross-section for collision between Ne ions and Mg atoms are obtained from intensity measurements, at various pressures of Ne, of Mg π lines in presence of Ne, and from the cross-section-energy discrepancy curve for the *s*, *d*, and *f* series. N. M. B.

Energy of agitation of positive ions in argon. F. L. JONES (Proc. Physical Soc., 1935, 47, 74—85).—Investigations were made over an electric force (*Z*) range 5—50 volts per cm., and pressure (*p*) range 3—0.24 mm., by measuring the lateral diffusion of a beam of ions moving in a uniform electric field. In pure A, for low vals. of *Z/p*, the energy was the same as that of the gas atoms, and independent of *p*; for higher vals. of *Z/p* the mean energy was increased by the field. N. M. B.

Effect of binding on the effective cross-section with respect to very rapid electrons. A. SIEBERT (Ann. Physik, 1934, [v], 21, 503—532).—Mathematical. A. J. M.

Interaction of light nuclei. I. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1935, A, 148, 206—224).—Theoretical. Assuming the vals. of the binding energies of the nuclei, ${}_1H^2$, ${}_1H^3$, and ${}_2He^3$, respectively, the following vals. have been calc.: (a) cross-sections and angular distributions for elastic scattering of neutrons by H^1 , H^2 , and He^4 nuclei; (b) cross-sections for the radiative combination of neutrons and protons, and for the interaction of γ -rays with diplons; (c) cross-sections for continuous radiation by protons in collision with neutrons; and (d) cross-sections for the disintegration of diplons by α -particles. The data are compared with experimental vals., where available. L. L. B.

Heavy isotope of hydrogen. R. H. FOWLER (Proc. Camb. Phil. Soc., 1934, 30, 225—241).—Liverpool lecture. N. M. B.

Chemical elements and natural atomic types from the viewpoint of the investigation of isotopes. O. HAHN (Ber., 1935, 68, [A], 1—15).—A review of work published between the end of 1933 and of 1934. H. W.

Nuclear synthesis and isotopic constitution. H. J. WALKE (Phil. Mag., 1935, [vii], 19, 33—59; cf. this vol., 7).—A discussion of the synthesis of elements as a result of the β -ray activity (or in certain cases the γ -ray activity) of the missing isotope of the previous element in the periodic table. The Pd isotopes in order of decreasing abundance are predicted as 106, 105, 104, 108, 110 (?), 100 (?), 102 (?). The existence of missing radioactive series is discussed. Pb^{210} may be the end product of a short-lived Th-Ra series which has died out. The heavy elements are considered as being synthesised in the same way as the lighter ones, their radioactivity being due to their instability. H. J. E.

Condensation phenomena in mercury vapour. P. C. HO (Proc. Camb. Phil. Soc., 1934, 30, 216—224).—Using a cloud chamber connected by a long tube to an expansion chamber, so that Hg could be vaporised by heat while the expansion chamber remained at room temp., data were obtained for crit. expansion ratios required to give a cloud, and for crit. supersaturation, over the temp. range 191—270° for a definite vol. change expansion. X-Rays did not appreciably increase the cloud density or change the expansion limit, indicating that there is no condensation on ions. Results in the case of definite pressure change expansions differed slightly from the first mentioned. N. M. B.

Theory of ionisation measurements in gases at high pressures. D. E. LEA (Proc. Camb. Phil. Soc., 1934, 30, 80—101).—Jaffé's columnar theory of the recombination of ions in α -particle tracks, extended to β -rays by taking account of the clusters of secondary ionisation, gives fair agreement with experiment. Recombination in proton tracks produced in H_2 by neutrons agrees with the columnar theory, but for N nuclear tracks in N_2 the recombination is only 0.01 of that predicted by theory. It is suggested that recombination is abnormally small for all heavy nuclei of velocities $> 5 \times 10^8$ cm. per sec. Data for the coeff. of recombination of ions in N_2 and H_2 at 20, 40, and 90 atm. are given. N. M. B.

Simple method for measuring and finding the range of polonium preparations. B. KARLIK and E. ROXA (Physikal. Z., 1935, 36, 27—28).—A method involving the luminescence (I) of a ZnS screen produced by bombardment with α -rays is used. It is employed to investigate the range distribution of particles from strong Po preps.; (I) \propto no. of particles reaching the screen. The curve connecting (I) and range can be explained by assuming that 50% of the particles have normal range, and 50% are decreased by 1.2 mm. The increase in inhomogeneity of rays with time was also investigated. The possibility of the penetration of the Po into its metallic support is discussed. With Au as the support, there was a marked decrease in range with time, not with Pd or Ni. A. J. M.

Cloud chamber. P. C. HO and E. C. HALLIDAY (Proc. Camb. Phil. Soc., 1934, 30, 201—205).—Using Wilson's improved apparatus (cf. A., 1933, 1266) photographs of electron, α - and β -ray tracks can be

obtained satisfactorily over the pressure range 1 atm—7 cm. N. M. B.

Heat of the penetrating radiation of radium. A. DORABIALSKA (Rocz. Chem., 1934, 14, 798—805).—The heat of penetrating radiation has been determined after filtration through screens of different opacities, using a modified adiabatic calorimeter. R. T.

Mesothorium. P. M. WOLF (Chem.-Ztg., 1935, 59, 66—68).—A review.

Radioactivity of potassium. F. H. NEWMAN and H. J. WALKE (Nature, 1935, 135, 98).—This may be due to $^{40}_{19}\text{K}$, produced by the action of neutrons on $^{40}_{20}\text{Ca}$, and present in amounts too small to be detected by the mass spectrograph. L. S. T.

Most probable ionisation curve of single Po α -particles and the occurrence of large numbers of ions at the end of the range. H. SCHULZE (Physikal. Z., 1935, 36, 68—69).—By dividing the no. of α -particles by the no. of ions produced at different points of the range, an ionisation curve is obtained which gives a max. at 5.4 mm. from the end of the range. The extrapolated val. of the range is 3.87 cm. A. J. M.

Range-velocity relation for α -particles and protons. W. E. DUNCANSON (Proc. Camb. Phil. Soc., 1934, 30, 102—113).—Various calculations and comparisons with available experimental data are given. N. M. B.

Absorption of α -rays and H particles by matter: penetration and retardation. G. MANO (J. Phys. Radium, 1934, [vii], 5, 628—634; cf. A., 1934, 579).—Recalc. vals. of the penetration in air of several groups of α -rays are in good agreement with experiment. The theory of penetration of H particles is examined, and vals. are calc. as a function of initial velocity and kinetic energy. Retardations and equiv. air thicknesses are given for H_2 , N_2 , O_2 , He, Ne, Ar, H_2O , Al, Cu, Ag, Au, Pb, and mica for velocities $> 6 \times 10^9$ cm. per sec. N. M. B.

Diffraction of β -rays. Verification of de Broglie's law for very high velocity electrons. J. V. HUGHES (Phil. Mag., 1935, [vii], 19, 129—145).—The law was verified for monochromatic β -rays (energy 250—1000 kv.), using sputtered Au on gelatin for the diffracting foils. H. J. E.

Low-energy β -rays of radium-E. H. O. W. RICHARDSON (Proc. Roy. Soc., 1935, A, 147, 442—454).—An energy distribution curve has been obtained, extending from 10 to 65 kv., which fails to fit the accepted energy distribution for Ra-E. It is suggested that the available data on branching are inadequate, or that a group of low-energy particles is emitted by Ra-E. L. L. B.

Upper limits of the continuous β -ray spectra of thorium-C and -C'. W. J. HENDERSON (Proc. Roy. Soc., 1935, A, 147, 572—582).—Accurate vals. are obtained for the upper limits of Th-C and -C', using the method of magnetic focussing and a coincidence counter. The max. energies liberated in the two branches of Th-C are found to be equal, as predicted by Ellis and Mott (A., 1933, 1100). L. L. B.

Emission of γ -rays in nuclear reactions. W. D. HARKINS and D. M. GANS (*J. Amer. Chem. Soc.*, 1934, **56**, 2786—2787).—The energy changes accompanying artificial disintegration by neutrons are recorded for 71 nuclear reactions. The results are discussed. E. S. H.

Kinetic energy of neutrons emitted by beryllium bombarded by Po α -radiation. L. WINAND (*J. Phys. Radium*, 1934, [vii], **5**, 597—600).—Determinations of the kinetic energy of N and O nuclei bombarded by neutrons from a Po+Be source show that the max. kinetic energy of the emitted neutrons is $< 10^7$ e.v. N. M. B.

Neutrons from deutons and the mass of the neutron. M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (*Physical Rev.*, 1933, [ii], **44**, 781).—Further experiments (cf. this vol., 142) corroborate the view that the deuteron disintegrates, liberating approx. 4.8×10^6 volts of energy, and that the neutrons produced in the process have a mass of approx. 1.0006 mass units. L. S. T.

Attempt to detect a neutral particle of small mass. J. CHADWICK and D. E. LEA (*Proc. Camb. Phil. Soc.*, 1934, **30**, 59—61).—Unsuccessful attempts to detect a particle of the nature of Pauli's "neutrino," in order to explain the continuous β -ray spectra of Ra-E, indicate that such particle would be of small mass and zero magnetic moment. N. M. B.

Possibility of a positron transformation of radium-C. H. HERSZFINKIEL and J. HERSZAFT (*Rocz. Chem.*, 1934, **14**, 957—958).—The isotope of Ra-B which should be obtained were Ra-C to undergo positron degradation was not detected. R. T.

Neutrons and positrons. Artificial radioactivity. F. JOLIOT and (MME.) JOLIOT (*Rev. gen. Sci.*, 1934, **45**, 229—235; *Chem. Zentr.*, 1934, ii, 1582—1583).—A summary and review. H. J. E.

Theory of artificial radioactivity. K. SITTE (*Compt. rend.*, 1935, **200**, 308—310).—The question of the average life of artificially radioactive elements is discussed on the basis of the theory of β -ray disintegration previously put forward (A., 1933, 1224). M. S. B.

Natural and artificial radioactivity of potassium. G. VON HEVESY (*Nature*, 1935, **135**, 96).—Bombardment of Sc_2O_3 by neutrons from a Be-Rn source produces K^{42} according to scheme ${}_{21}\text{Sc}^{45} + {}_0n^1 \rightarrow {}_{19}\text{K}^{42} + {}_2\alpha^4$. K^{42} decays with a period of 16 hr., emitting hard β -rays of approx. 1.2×10^6 e.v. The natural radioactivity of K is thus limited to K^{40} or K^{41} , but the difficulty of reconciling the computed long life of these isotopes with the 5×10^5 e.v. energy of the electrons emitted by K still remains. L. S. T.

Radioactivity induced by neutrons. L. SZILARD and T. A. CHALMERS (*Nature*, 1935, **135**, 98).—Irradiation of In by neutrons shows the existence of a third period of approx. 3.5 hr. One of the two isotopes of In thus appears to be activated with two periods. This has been previously observed only in the case of elements lighter than Zn. L. S. T.

New radioactive elements. Chemical proofs of transmutations. F. JOLIOT and (MME.) JOLIOT

(*J. Chim. phys.*, 1934, **31**, 611—620).—Possible types of transformation which may occur on bombardment of various atoms with α -particles, H atoms, H ions, and neutrons are discussed, and examples so far detected enumerated. On irradiation of BN by α -particles from Po, a radioactive element is formed which passes over with the NH_3 when the BN is treated with NaOH. Al similarly irradiated yields a product which is carried off with the H_2 on treatment with HCl and after oxidation is pptd. with P by a Zr salt. The products, half-life periods 14 and $3\frac{1}{4}$ min., respectively, are probably N^{13} and P^{30} . J. W. S.

New artificial radioactive elements. I. O. D'AGOSTINO (*Gazzetta*, 1934, **64**, 835—851; cf. A., 1934, 1284).—Details are given of the chemical methods used to identify 20 active elements obtained by neutron bombardment. O. J. W.

Experiments with high-velocity positive ions. IV. **Production of induced radioactivity by high-velocity protons and deuterons.** J. D. COCKCROFT, C. W. GILBERT, and E. T. S. WALTON (*Proc. Roy. Soc.*, 1935, A, **148**, 225—240).—Experiments described show that induced radioactivity can be produced in C by both proton and dipton bombardment, and in B and possibly N compounds by dipton bombardment. A study has been made of the decay period of the radioactive bodies and of the energy distribution of the positive electrons, and some evidence has been obtained bearing on the nature of the radioactive isotopes. L. L. B.

Induced radioactivity produced by neutrons liberated from heavy water by radium γ -rays. T. E. BANKS, T. A. CHALMERS, and F. L. HOPWOOD (*Nature*, 1935, **135**, 99).—Radio-I and -Br are produced when EtI and CHBr_3 , respectively, are bombarded by the neutrons liberated from H_2^{18}O by irradiation with γ -rays from Ra. L. S. T.

Artificial radioactivity produced by neutrons. J. C. McLENNAN, L. G. GRIMMETT, and J. READ (*Nature*, 1935, **135**, 147).—With a Ra-Be source the following half-life periods were obtained: Mo 25 min. and approx. 36 hr., Pd 14 hr., Ta slight activity after 24 hr. exposure, W 23 hr., and Pt 36 min. With intimate mixtures of 100 mg. of Ra and equal quantities of Be, B, and Al the relative activities excited in I were 13.0, 4.5, and 1.0, respectively. L. S. T.

Probability of artificial nuclear transformations and its connexion with the vector model of the nucleus. M. GOLDBABER (*Proc. Camb. Phil. Soc.*, 1934, **30**, 561—566).—By introducing into a discussion of artificial nuclear transformations the theorem of quantum mechanics that the spin part of the angular momentum is approx. a const. of the motion, provided that the interaction forces depending on the directions of the spins are small compared with the total forces, "probable" and "not probable" nuclear reactions can be defined. An explanation is offered for the greater probability of $\text{Li}^6 + \text{H}^1 \rightarrow \text{He}^4 + \text{He}^3$ than of $\text{Li}^7 + \text{H}^1 \rightarrow 2\text{He}^4$. From consideration of the nuclear transformations of Li^6 and Li^7 with H^2 the nuclear spin of Li^6 is 1. Similar derivations for the spins of H^3 , He^3 , and B^{11} each give $\frac{1}{2}$. W. R. A.

Formulæ and equations in nuclear chemistry. T. M. LOWRY (Nature, 1935, 135, 36).—It is suggested that the French system, e.g., $^{35}_{17}\text{Cl}$, be adopted.

L. S. T.

Formulæ and equations in nuclear chemistry. J. H. AWBERY (Nature, 1935, 135, 185).—Nomenclature.

L. S. T.

Atomic disintegrations with radium-B+C as source of rays. I. Method. G. ORTNER and G. STETTER (Sitzungsber. Akad. Wiss. Wien, IIa, 1933, 142, 493—508; Chem. Zentr., 1934, ii, 1583).—The method used with a Po source is modified by using very pure N_2 in the ionisation chamber.

H. J. E.

Disintegration of beryllium by γ -rays. Absorption of neutrons emitted. Effective cross-section of γ -rays. W. GENTNER (Compt. rend., 200, 310—312).—The fraction of the neutrons, emitted when Be is excited by γ -rays from different sources, which is absorbed by 7 cm. of Pb has been determined. It is thus shown that, in increasing the energy of the quantum supplied to the Be, the kinetic energy of the neutron emitted is also increased. The effective cross-section for the unfiltered γ -radiation of Ra-B+C is 2×10^{-28} sq. cm.

M. S. B.

Transformation of beryllium by rapid protons, and the mass of Be^9 . F. KIRCHNER and H. NEVERT (Physikal. Z., 1935, 36, 54—56).—There is a well-defined homogeneous group of particles of range 7.5 mm. (corresponding with total energy 2.2×10^6 e.v.), which leads to the conclusion that only two types of particles can be present. The process may be represented as ${}_4\text{Be}^9 + {}_1\text{H}^1 \longrightarrow {}_3\text{Li}^6 + {}_2\text{He}^4$. Using the val. 6.0145 for ${}_3\text{Li}^6$, found by disintegration experiments, the mass of ${}_4\text{Be}^9$ is 9.0110 ± 0.0006 , which is < the sum of the masses of two α -particles and a neutron (9.0123). The val. found would make a nucleus of this structure stable, whereas the mass-spectrograph val. of 9.0155 would make it unstable.

A. J. M.

Disintegration of boron by α -particles. H. MILLER, W. E. DUNCANSON, and A. N. MAY (Proc. Camb. Phil. Soc., 1934, 30, 549—560; cf. A., 1934, 1284).—B was bombarded with α -particles from Ra-C' and Po and protons emitted were examined. All have been ascribed to the disintegration of B^{10} . Four energy changes of 3.1, 0.4, -0.1, and -1.0 ($\times 10^6$) e.v. are necessary to explain the observed range distribution.

W. R. A.

Evidence for a new type of disintegration produced by neutrons. J. CHADWICK, N. FEATHER, and W. T. DAVIES (Proc. Camb. Phil. Soc., 1934, 30, 357—365).—A new type of disintegration, resulting in three heavy particles, has been studied by bombarding C with neutrons. It is not possible, on the available evidence, to decide between the reactions $\text{C}^{12} \longrightarrow 3\text{He}^4$ and $\text{C}^{12} + n^1 \longrightarrow 2\text{He}^4 + \text{He}^5$.

R. S. B.

Disintegration by slow neutrons. J. CHADWICK and M. GOLDBABER (Nature, 1935, 135, 65).—When Li is bombarded by neutrons from a Rn-Be source slowed down by passage through paraffin wax, singly-charged particles of max. range approx. 5.0 cm. and doubly-charged particles of range < 1.5

cm. are produced. The probable reaction is ${}_3\text{Li}^6 + {}_0n^1 \longrightarrow {}_2\text{He}^4 + {}_1\text{H}^3$ and the energy released is approx. 5×10^6 e.v. With B most of the particles are doubly-charged with ranges < 5 mm. and the reaction is ${}_5\text{B}^{10} + {}_0n^1 \longrightarrow {}_2\text{He}^4 + {}_2\text{He}^4 + {}_1\text{H}^3$. A small effect has been observed with N_2 and a doubtful one with Be. These reactions give a convenient and sensitive means for detecting slow neutrons.

L. S. T.

Disintegration by slow neutrons. J. TUTIN (Nature, 1935, 135, 153).—An alternative explanation of the ejection of heavy charged particles from light atoms by slow neutrons (see above) is that heavy particles are outside and not in the nucleus.

L. S. T.

Disintegration of nitrogen by neutrons. F. N. D. KURIE (Physical Rev., 1935, [ii], 47, 97—107).—The disintegration of N by neutrons, produced by bombardment of Be with H^2 , was investigated by cloud chamber photographs. The kinetic energy loss agrees with the momentary production of a radioactive N^{15} by a radiative capture of the neutron; the N^{15} disintegrates with emission of α -particles, the half-life being approx. 10^{-20} sec., and mass 15.0166. In disintegrations by neutrons the proper disintegration energy E , as opposed to absorbed energy, is a const. The val. 3.1 mv. found for E agrees with that from available data on transmutation of F, O, and Ne.

N. M. B.

Disintegration of fluorine nuclei by neutrons and the probable formation of a new isotope of nitrogen (N^{16}). W. D. HARKINS, D. M. GANS, and H. W. NEWSON (Physical Rev., 1933, [ii], 44, 945—946).—3200 pairs of photographs in a Wilson cloud chamber filled with 30% by vol. of CCl_2F_2 and 70% of He show 10 nuclear disintegrations, most probably those of F nuclei. Each disintegrating nucleus breaks into two parts, one of which has a range 2—11 times that of the other. For disintegrations in which the neutron is captured, the reaction is probably $\text{F}^{19} + n^1 \longrightarrow \text{F}^{20} \longrightarrow \text{N}^{16} + \text{H}^4$, where the subscripts represent isotopic nos. Kinetic energy always disappears when F is disintegrated, part of it probably being converted into γ -rays. The no. of disintegrations obtained with F is approx. the same as with N with equal concns. of atoms and neutrons. The no. decreases in the order N or F, O, Ne, C, and Cl.

L. S. T.

Disintegration of the nuclei of light atoms by neutrons. II. Neon, fluorine, and carbon. W. D. HARKINS, D. M. GANS, and H. W. NEWSON (Physical Rev., 1935, [ii], 47, 52—55; cf. A., 1933, 1225).—Measurements of cloud track photographs of disintegration, by capture of a neutron, of Ne and F nuclei indicate the reactions: ${}_{10}\text{Ne}^{20} + {}_0n^1 \longrightarrow {}_8\text{O}^{17} + {}_2\text{He}^4$ and ${}_9\text{F}^{19} + {}_0n^1 \longrightarrow {}_7\text{N}^{16} + {}_2\text{He}^4$, the N^{16} being a new isotope. Mechanism and energy changes are interpreted. Positive-ray data show that the change ${}_6\text{C}^{12} + {}_0n^1 \longrightarrow {}_4\text{Be}^9 + {}_2\text{He}^4$ requires a min. neutron kinetic energy of 6.9×10^6 e.v. Since only 1 of 6 disintegrations in 6400 photographs satisfied this condition, the neutron disintegration of C is not proved.

N. M. B.

Transmutations of sodium by deuterons. E. O. LAWRENCE (Physical Rev., 1935, [ii], 47, 17—27).—

Under deuteron bombardment Na emits protons, neutrons, and α -particles and yields radio-Na, half-life of 15.5 hr., and emitting electrons with energies up to 1.2 mv., and 5.5 ± 0.5 mv. γ -rays. One micro-amp. of 1.7 mv. deuterons bombarding NaCl produces about 4×10^6 radio-Na atoms per sec., equal approx. to the no. of emitted protons, and indicating the formation of Na^{24} . The max. proton range is 49 ± 2 cm. The nos. of emitted neutrons and protons are approx. equal. The α -particle range is 6.5 ± 0.3 cm., Ne^{21} probably being formed. Balance of energy in the reactions indicates the at. masses: Na^{23} , 22.992 ± 0.001 ; Na^{24} , 24.000 ± 0.003 ; Mg^{24} , 23.993 ± 0.003 .

N. M. B.

Artificial transformation of uranium by neutrons. O. HAHN and L. MEITNER (Naturwiss., 1935, 23, 37—38).—Of the four at. species (half-life periods 10 sec., 40 sec., 13 min., and 90 min., respectively) obtained by bombarding U with neutrons, the last two have been further investigated. After bombardment, the U was dissolved, KReO_4 and PtCl_4 added, and then NaOH to ppt. U. Pt was removed by H_2S . The ppt. was found to contain a considerable quantity of the 13-min. body (I), and some of the 90-min. body (II). The Re was pptd. from the filtrate by the addition of conc. HCl and further passage of H_2S , but was inactive. If, on the other hand, KReO_4 only was added at the start, and the above separation was carried out, the Re contained both (I) and (II). (I) thus appears to resemble Pt rather than Re, which, whilst excluding the possibility of its being element 90, 91, or 92, is not incompatible with its being 93. When Pt, Re, Zr, and U-Z are added to the U and transformation product, the Pt on separation was found to contain (I) and (II), but the U-Z did not. Hence (I) and (II) are not isotopes of Pa. It is probable that they belong to a radioactive series leading into the Ac series.

A. J. M.

Analysis of absorption curves of cosmic rays. B. GROSS (Z. Physik, 1934, 92, 755—758).

A. B. D. C.

Ultra-penetrating corpuscles of cosmic radiation. P. AUGER and P. EHRENFEST (Compt. rend., 1934, 199, 1609—1611).—Experiments using two counters, one above the other, separated by 50 cm. thickness of Pb, showed the existence of a highly penetrating type of radiation.

H. J. E.

Absorption of cosmic particles in copper and lead. G. ALOCCO (Nature, 1935, 135, 96—97).—Cu and Pb, although differing in at. no., absorb the more penetrating cosmic particles to the same extent.

L. S. T.

Connexion between atomic and cosmic constants in the expanding universe. H. ERTEL (Naturwiss., 1935, 23, 36—37).—Theoretical.

A. J. M.

Investigation of corpuscular rays with a double [ionisation] chamber and two valve electrometers. G. STETTER and J. SCHINTLMEISTER (Sitzungsber. Akad. Wiss. Wien, IIa, 1933, 142, 427—436; Chem. Zentr., 1934, ii, 1587).—A method of measurement by simultaneous recording of the ionisation in two chambers is described.

H. J. E.

Determination of the potential of interaction of corpuscles. L. GOLDSTEIN (Compt. rend., 1935, 200, 296—298).—A discussion of the limits of validity of the classical theory and quantum theory with regard to the regions in which the potential of interaction may be considered to exist.

M. S. B.

Are the formulæ for the absorption of high-energy radiations valid? J. R. OPPENHEIMER (Physical Rev., 1935, [ii], 47, 44—52).—Discrepancies between observed and calc. absorption of cosmic-ray electrons and γ -rays are discussed. A limitation of classical electron theory leads to improved agreement.

N. M. B.

Nuclear moments. D. R. INGLIS (Physical Rev., 1935, [ii], 47, 84—88).—The magnetic moments of nuclei can be explained on the assumption that nuclei are built of protons of spin $1/2$ and gyromagnetic ratio -5 , and of neutrons of spin $1/2$ and gyromagnetic ratio -1.1 .

N. M. B.

Properties of nuclear constituents. G. C. WICK (Nuovo Cim., 1934, [ii], 11, 227—234; Chem. Zentr., 1934, ii, 1731—1732).—The interaction between nuclear constituents is discussed. The binding energy of the neutron and proton in H^2 is 8.3×10^6 e.v.

H. J. E.

α -Particles in light nuclei. E. GAPON and D. IVANENKO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 275—277; cf. A., 1934, 827).—The mass defects of atoms of at. wt. 1—36 show maxima at every fourth no., indicating that α -particles or similar groups of 4 are present in the lighter nuclei.

J. W. S.

Stability of the proton and neutron. G. WENTZEL (Naturwiss., 1935, 23, 35—36).—Theoretical. The spontaneous occurrence of the changes $N \rightarrow P + e^- + \nu$ (I), and $P \rightarrow N + e^+ + \nu$, is considered. N =neutron, P =proton, e =electron, and ν =neutrino. Investigation of the breaking down of the H atom into N , n , and a light quant, $P + e^- \rightarrow N + n + \nu$, furnishes new criteria for the stability of N and P , and leads to the conclusion that the mass of N must be $<$ that of $P + e^-$. N is unstable with respect to process (I).

A. J. M.

I. Charge and field fluctuations. II. Production of pairs by charged particles. J. R. OPPENHEIMER (Physical Rev., 1935, [ii], 47, 144—145, 146—147).—I. The field fluctuations arising from the possibility of creating positron-electron pairs in Dirac's theory are calc.

II. The internal conversion by pair-production of the radiation emitted in the impact of charged particles is calc.

N. M. B.

Approximation method in the problem of many electrons. H. HELLMANN (J. Chem. Physics, 1935, 3, 61).—A new method is described.

F. L. U.

Born-Infeld field theory of the electron. E. FEENBERG (Physical Rev., 1935, [ii], 47, 148—157).

N. M. B.

Infinite distribution of electrons in the theory of the positron. P. A. M. DIRAC (Proc. Camb. Phil. Soc., 1934, 30, 150—163).—Mathematical. A precise meaning is found for a distribution in which every state is occupied, and for one in which nearly all the

negative-energy states are occupied and nearly all the positive-energy states unoccupied. N. M. B.

Annihilation radiation of the positron. O. KLEMPERER (Proc. Camb. Phil. Soc., 1934, 30, 347—354).—By means of two Geiger-Müller coincidence counters it has been shown that the radiation produced by the annihilation of a positron by an electron is emitted as a pair of γ -rays in opposite directions. The coincidence method of Becker and Bothe, and absorption measurements using Pb, establish that the radiation is soft and homogeneous, the energy of each ray being 0.5×10^6 e.v. The total energy is then nearly equal to the theoretical val. for the mass equiv. of the positron and electron, viz., 1.02×10^6 e.v. The positron source consisted of C and B (in $\text{Na}_2\text{B}_4\text{O}_7$) activated by bombardment with diplotons and protons. R. S. B.

Quantum theory of the diplon. H. BETHE and R. PEIERLS (Proc. Roy. Soc., 1935, A, 148, 146—156).—The following vals. have been calc.: cross-section for disintegration of a diplon by absorption of γ -rays, 1.6×10^{-27} sq. cm.; cross-section for capture of neutrons by protons, 2.7×10^{-29} sq. cm.; cross-section for scattering of γ -rays by diplotons, 2.0×10^{-31} sq. cm. The disintegration of diplotons under electron bombardment is considered. L. L. B.

Wave mechanical treatment of the molecule Li_2^+ . H. M. JAMES (J. Chem. Physics, 1935, 3, 9—14; cf. this vol., 15).—The dissociation energy of Li_2^+ is 1.30 ± 0.05 e.v. F. L. U.

Electromagnetic fields in the quantum theory. II. L. GOLDSTEIN (J. Phys. Radium, 1934, [vii], 5, 623—627; cf. this vol., 8).—Mathematical. N. M. B.

Heterogeneous electromagnetic ether capable of producing a quantic atomic field of force. M. BRILLOUIN (Compt. rend., 1935, 200, 275—279).—Theoretical. M. S. B.

Wave mechanical calculation of some atomic properties. G. PLATO (Ann. Physik, 1935, [v], 21, 745—760).—Mathematical. Properties of atoms connected with the three innermost shells are derived. Accurate ψ -functions for Ne and Ar and ions with this structure (K^+ , Cl^-) are calc., and the calc. diamagnetic susceptibility agrees with observation. A. J. M.

Spectroscopic determination of e/m . C. D. SHANE and F. H. SPEDDING (Physical Rev., 1935, [ii], 47, 33—37).—The val. $1.7579 \pm 0.0003 \times 10^7$ was obtained from accurate measurement of the wave-no. difference between the H_α lines of H and H^2 . The calc. mass ratio H atom/electron is $1835.6 \pm 0.2_5$. N. M. B.

Exchange in the Thomas-Fermi atom. H. JENSEN (Z. Physik, 1935, 93, 232—235).—Completion of previous work (A., 1934, 1054). A. B. D. C.

Elementary electric charge. E. SCHOPPER (Z. Physik, 1934, 93, 1—21).—This is given as 4.769 ± 0.004 e.g.s. units. A. B. D. C.

Multipole radiation and quantum selection rules for central field atoms. C. K. JEN (Sci. Rep. at. Tsing Hua Univ., 1934, 2, 413—418).—Mathematical.

Budde effect in iodine. I. Photo-expansion. II. Influence of temperature on the photo-expansion. T. S. NARAYANA (Indian J. Physics, 1934, 9, 111—115, 117—120).—I. An effect similar to that in Cl_2 and Br_2 (cf. A., 1934, 1295) was found in I_2 . Photo-expansion \propto light intensity and v.p. of I, and was a max. in the violet and orange regions at 70 mm. v.p. of I.

II. Vals. of 0.7 and 0.45 mm. for the photo-expansion at 200° and 350° , respectively, show that the effect diminishes with rise of temp. Results are interpreted with the help of Wood's data for the catalytic effect of dry and moist glass walls. N. M. B.

Relation between scattering and absorption of light in sols of silver, silver chloride, and colophony. G. P. LUTSCHINSKI and E. S. ALTMAN (Kolloid-Z., 1935, 70, 55—61).—The absorption of light by the sols is in accordance with Lambert's rule. The coeff. of total absorption is the sum of the coeffs. of real (I) and apparent absorption (II); in metal sols (I) > (II) and increases with increasing concn.; in colourless non-metal sols (I) increases with concn. to a limit and is independent of concn. thereafter. Beer's rule does not apply. E. S. H.

Formation and dissociation of diatomic molecules. R. RYDBERG (Z. Physik, 1934, 92, 693—704).—Formation and dissociation of AlH mols. was studied by observing absorption by an Al arc in H_2 at pressures up to 0.5 atm. A. B. D. C.

Ultra-violet transmission changes in glass as a function of the wave-length of the radiation stimulus. W. W. COBLENTZ and R. STAIR (Proc. Nat. Acad. Sci., 1934, 20, 630—635).— $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ glass exposed to ultra-violet radiation undergoes changes in spectral transmission, differing in magnitude for different wave-lengths, and occurring in a wide band from 405 μ to the extreme ultra-violet; the glass shows stages in photochemical equilibrium, not found in potash glass, indicating the soda as the photo-sensitive constituent. Using observed changes in transmission as a measure of changes in concn. of the photo-sensitive substance, the energies involved in the formation and disintegration of the latter are calc. N. M. B.

Flame spectrum of ethylene. W. M. VAIDYA (Proc. Roy. Soc., 1935, A, 147, 513—521).—When produced with the aid of a Smithells flame separator, the spectrum of the inner cone of the C_2H_4 flame includes, in addition to strong bands of C_2 , CH , and OH , a system of fainter bands extending from 4100 to 2500 Å. degraded towards the red. Conditions for the occurrence of these bands have been investigated, and their wave-lengths are tabulated. It is suggested that they are due to HCO , and supporting evidence is cited. L. L. B.

Modern spectroscopy. H. DINGLE (J. Soc. Arts, 1935, 83, 234—245, 258—272, 283—301).—Lectures.

Absorption spectrum of NaH^2 . E. OLSSON (Z. Physik, 1935, 93, 206—219).—The true quantum numbers for NaH and NaH^2 are deduced from isotope effects. A. B. D. C.

Spectra of CaH and CaH^2 . W. W. WATSON (Physical Rev., 1935, [ii], 47, 27—32).—Full data of

observed lines, quantum assignments, and combination differences are tabulated for the *B* and *C* systems of CaH^2 . The spectra of CaH and CaH^2 are compared. The calc. decrease for the equilibrium internuclear distance in CaH^2 is 0.059%. N. M. B.

OH^{2+} bands. A. CLARK and W. H. RODEBUSH (J. Amer. Chem. Soc., 1935, 27, 228).—The OH^{2+} bands in the electrodeless discharge in H_2O have been photographed. E. S. H.

Absorption spectrum of sulphur monoxide. G. KORNFIELD and M. McCAIG (Nature, 1935, 135, 185—186).—The absorption spectra of SO_2 before and after the production of an electrodeless discharge are identical, but the emission spectrum taken during the discharge shows the presence of SO . Small concns. of SO do not absorb between 3100 and 2500 Å.

L. S. T.

Spectrum of AsO . F. A. JENKINS and L. A. STRAIT (Physical Rev., 1935, [ii], 47, 136—139).—Measurements for the band heads of two systems due to AsO and equations for the vibrational structure are given. Heat of dissociation of AsO is 4.93 volts.

N. M. B.

Spectroscopic investigation of the structure of hydrogen halides. A. K. DUTTA and S. C. DEB (Z. Physik, 1934, 93, 127—140).—Emission spectra of the H halides are continuous with fixed long-wave limits. Electron configurations are given, and the continuous spectra ascribed to two neighbouring levels, the higher being unstable; it cannot be stated whether the linkings are at. or ionic. The electric moment is considered.

A. B. D. C.

Ultra-violet absorption spectra of alkali halide crystals. A. VON HIPPEL (Z. Physik, 1934, 93, 86—89).—The characteristic ultra-violet absorption spectrum of the alkali halides has two doublet bands corresponding with the different space-groups of cations around an anion.

A. B. D. C.

Nature of the red layer formed at the border of the coloured zone in alkali halide crystals. S. ARZIBISCHEV and A. TORPOREC (J. Phys. Radium, 1934, [vii], 5, 619—622).—When a crystal of rock-salt or KCl , containing a piece of Na sealed in a cavity, was heated to 700° a red layer formed in the crystal, the rapidity of formation being increased by the passage of a current. The distance of the layer from the anode varies with the duration of the current. Photometric and ultra-violet absorption suggest that the layer is due to the diffusion of colloidal Cu in the salt, and deposition following the neutralisation of Cu ions (from electrodes) by electrons emanating from the Na cathode. (Cf. this vol., 282.)

N. M. B.

Rotation structure of AlCl bands. W. HOLST (Z. Physik, 1934, 93, 55—64).—Six bands have been analysed, and the nuclear separation is given as 2.3 Å.

A. B. D. C.

Optical dissociation of InBr and InI . J. S. SEDOV and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 374—377).—The long-wave limits of absorption causing dissociation have been determined, and the fluorescence spectra examined. Heats of dissociation are 75.5 ± 2.5 kg.-cal. per mol. for InBr and 62 ± 2 for InI .

E. S. H.

Displacements of the absorption bands of certain rare-earth salts: spectrographic detection of rare earths. Y. UZUMASA (J. Fac. Sci. Hokkaido Imp. Univ., 1934, [iii], 2, 1—11).— Mg and La salts did not affect the appearance and persistence of Nd bands; in EtOH a broadening of band λ 5780 was observed. Addition of HCl to a solution of $\text{NdCl}_3 + \text{CO}(\text{NH}_2)_2$ progressively eliminated the displacement and broadening, due to the $\text{CO}(\text{NH}_2)_2$, of the λ 5780 band.

N. M. B.

Vibrational analysis of the absorption spectrum of lead sulphide. G. D. ROCHESTER and H. G. HOWELL (Proc. Roy. Soc., 1935, A, 148, 157—170).—A new, extensive absorption band spectrum ascribed to PbS has been discovered in the region 3140—7690 Å. The spectrum consists of overlapping progressions of bands degraded to the red. In the region of greatest dispersion, the bands show apparently simple rotational structure. By analogy with PbO , the electronic transition would appear to be $\leftarrow {}^1\Sigma$. Of 230 bands, 221 have been fitted into 6 systems with the same ground state, and the vibrational consts. for the states giving rise to these systems have been derived by a "least-squares" method. Interesting intensity anomalies not explained by the Condon theory have been found in system A.

L. L. B.

Absorption spectra of the sulphite and sulphate ions. S. M. KARIM and R. SAMUEL (Proc. Indian Acad. Sci., 1934, 1, A, 398—406).—Curves and data are given of measurements, as crystals or in solution, for NaHSO_3 , KHSO_3 , Na_2SO_3 , Na_2SO_4 , NaHSO_4 , KHSO_4 , NaMeSO_4 , Me_2SO_4 , Et_2SO_4 , and ClSO_3H . Results and structural deductions are discussed.

N. M. B.

General connexion between frequencies of the band spectra of aromatic hydrocarbons and their derivatives. D. RADULESCU and C. DRAGULESCU (Physikal. Z., 1935, 36, 66—68).—For the vapours of aromatic hydrocarbons, and their derivatives, all the luminescence, fluorescence, and absorption bands may be arranged together in series governed by the general formula, $F_x = F_0 \rho^x$, where F_0 is the frequency of a band, $\rho = 1.01048$, and x is a positive or negative integer. The formula is tested with the absorption max. of pyrene and of phenanthrene (both in EtOH), and the fluorescence bands of solid C_6H_6 .

A. J. M.

The azo chromophore.—See this vol., 207.

Continuous bands of glycerol. S. M. MITRA (Z. Physik, 1934, 93, 141—146).—The effect of KI and temp. on fluorescence of glycerol has been studied.

A. B. D. C.

Hydrogen sulphide band at 10,100 Å. P. C. CROSS (Physical Rev., 1935, [ii], 47, 7—14).—A detailed rotational analysis is developed. Observed lines and the spectrum calc. from the rotational term vals., and transition vals. explaining 84 of the 91 lines are tabulated; 7 lines are considered spurious. The moments of inertia of the normal vibrational state are 2.667, 3.076, and 5.845×10^{-40} g.-cm.², the axis of least inertia being perpendicular to the symmetry axis of the mol. The linking angle is $92^\circ 20'$, and the H—S distance 1.345 Å.

N. M. B.

Absorption bands of HCN in the photographic infra-red. G. HERZBERG and J. W. T. SPINKS (Proc. Roy. Soc., 1935, **A**, 147, 434—442).—Two strong HCN bands at 1.04 and 1.16 μ have been analysed. The rotational consts. are derived. $I_0 = 18.703 \times 10^{-40}$ g.-cm.² The internuclear distances, calc. from I_0 on the assumption that the C—H distance is the same as in C₂H₂, are < those in the free diat. radicals. The broadening of HCN lines by pressure is attributed to a strong intermol. interaction. L. L. B.

Frequency of vibrational and rotational bands and the chemical reactivity of gaseous molecules. W. HELLER (Compt. rend., 1934, **199**, 1611—1613; cf. this vol., 150).—The diminution in the near infra-red frequency of OH in a series of compounds of the type R·OH as the complexity of R is increased is parallel to increased reactivity of the corresponding Cl derivative of the radical, as measured by the reaction $R\dot{C}l + Na \rightarrow R + NaCl$. H. J. E.

Infra-red region of the spectrum. XI. Absorption spectrum and molecular structure of boron trichloride, and the effect of strain on plane groups of the type XY. A. B. D. CASSIE (Proc. Roy. Soc., 1935, **A**, 148, 87—103).—Nine bands in the infra-red absorption spectrum of BCl₃ have been located between 1 and 18 μ , and fundamental frequencies have been assigned from a consideration of the Raman displacements. The true val. of the force const. for the BCl linking is deduced from Morse's potential nuclear separation expression. The electron configuration is discussed. Evaluation of both the true and strain rigidities of the plane configuration shows that this is not due to repulsion of the Cl atoms alone. The CO₃' and NO₃' ions have been similarly investigated with respect to the true force consts. and true rigidity. Both ions would be pyramidal in the absence of the repulsion of the O ions. L. L. B.

Far infra-red absorption of benzene. R. B. BARNES, W. S. BENEDICT, and C. M. LEWIS (Physical Rev., 1935, [ii], 47, 129—130).—Five weak bands, interpreted as difference bands, were found in the region 40—135 μ ; the observations support the plane symmetrical hexagonal mol. model. N. M. B.

Rotational Raman effect in gases: carbon dioxide and nitrous oxide. S. BHAGAVANTAM and A. V. RAO (Nature, 1935, **135**, 150).—The distribution of intensity in the rotational Raman wings has been determined for gaseous CO₂ at 6 and 50 atm. and for N₂O at 6 and 40 atm. At the higher pressures these wings become similar to those obtained with liquids. The intensity max. at low pressures give 69×10^{-40} and 62×10^{-40} , respectively, for the moments of inertia of CO₂ and N₂O mols. (cf. A., 1933, 885). L. S. T.

Raman effect of binary mixtures of sulphuric and nitric acids. L. MEDARD (Compt. rend., 1934, **199**, 1615—1617; cf. A., 1933, 1102).—Mixtures of pure conc. HNO₃ and H₂SO₄ gave a new Raman line (1400 cm.⁻¹) attributed to a mol. association product. Other lines, characteristic of the separate acids, were observed. H. J. E.

Relation between the molecular spectrum and the electrons and electron rings of the con-

stituent atoms. H. DESLANDRES (Compt. rend., 1934, **199**, 1543—1546; cf. A., 1934, 1054).—Raman spectrum data for H₂O, CH₂O, MeOH, MeCl, and S₂Cl₂ are discussed on the author's theory.

H. J. E.

Raman effect and dipole moment in relation to free rotation. I. S. MIZUSHIMA, Y. MORINO, and K. HIGASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **25**, 159—221; cf. this vol., 12).—The dipole moments (I) of (CH₂Cl)₂, CH₂Cl-CH₂Br, (CH₂Br)₂, and (CH₂I)₂ in C₆H₁₄, amylene, C₆H₆, PhMe, Et₂O, CCl₄, and CS₂ were determined. (I) of these compounds increases with rise of temp. and with increasing dielectric const. of the solvent, except in C₆H₆ and PhMe solutions, where (I) are much > would be expected. In the rotation of the CH₂X groups in the ethylene halides, the *trans* position is most stable. The probability of deviation from this position increases with rise in temp. The mutual potential energy of the two groups increases with the at. wt. of the halogen. Observations of the intensities of the two Raman lines of (CH₂Cl)₂ and (CH₂Br)₂ lead to the same conclusions. A. J. M.

Relative intensities of the Raman and the Rayleigh lines in light scattering. J. DHAR (Indian J. Physics, 1934, **9**, 189—194).—Using the Hg 4358 line for excitation, relative intensities are given in the scattering by C₆H₆, CCl₄, SiCl₄, CHCl₃, and CHBr₃. N. M. B.

Raman spectrum of the esters of some derivatives of β -ketobutyric acid. M. MILONE (Gazzetta, 1934, **64**, 868—875).—The Raman spectra of the compounds COMe·CHR·CO₂R' (R' = Me or Et, R = alkyl) show that at room temp. there is a considerable amount of the enol form present.

O. J. W.

Raman effect of some aliphatic ethyl ketones. M. MILONE (Gazzetta, 1934, **64**, 876—882).—The Raman spectra of 9 ketones COEtR all give the characteristic C=O frequency at 1710 cm.⁻¹

O. J. W.

Raman spectrum of $\Delta^{1:3}$ -cyclohexadiene. J. W. MURRAY (J. Chem. Physics, 1935, **3**, 59—60).—Raman frequencies are given in comparison with C₆H₆ and C₆H₁₀. F. L. U.

Quasi-crystalline structure of liquids and the Raman effect. E. GROSS and M. VUKS (Nature, 1935, **135**, 100—101).—Investigation of the Raman spectrum of Ph₂O shows that the "wings" which accompany the primary line are due, not to a rotation of the mols. as hitherto assumed, but to a vibrational Raman effect. The theory of the quasi-cryst. structure of liquids is supported. L. S. T.

Chemiluminescence of dimethyldiacridylum salts. K. GLEU and W. PETSCH (Angew. Chem., 1935, **48**, 57—59).—NN'-Dimethyldiacridylum nitrate fluoresces intense green in neutral or acid solution. On adding alkali the fluorescence disappears immediately and the colour darkens with production of a dark brown ppt. On addition of H₂O₂ to a freshly prepared alkaline solution, however, a green chemiluminescence is obtained, similar in colour to the fluorescence. No light is emitted,

however, if OBr' , OCl' , KMnO_4 , or $\text{Fe}(\text{CN})_6'''$ is used, but a brief strong light emission is observed with reducing agents (HSO_3' , S'' , VO_3' , SnO_2'') in presence of atm. O_2 . The behaviour with H_2O_2 is attributed to its alternate oxidation and reduction action, light being emitted during the latter phase. Similar mechanism may account for light emission in biological processes. J. W. S.

Crystallisation fluorescence. H. DÖRING (Naturwiss., 1935, 23, 19; cf. this vol., 147).—The fluorescence previously observed is not now ascribed to a special crystallisation fluorescence. A. J. M.

Fluorescence of fluorite and the bivalent europium ion. K. PRZIBRAM (Nature, 1935, 135, 100).—In ultra-violet light EuCl_2 gives a brilliant purplish-pink fluorescence, showing a broad band in the blue identical with the well-known fluorite band. This confirms the view that the blue fluorescence of fluorspar in ultra-violet light is due to Eu'' (cf. A., 1934, 239). EuCl_2 also gives a line at 690 $\text{m}\mu$, and a diffuse band at 630 $\text{m}\mu$ closely resembling a band shown by some fluorites and by artificial "pure" CaF_2 . L. S. T.

Varying β - and γ -ray coloration of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass and causes of the pure violet colour of manganese-free glass. J. HOFFMANN (Sitzungsber. Akad. Wiss. Wien, IIa, 1933, 142, 437—444; Chem. Zentr., 1934, ii, 1097).—The violet colour produced on irradiation with rays from Ra was attributed to traces of Pt dissolved from the crucible in which the glass melt was prepared. Rapidly-cooled Na_2SiO_3 melts gave greyish-black irradiation effects. H. J. E.

Synthetic phosphors. I. External photo-electric effect in the ultra-violet region and the distribution of excitation of various alkaline-earth phosphors. S. HAKOMORI and Y. OKA (J. Electrochem. Assoc. Japan, 1934, 2, 182—186).—In ultra-violet excitation in the region of longer λ , direct excitation of the nucleus of phosphorescence occurs. At shorter λ secondary excitation of the electron emitted from CaS occurs. CH. ABS. (e)

Method of working of counter tubes and gas-filled photo-cells. P. GÖRLICH (Physikal. Z., 1935, 36, 36).—A method quoted by Teichmann (*ibid.*, 1934, 35, 637) for the stabilisation of the Townsend discharge in photo-cells is stated to be ineffective. The most important condition for the above stabilisation is the limitation of the c.d. to a val. $<$ a characteristic val. by the use of a high resistance. A. J. M.

Method of working of counter tubes and gas-filled photo-cells. H. TEICHMANN (Physikal. Z., 1935, 36, 37).—A reply to Görllich (preceding abstract). A. J. M.

Investigations with cuprous oxide photo-cells. II. Fatigue phenomena. W. BULIAN (Physikal. Z., 1935, 36, 33—34; cf. A., 1933, 1229).— Cu_2O photo-cells with cathodic sputtered Ag electrodes show a considerable decrease in the photo-current when illuminated over long periods. The nature of the electrodes plays no part in the effect, which can be prevented by enclosing the cell in a gas-tight

vessel. The fatigue is due to optical and chemical changes in the electrodes. For use at wave-lengths $> 6000 \text{ \AA}$, Cu_2O cells with thin Au electrodes may be used. They show no fatigue. A. J. M.

Spectral distribution of, and the effect of temperature on, the crystal photo-effect with single crystals of pyrargyrite and stephanite. J. BARISCH (Ann. Physik, 1935, [v], 21, 804—811).—The selective max. of the crystal photo-effect with single crystals of pyrargyrite and stephanite increases exponentially with fall in temp. At a certain temp. the exponential function changes, possibly due to the absorption of H_2O . The max. is displaced towards the shorter wave-lengths with fall in temp.; displacement \propto temp. change. This behaviour is characteristic of semi-conductors. A. J. M.

Loss and restoration of photo-conductivity in red mercuric iodide. F. C. NIX (Physical Rev., 1935, [ii], 47, 72—78).—Single crystals of red HgI lose their photosensitivity on ageing, with accompanying change from mono- to poly-cryst. fibrous state. Sensitivity can be restored by an impressed voltage. The rate of resensitisation and the magnitude of the attained sensitivity increase with increase of applied field and with fall in temp. N. M. B.

Spectral distribution of the photo-current in colloidal coloured alkali halide crystals. L. GROSHÉV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 378—382).—Observations on NaCl and KCl containing colloiddally dispersed Cu are recorded. The limit of the photo-effect is displaced from 300 to 600 $\text{m}\mu$, indicating a diminution of the work of elimination of electrons in colloidal Cu. (Cf. this vol., 280.) E. S. H.

Crystal photo-effect with coloured rock-salt. S. PELZ (Sitzungsber. Akad. Wiss. Wien, 1933, IIa, 142, 509—522; Chem. Zentr., 1934, ii, 1736).—Results are recorded for NaCl and KCl. The effect is due to diffusion of photo-electrons from the illuminated to the dark part of the crystal. The lag is $> 10^{-3}$ sec. H. J. E.

Surface-force theory of crystal rectification. S. R. KHASTGIR (Nature, 1935, 135, 148). L. S. T.

Energy levels of electrons in amorphous bodies. V. ZDANOV (J. Phys. Radium, 1934, [vii], 5, 614—616).—Mathematical. The case of electrons in an amorphous semi-conductor is examined. N. M. B.

Molecular rays. V. GUILLEMIN, jun. (J. Franklin Inst., 1935, 219, 73—85).—A survey of recent work on mol. rays in relation to scattering in gases, diffraction at crystal surfaces, magnetic and electric moments of atoms and mols., and other applications. N. M. B.

Space-charge measurements in beeswax during solidification and in the solid state. P. JAEGER (Ann. Physik, 1934, [v], 21, 481—502).—The space-charge distribution in liquid and solid beeswax was investigated by passing the electric discharge (10 and 20 kv.) between parallel electrodes in the wax just about to solidify. The space charge was fixed on solidification, and the solid wax was

cut into a no. of parallel layers, the space charge of each section being determined. A. J. M.

Pressure variation of residual ionisation current in different gases. J. A. PRIEBSCHE (Z. Physik, 1934, 93, 22—34).—The residual current of a 4-litre chamber was determined for air, A, and CO₂ to 15 atm., and for H₂ to 5 atm. Air and CO₂ gave the largest current. A. B. D. C.

Observation of motions due to electric fields acting on dielectric liquids. R. HOFMANN (Z. Physik, 1934, 92, 759—795).—The "schlieren" method was used to observe the motion of the surface of liquids under electric fields; velocity of wave motion was determined and related to conductivity and dipole character of the liquid. A. B. D. C.

Physical methods in chemistry. I. P. C. HENRIQUEZ and L. J. N. VAN DER HULST (Chem. Weekblad, 1935, 32, 35—39).—A general account of polarisation and absorption and the importance of ϵ and n . S. C.

Chemical applications of recent dielectric constant theory. J. W. WILLIAMS (J. Franklin Inst., 1935, 219, 47—72).—A general survey of the relation of dipole moment data to mol. structure, and the variation of dielectric const. as a function of temp. and concn. relative to mol. association and compound formation in solution. N. M. B.

Dipole moment of iodine. V. VASSILIEV, J. SYRKIN, and I. KENEZ (Nature, 1935, 135, 71).—Measurements of ϵ of 1—6% solutions of I in C₆H₆ and CS₂ between 15° and 70° and 15° and 35°, respectively, show that I has no dipole moment in either solvent. L. S. T.

Dipole moments and molecular structure of amides. W. D. KUMLER and C. W. PORTER (J. Amer. Chem. Soc., 1934, 56, 2549—2554).—The dipole moments of NH₂Ac, NHAcEt, NAcMe₂, NAcEt₂, NH₂CMc₂OEt, and *p*-NO₂·C₆H₄·NH₂ have been determined. The vals. are discussed in terms of resonance. The moment of the C:N linking has been evaluated. E. S. H.

Dipole moments of mono-substituted benzenes in the vapour state. K. B. McALPINE and C. P. SMYTH (J. Chem. Physics, 1935, 3, 55—57; cf. A., 1934, 1157).—Dielectric consts. of vapours of PhF, PhCl, and PhNO₂ have been determined. The calc. dipole moments are, respectively, 1.57, 1.70, and 4.19 $\times 10^{-18}$. F. L. U.

Dielectric constants of liquids and liquid mixtures. D. S. SUBBARAMAIYA (Proc. Indian Acad. Sci., 1934, 1 A, 355—362).—Mathematical. Narasimhaiah's refractivity theory (cf. this vol., 24) is extended to the dielectric const. of binary liquid mixtures, and is satisfactory for C₆H₆—PhMe mixtures. N. M. B.

Anisotropy of liquids around gaseous bubbles. F. GAUBERT (Compt. rend., 1935, 299, 304—306).—When two bubbles in a liquid touch without coalescing, optical examination of the area of contact indicates that the film of liquid of which it consists is anisotropic, optically uniaxial, and negative, and that the optical axes are along the radius of the bubble. M. S. B.

Natural and magnetic rotatory power of pinene vapour. P. GABIANO (Compt. rend., 1934, 199, 1607—1609).—The natural rotation of α -pinene vapour at 88° \propto its pressure (39—64 mm.). The sp. magnetic rotation of the vapour was 1.80×10^{-2} . H. J. E.

Time lags in magneto-optics. H. W. FARWELL and J. B. HAWKES (Physical Rev., 1935, [ii], 47, 78—84).—Using modified apparatus permitting photometric measurements, an indefinite min. was found for the Faraday effect for CS₂, but none in the case of HCl. The intensity of the transmitted light is that predicted from Verdet const. of the liquid, and the const. of the electrical circuit. N. M. B.

Valency angles of oxygen and sulphur. N. G. PAI (Indian J. Physics, 1934, 9, 121—130).—From Raman and infra-red frequencies and dipole moments of mols. the following valency angles are calc. for O: H₂O, 115° and 104—106°; Me₂O, 118°; (CH₃)₂O, 64°; Et₂O, 125.8°; Pr₂O, 124.8°; Ph₂O, 126.9°, and for S: H₂S, 90°; Me₂S, 100°; Et₂S, 87.8°; Pr₂S, 89.4°; Bu₂S, 87.8°; Ph₂S, 95.2°. N. M. B.

Course of the reaction involved in the recombination of hydrogen atoms to molecules. H. SENTFLEBEN and W. HEIN (Ann. Physik, 1935, [v], 22, 1—27).—A more detailed account of work already reviewed (this vol., 150). A. J. M.

Theory of free radicals and organo-alkali compounds. B. NILSEN (J. Chem. Physics, 1935, 3, 15—19).—The method of Pauling and Wheland (A., 1934, 15) is applied to electron affinities of radicals. F. L. U.

Investigation of the free alkali metals (1930—1933). H. ALTERTHUM and R. ROMPE (Physikal. Z., 1935, 36, 69).—Two additions are made to the previous review (A., 1934, 1285). A. J. M.

Parachor and chemical constitution. I. Structure of the carbohydrates. S. K. RAY (J. Indian Chem. Soc., 1934, 11, 843—847).—From rapid measurements of d and surface tension in the fused state, before decomp. begins, the following vals. of the parachor have been determined: fructose 360.7, glucose 358.8, sucrose 672.0, glucose penta-acetate 771.5, glucose octa-acetate 1331, maltose octa-acetate 1339. Measurements have also been made on H₂O and C₅H₅N solutions of fructose, glucose, sucrose, and maltose. Results support Haworth's ring formula. R. S. B.

Interpretation of the parachor. R. F. HUNTER and R. SAMUEL (Rec. trav. chim., 1935, 54, 114—117).—A discussion of the validity of parachor measurements as a test of the existence of co-ordinate covalencies and singlet linkings. E. S. H.

Temperature coefficient of the surface tension of liquids. A. BOUTARIC (J. Chim. phys., 1934, 31, 621—627).—At temp. $<$ b.p. the temp. coeff. of the surface tension, γ , of liquids is related to the coeff. of expansion by $(1/\gamma)(d\gamma/dt) = -(4/v)(dv/dt)$, where v is the sp. vol. of the liquid. This relation, combined with a knowledge of the vals. of the consts. a and b in $v = v_0(1 + at + bt^2)$, for any particular liquid, permits calculation of γ at any temp. $<$ b.p. if the val. at any

other temp. is known. The approx. validity of the conclusions is confirmed for 15 org. liquids.

J. W. S.

Surface tension and molecular structure of liquids and solid substances in the light of "space energetics." R. VON DALLWITZ-WAEGNER (*Kolloid-Z.*, 1935, **70**, 39—48).—Theoretical.

E. S. H.

Surface tension of unassociated organic liquids: simple method of interpolation. A. R. CARR and T. WOLCZYNSKI (*J. Amer. Chem. Soc.*, 1934, **56**, 2541—2542).—A method for interpolation of the surface tension of unassociated org. liquids valid over a wide range of temp.

E. S. H.

Inactivation of activated molecules. K. WEBER (*Arh. Hemiju*, 1934, **8**, 160—179).—A review.

R. T.

Addition of symmetrical diatomic molecules to benzene. A. SHERMAN, C. E. SUN, and H. EYRING (*J. Chem. Physics*, 1935, **3**, 49—55; cf. *A.*, 1934, 242, 736).—Activation energies are calc.

F. L. U.

Linking energies of hydrocarbons: corrections yielding additivity. V. DERTZ (*J. Chem. Physics*, 1935, **3**, 58).—Introduction of three corrections makes the linking energies of nine aliphatic hydrocarbons additive within the accuracy of the experimental data available. The heat of dissociation of C_6H_6 can be calc. accurately without assuming resonance energy.

F. L. U.

Normal frequencies of vibration of the plane square molecule AB_4 with reference to the structure of nickel carbonyl. E. B. WILSON, jun. (*J. Chem. Physics*, 1935, **3**, 59).—The model AB_4 is treated analytically and the results are given. The method used by Duncan and Murray (*A.*, 1934, 1289) is criticised.

F. L. U.

Spectrum of the frequencies of a polar crystal lattice. M. BORN and J. H. C. THOMPSON (*Proc. Roy. Soc.*, 1934, **A**, 147, 594—599).—A method for the determination of the frequency spectrum of a crystal lattice is briefly described.

L. L. B.

Lithium bromide crystal and polarisation effects. P. GOMBAS (*Z. Physik*, 1934, **92**, 796—814).—Lattice consts., lattice energy, compressibility, and infra-red characteristic frequency are calc., taking into account polarisation and van der Waals energies. Stability is determined for lattices of NaCl and CsCl type; the former is preferred.

A. B. D. C.

Capillary systems. XII (3). Sphere-spiral as a structure element in homogeneous and heterogeneous spherical packing. E. MANEGOLD (*Kolloid-Z.*, 1935, **70**, 1—13; *A.*, 1933, 458).—Mathematical.

E. S. H.

Experimental proof of the vibrational movements of physical molecules. U. SCHMIESCHEK (*Z. tech. Physik*, 1934, **15**, 178—180; *Chem. Zentr.*, 1934, ii, 1081).—Vibrational movements of very small suspended Ag crystals, produced by the same cause as the Brownian movement, have been observed by photographing the reflected light.

H. J. E.

Number of water drops condensing on various solids. G. TAMMANN and W. BOEHME (*Ann. Physik*,

1935, [v], **22**, 77—80).—Condensation centres are on the solid surface and not in the neighbouring air. The no. of drops (I) formed on hard and soft metallic plates is not greatly different. (I) is independent of the orientation of the crystallite planes. The difference in temp. of the condensation plate and the H_2O vapour does not affect (I). The base metals are more effective in the condensation than the noble metals, but are affected by oxide layers and adsorbed gases.

A. J. M.

Relative reflexion powers of some X-ray spectrometer crystals. A. FAESSLER and G. KUPFERLE (*Z. Physik*, 1935, **93**, 237—244).—Relative reflexion power is given for Zn blende, rock-salt, calcspar, fluorspar, Bi, quartz, gypsum, beryl, mica, and sugar for three wave-lengths, 560, 1932, and 4150 X.

A. B. D. C.

Precision methods for the measurement of the parameters of crystal lattices. V. I. IVERNOVA (*J. Tech. Phys. U.S.S.R.*, 1934, **4**, 459—475).—Vals. arc recorded from various crystal faces for Mg, Al, α -Fe, Cu, Zn, Rh, Pd, Ag, Cd, β -Sn, Re, Ir, Pt, Au, and Pb.

CH. ABS. (e)

[Laue diagrams and morphology.] V. GOLDSCHMIDT (*Beitr. Kryst. Min.*, 1934, **3**, 143—221; *Chem. Zentr.*, 1934, ii, 1093).—A discussion.

H. J. E.

Derivation of a group of X-ray absorption curves from a single curve. R. JAEGER (*Physikal. Z.*, 1935, **36**, 3—8).—By considering $\mu_{\infty}l$ instead of the thickness, l , as variable in the exponential function for X-ray absorption by filters, it is possible to derive the group of curves for different tube potentials from a single curve.

A. J. M.

Stability of ionic lattices. H. JENSEN (*Z. Physik*, 1935, **93**, 236).—Polemical, against Steensholt (this vol., 19).

A. B. D. C.

Laue diagrams of deformed crystals. W. F. BERG (*Z. Krist.*, 1934, **89**, 587—593).—The "smearing" of Laue spots, transmitted and reflected, is discussed, viewing the lattice as a series of two-dimensional gratings arranged along the path of the X-ray beam.

B. W. R.

Kinetics of crystallisation processes. A. HUBER (*Z. Physik*, 1935, **93**, 227—231).—A distribution function is deduced to give direct comparison of Goler and Sachs' theory (*A.*, 1932, 986) with experiment.

A. B. D. C.

Orientations of impurity molecules included in crystals. K. S. KRISHNAN and P. K. SESHAN (*Z. Krist.*, 1934, **89**, 538—540).—Small traces of naphthacene in anthracene and in chrysene can be detected by their absorption bands. Polarisation measurements can locate the planes of these impurity mols., and it is concluded that these are parallel to the mols. of the mother substance.

B. W. R.

Isomorphism of compounds of elements of different valencies. G. BRUNI and A. FERRARI (*Z. Krist.*, 1934, **89**, 499—504).—The $MgCl_2$ lattice can be derived from that of $LiCl$ by maintaining the anion network but filling only half the cation spaces. Isomorphism is discussed from this aspect, the

anions in general determining the lattice, in which the cations are by comparison unimportant. B. W. R.

The vitreous state. G. HAGG (J. Chem. Physics, 1935, 3, 42—49).—Formation of glass on cooling is attributed to the presence in the melt of large or irregular groups of atoms the direct addition of which to the lattice is difficult. The structure of silicates and metaborates is discussed in support of the theory. F. L. U.

Structure of liquid substances. P. BOGDAN (J. Chim. phys., 1934, 31, 647—663; cf. A., 1934, 133).—Theoretical. J. W. S.

Growth of magnesium crystals. M. STRAUMANN (Z. Krist., 1934, 89, 487—493).—When Mg crystals grow from the vapour phase, besides the faces of regular habit apparently curved surfaces may appear, especially if the growth is fast. The process is discussed. B. W. R.

X-Ray investigations of very finely divided crystals (active charcoal and lamp-black). D. WILLY and U. HOFMANN (Kolloid-Z., 1935, 70, 21—24).—With increasing subdivision of C crystals the distance between the planes of atoms increases from 3.347 to 3.59 Å., whilst in the direction of the *a* axis there is a contraction from 2.456 to 2.40 Å. Recrystallisation begins at > 1300°; the crystals grow particularly in the *c* axis. E. S. H.

Twin formation in graphite. V. S. VESSELOVSKI and K. V. VASSILIEV (Z. Krist., 1934, 89, 494—496).—There is definite X-ray evidence for the occurrence of twinning in the basal plane with a rotation of 30°. B. W. R.

X-Ray study of indium and the indium-silver system. L. K. FREVEL and E. ORT (J. Amer. Chem. Soc., 1935, 57, 228).—X-Ray determinations between -25° and 141° reveal only the face-centred tetragonal modification. At 22°, *a*=4.588, *c*=4.938 Å.; the linear expansion coeffs. are: $\alpha_a=1/a \cdot (da/dT)_p=5.6 \times 10^{-5}$, $\alpha_c=1.3 \times 10^{-5}$. In the In-Ag alloys 5 phases have been detected. E. S. H.

X-Ray determination of the FeAl₃ structure. E. BACHMETEV (Z. Krist., 1934, 89, 575—585).—FeAl₃ has a rhombic cell, *a*₀ 47.43, *b*₀ 15.46, *c*₀ 8.08 Å., 100 mols. in the cell, space-group *V*₂₃². B. W. R.

Structure of rhombic sulphur. B. E. WARREN and J. T. BURWELL (J. Chem. Physics, 1935, 3, 6—8).—The unit cell contains 16 S₈ mols. and has *a* 10.48, *b* 12.92, *c* 24.55 Å. Space-group *V*_h⁴ (*Fddd*). The 8 mols. are symmetrically puckered rings. B. W. R.

Fibrous sulphur and its fine structure. K. H. MEYER and Y. GO (Kolloid-Z., 1935, 70, 19—20).—The crystallisation brought about by strongly stretching fibres of plastic S resembles that produced in rubber by stretching. The arrangement of S atoms in the fibre is discussed in the light of X-ray evidence; identity period occurs per 8 atoms. E. S. H.

Physico-chemical properties and X-ray structure of certain ferric oxides and hydroxides. J. OWAKOWSKI and S. GAWRYCH (Rocz. Chem., 1934, 4, —524).—X-Ray studies indicate that ortho-Fe(OH)₃ (I), prepared in various ways, is

amorphous, that ferrous acids possess a structure of the type of γ -FeO₂H, and consist of particles < 10⁻⁵ cm. in diameter, that goethites (II) have the cryst. form of α -FeO₂H, and that Fe₂O₃ obtained from (I) or (II) consists of well-formed crystals of the α -Fe₂O₃ type. R. T.

X-Ray studies on the hydrous oxides. VI. Alumina hydrates. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1934, 38, 1175—1182; cf. A., 1933, 214).—The authors overlooked the metastable bayerite, Al₂O₃·3H₂O, reported by Fricke and Severin (A., 1932, 573). The material formerly called δ -Al₂O₃ is identical with bohmite, Al₂O₃·H₂O. D. R. D.

Constitution of the alkaline-earth hydrides. E. ZINTL and A. HARDER (Z. Elektrochem., 1935, 41, 33—52; cf. A., 1932, 326).—Carefully purified specimens of CaH₂, SrH₂, and BaH₂ have been prepared and examined by X-rays. The consts. of the rhombic elementary cells are: CaH₂, 5.936, *a*₂ 6.838, *a*₃ 3.600 Å., *d*_{calc.} 1.90; SrH₂, *a*₁ 6.364, *a*₂ 7.343, *a*₃ 3.875, *d*_{calc.} 3.27; BaH₂, *a*₁ 6.788, *a*₂ 7.829, *a*₃ 4.167, *d*_{calc.} 4.15. Space-group *V*_h¹⁸. Direct measurement gave for SrH₂ *d*₄ 3.26. The arrangement of metal and H atoms in the crystals is discussed. F. L. U.

Structure of vitreous BeF₂. B. E. WARREN and C. F. HILL (Z. Krist., 1934, 89, 481—486).—The diffraction pattern of vitreous BeF₂ in monochromatic radiation agrees with the "random network" hypothesis. This postulates definite interat. distances and co-ordination scheme, but random orientation of neighbouring groups, and consequently no regular repetition of the structure. B. W. R.

Crystal form and space-group of ZrF₄ and HfF₄. G. E. R. SCHULZE (Z. Krist., 1934, 89, 477—480).—These substances have the same monoclinic prismatic structure, space-group *C*_{2h}⁶, consts. *a*₀ 9.46, *b*₀ 9.87, *c*₀ 7.64 Å., β 94° 30' for ZrF₄, and *a*₀ 9.45, *b*₀ 9.48, *c*₀ 7.62 Å., β 94° 29' for HfF₄. B. W. R.

Crystal structure of mercuric chloride. H. BRÆKKEN and W. SCHOLTEN (Z. Krist., 1934, 89, 448—455).—The rhombic bipyramidal cell has *a*₀ 5.963, *b*₀ 12.735, *c*₀ 4.325 Å., space-group *Pmnb*. At. co-ordinates are located from intensity measurements. The structure differs from that of HgBr₂, the mol. Cl-Hg-Cl being straight. B. W. R.

Space-group of silver nitrate diammoniate, AgNO₃·2NH₃. R. B. COREY and K. PESTRECOV (Z. Krist., 1934, 89, 528).—The cell is orthorhombic, *a*₀ 8.00, *b*₀ 10.58, *c*₀ 6.29 Å.; space-group probably *C*_{2h}¹⁰. B. W. R.

Atomic arrangement in potassium trithionate crystals K₂S₃O₆ and the structure of the trithionate radical, S₃O₆²⁻. W. H. ZACHARIASEN (Z. Krist., 1934, 89, 529—537).—K₂S₃O₆ is orthorhombic, 4 mols. to the cell, *a*₀ 9.77, *b*₀ 13.63, *c*₀ 5.76 Å., space-group *Pnam*. The parameters are determined. B. W. R.

Crystal structure of lithium sulphate monohydrate. G. E. ZIEGLER (Z. Krist., 1934, 89, 456—461).—The cell is monoclinic, *a*₀ 5.43, *b*₀ 4.83, *c*₀ 8.14 Å.,

β 107° 35', space-group $P2_1$. The 23 parameters were adjusted by trial, and the detailed at. positions (not H) are given. B. W. R.

Crystal structure of sulphohalite. T. WATANABE (Proc. Imp. Acad. Tokyo, 1934, 10, 575—577).—In agreement with predicted vals., the material was cubic (a 10.15 Å.; 4 mols. $2\text{Na}_2\text{SO}_4\cdot\text{NaCl}\cdot\text{NaF}$ per unit cell; space-group O^3 or O_h^3). H. J. E.

Crystal structure of sulphohalite. A. PABST (Z. Krist., 1934, 89, 514—517).— $2\text{Na}_2\text{SO}_4\cdot\text{NaCl}\cdot\text{NaF}$ is cubic face-centred, a_0 10.08±0.01 Å. At. parameters are found. B. W. R.

Crystal structure of dimethylammonium stannichloride. R. B. COREY and R. W. G. WYCKOFF (Z. Krist., 1934, 89, 469—476).— $(\text{NH}_2\text{Me}_2)_2\text{SnCl}_6$ is orthorhombic, 2 mols. in cell, a_0 7.26, b_0 7.38, c_0 14.28 Å., space-group C_{2v}^2 . At. distances are determined; the structure may be regarded as a serious distortion of the CaF_2 grouping. B. W. R.

Crystal structure of cyanuric triazide. E. W. HUGHES (J. Chem. Physics, 1935, 3, 1—5).—The dimensions of the unit cell of $\text{C}_3\text{N}_3(\text{N}_3)_3$ are a 8.70, c 5.98 Å.; it contains 2 mols.; space-group $H6_3/m$. The N_3 groups are bent through 15° at the central N atom. F. L. U.

Directed primary and subsidiary valencies of the oxygen atom deduced from the space-lattice of arsenolite as a geometrical basis for quadrivalent oxygen in oxonium compounds. R. REINICKE (Z. Elektrochem., 1935, 41, 23—28; cf. A., 1934, 476, 941).—The lattice structure of arsenolite and of senarmontite is deducible on the assumption that the O tetrahedron can under certain conditions bring into action two pairs of additional weaker valencies directed from the centre of the faces. Oxonium compounds and the existence of certain elements in both metallic and non-metallic form are discussed. F. L. U.

Crystal structure of manganite. J. GARRIDO (Compt. rend., 1935, 200, 69—71).—The unit cell of manganite has a 8.84, b 5.23, c 5.74 Å., and contains 8 mols. of $\text{MnO}_2\cdot\text{H}$. The probable at. arrangement in the lattice is discussed. J. W. S.

Crystal structure of calaverite. G. TUNELL and C. J. KSANDA (J. Washington Acad. Sci., 1935, 25, 32—33).—Cell dimensions are a_0 7.18, b_0 4.40, c_0 5.07 Å., all ±0.03 Å., β 90°±30'. Space-group $C2/m$; 2 mols. per unit cell. C. W. G.

Space-group of resorcinol. J. M. ROBERTSON (Z. Krist., 1934, 89, 518).—The cell axes given for this compound in the "Strukturbericht" (1931) must be revised; they should be a_0 10.53, b_0 9.53, c_0 5.66 Å., space-group Pna . B. W. R.

Spectrometric measurements on hexamethylenetetramine and carbamide. R. W. G. WYCKOFF and R. B. COREY (Z. Krist., 1934, 89, 462—468).—Fourier analyses based on powder and single-crystal measurements agree with the accepted structures for these compounds. The consequent F curves for C, N, and O are discussed. B. W. R.

Reflexion of X-rays from powdered anthracene. B. W. ROBINSON (Proc. Roy. Soc., 1935, A,

147, 467—478).—The discrepancy previously found between the F (001) vals. for single crystals of anthracene obtained with two different X-ray wavelengths (A., 1934, 18) disappears when powder measurements are made, and a higher val. for F (34.3) is obtained. L. L. B.

Structure of some hydrocarbons related to the sterols. J. D. BERNAL and (MISS) D. CROWFOOT (J.C.S., 1935, 93—100).—The crystal structure of some hydrocarbons derived from the sterols and bile acids has been examined by X-ray and optical methods, and compared with that of synthetic hydrocarbons of known constitution. Crystallographically, the hydrocarbons fall into two classes, monoclinic and orthorhombic, which are not essentially different, since a compound may exist in both forms. Diels' $\text{C}_{18}\text{H}_{16}$ (A., 1928, 169) could not be distinguished from the synthetic γ -methylcyclopentenophenanthrenes of Bergmann (A., 1933, 1154) and Kon (A., 1934, 288). It is suggested that $\text{C}_{21}\text{H}_{16}$ is a methyl-naphthafluorene. $\text{C}_{25}\text{H}_{24}$, $\text{C}_{26}\text{H}_{26}$, and $\text{C}_{27}\text{H}_{28}$ are also investigated. The lengths of their mols. are > those given by formulae previously proposed, and probably part of the sterol chain is still intact. The probable formulae involve a naphthafluorene skeleton with Bu^{β} , CHMePr^{β} , and CHEtPr^{β} groups, respectively, attached at one end. A. J. M.

X-Ray studies of crystallite orientation in cellulose fibres. Natural fibres. W. A. SISSON (Ind. Eng. Chem., 1935, 27, 51—56).—X-Ray diagrams obtained with the beam parallel to and perpendicular to the fibre axis indicate that in fibres having a spiral arrangement of crystallites (flax, cotton, sisal, and wood), although the direction of the b axis (direction of cellulose chains) is fixed, the other two axes are randomly oriented. This is explained by the assumption of discontinuities in cryst. structure. A. G.

Micellar structure and deformation processes of fibre materials. O. KRATKY (Kolloid-Z., 1935, 70, 14—19).—X-Ray investigation established the cryst. nature of micelles of cellulose esters after swelling. The influence of stretching is discussed. E. S. H.

Structure of cellulose dinitrate. M. MATHIEU (Compt. rend., 1935, 200, 143—145; cf. A., 1933, 216).—Nitrated cotton with 10.5—12.9% N gives the X-ray diagram of cellulose dinitrate, but with 13.3% N that of the trinitrate. The NO_2 groups are arranged at random in the chain, but coplanar with the glucose residues and 13.86 Å. (the dimensions of a NO_2) distant. The monoclinic pattern of a cellulose nitrate with < 13% N has periods 13.86 Å. and 8.0 Å. along a and c axes, and d -periods of 5.2 and 3.5 Å. J. L. D.

Preparation of thin single crystals of silver and their investigation with electron beams. H. LASSEN and L. BRUCK (Ann. Physik, 1935, [v], 22, 65—72; cf. A., 1934, 352).—If the temp. of the rock-salt on which the Ag is deposited is > 100, single crystals are always obtained. Examination of the structure of the Ag layers by transmission of electron beams shows that the rock-salt completely

determines the structure and orientation of the Ag crystal, the lattice planes of the latter being parallel to those of the NaCl. Comparison of reflexion with transmission shows that the dissolution of the NaCl support required for the second method causes considerable mechanical strain in the Ag, and consequent distortion.

A. J. M.

"Extra" rings and bands in electron diffraction patterns. G. I. FINCH and A. G. QUARRELL (Nature, 1935, 135, 183—184).—Electron diffraction patterns from Pt, Au, Ag, Co, Ni, Cr, Fe, Sn, graphite, and ZnO show up to 14 "extra" rings, and circular bands in addition. The crystals must be oriented and for a given orientation the extra ring and band pattern is characteristic of the crystal lattice. Impurities are not a contributory factor, and secondary scattering appears to play no material role in the formation of extra rings. These and the bands appear to owe their origin to the boundary faces through which the electron beam leaves the crystals.

L. S. T.

Electron diffraction on oxide-coated filaments. H. GAERTNER (Phil. Mag., 1935, [vii], 19, 82—103).—Activated block Ni cathodes initially coated with a BaCO_3 - SrCO_3 paste showed diffraction rings of SrO. Incomplete activation gave additional rings due to BaO and to the carbonates.

H. J. E.

Oxidation of metals. I. G. D. PRESTON and L. L. BIRCHUMSHAW (Phil. Mag., 1935, [vii], 19, 160—176).—From electron diffraction measurements the oxide film on Sn above its m.p. had the tetragonal SnO_2 structure, with the c axes of the crystals oriented perpendicular to the surface of the drop. Traces of SnO were indicated. Pb melted in air gave a film with the orthorhombic (yellow) PbO structure, with traces of the tetragonal (red) form (I). The c axis was oriented perpendicular to the plane of the film. Oxidation of molten Pb gave a film consisting of (I).

H. J. E.

Hall effect of cuprous oxide. O. VON AUWERS (Z. Physik, 1934, 93, 90—91).—The Hall effect is anomalous, i.e., positive.

A. B. D. C.

Magnetic Barkhausen effect by irradiation with ultrasonic waves. H. E. HOLLMANN and W. BAUCH (Naturwiss., 1935, 23, 35).—The structural changes occurring in a ferromagnetic body on demagnetisation can be demonstrated by examining the variation of the magnetic Barkhausen effect over the magnetisation curve, while the specimen is irradiated with ultrasonic waves.

A. J. M.

Magnetic investigations of separating power of iron-nickel crystals. F. PREISACH (Z. Physik, 1935, 93, 245—268).—The change in magnetic properties on recrystallisation of Fe-Ni alloys, with Be and Cu as separating components, is dependent not only on the extent and distribution of separation, but also on the condition of the crystal lattice.

A. B. D. C.

Discontinuity of magneto-resistance in ferromagnetic materials. G. ALOCCO and A. DRIGO (Nuovo Cimento, 1934, [ii], 11, 224—226; Chem. entr., 1934, ii, 1099).—The interpretation of Heaps' results is criticised (cf. A., 1934, 480).

H. J. E.

Magnetic properties of thin films of nickel. A. ARON (Compt. rend., 1935, 200, 228—230).—The influence of temp. on the magnetic properties of very thin, non-ferromagnetic films of Ni prepared by cathodic sputtering in H_2 and N_2 has been studied. On heating in air an irreversible change first occurs, accompanied by ferromagnetism. Further heating gives a reversible change, which oxidation destroys. In one case the Curie point was $20^\circ >$ that determined for bulk Ni by the same method (360°).

R. S. B.

Thermal expansion and the ferromagnetic change in volume in nickel. C. WILLIAMS (Physical Rev., 1935, [ii], 47, 88; cf. this vol., 153).—A correction.

N. M. B.

Diamagnetism of mercury crystals. E. VOGT (Ann. Physik, 1935, [v], 21, 791—803).—The dependence of the diamagnetism on the orientation of the crystals with respect to the field was determined for a single Hg crystal. The anisotropy of the mass-susceptibility, χ , is $\chi_{\perp} - \chi_{\parallel} = -8.9 (\pm 0.2) \times 10^{-9}$, the abs. vals. being $\chi_{\perp} = -121 (\pm 2)$ and $\chi_{\parallel} = -112 (\pm 2)$, both $\times 10^{-9}$. A comparison of these results with those for Zn and Cd is made, differences being ascribed to differences in the crystal structure.

A. J. M.

Directions of discontinuous changes in magnetisation in monocrystal bars and discs of silicon-iron. R. F. CLASH, jun., and F. J. BECK, jun. (Physical Rev., 1935, [ii], 47, 158—165).—Using a cathode-ray oscillograph method, by which the amplified rectangular components of a single discontinuity in magnetisation could be reintegrated into a vector representing the nearly discontinuous increment in magnetisation, a crystallographic dependence of the Barkhausen effect was found.

N. M. B.

Magnetism of tin. K. HONDA and Y. SHIMIZU (Nature, 1935, 135, 108).—The paramagnetic susceptibility of white Sn changes its sign as the internal stress produced by cold-working increases. This is analogous to the change accompanying reduction in particle size (A., 1934, 1061). Both changes are attributed to an increased lattice const. of the surface layer.

L. S. T.

Magnetic induction in a superconducting lead crystal. G. N. RJABININ and L. V. SHUBNIKOV (Nature, 1935, 135, 109; cf. A., 1934, 1061).

L. S. T.

Penetration of a magnetic field into superconductive alloys. W. J. DE HAAS and J. M. CASIMIR-JONKER (Nature, 1935, 135, 30—31).— Bi_5Te_3 and a Tl-Pb alloy (approx. 65% Pb), made superconductive by cooling below 4° abs., are penetrated by an electromagnetic field $>$ a certain crit. val. The relation between this val. and temp. is given.

L. S. T.

Structure of thin metallic layers produced by cathodic sputtering or vaporisation. G. TAMMANN (Ann. Physik, 1935, [v], 22, 73—76).—Evidence from density, thermal and electrical conductivity, etc. indicates that pure metals do not exist in the amorphous state (I). Sb containing 5—20% SbCl_3 or Sb_2Se_3 is stable in (I).

A. J. M.

Wiedemann-Franz number of β -manganese at -190° . H. REDDEMANN (Ann. Physik, 1935, [v], 22, 28—30).—The thermal and electrical conductivities of β -Mn at -183° and -195° were determined, and the vals. at -190° obtained by extrapolation. At -190° the sp. electrical resistance is 10^{-4} ohm per cm. The thermal conductivity no. λ is 0.05 watt per cm. per degree. The Wiedemann-Franz no. L is 6.41×10^{-8} . The thermal conductivity of β -Mn decreases with temp., supporting the assumption of Brunke (this vol., 19) that β -Mn is a mixed crystal phase of γ -Mn. A. J. M.

Electrical breakdown of X-irradiated rock-salt exposed to light. A. VOROBJEV (Z. Physik, 1935, 93, 269—277).—Exposure to light decreases the electrical breakdown strength of X-irradiated rock-salt. A. B. D. C.

Time of relaxation in crystals of Rochelle salt. R. D. SCHULWAS-SOROKIN and M. V. POSNOV (Physical Rev., 1935, [ii], 47, 166—174).—A theory of the action of mechanical and electrical forces, based on two relaxation times, is given and explains "creep" of polarisation, asymmetrical rates of polarisation and depolarisation, and other experimental results. Data on dielectric const. and power loss and dispersion curves are examined on the theory. N. M. B.

Rochelle salt. H. MUELLER (Physical Rev., 1935, [ii], 47, 175—191).—Measurements of dielectric, pyroelectric, optical, and electro-optical properties and a theory correlating all observations are given, based on the assumption that all properties depend on the inner field and that the Curie point changes with temp. The theory explains observed variation of susceptibility with temp. and field strength, anomalies of the quadratic electro-optical effect, pyroelectric effect, hysteresis loop, abnormal temp. variation of the birefringence, and change of these properties if piezoelectric deformations are prevented. The electro-optical effect is a Kerr effect, and a longitudinal Kerr effect has been discovered. A small crystal represents a single Weiss region, but large crystals show a Barkhausen effect. N. M. B.

Simple method for demonstrating the piezoelectricity of crystals. L. BERGMANN (Physikal. Z., 1935, 36, 31—32).—A tuning-fork (I) is clamped vertically with its handle in contact with a crystal showing the phenomenon, the crystal resting on a metal plate (II). (I) is connected to the filament, and (II) to the grid, of a valve connected to an amplifier. When (I) is set into vibration, a note is heard in telephones. The piezo axis may be found by moving the crystal until the effect is greatest. A. J. M.

Action of radium and X-rays on piezo quartz. F. SEIDL [with H. FROHLICH and E. HOFER] (Sitzungsber. Akad. Wiss. Wien, IIa, 1933, 142, 467—469; Chem. Zentr., 1934, ii, 1738—1739).—Irradiation raised the piezo const., especially in samples for which it was low. H. J. E.

Optical properties of metals. N. F. MOTT and C. ZENER (Proc. Camb. Phil. Soc., 1934, 30, 249—270).—Mathematical. The quantum theory of the

periodic field is developed, and results are compared with available experimental data for a no. of metals. N. M. B.

New interference phenomenon observed with crystalline plates. K. S. SUNDARARAJAN (Indian J. Physics, 1934, 9, 141—151).—A subsidiary set of closely spaced interference fringes, superposed on the interference system due to birefringence, was observed for thin cryst. plates of chrysene mounted between Nicols. Similar results were found for KClO_3 and mica. The theory of the fringes is developed, and they are shown to be due to two sets of closely spaced fringes, the superposition of which gives rise to the birefringence system, complementary to the Haidinger fringes. N. M. B.

Scattering of light by thin metallic films. S. R. SWAMY (Proc. Indian Acad. Sci., 1934, 1, A, 347—353).—The light scattered by thin films of Ag, Al, and Sn evaporated on glass or mica in vac., and of Ag, Cu, and Au sputtered on mica, showed anomalous depolarisation characteristic of metallic surfaces; the thin film has no metallic reflexion and a very large electrical resistance. It is suggested that the film has three possible different states: cryst. with metallic properties, two-dimensional gaseous non-metallic and non-conducting, and an intermediate state with high resistance. N. M. B.

[Theory of practical strength.] A. SMEKAL (Z. Physik, 1934, 93, 125—126).—A reply to Stepanov (this vol., 19). A. B. D. C.

Mechanical behaviour of single crystals of mercury. E. N. DA C. ANDRADE and P. J. HUTCHINGS (Proc. Roy. Soc., 1935, A, 148, 120—146).—The rhombohedral faces are glide planes, and the short diagonal is the glide direction. The crystal twins under strain on a plane through the long diagonals of two opposite faces, acting as glide planes. Twinning takes place when the twinning plane makes an angle of 45° with the direction of the applied force. Whereas the packing of the rhombohedral line and that of the hexagonal base are the same, the former contains a much more closely-packed line, which probably confers on this face its prerogative as a glide plane. The distribution of planes of pronounced glide at approx. equal intervals, of the order of 10^4 times the at. lattice spacing, appears to be a fundamental feature of the metal lattice which does not depend on metallic impurities or dissolved gas. The crit. shear stress is 9.3 g. (wt.) per sq. mm. at -43° . L. L. B.

Directional variation of the translation mechanism of rock-salt crystals at high temperatures. H. WOLFF (Z. Physik, 1935, 93, 147—165).—Directional variation of translation properties of rock-salt crystals was determined at 400° , and shows that the slip planes for homogeneous extension are (100), (110), and (111). A. B. D. C.

Translation conditions. A. SMEKAL (Z. Physik, 1935, 93, 166—172).—Translation conditions for plastic flow of single crystals are summarised; rock-salt shows the further condition that of possible flow systems that of "shortest" direction of slip is preferred. A. B. D. C.

Polymorphism of metals. V. N. SVECHNIKOV (J. Tech. Phys. U.S.S.R., 1934, 4, 253—267).—Fe and Sn tend to pass into the form with the lesser sp. lattice vol. at a given temp. The effect of admixtures on the $\alpha \rightleftharpoons \gamma$ Fe conversion depends on the at. vol. of the mixture. Pure Fe may not have a γ phase. The speed of crystallisation of Sn is lowered by Cd, Sb, and Bi in the order of their at. vols.

CH. ABS. (e)

Time of melting of thin fuses. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Z. Physik, 1934, 93, 100—110).—Results are given for Cu, Zn, Pt, Ni, Mn-Ni, constantan, monel, "Kruppin," and Ag wire fuses.

A. B. D. C.

Refraction of ultrasonic waves. W. BEZ-BARDILI (Physikal. Z., 1935, 36, 20—24).—Photographs show the refraction of ultrasonic waves at an Al prism, their deviation at an Al plate, the action of cylindrical lenses of Al in xylene, the effect at a wire grating, and other examples of reflexion and refraction.

A. J. M.

Effect of pressure and addition of foreign gases on the relaxation time of the vibrational heat in carbon dioxide. M. H. WALLMANN (Ann. Physik, 1935, [v], 21, 671—681).—The velocity of sound (I) in CO_2 , H_2 , N_2 , and $\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-N}_2$ mixtures has been determined, and its variation with frequency investigated. From the dispersion curve, the relaxation time of the vibrational heat (II) in CO_2 at 21° and 600 mm. is 4.6×10^{-6} sec. (I) in H_2 was const. at frequencies between 359 and 1481 k.-hz., and equal to the val. for audible frequencies. In $\text{CO}_2\text{-H}_2$ mixtures, (II) $\propto 1/[\text{H}_2]$. (II) $\propto (\text{pressure})^{-1}$.

A. J. M.

Relaxation time of vibrational energy in oxygen and the effect of foreign gases on it. H. O. KNESER and V. O. KNUDSEN (Ann. Physik, 1935, [v], 21, 682—696).—The absorption of sound in O_2 and binary mixtures of O_2 and other gases (H_2 , He, CO, CO_2 , O_3 , H_2S , C_2H_2 , C_6H_6 , EtOH, CHCl_3 , CCl_4 , CS_2) was determined. The relaxation time of the vibrational heat (I) and the mean life of the vibrational quanta in O_2 is obtained from the absorption curves. The curve between absorption and concn. of foreign gas usually shows a max., but not with CHCl_3 , CCl_4 , O_3 , CO_2 , CO, and He; N_2 has small effect. The probability of conversion of nuclear vibration of O_2 into translational and rotational energy by collision is calc.

A. J. M.

Velocity of sound in liquid oxygen. R. BAR (Nature, 1935, 135, 153).—The scattering of light by ultrasonic waves gives 903 m. per sec. for the velocity of sound in liquid O_2 . The calc. adiabatic and thermal compressibilities are 105.6×10^{-6} and 172.0×10^{-6} cm.² per kg., respectively.

L. S. T.

Paramagnetism in the palladium series. B. CABRERA and H. FAHLENBRACH (Ann. Physik, 1935, [v], 21, 832—840).—The magnetism (I) of PdCl_2 , RhCl_3 , and RuCl_3 between -50° and 150° follows a law of the form $(\chi + a)T = C$, where a and C are consts. (I) of an aq. solution of PdCl_2 was also investigated. The paramagnetism of the solution is $>$ that of H_2O .

A. J. M.

Hydrates and diamagnetism. S. R. RAO and P. S. VARADACHARI (Current Sci., 1934, 3, 249—250).—Investigation of solid Na_2SO_4 and in conc. solution showed no change in magnetic susceptibility at temp. $> 33^\circ$. Deviations of 3—4% occurred with aq. H_2SO_4 corresponding with different hydrates. Vals. for diamagnetic susceptibility of cryst. sulphates of Li, Na, K, and Mg did not support the theory of enlargement of ionic radii in solution with rising temp.

P. G. M.

Magnetic susceptibility of organic liquids; applications to the additivity law. C. SALCEANU and D. GHEORGHIU (Compt. rend., 1935, 200, 120—123).—A modification of the method of Sibaiya and Venkataramiah (A., 1933, 455) is described. The magnetic susceptibilities of $\text{COMc}_2\text{-PhNO}_2$ and $\text{COMc}_2\text{-1-C}_{10}\text{H}_7\text{Me}$ follow the additivity law to within 1%. This is contrary to the view of Ranganadham (A., 1932, 216), who attributes deviations from the law to mol. deformations produced by the mutual influence of polar mols.

J. W. S.

Susceptibility constants for co-ordinate linking in additive compounds. I. S. S. BHATNAGAR, M. R. VERMA, and P. L. KAPUR (Indian J. Physics, 1934, 9, 131—139).—Magnetic susceptibility data were obtained for compounds containing a co-ordinate linking and formed between $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ and benzidine, C_{10}H_8 , and $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$, and between picric acid and C_{10}H_8 , anthracene, phenanthrene, and $1\text{-C}_{10}\text{H}_7\text{Me}$. Results show that the additive compounds become more diamagnetic than expected on the additivity law. The susceptibility increase varies between 77×10^{-7} and 140×10^{-7} per g.-mol. Explanations are discussed.

N. M. B.

Ebulliometric and tonometric studies of chemically pure liquids. A. ZMACZYNSKI (Rocz. Chem., 1934, 14, 691—701).—The b.p. of C_6H_6 and H_2O have been determined at pressures of 289.1—2347.4 mm.

R. T.

Specific heat of some lanthanum and scandium salts, and of monazite. E. TURSKA (Rocz. Chem., 1934, 14, 760—763).—The sp. heats are: $(\text{HCO}_2)_3\text{La}$ 0.2910, $(\text{HCO}_2)_3\text{Sc}$ 0.2985, $\text{Sc}_2(\text{C}_2\text{O}_4)_3$ 0.3455, monazite 0.1223.

R. T.

Approximate equation for heat capacities at high temperatures. J. CHIPMAN and M. G. FONTANA (J. Amer. Chem. Soc., 1935, 57, 48—51).—The expression $C_p = a + bT + cT^{-1}$ holds approx. for solids and gases at high temp.

E. S. H.

Specific heat of liquid pure hydrocarbons and petroleum fractions. L. P. GAUCHER (Ind. Eng. Chem., 1935, 27, 57—64).—Each of the purely empirical equations $C_p = 0.6230 - 0.0187T^{0.5}/S^{1.5} + 0.000355T/S^3 + 0.00045(t-32)$ and $C_p = 1.323 - 0.2005T^{1/3}/S + 0.0107T^{2/3}/S^2 + 0.00045(t-32)$ expresses the sp. heat at const. pressure of pure hydrocarbons in terms of the b.p. T , the sp. gr., S , and the temp. t in $^\circ\text{F}$, with a mean error of 1.3%. For petroleum fractions Watson and Nelson's correlation is the best.

A. G.

Specific heats of technical gases and vapours at higher temperatures. E. JUSTI (Forsch. Ingenieurw., 1934, A, 5, 130—137; Chem. Zentr.,

1934, ii, 1741—1742).—Data are calc. for C_p from 20° to 5000° abs. for H_2 , N_2 , CO , NO , O_2 , Cl_2 , H_2O , and CO_2 .
H. J. E.

Latent heat of vaporisation and characteristic temperature. R. LAUTIE (Compt. rend., 1935, 200, 58—59)—Theoretical.
J. W. S.

Molar heats of fusion of organic compounds and their dependence on the position of the m.p. J. PIRSCH (Ber., 1935, 68, [B], 67—72; cf. A., 1934, 951).—The mol. latent heats of fusion (I) of all ketones and halogenated hydrocarbons of the *dicycloheptane*-[1:2:2]-ring system diminish linearly with the m.p.; *dicyclooctane* compounds appear to behave similarly. A like but less exact relationship exists among *dicycloheptane* hydrocarbons, for which the vals. of (I) are > in the case of ketones of corresponding m.p. Similar relationships are observed with ketones related to α -*dicyclopentadiene* and the corresponding hydrocarbons. The relationships do not appear to depend on the presence or absence of double linkings in the mol., so that the great change in m.p. frequently produced by hydrogenation is accompanied by corresponding change in (I). The magnitude of (I) is controlled by the form and size of the space demand of the mol. With compounds of approx. the same space demand and m.p., the mol. depression \propto mol. wt. H. W.

Further experiments with the magnetic cooling method. N. KURTI and F. SIMON (Nature, 1935, 135, 31; cf. A., 1934, 836).—Zr becomes superconductive at 0.7° abs. and Hf at 0.3—0.4° abs. Cu, Au, Ge, Bi, and Mg do not become superconductive at temp. down to 0.05° abs. Using magnetic cooling, 0.04° abs. has been reached with Fe alum.
L. S. T.

New interpretation of the Helmholtz equation and of Nernst's theorem. C. GRABOWSKI (Rocz. Chem., 1934, 14, 806—822).—Theoretical. All three theses of Nernst's theorem are regarded as proved.
R. T.

Rapid calculation of fugacities of pure substances. G. VAN LERBERGHE (J. Chim. phys., 1934, 31, 577—582).—The method described is based on the use of "reduced" temp., pressure, and vol. Examples are given.
F. L. U.

Phase equilibria in hydrocarbon systems. VI. Thermodynamic properties of normal pentane. B. H. SAGE, W. N. LACEY, and J. G. SCHAAFSMA (Ind. Eng. Chem., 1935, 27, 48—50).—Data are given for sp. gr., v.p., sp. heat at const. pressure of 1000 lb. per sq. in., fugacity/pressure, and heat content within the limits 21—104° and 100—3000 lb. per sq. in.
A. G.

Density of liquid hydrogen sulphide. J. P. BAXTER, L. J. BURRAGE, and C. C. TANNER (J.S.C.I., 1934, 53, 410—413r).—The density of liquid H_2S , prepared synthetically in a system from which all traces of H_2O were excluded, has been determined over the temp. range —81° to 58°, six independent density tubes being used.

Vapour-pressure curves, m.p., and chemical constants of di- and tri-methylamine and isobutylamine. A. SIMON and J. HUTER (Z. Elektro-

chem., 1935, 41, 28—33).—V.p. have been measured between —78° and 15° for $NHMe_2$, —90° and 12° for NMe_3 , and —37° and 74° for NH_2Bu^{β} . The respective m.p. are —93.3°, —123.8°, and —86.7°. Chemical consts. have been calc. from the v.p.
F. L. U.

Vapour pressure of ketones. M. G. MAYBERRY and J. G. ASTON (J. Amer. Chem. Soc., 1934, 56, 2682—2683).—The v.p. of the following are measured: $COMeEt$, $COMePr^{\alpha}$, $COMePr^{\beta}$ (I), $COMeBu$, $COMeBu^{\beta}$, $COEtPr^{\beta}$, $COPr^{\beta}_2$, $COPr^{\alpha}Pr^{\beta}$, $COPr^{\beta}Bu^{\beta}$, $COBuPr^{\beta}$, and *cyclohexyl Me* and *Et* ketones. Dühring's rule (cf. White, B., 1930, 443) for predicting v.p. applies; (I) is used as standard. Calculation of Trouton's const. shows that the ketones are slightly associated.
H. B.

Viscosity anomalies. M. PICHOT (Physics, 1934, 5, 200—206).—Data for H_2O and for a 0.7% gelatin solution flowing between parallel plates under const. head indicate parabolic velocity distribution for the H_2O and a flat distribution, similar to that in turbulent flow, for the solution. An hypothesis of structural viscosity is derived, supported by other data on aq. Na stearate solutions.
CH. ABS. (c)

Fluidity method for the determination of association. II. E. C. BINGHAM and L. W. SPOONER (Physics, 1933, 4, 387—400; cf. A., 1932, 566).—Fluidity data for 346 liquids are recorded and discussed.
CH. ABS. (c)

Measurement of the viscosity of the alkali metals *in vacuo*. F. SAUERWALD [with K. GERING] (Z. Metallk., 1934, 26, 259—260).—Measurements in a capillary in vac. gave the following vals. for η : Na (at 100°) 0.0077; K (at 79°) 0.00520, (at 183°) 0.00346. The extrapolated vals. for η at the m.p. are Na 0.0077, K 0.0056, which are about 30% > those calc. by Andrade's rule.
A. R. P.

Viscosity of phosphoric acid. N. D. LITVINOV, T. A. KRIUKOV, and E. A. KOROTSHKINA (J. Appl. Chem. Russ., 1934, 7, 1121—1124).—The η of H_3PO_4 varies approx. exponentially, and the d linearly, with the temp.
R. T.

Fluidity of anisole. J. A. GEDDES and E. C. BINGHAM (J. Amer. Chem. Soc., 1934, 56, 2625—2626).—Data for the temp. range 2—100° are recorded. The degree of association is calc.
E. S. H.

Viscosity of supercooled liquid glucose. G. S. PARKS, L. E. BARTON, M. E. SPAGHT, and J. W. RICHARDSON (Physics, 1934, 5, 193—199).—Vals. are recorded between 145° and 22°. Considerable association is indicated.
CH. ABS. (c)

Glycol-water mixtures. Vapour pressure-b.p.-composition relations. H. M. TRIMBLE and W. POTTS (Ind. Eng. Chem., 1935, 27, 66—68).—Data are recorded for mixtures at 228, 430, 603, and 747 mm. pressure. Raoult's law is approx. obeyed and the results are reproduced by $\log p - A + B/T$, in which the vals. of the consts. depend on the % H_2O .
A. G.

Rapid evaporation of liquid mixtures. I. Mixtures of acetic and benzoic acids. Z. BEASZKOWSKA (Rocz. Chem., 1934, 14, 919—924).
R. T.

Physico-chemical properties of carbamide nitrate. M. TOKUOKA and H. MOROOKA (Bull. Agr. Chem. Soc. Japan, 1934, 10, 127—129).—The solubility, together with the d and v.p. of aq. solutions, are recorded. CH. ABS. (r)

Viscosity of nitrocotton in various solvents and mixtures. J. W. MCBAIN, E. M. GRANT, and L. E. SMITH (J. Physical Chem., 1934, 38, 1217—1231; cf. B., 1926, 482).—Previous results are confirmed. The η of solutions of cellulose nitrate (I) falls nearly to the val. for the pure solvent in 3 years at 55°. For solutions in benzyl- (II) and ethyl-formanilide (III) and o -C₆H₄(CO₂Et)₂, η passes through a min., and with (II) and (III) a jelly is ultimately formed. Solvent power for (I) may be measured (a) by adding solvent to diluent until gelatinisation occurs; (b) by adding solvent in C₆H₁₄ and comparing swelling; (c) by measuring amount of solvent absorbed from C₆H₁₄, and (d) by measuring the rise of temp. on adding (I) to the liquid. D. R. D.

Viscosity of solutions of cellulose nitrate. (MME.) A. DOBRY (J. Chim. phys., 1934, 31, 568—576).—The viscosity (η) of solutions of cellulose nitrate (I) in 12 org. liquids has been measured at 25°. The ratio $(\eta - \eta_0)/\eta_0 c = R$ (c = concn., η_0 = viscosity of solvent) is the same for all solvents at $c=0$, but varies greatly when c increases; e.g., at $c=1\%$, $R=630$ for cyclohexanone and 2770 for PhNO₂. At great dilutions $\eta = \eta_0(1 + R_0 c)$. The fact that R_0 is independent of the solvent indicates that the vol. of the particles is the same in all solvents despite large differences in their solvent power. The solvation must therefore be negligibly small. Staudinger's "vol. of encumbrment" is not the sole cause of the large increase of η caused by (I). F. L. U.

System pyridine-acetic acid. III. L. E. SWEARINGEN and R. F. ROSS (J. Physical Chem., 1934, 38, 1141—1144).—Sp. conductance passes through a max. at 83 mol.-% AcOH at all temp. between 0° and 40°. D. R. D.

Copper-gold alloys, especially at high temperatures. L. VEGARD and A. KLOSTER (Z. Krist., 1934, 89, 560—573).—Precision lattice consts. have been determined for 0, 25, 50, 75, and 100 at.-% Cu at 475° and at room temp. The cell size does not increase linearly with at.-%. B. W. R.

Fine structure of X-ray absorption edges of copper and zinc in copper-zinc alloys. D. COSTER and R. SMOLUCHOWSKI (Physica, 1935, 2, 1—12).—The positions of the absorption max. and min. in the X-ray absorption edges due to Cu and Zn in α -, β -, and γ -brass are related to those of the pure metals in the same kind of crystal lattice, in agreement with Kronig's theory (A., 1931, 993; 1932, 553). Deviations in the form of the max. or min. are interpreted. J. W. S.

Transformation of the β -phase of copper-aluminium alloys. E. KAMINSKY, G. KURDJUMOW, and W. NEUMARX (Metallwirts., 1934, 13, 373; Chem. Zentr., 1934, ii, 1986).—The transformation $\beta \rightarrow \alpha + \gamma$ (I) is easily suppressed. Slow cooling in air gives β' , Wassermann's results for the

transition $\beta' \rightarrow \alpha + \gamma$ being confirmed (cf. this vol., 23). The transitions $\beta \leftarrow \beta_1$ and $\beta_1 \leftarrow \beta'$ occur very rapidly and without diffusion. $\alpha + \gamma$ is stable at $< 570^\circ$, and is always formed if the diffusion rate is sufficient. When (I) does not occur, β forms β at 520° . H. J. E.

Alloys of aluminium with gallium. E. JENCKEL (Z. Metallk., 1934, 26, 249—250).—Thermal analysis and X-ray examination of Al-Ga alloys have failed to confirm the existence of any compounds (cf. Pushin *et al.*, A., 1933, 118); the alloys form a simple eutectiferous system with the eutectic at 26.3° and almost 100% Ga. A. R. P.

Under-cooling of high-melting intermetallic compounds in aluminium alloys. [System aluminium-titanium.] H. BOHNER (Z. Metallk., 1934, 26, 268—271).—When alloys of 99.99% Al with 0.5% Ti are chilled from 900° , needles of Al₃Ti cannot be seen in the microstructure, and the electrical properties are those of a complete solid solution. Prolonged annealing at 550 – 640° or casting at $<$ the solidus temp. produces the characteristic needles in the structure and the conductivity rises to that of the saturated solid solution of Ti (0.02%) in Al. On slow cooling from 900° the bottom of the ingot is very rich in Al₃Ti, whereas the top contains only 0.03%. Similar effects have been observed with Mn-Al alloys. A. R. P.

Transformations in eutectoid alloys. G. WASSERMANN (Z. Metallk., 1934, 26, 256—259).—Similarities in the decomp. of cementite, β -Cu-Al, β -Cu-Sn, and β -Cu-Be alloys into the $\alpha + \gamma$ eutectoids are pointed out and explained by means of lattice diagrams. A. R. P.

Properties of alloys of Be, Mg, Zn, Cd, Hg, Al, and Sn. U. DEHLINGER (Z. Elektrochem., 1935, 41, 20—23; cf. A., 1934, 1065, 1158).—The influence of at. radius and polarisability on the formation of compounds and on miscibility in the solid and liquid phases is discussed. F. L. U.

Criticism of the iron-cementite eutectoid diagram and a proposed new diagram. J. SEIGLE (Rev. Met., 1934, 31, 547—548).—The proposed diagram is based on experiments which indicate that the eutectoid transformation does not occur at a fixed temp., and that the $\alpha \rightarrow \gamma$ change of pure Fe also occurs over a temp. range. W. P. R.

Magnetic study of the system cobalt-palladium. G. GRUBE and O. WINKLER (Z. Elektrochem., 1935, 41, 52—60).—Magnetisation-temp. curves for Co and its binary alloys containing up to 90 at.-% Pd show that a transformation, setting in at different temp. for heating and for cooling, occurs only with pure Co and with alloys containing 5 and 10 at.-% Pd. The Curie temp. falls steadily with increasing Pd content. The course of the transformation closely resembles that of Fe-Ni alloys. The existence of a continuous series of β mixed crystals extending to 90 at.-% Pd is probable. The construction of a special magnetometer is described. F. L. U.

Disturbance of superconductivity of an alloy by an electric current. W. H. KEESOM (Physica, 1935, 2, 35—36).—Measurements with a eutectic Pb-Bi

alloy indicate that the disturbance of the superconductivity by a current does not depend on the val. of the magnetic field due to the current in the manner which Silsbee's hypothesis prescribes for pure metals.

Replaceability of zinc by magnesium and vice versa. I. Miscibility of Mg_3Sb_2 and Zn_3Sb_2 and structure of mixed crystals. K. LOHBERG (Z. physikal. Chem., 1934, B, 27, 381—403).— Mg_3Sb_2 dissolves up to 46 at.-% Zn_3Sb_2 , the c/a ratio of the hexagonal mixed crystal changing linearly from 1.581 to 1.636. The mixed crystals have the structure of the A modification of the rare-earth sesquioxides. The distribution of the Zn atoms over the Mg sites is such that the Mg atoms of the twofold, but not those of the onefold, point positions are replaceable by Zn.

R. C.

Mixed crystals in the vitriol series. IV. A. BENRATH and W. THIEMANN (Z. anorg. Chem., 1935, 221, 423—426).—Solubility curves for CdSO_4 (A., 1932, 229) indicate a transition point at 75° attributed to $(\text{CdSO}_4 \cdot \text{H}_2\text{O})_3 \rightarrow 3\text{CdSO}_4 \cdot \text{H}_2\text{O}$. $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ should be miscible in all proportions with other kieserites, but the product obtained above 75° is not miscible with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. The solubility curve at 75° is, therefore, not discontinuous and the observed relations may be due to the gradual dissociation of the associated mol.

M. S. B.

Significance of anomalous mixed crystals in the determination of the equilibrium in mixed salt solutions. A. BENRATH and H. SCHACKMANN (Z. anorg. Chem., 1935, 221, 418—422; cf. A., 1934, 725).—The mixed crystals which separate from a solution of FeCl_3 supersaturated with respect to NH_4Cl are not in equilibrium with the mother-liquor. When equilibrium is reached the mixed crystals disappear. A similar phenomenon is observed with MnCl_2 and NH_4Cl .

M. S. B.

Heterogeneous binary systems. Physical properties of liquid systems in two layers. (MLLE.) H. SCHLEGEL (J. Chim. phys., 1934, 31, 668—688; cf. this vol., 25).—Measurements have been made of d , n , viscosity, and surface tension of cyclohexane- NH_4Ph mixtures near the crit. solution temp. and concns. Viscosity measurements have also been made for C_6H_{14} - PhNO_2 mixtures.

J. W. S.

Miscibility of sulphides of copper, lead, and iron with lead in the liquid state. W. LEITGEBEL and E. MIKSCHE (Metall u. Erz., 1934, 31, 290—293; Chem. Zentr., 1934, ii, 1985—1986).—Addition of Pb lowers the f.p. of FeS to 1000° (30% Pb) and of Cu_2S to 1060° (7% Pb). Further additions cause two layers to separate. Pb and PbS are completely miscible. The systems Pb- FeS -PbS, Pb- Cu_2S -PbS, and Pb- Cu_2S - FeS are discussed.

H. J. E.

Solubility of antimonious acid in water. S. GLIXELI and A. PRZYSZCZYŃSKI (Rocz. Chem., 1934, 14, 474—486).—The proportion of larger particles in the heterodisperse system Sb_2O_3 - H_2O increases with increasing temp. of hydrolysis of the SbCl_5 from which the Sb_2O_3 was prepared. The highest solubility of Sb_2O_3 was found when SbCl_5 was hydrolysed at 0° (0.186 g. of the product dissolved in 100 c.c. of H_2O at 25°).

R. T.

Solubility of chemically-defined hydrates of silicon dioxide. R. SPYCHALSKI (Rocz. Chem., 1934, 14, 915—918).—The stability of the hydrates described by Thiessen *et al.* (A., 1930, 720) increases with time. The solubility of the hydrates increases with diminishing H_2O content.

R. T.

Method for experimental investigation of hydrothermal solutions and its application to the solubility of silica. C. S. HITCHEN (Bull. Inst. Min. Met., 1935, No. 364, 26 pp.).—A pressure-vessel of Ni-Cr steel for studying the action of H_2O on solid substances at temp. up to 400° and at a max. pressure of 800 atm. is described. The apparatus has been used to measure the solubility of SiO_2 in H_2O between 128° and 336° . Data for this and for the influence of Na_2SiO_3 on the solubility are given. The results are discussed from the point of view of the formation of quartz veins. Previous work is reviewed.

F. L. U.

Solubility of sulphur dioxide in sulphuric acid. E. K. LOPATTO and A. M. SAVINAEV (J. Appl. Chem. Russ., 1934, 7, 881—886).—The v.p. of SO_2 over aq. H_2SO_4 is given by $\log p = A + B/T$, where A and B are consts. depending on the concn. of SO_2 and of H_2SO_4 , respectively.

R. T.

Solubility of sodium thiosulphate in ethyl alcohol-water mixtures [at 20°]. R. DOLIQUE (Bull. Soc. chim., 1934, [v], 1, 1745—1752).—The relative concns. for which the ternary system affords two co-existing liquid phases have been determined. The solubility of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in EtOH containing small quantities of H_2O is very small.

J. G. A. G.

Solubility of cuprous chloride in concentrated hydrogen chloride. K. S. CHANG and Y. T. CHA (J. Chinese Chem. Soc., 1934, 2, 298—306).—The solubility of CuCl in 0.73—12.0N-HCl is determined by two methods. Vals. of $a_{\text{CuCl}}/a_{\text{H}^+}^2$ and $a_{\text{HCl}}/a_{\text{Cl}^-}$ at 25° are 0.0204 and 0.85, respectively, whence the activity coeff. of CuCl_2 is calc.

R. S. C.

Solubility of cuprous chloride in alcoholic hydrogen chloride. K. S. CHANG and Y. M. LIU (J. Chinese Chem. Soc., 1934, 2, 307—310).— CuCl , insol. in abs. EtOH, dissolves in HCl-EtOH, K for the formation of CuCl_2 being about 5.84 at 25° . CuCl_3 is not formed.

R. S. C.

Solubility of cellulose nitrate. T. URBANSKI (Rocz. Chem., 1934, 14, 944—956).—The solubility, S , of cellulose nitrate (I) in mixtures of EtOH and various solvents (Me, Et, Pr^a, Pr^b, Bu^a, Bu^b, and iso-C₅H₁₁ formate and acetate, EtCO₂Et, PrCO₂Et, BuCO₂Et, CH₃Ac-CO₂Et, COMe₂, and COMeEt) is expressed by $S = jr/dc$, where r is the % of (I) dissolved by the given mixture, and c the concn. of solvent. For the series R-CO₂R', S increases with increasing mol. wt. of R'; at the same time, the dielectric const. μ of the solvent diminishes, and the dipole moment k increases, so that S varies parallel with μ^2/k . Analogous relationships are not found between the val. of S and the mol. wt. of R.

R. T.

Velocity of crystallisation and certain other physico-chemical properties of supersaturated arsenious acid solutions. G. BIRSTEIN and J.

KRONMAN (Rocz. Chem., 1934, 14, 975—993).—The mols. of H_3AsO_3 undergo increasing association with increasing concn., to a limiting val. corresponding with As_2O_3 . The d and n of the solutions increase linearly with concn. The velocity of crystallisation corresponds with $-dc/dt = kc^4$, where c is the concn.; the temp. coeff. for the interval $0-25^\circ$ is zero.

R. T.

Growth of crystals. VI. Variations of form of crystals grown in the presence of cations which favour their growth. T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 61—65).—The development of star-like crystals (I) of NaCl and KCl in presence of Bi^{+++} and (I) of NH_4Cl in presence of Ti^{+++} , ZrO^{++} , Cd^{++} , Pb^{++} , Fe^{++} , Cr^{+++} , etc. has been studied microscopically. Small cubes are formed which become pyramidal, and the base of the pyramid then extends diagonally to give (I). The structure of the crystal planes is discussed.

R. S.

Complex isomerism. Formation of crystal nuclei and crystall lattices of complex isomerides. Thermochemical studies. E. HERTEL and H. FRANK (Z. physikal. Chem., 1934, B, 27, 460—466; cf. A., 1931, 1114).—The metastable red form (I) of the compound of $4:1\text{-C}_{10}\text{H}_8\text{Br}\cdot\text{NH}_3$ with $2:6$ -dinitrophenol has a greater power of spontaneous nucleus formation and a larger linear rate of crystallisation than the yellow form (II). In a molten mixture of the components nuclei of (I) and (II) are formed independently. The heat of formation of (I) from its components is negligible, whilst that of (II) ~ 3 kg.-cal.

R. C.

Rhythmic precipitates. IV. Distances between rhythmic layers. T. ISEMURA (J. Chem. Soc. Japan, 1934, 55, 809—810).—The formula $d = a + bn + cn^2$ (d being the distance between two successive layers and a , b , and c consts.) holds for ring formation of Cu chromate in SiO_2 gel.

CH. ABS. (e)

Partition of tartaric and citric acids between water and isoamyl alcohol. N. A. DE KOLOSOWSKI and F. S. KULIKOV (Ukrain. Chem. J., 1934, 9, 143—147).—The relative concn. of the acids in the aq. layer increases with increasing dilution.

R. T.

Diffusion of gases through metals. L. N. KHITRIN (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 160—170).—The Richardson formula reproduces the experimental data for the diffusion of H_2 , CO , CO_2 , C_2H_2 , CH_4 , and N_2 through Fe at $300-1000^\circ$. H_2 and CO diffuse readily, C_2H_2 and CH_4 more slowly, CO_2 and N_2 only slightly at 300° . The rate for H_2 is a max. at 550° .

CH. ABS. (e)

Sorption of hydrogen by reduced nickel. IV. Velocity of sorption of hydrogen at the early stage. S. IJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 45—69; cf. A., 1934, 358).—The influence of pressure and temp. on the sorption velocity (v) has been studied, and two points of inflexion a and b have been observed in the v curve. The relation between pressure and sorption at a is given by the Langmuir equation. Between a and b , $v = Ap^{1/n}$, where $n = 1.48$ at 21° . It is suggested that the initial rapid sorption is of the van der Waals

type and beyond a is activated. The v between a and b is governed by the rate of activation, whilst the slower v beyond b is due to diffusion.

R. S.

Adsorption of hydrogen on tungsten. J. K. ROBERTS (Proc. Camb. Phil. Soc., 1934, 30, 74—79).—The change in the accommodation coeff. (I) of Ne on a clean W wire is largely increased when the wire is covered by an adsorbed layer of hydrogen. The vals. of (I) recorded are 0.07 for a clean wire as compared with 0.17 at 295° abs., and 0.32 at 79° abs., for a film-covered wire. The mechanism of the adsorption is discussed.

N. M. B.

Heat of adsorption of hydrogen on tungsten. J. K. ROBERTS and B. WHIPP (Proc. Camb. Phil. Soc., 1934, 30, 376—379).—The heat evolved on admitting H_2 at pressures 10^{-6} — 10^{-4} mm. to a clean W wire in a vac. has been determined, and is approx. independent of the pressure and amount adsorbed; the mean val. $= 2.8 \times 10^4$ g.-cal. per mol. The max. no. of mols. adsorbed $= 2.9 \times 10^{14}$ per 0.54 cm^2 , and saturation is reached at $< 10^{-4}$ mm.

R. S. B.

Desorption of gases from sooted metallic surfaces in a vacuum. R. BEHNE and H. LOHNER (Ann. Physik, 1935, [v], 22, 92—96).—The desorption has been followed by measuring the pressure in the neighbourhood of a sooted brass plate at definite intervals during the evacuation, and at different distances from the plate. The rate of adsorption of gas after desorption was also studied.

A. J. M.

Adsorption on homogeneous surfaces. H. LACHS and Z. SOBIERAJ (Rocz. Chem., 1934, 14, 968—974).—The amount of methylene-blue adsorbed from aq. solution by glass spheres is 30 , and by glass plates 6 , times $>$ would correspond with the formation of a unimol. layer on the geometrical surface; the result is ascribed to development of active surface as a result of the existence of minute cracks and fissures.

R. T.

Adsorption of cuprous salts from Illosvay's reagent in precipitating cuprous acetylide. D. F. NOVOTNY (Coll. Czech. Chem. Comm., 1934, 6, 514—527).—Absorption of C_2H_2 is complete only when the reagent is conc. Sources of error in the determination are discussed, and modified procedure is recommended.

E. S. H.

Relation between the phenomenon of cation exchange with silica-alumina complexes and their crystal structure. J. B. VAN DER MEULEN (Rec. trav. chim., 1935, 54, 107—113).—A survey of published work indicates that cation exchange occurs in silicates containing Al atoms with the co-ordination no. 4.

E. S. H.

(A) Adsorption potentials of ions and dipoles. (B) Electrostatic potential and flotation phenomena. (C) Surface tension and electrical potential. B. KAMIENSKI and K. KARCEWSKI (Rocz. Chem., 1934, 14, 375—382, 383—393, 394—400).—(A) The potential ϵ of so-called irreversible (chemically inert) electrodes (I) is a consequence of the adsorption of ions and dipoles; electrolytes affect chiefly the electrode-solution interface, whilst non-electrolytes are conc. chiefly at the air-solution interface, and have consequently little influence on the ϵ of (I).

(B) The ϵ of (I) (Pt, Au, Ag, carborundum, graphite, chalcopryrite, marcasite, galena, and hæmatite) is greatly lowered by aq. K xanthate (II), whilst that of electrodes (CuO, Pb, Zn) which react with (II) rises at first, and then falls to a far smaller extent than in the case of (I). Other collectors, such as *o*-, *m*-, and *p*-tolylhydrazine (III), act similarly to (II), but to a much less marked extent. The ϵ of substances not possessing catalytic properties is scarcely affected by (III) and NH_2 -acids, whilst that of hæmatite or Pt is greatly lowered, particularly in presence of O_2 . Substances lowering surface tension, such as terpineol, have only an inconsiderable effect on the ϵ of (I).

(c) The fall in ϵ for (I) on adding (II) or other collectors conforms to the adsorption law; this effect is not obtained with other electrodes, or with substances lowering surface tension. R. T.

Adsorption of certain colloids on metallic surfaces and its influence on the structure of electrical deposits. P. JACQUET (Compt. rend., 1935, 200, 226—227; cf. A., 1933, 458).—Gelatin, serum-albumin, and Na caseinogenate, and the peptones are adsorbed by a Cu surface etched by dil. HNO_3 and considerably reduce the crystal size of electrolytic deposits of Cu on the surface. With polished Cu there is no apparent effect, since the grain of the initial electrolytic deposit is very fine. With etched cathodes the continuity of the metallic deposit is hindered by a colloid film except with supports of electrolytic Cu, for which the crystal growth is regular but the crystallites do not grow larger. Gums arabic and tragacanth are not adsorbed and have no influence on the deposit. R. S. B.

Influence of atmospheric carbon dioxide on the surface tension of sodium salts of fatty acids. A. LOTTERMOSE (Trans. Faraday Soc., 1935, 31, 200—204).—An apparatus for the determination of surface tension, σ , in an atm. containing CO_2 is described. For salts of fatty acids ranging from HCO_2Na to Na stearate, σ remains const. in absence of CO_2 , but, in presence of CO_2 , it falls to a min. after some hr. or days, and then gradually rises again. The influence of CO_2 increases with increasing mol. wt. of fatty acid up to myristate, due to the diminishing strength of the acid set free by CO_2 . The effect decreases with palmitate and stearate owing to pptn. and consequent diminution of concn. The influence of CO_2 also increases with salt concn. for salts of low mol. wt., but diminishes with rising concn. of typical soap solutions. σ diminishes linearly with rising temp., the temp. coeff. becoming smaller as mol. wt. and salt concn. increase. The temp. coeff. for HCO_2Na alone rises with increasing concn. σ also diminishes linearly as log concn. increases within certain limits of concn. Na oleate behaves similarly to the salts of the saturated fatty acids if measurements are made in an atm. of N_2 free from O_2 and CO_2 , but its capillary activity is greater. When CO_2 is excluded, the static σ of soap solutions reaches equilibrium within 1 min. Below the laurate the time is too short to be measured, but the time becomes longer the higher is the no. of C atoms in the mol., the more dil. the solution, and the lower the temp.

M. S. B.

Influence of capillarity on the m.p. of iodine. W. A. PATRICK and W. E. LAND (J. Physical Chem., 1934, 38, 1201—1210).—The adsorption isotherm of I on SiO_2 gel at 92.5° shows a break which is explained by assuming that the adsorbed I melts in the capillaries to a liquid which wets the walls. D. R. D.

Oxide films on liquid metals studied by means of electron-diffraction. R. O. JENKINS (Proc. Camb. Physical Soc., 1935, 47, 109—124).—Electron-diffraction patterns (I) obtained by reflexion from molten Pb, Zn, Bi, and Sn show that the surfaces are covered with thin oxide films consisting of small flat crystals resting on their (001) faces. The films can be removed by Ni gauze, and give (I) by transmission, which show that, after removal, the chemical composition is unchanged but the orientation is disturbed and distribution is approx. Maxwellian. N. M. B.

Properties of liquid films in fine-pored systems. B. H. WILSDON, D. G. R. BONNELL, and M. E. NOTTAGE (Nature, 1935, 135, 186—187).—The hydrostatic suction necessary to remove H_2O from finely-pored plastic materials is of a different order from that expected from the v.-p. relation. Osmotic pressure and electrical properties are also abnormal. The behaviour of thin films may be due to the formation of oriented chains of mols. L. S. T.

Spreading of pepsin and of trypsin. E. GORTER (J. Gen. Physiol., 1935, 18, 421—426).—Pepsin in aq. buffered solution shows max. spreading (I) (approx. 1 sq. m. per mg.) at approx. p_H 3 and 1 and a min. at approx. p_H 6. At p_H 6 addition of cations significantly influences (I). Trypsin gives a (I) curve showing no max. but a definite min. at p_H 3 and responds at p_H 3 to the valency effect of Cl' , SO_4'' , and $\text{CH}(\text{SO}_2\text{O}')_3$ and to the lyotropic series Cl' , Br' , I' , and CNS' . On the acid side of the isoelectric point, glutathione but not glutamic acid influences (I). F. O. H.

Determination of the ebullioscopic constants of ethyl and isobutyl alcohols, benzene, and chloroform. M. ŁAŻNIEWSKI (Rocz. Chem., 1934, 14, 560—569).—The ebullioscopic consts. are: EtOH 11.60, BuOH 21.66, C_6H_6 26.42, and CHCl_3 38.02. R. T.

Physico-chemical studies on gum arabic solutions. III. Osmotic pressures of arabic acid and sodium arabate. D. R. BRIGGS (J. Physical Chem., 1934, 38, 1145—1160).—The osmotic pressure of gum arabic in HCl-NaCl solutions has been studied in relation to the p_H difference across the (collodion) membrane. The distribution of diffusible ions agrees with Donnan's membrane theory, but the observed osmotic pressure is lower than that predicted by an amount \propto the concn. of salt (other than colloid) inside the membrane, the no. of small ions produced per g. of colloid, and the p_H difference across the membrane, but is independent of the presence of EtOH up to 0.5 molar. D. R. D.

Significance of the measurements of dielectric constants in aqueous solution. G. DEVOTO (Ber., 1934, 67, [B], 1985—1987).—Measurements of μ in non-polar solvents (I) and $d\varepsilon/dc$ in H_2O for NH_2Ph , PhOH , MeOAc , $\text{C}_5\text{H}_5\text{N}$, COMe_2 , MeNO_2 , MeCN , and

$\text{CO}(\text{NHMe})_2$ show proportionality between the vals. Theories developed for (I) are not applicable to aq. solutions. Kuhn's relation, $de/dc \sim l^2$, is not supported by data for $\text{CO}(\text{NH}_2)_2$ and $\text{SO}_2(\text{NH}_2)_2$, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, $\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2$ and $\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3$, or $p\text{-NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2$ and $p\text{-NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2$. The observations exclude the possibility of the existence of spiral forms or pronounced coiling in fatty NH_2 -acids with $\gamma \geq 8$ C. H. W.

Constitution of water in solutions of electrolytes as studied by the Raman effect. C. S. S. Rao (Indian J. Physics, 1934, 9, 195—230).—The intensity curves of Raman bands for solutions of electrolytes, excited by the Hg λ 4047 line or λ 3650—3653 group, show that the H_2O band for solutions is sharper than for pure H_2O . With aq. solutions of HNO_3 , H_2SO_4 , and NaNO_3 the band becomes sharper with increasing concn., and shifts as a whole towards greater frequency; the opposite is found for aq. HCl . There is a progressive shift towards higher frequencies in the H_2O band in solutions at the same concn., passing from LiCl to NaNO_3 and from HCl to H_2SO_4 and HNO_3 ; with the same H_2O content these differences tend to vanish. Results are attributed to hydration of solute ions, or to change in the H_2O equilibrium due to mol. association of H_2O . The cation exerts little influence on the behaviour of the solvent. The curves for NaNO_3 are much sharper than those for HNO_3 , even at higher concns. of the latter; this is due partly to formation of complex hydrates, and partly to superposition of the 3420 cm^{-1} HNO_3 band on the H_2O band. N. M. B.

Magnetic birefringence of cerous salts in solution. C. HAENNY (Compt. rend., 1935, 200, 56—58).—The magnetic birefringence of Ce^{III} salt solutions varies with the nature of the anion and of the solvent, being very high for aq. solutions of salts of strong acids, less for EtOH solutions, and very small for $\text{Ce}(\text{OAc})_3$. J. W. S.

Diffusion of potassium chloride in aqueous solution. J. W. McBAIN and C. R. DAWSON (Proc. Roy. Soc., 1935, A, 148, 32—39).—Measurements for 0.1—2.0*N* solutions have been made at 25° by the porous membrane method, using sintered glass discs. The data include both "integral" vals. for diffusion into H_2O , and "differential" coeffs. for diffusion into a second solution of slightly less concn. The results are the same for alundum as for glass membranes of varying porosity. Comparison with previous results shows that the integral vals. most nearly resemble those of Ohlm up to 0.5*N*, whilst the differential vals. are most like those of Clack. In conc. solution the ions of KCl are much more mobile than at infinite dilution, the only apparent explanation being that the ions carry less H_2O with them in conc. than in dil. solution. L. L. B.

Viscosity of moderately and highly concentrated solutions of some electrolytes in water and methyl, ethyl, and *n*-propyl alcohols; relation between conductance and fluidity. H. N. DESAI, D. B. NAIK, and B. N. DESAI (J. Univ. Bombay, 1934, 3, 109—120).—Data for NaI and BaI_2 in H_2O ,

CaCl_2 in MeOH , MgCl_2 in EtOH , and NaI in Pr^{OH} fit the equation $\eta = \eta_0 + D_1C^2 + D_2C^3$, where $\eta_0 = \eta$ of solvent, D_1 , D_2 are consts. differing with salt and solvent. Results are correlated with the authors' conductivity data (cf. A., 1934, 967). D. R. D.

Temperature variation of viscosities of aqueous solutions of strong electrolytes. G. R. PARANJPE and E. B. RAJDERKAR (J. Univ. Bombay, 1934, 3, 21—52).— η has been measured for Li, Na, K, Rb, Ca, Sr, Ba, and NH_4 chlorides (0.25—1.0*N*) at 30—75°. The data fit Raman's equation (Nature, 1923, 111, 600). D. R. D.

Compressibility of solutions of amino-acids. P. W. BRIDGMAN and R. B. DOW (J. Chem. Physics, 1935, 3, 35—41).—Compressibilities of aq. solutions of $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{NH}_2\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{H}$, and $\text{NH}_2[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$ at concns. 0.5—2.5*M* have been measured at 25° and 75° up to 8000 kg. per sq. cm. The substances, selected because they yield zwitterions in solution, differ from all solutes hitherto examined in that at the lower pressures their apparent mol. vol. decreases with increase of pressure. This behaviour is probably related to the action of zwitterions in raising the dielectric const. of H_2O . The abnormality increases with dilution. The curves obtained are too complicated to admit detailed explanation. F. L. U.

Properties of electrolytes as related to their constitution. C. A. KRAUS (Trans. Electrochem. Soc., 1934, 66, 385—409).—The conditions under which ions may associate to form ion-pairs, "triple ions," and more complex charged or neutral aggregates are discussed in relation to the properties of the solvent and sp. characters of the ions (cf. A., 1933, 230, 353, 464, 785; 1934, 25). A general theory of electrolytes is developed on this basis, and its validity tested by comparison with recent experimental data for conductance, f.p., and other properties of electrolyte solutions in solvents of low dielectric const. (cf. A., 1933, 908, 1120; 1934, 1304). H. J. T. E.

Effect of the magnetic field on Brownian movement. A. TURPAIN and R. DE B. DE LAVERGNE (Compt. rend., 1935, 200, 301—303).—Criticism of a paper by Métadier (this vol., 31). M. S. B.

Colloids in the atmosphere. B. N. DESAI (J. Univ. Bombay, 1934, 3, 195—218).—A detailed review is given of present knowledge of ions, solid and liquid particles in the air, their composition, charges, influence on transparency and conductivity of the air, and rates of settling. D. R. D.

Colloidal air, and determination of the size of the particles. A. KRAUZE and K. KAPITANCZYK (Rocz. Chem., 1934, 14, 487—503).—The colloidal air sol obtained by adding 10 c.c. of 18*N*- NaOH (I) to 1 c.c. of H_2O is diluted with (I); the diameter of the bubbles diminishes with increasing dilution to a limiting val. of 24—27 μ at 8192-fold dilution. The capillary pressure of such bubbles amounts to 190 atm., and, taking this factor into consideration, the actual diameter of the bubbles is $< 5 \mu$. R. T.

Are not liquid sodium amalgams colloidal? R. M. JOSHI (Indian J. Physics, 1934, 9, 153—159).—Polemical against Bent (cf. A., 1933, 561). The

possibility of dil. liquid Na amalgams being colloidal is discussed. N. M. B.

Doubly refracting selenium sol. F. B. GRIBNAU (Chem. Weekblad, 1934, 32, 53).—A Se sol as prepared by Jannek and Meyer (A., 1913, ii, 948), originally orange-red in colour, changes to greyish-brown on ageing in the dark for three weeks and then shows streaking phenomena in polarised light. The refracting particles are either spheres or flat plates, and so differ from those in an aged V_2O_5 sol, in which they are needle-shaped. S. C.

Electrochemical properties of colloidal silica. V. A. KARGIN and A. J. RABINOVITCH (Trans. Faraday Soc., 1935, 31, 284—297).—Very pure SiO_2 sols, prepared by hydrolysis of $SiCl_4$ and purified by dialysis and prolonged electro dialysis, give no perceptible conductivity to twice-distilled H_2O . "Acid" SiO_2 sols previously obtained (cf. A., 1928, 835) owe their acidity to the presence of HCl. SiO_2 gels, due to coagulation on prolonged electro dialysis, are readily peptised by HCl. Very pure SiO_2 sols are prepared by oxidation of SiH_4 by O_3 in H_2O . They have no acid properties, the p_H being approx. 7. The stability of pure SiO_2 sols must be due to their lyophilic properties. Electrometric measurements on acid SiO_2 sols give the ion concn. in the intermicellar liquid only. Cataphoretic measurements show that the potential of acid SiO_2 sols is small or zero. In the coagulation of acid sols by electrolytes there is no appreciable cation adsorption. In the coagulation of alkaline SiO_2 sols by $BaCl_2$, Ba^{++} is adsorbed, but there is no equiv. displacement of Na^+ or H^+ . In the interaction of Na silicates with aq. $CaCl_2$, solution pressure determinations, X-ray examination, and changes of viscosity with time indicate that adsorption compounds only are formed. M. S. B.

Polymerisation phenomena of silicic acid. W. D. TREADWELL (Trans. Faraday Soc., 1935, 31, 297—302).—Anomalies in the potentiometric titration curves of Na_2SiO_3 with HCl probably indicate polymerisation of H_2SiO_3 . Pure sols were prepared by electrolysing Na_2SiO_3 with a Hg cathode. On keeping in a closed vessel for 5 days, the sol showed a fall in p_H from 5.4 to 3.4, indicating that polymerisation precedes the formation of an acid sol. The mol. wt. of H_2SiO_3 in a freshly prepared solution, determined by the f.p. method, was 149.4. This increased initially at the rate of 22.2 per hr. and then more slowly, reaching 1240 after 86 hr. The viscosity increases with time. The min. time required for gelatination of a 0.5M-sol is at p_H 5.8. M. S. B.

New type of tungsten oxide sol and its electrochemical behaviour. F. ERICH (Trans. Faraday Soc., 1935, 31, 415—421).— WO_3 sols, prepared by d.c. between W wires in $10^{-3}N$ -NaOH, are acid, p_H approx. 5, and the acidity is increased by electro dialysis, p_H 3.0—3.3. The WO_3 mols. tend to become hydrated and react with bases. The no. of WO_3 mols. corresponding with an active H^+ , i.e., the colloidal equiv., is 100—200 and increases with concn. The electrical conductivity therefore decreases. Conductometric and potentiometric titration curves indicate the presence of two main constituents, probably different

types of tungstic acid built up of WO_3 hydrates. As observed in other colloids, the electrometric activity is $>$ corresponds with the conductivity vals. Flocculation takes place with positive ions or colloids, and reversal is observed with Al_2O_3 sols of very small colloidal equiv. It can be followed by conductivity measurements. M. S. B.

Formation of emulsions under the influence of ultrasonic waves. W. DANIEWSKI (Acta Phys. Polon., 1933, 2, 45—49).—The rate of formation of H_2O -kerosene emulsions at const. frequency (150—9000 kc.) \propto the strength of vibration (I). With increasing frequency, at const. (I), the rate decreases, being a max. at 150 kc. CH. ABS. (e)

Influence of electrolytes on the formation and stability of metallic colloids formed by ultrasonic waves. M. REGGIANI (Compt. rend., 1935, 200, 123—125).—When ultrasonic waves are passed through Hg, above which is a layer of liquid, the velocity of formation of a colloidal solution and the stability and diameter of the colloid particles produced vary with the liquid. Formation of a sol proceeds with difficulty in 0.01—0.1N-HCl, -AcOH, -tartaric acid, -KOH, -NaOH, or -NaCl, the particles being larger than those formed in pure H_2O . If, however, $<0.1\%$ of gelatin or ovalbumin is added to the electrolyte solution, atomisation occurs as readily as, or even more readily than, in pure H_2O . J. W. S.

Physico-chemical properties of solutions of basic ferric sulphate. A. L. ZAIDES and V. N. SVESHNIKOVA (Tzent. Nauch.-Issl. Inst. Koz. Prom., Sborn. Rabot, 1934, No. 2, 92—106).—Increase in basicity of the salt increases the colloidal properties, as shown by increased adsorption by hide powder (I) and C. If aq. $Fe_2(SO_4)_3$ is heated and then cooled and alkali added, a highly basic salt is obtained without pptn. Adsorption by (I) is increased by using an equimol. $Fe_2(SO_4)_3$ - $FeCl_3$ mixture. CH. ABS. (e)

Potentiometric studies in the formation and stability of colloidal solutions. I. Ferric oxide sols. M. P. V. IYER (Proc. Indian Acad. Sci., 1934, 1, A, 372—382).—Titration curves of acidified and unacidified $FeCl_3$ solutions against carbonate-free NaOH show that the range of stability of Fe_2O_3 sols extends from p_H 3.20 to 4.45; pptn. commences at approx. 4.5, and is complete at 6.0. The composition of the ppt. varies with the neutral salt (KCl, K_2SO_4 , KNO_3 , $BaCl_2$) added. The mol. ratio $FeCl_3/NaOH$ varies in the range 1/2.69—1/2.85, against the theoretical val. 1/3. The mol. ratio at the end-point follows the series $SO_4^{--} < Cl^- < NO_3^- < H_2O$. The different stages in the formation of micelles of Fe_2O_3 and their coagulation are elucidated. The development of alkalinity on adding neutral salts is explained, and the liberation of OH^- is correlated with the lower mol. ratio obtained in titrating $FeCl_3$ against alkali. N. M. B.

Action of acids on hydrous alumina. A. W. THOMAS and R. D. VARTANIAN (J. Amer. Chem. Soc., 1935, 57, 4—7).—The dispersing action of different aq. acids on Al_2O_3 has been measured. The order of effectiveness inversely \propto the tendency of the corresponding neutral salts to raise the p_H of Al oxychloride

sols. Acids with anions which have a weak tendency to bind co-ordinately to the Al atom have the strongest peptising power. E. S. H.

New type of osmometer for low pressures with some preliminary results for gum arabic. H. B. OAKLEY (Trans. Faraday Soc., 1935, 31, 136—147).—An osmometer capable of measuring pressures of a few mm. of H_2O with an accuracy of 0.1 mm. is described. Osmotic pressures of solutions of gum arabic of concn. 0.5—3.5% have been measured at 25°. The Na gum (I) prepared by neutralising the electro dialysed prep. has an apparent mol. wt. 70% > the undialysed product. The acid electro dialysed gum (II) appears to be an equilibrium mixture with its two products of autohydrolysis. 0.2N-HCl apparently causes two parallel hydrolyses, one of which proceeds to completion more rapidly than the other. The fall of osmotic pressure of (I) with increasing concn. of NaCl is attributed to progressive suppression of the ionic pressure difference. The effect of $CaCl_2$ and of HCl is still more marked. The following provisional consts. are suggested for (II): equiv. wt. 1200, mol. wt. 290,000, max. valency 240, effective valency in 1% solution 40. M. S. B.

Stability of colloids. Stability of negatively charged colloidal silver iodide. A. BASINSKI (Rocz. Chem., 1934, 14, 1017—1037).—The stabilising action (I) of halides is up to a certain limiting concn. (II) independent of the nature of the cation; at higher concns. (I) diminishes in the order $Li^+ > Na^+ > K^+ > NH_4^+$. The val. of (II) for different anions varies in the order $Cl^- > Br^- > I^-$. A theoretical interpretation is advanced. R. T.

Velocity of coagulation of colloids. J. SZPER and S. UZDANSKA (Rocz. Chem., 1934, 14, 579—589).—Coagulation of SiO_2 sols takes place at p_H 3—10 and shows max. velocity (v) at p_H 4.8. v rises with rise of temp. The velocity of denaturation of albumin (unspecified) attains a max. at a certain limiting concn. of HCl. The reaction is of the third order, and involves autocatalysis. The results indicate that coagulation and crystallisation are analogous processes. R. T.

Determination of the stability and type of emulsions. B. PUCHKOVSKI and E. STRUKOVA (Masl.-Zhir. Delo, 1933, No. 6, 28—29).—The stability and type of margarine emulsions can be determined by centrifuging a 10-c.c. sample for 60 sec. at 1000 r.p.m. CH. ABS. (e)

Anomalous flow of colloidal systems. A. S. C. LAWRENCE (Proc. Roy. Soc., 1935, A, 148, 59—87).—The velocity distribution for liquids where the distribution is not parabolic (Poiseuille's law not obeyed) has been examined by a new method. Gelating systems and non-gelating but elastic sols can be distinguished by this method. Anomalous flow in oil solutions is caused by the greater effective vol. of anisodimensional micelles resulting from rotation and increasing mutual interference. If the effective vol. or the solvent = the vol. of the solution, mutual interference increases rapidly with increasing concn. This should be called anomalous viscosity. Systems not obeying the Poiseuille equation have "apparent

viscosity," and these systems are characterised by "anomalous flow." The effective vol. occupied between collisions \propto the square of the length of the particle. Whether an elastic gel or sol is formed depends on dispersion and solvation. In mol. colloids degree of dispersion and solvation run parallel. All anomalous systems show "ageing" effects which are due to slow equilibration. Segregating mixtures, emulsions, and nematic liquid crystals are anomalous. L. L. B.

Radiocolloids. H. HERSZFINKIEL and A. WRONBERG (Rocz. Chem., 1934, 14, 959—967).—The particles (I) in aq. suspension which act as centres for the adsorption of the products of degradation of Ra appear not to be electrically charged. (I) are absent from EtOH, C_6H_6 , and $COMe_2$, but solutions in these solvents lose part of their activity on centrifuging, pointing to formation of true colloidal solutions. R. T.

Potassium ethyl sulphate gels. H. HENSTOCK (Trans. Faraday Soc., 1935, 31, 446—451).— $KEtSO_4$ forms a white opaque gel by pptn. from aq. solution by EtOH. At 15° the gel persists for 48 hr., but rapidly crystallises at higher temp. More stable gels are obtained by pptn. with various org. solvents from MeOH solutions. Their permanence varies from 3 weeks when pptd. with $CHCl_3$ to 10 sec. with $o-OH \cdot C_6H_4 \cdot CO_2Me$. All are readily disintegrated by heating and crystallise at low temp. The gel made with $CHCl_3$ is slightly alkaline. Electrical conductivity measurements indicate that gel formation is not complete until after approx. 30 min. Syneresis and deterioration set in a little later, and, after a preliminary arrest, proceed slowly to the end. There is a small rotation of polarised light. Refractive indices and radii of capillaries have been determined. The process of deterioration has been followed in the ultramicroscope. Gels in EtOH are best formed by evaporating a boiling solution and cooling. It is also possible to form a gel in PrOH by this method. M. S. B.

Complex relations in lyophilic colloidal systems. VII. Complex and autocomplex sols. H. G. B. DE JONG, W. A. L. DEKKER, and P. VAN DER LINDE. **VIII. Essential and non-essential specific characteristics of the colloidal components of importance for complex relations.** H. G. B. DE JONG, P. VAN DER LINDE, and A. DE HAAN (Rec. trav. chim., 1935, 54, 1—16, 17—37; cf. A., 1934, 843).—VII. The separation of complex coacervates in mixtures of positive gelatin and negative gum arabic sols is inhibited when these are in certain proportions, although the particles are shown viscosimetrically to be dehydrated. Such complex sols are distinguished from complex coacervates by their miscibility with the dispersion medium. The influence of neutral salts and p_H on the relative viscosity of clupein sulphate sol (I) has been determined. Observations on the coacervation of (I) with $CH(SO_3K)_3$, $K_4Fe(CN)_6$, and K_2SO_4 show that (I) is an autocomplex sol in which the opposition of charge is produced by adsorption of some of the SO_4^{2-} in the inner part of the double layer.

VIII. The density of the centres of capillary

electric charges and their chemical nature determine the conditions for the production of condensed complex or autocomplex systems. E. S. H.

New researches on colloids. [I. The electrical double layer. II. Coacervation.] H. R. KRUYT (Bull. Soc. chim. Belg., 1934, 43, 559—578, 578—596).—Two lectures. A comprehensive survey of the present position and the author's views.

J. G. A. G.

Colloid electrolytes; nature and importance for colloidal science. H. FREUNDLICH (Trans. Faraday Soc., 1935, 31, 4—9).—The development of the conception of ionic micelles is described. These may be classified into three types: (1) sensitive to dilution forming small monomeric dialysable ions, *e.g.*, soaps; (2) sensitive to dilution but forming ions which cannot be dialysed, *e.g.*, Congo-dyes; (3) practically insensitive to dilution, *e.g.*, certain proteins. The particle size of colloidal electrolytes is comparatively small, the mol. wt. not usually exceeding 100,000. There are no exact methods for detecting micelles of small size, and anomalies in the electrical behaviour of conc. solutions of electrolytes may often be due to the presence of ionic micelles. M. S. B.

Relations between electrochemical behaviour and the structure of colloids. W. PAULI (Trans. Faraday Soc., 1935, 31, 11—27).—The earlier view of the origin of the charge on a colloid particle as due to simple adsorption of an ion has given place to the theory of the formation of a distinct ionogenic complex attached to the surface of the colloid particle. The methods of determining the ionogenic complex for different types of sols are given. The theory has been especially successful in its application to the metallic sols, such as Au, Ag, and Pt, which give the best examples of the connexion between colloidal behaviour and the structure of the complex. Oxide sols, Congo-dyes, and gums are also considered. By electrodialysis or electro-decantation, or by the action of electrolytes, chemical and electrochemical changes take place in the complex, and thus change the character of the sol. M. S. B.

Ionic micelle or electric double layer. H. R. KRUYT (Trans. Faraday Soc., 1935, 31, 28—31).—In attempting to account for the behaviour of colloids it is more convenient, for the quant. interpretation of the facts, to adopt the conception of an electrical double layer at the surface of the particle than to regard the whole particle as a highly multivalent ion with an enormous ionic radius. The inner layer in the electrical double layer is probably often built up by ions of the same material as the particle, but other structures are possible. M. S. B.

Application of the Debye-Hückel theory to colloidal electrolytes. G. S. HARTLEY (Trans. Faraday Soc., 1935, 31, 31—50).—The difficulties encountered in the extension of the Debye-Hückel theory of electrolytes to colloids are discussed. Calculations by Muller's method, relating to the ionic atm. and the magnitude of its effects, indicate that, in pure solutions of colloidal electrolytes, activity coeffs. < those predicted by the extended Debye-Hückel equation, and micellar mobilities < those predicted

by a corresponding equation derived by the author, are not likely to be found. It is necessary to postulate some kind of association between micelles and their compensating ions. The effect of this on the properties of the solution may be numerically > the direct effects of the ionic atm. M. S. B.

Are lyophobic colloids colloidal electrolytes?

A. J. RABINOVITCH and V. A. KARGIN (Trans. Faraday Soc., 1935, 31, 50—66).—There are considerable difficulties in the application of the colloidal electrolyte theory to lyophobic colloids. Colloidal acids, such as WO_3 and V_2O_5 , behave like buffer solutions on dilution. This appears to be due to a gradual dissolution of the colloidal particles on dilution, giving a true solution. Where the acidity is caused by the presence of foreign electrolytes, and is not inherent in the colloid, a different behaviour is observed. Potentiometric measurements of ionic concn. give the equilibrium concn. of electrolytes in the intermicellar solution only, and not the concn. of the compensating ions. Considerable amounts of both ions of the stabilising electrolyte may be detected in the intermicellar liquid, and insol. salt formation may occur on the addition of other electrolytes. The equilibrium adsorption on the particles is thus shifted, and may lead to coagulation. Direct experimental data at present available are insufficient for solving the question of the equivalence or non-equivalence of exchange adsorption of compensating ions. Although equivalence of exchange adsorption of ions in the double layer may be admitted for typically lyophilic systems, which may be definitely regarded as colloidal electrolytes, it is probably not necessary in the case of lyophobic colloids. The non-equivalence of exchange adsorption leads necessarily to variability of the ϵ - and ζ -potentials. A theory of coagulation should take into account variation of the attractive, as well as repulsive, forces between particles, with varying electrolyte concn. M. S. B.

Molar (micellar) mass, electrovalency of ions, and osmotic pressure of colloidal electrolytes. F. G. DONNAN (Trans. Faraday Soc., 1935, 31, 80—98).—The thermodynamic theory of membrane equilibria has been applied to the determination of osmotic pressures and mol. masses for the following types of colloidal electrolytes: monodisperse, singly and multiply ionised electrolytes, monodisperse multiply ionised ampholytes, and polydisperse multiply ionised electrolytes. The theory has also been applied to the determination of the electrovalencies of colloidal ions. The conclusions reached are independent of any definitely "chemical" formulation of colloidal electrolytes and are not essentially affected by the consideration or otherwise of mol. or ionic adsorption. M. S. B.

New determination of the capacity of the electrical double layer. M. PROSKURNIN and A. FRUMKIN (Trans. Faraday Soc., 1935, 31, 110—115).—Measurements of the capacity of the electrical double layer at a Hg surface in $\text{N-Na}_2\text{SO}_4$, -KCl , -NaOH , and $\text{-H}_2\text{SO}_4$, and in $\text{N-Na}_2\text{SO}_4$ saturated with octyl alcohol, have been made and the vals. plotted against cathodic polarisation. The observed vals. are > those of

previous investigators, but agree fairly well with those calc. from electro-capillary data. M. S. B.

Cataphoresis of colloidal electrolytes. I. KEMP and E. K. RIDGAL (Trans. Faraday Soc., 1935, 31, 116—120).—The Debye-Henry expression for cataphoretic velocity has been applied to two systems in NaOAc buffers: sols of gliadin and suspensions of quartz particles covered with gliadin. The experimentally determined mobilities are in agreement with theory for a very limited range of ionic strength, μ 0.008—0.13. Both above and below this range the experimental vals. are < required by theory. At high vals. of μ appreciable adsorption of anions leads to discrepancies. In very dil. solutions the effective valency of the ion is reduced by a Donnan equilibrium at the ionic envelope. M. S. B.

Significance and determination of mobilities in the study of colloidal electrolytes. J. L. MOULLET, B. COLLIE, C. ROBINSON, and G. S. HARTLEY (Trans. Faraday Soc., 1935, 31, 120—129).—The transport no. (T), for colloidal electrolytes, affords evidence of aggregation to form ionic micelles, when conductivity determinations fail to do so owing to the inclusion of compensating ions in the micelles (inclusion effect) and to coulomb forces between the ions (atm. effect). The influence of these two factors on T is discussed. Confirmation of the purity of a colloidal electrolyte may be obtained by plotting mobilities of the simple ion against concn. For very low mobilities the balanced-boundary method must be used. The conditions for the satisfactory application of the moving-boundary method to the measurement of cataphoretic velocity are discussed.

M. S. B.

Determination of the electric charge of colloidal ions. G. S. ADAIR and M. E. ADAIR (Trans. Faraday Soc., 1935, 31, 130—135).—Approx. agreement only, between the vals. of the apparent valency of colloidal ions, determined by different methods, can be obtained. This is due to interionic forces and the combination of ions with the colloid. The nearest approximation to the true val. is probably best obtained by the use of membrane potentials. A range of concn. of electrolytes for which the potentials are small should be employed for purposes of extrapolation to the limiting val. for very low concn., and the colloidal solution should be dialysed with repeated changes of standard buffer solutions until osmotic pressures and membrane potentials are const. M. S. B.

Equilibrium between micelles and simple ions, with particular reference to the solubility of long-chain salts. R. C. MURRAY and G. S. HARTLEY (Trans. Faraday Soc., 1935, 31, 183—189).—The anomalous solubility-temp. curves of long-chain salts, which show a very sharp rise in solubility above a certain temp., can be explained by the equilibrium between simple ions and micelles. Since the transition a normal temp. coeff. to the extremely high one characteristic of the long-chain salts is less abrupt than the changes in the conductivity- and surface tension-concn. curves, it may be concluded that ionic aggregation predominates in dil. solution. M. S. B.

Soap micelles. A. S. C. LAWRENCE (Trans. Faraday Soc., 1935, 31, 189—195).—The size and

structure of the ionic and neutral micelles are discussed. It is suggested that in the micelles undergoing the Krafft transition, the mols. are associated in pairs by their $\cdot\text{CO}_2\text{Na}$ groups, giving the neutral or secondary micelle. The transition is due to the loosening of the attractive forces between hydrocarbon chains throughout the micelle resulting in a great increase of the degree of dispersion. With the increase of free $\cdot\text{CO}_2\text{Na}$ groups the no. of ionised micelles will also increase in accordance with the mass law. The formation of curd is due to a phase change. X-Ray examination shows that the structure alters in curdling. There are indications that the curd form is lamellar.

M. S. B.

Relation of electrokinetic and electrolytic movement, as illustrated by the transport of electricity through soap curds. (MRS.) M. E. L. MCBAIN (Trans. Faraday Soc., 1935, 31, 153—164).—Evidence for the interchangeability of electrokinetic and electrochemical quantities is afforded by calculation of electro-osmosis and cataphoresis from transport data for soaps, either alone or mixed with curd fibres, for both mixed with NaCl or KCl, and for curd fibres mixed with simple electrolytes. Insol. curd fibres in NaCl or KCl up to 1N give marked electro-osmosis, with ζ -potentials of 14—65 mv. compared with 39—86 mv. for Cl' under similar conditions. The surface conductance of N-Na palmitate curd fibres (I) is compared with that of 0.07N-NaCl. 7% of the mols. in (I) are ionised, 0.6 of the current being carried by the negatively-charged fibres and the remainder by Na'. The mobility of the latter is little < that of Na' in ordinary solutions. A negative charge on the curd conducts practically as well as on Cl'. M. S. B.

Diffusion of dyes. E. VALKÓ (Trans. Faraday Soc., 1935, 31, 230—245).—Diffusion coeffs. at 25° have been determined by the porous-plate method for Orange II (I), Azogrenadin S (II), Benzopurpurin 4B, Congo-red, and Chicago-blue 6B in pure H₂O and in aq. NaCl. The results indicate that (I) and (II), under the conditions employed, are mol. dispersed, whilst the others are aggregated, the aggregation increasing rapidly with increase in concn. of NaCl. The mechanism of the salt effect on aggregation is discussed. Comparison with mobilities derived from conductance data indicates that the frictional resistance of large colloid ions against osmotic forces is < against electrical forces. M. S. B.

Nature of the aqueous solution of dyes. C. ROBINSON (Trans. Faraday Soc., 1935, 31, 245—253).—Investigation of solutions of some highly purified dyes indicates that they contain micelles consisting of a no. of anions with some included Na'. If > one micellar type exists equilibrium must be established rapidly. The micelle has probably a definite structure, the ions having a definite orientation as in a micro-crystal. From diffusion and osmotic pressure data, Benzopurpurin 4B and *meta*-Benzopurpurin have probably about 10 particles in the micelle. Congo-red has a somewhat smaller micelle. Bordeaux Extra is much more nearly in true solution. The conductivity curve of methylene-blue shows that it

forms micelles to some extent, although formerly supposed to be in true solution. M. S. B.

Thermodynamics of swelling. R. L. STEINBERGER (Textile Res., 1934, 4, 451—462).—A discussion. CH. ABS. (e)

Application of Gibbs' fundamental equation to protein systems. G. S. ADAIR (Trans. Faraday Soc., 1935, 31, 98—106).—Gibbs' equations have been applied to protein systems of many components containing protein salts and ions, other salts and ions, and diffusible non-electrolytes. The theory of membrane equilibria has been extended to determine the activities of all the components of such systems. The determination of mol. wts., hydration, reactions which do not obey the law of const. proportions, and the equilibrium distribution of a protein in gravitational and centrifugal fields of force are also considered. M. S. B.

Proteins as colloidal electrolytes. (Miss) D. J. LLOYD (Trans. Faraday Soc., 1935, 31, 317—324).—The electrolytic character of proteins can be explained by their constitution as long polypeptide chains containing approx. 200 NH_2 -acid residues. They thus form zwitterions, but both charged centres never act together, one or other predominating according as the solution is acid or alkaline. The enormous mol. wts. of proteins indicate their colloidal character, but many proteins are fairly sol. in H_2O at their isoelectric points, probably due to definite hydration centres at which H_2O is held by co-ordinate linkings, and also to the orientation of H_2O mols. around charged centres. The electrolytic properties of proteins are illustrated by the reactions taking place in tanning. Differences in behaviour between colloid and crystalloid electrolytes may be explained by the bulk of the former. M. S. B.

Electrochemical properties of a simple protein. K. LINDERSTRÖM-LANG (Trans. Faraday Soc., 1935, 31, 324—335).—Clupein has been fractionated until it gave nearly pure proteins. One of these fractions has been titrated electrometrically with NaOH and the data employed for the calculation of the acidic and basic ionisation consts. Assuming an average mol. wt. of 4150, each mol. contains one free NH_2 or NH and one free CO_2H . M. S. B.

Reaction between gelatin and electrolytes in gelatin gels. E. J. BIGWOOD (Trans. Faraday Soc., 1935, 31, 335—348).—Blocks of gelatin gel, placed in aq. NaCl containing (a) some acid, (b) AcOH - NaOAc buffer solution of p_{H} 4.8, (c) NaCl only, were left at const. temp. until the p_{H} was const. and gel and solution were analysed for Na^+ and Cl^- . The distribution corresponds with the Donnan membrane equilibrium, as previously observed for CaCl_2 (A., 1931, 306). The reactions are chiefly due to electrolytic dissociation of acid and basic org. radicals at the protein surface. In slightly acid solutions, p_{H} 3—7, surface adsorption is almost negligible. The same behaviour is observed with MgSO_4 in solutions of p_{H} < 4.7 only. At higher p_{H} there is excess MgSO_4 in the gel. When a swollen block of gelatin is placed in dil. aq. NaOH, diffusion to the interior takes place, but penetration never becomes uniform and a

stationary concn. gradient of diffusible ions is set up and is maintained until the gel disintegrates. The effect is explained by the fact that the concn. of gelatin at the centre of the swollen block is > at the exterior, due to uneven swelling. A membrane equilibrium is set up with a concn. gradient of the free ions in the gel, due to the concn. gradient of the protein. Comparison with the behaviour of an agar gel shows that diffusion of ions in the latter proceeds steadily until distribution is uniform. M. S. B.

Diffusion potentials and mobilities of ionised gelatin. Acid and neutral solutions. E. B. R. PRIDEAUX (Trans. Faraday Soc., 1935, 31, 350—354).—Measurements of the diffusion potential (D.P.) between gelatin chloride and KCl in HCl solutions of p_{H} 3 seem to indicate that the mobility is > 0, whilst electrical conductivities give 10—20. Measurements in acetate buffers of p_{H} 3.62 gave a D.P. agreeing with a mobility of the order of 30. Conductivity measurements gave 34.8. Determinations of the D.P. in solutions at or near the neutral point, to eliminate effects due to inequalities of $[\text{H}^+]$, gave 10, whilst two other gelatin solutions of p_{H} 6.2 and 6.45, respectively, gave 30—40 with the flowing junction. M. S. B.

Metaphosphoric acid and proteins. R. K. SCHOFIELD (Trans. Faraday Soc., 1935, 31, 390—394).—When a protein is titrated electrometrically with a strong mineral acid an end-point is usually obtained near p_{H} 2. It represents the point at which the acid added is sufficient to combine with all the ionisable NH_2 -groups and to prevent the ionisation of the CO_2H . The amount cannot be very accurately determined, partly because of the effect of the anions loosely bound to the protein on the activity of the solution and the difficulty of separating, for back-titration of excess acid, an aliquot portion of the solution free from protein. It is suggested that the difficulties might be overcome by titrating with HPO_3 , since, as PO_4 coagulates protein, it should become firmly bound to it and both should be removed together from the solution. Views, which also account for the lack of coagulating power of polymerised HPO_3 , are put forward to explain the nature of the association of PO_3 with protein. M. S. B.

Influence of electrolytes on the p_{H} of gelatin solutions. W. GIEDROYĆ (Rocz. Chem., 1934, 14, 1409—1417).—At p_{H} < the isoelectric point of gelatin (I) the change in $[\text{H}^+]$ due to addition of salts varies in the order chlorides < sulphates < acetates and oxalates, both in absence and presence of (I); in the latter case the effect obtained is smaller, owing probably to buffer action of (I). R. T.

Gelatinisation of proteins by acids. W. KOPACZEWSKI (Compt. rend., 1935, 200, 418—421; cf. A., 1934, 547, 792; this vol., 374).—Dispersions in 0.01N-NaOH of casein, fibrin, globulin, myxoprotein, and albumin, but not of fibrinogen, nuclein, or elastin, are gelatinised by 1—2N-lactic acid. As with serum gels, they are liquefied on heating, but set again on cooling, and they also return to the liquid state on dialysis. Gelatinisation always precedes coagulation. The gelatinisation of sera is attributed to the proteins, and especially to the globulins. J. W. S.

Effect of variations in ionic strength on the apparent isoelectric point of ovalbumin. E. R. B. SMITH (J. Biol. Chem., 1935, 108, 187—194).—The apparent isoelectric point of ovalbumin varies with the ionic strength (I) of the buffer used, and with the protein concn. (II). The "true" isoelectric point at zero (I) and (II) is at p_H 4.86+0.01.

A. E. O.

Mordanting and dyeing processes. XXI. Investigation of chemical reactions in gelatin by means of measurements of light absorption. E. ELOD and T. SCHACHOWSKOY (Trans. Faraday Soc., 1935, 31, 216—230).—In order to determine the composition of the metal compounds which have the actual tanning effect on gelatin, and also the nature of the interaction of these substances with proteins, the change of light absorption of aq. and gelatin solutions of complex compounds of Fe^{III} and Cr^{III} has been studied. It is shown that stable complexes have no tanning effect. The extent of change in a complex, ascertained from the course of the absorption curve, runs parallel with the increase in the time required for the dissolution of the gelatin treated with the same complex. From a similar investigation using Co^{III} complex compounds it was found that the actual tanning substance in this case is $Co(OH)_3$ produced by decomp. of the complex. Interaction with gelatin produced very little change in the light absorption of $Co(OH)_3$ sols. This does not exclude the possibility that tanning also may be brought about by substances other than metal oxides.

M. S. B.

Colloidal ions of starch. M. SAMEO (Trans. Faraday Soc., 1935, 31, 395—410).—The negative charge of starch is due to H_3PO_4 present in combination as a polysaccharide ester forming amylophosphoric acid (I). In some starches fatty acids similarly combined are also present. By heating potato starch solution under pressure H_3PO_4 is gradually removed and the starch loses its charge. Osmotic pressure measurements seem to indicate that the amylophosphate ion has a mol. wt. of 200,000. (I) reacts as a dibasic acid, giving salts with bases. The migration velocity of the ion is 6.1×10^{-5} cm./sec. per volt/cm. The conductivity of (I) is < corresponds with the $[H]$ observed electrometrically. In some starches H^+ activity and conductivity are < corresponds with the amount of H_3PO_4 present. This seems to be due to the presence of N compounds. It is possible to remove these from wheat starch without affecting the P content; the electrochemical behaviour is then the same as that of potato starch of similar P content. The viscosity changes can be explained on the basis of displacements of the ionisation in presence of electrolytes, as well as by Smoluchowski's theory of the electro-viscous effect.

M. S. B.

Very fine wood fibres as colloid electrolytes. A. LOTTERMOSER and T. WILHELM (Trans. Faraday Soc., 1935, 31, 411—414).—The electric potential of "cement pulp," and the effect on it of different electrolytes, have been determined by an ultramicroscopic method. The influence of cations in reducing the negative potential increases with their valency, Al^{+++} and Th^{++++} giving a positive charge;

the opposing influence of anions is small except in the case of K salts, where it overcomes the positive action of K^+ : NaOH produces a strong negative charge. The flocculating action of different electrolytes on cement pulp, cellulose, and lignin sols has been compared. The flocculating power increases with the valency of the cations, and readiness of flocculation increases in the order lignin < cement pulp < cellulose. With $ThCl_4$ the results are irregular. The amounts of salt adsorbed are very small.

M. S. B.

Chemical equilibria in homogeneous systems, and the validity of the Le Chatelier principle. B. G. CARBONERI (L'Ind. Chimica, 1934, 9, 1327—1331).—Theoretical. The conditions under which the principle is valid are defined.

H. F. G.

A thermodynamical problem. R. LUTHER (Z. Elektrochem., 1935, 41, 20).

F. L. U.

Calculation of free energies, entropies, specific heats, and equilibria from spectroscopic data and the validity of the third law. IV. Homogeneous gas equilibria calculated from spectroscopic data. H. ZEISE (Z. Elektrochem., 1934, 40, 885—890).—A review.

Families of thermodynamic equations. I. Method of transformations by the characteristic group. F. O. KOENIG (J. Chem. Physics, 1935, 3, 29—35).—Mathematical.

F. L. U.

Calculation and graphical representation of elementary displacements in the [reversible] reactions of homogeneous equilibrium. P. MONTAGNE (Compt. rend., 1935, 200, 234—236; cf. A., 1933, 464).—The influence of temp. and pressure on the equilibrium of the system $\alpha A + \beta B + \gamma C$ are discussed in relation to the law of mass action and representation on a ternary diagram.

R. S. B.

Influence of thermal diffusion in certain equilibrium measurements. E. D. EASTMAN and S. RUBEN (J. Amer. Chem. Soc., 1935, 57, 97—98).—The conclusions of Emmett and Shultz (cf. A., 1933, 570) are confirmed.

E. S. H.

Equilibrium constant for esterification in the gaseous phase. J. SALCEWICZ (Rocz. Chem., 1934, 14, 702—721).—EtOH-AcOH mixtures have been examined.

R. T.

Dissociation constant of carbonic acid. J. CARLBERG (Suomen Kem., 1935, 8, B, 4).—MacInnes' vals. (A., 1933, 904) depend on faulty extrapolation. Recalculation of data brings the results more closely into line with the author's.

A. G. P.

Thermodynamics of aqueous sulphuric acid solutions from electromotive force measurements. H. S. HARNED and W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 27—33).—The e.m.f. of the cells $H_2|H_2SO_4(m)|Hg_2SO_4|Hg$ have been determined over the range 0.05—17.5M and 0—60°. The activities of H_2O in H_2SO_4 solutions and of H_2SO_4 (0.0005—17.5M and 0—60°) have been calc. The normal electrode potential of the $Hg_2SO_4|Hg$ electrode between 0° and 60° is given by $E_0' = 0.63495 - 781.44 \times 10^{-6}t - 426.89 \times 10^{-9}t^2$. The relative partial mol. heat content of H_2SO_4 has been calc.

E. S. H.

Dissociation constants of mono- and trichloroacetic acids in ethyl alcohol. F. J. WELCHER and H. T. BRISCOE (Proc. Indiana Acad. Sci., 1934, 43, 142—153).—The dissociation consts., derived from the e.m.f. of cells without liquid junctions, are $\text{CCl}_3\text{-CO}_2\text{H}$ 3.236×10^{-6} , and $\text{CH}_2\text{Cl-CO}_2\text{H}$ 5.224×10^{-7} (5.720×10^{-7} when Pt electrodes coated with bright Pt are used). CH. ABS. (e)

Dissociation constants of chlorophenols. J. W. MURRAY and N. E. GORDON (J. Amer. Chem. Soc., 1935, 57, 110—111).—The dissociation consts. of PhOH , $\text{C}_6\text{H}_4\text{Cl-OH}$ (I), and $\text{C}_6\text{H}_3\text{Cl}_2\text{-OH}$ (II) are determined electrometrically in 50% (vol.) MeOH. The estimated vals. for (I) and (II) in H_2O are given and compared with those of $\text{C}_6\text{H}_2\text{Cl}_3\text{-OH}$, $\text{C}_6\text{HCl}_4\text{-OH}$, and $\text{C}_6\text{Cl}_5\text{-OH}$ (Tiessens, A., 1929, 1173). H. B.

Dissociation constants of organic acids. XI. Thermodynamic primary dissociation constants of some normal dibasic acids. G. H. JEFFERY and A. I. VOGEL (J.C.S., 1935, 21—30; cf. A., 1934, 1307).—From conductivity measurements at 25° on the salts $\text{Na}_2\text{X}=\text{CO}_2\text{Na}[\text{CH}_2]_x\text{CO}_2\text{Na}$, where $x=1-6$, the limiting mobilities (l_0) of the ions X'' have been calc., using a new combined solvent and hydrolysis correction. Assuming that vals. of l_0 for the amic acid ions $\text{NH}_2\text{-CO}[\text{CH}_2]_x\text{CO}_2'$ (cf. A., 1934, 963), are equal to those for the acid ions $\text{HX}'=\text{CO}_2\text{H}[\text{CH}_2]_x\text{CO}_2'$, the approx. relation $l_{\text{OHX}}=0.53l_{\text{OX}}$ has been established. The primary thermodynamic consts. (K_1) have been calc. Vals. of $K_1 \times 10^5$ for $x=1-6$ are 139.7, 6.626, 4.535, 3.715, 3.097, and 2.994, and vals. of the limiting equiv. conductivity are 383.5, 379.5, 378.0, 376.6, 374.6, 373.1, respectively. R. S. B.

Electrolytic solutions. XV. Thermodynamic properties of very weak electrolytes. R. M. FUOSS and C. A. KRAUS (J. Amer. Chem. Soc., 1935, 57, 1—4; cf. this vol., 13).—Mainly theoretical. The osmotic properties of a very weak electrolyte, triisomylammonium picrate in C_6H_6 , are in agreement with the hypothesis that ion pairs may associate into groups containing four ions. E. S. H.

Vapour pressures and activity coefficients of aqueous solutions of calcium and aluminium nitrates at 25° . J. N. PEARCE and L. E. BLACKMAN (J. Amer. Chem. Soc., 1935, 57, 24—27).—V.p. of aq. $\text{Ca}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$, ranging in concn. from 0.1M to the saturated solutions, have been determined at 25° . The activity of the solvent, the activity coeffs. of the ions, the free energy of dilution of solute and solvent, and the partial mol. vols. of the solvent and solutes have been calc. E. S. H.

Activity coefficients in mixed solutions and the Gibbs-Duhem and Gibbs-Margules formulæ. P. VAN RYSELBERGHE (J. Physical Chem., 1934, 38, 1161—1168).—Theoretical. D. R. D.

Activity of soap solutions at 90° . J. W. MCBAIN and (Miss) M. M. BARKER (Trans. Faraday Soc., 1935, 31, 149—152).—The activity coeffs. for Na and K soaps at 90° have been recalcd. (cf. Randall *et al.*, A., 1926, 1208). For the higher soaps in conc. solution the vals. are similar to those for a transition electrolyte of dissociation const. 0.01, but the effect is

due to disappearance of soap mols. and fatty ions to form neutral and ionic micelles, respectively. Even in more dil. solution, however, when colloid has disappeared, the soaps, although now behaving as much stronger electrolytes, are definitely not as strong as KCl.

M. S. B.

M.-p. and transition curves of the forms of ice from heavy water. G. TAMMANN and G. BANDEL (Z. anorg. Chem., 1935, 221, 391—396).—A mixture (H) containing 58.3% of H_2O was employed. The m.-p. curve for ice I for H is about $2^\circ >$ for ordinary H_2O (W). The equilibrium pressure p for ice I and III for W is 2096 ± 8 kg. per sq. cm. at -30.4° and ΔV 0.2 c.c. per g. For H p is 2188 ± 13 kg. per sq. cm. at -30.8° and ΔV 0.16 c.c. per g. Between ice I and II for H the equilibrium p is approx. 2277 kg. per sq. cm. at -61° and for W 1948 kg. per sq. cm. The transition temp. of ice II to ice III for W is $0.5^\circ <$ for H at the same p . By extrapolation from the vals. for H the p - t curves for H_2O have been deduced. M. S. B.

Systematic studies in combination. LXIII. System rhodium-phosphorus. H. HARALDSEN (Z. anorg. Chem., 1935, 221, 397—417).—Re and P react when heated above $750-800^\circ$, but the products do not melt even at 1200° . Tensimetric and X-ray investigations indicate the existence of the compounds: ReP_3 , ReP_2 , ReP , and Re_2P . The mol. vols. are additive, the increment for Re being 8.1 c.c. and for P 10.1 c.c. Heats of formation from P_2 and P_4 have been derived for the first three phosphides. These and temp. of decomp. at 1 atm. have been compared with those for other phosphides. M. S. B.

[Solubility] diagram potassium nitrite-water. Hydrate $\text{KNO}_2 \cdot 0.5\text{H}_2\text{O}$. J. BUREAU (Compt. rend., 1935, 200, 395—397).—Pure KNO_2 is perfectly white, d_4^{20} 1.926, m.p. 441° . The eutectic temp. is -40.2° (64.9% KNO_2). The stable solid phase between -40.2° and -8.8° is $\text{KNO}_2 \cdot 0.5\text{H}_2\text{O}$. J. W. S.

Dissociation pressures of some salt hydrates. D. G. R. BONNELL and L. W. BURRIDGE (Trans. Faraday Soc., 1935, 31, 473—478).—The dissociation pressures of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ have been determined at 10° , 15° , 20° , and 25° by a dynamic method and compared with the results of other investigations at 25° . Heats of hydration have been calc. A new type of H_2O vapour saturator is described. M. S. B.

Thermal analysis of the system picric acid-dinitronaphthalene. T. URBANSKI and B. KWIATKOWSKI (Rocz. Chem., 1934, 14, 941—943).—Neither 1 : 5- nor 1 : 8- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ gives rise to compounds or solid solutions. R. T.

Thermal analysis of binary mixtures containing organic nitrates. T. URBANSKI (Rocz. Chem., 1934, 14, 925—940).—The m.-p. diagrams of the systems mannitol hexanitrate (I)- $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$ (II), $p\text{-C}_6\text{H}_4\text{Cl-NO}_2$, $p\text{-C}_6\text{H}_4(\text{OMe})_2$, m - (III), and p - (IV) $\text{-NO}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{Et}$, m - (V) and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$, $m\text{-NH}_2\text{-C}_6\text{H}_4\text{-NO}_2$, and 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ (VI); erythritol tetranitrate (VII)-(II) and 2 : 4 : 6-trinitrotoluene (VIII); pentaerythritol tetranitrate

(IX)-(VI), trinitrophenylmethylnitroamine, NH_2Ph , and camphor (X), indicate the unstable compounds 2(I), (III), 2(I), (IV), (I), 2(V), and (VII), 4(VIII). Solid solutions are formed in the system (IX)-(X), whilst in the remaining systems only ordinary eutectic mixtures are observed. R. T.

Equilibria in the systems $\text{KCl-H}_2\text{O-NH}_4\text{Cl}$ and $\text{NaCl-H}_2\text{O-NH}_4\text{Cl}$. M. M. JARLIKOV (J. Appl. Chem. Russ., 1934, 7, 902-905).—Solubility and density data are given for 0-80°. R. T.

System $\text{CaSO}_4\text{-CaO-SO}_3$. S. ZEROMSKI and Z. SEUBICKI (Rocz. Chem., 1934, 14, 849-856).—The pressure-% decomp. curves of CaSO_4 heated at > 1000° exhibit irregularities and spurious equilibrium points; these effects are ascribed to formation of metastable solid solutions of the products of decomp., and to surface phenomena. The system is univariant. R. T.

System antimony iodide-potassium iodide-water. F. FRANÇOIS (Compt. rend., 1935, 200, 393-395).—Between 16° and 48° $\text{SbI}_3 \cdot 2\text{KI} \cdot \text{H}_2\text{O}$ separates in dark red quadratic prisms, isomorphous with $\text{BiI}_3 \cdot 2\text{KI} \cdot \text{H}_2\text{O}$ (this vol., 36). J. W. S.

Equilibrium diagrams of salts for salt baths. III. **System $\text{Na}_2\text{CO}_3\text{-BaCl}_2\text{-KCl}$.** T. SATO (Kinz. no Kenk., 1933, 10, 448-463).—The m.p. and transition temp. of BaCl_2 are 963° and 927°, respectively. Equilibrium data are recorded for binary and ternary mixtures of Na_2CO_3 , BaCl_2 , and KCl . $\text{BaCl}_2 \cdot \text{Na}_2\text{CO}_3$, which yields two immiscible liquid phases at 730°, and $2\text{KCl} \cdot \text{BaCl}_2$, m.p. 670°, are formed in the binary systems. In the ternary system there are two ternary eutectic points and one peritecto-eutectic point. CH. ABS. (e)

System iron-iron oxide-calcium orthoferrite. E. MARTIN and R. VOGEL (Arch. Eisenhüttenw., 1934-1935, 8, 249-254).—Thermal and micrographic observations have disclosed two compounds, $\text{CaO} \cdot 9\text{FeO}$ (I), m.p. 1310°, and $4\text{CaO} \cdot 3\text{Fe}_3\text{O}_4$, m.p. 1200°. The system may be divided into five 3-phase fields and one 2-phase field, the other solid phases present being Fe , Fe_3O_4 , wüstite, CaFe_2O_4 , and $\text{Ca}_2\text{Fe}_2\text{O}_5$. Eutectics are formed at Fe_2O_3 62.8, CaO 26.9, Fe 10.3%, 1110° [(I) + $\text{Ca}_2\text{Fe}_2\text{O}_5$]; Fe_2O_3 65.3, CaO 25.8, Fe 8.9%, 1120°; and Fe_2O_3 72.0, CaO 24.5, Fe 3.5%, 1240° (Fe_3O_4 + $\text{Ca}_2\text{Fe}_2\text{O}_5$). Free Fe occurs in the melts when the Fe content is > that corresponding with the sections (I)- $\text{Ca}_2\text{Fe}_2\text{O}_5$ and (I)-wüstite. A. R. P.

Equilibrium between molten metals and slags. W. KRINGS (Z. Metallk., 1934, 26, 247-249).—Deviations from the ideal mass action law in the equilibrium between molten metals and slags are attributed to the formation of stable compounds in one of the liquid phases. In the case of systems involving a metal, P, and O, the more stable is the metal phosphide the looser is the combination between the metal oxide and P_2O_5 in the slag, and hence the greater is the P content of the metal phase; this accounts for the fact that in the Mn-P-O system at 1450° no P_2O_5 is detected in the slag until the metal contains > 10% P, whereas in the Cu-P-O system no P remains in metal until the P_2O_5 content of the slag exceeds 40%. A. R. P.

Condensed phase equilibria in the system water-alcohol-ether. A. LALANDE (J. Chim. phys., 1934, 31, 583-610; cf. A., 1934, 137, 845).—The three binary systems and the ternary system have been investigated at temp. from 0° downwards. There is no evidence for the formation of any intermol. compound. All three binary systems form eutectics, and there is a ternary eutectic at -127°. $\text{EtOH-Et}_2\text{O}$ mixtures remain homogeneous even when supercooled. F. L. U.

System butyric acid-sodium hydroxide-water. C. R. BURY and R. D. J. OWENS (Trans. Faraday Soc., 1935, 31, 480-482).—Four solid phases, $\text{NaOH} \cdot \text{H}_2\text{O}$, PrCO_2Na , $\text{PrCO}_2\text{Na} \cdot \text{H}_2\text{O}$, and $2\text{PrCO}_2\text{Na} \cdot \text{PrCO}_2\text{H}$, are formed. Alkali strongly represses the solubility of the neutral salt, whilst excess acid increases it. M. S. B.

Thermal equilibria in ternary systems. Phenacetin-antipyrine-sulphonol. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1934, 14, 466-473).—Compound formation does not take place; the ternary eutectic mixture, m.p. 69°, contains phenacetin 26, antipyrine 42, and sulphonol 32%. R. T.

Ternary systems of organic compounds and their classification. K. HRYNAKOWSKI (Rocz. Chem., 1934, 14, 451-465).—Three chief types are distinguished, differing in the intermiscibility of the fused components, and in the formation or otherwise of solid solutions and compounds. R. T.

Calorimetry of salt solutions (system sodium sulphate-magnesium sulphate-water). J. PERREU (Compt. rend., 1935, 200, 237-241).—The sp. heats of mixed solutions of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ of concns. c_1 and c_2 mol. per mol. of total H_2O , respectively, are given by $\gamma_{c,c} = \frac{+1}{(b_1c_1 + b_2c_2 + 1)}$ at 19-23°, where $a_1 = 17.641$, $b_1 = 27.278$, $a_2 = 11.481$, and $b_2 = 21.043$. Heats of dissolution, dilution, and crystallisation have also been determined. R. S. B.

Hydrazine: heat capacities of aqueous hydrazonium salts at 20° and 25°. A. W. COBB and E. C. GILBERT (J. Amer. Chem. Soc., 1935, 57, 35-39).—The heat capacities of 0.1-1M hydrazonium dichloride, dibromide, monochloride, monobromide, and monoperchlorate have been determined and the apparent and partial mol. heat capacities of the solute and the partial mol. heat capacity of H_2O calc. E. S. H.

Hydrazine: heats of dissolution of hydrazonium salts at 25°. E. C. GILBERT and A. W. COBB (J. Amer. Chem. Soc., 1935, 57, 39-41).—Data are recorded for $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$, $\text{N}_2\text{H}_4 \cdot \text{HCl}$, $\text{N}_2\text{H}_4 \cdot \text{HBr}$, $\text{N}_2\text{H}_4 \cdot \text{HClO}_4 \cdot 0.5\text{H}_2\text{O}$, and $\text{N}_2\text{H}_4 \cdot \text{HClO}_4$. The partial mol. heats of dissolution of solvent and solute have been calc. E. S. H.

Relation of volume shrinkage to the heat of formation and electrolytic decomposition potential of the alkali and alkaline-earth metal halides. S. BALCE (Univ. Philippines Nat. App. Sci. Bull., 1934, 4, 119-121).—The heats of formation of the alkali and alkaline-earth halides are given by $H = 1.33z \times 10^5 \times \sqrt[3]{(\Delta V)}$, where z is the valency of the

metal, and ΔV is the shrinkage in vol. per unit vol. on formation of the salt from the elements. The electrolytic decomp. potential $P=5.7\sqrt{(\Delta V)}$.

CH. ABS. (e)

Determination of free energy and heat of formation of aluminium chloride from the potential of the chlorine-aluminium cell. W. D. TREADWELL and L. TEREBESI (Helv. Chim. Acta, 1935, 18, 103—120).—The e.m.f. of the cell $\text{Al}|\text{Al}_2\text{Cl}_6+\text{KCl}+\text{NaCl}|\text{Cl}_2(\text{Pt})$ has been measured at 90° to 250°. The electrolyte used was the ternary eutectic, the v.p. of Al_2Cl_6 in which, measured over the same temp. range, is given by $\log p=21.039-5700/T-0.014687T$. The free energy of formation of Al_2Cl_6 vapour, calc. from the e.m.f. and from the equilibrium const. of the reaction $\text{Al}_2\text{O}_3+6\text{HCl}\rightleftharpoons 2\text{AlCl}_3+3\text{H}_2\text{O}$, is $1.997-4.57\times 10^{-4}(T-500)$ volts up to 930° abs., and $1.766-4.85\times 10^{-4}(T-1000)$ volts from 930° to 1500° abs. Heats of formation calc. from ΔF are 307.98 kg.-cal. for Al_2Cl_6 vapour, and 336.85 kg.-cal. for the solid at 20°. Available thermal data lead to 335.3 kg.-cal. for the latter. A method for preparing large quantities of pure AlCl_3 is described.

F. L. U.

Approximate value for the heat of formation of an iron phosphide $[\text{Fe}_2\text{P}]$. W. A. ROTH, A. MEICHSNER, and H. RICHTER (Arch. Eisenhüttenw., 1934—1935, 8, 239—241).—By dissolution of FePO_4 crystals in HCl its heat of formation from Fe_2O_3 and P_2O_5 has been found to be +21.6 kg.-cal., and from Fe , O , and red $\text{P}+303.9$ kg.-cal. The heat of formation of Fe_2P has been determined by oxidation of Fe_2P and of a mixture of $2\text{Fe}+\text{P}_{\text{red}}$ in a bomb calorimeter; the most probable val. is +41 kg.-cal. $\pm 10\%$. Attempts to prepare pure Fe_2P by direct union of the elements in vac. failed.

A. R. P.

Theory of concentrated solutions. XII. Application of thermal analysis to the determination of the heats of fusion of organic compounds. J. TIMMERMANS (Bull. Soc. chim. Belg., 1934, 43, 626—638).—The f.p. data for the binary systems afford the following vals. for the heat of fusion: $n\text{-C}_5\text{H}_{12}$ 2.0, $n\text{-C}_6\text{H}_{14}$ 3.0, methylcyclohexane 1.6, PhMe 1.6, CS_2 1.35, EtBr 1.4, Pr^nBr 1.56, Bu^nBr 1.6, Bu^sBr 0.6, Bu^nCl 0.5, CH_2Cl_2 1.0, $\text{C}_2\text{H}_4\text{Cl}_2$ 1.25, PhF 1.95, PhCl 1.8, PhBr 2.0, $o\text{-C}_6\text{H}_4\text{MeCl}$ 2.0, $m\text{-C}_6\text{H}_4\text{Cl}$ 2.5, Et_2O 1.8, methylal 1.9, ethylal 3.6, HCO_2Et 2.2, EtCO_2Et 3.0, EtCO_2H 1.8, $\text{Pr}^s\text{CO}_2\text{H}$ 1.2, $\text{Bu}^n\text{CO}_2\text{H}$ 1.85, $\text{Bu}^s\text{CO}_2\text{H}$ 1.75 kg.-cal. per mol. J. G. A. G.

Heats of dissolution, heats of dilution, and specific heats of aqueous solutions of certain amino-acids. C. A. ZITTE and C. L. A. SCHMIDT (J. Biol. Chem., 1935, 108, 161—185).—The sp. heats of solutions of glycine, *dl*-alanine, and *dl*-valine, and the heats of dilution and dissolution of 18 NH_2 -acids (I), have been measured at 25°. The relation between free energy change and temp. for certain (I) is also discussed. The heat of hydration of asparagine determined from heats of dissolution of the hydrated and anhyd. form is in agreement with the val. deduced from heats of combustion.

A. E. O.

Heats of organic reactions. I. Apparatus and heat of hydrogenation of ethylene. G. B. KISTIAKOWSKY, H. ROMBYN, jun., J. R. RUHOFF, H. A.

SMITH, and W. E. VAUGHAN (J. Amer. Chem. Soc., 1935, 57, 65—75).—The calorimeter described is designed to measure the heats of gaseous reactions at $\geq 150^\circ$ with a precision of about 0.1%. From the measured heat of hydrogenation of C_2H_4 at 82° ($-32,824\pm 50$ g.-cal.) the following vals. have been calc.: $\Delta H_{998} -32,575\pm 50$, $\Delta H_{273} -32,460\pm 50$, $\Delta H_0 -31,000\pm 150$ g.-cal. E. S. H.

Thermal data. II. Heats of combustion of *l*-cysteine, *l*-cystine, β -thiolactic acid, and $\beta\beta'$ -dithiodilactic acid. III. Heat capacities, entropies, and free energies of four organic compounds containing sulphur. H. M. HUFFMAN and E. L. ELLIS (J. Amer. Chem. Soc., 1935, 57, 41—46, 46—48; cf. A., 1933, 27).—II. The mol. heats of combustion at const. pressure at 25° are: β -thiolactic acid $511,500\pm 800$, $\beta\beta'$ -dithiodilactic acid $946,800\pm 900$, *l*-cysteine $532,420\pm 500$, *l*-cystine $998,170\pm 900$ g.-cal. III. The heat capacities, entropies, and free energies between 90° and 298° abs. are calc. for the above compounds. E. S. H.

Apparent molal isochoric heat capacity of electrolytes. F. J. GUCKER, jun., and T. R. RUBIN (J. Amer. Chem. Soc., 1935, 57, 78—82).—Theoretical. E. S. H.

Calculation of heat of reaction from values of the equilibrium constant at two temperatures. T. B. DOUGLAS and H. D. CROCKFORD (J. Amer. Chem. Soc., 1935, 57, 97).—Theoretical. E. S. H.

Diffusion coefficients of electrolytes, and ionic mobilities. S. PLESNIEWICZ (Rocz. Chem., 1934, 14, 764—797).—The diffusion coeffs. have been determined by a new method. The calc. ionic mobilities (I) of the isobaric anions $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, and $\text{Cr}_2\text{O}_7^{2-}$ are as $\frac{1}{3}:\frac{1}{2}$, indicating that (I) are inversely oc to the charge of the ions. R. T.

Purification of certain solvents for conductivity determinations. E. MICHALSKI (Rocz. Chem., 1934, 14, 1052—1060).— $\text{H}\cdot\text{CO}_2\text{H}$, AcOH , H_2O , and other solvents are purified by fractional crystallisation in special apparatus ensuring isolation from atm. CO_2 and NH_3 . R. T.

Direct determination of the limiting conductivity of strong electrolytes, and the conductivity of very dilute weak electrolytes. M. HEASKO and A. SALITÓWNA (Rocz. Chem., 1934, 14, 1038—1051).—Specially purified H_2O is used for diluting various salt solutions and the limiting conductivities, λ_∞ , are measured directly in special SiO_2 vessels. The vals. of λ_∞ obtained differ by $\geq 0.2\%$ from those calc. from Kohlrausch's equation; is attained at $2\times 10^{-6}\text{N}$. TlOH , 10^{-7}N . $\text{Ba}(\text{OH})_2$, and 10^{-6}N . HCl . R. T.

Influence of the bubbles of gas evolved on the conductivity of solutions during electrolysis. L. E. KRAUZE and P. I. SOKOLOV (J. Appl. Chem. Russ., 1934, 7, 887—901).—The increased resistance of the electrolyte due to formation of bubbles of gas increases directly with the c.d., and inversely with the distance between the electrodes. R. T.

Conductivity of glycerol solutions of calcium, strontium, and barium chlorides. J. SZPER and Z. GAJEWSKI (Rocz. Chem., 1934, 14, 570—578).—At 25—200° the mol. conductivity, follows Kohl-

rausch's law; has the same val. in all three cases (3.67×10^{-4} at 25°). The mobility of the cations augments in the order $\text{Ca} < \text{Sr} < \text{Ba}$. rises with rise of temp., exponentially from 25° to 130° , and linearly from 130° to 200° . R. T.

Potentials of electrodes in non-aqueous solutions. K. DREWSKI (Rocz. Chem., 1934, 14, 865—898).—The potential of a H electrode in MeOH , EtOH , and PrOH solutions of HCl differs from that in aq. solution, to an extent \propto to the difference in dielectric const. and in the hydration of H^+ ; for solutions in HCO_2H and AcOH the chemical nature of the solvent enters as a further factor. R. T.

Potential of azides. E. H. RIESENFELD and F. MÜLLER (Z. Elektrochem., 1935, 41, 83—86).—The potential (E) of a Pt anode in NaN_3 has been determined. At the anode $\text{N}_3' \rightarrow \text{N}_3 + e$, $\text{N}_3 \rightarrow \text{N}_2 + \text{N}$, $\text{N} + \text{N} \rightarrow \text{N}_2$. For $-\log c.d. -1.5-3.5$, Tafel's formula $E = a + b \log i$ holds, where i = current, $b = RT/F \log e$, and $a = \text{const.}$ Smooth Pt gives on previous treatment with O_2 and N_2 the same p.d., but with H_2 a lower val. Platinised Pt gives a p.d. approx. 0.06 volt < for smooth Pt owing to catalysis of the conversion of N_3 into N_2 on the former. The val. of E depends on $[\text{N}_3']$ according to the Nernst formula, and is independent of $[\text{H}^+]$ and $[\text{OH}^+]$ at const. $[\text{N}_3']$. From measurements on the cells $\text{Ag}|\text{AgN}_3|\text{N-NaN}_3|0.1\text{N-KCl}|\text{Hg}_2\text{Cl}_2|\text{Hg}$ at 0° , $\text{Ag}|\text{AgN}_3|\text{N-NaN}_3|0.1-0.001\text{N-NaN}_3|\text{AgN}_3|\text{Ag}$ at 20° , and $\text{Ag}|\text{AgN}_3|0.1\text{N-AgNO}_3|\text{Ag}$ at 18° , the normal potential of the $\text{AgN}_3|\text{Ag}$ electrode has been found to be 0.384 volt, with a temp. coeff. 0.0006 volt per 1° . The aq. solubility of AgN_3 is 8.43×10^{-3} g. per litre at 18° . R. S. B.

Systematic p_H values of some solutions in the alkaline range. S. J. KIEHL and R. D. LOUCKS (Trans. Electrochem. Soc., 1935, 67, 77—96).—The p_H at 30° has been determined for NaOH in admixture with Na_2HPO_4 , H_3BO_3 , and NaHCO_3 ; H_3BO_3 mixed with $\text{Na}_2\text{B}_4\text{O}_7$, Na_3PO_4 , Na_2HPO_4 , and Na_2CO_3 , and $\text{Na}_2\text{B}_4\text{O}_7$ mixed with Na_3PO_4 , Na_2HPO_4 , NaHCO_3 , and Na_2CO_3 . The p_H of solutions of H_3BO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, Na_2HPO_4 , and Na_2CO_3 , with and without the addition of NaOH , has also been determined at 60° . In all cases except H_3BO_3 , for which the ionisation decreases with fall of temp., $p_{H60} < p_{H30}$. The p_H of NaHCO_3 and Na_2HPO_4 solutions increases with decreasing concn. from 0.05M to 0.5M, with a max. at $< 0.05\text{M}$. R. S. B.

Physico-chemical studies of complex formation involving weak acids. XII. Complex anions of cuprous and auric cyanides. H. T. S. BRITTON and E. N. DONN (J.C.S., 1935, 100—104).—The results of adding aq. KCN to CuSO_4 , to CuCN , and to NaAuCl_4 have been followed by potentiometric titration using the Cu electrode, and by measurements of (a) p_H by the glass electrode, (b) conductivity, and (c) v.p. of hydrolysed HCN . It is inferred that in these solutions only the complex ions $\text{Cu}(\text{CN})_3^-$ and $\text{Au}(\text{CN})_4^-$ exist. R. S. B.

Potential of the lead dioxide-lead sulphate electrode at various temperatures. W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 9—15).—The e.m.f. of the cell $\text{H}_2|\text{H}_2\text{SO}_4(m)|\text{PbSO}_4|\text{PbO}_2|\text{Pt}$ has been

measured over the range 0.0005—7.0M and 0— 60° . Vals. of the mol. electrode potential of the PbSO_4 — PbO_2 —Pt electrode between 0° and 60° have been calc. E. S. H.

Molal electrode potentials and the reversible electromotive forces of the lead accumulator from 0° to 60° . H. S. HARNED and W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 33—35).—The e.m.f. of Pb (2-phase amalgam)| $\text{PbSO}_4|\text{Na}_2\text{SO}_4|\text{Hg}_2\text{SO}_4|\text{Hg}$ has been determined between 0° and 60° . The mol. electrode potentials of the electrodes reversible to SO_4^{2-} and those related to the electrodes of the Pb accumulator have been evaluated. Equations for the e.m.f. of $\text{Pb}|\text{PbSO}_4|\text{H}_2\text{SO}_4(m)|\text{PbSO}_4|\text{PbO}_2|\text{Pt}$ at 0.05—7M and 0— 60° have been developed. E. S. H.

Polarographic studies with the dropping mercury cathode. XLIV. Dependence of limiting currents on the diffusion constant, the rate of dropping, and the size of drops. D. ILKOVIČ (Coll. Czech. Chem. Comm., 1934, 6, 498—513).—Equations are derived from theoretical principles and confirmed experimentally. E. S. H.

Polarographic studies. Measurement of "limiting currents" in solutions of pure salts by means of the Kucera-Heyrovsky dropping mercury electrode. W. KEMULA and B. WENIGERÓWNA (Rocz. Chem., 1934, 14, 406—413).—Reproducible results are obtained when the size of the drops of Hg and the rate of flow are strictly const. R. T.

Capacity of the polarised mercury electrode at very low frequencies. N. THON (Compt. rend., 1935, 200, 54—56; cf. A., 1934, 846).—The capacity of the polarised Hg electrode in LiCl_2 is the same at frequencies of 9 and 31 per sec. The vals. calc. from the cathodic and anodic polarisations are concordant (cf. A., 1932, 24) and are in agreement with the vals. determined from the electro-capillary curve. Since the capacity is independent of frequency over the voltage range investigated, the vals. measured are the true capacities of the Hg-solution double layer. The capacity is a min. at about -0.8 volt. Its decrease with increasing voltage below 0.8 volt is attributed to increase in the proportion of cations in the ionic layer, and its increase with increasing voltage beyond -0.8 volt to decreasing distance between the two layers as a result of dehydration of the cations. J. W. S.

Reduction potentials of organic compounds. XIX. Limiting currents of the current-voltage curves. M. SHIKATA and I. TACHI (J. Electrochem. Assoc. Japan, 1934, 2, 201—206).—Limiting currents found on the polarograms of many org. compounds are compared and discussed. Solubilities of various org. compounds in H_2O at 25° are recorded. CH. ABS. (e)

Effect of addition of colloidal substances on the polarisation potential in the electrodeposition of zinc from aqueous solutions of zinc sulphate. T. ISHIHARA, T. ONODA, and K. UMETU (Kinz. no Kenk., 1933, 10, 365—382).—The potential decreases with increasing amount of colloid, whereas the min. overvoltage of O and the decomp. voltage increase.

A discontinuity was observed at 0.1 g. of colloid (glue or gelatin) per litre. CH. ABS. (e)

Effect of supersonic waves on chemical phenomena. III. Effect on the concentration polarisation. IV. Effect on overvoltage. N. Moriguchi (J. Chem. Soc. Japan, 1934, 55, 749—750, 751—754).—When supersonic waves (I) are applied in the electrolysis of 0.1N-CuSO₄ the voltage-c.d. curve becomes a straight line. The overvoltage in the electrolysis of N-KOH, -NaOH, or -H₂SO₄ is eliminated when (I) are applied. (I) is supposed to eliminate the diffusion layer between electrode and electrolyte. CH. ABS. (e)

Limiting effect of the Debye equation on polarisation concentration curves. W. D. KUMLER (J. Amer. Chem. Soc., 1935, 57, 100).—Theoretical. E. S. H.

Determination of potential-current curves of electrolytes. J. LIGER (Bull. Soc. chim., 1934, [v], 1, 1679—1702).—Using a large Pt anode with wire cathodes of Pt, Fe, Cu, and Ag embedded in glass, current-voltage curves have been obtained from successive throws of a ballistic galvanometer produced by applying known p.d. for about 0.1 sec. A fresh electrode surface was made by abrading the exposed end of the wire between each throw. A rocking device permitted the electrode to make and break the circuit. Results were reproducible to within 2—5 mv. NaCl and NaOH solutions afforded four inflexions, corresponding with four discharge potentials (I) which depended on the electrode metal, rose with decreasing diameter of the Pt wire, and varied with dilution more rapidly than the Nernst equation requires. The curves for BaCl₂ and NiSO₄ solutions had four and three inflexions, respectively. The significance of these (I) is discussed. The (I) of Cu⁺ at Pt (0.4 mm. diam.) is 0.45—0.5 volt and that of Cu⁺⁺ at Fe (0.5 mm.) is 0.16. J. G. A. G.

Electrochemical potential and corrosion phenomena of iron. N. NEKRASSOV, I. STERN, and Z. GULANSKAJA (Z. Elektrochem., 1935, 41, 2—9).—The change of electrode potential of Fe with time has been measured in aq. solutions of Na₂SO₄, NaHCO₃, Na₂CO₃, Na₂SiO₃, NaH₂PO₄, Na₂HPO₄, Na₃PO₄, NaCl, NaOAc, and Na₂C₂O₄, all containing air. An increased rate of corrosion is associated with displacement of the potential towards more negative vals., and the converse is also true. The val. of p_H above which corrosion is greatly diminished is not necessarily 9, but depends on the anions present. F. L. U.

Exact method for the direct measurement of cathodic current distribution. E. MANTZELL (Z. Elektrochem., 1935, 41, 10—20).—The method described consists in measuring the c.d. at each separate part of a symmetrically divided cathode, the subdivisions being insulated from one another and connected by low-resistance leads to a bus bar. The method has been applied to the determination of the current distribution with varying distance between the electrodes and with the interposition of screens and slits of varying dimensions. F. L. U.

Acoustic electrochemical phenomena. L. V. NIKITIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 309—313).—When acoustic waves are passed through an electrolyte during electrolysis, a periodic variation of 0.05—0.1 mv. occurs in the electrode potential, of the same frequency as the wave motion. The character of the variation varies with time, and it disappears after some min. to reappear after a further lapse of time. The phenomenon is associated with the release of the gas films from the electrodes. J. W. S.

Electrolysis of sodium chloride in liquid ammonia. E. I. ACHUMOV and B. B. VASSILIEV (Z. Elektrochem., 1935, 41, 96—101).—For saturated solutions the conductivity (κ) is a max. when the solid phases NaCl and NaCl, 5NH₃ are both present. The decomp. p.d. is 3.54 volts. The electrolysis has been studied in an autoclave which acts as cathode, with a C anode, at -10°, 0°, and room temp. The reaction at the anode is 8NH₃ + 3Cl₂ = 6NH₄Cl + N₂, and at the cathode Na + NH₃ = NaNH₂ + 0.5H₂, the NaNH₂ forming a white powder. An asbestos diaphragm separates the anodic and cathodic compartments, preventing the reaction NH₄Cl + NaNH₂ = NaCl + 2NH₃. R. S. B.

Theory of passivation. XXVI. Limiting current for anodic polarisation of metals in water solution. W. J. MULLER (Z. Elektrochem., 1935, 41, 83—86).—Photographs of the anode surface at various points on the i - t curves for Fe in N-H₂SO₄ (alone and saturated with FeSO₄) show that i falls rapidly only when the surface is almost completely covered with crystallites. E. Muller's results are readily interpreted in terms of the author's passivation theory. R. S. B.

Influence of gelatin on the processes taking place in the systems Zn-ZnSO₄ and Zn-CuSO₄. A. GALECKI [with E. HOJA, J. NETEROWICZ, and F. MODRZEJEWSKI] (Rocz. Chem., 1934, 14, 414—429).—The quantity of Cu deposited on Zn from aq. CuSO₄ containing gelatin (I) is > in its absence. The Zn and (I) contents of the deposit increase with increasing (I) concn., and the deposits become darker and more tenacious. Substantially the same results are obtained in stirred and unstirred systems. The potential of a Zn electrode in aq. ZnSO₄ becomes more negative in presence of (I), whilst that of Zn electrodeposited from aq. ZnSO₄ containing (I) is more positive than that of pure Zn. (I) is deposited on the cathode in amount varying directly with time, and inversely with c.d. R. T.

Entropy and the absolute rate of chemical reactions. I. Steric factor of bimolecular associations. O. RICE and H. GERSHINOWITZ (J. Chem. Physics, 1934, 2, 853—859).—Theoretical. M. S. B.

Application of wave mechanics to reactions involving hydrogen and diplogen. R. A. СМІТН (Proc. Camb. Phil. Soc., 1934, 30, 508—513).—A chemical reaction is treated as a problem of transitions between two stationary states. In a collision between two heavy mols., XH and XH₂, the initial and final stationary states are taken to have the same energy. Using Fowler and Bernal's method the probability of

exchange of a proton and a dipton in collisions between H_2O and H_3O^+ is calc. The effects of temp. and of OH^+ and OH_3^+ ions on the exchange are discussed. Lower limits to the heights of the potential barriers, through which a proton and dipton have to pass in exchange between H_3^+ and H_2O and OH_3^+ in order that the rates of reaction are as slow as the observed rates, are calc.

W. R. A.

Kinetics of the reaction between hydrogen and sulphur. I. Reaction at 265–350° and 290–820 mm. E. E. AYNSLEY, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1935, 58–68; cf. A., 1933, 469).—The reaction was studied by dynamic and static methods. The velocity of the homogeneous reaction $\propto [\text{S}]^{\frac{1}{2}}[\text{H}_2]$ and is not affected by N_2 , H_2S , or the glass surface, but is markedly catalysed by traces of O_2 at the lower temp. The temp. coeff. is 1.90 corresponding with the heat of activation 43.3 kg.-cal. The velocity of the heterogeneous reaction \propto the area of the molten S and $\propto [\text{H}_2]$, but is not affected by N_2 and is independent of the v.p. of S. The temp. coeff. is 1.95 and the heat of activation is 45.5. Earlier investigations (J.C.S., 1923, 123, 696) are discussed and the following mechanism is proposed: (1) $\text{H}_2 + \text{S}_2 \rightarrow \text{H}_2\text{S} + \text{S}$, (2) $\text{S} + \text{S}_x \rightarrow \gamma \text{S}_{(x+1)/2}$ and $\text{S} + \text{H}_2 + \text{M} \rightarrow \text{H}_2\text{S} + \text{M}^*$.

J. G. A. G.

Influence of temperature on the explosion of mixtures of air and hydrocarbons. P. MONDAIN-MONVAL and R. WELLARD (Compt. rend., 1935, 200, 232–234; cf. B., 1931, 705).—The max. pressure produced by exploding mixtures of air and $n\text{-C}_6\text{H}_{14}$ is independent of the temp. up to 180°, and then begins to increase rapidly with rise of temp. up to the point of spontaneous inflammability, 232°. Commercial oils behave similarly, but with C_6H_6 the max. pressure is independent of temp. from 50° to 350°. Results are interpreted in terms of unstable alcohol peroxides of high latent energy formed in the region of rapid change of max. pressure with temp., and the application of this view to the overheated motor cylinder is discussed.

R. S. B.

Oxidation of carbon monoxide by nitrous oxide. C. E. H. BAWN (Trans. Faraday Soc., 1935, 31, 461–473).—The oxidation of CO by N_2O in quartz vessels near 550° is a surface reaction. The rate \propto the initial $[\text{N}_2\text{O}]$ and inversely as $[\text{CO}]$, indicating that CO is strongly adsorbed. Inert gases and NO have very little effect, but CO_2 , either added or produced by the reaction, accelerates the reaction. Between certain limits of temp. and pressure explosion takes place. The lower explosion limit is depressed by excess of CO and N_2O . The effect of inert gases depends on their physical properties in a way which indicates that the reaction is governed by the temp. of the surface layers. Small amounts of NO inhibit the explosion. A chain mechanism is suggested.

M. S. B.

Inert gas effects at the lower explosion limit of phosphine-oxygen mixtures. S. C. GRAY and H. W. MELVILLE (Trans. Faraday Soc., 1935, 31, 462–461; cf. this vol., 47).— H_2 , Ne, Ar, N_2 , CO_2 , and SO_2 all depress the lower explosion limit of $\text{rH}_3\text{-O}_2$ mixtures by impeding diffusion of the chains to the walls. There is no measurable gas phase

inhibition for pressures of the inert gas of the same order as that of PH_3 and O_2 . Contrary to their accelerating effect with $\text{P}_4\text{-O}_2$ mixtures, C_2H_4 , C_6H_6 , PbMe_4 , and CCl_4 all raise the lower limit for $\text{PH}_3\text{-O}_2$. This is explained as due to a smaller probability of branching of the chains in the latter case. The inhibition coeff. of C_2H_4 has practically the same val. as in the stable photo-oxidation of PH_3 .

M. S. B.

Kinetics and activation energy of the thermal decomposition of acetaldehyde vapour. M. LETORT (Compt. rend., 1934, 199, 1617–1619; cf. A., 1934, 1073).—In agreement with Fletcher and Hinshelwood's results (A., 1933, 910), the true order of the reaction was 1.5 (from 0.3 to 1160 mm. pressure). The mean activation energy, 45,700 kg.-cal., was independent of pressure (50–400 mm.) at 447°.

H. J. E.

Kinetics of the thermal decomposition of acetaldehyde vapour in presence of traces of oxygen. M. LETORT (Compt. rend., 1935, 200, 312–314).—The increased velocity, v'_0 , of the pyrolysis of MeCHO , due to the presence of O_2 , has been determined at different temp. for a practically const. concn. of MeCHO vapour. The temp. coeff. of v'_0 is negative.

M. S. B.

Substitution by free atoms and Walden inversion. Decomposition and racemisation of optically active *sec.*-butyl iodide in the gaseous state. R. A. OGG, jun., and M. POLANYI (Trans. Faraday Soc., 1935, 31, 482–495).—The homogeneous gas phase decomp. of *sec.*-BuI (I) at 238–276° consists of a unimol. dissociation into a free radical and I atom and a bimol. reaction of a (I) mol. with an I atom giving I_2 and a free *sec.*-Bu radical. Racemisation of the undecomposed fraction also occurs as a result of a Walden inversion caused by at. exchange through collision between an I atom and a (I) mol. A heterogeneous racemisation of optically active (I) by added I at a soft glass surface, apparently due to I atoms adsorbed at the surface, takes place at temp. as low as 150°. Heats of activation of the different reactions are given. The racemisation observed is evidence for the hypothesis that substitution by free atoms in org. mols. causes optical inversion.

M. S. B.

Kinetics of the depolymerisation of bimolecular nitrosoisopropylacetone. K. D. ANDERSON and D. L. HAMMICK (J.C.S., 1935, 30–32).—The rate of depolymerisation of colourless nitrosoisopropylacetone in C_6H_6 solution in the dark has been determined between 8° and 22° by the intensity of the colour of the monomeric form produced. The heat of activation is 26,600 g.-cal., assuming that the necessary energy is derived from binary collisions between solvent and solute. The no. of degrees of freedom involved in the activation of the reactant is 5.

J. G. A. G.

Thermal decomposition of propylamine. D. V. SICKMAN and O. K. RICE (J. Amer. Chem. Soc., 1935, 57, 22–24).—The reaction is of the first order at < 4 mm. pressure, but is strongly inhibited by increase of surface; this effect diminishes and finally disappears as the pressure is increased. A chain mechanism is probable.

E. S. H.

Kinetics of the oxidation of gaseous propaldehyde. E. W. R. STEACIE, W. H. HATCHER, and S. ROSENBERG (J. Physical Chem., 1934, **38**, 1189—1200).—Between 120° and 170° the reaction is a chain process and resembles the oxidation of MeCHO. The heat of activation is 15,400 g.-cal. per mol. No evidence of explosion limits was found. A surface reaction is also present. D. R. D.

Kinetics of the decomposition of nickel carbonyl. C. E. H. BAWN (Trans. Faraday Soc., 1935, **31**, 440—446).—The decomp. of Ni(CO)₄ into Ni and CO, in Ni-coated glass vessels, goes practically to completion at 100—128°. 20% of the reaction is heterogeneous, but this and the homogeneous reaction also are inhibited by CO and give the same velocity relationship $dx/dt = k_{i[Ni(CO)_4]} / (1 + k'_{[CO]})$. It is suggested that the dissociation takes place in > one stage. The activation energy is 10,250 g.-cal. The results are in agreement with those of Garratt and others (this vol., 40). M. S. B.

Decomposition of substances at linearly increasing temperatures. P. VALLET (Compt. rend., 1935, **200**, 315—317).—An expression is developed for the irreversible unimol. decomp. of a solid when the temp. is increasing linearly with time. Its validity is confirmed by reference to previous experimental results (A., 1934, 859). M. S. B.

Kinetics of decomposition of single crystals of calcite. S. BRETSZNAJDER (Rocz. Chem., 1934, **14**, 843—848).—The velocity, v , of decomp.-% decomp. curves of single crystals of calcite (I) present irregularities not observed with numerous crystals. This effect is ascribed to differences in the no. and distribution of active centres (II) originally present, and in the rate of formation of new (II) during the reaction. The initial v of (I) is increased by scratching the crystals, also as a result of increase in the no. of (II). R. T.

Electrostatic factors affecting acidity and chemical reactivity. W. A. WATERS (Helv. Chim. Acta, 1935, **18**, 5).—A claim for priority against Schwarzenbach and Egli (A., 1934, 1310).

F. L. U.

[Electrostatic factors affecting acidity and chemical reactivity.] G. SCHWARZENBACH and H. EGLI (Helv. Chim. Acta, 1935, **18**, 6).—A reply to Waters (preceding abstract).

F. L. U.

Kinetic salt effect in the fourth-order reaction $BrO_3' + Br' + 2H' \rightarrow$ Ionisation quotients for HSO_4' at 25°. W. C. BRAY and H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1934, **57**, 51—56).—The initial rates of the reaction $BrO_3' + 5Br' + 6H' = 3Br_2 + 3H_2O$ (1) have been measured at 25°, and compared with published data for the reaction $BrO_3' + 3H_2O_2 = 3O_2 + Br' - 3H_2O$ (2) and with published kinetic data for (1) and (2) in H_2SO_4 solutions. At low ionic concns., k_1 increases rapidly with decreasing ionic concn., and the extrapolated val. agrees with k_2 . At ionic concns. > 0.02, k_2 and the difference increases with increasing ionic concn. High vals. of k_1 obtained at high concns. of NaBr indicate the existence of a fifth-order $BrO_3' - Br'$ reaction. Ionisation quotients

for HSO_4' have been calc. from the kinetic data for H_2SO_4 solutions. E. S. H.

Kinetics of absorption of oxides of nitrogen by sulphuric acid. I. N. KUZMINICH, E. L. JACHONTOVA, and E. I. SURKOV (J. Chem. Ind. Russ., 1934, **10**, No. 11, 38—45).—The velocity V of absorption of NO₂ by H_2SO_4 (I) is at a min. for 85% (I), corresponding with max. η . V diminishes with rise in temp., owing to increase in the η of the gaseous phase. The gas is absorbed as NO₂, and not N₂O₄. In the case of N₂O₃, V increases with increasing concn. of (I), and falls with rise in temp. R. T.

Theory of semiquinone formation and its application. B. ELEMA (Rec. trav. chim., 1935, **54**, 76—78).—The formation const., K , of semiquinones can be determined accurately by the author's electrode equation (4) or by direct titration. Vals. obtained by means of A for hepato- and photohepato-flavin differ from those given in the lit. R. S. C.

Electromotive force measurements of hydrochloric acid solutions with and without sucrose and their relation to the rate of sucrose hydrolysis. V. K. KRIEBLE and F. M. REINHART (J. Amer. Chem. Soc., 1935, **57**, 19—22).—The activities have been calc. from e.m.f. measurements of HCl and of HCl+sucrose (1—4M) at 20°. The velocity coeffs. of hydrolysis of sucrose (0.292M) by HCl (1—9M) have been determined. A relation between velocity coeff. and the calc. activity has been noted.

E. S. H.

Activities and the hydrolysis of sucrose with concentrated acids. V. K. KRIEBLE (J. Amer. Chem. Soc., 1935, **57**, 15—19).—Velocity coeffs. for the hydrolysis of sucrose by HCl, H_2SO_4 , and HBr are not directly \propto acid concn. or H^+ activity. The results with HCl suggest that the hydrolysis is catalysed partly by H^+ and partly by HCl or $H^+ + Cl^-$.

Mechanism of dissolution of metals. M. CENTNERSZWER and W. HELLER (Rocz. Chem., 1934, **14**, 525—559).—A description of the methods involved in the study of the kinetics of dissolution of metals is given, and the nature of the processes taking place is discussed on the basis of a comprehensive survey of the literature. R. T.

Action of acids on zinc. T. O. POULTER and G. E. FRAZER (J. Physical Chem., 1934, **38**, 1131—1140).—The great decrease in the rate of reaction under pressure previously reported was not confirmed and was due to grease on the Zn. The e.m.f. of the cell $Zn|N-H_2SO_4|Pt$ (platinised) is reversed under pressure because of the reduction to H_2S . Reversal does not occur with bright Pt or in HCl. D. R. D.

Velocity of dissolution of sodium in solutions of alcohols in benzene, toluene, and xylene. J. SZPER [with M. JASIŃSKA, K. PRZYBYSZEWSKA, T. BRODZKA, and L. WIZENFELD] (Rocz. Chem., 1934, **14**, 590—597).—The velocity of dissolution (v) of Na in solutions of EtOH or MeOH in C_6H_6 , PhMe, or xylene falls with time, probably owing to decomp. of traces of H_2O originally present. $v \propto [H^+]$. The temp. coeff. of the reactions, and the accelerating

effect of stirring, point to the diffusive nature of the process. R. T.

Relation between rate of dissolution, solvent, and lattice forces in single copper crystals. R. GLAUNER (Ber. Korros.-Tag., 1934, 1933, 36—41; Chem. Zentr., 1934, ii, 2129).—With acid- H_2O_2 mixtures two types of dissolution mechanism operate: (1) the Cu^{++} accelerates dissolution by the process $\text{Cu} + \text{Cu}^{++} = 2\text{Cu}^+$ (e.g., with HCl), and (2) the Cu^{++} has no effect (e.g., with H_2SO_4 , HNO_3 , and H_3PO_4). In dil. solution without H_2O_2 the Cu^{++} accelerates dissolution by the above mechanism. The rate of dissolution from different crystal faces in the same solution is const. The nature of the anion is the decisive factor in the mechanism of dissolution.

H. J. E.

Catalytic action of silver ions on the velocity of oxidation of manganous salts by persulphates. E. BEKIER and W. KIJOWSKI (Rocz. Chem., 1934, 14, 1004—1016).—The velocity of the reaction between MnSO_4 in 2.24*M*- H_2SO_4 and $\text{K}_2\text{S}_2\text{O}_8$ in presence of Ag_2SO_4 is independent of the $[\text{MnSO}_4]$, and $\propto [\text{K}_2\text{S}_2\text{O}_8]$ and $[\text{Ag}_2\text{SO}_4]$. The process consists of the relatively slow reaction $\text{Ag}^+ + \text{S}_2\text{O}_8^{--} \rightarrow \text{Ag}^{+++} + 2\text{SO}_4^{--}$, and of the instantaneous reaction $5\text{Ag}^{+++} + 2\text{Mn}^{++} + 8\text{H}_2\text{O} \rightarrow 5\text{Ag}^+ + 2\text{MnO}_4^- + 16\text{H}^+$. The velocity of the former reaction varies with the total ionic concn. in accordance with Bronsted's theory. R. T.

Catalytic action of salts on the velocity of ionic reactions. Specific action of ions on the velocity of the reaction $\text{CH}_3\text{Cl} \cdot \text{CO}_2' + \text{S}_2\text{O}_3^{--} \rightarrow \text{S}_2\text{O}_3 \cdot \text{CH}_3 \cdot \text{CO}_2' + \text{Cl}'$. E. BEKIER and Z. ŻELAZNA (Rocz. Chem., 1934, 14, 994—1003).—The reaction is accelerated by cations in the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+$; $\text{Ba}^{++} > \text{Sr}^{++} > \text{Ca}^{++}$, and by anions in the order $\text{Br}^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{--}$. The activities of Na^+ , Ca^{++} , and La^{++} are as 1 : 1.5 : 3.25. R. T.

Influence of temperature on catalysis. Hydrolysis of ethyl acetate at 25—60°. W. WYCZALKOWSKA (Rocz. Chem., 1934, 14, 1118—1122).—The temp. coeff. τ of the reaction $\text{EtOAc} \rightleftharpoons \text{EtOH} + \text{AcOH}$ is independent of the concn. of HCl present; the heat of activation, Q , at 25—60°, and at various HCl concns., is const. at 16,405 g.-cal. The vals. of τ and Q in presence of HCl and NaCl or NaNO_3 are < in presence of HCl alone. R. T.

Catalytic decarboxylation of β -keto-acids. K. BENIYA (J. Biochem. Japan, 1934, 20, 451—463).—The catalysis (I) by 32 N-containing org. substances of the decarboxylation (II) of acetonedicarboxylic acid and $\text{CHAc} \cdot \text{CO}_2\text{H}$ at various $[\text{H}^+]$ was investigated. (II) occurs spontaneously and increases with increasing acidity. With (I), optimum p_{H} vals. occur, e.g., at p_{H} 3.8 and 3.7 for 0.1*M*- NH_2Ph and 0.01*M*- α - $\text{C}_6\text{H}_4(\text{NH}_2)_2$, respectively, on $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{H}$.

F. O. H.

Catalytic oxidation of carbohydrates and related compounds by oxygen in presence of iron pyrophosphates. XII. Ethyl alcohol, acetaldehyde, acetic acid, and sodium acetate. E. F. DEGERING (Proc. Indiana Acad. Sci., 1934, 43, 105—106; cf. A., 1932, 476).—Of the above, only MeCHO is oxidised under the conditions described.

CH. ABS. (r)

Influence of H_2O and $\text{H}^+\text{H}_2\text{O}$ on the mutarotation of glucose. W. H. HAMMILL and V. K. LA MER (J. Chem. Physics, 1934, 2, 891).—Determinations of the velocity of mutarotation of α -*D*-glucose in heavy H_2O mixtures at 25° and p_{H} 4—6, at which there is mol. catalysis only, and not ionic, give vals. which deviate appreciably from a linear function of the mol. fraction of H_2O . $k_{\text{H}_2\text{O}} = 9.01 \times 10^{-5}$. Experiments in more acid solutions indicate that the acidic catalytic const. in mixtures, is an approx. linear function of the vals. of k_{H^+} and $k_{\text{H}_2\text{O}}$.

M. S. B.

Poisoning and activation of aluminium. T. PIERZCHALSKI (Rocz. Chem., 1934, 14, 608—613).—The velocity of dissolution (v) of Al in 1.4*N*- HCl at 25° falls to half the original val. (I) as the concn. of HCNS increases to 0.0005*N*, thereafter rising to attain (I) at 0.05*N*- HCNS . $\text{CS}(\text{NH}_2)_2$ reduces v to an extent \propto its concn., whilst $\text{CO}(\text{NH}_2)_2$ has no action. H_2S , CS_2 , KCl , K_2SO_4 , AlCl_3 , and FeCl_3 accelerate the reaction. v is gradually decreased by HCN , whilst I , similarly to other oxidising agents, passivates Al .

R. T.

Reduction of the rate of dissolution of aluminium in hydrochloric acid by β -naphthoquinoline. E. JENCKEL and E. BRAUCKER (Z. anorg. Chem., 1935, 221, 249—276).—In order to investigate the action of protective agents in the dissolution of metals, the inhibiting effect of β -naphthoquinoline (I) on the dissolution of Al in 3—6*N*- HCl has been determined at 0°, 25°, and 50°. The rate falls quickly at first with increase in concn. of (I), and then more slowly. For the same concn. of (I), the effect diminishes with rise of temp. and increases with increase in $[\text{HCl}]$. Current-voltage curves for different concns. of (I) in 1.5*N*- HCl shows a diminution in current strength with increase in concn. of (I). The results are explained on the assumption that dissolution of the metal is due to local electrolytic action, and the inhibiting effect of (I) is due to formation of a protective layer on the local cathode. The potential of the metal and the surface tension of the solution are so little affected by (I) that it is not possible to ascribe the inhibiting action to these influences. In presence of (I), Cu may be deposited on Al as a smooth adherent film, probably owing to complex formation. In absence of (I) the Cu deposit is spongy.

M. S. B.

Kinetics of the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ with a vanadium catalyst. N. F. MAKLAPOV and M. S. ARKHIPOV (Khimstroi, 1934, 6, 318—321).—At 450—500° the kinetics of the reaction with Ba-V and Ca-V catalysts resembles that with a Pt catalyst. At < 450° the velocity falls sharply with a V catalyst. Ba-V is more active than Ca-V at 450—500°.

CH. ABS. (e)

Catalytic action of Japanese acid earth. IX. Promotion and poisoning of the catalytic action. K. ISHIMURA (Bull. Chem. Soc. Japan., 1934, 9, 521—530; cf. this vol., 44).—The activity of Japanese acid earth (I), measured in terms of the yield of resinous substance produced from C_{10}H_8 under conditions already described (*loc. cit.*), decreases with rise in the temp. of drying from 100° to 800°, but increases

with increase of H_2O "retained" after a subsequent adsorption and drying treatment. With other adsorbates, the "degree of promotion" effected per millimol. of "retained" vapour is $\text{Et}_2\text{O} > \text{EtOH} > \text{MeOH} > \text{COMe}_2 > \text{H}_2\text{O}$, parallel with the order of increasing heat of adsorption on fuller's earth and decreasing order of solubility of C_{10}H_8 . The recovery of catalytic activity is accomplished by the adsorbate "retained" forming active centres after the dried (I) has been treated with vapour. "Retained" EtOAc is a weak catalyst and AcOH and HCl are weak poisons, whilst NH_3 , NH_2Me , MeCN , and amyl nitrite are strong poisons. C_6H_6 , PhMe , *cyclohexane*, *cyclohexene*, *methylcyclohexenes*, and PhCl have no effect.

J. G. A. G.

Kinetics of the catalytic dehydrogenation of dimethylcyclohexane. A. A. BALANDIN and J. K. JURIEV (J. Phys. Chem. U.S.S.R., 1934, 5, 393—406).—The reaction rate was measured as a function of temp. and concn. on Ni and Al oxide catalysts, using mixtures of dimethylcyclohexane (I) and xylene (II). For mixtures with 20—100% of (I) the energy of activation (200—350°) was 14,700 g.-cal. per mol. It fell to 12,300 g.-cal. per mol. in a 10% mixture. CH_4 formation was slight when (I) was pure. The rate of dehydrogenation of (I) was slightly > that for *cyclohexane*. The val. of N for mixtures of (I) and (II) \propto the composition. CH. ABS. (e)

Preparation of anhydrous aluminium chloride by catalytic chlorination of kaolin.—See B., 1935, 99.

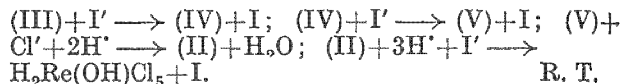
Titanomagnetite as a catalyst for ammonia synthesis.—See B., 1935, 99.

Catalytic hydrolysis of chlorobenzene by steam.—See B., 1935, 137.

Sulphuric acid as catalyst for the ethylation of arylamines by alcohol.—See B., 1935, 137.

Anomalous electrolysis of water. M. KATALINIĆ (Arh. Hemiju, 1934, 8, 145—149).—The results previously described, in connexion with liquid currents and space charge around wire electrodes (A., 1932, 981), are discussed. R. T.

Reduction of perrhenic acid. B. JEŻOWSKA (Rocz. Chem., 1934, 14, 1061—1087).— KReO_4 (I) in 6*N*- HCl undergoes electro-reduction to yield Re^{V} . Pt electrodes readily undergo polarisation, and platinised Pd electrodes are recommended; depolarisation may also be effected by adding HI to the electrolyte. The reduction of cold aq. (I) by HI proceeds in two stages: $\text{Re}^{\text{VII}} + 2\text{I}^- \longrightarrow \text{Re}^{\text{V}} + 2\text{I}$; $\text{Re}^{\text{V}} + \text{I}^- \longrightarrow \text{Re}^{\text{IV}} + \text{I}$. Re^{V} is characterised, in contrast to Re^{IV} , by the facility with which it is hydrolysed by H_2O , to yield chiefly hydrated ReO_2 , originating as follows: $3\text{Re}^{\text{V}} + 2\text{H}_2\text{O} \longrightarrow 2\text{Re}^{\text{IV}} + \text{Re}^{\text{VII}}$. A by-product of reduction of (I) is the yellowish-green ion ReOCl_5^- (II); the salts K_2ReOCl_5 and $(\text{NH}_4)_2\text{ReOCl}_5$, obtained by adding 2 equivs. of HI to cold (I) in conc. HCl , are described. The process of electro-reduction consists of the stages: $\text{ReO}_4^- + 4\text{HCl} \longrightarrow \text{ReO}_2\text{Cl}_4^-$ (III) + H_2O ; (III) $\longrightarrow \text{ReO}_2\text{Cl}_4^{2-}$ (IV) $\longrightarrow \text{ReO}_2\text{Cl}_4^{3-}$ (V); (V) + $\text{H}^+ + \text{HCl} \longrightarrow$ (II) + H_2O ; (IV) \longrightarrow (III) + (V), whilst reduction with HI involves the reactions:



R. T.

Simultaneous discharge [of ions] at the cathode in the electrolysis of zinc [sulphate]. O. ESSIN and A. BALABAJ (J. Chim. phys., 1934, 31, 559—567; cf. A., 1933, 468).—A general equation giving the current yields of two species of ion when discharged simultaneously agrees well with the results of Roentgen and Hoegel on the electrolysis of aq. ZnSO_4 containing varying amounts of H_2SO_4 .

F. L. U.

Electrodeposition of zinc.—See B., 1935, 154.

Effect of germanium in the electrolysis of zinc sulphate solutions.—See B., 1935, 154.

Electrolytic preparation of sodamide.—See B., 1935, 107.

Regulation of the bath solution for the electrolytic oxidation of aluminium.—See B., 1935, 154.

Electrolytic reduction of methyl *n*-propyl ketone to *n*-pentane. S. SWANN, jun., and J. FELDMAN (Trans. Electrochem. Soc., 1935, 67, 19—24; cf. A., 1932, 1005).—In aq.- EtOH H_2SO_4 solutions of COMePr^2 the best yields of *n*- C_5H_{12} are obtained at cathodes of Cd, Zn, Pb, and Hg, the efficiency of electrolytic reduction decreasing in this order. Variation of c.d. between 0.05 and 0.22 amp. per sq. cm. has little effect on the yield, except at Pb cathodes where the lower c.d. is advantageous and at Fe cathodes where the higher c.d. is better. The optimum $[\text{H}_2\text{SO}_4]$ is 30%, except with Pb cathodes, where a lower concn. is better, and with Hg cathodes, where the concn. should be higher. H. J. T. E.

Cathodic combustion of hydrogen and carbon monoxide. G. I. FINCH (J.C.S., 1935, 32—39).—From a survey of the results obtained by the author and others it is concluded that the cathodic combustion of dry CO-O_2 mixtures in the absence of metal, M, atoms (non-sputtering cathode) involves $2\text{CO} = \text{CO}_2 + \text{C}$ followed immediately by the oxidation of the C, but direct oxidation of CO to CO_2 is not excluded. In the presence of M atoms (sputtering cathode), an unstable oxide, MO, first formed leads to $\text{CO} + \text{MO} = \text{CO}_2 + \text{M}$. With $\text{CO-O}_2\text{-H}_2$ mixtures in the absence of M atoms, the H_2 burns by way of OH to H_2O , and the CO is then oxidised by the processes $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ and $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. The initial step in the combustion of rigidly dried $\text{H}_2\text{-O}_2$ mixtures in the absence of M atoms is $\text{H}_2 + \text{O}_2 = 2\text{OH}$, but with traces of H_2O , $2\text{H}_2\text{O} = 2\text{OH} + \text{H}_2$, and the OH formed promotes the succeeding stages of the combustion. This probably explains the effect of traces of steam on the ignitability by an electric discharge of a $2\text{CO} + \text{O}_2 + (\text{H}_2)$ mixture. With atoms of M, MO is first formed and reacts $\text{H}_2 + \text{MO} = \text{H}_2\text{O} + \text{M}$. The relation of these results to flame combustion is considered.

J. G. A. G.

Mechanism of carbon dioxide and hydrogen peroxide formation. W. F. JACKSON (J. Amer. Chem. Soc., 1935, 57, 82—89).—CO is oxidised by the products of an electrical discharge through H_2O vapour at pressures < 1 mm. Large quantities of H_2O_2 are found in the products of discharge. The

effects of added gases, of varying the discharge current, and of interposing dehydrogenation and dehydration catalyst surfaces, on the yields of CO_2 and H_2O_2 have been studied. The yields of H_2O_2 and CO_2 from mixtures of O_2 , CO , H_2 , and H_2O under various conditions have been determined. Mechanisms of reaction are suggested. E. S. H.

Unsaturated silicon hydride. R. SCHWARZ and F. HEINRICH (Z. anorg. Chem., 1935, 221, 277—286).—The decomp. of SiH_4 by the silent electrical discharge in an ozoniser gives highly polymerised solid unsaturated hydrides. The composition varies between $\text{SiH}_{1.2}$ and $\text{SiH}_{1.7}$ according to conditions. The product consists of brown leaflets with a metallic lustre, easily sol. in aq. NaOH , but stable towards 30% H_2O_2 and aq. KMnO_4 . By the decomp. of CaSi with glacial AcOH or HCl in abs. EtOH , polysilene, $(\text{SiH}_2)_x$, is obtained; it is light brown, ignites spontaneously in air, and is decomposed by acids or alkalis forming H_2 and SiO_2 , but no SiH_4 , thus differing in behaviour from polygermene. By heating $(\text{SiH}_2)_x$ in vac. a series of saturated silanes is formed, as also by hydrolysing CaSi with aq. HCl , polysilenes of low mol. wt. being formed as intermediate products. M. S. B.

Mercury-sensitised decomposition of azoimide. A. E. MYERS and A. O. BECKMAN (J. Amer. Chem. Soc., 1935, 57, 89—96).—The final products of decomp., using λ 2537 Å. over the pressure range 0.3–20 mm., are NH_3 and N_2 . NH_4N_3 and H_2 are formed as intermediate products during the earlier stages of decomp. The quantum yield for the initial stage is approx. 2.86 mols. of HN_3 decomposed per quantum absorbed when calc. to the formation of NH_4N_3 , or 3.6 when calc. to the formation of NH_3 . E. S. H.

Influence of irradiation on the formation and decomposition of colloidal sodium in rock-salt. S. A. ARZIBISCHEV, L. B. MILKOVSKAJA, and M. V. SAVOSTJANOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 382—389).—The absorption max. and max. absorption coeff. have been determined for crystals heat-treated in different ways. E. S. H.

Energytransformations at surfaces. VIII. Importance of metastable conditions for sensitised photo-oxidations. H. KAUSKY, A. HIRSCH, and W. FLESCH (Ber., 1935, 68, [B], 152—162; cf. A., 1933, 1256).—In the photo-sensitised oxidation of isoamylamine (I) and allylthiocarbamide (II) in presence of haematoporphyrin (III), chlorophyll (IV), and other pigments, O_2 is regarded as the substance which withdraws the exciting energy from (III) and (IV), since it is the sole type of mol. which depresses the fluorescence of (III) and (IV). (I) and (II) have no visible effect on the fluorescence of (III) and (IV). Fluorescence is not completely destroyed in presence of (II) (cf. Gaffron, A., 1927, 429), and the presence of long-lived metastable conditions of excitation is established by the observation of phosphorescence which may persist for 10^{-2} sec. in very dil. solutions of many dyes in absence of O_2 . The influence of concn., temp., and solvent on phosphorescence is described. In all media, very small amounts of O_2 quench phosphorescence, which is not affected by

acceptors. The primary process in the photo-oxidation of (I) and (II) in solution is activation of the O_2 mols. by the dye. Oxidation of the acceptor by the activated O_2 mols. is a secondary process. The mechanism of the change is the same in solution and in heterogeneous systems. A new interpretation of Gaffron's observations on rubene is given. H. W.

Action of water on the latent photographic image. T. H. JAMES, F. E. E. GERMANN, and J. M. BLAIR (J. Physical Chem., 1934, 38, 1211—1216).—Vapours of H_2O , HCO_2H , AcOH , and $(\text{CH}_3)_2\text{OH}_2$ cause fading of the undeveloped image. Et_2O , dry EtOH , CCl_4 , CS_2 , C_6H_6 , and PhNO_2 have no effect. The former materials swell gelatin; the latter do not. Exposure to H_2O vapour sensitises an emulsion. Age mottle is due to moisture and does not develop over P_2O_5 . D. R. D.

Water effect in infra-red plates. K. WEBER (Phot. Korr., 1934, 70, 105—106; Chem. Zentr., 1934, ii, 1721).—The H_2O effect (I) (i.e., increased sensitivity on wetting the plates and drying before exposure) is especially marked in the red and infra-red. H_2O has no such effect after exposure. (I) is attributed to a more intense dyeing of the Ag halide during swelling of the gelatin by dye particles present in it. H. J. E.

Colloidal electrolytes in photography. F. WEIGERT (Trans. Faraday Soc., 1935, 31, 359—365).—On the basis of the photodichroism of dry photographic emulsions, a scheme is suggested for the reaction mechanism between AgBr and the micelles of the photo-sensitive colloidal electrolyte composing the emulsion, when light acts on a photographic plate. M. S. B.

Blackening of photographic plates by very slow electrons. O. MEIER (Physikal. Z., 1935, 36, 8—14).—Blackening of special photographic plates by electrons of only 5 volts energy has been obtained. This limit is imposed by the apparatus, and is not necessarily the lowest that can be recorded. A. J. M.

Systematic calculation and technique of the preparation of heavy water. P. GOLDFINGER and L. SCHEEPERS (J. Chim. phys., 1934, 31, 628—646).—After reduction of the initial vol. of the H_2O to 1/20—1/30 it is economic to recombine the gases evolved and re-electrolyse. The addition of further H_2O during electrolysis to maintain a const. level diminishes the yield. 1 g. of solution containing 90% H_2^{18}O can be obtained by decomp. of 10—15 litres of ordinary H_2O , corresponding with 30,000—45,000 amp.-hr. Electrolytic cells of Fe are described, with electrodes 6 mm. apart and permitting of the passage of 400 amp. at a c.d. of 0.1—0.3 amp. per sq. cm. Working at 2.5—3 volts with 1—8% aq. NaOH as electrolyte 100—150 kw.-hr. are consumed per g. of 90% H_2^{18}O solution prepared. Apparatus is also described for the safe recombination of the gases evolved. The equipment works with a separation factor of about 6. J. W. S.

Preparation of heavy water. B. KAMIENSKI (Rocz. Chem., 1934, 14, 401—405).—Electrolysis of 30 litres of H_2O yielded a residue of 27 c.c., containing 0.1% of H_2^{18}O ; of the H_2O removed, $\frac{1}{3}$ was accounted

for by electrolytic decomp., and $\frac{2}{3}$ by evaporation. In view of the lower surface tension and dielectric const. of H_2O , the latter might be assumed to undergo concn. at the air- H_2O interface, and to be hence the most exposed to evaporation, and the unsatisfactory concn. of H_2O achieved is ascribed to this circumstance. The isotopic identity of Dead Sea H_2O with ordinary H_2O is due to the same factors. R. T.

Cleaning liquid sodium-potassium alloy. J. F. BIRMINGHAM, jun. (Ind. Eng. Chem. [Anal.], 1935, 7, 53).—The globules are cleaned with a dil. solution of EtOH in C_6H_6 . E. S. H.

Complex salts of tartar emetic. J. V. DUBSKÝ and T. BERGER (Z. anorg. Chem., 1935, 221, 367—368).—By replacement of K in tartar emetic (I) by the action of amines the following compounds have been obtained: $(\text{C}_2\text{H}_4\text{O}_2\text{Sb}=\text{E}) \cdot \text{E}_2[\text{Co}(\text{NH}_3)_6]\text{Cl} \cdot 4\text{H}_2\text{O}$, yellow; $\text{E}_4[(\text{NH}_3)_4\text{Co}(\text{OH})_2 \cdot \text{Co}(\text{NH}_3)_4] \cdot 3\text{H}_2\text{O}$, violet; $\text{E}_4[(\text{H}_2\text{O})_2\text{Co}\{(\text{OH})_2 \cdot \text{Co en}_2\}_2] \cdot 4\text{H}_2\text{O}$, rose; $\text{E}_3[\text{Co}\{(\text{OH})_2 \cdot \text{Co en}_2\}_3](\text{NO}_3)_3 \cdot 5.5\text{H}_2\text{O}$, brown. The formation of these compounds can be used as a qual. test for (I). M. S. B.

Precipitation of copper under pressure by means of organic reducing agents. V. I. LAINER E. V. NATANSON, and A. A. ORIONOV (Tsvet. Met., 1933, No. 6, 87—102).—By reduction with substances containing cellulose, e.g., sawdust, at $160\text{--}170^\circ/6\text{--}8$ atm., 80—85% pptn. of Cu is possible. The yield is practically independent of [Cu]. Ag and Hg can be recovered similarly. CH. ABS.

Preparation and properties of some cupritetra-chlorides and -bromides. J. AMIEL (Compt. rend., 1935, 200, 138—140).—By interaction in aq. solution of CuCl_2 or CuBr_2 with the amine hydrochloride, followed by evaporation below 100° at reduced pressure, the following compounds have been obtained: $[\text{CuCl}_4](\text{NH}_3\text{Me})_2$; $[\text{CuCl}_4](\text{NH}_3\text{Et})_2$; $[\text{CuCl}_4](\text{NH}_3\text{Pr}^e)_2$; $[\text{CuCl}_4](\text{NH}_3 \cdot \text{CH}_2\text{Ph})_2$; $[\text{CuCl}_4](\text{NH}_3 \cdot \text{CH}_3)_2$; $[\text{CuBr}_4](\text{NH}_3\text{Me})_2$; $[\text{CuBr}_4](\text{NH}_3\text{Et})_2$; $[\text{CuBr}_4](\text{NH}_3\text{Pr}^e)_2$; $[\text{CuBr}_4](\text{NH}_3 \cdot \text{CH}_2\text{Ph})_2$; $[\text{CuBr}_4](\text{NH}_3 \cdot \text{CH}_3)_2$. They have also been prepared by action of Cl_2 , HCl, or HBr on the complex chlorates (cf. A., 1934, 978, 1080). The cupritetra-chlorides and -bromides form small yellow and black plates, respectively. They are all very sol. in H_2O , dil. solutions being blue owing to dissociation of the complex. They melt (decomp.) at $125\text{--}150^\circ$ or a little above 200° [$(\text{CH}_2\text{NH}_2)_2$ compounds]. Addition of NH_3 produces a deep blue colour, and conc. KOH ppts. $\text{Cu}(\text{OH})_2$ with liberation of the amine. The Cl compounds are converted into the Br compounds by action of HBr; treatment with Cl_2 effects the reverse change. J. W. S.

Preparation and properties of copper ferrite. F. S. WARTMAN and A. J. THOMPSON (U.S. Bur. Mines, Rept. Invest., 1934, No. 3228, 15—21).—Vals. are recorded for the ferrite formation on heating mixtures of Fe and Cu oxides at a series of temp. from 110° to 1000° . Quenching in H_2O after heating at $900\text{--}1000^\circ$ gave a magnetic product (cubic; a 8.40 Å.; almost identical with magnetite). Slow cooling, or annealing at 350° , gave a tetragonal structure (a 8.28,

c 8.68 Å.). Cu ferrite was hexagonal (a 6.06, c 2.82 Å.). Solubilities in HCl, H_2SO_4 , and HNO_3 are recorded.

CH. ABS. (e)

Chemical reactivity of redistilled magnesium. Action of water and of carbon dioxide on magnesium at room temperature. P. REMY-GENNETÉ (Bull. Soc. chim., 1934, [v], 1, 1674—1678).—Mg redistilled in vac. liberates H_2 from H_2O at room temp. and slowly absorbs dry CO_2 forming Mg carbide at the surface. J. G. A. G.

Action of mercury vapour on calcium at room temperature. P. REMY-GENNETÉ (Bull. Soc. chim., 1934, [v], 1, 1671—1674).—Under the conditions, redistilled Ca absorbs, in vac. during 4 months, approx. 5% of its wt. of Hg vapour. J. G. A. G.

Reactions in systems consisting of three phases (two solid and one gaseous). J. ZAWADZKI (Rocz. Chem., 1934, 14, 823—842).—The mechanism of the reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ is discussed. R. T.

Study of the reaction between calcium oxide and sulphur dioxide by the flow method. M. ILINSKI (Rocz. Chem., 1934, 14, 857—864).—The system is univariant; irregularities in the % decomp.-pressure curves are due to the same causes as in the case of CaSO_4 (this vol., 303). R. T.

The hydrotimetric method. M. LEMARCHANDS and LE VIET KHOA (Ann. Chim. Analyt., 1935, [iii], 17, 5—16).—The formation of a lather is conditioned by: (1) a lowering of the surface tension of the H_2O by the soap, (2) the hydrolysis of the soap which forms, depending on the p_{H} , acid salts of the fatty acids of the soap or free fatty acid, and (3) the presence of unhydrolysed soap. There is an optimum relation between acid mols. and soap, and within limits, the smaller are the particles of the disperse phase, the smaller is the quantity of soap required. Neutral salts of K, Na, and NH_4 alone have little effect on lather formation, but hinder the pptn. of Ca salts and in some cases prevent pptn. of Mg salts, thus indicating a source of error in the analysis of saline H_2O . Except with low $[\text{Ca}^{++}]$, the quantity of soap required to produce a lather does not increase in direct proportion to $[\text{Mg}]$ and $[\text{Ca}]$. J. G. A. G.

Monocalcium phosphate as basis of organophosphors. E. TIEDE and H. CHOMSE (Ber., 1935, 68, [B], 146—148; cf. this vol., 234).—Weighed quantities of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and the org. compound are intimately mixed in a porcelain mortar and heated at about 250° on Pt foil or porcelain until the mass has become plastic. (I) is thereby converted into a mixture of $\text{Ca}(\text{PO}_3)_2$ and $\text{Ca}_2\text{P}_2\text{O}_7$. Luminous preps. are obtained with uranin, $m\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, phenanthraquinone, $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$, $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$, poor results with 1-hydroxynaphthoic acid, and negative results with $o\text{-OH-C}_6\text{H}_4\text{CO}_2\text{H}$ and anthracene. Small amounts of metals (Cu, Bi, Mn) do not induce luminescence. Comparison is made with H_3BO_3 phosphors. H. W.

Complex salts of 2 : 2'-dipyridyl with zinc and cadmium. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 753—760).—The prep. and crystallographic characteristics of the

following complex salts with dipyrldyl (R) are described: $[\text{ZnR}_3]\text{SO}_4 \cdot 7\text{H}_2\text{O}$; $[\text{ZnR}(\text{H}_2\text{O})_2]\text{SO}_4$; $[\text{ZnRCl}_2]$; $[\text{ZnR}_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$; $[\text{CdR}_2](\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$; $[\text{CdR}_3](\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$; and $[\text{CdR}(\text{H}_2\text{O})_2](\text{NO}_3)_2$.

J. W. B.

Reduction of alkaline-earth arsenates by carbon. Tribarium arsenate. H. GUÉRIN (Compt. rend., 1935, 200, 129—131).—A mixture of $\text{Ba}_3(\text{AsO}_3)_2 + 8\text{C}$ reacts in vac. at 750—800°, successive reduction occurring to $\text{Ba}_3(\text{AsO}_2)_2$ and then to BaO and As . The latter reaction is slower than the former. Above 850° the products contain BaO , C , $\text{Ba}_3(\text{AsO}_2)_2$, and Ba_3As_2 . Inefficient removal of the CO formed favours the formation of Ba_3As_2 .

J. W. S.

Preparation of phosphorescent substances. VII. Boric anhydride. N. F. SHIROV (J. Appl. Chem. Russ., 1934, 7, 921—925).—The product of heating H_3BO_3 at 800° with 0.1 p.p.m. of sucrose exhibits fairly intense greenish-yellow phosphorescence. The structure of the active centres is discussed.

R. T.

Thermal decomposition of metallic borofluoride amines. G. BALZ and W. ZINSER (Z. anorg. Chem., 1935, 221, 225—248).— $\text{Ni}(\text{NH}_3)_6(\text{BF}_4)_2$ is irreversibly decomposed by heat giving NiF_2 , NH_3 , and a sublimate of $\text{BF}_3 \cdot \text{NH}_3$. An attempt was made to employ this reaction for the prep. of anhyd. NiF_2 , but it was not possible to remove the last traces of NH_3 . V.p. determinations of $\text{BF}_3 \cdot \text{NH}_3$ have been made. The compound $\text{Zn}(\text{NH}_3)_6(\text{BF}_4)_2$ has been prepared by the action of NH_3 on the tetrammine. Both the Zn and Cd hexammines form the corresponding tetrammines reversibly. The further decomp., giving ZnF_2 or CdF_2 , $\text{BF}_3 \cdot \text{NH}_3$, and NH_3 , takes place irreversibly. The heats of formation of the Zn and Cd hexammines from the tetrammines at 0° and 100°, respectively, are 10.9 and 16.7 kg.-cal.

$\text{Cr}(\text{NH}_3)_6(\text{BF}_4)_3$ behaves similarly to the Ni compound giving CrF_3 . $\text{Co}(\text{NH}_3)_6(\text{BF}_4)_3$ is at the same time partly reduced giving CoF_2 . $\text{Ag}(\text{NH}_3)_2\text{BF}_4$ gives Ag . Determinations of d have been made for some borofluoride amines and hydrates and also for NiF_2 and CoF_2 .

M. S. B.

Boron acids and alkali borates. V. Transition of sodium borate pentahydrate into decahydrate. H. MENZEL (Sitzungsber. u. Abh. naturwiss. Ges. Isis. Dresden. Festschr., 1934, 204—207; Chem. Zentr., 1934, ii, 2059; cf. A., 1928, 32).—The transition occurs readily at room temp. on seeding a supercooled solution previously heated at 80°.

H. J. E.

Aluminium subacetate solution. E. V. CHRISTENSEN and J. STRÖYBERG (Arch. Pharmac. og Chem., 1934, 41, 437—447; Chem. Zentr., 1934, ii, 2100).—Acquisition of insufficient AcOH to equiv. quantities of CaCO_3 and $\text{Al}_2(\text{SO}_4)_3$ in solution forms readily gelatinising products.

R. N. C.

Pertitanates and pervanadates. (MME.) M. E. P. KUMPF (Compt. rend., 1935, 200, 317—319).—An unstable, yellow to reddish-brown pertitanate is formed in solution by the action of H_2O_2 on TiCl_4 in aq. HCl . Its dissociation const. is 1.12×10^{-4} . Similarly, a red unstable pervanadate, dissociation

const. 2.36×10^{-4} , is formed by the action of H_2O_2 on an acid solution of NaVO_3 .

M. S. B.

Decomposition products of ammonium perchlorate. M. DODE (Compt. rend., 1935, 200, 63—66).— NH_4ClO_4 , purified by 4 recrystallisations from H_2O and dried in vac. over P_2O_5 , decomposes slowly above 150° and deflagrates about 400°. During slow decomp. the principal reaction is $4\text{NH}_4\text{ClO}_4 = 2\text{Cl}_2 + 8\text{H}_2\text{O} + 2\text{N}_2\text{O} + 3\text{O}_2$; a little Cl oxide (probably ClO_2) and traces of N_2 and NO_2 are also formed, the last two especially above 300°. Some recombination occurs in the cool parts of the vessel, yielding apparent sublimation. The explosive reaction yields H_2O and a complex mixture corresponding with the equilibrium of the system $\text{Cl}_2 - \text{O}_2 - \text{NO}_2 - \text{N}_2\text{O}_3 - \text{NOCl}$.

J. W. S.

Oxidation of hydrazine. IX. Mono- and di-deelectronation of hydrazine by permanganate in hydrochloric acid solution. A. G. HOUTP, K. W. SHERK, and A. W. BROWNE (Ind. Eng. Chem. [Anal.], 1935, 7, 54—57; cf. A., 1928, 380).—Two reactions occur concurrently, viz., (1) $\text{N}_2\text{H}_4 + 2\text{O} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, (2) $2\text{N}_2\text{H}_4 + \text{O} \rightarrow \text{N}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$. Since the relative amounts of N_2H_4 oxidised by (1) and (2), respectively, vary with several factors, the reaction is unsatisfactory for the determination of N_2H_4 or the standardisation of KMnO_4 .

E. S. H.

Reduction of vanadium oxides by carbon monoxide and by carbon. A. MORETTE (Compt. rend., 1935, 200, 134—136).— CO reduces V_2O_5 to V_2O_3 , and the CO_2 produced does not react with the latter. Reaction is slow at 500°, but very rapid at 600°. If insufficient CO is present V_2O_4 may be formed. A mixture of V_2O_5 and C heated in vac. yields V_2O_4 at 400—700°, and V_2O_3 at 1000°, CO_2 being the main gaseous product during the former reaction and CO during the latter. Reduction of V_2O_3 by C commences at 1200°, but is complete only at 1700°. Carbide formation commences considerably below the latter temp.

J. W. S.

Compounds of tervalent vanadium. S. BODFORSS, K. J. KARLSSON, and H. SJODIN (Z. anorg. Chem., 1935, 221, 382—390).—By heating V_2O_3 in excess of CCl_4 vapour VCl_4 is readily formed and can be converted into VCl_3 by Meyer and Backa's method (A., 1924, ii, 558). VCl_3 is not sol. in inert org. solvents, but dissolves in org. bases with a violet-red colour, forming a no. of additive compounds with aliphatic amines and $\text{C}_5\text{H}_5\text{N}$. Facility of formation is in the order primary > sec. > tert.-amines. From aq. solutions of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ complex salts of V^{III} are formed by pptn. with org. acids: $\text{V}(\text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH})$, $\text{V}(\alpha\text{- and } \beta\text{-CO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH})$, $\text{V}[\text{C}_6\text{H}_5\text{N}(\text{NO}) \cdot \text{O}]_3$, $\text{V}(\beta\text{-C}_{10}\text{H}_6 \cdot \text{O} \cdot \text{NO})_2$. With $\text{K}_4\text{Fe}(\text{CN})_6$ an amorphous reddish-brown ppt. or a red sol is formed. The sol is negatively charged, so that flocculation depends on the cation, the concn. of salt required being in the order $\text{KCl} > \text{K}_2\text{SO}_4 > \text{CaCl}_2 > \text{AlCl}_3$.

M. S. B.

Preparation of hydrogen selenide by the interaction of selenium and hydrocarbons. C. GREEN and W. E. BRADT (Proc. Indiana Acad. Sci., 1934, 43, 116—118).—A max. yield (96.8% H_2Se based on Se used) was obtained by heating 50 g. of a

paraffin-base motor oil with 1 g. of Se for 1 hr. at 380°. The H_2Se yield increases with rise in temp., being negligible at < 300° (cf. Scudder and Lyons, A., 1932, 578).

CH. ABS. (e)

Metal carbonyls. XX. Metal hexacarbonyls of the chromium group, their mode of formation and reaction mechanism. **XXI.** Thermochemical investigations of metal hexacarbonyls. W. HIEBER and E. ROMBERG. **XXII.** Reactions and derivatives of the hexacarbonyls of chromium and molybdenum. W. HIEBER and F. MUHLBAUER. **XXIII.** Derivatives of tungsten hexacarbonyl. W. HIEBER and E. ROMBERG (Z. anorg. Chem., 1935, 221, 321—331, 332—336, 337—348, 349—353).—XX. $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been prepared by the action of CO on the corresponding chlorides in presence of Grignard's reagent (cf. Job *et al.*, A., 1928, 1201). The product is hydrolysed by a mixture of ice and dil. H_2SO_4 and the carbonyl removed together with Et_2O and C_6H_6 by steam-distillation, separated, and purified by vac.-sublimation. The yield is not large. The mechanism of the reaction is discussed. There are several concurrent reactions. Carbonyls low in CO, or org. metal carbonyls, are probably first formed, and break up into compounds containing more or less CO. The three carbonyls are isomorphous, all forming colourless, strongly refracting, volatile, orthorhombic crystals readily sol. in inert org. solvents. Compared with other metal carbonyls they are very stable; the vapour decomposes slowly above 120° only; the metal then separates in a very pure form as a mirror. They are stable at room temp. to conc. HCl and H_2SO_4 , but decomposed by fuming HNO_3 and by alkalis. $Cr(CO)_6$ is the most stable towards halogens, being attacked by Cl_2 only. They have no appreciable dipole moment.

XXI. Saturation pressures at different temp. have been determined. B.p. (abs.)/1 atm. are: $Cr(CO)_6$ 420.5°, $Mo(CO)_6$ 429.4°, $W(CO)_6$ 448.0°, and heats of sublimation are 17.18, 16.29, and 17.71 kg.-cal., respectively. The anomalous position of $W(CO)_6$ in the carbonyl series, as shown by thermal data, is evident also from d determinations.

XXII. The following *organo-carbonyls* of Mo and Cr have been prepared: $(Mo \text{ or } Cr)(CO)_6(C_2H_5N)_2$, $(Mo \text{ or } Cr)(CO)_4(o-C_{12}H_8N_2)$, $(Mo \text{ or } Cr)(CO)_3(C_5H_5N)(o-C_{12}H_8N_2)$, $Mo_2(CO)_6[C_2H_4(NH_2)_2]_3$, $Cr_2(CO)_7(C_5H_5N)_5$, $Cr(CO)_4(C_5H_5N)_2$.

XXIII. The following *organo-carbonyls* of W have been prepared: $W(CO)_3(C_5H_5N)_3$, $W(CO)_4(C_5H_5N)_2$, $W(CO)_4(o-C_{12}H_8N_2)$, $W(CO)_4(\alpha\alpha'-C_{10}H_8N_2)$, $W(CO)_3(C_5H_5N)(o-C_{12}H_8N_2)$. M. S. B.

Polyacids. E. H. RIESENFELD and M. TOBIANK (Z. anorg. Chem., 1935, 221, 287—317).—Theoretical. The constitutional formulae of poly- and heteropolyacids of W, Mo, P, As, and Si are discussed.

M. S. B.

Action of heat on some oxides of manganese. S. PAVLOVITCH (Compt. rend., 1935, 200, 71—73; cf. A., 1931, 930).—The network formation observed previously on hausmannite crystals at high temp. is accompanied in air or N_2 by absorption of heat at

950° and 1160°, without apparent variation in wt. or crystal structure. The same result is obtained in O_2 , no oxidation occurring. Thermal analysis of polianite in air or N_2 shows two endothermic inflexions at 570° and 950°, respectively, due to transformation into Mn_2O_3 and Mn_3O_4 . Manganite shows similar inflexions at 370° and 940° due to dehydration to Mn_2O_3 and conversion into Mn_3O_4 , respectively. In O_2 the last two compounds also show inflexions due to O_2 absorption by the Mn_3O_4 on cooling. J. W. S.

Preparation of anhydrous chlorides of certain heavy metals. D. I. RIABTSCHIKOV and V. M. SCHULMAN (J. Appl. Chem. Russ., 1934, 7, 1162—1165).—Anhyd. $MnCl_2$, $NiCl_2$, and $CoCl_2$ are obtained by passing dry HCl over the heated hydrates, $FeCl_3$ from Fe and HCl, and $CrCl_3$ from Cr_2O_3 and $CO-Cl_2$ mixtures, or from Cr_2O_3-C mixtures and Cl_2 .

R. T.

Dilatometric study of the dehydration and thermal decomposition of some manganese compounds. P. DUBOIS and E. RENCKER (Compt. rend., 1935, 200, 131—134).—The temp. variation of the length of a pressed pellet of $MnCl_2 \cdot 2H_2O$ confirms the existence of $MnCl_2 \cdot H_2O$ (cf. A., 1934, 617). Similar study of pellets of synthetic $Mn_2O_3 \cdot H_2O$ and of cryst. blocks of manganite shows that in absence of air $Mn_2O_3 \cdot H_2O$ passes into $\alpha-Mn_2O_3$ at about 250°, this passing further into $\beta-Mn_2O_3$ at about 600° and finally yielding Mn_3O_4 at about 930°. The change from $\alpha-Mn_2O_3$ into $\beta-Mn_2O_3$ is irreversible (cf. this vol., 181).

J. W. S.

Keeping properties of ferric chloride solutions for reagent purposes. U. CARISI (Boll. Chim. farm., 1935, 74, 3—4).—Acid solutions keep indefinitely, but neutral solutions must be freshly made.

D. R. D.

Microcrystalline ferric hydroxides and sodium, silver, and barium ferrites. A. KRAUZE and S. KRZYZANSKI (Rocz. Chem., 1934, 14, 504—514).—A highly unstable, colourless, microcryst. Na ferrite (I) is obtained by dissolving ortho- $Fe(OH)_3$ (II) in conc. NaOH and cooling; when aq. (I) is boiled, a second, stable, brown, microcryst. ferrite, $NaFeO_2$, separates. Unstable colourless Ba ferrites, in which $Fe_2O_3 : BaO = 1 : 3.9-4.5$ are obtained by adding $Ba(OH)_2$ to hot aq. (I), and cooling, whilst when the solution is boiled stable brown ferrites ($Fe_2O_3 : BaO = 1 : 1.37-1.48$) crystallise on cooling. The sole product of the action of Ag_2O on aq. (I) was $AgFeO_2$ (III). (II) and aq. KOH do not afford ferrites, but only microcryst. $Fe_2O_3 \cdot H_2O$, yielding (III) on treatment with Ag_2O .

R. T.

Preparation and properties of sodium ferroate. X. THIESSE (Compt. rend., 1935, 200, 136—138).—If a solution of $FeSO_4 \cdot 7H_2O$ (100 g. per litre) be added dropwise to a boiling solution of NaOH (34—57%) in an atm. of N_2 , the $Fe(OH)_2$ dissolves in the NaOH yielding an emerald-green solution, which on cooling rapidly to 40° deposits white hexagonal or cubic crystals of sodium ferroate ("hypoferrite") (I). Addition of excess of H_2O to the solution ppts. $Fe(OH)_2$, but a limited amount of H_2O at a high temp. slowly oxidises (I) to Fe_3O_4 , with liberation of H_2 . presence of a large excess of NaOH no oxidation

occurs in the atm. in the cold. H_2O immediately hydrolyses solid (I), and the air rapidly oxidises it to Fe_2O_3 , but it can be redissolved in NaOH without decomp. The formula cannot be determined owing to difficulty in removing mother-liquor. J. W. S.

Tartrates of bivalent metals. J. P. MATHIEU (Bull. Soc. chim., 1934, [v], 1, 1713—1744).—Absorption spectra, optical activity, circular dichroism, and conductivity and electrometric determinations with aq. solutions of the tartrates of Co, Ni, Mn, Fe, Cr, and Zn show that at least part of the metal, M, is not ionised. The general formula of the complexes isolated is $[\text{TM}(\text{H}_2\text{O})_2]$, where $\text{T}=\text{C}_4\text{H}_4\text{O}_6$, and these dissociate with increasing dilution. Co, Ni, and Fe form the double salts TM, TNa_2 . The tendency of the alkaline solutions to oxidise is slight for Co, strong for Mn and Fe, and prevents further investigation in the case of Cr. With $\frac{1}{2} 2\text{NaOH} : 1[\text{TM}(\text{H}_2\text{O})_2]$, sol. metatartarates, $[\text{TM}(\text{OH})_2]\text{Na}_2$, have been isolated; these, on dilution, afford insol. basic tartrates, $[\text{TM}(\text{OH})_2]\text{M}$, except Zn, which yields $\text{Zn}(\text{OH})_2$, and these are identical with the corresponding ppts. obtained by adding NaOH to $[\text{TM}(\text{H}_2\text{O})_2]$. The hydrolysis of $[\text{TM}(\text{OH})_2]\text{Na}_2$ is diminished by NaOH and Na_2T . The facile hydrolysis of $[\text{TZn}(\text{OH})_2]\text{Na}_2$ is in keeping with the inability of tartrates to prevent the pptn. of Zn by alkalis. The colloidal nature of some Ni tartrate solutions is emphasised. J. G. A. G.

Potassium cobaltic trioxalate. R. F. RECODER (Chemia, Rev. Centr. Estud. Doct. Chim., 1932, 9, 31—34).—The prep. is described and the stereochemistry of the compound discussed. CH. ABS.

Spectral analysis. F. PAVELKA and H. MOLLERER (Mikrochem., 1935, 17, 47—102).—A review.

Quantitative spectroscopy and its analytical applications. S. J. LEWIS (Analyst, 1935, 60, 10—17).—Several examples are given showing the val. of spectrographic analysis in the determination of small quantities of metals in org. materials by the ratio quant. system. A. R. P.

Quantitative emission spectrum analysis. A. WENDT and H. HEUN (Z. Physik, 1934, 93, 92—99).—The electrical conditions of an arc of an alloy can be varied to give a spark line from one metal of the same intensity as an arc line from the other; this is used for quant. analysis, and has given the distribution of Cd in Zn with respect to depth below the electrode surface. A. B. D. C.

Accuracy of log sector method of quantitative spectroscopic analysis. L. C. MARTIN, S. A. LAKE, and E. G. KNOWLES (Trans. Faraday Soc., 1935, 31, 495—502).—The "log sector" method is especially suitable for the determination of metals present as minor constituents of mixtures. The difficulties involved in the photographic photometry associated with the method are discussed. The apparatus employed for line length measurement is described. The error in the photometric measurement should be $\pm 5\%$. M. S. B.

Use of logarithmic sector for the quantitative analysis of precipitates. E. G. KNOWLES and L. C. MARTIN (Trans. Faraday Soc., 1935, 31, 502—508).—The determination by the log sector of a foreign

element carried down by a ppt. has been applied to the case of Zn pptd. with Cu as sulphide in solutions of varying acidity. A fairly good average accuracy is obtained, but there are large individual variations. The determination, by this method, of K carried down by BaSO_4 was not successful. M. S. B.

Application of fluorescence analysis in micro-chemistry. M. HAITINGER (Mikrochem., 1935, 16, 321—356).—A review.

Drop analysis in practice. J. WINCKELMANN (Mikrochem., 1935, 16, 203—210; cf. A., 1933, 135). J. S. A.

Accurate micro-analysis by Pregl's method. C. TIEDCKE (Mikrochem., 1935, 16, 171—186).—Minor points of technique are discussed. J. S. A.

Rapid method for making standard solutions of specified normality. O. JOHNSON (Ind. Eng. Chem. [Anal.], 1935, 7, 76). E. S. H.

Theory of the error of acid-base titration. P. S. ROLLER (J. Amer. Chem. Soc., 1935, 57, 98—100).—Theoretical. E. S. H.

Fluorescence acidimetric and adsorption indicators. H. R. FLECK, R. F. G. HOLNESS, and A. M. WARD (Analyst, 1935, 60, 32—33).—In titrating acids with alkalis in ultra-violet light the Mg salt of 8-hydroxyquinoline serves as a good indicator, a change from colourless to golden-yellow taking place at p_H 7. For the titration of chlorides with AgNO_3 dichlorofluorescein changes from a fluorescent yellow-green to a chocolate-coloured suspension without fluorescence; eosin behaves similarly with bromide and iodide titrations. A. R. P.

Sodium carbonate as a standard in alkali-acidimetry. J. STALONY-DOBZAŃSKI (Rocz. Chem., 1934, 14, 1106—1117).— Na_2CO_3 suitable for standardisation purposes is obtained by heating NaHCO_3 at 150 — 280° ; at the b.p. of PhNO_2 the decomp. of NaHCO_3 is completed after 100 min. R. T.

Carbonate error in acidimetry. T. MIŁOBĘDZKI and W. SZCZYPYŃSKI (Rocz. Chem., 1934, 14, 1088—1105).—The presence of carbonate in standard aq. NaOH used for acidimetry is the most serious source of error, the magnitude of which varies according to the conditions of addition of the alkali to the acid, and to the indicator used; the use of carbonate-free solutions, prepared according to Sørensen, is recommended. The indicator properties of red-cabbage extracts appear to be due chiefly to the crude anthocyanin rubrobrassicin, elimination of sinapic acid from which yields a product unsuitable for the purpose. R. T.

Standardisation of hydrochloric acid with calcite. J. W. YOUNG (Canad. Chem. Met., 1934, 18, 218).—A method for the standardisation of $N\text{-HCl}$ using calcite is described. With $0.1N$ -acid, deviations are high and several determinations are necessary to obtain an accuracy $> 0.1\%$. H. G. R.

Indicator properties of dinitroaniline azo-dyes. H. WENKER (Ind. Eng. Chem. [Anal.], 1935, 7, 40—41).—Many dinitroanilineazonaphtholsulphonic acids are described. α -Naphthol, 1:6-, 1:7-, and 1:8- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ as azo-components give indic-

ators of strong colour contrast over a narrow p_H range. 2:4-Dinitroaniline derivatives give bluer and brighter shades than the 2:6-compounds, which are redder and duller. None of the dyes now described is as good an indicator as nitrazine-yellow (cf. A., 1934, 500), the blue form of which contains 3 Na atoms.

J. L. D.

Colorimeter tube for p_H determination. K. BUCH (Finska Kem. Medd., 1934, 43, 112—114).—The tube is protected from the atm. A fixed amount of indicator is introduced by a pocketed stopcock and the colour is observed between parallel glass plates. The buffer tube is fitted with similar plates having the same separation.

R. S.

β -Methylumbelliferone, a fluorescing indicator. A. G. PUKIREV and M. S. MASLOVA (Zavod. Lab., 1934, 3, 1038—1039).—Coloured solutions may be titrated by observing the point at which fluorescence due to β -methylumbelliferone appears or disappears (p_H 7.2).

R. T.

Application of V. Meyer's method to determination of moisture content. W. SWIENTOSŁAWSKI, H. BRZUSTOWSKA, and M. KRAKOWSKI (Rocz. Chem., 1934, 14, 633—639).—The H_2O content of various products can be rapidly and conveniently determined by measuring the vol. of vapour evolved when the sample is heated at the appropriate temp. in a modified V. Meyer apparatus.

R. T.

Determination of chloride. Modification of the Volhard method. J. R. CALDWELL and H. V. MOYER (Ind. Eng. Chem. [Anal.], 1935, 7, 38—39).—Addition of $PhNO_2$ obviates the necessity of removing the pptd. $AgCl$ before titrating back with KCN .

E. S. H.

Colorimetric determination of small quantities of chlorides in waters. H. B. RIFFENBURG (Ind. Eng. Chem. [Anal.], 1935, 7, 14).—The $AgNO_3$ - K_2CrO_4 method is modified.

E. S. H.

Drop method of detection of anions. N. A. TANANAEV and A. M. SCHAPOVALENKO (J. Appl. Chem. Russ., 1934, 7, 1258—1269).—Directions are given for the drop detection of Cl' , Br' , I' , S'' , SO_3'' , S_2O_3'' , SO_4'' , CN' , CNS' , $Fe(CN)_6'''$, $Fe(CN)_6''''$, NO_2' , NO_3' , AsO_3''' , AsO_4''' , IO_3' , CrO_4'' , OCl' , BO_3''' , and BO' alone, or together.

R. T.

Determination of free chlorine in water [using o-tolidine].—See B., 1935, 128.

Determination of perchlorates. M. L. NICHOLS (Ind. Eng. Chem. [Anal.], 1935, 7, 39).— ClO_3' is quantitatively reduced in the cold by $TiCl_3$, whilst ClO_4' is quantitatively reduced by conc. aq. $TiCl_3$ containing H_2SO_4 .

E. S. H.

Determination of bromine in solutions containing potassium, sodium, and magnesium chlorides. S. K. TSCHIRKOV and A. I. SCHPIKELMAN (J. Appl. Chem. Russ., 1934, 7, 1270—1276).—Br may be determined potentiometrically in solutions containing KCl , $NaCl$, and $MgCl_2$; the $[Br']$ should be 0.007—0.015% for $MgCl_2$ concns. of $> 10\%$, and 0.011—0.015% for higher $MgCl_2$ concns.

R. T.

Volumetric determination of iodide ions by Fajans' method. E. A. KOCIS (Z. anorg. Chem.,

1935, 221, 318—320).—Diamine-fast-bordeaux 6BS (I) and diamine-fast-violet BBN (II) may be used as indicators in the titration of I' by $AgNO_3$ in neutral solution, but not for the titration of Ag' by KI . (II) may also be used in acid solution, although the end-point is not quite so sharp, and in presence of Cl' , but not of Br' .

M. S. B.

Determination of fluorine in drinking-water. Comparison of several methods and establishment of toxic concentration by these methods. H. V. SMITH (Ind. Eng. Chem. [Anal.], 1935, 7, 23—25).—A comparison of the F' content of 44 waters by 4 different standard methods has been made. H_2O containing > 1.0 p.p.m. F' is associated with the production of mottled enamel in teeth, whilst no H_2O containing < 0.8 p.p.m. is known to cause mottled enamel.

E. S. H.

[Detection of traces of fluoride and the volumetric determination of zirconium.] R. CHARONNAT (Compt. rend., 1934, 199, 1620—1622; cf. this vol., 190).—The origin of the colour change in de Boer's method (cf. A., 1926, 40) is discussed. The min. ratio of Zr atoms to Na alizarinsulphonate mols. for all the Zr to remain in the (violet-red) solution (I) is 4:1. The min. concns. of acids to produce the yellow colour are HF , 0.001N; H_3PO_4 , 0.16N; H_2SO_4 , 4.1N; HBr , 10.5N. (I) is stable only when neutral or alkaline. The action of acids on (I) occurs in 4 stages which depend on the nature and concn. of the acid.

H. J. E.

Determination of sulphide-sulphur, especially in effluents.—See B., 1935, 176.

Determination of sulphuric acid in presence of copper salts. J. G. TITOVA (J. Appl. Chem. Russ., 1934, 7, 1277—1281).— H_2SO_4 is determined in presence of $CuSO_4$ by titrating with standard $NaOH$ to the appearance of a turbidity, due to $Cu(OH)_2$, of equal intensity to that given by addition of the theoretical amount of $NaOH$ to a H_2SO_4 solution of known concn., also containing $CuSO_4$.

R. T.

Microscopical chemical reactions of some polythionic acids. E. M. CHAMOT and R. W. BRICKENKAMP (Mikrochem., 1935, 16, 121—132).—Benzyl- ϕ -thiocarbamide forms characteristic cryst. ppts. with S_2O_6'' , S_3O_6'' , S_4O_6'' , S_5O_6'' ; nitron sulphate does so with S_2O_6'' , S_3O_6'' , and S_5O_6'' only. $[Ni en_3](NO_3)_2$ is sp. for S_2O_6'' , but S_2O_3'' reacts also $[en = C_2H_4(NH_2)_2]$. $[Co en_3]Cl_2$ reacts with S_2O_6'' and S_4O_6'' only. $[Co(NH_3)_6]Cl_3$ gives cryst. ppts. with S_2O_6'' , S_3O_6'' , and S_5O_6'' , but not S_4O_6'' . The reactions of other acids with the above reagents are described, and a general group separation of the S oxy-acids is outlined.

J. S. A.

New tests [for nitrites, chromates, dichromates, tungstates, and auric salts]. L. R. CATALANO (Rev. Minera, 1931, 1, 16—17).—Aq. $NH_2Ph.H_2SO_4$ containing 2—4% of H_2SO_4 (I) gives with aq. nitrites and excess of aq. NH_3 a yellow-chestnut colour and ppt., not produced by NO_3' , ClO_3' , or ClO_4' . CrO_4' , Cr_2O_7'' , or vanadates give with (I) a greenish-blue colour, changing to violet with aq. NH_3 . Au''' salts give a permanent orange colour.

CH. ABS. (c)

Rapid micro-determination of phosphoric acid in water.—See B., 1935, 176.

Determination of active silica in puzzuolana. P. P. BUDNIKOV and L. G. GULINOVA (Kolloid-Z., 1935, 70, 100—105).— SiO_2 is determined by following its reaction with finely-divided Ca(OH)_2 , calorimetrically or by electrical conductivity in aq. solution.

E. S. H.

Analysis of dust samples employing X-ray diffraction. W. F. BALE and W. W. FRAY (J. Ind. Hygiene, 1935, 17, 30—32).—A Debye-Scherrer photograph is made from the dust, using pure SiO_2 or other suspected constituent as a comparison.

J. S. A.

Determination of free silica. Modified petrographic immersion method. H. L. ROSS and F. W. SEHL (Ind. Eng. Chem. [Anal.], 1935, 7, 30—32).— SiO_2 in powders or dust is determined by counting and weighting the particles, immersed successively in fennel-seed oil and PhNO_2 , under a microscope equipped with a Whipple disc.

E. S. H.

Determination of impurities in commercial carbon monoxide.—See B., 1935, 146.

Photronic photo-electric turbidimeter for determining hydrocyanic acid in solutions. E. T. BARTHOLOMEW and E. C. RABY (Ind. Eng. Chem. [Anal.], 1935, 7, 68—69).—With the apparatus described HCN can be determined by titration with AgNO_3 to within 0.00054 mg. Original colour or turbidity of the solutions does not vitiate the results.

E. S. H.

Disturbance by cations of tests for anions in alkaline solution. A. HEMMELER and M. ANGELINI (L'Ind. Chimica, 1934, 9, 1343—1353).—Difficulties arising from the presence of heavy metals, either as hydroxide or in anions or complex salts, are considered. A classification of anions is given according to their behaviour when the alkaline solution is neutralised, acidified, oxidised, or reduced, or when they are caused to form stable complex anions, to unite with a second anion (e.g., $\text{CN}^+ + \text{S}^{''}$), to decompose (e.g., $\text{S}_2\text{O}_3^{''}$), or to yield salts stable towards Na_2CO_3 .

H. F. G.

Volumetric determination of potassium by the cobaltinitrite method. C. S. PIPER (J.S.C.I., 1934, 53, 392—396r).—The method was modified so as to obtain quant. recoveries over the range of 0.1—mg. K_2O . The ppt. has the composition $\text{R}_3\text{Co(ONO)}_2$, aq. ($\text{R}=\text{K}$ and Na), but the relative amounts of these elements depend on the amount of K , the amount and nature of pptg. reagent, the amount of Na salts, and the temp. If standard amounts of reagent and NaCl are used at room temp., K_2O in mg. = $0.354x + 0.00034x^2$, where x is the KMnO_4 val. in ml. of 0.05N solution. The cobaltinitrite ppt. is appreciably sol. in H_2O and in 2.5% aq. Na_2SO_4 . The most suitable wash liquids are either 35% EtOH or a freshly prepared saturated solution of K cobaltinitrite. The titration with IO_4 is quant. when the ppt. is added to cold acidified KMnO_4 and then boiled. 11 equivs. of O are required per mol. of $\text{R}_3\text{Co(ONO)}_2$.

Standardisation of potassium dichromate. H. WILLARD and P. YOUNG (Ind. Eng. Chem.

[Anal.], 1935, 7, 57—58).— $\text{K}_2\text{Cr}_2\text{O}_7$ is standardised by treatment of H_3AsO_3 in H_2SO_4 solution with < its equiv. of $\text{K}_2\text{Cr}_2\text{O}_7$, and titrating the excess of reducing agent with $\text{Ce(SO}_4)_2$ or KMnO_4 , using OsO_4 as catalyst and *o*-phenanthroline ferrous complex as indicator. The titration may be performed potentiometrically with KBrO_3 in aq. HCl .

E. S. H.

Mechanism of precipitation processes. XV. Reactions in the precipitation of $\text{Ba}^{''}$, $\text{Pb}^{''}$, or $\text{SO}_4^{''}$ ions as barium sulphate or lead sulphate. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1935, 221, 369—381; cf. A., 1934, 604).—When $\text{Ba(NO}_3)_2$ is pptd. with H_2SO_4 the ppt. contains more Ba than corresponds with the amount of H_2SO_4 employed, the excess of Ba being the smaller the more slowly pptn. takes place. The presence of HCl has practically no influence, but excess of HNO_3 causes an increase in the ratio of $\text{Ba}^{''}$ to $\text{SO}_4^{''}$. The results are to be explained, not by adsorption, but by formation of a secondary product, possibly of the form $(\text{BaNO}_3)_2\text{SO}_4$; > 20% of this product may be formed. A similar reaction takes place in presence of H_3PO_4 , probably forming $(\text{BaH}_2\text{PO}_4)_2\text{SO}_4$. Other secondary reactions occur in presence of electrolytes such as KCl or FeCl_3 , probably giving products of the form $\text{Ba(KSO}_4)_2$ or $\text{Ba}_3[\text{Fe(SO}_4)_3]_2$. BaCl_2 with H_2SO_4 will result in a secondary product such as $(\text{BaCl})_2\text{SO}_4$. Formulae other than those suggested are possible. The pptn. of PbSO_4 from $\text{Pb(NO}_3)_2$ and H_2SO_4 is very little influenced by conditions; hence it is unlikely that secondary products are formed.

M. S. B.

Determination of magnesium, manganese, silicon, and iron in duraluminium by quantitative spectral analysis. P. A. BAZHULIN, A. A. BASKAKOV, and A. P. STRIGANOV (J. Tech. Phys. U.S.S.R., 1934, 4, 578—586).—0.03—0.07% of Mn or Mg , 0.1—0.7% of Fe or Si , and 3.5—5% of Cu may be determined with an error < 10%. Spectral lines used are tabulated.

CH. ABS. (e)

Detection of cations without the use of hydrogen sulphide. L. G. BERDITSCHESKI and I. G. VASSERBERG (Ukrain. Chem. J., 1934, 9, 161—166).—An analytical procedure is described.

R. T.

Effect of salts on the determination of traces of lead by the chromate method. A. W. MIDDLETON (J. Ind. Hygiene, 1935, 17, 7—11).— Pb cannot be determined as PbCrO_4 in presence of > very small amounts of other heavy metals.

J. S. A.

Simple test for the formation of complex lead alkali halides. H. J. BORN and R. MUMBRAUER (Z. anorg. Chem., 1935, 221, 354—362).—By the radioactive indicator method, using Th-B , the formation of complex chlorides of PbCl_3 with KCl and NH_4Cl is confirmed. None, however, is formed with NaCl .

M. S. B.

Micro-determination of lead. Electrolytic-colorimetric method. M. RANDALL and M. N. SARQUIS (Ind. Eng. Chem. [Anal.], 1935, 7, 2—3).—2—15 mg. of Pb can be determined with an accuracy of about 1% by pptg. electrolytically 95—99% as PbO_2 and determining the remainder colorimetrically as PbS .

E. S. H.

Iodometric determination of copper. J. R. CALDWELL (J. Amer. Chem. Soc., 1935, 57, 96—97).—The absorption of starch iodide by the pptd. CuI is reduced by adding a solution of white shellac in EtOH .
E. S. H.

Drop method of detection of copper. L. M. KULBERG (J. Appl. Chem. Russ., 1934, 7, 1079—1080).—A few ml. of solution are heated for 1—1.5 min. with Sn and conc. HCl , the solution is poured off, the Sn washed and boiled for 1 min. with 1.5 ml. of 65% HNO_3 , the solution diluted, and 0.2 ml. of saturated aq. NaF , 0.2 g. of ZnSO_4 , and 0.3 ml. of saturated aq. $(\text{NH}_4)_2\text{Hg}(\text{CNS})_4$ are added, when a lilac ppt. of $\text{ZnHg}(\text{CNS})_4$, $\text{CuHg}(\text{CNS})_4$ indicates $\leq 10^{-7}$ g. Cu. Co, Pb, Fe, Sn, As, Sb, and Bi do not interfere. R. T.

Colorimetric determination of copper as cupric sulphide. L. DE BROUCKERE and S. SOLOWIEJCZYK (Bull. Soc. chim. Belg., 1934, 43, 597—625).—The conditions for obtaining stable hydrosols of reproducible colour for which Beer's law is valid have been investigated. 25 ml. of solution containing 0.003—0.03 g. of Cu per litre, 0.1—0.5N with respect to HCl , HNO_3 , or H_2SO_4 , and stabilised with 1 ml. of 1% aq. gelatin (Ostwald) are added to 2.5 ml. of fresh saturated aq. H_2S . The colour is compared, over a period, with that of a simultaneously prepared standard, in a Duboseq colorimeter. In general, the determinations are accurate to within 1% in the presence of 0.05—1.0M KCl , NaCl , KNO_3 , NaNO_3 , K_2SO_4 , Na_2SO_4 , MgCl_2 , CaCl_2 , BaCl_2 , MnSO_4 , ZnSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ even if the concns. are not identical in the solutions compared. The results are not reproducible in presence of Fe. Dextrin and aq. Na_2S are less satisfactory reagents. J. G. A. G.

Quinaldinic acid as a micro-reagent. I. Determination of zinc, and its separation from manganese. P. R. RAY and M. K. BOSE. II. Determination of copper, and its separation from cadmium, manganese, nickel, cobalt, etc. P. R. RAY and J. GUPTA (Mikrochem., 1935, 17, 11—13, 14—16; cf. A., 1934, 270).—I. The Zn solution (about 1 mg. in 1—1.5 c.c. of H_2O) is acidified with 0.02—0.04 c.c. of glacial AcOH , and pptd. with slight excess of 1% Na quinaldinate solution. The ppt. is washed 5—6 times with 0.5—1 c.c. of hot H_2O and dried at 125° . In presence of Mn 0.05—0.1 c.c. of AcOH is used and preliminary washing H_2O contains 2.5% AcOH and 5% Na quinaldinate solution. The AcOH is reduced in presence of Mg and alkaline earths. Pptn. of Fe, Al, Be, Ti, and U can be prevented by addition of alkaline tartrate solution.

II. 0.1—0.9 mg. of Cu in 1—2 c.c. of H_2O is acidified with 0.025 c.c. of 0.7N- H_2SO_4 , and 1% quinaldinic acid solution added dropwise to the hot Cu solution, until 0.1 c.c. in excess is present. The ppt. is washed with hot H_2O and dried at 135° . This method also separates Cu from Cd, Pb, Mn, Ni, Co, PO_4^{3-} , AsO_3^{3-} , and AsO_4^{3-} , if precautions are taken in washing.

J. W. S.

Microchemical detection of mercury. I. M. KORENMAN (Mikrochem., 1935, 16, 223—226).—Hg gives characteristic crystals of $\text{Zn}[\text{Hg}(\text{CNS})_4]$, advantageously coloured by addition of Fe^{3+} , with ZnSO_4 +

NH_4CNS . Ag and Cd also give cryst. ppts. with the reagent. J. S. A.

Rapid detection of mercury. P. I. TRISCHIN (J. Appl. Chem. Russ., 1934, 7, 1282—1284).— $\text{Br-H}_2\text{O}$, aq. NaOH , and KI are added to the solution, the solution is filtered, excess of aq. Na_2S added, the solution again filtered, and HCl added to the filtrate, when a black ppt. of HgS indicates Hg. Other cations do not interfere. R. T.

Quantitative spectral analysis of slightly volatile substances in the arc. Lanthanum oxide. H. BAUER (Z. anorg. Chem., 1935, 221, 209—224).—Since 0.01% of La_2O_3 mixed with CaO can be readily detected by examination of spectral photographs, whilst below that concn. there is a marked fall in intensity or practical disappearance of some lines, visual comparison of photographs affords an approx. quant. method of determination of small concns. Greater accuracy can be obtained by a photometric method, using ZrO_2 lines as a comparison standard. In the determination of 0.1% of La_2O_3 the error is ± 5 —10%. Using 1.5 mg. of material only, 0.001% La_2O_3 in Al_2O_3 or 0.0025% in CaO can be detected.

M. S. B.

Sensitive drop reaction for indium. A. S. KOMAROVSKI and N. S. POLUKTOV (Mikrochem., 1935, 16, 227—232).—The solution is applied to paper impregnated with alizarin or quinalizarin, and exposed to NH_3 vapour. On neutralising with H_3BO_3 , In leaves a red, or a purple, lake, respectively; limit, for both, 0.05×10^{-6} g. Al if present is suppressed by addition of NaF . Zn, Ni, Co, Mn, and Fe (first reduced to Fe^{2+} by $\text{Na}_2\text{S}_2\text{O}_3$) are removed by treating the coloured spot with KCN . J. S. A.

Hexamethylenetetramine and bromate methods of determining manganese in presence of iron. V. F. STEFANOVSKI (J. Appl. Chem. Russ., 1934, 7, 1288—1293).—Ray and Chattopadhyaya's method (A., 1929, 614) is laborious, and cannot be applied in presence of Ni and other metals. Kolthoff and Sandell's method (A., 1929, 1414) gives trustworthy results, with the following modifications: the acidity of the medium during oxidation should correspond with 1.2N, and the filtrate from MnO_2 should be treated a second time with KBrO_3 . Fe, Ni, Zn, and other metals present in Fe alloys do not interfere.

T

Determination of titre of permanganate solutions by means of calcium carbonate. A. V. FILOSOFOV (J. Appl. Chem. Russ., 1934, 7, 1085—1086).—0.5 g. of CaCO_3 is dissolved in 50 ml. of 20% HCl , 250 ml. of 0.1N- $\text{H}_2\text{C}_2\text{O}_4$ are added, the solution is made alkaline with 20% aq. NH_3 at 95° , diluted to 500 ml., filtered after 3 hr., and excess of $\text{H}_2\text{C}_2\text{O}_4$ is determined by KMnO_4 titration; the titre of the latter is hence calc. R. T.

Arsenic test for reduced iron. M. OAKLEY and J. C. KRANTZ, jun. (J. Amer. Pharm. Assoc., 1934, 23, 1196—1197).—The Fe is dissolved in aq. Br, heated on a H_2O -bath for 15 min., and the normal U.S.P. Gutzeit method applied, the order of addition of acid SnCl_2 and of KI being reversed. F. O. H.

Separation of iron from indium with cupferron. F. C. MATHERS and C. E. PRICHARD (Proc. Indiana Acad. Sci., 1934, 43, 125—127).—Cupferron will ppt. Fe completely in presence of In. Most of the Fe should be removed previously by some other method. InCl_3 is sol. in a mixture of Et_2O and conc. HCl saturated with HCl; consequently the method of Gooch and Havens (A., 1897, ii, 232) for separating Al and Fe cannot be applied to In and Fe. CH. ABS. (e)

Determination of ferrous iron in materials containing metallic iron and ferric iron. T. TAZAWA (Seitetsu Kenkyu, 1933, No. 134).—Free Fe is removed by treatment with aq. HgCl_2 , pptd. Hg being removed with a solution of I in EtOH. Fe^{II} and Fe^{III} are determined in the mixed oxide residue. CH. ABS. (e)

Potentiometric and conductometric titration of ferric salts. A. L. ZAIDES (Tzent. Nauch. Issl. Inst. Koz. Prom. Sborn. Rabot, 1934, No. 2, 107—111).—In the conductometric determination of $\text{Fe}_2(\text{SO}_4)_3$ min. were observed at $[\text{NaOH}]$ approx. 0.5 and 3.0 equiv. per atom of Fe. Similar breaks were found in the potentiometric curve. Their origin is discussed. CH. ABS. (e)

Quantitative micro-analytical determination of certain metals in complex salts. J. MEYER and K. HOEHNE (Mikrochem., 1935, 16, 187—192).—Co and Ni in complex salts are weighed as the metal by igniting first in O_2 and subsequently in H_2 , without addition of H_2SO_4 . Compounds of Fe, Cr, and V are converted into Fe_2O_3 , Cr_2O_3 , and V_2O_5 by ignition in O_2 . Preliminary heating in air is advantageous in some cases. J. S. A.

Micro-colour reaction of chromium. S. AUGUSTI (Mikrochem., 1935, 17, 17—21).— CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ (or Cr^{III} oxidised with H_2O_2) yield a violet colour, passing into red, when treated with a 1% solution of strychnine in conc. H_2SO_4 . The limit of sensitivity as a drop reaction is 0.98×10^{-6} g. CrO_4^{2-} (0.348×10^{-6} g. Cr). Mn^{II} and Co^{II} , which interfere with the test, can be removed with BaCO_3 and 1:2- $\text{NO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, respectively. $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ also interfere, but can be decomposed with conc. H_2SO_4 before the test. J. W. S.

Critical study of cacotheline for the determination of tin. I. L. NEWELL, J. B. FICKLEN, and L. S. MAXFIELD (Ind. Eng. Chem. [Anal.], 1935, 7, 26—27).—2 p.p.m. of Sn^{II} can be detected when present alone, but the presence of Sb^{III} , Cr^{III} , Cr^{II} , Co^{II} , Cu^{II} , Fe^{II} , Hg^{II} , Ni^{II} , Ag^{I} , Ti^{IV} , HSO_3^{I} , CrO_4^{2-} , MoO_4^{2-} , NO_3^- , SeO_3^{2-} , SO_3^{2-} , or VO_4^{3-} interferes with the test. The sensitivity of the test is increased in presence of HCl. E. S. H.

n-Propylarsinic acid as a reagent for the determination of zirconium. F. W. ARNOLD, jun., and G. C. CHANDLEE (J. Amer. Chem. Soc., 1935, 57, 8).—The procedure is applicable in presence of a large no. of other metals, including Sn. The error is about 1%. Allylarsinic acid can be substituted when Zr is alone or accompanied by Th, Ti, or Sn. E. S. H.

Detection and determination of germanium in organic matter.—See this vol., 369.

Gravimetric determination of vanadium with ammonium benzoate, and of titanium with tannin. F. M. SCHEMJAKIN (Zavod. Lab., 1934, 3, 986—987).—25 c.c. of solution, containing 0.1—0.15 g. of V_2O_5 , are boiled with 10 c.c. of 2N-HCl; $(\text{NH}_4)_2\text{SO}_4$ is added to reduction of V^{V} to V^{IV} . A hot saturated solution of 1 g. of NH_4OBz is then added, the solution boiled for 2 min., the ppt. of $\text{VO}(\text{OBz})_2$ collected after 4 hr., washed with saturated aq. BzOH , ignited, and weighed as V_2O_5 . Fe and Cr should be absent; Mg, Al, Cu, Mo, W, and Ti do not interfere. Das-Gupta's method for determination of Ti (A., 1930, 566) is not as accurate as the 8-hydroxyquinoline method. R. T.

Microchemical mineral analysis. V. A. MARTINI (Mikrochem., 1935, 16, 233—235).—Rh gives a yellow cryst. ppt. with $(\text{NH}_4)_2[\text{Hg}(\text{CNS})_4]$. Pyramidone + aq. NH_4CNS gives characteristic cryst. ppts. with Fe, Zn, Cd, Sn, Cu (amorphous), and Co, but not with Ni; 1% of Co in Ni may be so detected. J. S. A.

Recent advances in calorimetry and thermometry. W. A. ROTH (Z. Elektrochem., 1935, 41, 112—122).—A review.

Isothermal calorimeter. H. B. SREERANGACHAR and M. SREENIVASAYA (Biochem. J., 1935, 29, 295—299).—A simple isothermal calorimeter using CH_2Ph_2 and its calibration are described. The heat liberated in the peroxidase-quinol system is 68.2 μ -cal. per g. of quinol. P. W. C.

Construction of a tubular oven for the thermostatic conduction of reactions in sealed tubes. E. SUCHARDA, T. MAZONSKI, and J. MOKRZYCKI (Rocz. Chem., 1934, 14, 1166—1171).—Apparatus is described. R. T.

Induction furnace without molten metal movement suitable for melting of light metals. E. F. RUSS (Z. Physik, 1935, 93, 220—226). A. B. D. C.

Temperature regulator for high temperatures. J. FÖRSTER and E. GRÜNER (Z. Elektrochem., 1935, 41, 9—10).—The winding of the electric furnace, the temp. of which is to be regulated, is placed in series with a second heating element having a resistance about 0.1 of that of the former. This second element is wound on the bulb of a Hg regulator which operates a relay cutting out one of two parallel resistances, thus decreasing the current through both main and subsidiary windings. Temp. between 300° and 1000° can be maintained with an accuracy of 1—2°. F. L. U.

Thermostatic relay. K. V. TSCHMUTOV (J. Appl. Chem. Russ., 1934, 7, 1103).—A simple relay for currents of 6—7 amp. is described. R. T.

Thermo-regulator for heating and cooling baths. A. E. BRADFIELD (J.S.C.I., 1935, 54, 6T).—The temp. is altered at a steady rate by moving the position of the upper contact by means of a clockwork drive. J. S. A.

Accurate thermostat of small capacity. I. G. NAGATKIN (Zavod. Lab., 1934, 3, 1036).—The thermostat, of 1 litre capacity, and of simple construction, can be maintained at $20\text{—}150 \pm 0.1^\circ$. R. T.

Micro-thermal conductivity apparatus for gas analysis. P. GROSS and H. STEINER (*Mikrochem.*, 1935, **17**, 43—46).—A modification of the Schleiermacher apparatus is described for measurement of the thermal conductivity of vols. of gas down to 0.2 c.c. The measurements can be applied to the analysis of gas mixtures and indicate the concn. of H_2^2 in H_2 to 0.5%.

J. W. S.

Hydrogen discharge tube for spectrographic work. H. J. J. BRADDICK (*Proc. Camb. Phil. Soc.*, 1934, **30**, 355—356).—The tube is made of Pyrex, with a cryst. SiO_2 window, and runs at 3000 volts and 0.5—1.0 amp. It is claimed that it is easy to construct and align with other apparatus, is robust, and permits a rather higher power input than is usual.

R. S. B.

High-power hydrogen lamp. L. HENRY (*J. Chim. phys.*, 1934, **31**, 665—667).—A form of H_2 lamp is described, constructed in Pyrex glass and with 50 sq. cm. Al electrodes, which can operate up to 4000 watts.

J. W. S.

Light filters for the mercury lamp. E. J. BOWEN (*J.C.S.*, 1935, 76).—A list of filters for isolating lines and groups of lines between 2480 and 5790 Å. is given (cf. A., 1932, 1013).

J. G. A. G.

Possibility of approximate spectro-photometry without analysis of the spectrum. N. NIUBERG (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4**, 278—285).—Theoretical.

J. W. S.

Instruments used for spectrum analysis and absorption spectrophotometry. F. TWYMAN (*Analyst*, 1935, **60**, 4—9).—A brief description is given of the Hilger const.-deviation wave-length spectrometer, the quartz spectrograph, the logarithmic sector, and the "Spekker" spectrophotometer, and their uses.

A. R. P.

Sources of error in absorption spectroscopy. C. P. SNOW and E. EASTWOOD (*Nature*, 1935, **135**, 186).—Sources of error in determining the absorption spectrum of vapours are the possible presence of small amounts of impurities and the effect of interference bands from the quartz plates of the apparatus.

L. S. T.

Microphotometric methods in divided-beam spectrophotometry. D. H. FOLLETT (*Proc. Physiol. Soc.*, 1935, **47**, 125—135).—A microphotometer is described in which two photocells, connected differentially, are used to indicate the difference in transmission of the individual spectra in the pairs produced in divided-beam methods of spectrophotometry.

N. M. B.

Roulette comparator for colorimetric analysis. J. H. YOE and T. B. CRUMPLER (*Ind. Eng. Chem. [Anal.]*, 1935, **7**, 78).—Apparatus and procedure are described.

E. S. H.

New precision colorimeter. J. J. MANLEY (*Proc. Physical Soc.*, 1935, **47**, 69—73).—The length of the standard solution column is controlled by a plunger working in a vertical connected tube; the two beams of light are juxtaposed by a simple optical system.

N. M. B.

Sonic interferometer for the study of absorption in liquids. A. L. QUIRK and G. D. KOCK (*Rev.*

Sci. Instr., 1935, [ii], **6**, 6—7).—The oscillations of a quartz crystal, protected from direct contact with the liquid by a thin metal diaphragm, are amplified.

G

Apparatus for converting photograms into intensity curves. K. HABERL (*Physikal. Z.*, 1935, **36**, 59—61).—The apparatus is a type of planimeter.

A. J. M.

Simple registering micro-photometer. H. KULENKAMPFF (*Physikal. Z.*, 1935, **36**, 56—59).

A. J. M.

Direct photography of dust in air. L. H. OTT and J. B. FICKLEN (*Rev. Sci. Instr.*, 1935, [ii], **6**, 4—5).—A dust chamber attached to the camera is illuminated from the side by a photo-flash lamp.

C. W. G.

Micro-refractometer and its use in chemical microscopy. E. E. JELLEY (*J. Roy. Microsc. Soc.*, 1934, [iii], **54**, 234—245).—Using only 0.0001 ml. of liquid, n can be determined to ± 0.001 between 1.330 and 2.000.

C. W. G.

Technique of Kerr cells. H. J. WHITE (*Rev. Sci. Instr.*, 1935, [ii], **6**, 22—26).—The purification of $PhNO_2$ by fractional distillation and freezing is described. Kerr cells are made of plate glass cemented with ceresin wax.

C. W. G.

Sensitivity of the γ -ray method of radiography. J. T. NORTON and A. ZIEGLER (*Trans. Amer. Soc. Met.*, 1934, **22**, 271—279).—The sensitivity is arbitrarily defined as the change in thickness of a steel block which produces a 2% change in density of the exposed film. Capsules containing 100 millicuries of Rn were used as the source of the γ -rays. The sensitivity is lower for a small thickness of steel, but improves up to a thickness of 2.5 in., after which it is practically const. at 1.3%.

W. P. R.

Valve potentiometer. D. N. MEHTA and S. K. K. JATKAR (*Proc. Indian Acad. Sci.*, 1934, **1**, A, 390—397).

N. M. B.

Lamp potentiometer and its application to the glass electrode. S. I. SOKOLOV and V. A. PTSCHELIN (*J. Appl. Chem. Russ.*, 1934, **7**, 1316—1322).

R. T.

Calomel electrodes. M. CHANOT, G. FLORENCE, and (Mlle.) PERROTTET (*Compt. rend. Soc. Biol.*, 1935, **118**, 245—247).—Theoretical.

R. N. C.

Cataphoretic measurements by the aid of resistance lamps, using a direct current. R. SPYCHALSKI and J. NETEROWICZ (*Rocz. Chem.*, 1934, **14**, 909—914).—Apparatus for cataphoresis experiments is described, in which accumulators are replaced by direct lighting current.

R. T.

Haber glass electrode. B. P. NIKOLSKI and K. S. EVSTROPIEV (*Proc. Leningrad Lab. [N.S.]*, 1930, No. 12, 5—24).—The glass electrode (I) gives accurate readings up to p_H 11.5, departures beyond this p_H depending on the cation. Ca and Ba do not affect the accuracy. (I) is especially valuable in heterogeneous solutions.

CH. ABS. (e)

Improvements in the technique of counting small ions. N. WEGGER (*Physikal. Z.*, 1935, **36**, 15—20).—Apparatus for counting and determining the velocities of small ions is described.

A. J. M.

Water-cooled resistors. E. M. THORNDIKE (Science, 1934, 80, 619—620).—Two types of resistor, consisting essentially of nichrome wire cooled by a flow of H_2O , and capable of carrying 40 amp., are described. L. S. T.

Device for holding electrodes during electro-metric titrations. M. L. HERZOG (Ind. Eng. Chem. [Anal.], 1935, 7, 47). E. S. H.

Radio-frequency high-voltage generator. D. H. SLOAN (Physical Rev., 1935, [ii], 47, 62—71).—The resonance transformer, generating 800,000 volts, is contained in an evacuated, H_2O -cooled, Cu-lined steel tank, and is wound of H_2O -cooled concentric Cu pipes, without insulation. N. M. B.

Apparatus for measuring the magnetic susceptibility of solids and liquids at high temperatures. R. B. SOSMAN and J. B. AUSTIN (J. Washington Acad. Sci., 1935, 25, 15—32).—The pull on a sample suspended inside a vertical solenoid is measured directly by means of a sensitive balance. The shape of the hysteresis loop of a ferromagnetic powder is estimated by combining a uniform field with a non-uniform one. C. W. G.

Accuracy of the Curie-Cheneveau magnetic balance. F. W. GRAY and J. H. CRUICKSHANK (Nature, 1935, 135, 152).—The accuracy of the balance is defended. The unexplained variations sometimes obtained with H_2O are not due to its untrustworthiness (cf. this vol., 149). L. S. T.

Apparatus for measuring Curie points at low temperatures. R. FORRER and V. MARIAN (J. Phys. Radium, 1934, [vii], 5, 617—618).—A simple instrument, consisting of a small three-pole magnet in contact with a thermometer and acting on a magnetometer, can be used at temp. $\geq 400^\circ$. The substance under investigation is placed between two of the poles. N. M. B.

Wash-bottle for quantitative work. E. J. DE BEER (Ind. Eng. Chem. [Anal.], 1935, 7, 67).—The apparatus permits the use of a measured amount of washing liquid. E. S. H.

Viscosity determinations at high temperatures by means of freely falling spheres. W. M. COHN (Ann. Physik, 1935, [v], 21, 761—782).—Pt-Rh spheres were dropped through silicate melts (900—1400°), the time taken to fall a measured distance being determined electrically. The viscosity is calc. from Stokes' equation. Comparison with the rotating-cylinder method shows good agreement. A. J. M.

Determination of the degree of purity of liquid substances and azeotropic mixtures. W. SWIENTOSLAWSKI (J. Physical Chem., 1934, 38, 1169—1172).—A standard apparatus is described (cf. A., 1932, 1226). D. R. D.

Apparatus for control of pressure in distillation. G. W. JACOBS (Ind. Eng. Chem. [Anal.], 1935, 7, 10—71). E. S. H.

Fractional distillation under reduced pressure. E. BRADFELD (J.S.C.I., 1935, 54, 6T).—A vacuum-jacketed fractionating column is described. J. S. A.

Distillation apparatus. W. SWIENTOSLAWSKI (Rocz. Chem., 1934, 14, 614—620).—Apparatus for fractional distillation of small vols. of liquids is described. R. T.

Milling of small quantities of material for analysis. J. HUDIG (Chem. Weekblad, 1935, 32, 54).—The laboratory disintegrator described mills and sieves 50-g. samples of plant materials quantitatively in 3 min. S. C.

Preparation of very thin tungsten wires by sputtering a thicker wire in a gas discharge. J. F. H. CUSTERS (Nederl. Tijds. Natuurk., 1934, 1, 8—15; Chem. Zentr., 1934, ii, 1738).—A W wire of 2×10^{-4} cm. diam. was made by sputtering one of 10^{-3} cm. diam. in an A atm. H. J. E.

Preparation of graded collodion membranes and their use in study of filterable viruses.—See this vol., 257.

Vacuum regulator. C. W. MCCONNELL (Ind. Eng. Chem. [Anal.], 1935, 7, 4). E. S. H.

Compact rotatable vacuum gauge with three ranges for pressures of 700—0.0001 mm. H. MOSER (Physikal. Z., 1935, 36, 1—2).—An instrument based on the MacLeod principle is described. A. J. M.

Magnesium perchlorate ("anhydron") as a drying agent. J. G. F. DRUCE (Chem. and Ind., 1935, 54—55).—A review. $Mg(ClO_4)_2$ is as effective as P_2O_5 as a drying agent, is readily regenerated, and is not subject to the chemical limitations imposed on the use of P_2O_5 . $Mg(ClO_4)_2 \cdot 3H_2O$ is almost as effective as P_2O_5 . R. S. B.

Magnesium perchlorate as a drying agent. J. G. F. DRUCE (Chem. and Ind., 1935, 133; cf. preceding abstract).— $Mg(ClO_4)_2$ can be heated with NH_4Ac at 220° without any sign of violent action, but caution must be used in heating with some org. compounds, or explosions may occur. P. G. M.

Glass-blowers' holder for large flasks. A. F. SCOTT (Science, 1934, 80, 620). L. S. T.

Apparatus for extraction of solids by upward flow of solvent. F. E. HOLMES (Ind. Eng. Chem. [Anal.], 1935, 7, 75—76). E. S. H.

Hot-water funnel. J. R. CALDWELL (Ind. Eng. Chem. [Anal.], 1935, 7, 76). E. S. H.

Filling of instruments with liquids through capillary tubes. V. G. SHIVOV (Zavod. Lab., 1934, 3, 1037).—Electrical heating is recommended for filling thermoregulator bulbs with PhMe. R. T.

Determination of solubility, density, viscosity, and conductivity of solutions of salts. S. K. TSCHIRKOV (J. Appl. Chem. Russ., 1934, 7, 1323—1328).—Apparatus is described. R. T.

Nomogram for centrifugal force. H. SHAPIRO (Ind. Eng. Chem. [Anal.], 1935, 7, 25).—The nomogram may be used for machines having a radius up to 27 cm. and speed up to 2000 r.p.s. E. S. H.

Geochemistry.

Atmospheres of the planets. H. N. RUSSELL (Science, 1935, 81, 1—9).—A lecture. L. S. T.

Origin of the helium in natural gases. Helium and ekacæsium (element no. 87). A. LEPAPE (Compt. rend., 1935, 200, 336—338).—A small portion only of the He found in natural gases can be accounted for by known radioactive elements. Owing to the frequent association of the rarer alkalis, Li, Rb, and Cs, with the sources of these gases, it is suggested that the origin of the He was eka-Cs which has probably now practically disappeared. M. S. B.

Origin of the helium in natural gas; relation between helium and lithium contents in certain sodium chloride mineral springs. A. LEPAPE (Compt. rend., 1935, 200, 163—165).—Of 14 French mineral spring-waters examined, those yielding gases richest in He are the NaCl springs richest in Li, and originating in triassic strata. No relationship exists between the He in the gas and the radioactivity of the H₂O. NaCl springs originating from tertiary formations are poor in He, whatever their [Li] or radioactivity. In all springs very rich in He the Li is accompanied by Rb and Cs. J. W. S.

Abnormal temperature stratification in lakes Maru-numa and Ooziri-numa, Gunma Prefecture, Japan, and the chemistry of their waters. S. YOSHIMURA (Japan. J. Geol., 1934, 11, 259—271).—Data are recorded. CH. ABS. (e)

Radium content of some connate waters. H. G. BOTSET (Physics, 1934, 5, 276—280).—H₂O from oil wells gave vals. from 208 to 1956 × 10⁻¹² g. Ra per litre. There was a fairly definite correlation between the heavy mineral content of a sample and its Ra content. CH. ABS. (e)

Colloid lake at Witzenhausen a.d. Werra. E. WEDEKIND (Kolloid-Z., 1935, 70, 39).—The H₂O contains Fe(OH)₃, Al(OH)₃, and SiO₂ as a reversible sol. E. S. H.

Acid-base equilibrium in sea-water. L. IRVING (Science, 1934, 80, 587—588).—A discussion. L. S. T.

Microbiology and the marine limestone. R. M. FIELD (Trans. Amer. Geophys. Union, 1932, 230—233).—Ca(HCO₃)₂ in solution, and pptn. of CaCO₃ in the waters of the Bahamas, may be due to bacterial action. CH. ABS. (e)

Metallic sulphides in the Shotover River district. C. O. HUTTON (New Zealand J. Sci. Tech., 1934, 16, 154—155).—Analytical data are recorded for a chalcopyrite outcrop and for a pyrrhotite ore containing an abnormally high proportion of S relative to Fe. A. G. P.

Halloysite and allophane. C. S. ROSS and P. F. KERR (U.S. Geol. Survey, 1934, Prof. Paper 185-G, 135—148).—12 analyses of halloysite show SiO₂:Al₂O₃ ratios 206:100 to 165:100 with only approx. agreement with the usually accepted formula H₂Al₂Si₂O₈. The material may be white and friable or grey and porcellaneous. Most is optically isotropic, but sometimes feebly birefringent (< 0.001), *n* 1.543—1.648.

X-Ray patterns with somewhat diffused bands show that the material is minutely cryst., with some relation to, but distinct from, kaolinite. The dehydration curve shows a gradual loss of H₂O to 400—430° and a rapid loss to 500°. Halloysite is a product of weathering, especially in association with sulphide ores, and it is often associated with alunite. Allophane is truly amorphous and shows a wider range in composition, often containing evansite and other minerals in solid solution. X-Ray patterns show traces of diffused bands. *n* 1.472—1.512. The dehydration curve shows a gradual loss of H₂O throughout. L. J. S.

Alkalinity of silicate minerals. R. E. STEVENS (U.S. Geol. Survey, 1934, Prof. Paper 185-A, 1—13).—Various minerals were ground with a few drops of H₂O free from CO₂ in an agate mortar for 2 min., and the *p*_H of the solution was determined colorimetrically and electrometrically. Vals. include: beryl 7.2, muscovite 7.8—9.0, calcite 9.0, orthoclase 8.8—9.2, albite 9.4—9.8, olivine 10.2, wollastonite 10.8, glass 11.2—11.4. This is the order of stability of the minerals with respect to their resistance to weathering. The effects of silicate minerals on underground waters and geochemical changes is discussed. L. J. S.

Constancy of the uranium-actinium ratio in minerals. F. H. BRUNER and H. SCHLUNDT (J. Physical Chem., 1934, 38, 1183—1188).—U was determined gravimetrically and Ac by Meyer and Hess' method (A., 1920, ii, 658). The ratio was const. within the limits of experimental error (5%) in soddite, thorianite, and pitchblende from Bohemia and two Canadian sources. D. R. D.

Spring Hill gold deposit near Helena, Montana. V. JONES (Econ. Geol., 1934, 29, 544—559).—The sulphides are pyrrhotite, arsenopyrite, and pyrite (I), Au occurring mainly with (I). CH. ABS. (e)

Characteristics of organic content of rocks. W. L. RUSSELL (Bull. Amer. Assoc. Petroleum Geol., 1934, 18, 1103—1125).—The org. substances and NH₃ evolved on distilling > 700 samples of shale, limestone, and dolomite in a closed tube have been studied. CH. ABS. (e)

Role of volatiles in the formation of Virginia titanium deposits. C. S. ROSS (Trans. Amer. Geophys. Union, 1934, 245).—The development of the minerals is discussed. CH. ABS. (e)

Rare elements in Oklahoma sphalerite. E. L. HASSLER and H. C. ROYS (Proc. Oklahoma Acad. Sci., 1934, 14, 67—68).—Ga, Ge, Fe, Zn, Cd, Pb, and Sn were detected, indicating the magmatic origin of this Zn ore. CH. ABS. (e)

Eclogites from the eastern Alps. H. WIESENER (Tsch. Min. Mitt., 1934, 46, 174—210).—Descriptions with chemical analyses are given of eclogites from several localities. L. J. S.

Magmatic rocks. E. TROGER (Tsch. Min. Mitt., 1934, 46, 153—173).—Detailed chemical analyses are given of ten rarer types of igneous rocks—greisen,

carbonate-beresite, weiselbergite, sanukite, ornoite, bojite, corsite, lakarpite, alnoite, and olivine-melilitite.

L. J. S.

Pyromorphism of inclusions in volcanic rocks. K. SCHOTLITSCH (Tsch. Min. Mitt., 1934, 46, 127—152).—Inclusions of various plutonic rocks and cryst. schists in volcanic rocks on the borders of the eastern Alps are described and the mineral changes in them noted.

L. J. S.

Plagioclase from Linosa: the anemousite question. E. ERNST and H. NIELAND (Tsch. Min. Mitt., 1934, 46, 93—126).—Crystals of felspar from the same spot on the island of Linosa, Mediterranean, as those described as anemousite by Washington and Wright (1910) were examined in detail. They show a variation in their optical data, d , and composition; four analyses range from Ab 61.38, An 34.02, Or 4.60 to Ab 44.62, An 51.55, Or 3.83 mol.-%, d 2.660—2.693. The optical data are found to agree with the normal plagioclase series, and there is no need to assume a carnegite mol. The assumed anemousite and pacificite from Hawaii (Barth, A., 1930, 448; 1931, 708) are not accepted.

L. J. S.

Boehmite and diaspore in Ayrshire fireclays (Scotland). J. DE LAPPARENT (Compt. rend., 1934, 199, 1629—1631).—Well-developed boehmite crystals and diaspore were observed. The Ayrshire fireclays are analogous to bauxites in the Pyrenees (Ariege).

H. J. E.

Separation of argillaceous fraction of sedimentary rocks. M. DREYFUSS (Compt. rend., 1934, 199, 1631—1633).—Argillaceous constituents (I) are separated by using suspending agents (K soaps, gum arabic, or gelatin). (I) is recovered from the suspension by pptg. and washing.

H. J. E.

Thermal decomposition of carbonate minerals. R. C. WELLS (Trans. Amer. Geophys. Union, 1934, 237—240).—Data for the rate of thermal decomp. of magnesite (I), brucite, and hydromagnesite are given. Decomp. of (I) begins at $> 560^\circ$, increasing rapidly for the first third of the decomp. and then remains approx. const.

CH. ABS. (e)

Stilpnomelane and related minerals as constituents of schists from Western Otago, New Zealand. F. J. TURNER and C. O. HUTTON (Geol. Mag., 1935, 72, 1—8).—Minerals of the stilpnomelane group are common constituents of the schists and semi-schists of various parts of W. Otago. The genesis of stilpnomelane is discussed.

L. S. T.

Analysis of Egyptian igneous and metamorphic rocks. W. F. HUME, H. F. HARWOOD, and L. S. THEOBALD [with A. I. AWAD] (Geol. Mag., 1935, 72, 32; cf. A., 1929, 56).—Analyses and petrographic descriptions of a gneiss, four schists, a diorite, a eclogite, four Baramia serpentines, a dolomite, and a typical Aswan monumental granite are discussed.

L. S. T.

Dehydration of fibrous parasepiolite. (MILE.) S. CALLERE (Compt. rend., 1934, 199, 1626—1628).—Hydration in vac. occurs in two stages (190—290° 465—675°), and is complete at 720°. From X-ray measurements, the material is non-cryst. at 190°, but becomes cryst. at 1000°. The decomp. of

sepiolite on heating is $H_4Mg_2Si_3O_{10} = 2H_2O + 2MgSiO_3 + SiO_2$. Changes in optical properties on heating, and analytical data are recorded.

H. J. E.

Hessian bauxite deposits. M. MOLDENHAUER (Chem.-Ztg., 1935, 59, 125—127).—The location of the deposits is given, and the composition of samples discussed.

A. J. M.

Origin of the crystalline slates of Kabylie de Collo (Department of Constantine, Algeria). M. ROUBAULT (Compt. rend., 1935, 200, 145—147).—These rocks include complete slate formations (satin and mica slates), gneissic formations (biotite, granulitic and amphibolic gneiss), more basic amphibolites, and some strata of cipolins. The origin of these formations is discussed.

J. W. S.

Schroëckerite from Bedford, New York. E. J. ARMSTRONG (Amer. Min., 1935, 20, 62—63).—The mineral which occurs in pegmatite specimens from Kinkel's quarry has n_a 1.658, n_e 1.682, n 1.685 \pm 0.003.

L. S. T.

Soda-alunite from Molokai, Hawaiian islands. J. D. LAUDERMILK (Amer. Min., 1935, 20, 57—58).—A white, chalky mineral from the desert strip of Molokai has been identified as soda-alunite; SiO_2 0.04, Al_2O_3 34.64, Fe_2O_3 2.16, MgO trace, CaO 0.28, K_2O 6.08, Na_2O 4.62, H_2O 15.38, TiO_2 0.60, SO_3 37.02, total 100.82%.

L. S. T.

Burkeite, a new mineral species from Searles Lake, California. W. F. FOSHAG (Amer. Min., 1935, 20, 50—56).—The analysis Na₂O 47.89, K_2O none, SO_3 39.96, CO_2 11.72, H_2O 0.04, Cl 0.09, insol. 0.04, total 99.74%, agrees with the formula $2Na_2SO_4 \cdot Na_2CO_3$. The mineral is biaxial, negative with n_a 1.448—1.449, n_β 1.488—1.489, n_γ 1.491—1.493; d 2.57, hardness 3.5.

L. S. T.

Unit cell and space-group of realgar. M. J. BUERGER (Amer. Min., 1935, 20, 36—43).—Weissenberg photographs for realgar from Allchar, Macedonia, give a 9.27, b 13.50, c 6.56 Å., β 73° 22' with 16 formula wts. per unit cell, space-group C_{2h}^2 , $P2_1/n$, referred to a new orientation chosen by taking the a -axis in Goldschmidt's [101] direction. X-Ray methods confirm the monoclinic holohedral nature of realgar.

L. S. T.

Formula and crystal system of alleghanyite. A. F. ROGERS (Amer. Min., 1935, 20, 25—35).—Alleghanyite from Bald Knob, Alleghany County, N.C., has the formula $2Mn_2SiO_4 \cdot Mn(OH, F)_2$ and not $5MnO \cdot 2SiO_2$ (A., 1932, 1228). It is monoclinic, and isomorphous with chondrodite; n_a 1.756, n_β 1.780, n_γ 1.792; d 4.020. SiO_2 22.75, Al_2O_3 0.75, Fe_2O_3 0.73, MgO 0.71, CaO 1.34, H_2O 2.56, CO_2 1.92, TiO_2 0.15, MnO 67.85, F 0.30, S 0.11, total 98.82%.

L. S. T.

Pegmatites of Fitchburg, Massachusetts. C. S. HITCHEN (Amer. Min., 1935, 20, 1—24).—The pegmatites described are classified into the following types: biotite, tourmaline, beryl, titanite, and allanite. Their origin is discussed.

L. S. T.

Stibnite in quartz. N. H. STEARN (Amer. Min., 1935, 20, 59—62).—Inclusions of stibnite and prob-

ably cinnabar occurring in small quartz crystals from the Parnell Hill and Gap Ridge mines, Pike County, Arkansas, are described. The order of crystallisation appears to be stibnite, cinnabar, quartz. L. S. T.

X-Ray study of opals. F. P. DWYER and D. P. MELLOR (J. Proc. Roy. Soc. New South Wales, 1934, 68, 47—50).—The presence of β -cristobalite and α -quartz in opals is correlated with their thermal history. F. N. W.

Mineral occurring in Germany containing rare-earths as main constituent. F. HENRICH (J. pr. Chem., 1935, [ii], 142, 1—5).—Weinschenkite (A., 1922, ii, 860) is a rare-earth phosphate dihydrate ($X^{III}PO_4 \cdot 2H_2O$) and contains Y (main constituent), Gd, Dy, Er, Ho, Tb (trace), Yb (trace), and small amounts of Ce-earths. H. B.

Origin of natural oil. E. BERL (Science, 1935, 81, 18).—A reply to criticism (cf. this vol., 191).

L. S. T.

Soil profiles developed on carboniferous limestone in Somerset and Derbyshire. A. J. LOW (J.S. East. Agric. Coll. Wye, 1934, No. 34, 155—165).

CH. ABS. (p)

Soil profile in view of field studies in Somerset, Derbyshire, and Cheshire. A. J. LOW (J.S. East. Agric. Coll. Wye, 1934, No. 34, 166—196).

CH. ABS. (p)

Meteorite from Lanton, Howell County, Missouri. J. S. CULLISON and G. A. MULLENBURG (J. Geol., 1934, 42, 305—308; Chem. Zentr., 1934, ii, 1755).—The outer crust consisted of reddish-brown oxides. The composition was Fe 90.40, Ni 8.33, Co 0.61, P 0.18, SiO_2 0.005% (no Mn or Cu). The chief minerals were kamazite, taenite, schreibersite, and plessite.

H. J. E.

Organic Chemistry.

Electronic theory of organic chemical reactions. F. ARNDT and B. EISTERT (Ber., 1935, 68, [B], 193—199).—Theoretical. H. W.

Isomerism. II. F. P. A. TELLEGEN (Chem. Weekblad, 1935, 32, 40—45; cf. this vol., 191).—An account of stereo- and geometrical isomerism.

S. C.

Bruto-isomerism. J. VAN ALPHEN (Chem. Weekblad, 1935, 32, 39—40). F. P. A. TELLEGEN (*ibid.*, 53—54).—A discussion.

S. C.

Occurrence of optical asymmetry. F. ROST (Angew. Chem., 1935, 48, 73—75).—A review.

E. S. H.

Electrolytic syntheses in organic chemistry. F. FICHTER (Bull. Soc. chim., 1934, [v], 1, 1585—1609).—A lecture.

Improvements in the Sabatier-Senderens process for the preparation of paraffins. P. K. SAKMIN (Ber., 1935, 68, [B], 164—166).—The olefine is mixed with an excess (instead of a deficiency) of H_2 and passed over a Ni catalyst at 150° . The product contains 1% of C_nH_{2n} , 9% of N_2 , 30% of H_2 , and 60% of C_nH_{2n+2} . It is strongly cooled (apparatus described), whereby all paraffins are condensed but H_2 and N_2 escape. The advantage of the process lies in its avoidance of olefine and use of Br; the paraffins are free from olefine dibromides and are 92—94% (instead of 80%) pure. H. W.

Oxidation of ethane. E. W. R. STEACIE (Chem. and Ind., 1935, 62—63).—A reply to Bone (this vol., 40).

R. S. B.

Oxidation of ethane. W. A. BONE (Chem. and Ind., 1934, 63—64; cf. preceding abstract).—A reply to Steacie with further criticism.

R. S. B.

Catalytic isomerisation of *n*-heptane, *n*-octane, and Δ^a -hexene. A. D. PETROV, A. P. MESCHT-SCHERJAKOV, and D. N. ANDREEV (Ber., 1935, 68, [B], 1—5).—With olefines, the temp. ranges of isomerisation, cracking, and, particularly, of polymerisation

lie very close to one another. In presence of $ZnCl_2$, *n*-heptane (I) undergoes 20—25% isomerisation in 6 hr. at 300 — 400° under pressure of H_2 or N_2 . In presence of MoS_3 at 420° (I) is appreciably isomerised at 420° to an extent which increases markedly with time over 3—14 hr. *n*-Octane in presence of MoS_3 is isomerised at 410° and at 440° suffers profound transformation accompanied by marked cracking. MoS_3 is more powerful than $ZnCl_2$ but weaker than $AlCl_3$ as isomerising agent. Δ^a -Hexene remains unchanged in presence of MoS_3 at 300° , but commences to polymerise at 350° ; the process is more marked at 400° . It differs from the paraffins in that it scarcely yields fractions of b.p. < that of the initial material. After 1 hr. at $400^\circ/140$ atm., the product contained Δ^a - and Δ^v -hexene, but *isohexenes* could not be detected.

H. W.

Hydrocarbon in basking shark.—See this vol., 233.

Determination of unsaturation in aliphatic hydrocarbons by bromide-bromate titration. S. P. MULLIKEN and R. L. WAKEMAN (Ind. Eng. Chem. [Anal.], 1935, 7, 59).—The procedure is applicable to alkenes, *cycloalkenes*, and alkadienes; its application under ordinary conditions to alkynes and *cycloalkdienes*, such as terpenes, is doubtful.

E. S. H.

Addition of hydrogen bromide to olefines. J. C. SMITH and P. L. HARRIS (Nature, 1935, 135, 187).—*iso*Undecenoic acid adds HBr relatively slowly and yields the same proportions of 0- and *i*-bromo-undecenoic acid whether oxidants or anti-oxidants are present. Since undecenoic acid shows the peroxide effect, this is now evidence that only terminal double linkings are susceptible.

L. S. T.

Preparation of butadiene from ψ -butylene (butene). B. P. FEDOROV, A. I. SMIRNOVA, and P. A. SEMENOV (J. Appl. Chem. Russ., 1934, 7, 1166 1180).—Butadiene (I) is obtained in 21% yield by passing 7 : 1 N_2 -CHMe:CHMe (II) mixtures through

porcelain tubes at 700°; at the same time, 18—24% of the (II) is decomposed, and the remainder may be recovered. Lower yields of (I) are obtained in presence of ZnO, Cr₂O₃, SiO₂ gel, Pt, Fe, Cu, and C, whilst in presence of MgO 25—29% yields of (I), with 27—29% decomp. of (II) to other products, are obtained.

R. T.

Addition of sulphur dichloride to butadienes. H. J. BACKER and J. STRATING (Rec. trav. chim., 1935, 54, 52—56).— β -γ-Dimethylbutadiene and isoprene with SCl₂ in ligroin give 1% yields of 3:4-dichloro-3:4-dimethyl-, m.p. 174° (HgCl₂ compound, decomp. 130—131°), and -3-methyl-thiacyclopentane, b.p. 68—70°/3 mm. (HgCl₂ compound, decomp. 158°), oxidised to 3:4-dichloro-3:4-dimethyl-, m.p. 265° (decomp.), and -3-methyl-thiacyclopentane 1:1-dioxide, m.p. 144.5—145.5°, respectively. Butadiene, however, gives the tetrachloride, m.p. 73—74°, as sole product.

R. S. C.

Polymerisation of pentenes. H. I. WATERMAN, J. J. LEENDERTSE, and W. MOKLAZINGAL (Rec. trav. chim., 1935, 54, 79—84).—*n*-C₅H₁₂ (I) and AlCl₃ at 0° give 80% of "partly cyclised" polymerisation product (II). At 400° alone or with Al₂O₃ (I) gives a larger yield of (II). A mixture of branched-chain pentenes, mainly CH₂:CHPr^s (III), at 400° or in C₆H₆ at 85° or 200° undergoes much isomerisation (to a product giving CMe₂EtCl with HCl) and polymerisation to "partly cyclised" products.

R. S. C.

Low-temperature hydrogenation and polymerisation of acetylene in presence of nickel catalysts. A. D. PETROV and L. I. ANTZUS (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 295—303).—C₂H₂ and H₂ at 300°/1 atm. (a), or at 40°/20—25 atm. (b), give alkenes principally, but isoalkenes, alkadienes, more highly unsaturated hydrocarbons, and aromatic hydrocarbons (I) have been found. Conditions (b) favour the formation of (I). Reactions involved are discussed.

F. N. W.

Oxygen additive compounds of acetylenes. C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J.C.S., 1935, 115; cf. A., 1934, 1089).—Acetylenes which are normally liquids or are in fused condition form peroxides, but C₂H₂ does not.

F. R. G.

Reaction between acetylene and sulphur. C. T. BHATT, K. S. NARGUND, D. D. KANGA, and M. S. SHAH (J. Univ. Bombay, 1934, 3, No. 2, 159—160).—Passage of C₂H₂ through S heated at 290—390° (reaction becomes rapid at 320°) in a glass flask gives C, H₂S, CS₂, thiophen, and PhSH.

H. W.

Reactions between ethylene chloride and chloral. S. HAMAI (Bull. Chem. Soc. Japan, 1934, 9, 542—548).—No measurable reaction occurs between liquid (CH₂Cl)₂ (I) and Cl₂ at 25°, 30°, or 50°, but in presence of HCl as catalyst CHCl₂:CH₂Cl is formed. Gaseous (I) and Cl₂ at room temp. give a trace of C₂Cl₆. Both reactions are preceded by an induction period.

F. N. W.

Preparation and solubilities of aluminium alkoxides. E. V. ZAPPI and E. RESTELLI (Anal. Assoc. Quim. Argentina, 1934, 22, 87—90).—Al amalgams do not react satisfactorily with all alcohols. In presence of HgCl₂ clean Al filings begin to react with anhyd. alcohols at room temp.; Al powder is less

satisfactory, owing probably to greater surface oxidation. The solubilities of Al(OR)₃, where R=Me, Et, Pr^s, Bu^s, Bu^t, CH₂Ph, and CH₂:CH:CH₂, in the corresponding alcohol, are recorded. All, except the first and last-named, are sol. (12—47%).

H. F. G.

Preparation of propylene glycol from propylene chloride. A. L. KLEBANSKI and I. M. DOLGOPOLSKI (J. Appl. Chem. Russ., 1934, 7, 1181—1191).—CHMeCl:CH₂Cl and saturated aq. NaHCO₃ at 210°/182 atm. yield 60—65% of OH:CHMe:CH₂:OH (I) and 7—8% of unsaturated compounds (chiefly CH₂Cl:CH:CH₂); when Na₂CO₃ is substituted for NaHCO₃ the yields of (I) are > 48%.

R. T.

Oxonium compounds. Complex acidic oxonium compounds of organic oxygen compounds. V. V. TSHELINTZEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 304—309).—Saturated solutions of many org. O compounds (I) (R·OH, R·CHO, etc.) in varying concns. of HCl are found to contain (I) and HCl in equimol. proportions. Formation of acid oxonium compounds is assumed.

F. N. W.

Reactions of cobalt sulphate in glycerol. M. CHATELET (Compt. rend., 1935, 200, 62—63).—The red solution (I) of CoSO₄·7H₂O (II) in glycerol on addition of EtOH deposits a viscous mass which after prolonged washing with C₆H₆ is approx. (CoSO₄)₃·C₃H₈O₃. Addition of aq. NH₃ to (I) gives no ppt., but yields a yellow solution which on addition of an equal vol. of EtOH deposits crystals of the compound (CoSO₄·4NH₃)₃·(C₃H₈O₃), stable in dry air but decomposed by traces of H₂O with pptn. of Co(OH)₂. If dry HCl is passed through saturated (I) heat is generated and further amounts of (I) can be dissolved until the HCl yields a ppt., probably CoCl₂·C₃H₈O₃·*n*HCl, which on washing with C₆H₆ and Et₂O yields the violet compound CoCl₂·C₃H₈O₃.

J. W. S.

Constitution of benzylidene-*d*-sorbitol. Synthesis of *l*-xylose. L. VON VARGHA (Ber., 1935, 68, [B], 18—24).—Sorbitol is converted by PhCHO in H₂O-HCl at room temp. into αγ-benzylidene-*d*-sorbitol (I), m.p. 172—173°, [α]_D²⁰ +5.6° in H₂O, transformed by COMe₂-CuSO₄ into αγ-benzylidene-ε-*isopropylidene-d*-sorbitol, m.p. 179°, [α]_D²⁰ +19.0° in CHCl₃, and αγ-benzylidene-βδεζ-*diisopropylidene-d*-sorbitol, m.p. 131—132°, [α]_D²⁰ +26.7° in CHCl₃. (I) is oxidised by Pb(OAc)₄ in AcOH to 3:5-benzylidene-*l*-xylofuranose (II), m.p. (indef.) 184° (decomp.), [α]_D²⁰ +36.5° in EtOH (phenylhydrazone, m.p. 185°, [α]_D²⁰ +28.0° in MeOH). (II), Ac₂O, and C₅H₅N at 15—20° afford 3:5-benzylidene-*l*-xylofuranose 1:2-diacetate, m.p. (indef.) 90°, [α]_D²⁰ +20.6° in CHCl₃, which does not react with NHPh·NH₂ or redden fuchsin-H₂SO₃. Hydrolysis of (II) with boiling 10% AcOH leads to β-*l*-xylose (III), m.p. 144°, [α]_D²⁰ -79.3° (initial), -18.6° (equil.), in H₂O (tetra-acetate, m.p. 126°, [α]_D²⁰ +25.7° in CHCl₃). Treatment of (III) according to Schmidt *et al.* (A., 1934, 173) gives *l*-xyloketose identical with that obtained by Levene *et al.* (A., 1914, i, 1027) from urine.

H. W.

Detection of trichlorotribenzylidenesorbitol with acetone. G. REIF (Z. Unters. Lebensm., 1934, 8, 468—473).—The [H₂SO₄] required to liberate

α - $C_6H_4Cl \cdot CHO$ from trichlorotribenzylidenesorbitol (I) (equal vols. of H_2O and H_2SO_4 of d 1.84) is $>$ that required to liberate $PhCHO$ from benzylidenesorbitol (9 vols. of H_2O to 5 vols. of H_2SO_4), and the more conc. acid is also necessary to produce a coloration with $COMe_2$. With the more conc. acid benzylidenemannitol may also give a coloration with $COMe_2$, but instructions are given for differentiating the two. The purification of the pptd. (I) and the method of carrying out the test are described. E. C. S.

Synthesis of glycerides. I. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 812—818).—On the basis of lit. data concerning the wandering of acyl groups in the hydrolysis of CPh_3 from $OR \cdot CH_2 \cdot CH(OR') \cdot CH_2 \cdot O \cdot CPh_3$ (R, R' or $R'' = \text{acyl}$), the following general method for the synthesis of glyceryl esters (of known structure) containing three different acid radicals is outlined: the α -monoglyceride $OR \cdot CH_2 \cdot CH(OH) \cdot CH_2OH$ (from isopropylideneglycerol and RCl) with 1 mol. of CPh_3Cl and C_6H_5N (or triphenylmethylglycerol and RCl) affords $OR \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot CPh_3$, converted by $R'Cl \cdot C_6H_5N$ in $CHCl_3$ into $OR \cdot CH_2 \cdot CH(OR') \cdot CH_2 \cdot O \cdot CPh_3$, hydrolysis of which gives either the $\alpha\gamma$ -, $OR \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OR'$ (I) or $\alpha\beta$ -, $OR \cdot CH_2 \cdot CH(OR') \cdot CH_2 \cdot OH$ (II), -diglyceride, the constitution of which is readily determined by known methods. Further action of $R''Cl$ on (I) and (II) gives, respectively, the triglycerides $OR \cdot CH_2 \cdot CH(OR'') \cdot CH_2 \cdot OR'$ and $OR \cdot CH_2 \cdot CH(OR') \cdot CH_2 \cdot OR''$. J. W. B.

Production of an optically active phosphoglyceric acid by glycolysis in muscle.—See this vol., 250.

Reaction of alkyl sulphates and *p*-toluenesulphonates with the Grignard reagent and preparation of magnesium dialkyls. C. M. SUTER and H. L. GERHART (J. Amer. Chem. Soc., 1935, **57**, 107—109; cf. Cope, A., 1934, 991).—Contrary to the previous statement (A., 1933, 1033), $MgBu^aBr$ and $Bu^a_2SO_4$ do not give $Bu^a(MgBu^a)SO_4$ (I); if (I) is produced to any appreciable extent it undergoes disproportionation to $MgBu^a$, and $Mg(Bu^aSO_4)_2$. The reactions of various Alk_2SO_4 and p - $C_6H_4Me \cdot SO_3Alk$ with $MgBu^aBr$ and $MgPhBr$ are investigated; the decreases in the % of basic Mg (Gilman *et al.*, A., 1929, 800) and Br^- are determined. A solution of nearly pure $MgBu^a$, is obtained from $MgBu^aBr$ and Et_2SO_4 (slightly $>$ 1 mol. per equiv. of Br). Reaction between Mg and $Bu^a_2SO_4$ occurs only in presence of a little Mg halide; $MgBu^a_2$ and $Mg(Bu^aSO_4)_2$ are produced (cf. *loc. cit.*). The catalytic effect of, e.g., MgI_2 is explained thus: $2Bu^a_2SO_4 + MgI_2 \rightarrow 2Bu^aI + Mg(Bu^aSO_4)_2$; $2Bu^aI + Mg \rightarrow MgBu^a_2, MgI_2$. $MgBu^a_2 + MgI_2$. Me_2SO_4 , Mg , and MgI_2 similarly afford a low yield of $MgMe_2$ owing to the production of C_2H_6 (evolved rapidly towards the end of the reaction): $2Me_2SO_4 + MgMe_2 \rightarrow 2C_2H_6 + Mg(MeSO_4)_2$. H. B.

Esters of thiosulphurous acid, $H_2S_2O_2$. A. MEUNSEN [with G. DEGEL] (Ber., 1935, **68**, [B], 121—127).—Addition of $NaOMe$ or $NaOEt$ (prep. described) to a well-cooled solution of S_2Cl_2 in light petroleum leads to $Me_2S_2O_2$ (I), b.p. 44.2—44.4°/28—29 mm., and

$Et_2S_2O_2$ (II), b.p. 62.0—62.7°/15—16 mm., thiosulphite as greenish-yellow liquids which dissolve S, mix with org. media, are decomposed by acids, and are stable to air. Addition of S_2Cl_2 in light petroleum to $NaOAlk$ in the same medium gives the isomeric $Me_2S_2O_2$ (III), b.p. 33—33.5°/15 mm., and $Et_2S_2O_2$ (IV), b.p. 67—68°/16 mm., esters. (III) and (IV) dissolve S very sparingly and are distinguished from (I) and (II) in that they are scarcely affected by Hg , by which (I) and (II) are rapidly decolorised with production of HgS . Small amounts of $KOH \cdot MeOH$ rapidly cause copious separation of S from (I) and (II), whereas from (III) and (IV) a slight pptn. occurs only after considerable time. (I) and (II) colour $KI \cdot MeOH$ brown, whilst (III) and (IV) give only a pale yellow colour. Treatment with $NaOMe$, prolonged boiling under reduced pressure, or long keeping at 15—20° isomerises (I) to (III). The structure $S \cdot SCl_2$ being assigned to S_2Cl_2 , (I) and (II) are therefore considered to be $S \cdot S(OAlk)_2$, whereas (III) and (IV) are $OAlk \cdot S \cdot S \cdot OAlk$. The alternative structure $SR \cdot SO \cdot OR$ is improbable, since (III) and (IV) have no mercaptan odour and do not yield mercaptan when hydrolysed by acid or alkali. Attempts to obtain a compound of this structure from *Et chlorosulphinic acid*, b.p. 45.1—45.3°/38—39 mm., 171°/760 mm. (from $SOCl_2$ and $EtOH$), were unsuccessful. The discrepancy in b.p. excludes the possible formulation $SR \cdot SO_2R$, but the alternative structure $OR \cdot S \cdot SR \cdot O$ is not excluded.

H. W.

Isomerism of cyclic isoprene sulphones. J. BOESEKEN and E. DE R. VAN ZUYDEWIJN (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 760—762).—The conversion of cyclic isoprene sulphone ($R=Me$), in 0.5*N*- KOH , into an isomeride occurs in the dark and is due, not to *cis-trans* isomerisation (Eigenberger, A., 1931, 600, 1268), but to a three-carbon prototropic change (Ingold *et al.*, A., 1929, 300), $SO_2 \cdot \begin{smallmatrix} CH_2 \cdot CH \\ | \\ CH_2 \cdot CR \end{smallmatrix} (I) \rightleftharpoons SO_2 \cdot \begin{smallmatrix} CH_2 \cdot CH \\ | \\ CH=CR \end{smallmatrix} (II)$, since O_3 in aq. $CHCl_3$ affords, after removal of HCO_2H and addition of $BaCO_3$, a *Ba* salt $(CH_2Ac \cdot CH_2 \cdot SO_3)_2Ba$ or $(CHO \cdot CHMe \cdot CH_2 \cdot SO_3)_2Ba$ (slight reducing properties and gives $CHBr_3$ with $NaOBr$). Similar equilibration of butadiene sulphone ($R=H$), m.p. 63°, affords an isomeride, m.p. 45—50°, the equilibrium being at approx. 66.6% of (I). J. W. B.

Steric hindrance. *tert*-Butyl chlorotrithio-ortho-silico- and -germano-formate. H. J. BACKER and F. STIENSTRA (Rec. trav. chim., 1935, **54**, 38—46).— Bu^t_3 chlorotrithio-orthosilicoformate (I), $SiCl(SBu^t)_3$, m.p. 71°, b.p. 161—163°/3—4 mm. [from $NaSBu^t$ (3.3 mols.) and $SiCl_4$; 60% yield], with the appropriate alkyl mercaptide gives *Me* (II), m.p. 43—44°, b.p. 159—160°/4 mm. (66%), *Et* (III), m.p. 26—27°, b.p. 163—164°/4 mm. (75%), and *Pr* m.p. 105°, b.p. 161—163°/3—4 mm. (25%), Bu^t tetrathio-orthosilicate (IV), $Si(SBu^t)_3 \cdot SR$, and Bu^t tetrathio-orthosilicate, m.p. 160—161°, sublimes at 4 mm. (46%). Presence of a little $NaOH$ during the prep. of (IV) leads to formation of *tritert*-butylthio-silicon oxide, $[Si(SBu^t)_3]_2O$, m.p. 248—249° (decomp.), but the formation of (II) and (III) is more rapid than that of (IV), and thus $NaOH$ does not in these cases

lead to oxides. (I) is unchanged by H_2O (1 mol.) in EtOH, but with KOH-EtOH affords *tritert.-butylthiolsilicon hydroxide* (46%), m.p. 90–91°. GeCl_4 and NaSBu^\vee (3 mols.) in hot C_6H_6 give *Bu \vee ₃ chlorotrihydrogermanoformate*, m.p. 66–67°, b.p. 156–157°/3–4 mm., also formed, together with half its wt. of $\text{Ge}(\text{SBu}^\vee)_4$, m.p. 173–174°, when 4.4 mols. of NaSBu^\vee are used. Crystallographic data are given.

R. S. C.

Electrolysis of crotonic acid and thermal decomposition of dicrotonyl peroxide. F. FICHTER and J. ROSENZWEIG (Helv. Chim. Acta, 1935, 18, 238–242).—In the electrolysis of crotonic acid (I) between a Pt anode and Sn cathode about 25% of the current yield is consumed by oxidative decomp., about 75% by decomp. of H_2O , and only about 1.3% by the production of propylene. Thermal decomp. of dicrotonyl peroxide (II) affords CO_2 and $\Delta^{8,8}$ -hexadiene with some $\text{CHMe}\cdot\text{CH}_2$. The behaviour of (I) and (II) is thus similar to that of BzOH and Bz_2O_2 under analogous conditions, thus supporting the hypothesis that the inability of BzOH to undergo Kolbe's synthesis is due to its unsaturated nature (double linking $\alpha\beta$ to CO_2H). The prep. of percrotonic acid is hindered by its great instability; the products give the same substances as does (II) when thermally decomposed and probably contain (II). H. W.

Determination of lactic acid. F. GIRAULT (Bull. Sci. pharmacol., 1934, 41, 331–338; Chem. Zentr., 1934, ii, 1815).—An improved method for the determination of the purity of lactic acid is described.

H. N. R.

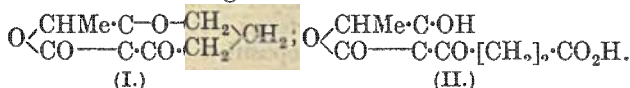
Catalytic decarboxylation of β -keto-acids.—See this vol., 309.

Glycol esters of dibasic acids. Di- β -hydroxyethyl esters. F. B. SHORLAND (J. Amer. Chem. Soc., 1935, 57, 115–116).— $(\text{CH}_2)_n(\text{CO}_2\text{H})_2$ ($n > 1$) (0.05 g.-mol.) and $(\cdot\text{CH}_2\cdot\text{OH})_2$ (0.5 g.-mol.) at 100° give good yields of $(\text{CH}_2)_n(\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ (I), which polymerise slowly at 160° to $\text{H}[\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot(\text{CH}_2)_n\cdot\text{CO}]_x\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and when heated to 260° afford the corresponding polyesters (Carothers and Arvin, A., 1929, 1165). *Hydroxyethyl sebacate* has m.p. 46°. β -Hydroxyethyl formate and acetate are similarly obtained from $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CH}_2(\text{CO}_2\text{H})_2$, respectively. Acetylation of the appropriate (I) gives *di- β -acetoxyethyl succinate*, u.p. 196°/5 mm., *glutarate*, b.p. 198°/5 mm., *adipate*, b.p. 210°/5 mm., and *sebacate*, b.p. 242°/5 mm., m.p. 25.5°.

H. B.

Biochemistry of micro-organisms. XLI. Metabolic products of *Penicillium Charlesii*. G. MATH. II. Molecular constitution of carolic carolinic acids. P. W. CLUTTERBUCK, H. RAISTRICK, and F. REUTER (Biochem. J., 1935, 29, 321).—Carolic acid (I) (A., 1934, 452), $\text{C}_9\text{H}_{10}\text{O}_4$, m.p. 132°, $[\alpha]_{5461}^{20} + 84^\circ$ in H_2O , monobasic and acid Congo-red, containing no active H in anisole and active H in $\text{C}_5\text{H}_5\text{N}$, gives on bromination (a) in gl. ac. COH *d-bromocarolic acid*, $\text{C}_9\text{H}_9\text{O}_4\text{Br}$, m.p. 132°, $[\alpha]_{5461}^{20} + 39^\circ$ in H_2O , monobasic, containing its active H in the side-chain, (b) in 50% AcOH and in H_2O *romo- γ -methyltetronic acid*, $\text{C}_9\text{H}_9\text{O}_3\text{Br}$, m.p. 172°, $[\alpha]_{5461}^{20} + 9.5^\circ$ in H_2O , monobasic, with *d- α -dibromo-*

γ -methyltetronic acid, $\text{C}_9\text{H}_9\text{O}_3\text{Br}_2$, m.p. 88°, monobasic (*monohydrate*, m.p. 135°, $[\alpha]_{5461}^{20} + 36.2^\circ$ in H_2O , monobasic). These C_9 mono- and di-bromotetronic acids with $\text{Pd}-\text{C}-\text{H}_2$ give *l- γ -methyltetronic acid*, $\text{C}_9\text{H}_9\text{O}_3$, m.p. 115°, $[\alpha]_{5461}^{20} - 21^\circ$, monobasic (*dinitrophenylhydrazone*, m.p. 235°), red FeCl_3 and violet NaNO_2 colours, hydrolysis products 1 mol. each of CO_2 and acetoin. (I) on hydrolysis gives 1 mol. each of CO_2 , acetoin, and butyrolactone (*phenylhydrazide*, m.p. 94°). (I) on reduction with $\text{Pd}-\text{C}-\text{H}_2$ gives an acid, $\text{C}_9\text{H}_{14}\text{O}_4$, monobasic (on distillation in vac. gives a substance, $\text{C}_9\text{H}_{12}\text{O}_3$, m.p. 45°, neutral), which on hydrolysis gives a *ketol*, $\text{C}_9\text{H}_{16}\text{O}_3$ (*bisdinitrophenylhydrazone*, m.p. 225°). (I) in H_2O becomes $\text{C}_9\text{H}_{12}\text{O}_5$, which gives *mono-* and *bis-dinitrophenylhydrazones*, m.p. 176° and 225°, respectively. (I) with CH_2N_2 gives a *Me₁ ether* readily hydrolysable with NaOH . Carolinic acid (II), $\text{C}_9\text{H}_{10}\text{O}_6$, m.p. 129°, $[\alpha]_{5461}^{20} + 60^\circ$ in H_2O (*monohydrate*, m.p. 123°; *dinitrophenylhydrazone*, m.p. 228°), dibasic, containing 2 active H in anisole, gives on hydrolysis 1 mol. each of CO_2 , acetoin, and $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, on reduction the *dibasic* $\text{C}_9\text{H}_{12}\text{O}_5$, m.p. 143° [hydrolysis product a *ketol-monobasic acid*, $\text{C}_9\text{H}_{14}\text{O}_4$ (*bisdinitrophenylhydrazone*, m.p. 248°)], and with CH_2N_2 a *ether Me₁ ester*. The structures assigned are:



A complete analogy is obtained between all the reactions of these acids and of synthetic α -acetyltetronic acid (III). (III) hydrolyses at the same speed as (I) and (II), giving 1 mol. each of CO_2 , acetol, and AcOH , on bromination loses its α -side-chain giving α -bromotetronic acid, and on reduction gives α -ethyltetronic acid, gives a readily hydrolysable *Me₁ ether* and a *dinitrophenylhydrazone*, m.p. 226°. Attention is directed to the relationship in structure of these acids and ascorbic acid (vitamin-C).

P. W. C.

Reducing substance obtained by hydrolysis of alginic acid. II. H. UGAMI (J. Agric. Chem. Soc. Japan, 1934, 10, 727–730).—Hydrolysis of alginic acid yields a substance, $\text{C}_5\text{H}_6\text{O}_3$, m.p. 207–207.5° (*phenylosazone*, m.p. 246°; *Ac₁ derivative*, m.p. 195°), which yields $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ on oxidation and is considered to be reductive acid (A., 1934, 511).

CH. ABS. (r)

Tartrates of bivalent metals.—See this vol., 315.

Complex salts of tartar emetic.—See this vol., 312.

Preparation of trihydroxyglutaric acid from xylose. E. Z. PLIUSCHKIN (J. Appl. Chem. Russ., 1934, 7, 1004–1007).—Trihydroxyglutaric acid is obtained in 50% yield from xylose by oxidation with HNO_3 according to Acree (B., 1930, 1084) and 97% of the HNO_3 can be regenerated.

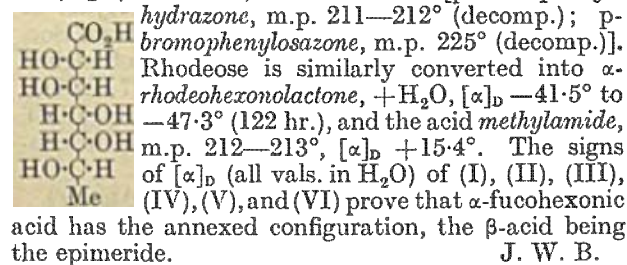
R. T.

Action of barium hydroxide on monobasic sugar acids. W. D. ALBERT and F. W. UPSON (J. Amer. Chem. Soc., 1935, 57, 132–134).—The amounts of CO_2 , HCO_2H , other volatile acids (mainly AcOH), $\text{H}_2\text{C}_2\text{O}_4$, and lactic acid (I) formed (as Ba salts) when the Ba salts of *d*-gluconic (II), *l*-arabonic, and *dl*-glyceric acids are treated with $3N\text{-Ba}(\text{OH})_2$ at 140°

for 24 hr. are determined. (I) is the main product and is obtained in yields of 65.2, 59.9, and 65.2% (of recovered C), respectively. Possible mechanisms (involving enediol formation) for the production of (I) are discussed. A little *meso*- $\alpha\alpha'$ -dihydroxyadipic acid [Ca salt; *phenylhydrazide*, m.p. 215° (corr.)] is also produced from (II). *dl*-Lactic acid is largely unaffected by the above treatment. Much less (I) but more HCO_2H and AcOH are obtained from glucose [as compared with (II)]. H. B.

Determination of glycuronic and galacturonic acids by Bertrand's method. Z. I. KERTESZ (J. Biol. Chem., 1935, 108, 127—129).—Cu equivs. for the determination of these acids by Bertrand's method are given. A. E. O.

Configuration of fucohexonic and rhodeohexonic acids. E. VOTOCEK (Coll. Czech. Chem. Comm., 1934, 6, 528—548).—Fractional crystallisation of the Ba α - and β -fucohexonates (I) obtained by the HCN synthesis from fucose affords the pure α -salt, $[\alpha]_D -6.6^\circ$, from which α -fucohexonolactone, $+\text{H}_2\text{O}$ and anhyd. (II), sinters 110° , m.p. 126° (decomp.), $[\alpha]_D +43.6^\circ$ to $+48.0^\circ$ (12 days), is obtained, together with a substance, m.p. 187 — 188° , $[\alpha]_D 0^\circ$ to $+35.7^\circ$ (16 days), which is possibly the compound erroneously described by Mayer *et al.* (A., 1907, i, 588) as (II). From the lactones obtained from the mother-liquor of (I), after deposition of more (II), is isolated Ba β -fucohexonate, $[\alpha]_D +4.3^\circ$, whence pure β -fucohexonolactone (III), sinters 125° , m.p. 130° , $[\alpha]_D +69.2^\circ$ to $+28.9^\circ$ (11 days), is obtained. With NH_4R -MeOH, (II) gives the α -acid amide, m.p. 218° , and methylamide (IV), m.p. 213° (decomp.), $[\alpha]_D -15.4^\circ$, diethylamide, m.p. 173 — 174° , and di-*n*-amylamide, m.p. 170° ; (III) similarly gives the β -acid amide, m.p. 199 — 200° (decomp.), and methylamide (V), m.p. 207 — 208° (decomp.), $[\alpha]_D +44.5^\circ$. Reduction of (II) with 2% Na-Hg- H_2O gives α -fucohexose, isolated as its benzylphenylhydrazone (VI), m.p. 176 — 177° , $\alpha_D +0.18^\circ$ to $+0.22^\circ$ in 2.5 hr. [p-bromophenylhydrazone, m.p. 211 — 212° (decomp.); p-bromophenylosazone, m.p. 225° (decomp.)]. Rhodose is similarly converted into α -rhodohexonolactone, $+\text{H}_2\text{O}$, $[\alpha]_D -41.5^\circ$ to -47.3° (122 hr.), and the acid methylamide, m.p. 212 — 213° , $[\alpha]_D +15.4^\circ$. The signs of $[\alpha]_D$ (all vals. in H_2O) of (I), (II), (III), (IV), (V), and (VI) prove that α -fucohexonic acid has the annexed configuration, the β -acid being the epimeride. J. W. B.



Symmetrical esters of methanetetra-acetic acid. H. J. BACKER (Rec. trav. chim., 1935, 54, 62—67).— $\text{C}(\text{CH}_2\text{CO}_2\text{H})_4$ (modified prep.; 4% yield from citric acid) gives the tetrachloride, m.p. about 45° , whence good yields of the following esters are obtained: Me_4 , b.p. 192 — $195^\circ/12$ mm., m.p. 23° ; Et_4 , b.p. $211^\circ/20$ mm.; Pr_4 , b.p. 212 — $213^\circ/5$ mm.; tetracyclohexyl, m.p. 73.5° ; tetramenthyl, m.p. 82 — 83° ; Ph_4 , m.p. 116.5° [(p- NO_2) $_4$ -derivative, m.p. about 100°]; (p- $\text{C}_6\text{H}_4\text{Me}$) $_4$, m.p. 127° ; (p- $\text{C}_6\text{H}_4\text{Bu}^t$) $_4$, m.p. 166.5° {[2:6-(NO_2) $_2$] $_4$, m.p. about 250° (decomp.) after sintering from about 130° , and (2:6- Br_2) $_4$ -derivative, m.p. 222 — 224°]; (o- $\text{C}_6\text{H}_4\text{CMe}_2\text{Et}$) $_4$, m.p. 122 — 122.5° ; (o- $\text{C}_6\text{H}_4\text{OMe}$) $_4$, m.p. 121° ; (α - C_{10}H_7) $_4$,

m.p. 148° ; and (β - C_{10}H_7) $_4$, m.p. 171.5° . The esters are not volatile and show the ready crystallising power and high m.p. of symmetrical compounds.

R. S. C.

Action of phosphorus pentachloride on ethylenetetracarboxylic acid. R. MALACHOWSKI and R. J. SIENKIEWICZOWA (Ber., 1935, 68, [B], 29—37).— $\text{CHBr}(\text{CO}_2\text{Et})_2$ is converted by K_2CO_3 in boiling C_6H_6 saturated with H_2O into $\text{C}_6(\text{CO}_2\text{Et})_4$, m.p. 55.5 — 57° (yield 80%), transformed by hydrolysis and treatment of the product with AcOH into $(\text{CO}_2\text{H})_2\text{C}_2(\text{CO}_2\text{K})_2$ (I), (I) cannot be converted into $\text{C}_2(\text{CO}_2\text{H})_4$ (II), m.p. 184° (corr.), by the usual method, but transformation is effected by passing HCl through its suspension in C_6H_6 saturated with H_2O . Treatment of (II) with PCl_5 and POCl_3 under varied conditions leads to evolution of CO_2 and production of a mixture of chlorides (III) which cannot be separated by fractional distillation. (III) is converted by NH_2Ph in Et_2O into ethylenetetracarboxytetra-anilide, m.p. 224° (corr.) [transformed when melted or treated with boiling AcOH into ethylenetetracarboxydianilideanil,

$\text{NPh}-\begin{array}{c} \text{CO}-\text{C}-\text{CO}-\text{NHPH} \\ | \quad | \\ \text{CO}-\text{C}-\text{CO}-\text{NHPH} \end{array}$, m.p. 195°], anilinoethylenetricarboxytetranilide, m.p. 188° (corr., decomp.) [whence anilinoethylenetricarboxyanilideanil (IV), m.p. 232° , and (IV). Successive treatment of $\text{C}_2(\text{CO}_2\text{H})_4$ with PCl_5 and EtOH yields $\text{C}_2(\text{CO}_2\text{Et})_4$ and Et_3 chloroethylenetricarboxylate, b.p. 163 — $164.5^\circ/10$ mm., converted by condensation with $\text{CHNa}(\text{CO}_2\text{Et})_2$ and subsequent hydrolysis with boiling 20% HCl into aconitic acid. Treatment of $\text{C}_2(\text{CO}_2\text{H})_4$ with PCl_5 and POCl_3 under defined conditions followed by distillation of the product in vac. leads to anhydroethylenetetracarboxyl dichloride (V), $\text{O}-\begin{array}{c} \text{CO}-\text{C}-\text{COCl} \\ | \quad | \\ \text{CO}-\text{C}-\text{COCl} \end{array}$, b.p. 115.5 — $116^\circ/8$ mm., which with PCl_5 at 50° affords a mixture of $\text{C}_2(\text{COCl})_4$ and $\text{C}_2\text{Cl}(\text{COCl})_3$. (V) and hot EtOH yield Et_3 H ethylenetetracarboxylate, which passes when distilled in vac. into Et_2 anhydroethylenetetracarboxylate, m.p. 33 — 35° , b.p. 162 — $163^\circ/9$ mm. (whence Et , H_2 ethylenetetracarboxylate, m.p. 103 — 104°). Ph_2 anhydroethylenetetracarboxylate has m.p. 103 — 104° . W

Reduction of aldehyde- or ketone-nitrite mixtures. III. A. OGATA, T. HOSOI, H. NISHIMATSU, and S. TOMIOKA (J. Pharm. Soc. Japan, 1934, 54, 280—291).—In the above the most important factor is the absorption of the CO_2 produced; other necessary precautions are discussed. CH. ABS. (r)

Chloralides of α -hydroxycarboxylic acids. A. N. MELDRUM and D. M. BHATT (J. Univ. Bombay, 1934, 3, No. 2, 149—152).—Chloralides are obtained by treatment of $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ with the requisite acid and H_2SO_4 at room temp. (method 1; yield > 80% with aliphatic acids, smaller yields with aromatic acids, and failure with $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$) or from $\text{CCl}_3\cdot\text{CHO}$ and the acid at 150° (method 2). Chloralides of the following acids are described: *l*-lactic acid, m.p. 45° (by 1 and 2); malic acid, m.p. 139 — 140° (by 1 and 2), and the *Et* ester $\text{C}_6\text{H}_5\text{O}_5\text{Cl}_3$, m.p. 44° ; *d*-tartaric acid (III), m.p. 160° (by 1); *r*-tartaric acid, m.p. 128 — 130° (by 2) or from (III) and H_2SO_4 at 115 — 120° , converted by KOH into *r*-tartaric acid; citric acid (also

+0.5PhNO₂), m.p. 161° (by I) (converted by PCl₅ into the *chloride*, C₈H₅O₅Cl₅, m.p. 78–79°; Me₂ ester, C₁₀H₁₁O₇Cl₃, m.p. 68–69°; Et₂ ester, b.p. 215–225°/33 mm.); *mucic acid*, C₁₂H₇O₈Cl₉, m.p. 200–201°; *r*-mandelic acid, m.p. 82–83°. H. W.

Action of metallic sodium on aliphatic ketones.

III. Reaction between sodium and isobutyron. I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 288–294).—Na with CO(CHMe₂)₂ (I) produces the *pinacol alcoholate* [(ONa)C(CHMe₂)₂]₂ (II), which on hydrolysis gives (I) and Bu^oOH together with the *pinacol* [OH·C(CHMe₂)₂]₂ (III), m.p. 90–91°. The *dibenzozate*, b.p. 150–153°/19 mm., is formed from (II) and BzCl, whilst (II) and MeI give an ether (?) and a trace of (III). F. N. W.

Electrolytic reduction of methyl *n*-propyl ketone to *n*-pentane.—See this vol., 310.

Action of Grignard salts on hydroxymethylene ketones. R. E. MEYER (Helv. Chim. Acta, 1935, 18, 101–103).—In the hope of preparing αβ-unsaturated aldehydes, the OH·CH: compound of methylheptenone (I) has been treated with MgMeI; the non-homogeneous product does not yield H₂O with NHPH·NH₂ or NH₂Ph, reddens fuchsin-H₂SO₃, reduces AgOH-NH₃, and decomposes when heated into MeCHO and (I). H. W.

Internal energy relationships of organic compounds. III. Experimental foundations of the double linking rule. Fission of sugars. O. SCHMIDT (Ber., 1935, 68, [B], 60–67; cf. this vol., 73).—Numerous examples are cited in favour of the view that in a C chain or ring the single linking proximate to a double linking is strengthened and the following linking is weakened, and that this alternating process extends with diminishing intensity throughout the mol. The fission of sugars at C3 during fermentation or under the action of alkali is explained by assuming that the cyclic form passes initially into the ring-free aldose, which affords an αβ-dienol, thus weakening the linking from C3. Evidence of a less pronounced fission at C5 is found in the presence of *n*-amyl alcohol in fusel oil. Examples are quoted of similar fissions at C5, particularly at higher temp. Scission of hexitols when hydrogenated under pressure similarly involves the production of αβ-dienols and, to a smaller extent, of βγ-dienols. Like relationships exist among pentitols and pentoses. The cracking of paraffins is considered from a similar viewpoint. The distance of the double from the single linking is considered to be so great that at. forces are not involved, and the phenomena are attributed to the action of the B electrons. The phenomena of alternating polarity are therefore not due to alternating charge, but to alternating spin. H. W.

Determination of sugars by Bertrand's method in presence of phosphates. VI. Oxidation of sugars by cupric oxide in alkaline solutions. A. MALKOV (J. Appl. Chem. Russ., 1934, 7, 1254–1257).—Reduction of Cu^{II} to Cu^I by invert-sugar, but not by glucose, is retarded by Na₂HPO₄ and Na₄P₂O₇ to an extent increasing with the duration of the reaction. R. T.

Transformations of isomeric sugars. J. W. H. OLDHAM and G. J. ROBERTSON (Nature, 1935, 135, 103; cf. A., 1934, 871).—*d*-Glucose has been converted into *d*-galactose and *l*-gulose. By a series of consecutive reactions α-methylglucoside is converted into 3:4-anhydro-6-triphenylmethyl-α-methylhexoside 2-acetate, which gave two *isopropylidenemethylhexoside acetates*, (I) m.p. 101–102°, [α]_D +127.3° in CHCl₃, and (II) m.p. 176–178°, [α]_D +76.8° in CHCl₃. Deacetylation of (I) gives an *isopropylidenemethylhexoside*, m.p. 109–110°, [α]_D +147.2°, which on partial hydrolysis yields α-methylgalactoside. From this *d*-galactose is isolated. Similarly, (II) gives an *isopropylidenemethylhexoside*, m.p. 132–133°, [α]_D +88.5°, and complete hydrolysis yields *l*-gulose, [α]_D –17.9°. L. S. T.

Precipitation of sugars with methyl-alcoholic barium hydroxide. T. BABA (Biochem. Z., 1935, 275, 253–260).—The sugars are pptd. with MeOH-Ba(OH)₂, recovered from the ppt. by treatment with CO₂, and determined in the filtrate by polarimetric and reduction methods. The recovery of sugar for glucose, mannose, maltose, lactose, sucrose, and cellobiose is in each case 100%, for fructose 67%, galactose 89%, arabinose 80%, and xylose 87%. The pptn. in the latter cases can be rendered quant. by adding Et₂O. Rhamnose is not pptd. by the reagent and only 57% pptd. on adding Et₂O. P. W. C.

Action of 132-volume aqueous hydrogen peroxide on carbonaceous substances obtained by action of concentrated sulphuric acid on sucrose, glucose, etc. G. SOLLAZZO (Boll. Chim. farm., 1934, 73, 917–922).—The C-like substances (I) obtained by action of H₂SO₄ on sugars and starches are oxidised very slowly by cold 132-vol. H₂O₂ to a colourless liquid and a white infusible solid; at 60–80°, oxidation is rapid, and there is no residue, the products being CO₂, HCO₂H, and H₂C₂O₄. The residue after interrupted oxidation explodes when heated. It is suggested that (I) are not impure C, but dehydration products containing H and O. E. W. W.

***d*-Adonose (*d*-erythro-2-ketopentose).** C. GLATTHAAR and T. REICHSTEIN (Helv. Chim. Acta, 1935, 18, 80–81; cf. A., 1934, 1205).—Boiling C₅H₅N transforms *d*-arabinose (I) into a mixture of isomers from which unchanged (I) is mainly removed by crystallisation. Treatment of the non-cryst. residue with *o*-NO₂·C₆H₄·NH·NH₂ in boiling abs. EtOH affords *d*-adonose-*o*-nitrophenylhydrazone, m.p. 168–169.5° (corr., decomp.), [α]_D²⁰ –48.3° (±3°) in MeOH. H. W.

Modification of the Hagedorn-Jensen method for semi-macro-quantities of glucose. G. A. SCHRADER (Ala. Agric. Exp. Sta., 42nd Ann. Rept., 1931, 39–42).—10 c.c. of the glucose solution are added to 5 c.c. of 0.04N-K₃Fe(CN)₆ and heated for 15 min. on a water bath. After cooling, 5 c.c. of KI (25 g. of KI, 50 g. ZnSO₄·7H₂O, and 250 g. NaCl in 1 litre of H₂O) are added. Liberated I [from unchanged K₃Fe(CN)₆] is titrated with 0.02N-Na₂S₂O₃. CH. ABS. (e)

Effect of asparagine on the reducing power of fructose. I. WEBER, E. J. POSEN, and N. G. CREBOOLSKY (Ind. Eng. Chem. [Anal.], 1935, 7, 77).—

Asparagine does not affect the determination of fructose by Jackson's method. J. L. D.

Determination of sucrose in very small amounts of liquid by measurement of specific gravity and specific rotation. R. BEUTLER (Mikrochem., 1935, 16, 133—140).—The sugar content of 5—30 mg. of solution may be determined within 2% by measurement of the sp. gr. by direct weighing in a calibrated glass capillary, or from the $[\alpha]$ as measured for a 2-mm. column contained in a glass ring held between plane cover glasses. J. S. A.

Physico-chemical properties of lactose. V. Influence of other substances on the equilibrium rotation of lactose. B. L. HERRINGTON (J. Dairy Sci., 1934, 17, 701—707; cf. this vol., 200).—In glycerol the equilibrium mixture of the high- and low-rotating forms of lactose (I) contains more of the former than is the case in aq. solutions. $[\alpha]$ of (I) is altered by the presence of neutral salts (II). Changes in concn. of (I) or (II) alter the equilibrium rotation. A. G. P.

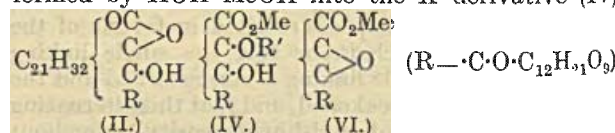
Effect of liquid ammonia on sugar derivatives. L. ZECHMEISTER and G. TÓTH (Naturwiss., 1935, 23, 35).—Cellobiose octa-acetate is de-acetylated by heating to 50° with liquid NH_3 in a sealed tube. Re-acetylation in $\text{C}_5\text{H}_5\text{N}$ leads to N-containing per-acetates, the principal product being formed by linking of cellobiose residues through N (3.3% N; m.p. 192—193°). A. J. M.

Acetyl derivative of a new anhydride of gentiobiose. L. KAMIENSKI (Rocz. Chem., 1934, 14, 1342—1347).—1-Dimethylamino gentiobiose hepta-acetate, m.p. 169°, $[\alpha]_D^{20} -10.84^\circ$ in CHCl_3 , is obtained from α -bromogentiobiose hepta-acetate (I) and NHMe_2 in C_6H_6 . (I) and NMe_3 in C_6H_6 yield gentiobiosetri-methylammonium bromide hepta-acetate, m.p. 140—144° (decomp.), and isooxygentiobial hepta-acetate, m.p. 140—141°, $[\alpha]_D -30.81^\circ$ in CHCl_3 , from which the parent anhydride was not obtained by hydrolysis. R. T.

Derivatives of phenol- β -D-glucoside. B. HELFERICH and F. STRAUSS (J. pr. Chem., 1935, [ii], 142, 13—22).—Successive treatment of phenol- β -D-glucoside (I) (A., 1933, 379) [tetrabenzoate, m.p. 177° (corr.), $[\alpha]_D +27.5^\circ$ in CHCl_3] with CPh_3Cl and Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 100° (bath) and room temp., respectively, gives 6-triphenylmethylphenol- β -D-glucoside 2:3:4-triacetate (II) ($+\text{C}_6\text{H}_6$), m.p. 110—116° (corr.), $[\alpha]_D^{25} (\text{C}_6\text{H}_6\text{-free}) +16.93^\circ$ in CHCl_3 , converted by cold AcOH-HBr into phenol- β -D-glucoside 2:3:4-triacetate (III), m.p. 114° (corr.), $[\alpha]^{20} -28.3^\circ$ in CHCl_3 . (III) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ at room temp. afford the 6-p-toluenesulphonate, m.p. 161—162° (corr.), $[\alpha]^{19} -25.96^\circ$ in CHCl_3 , hydrolysed (method: Zemlen, A., 1926, 822) to phenol- β -D-glucoside 6-p-toluenesulphonate (IV), m.p. 127—128° (corr.), $[\alpha]^{25} -66.6^\circ$ in EtOH . Short treatment of crude (III) with a little 0.1N-KOH in EtOH at room temp. gives phenol- β -D-glucoside 2:3:6(?)-triacetate, m.p. 130° (corr.), $[\alpha]_D -52.2^\circ$ in CHCl_3 , the 4(?)-p-toluenesulphonate, m.p. 160° (corr.), $[\alpha]^{20} -20.62^\circ$ in CHCl_3 , of which is hydrolysed (Zemlen) to anhydrophenol- β -D-glucoside (?) (V), m.p. 149—150° (corr.), $[\alpha]_D^{18} -161^\circ$ in H_2O (di-

acetate, m.p. 120—123°, $[\alpha]^{19} -104.5^\circ$ in CHCl_3), and a little phenol- β -D-glucoside 4(?)-p-toluenesulphonate (VI), m.p. 142—144° (corr.), $[\alpha]_D^{24} -49.95^\circ$ in EtOH . 6-Triphenylmethylphenol- β -D-glucoside 2:3:4-tribenzoate, m.p. 110—120°, $[\alpha]_D^{20} +27.37^\circ$ in CHCl_3 [from (I), CPh_3Cl , and BzCl (as above)], and AcOH-HBr give phenol- β -D-glucoside 2:3:4-tribenzoate (VII), amorphous, $[\alpha]_D^{21} +15.16^\circ$ in CHCl_3 , hydrolysed (0.1N-KOH in EtOH) to the 2:3-dibenzoate (?), m.p. 174—176°, $[\alpha]^{20} +63.4^\circ$ in CHCl_3 . The 6-OH in (III) and (VII) could not be methylated (quant.), showing that the glucosidic substituent can influence the properties of C6 (cf. A., 1925, i, 9). (IV) and (VI) are practically unaffected by emulsin. H. B.

Cardiac glucosides. VIII. Transformation products of scillaren A. A. STOLL and A. HOFMANN (Helv. Chim. Acta, 1935, 18, 82—95; cf. A., 1934, 1206).—Lactone fission, formation of carboxylic ester (I) and Ph ether, ester hydrolysis, and production of the *iso*-ring occur in the same manner with scillaren A (II) as with scillaridin A (III) (*loc. cit.*). Quant. hydrolysis of (I) gives the theoretical yield of aglucone and sugar, proving that the glucosidic linking remains intact until this stage is reached. The aglucone of (II) contains a fourth O to which the scillabiose residue is attached; in harmony, all the glucosides contain 1 $\text{H}_2\text{O} > \text{calc.}$ from the corresponding scillaridin derivative and sugar. (II) is changed in a complex manner by 20% aq. KOH, but is transformed by KOH-MeOH into the K derivative (IV)



($\text{R}'=\text{K}$), m.p. 220—230° (decomp.), $[\alpha]_D^{20} -66.4^\circ$ in H_2O , which when slightly acidified and immediately treated with an excess of CH_3N_3 gives *Me scillarenate A Me ether* (V) (cf. IV; $\text{R}=\text{Me}$), m.p. 223—226° (corr.), $[\alpha]_D -42.8^\circ$ in dioxan. Cautious hydrolysis of (V) leads to methylscillarenic acid A, m.p. 214° (corr., decomp.), $[\alpha]_D^{20} -46.4^\circ$ in dioxan, re-converted by CH_2N_2 into (V). (IV) passes very readily when acidified into *Me isoscillarenate A* (VI), m.p. (indef.) 180—190° (corr.) after softening at 135°, $[\alpha]^{20} -104^\circ$ in dioxan. Quant. hydrolysis of (VI) yields (III), m.p. 175° (corr.), glucose, and rhamnose. Cautious alkaline hydrolysis of (V) gives isoscillarenic acid A, m.p. 218—222° (corr., decomp.), $[\alpha]_D^{20} -109^\circ$ in dioxan. It is recommended that the Liebermann reaction should be standardised and made quant., 1 mg. of aglucone or the equiv. quantity of glucoside being dissolved in 1—2 drops of AcOH and treated with the fresh reagent prepared with 10 c.c. of Ac_2O and 0.2 c.c. of conc. H_2SO_4 . H. W.

Cardiac glucosides. IX. True glucosides of Digitalis purpurea; purpureagluconide-A and -B. A. STOLL and W. KREIS (Helv. Chim. Acta 1935, 18, 120—141; cf. A., 1933, 877, 1146).—The fresh leaves of *Digitalis purpurea* are extracted under conditions which exclude enzymic action and the extracts are purified and freed from tannin-like

impurities as described for *D. lanata* (I) (*loc. cit.*). The product is non-cryst. and contains much more ballast than is the case with (I). It is purified by distribution between CHCl_3 , MeOH, and H_2O . Thus isolated, purpleagluconide-A and -B are shown by analysis, $[\alpha]_D$, lactone titration, colour reactions, decomp. temp., solubility, and enzymic or acid hydrolysis to be identical with deacetyldigilanic-A and -B, respectively. H. W.

Heteroside of *Primula acaulis*, Jacq.—See this vol., 268.

Xylan esters. N. J. SOLETSCHNIK (*J. Appl. Chem. Russ.*, 1934, 7, 1029—1036).—*Xylan diacetate*, from xylan and 100 : 1 $\text{Ac}_2\text{O} \cdot \text{H}_2\text{SO}_4$ at 28—30°, gives solutions in 9 : 1 CHCl_3 -EtOH from which films may be prepared. Xylan heated for 15 min. with stearyl chloride in quinoline at 145° gives the *stearate*, $\text{C}_{10}\text{H}_{12}\text{O}_4(\text{OH})(\text{CO}_2 \cdot \text{C}_{17}\text{H}_{35})_3$, m.p. 48°, sol. in C_6H_6 , xylene, and CHCl_3 . The *oleate*, $\text{C}_8\text{H}_9\text{O}_2(\text{OH}) \cdot \text{CO}_2 \cdot \text{C}_{17}\text{H}_{33}$, decomp. 250°, prepared by heating xylan with oleyl chloride in $\text{C}_5\text{H}_5\text{N}$ at 135° for 2 hr., is insol. in org. solvents. *Benzylxylan*, $\text{OH} \cdot \text{C}_{15}\text{H}_{18}\text{O}_6(\text{O} \cdot \text{CH}_2\text{Ph})_5$, m.p. 158—159°, prepared by heating xylan at 100° for 4 hr. with CH_2PhCl and aq. NaOH, adding an equal amount of NaOH, and heating for a further 3 hr., has similar properties to the corresponding benzylcellulose. R. T.

Benzyl ethers of polysaccharides. I. Benzyl ethers of starches of various origins. T. ASAHINA and G. NARA (*Bull. Chem. Soc. Japan*, 1934, 9, 530—534).—With CH_2PhCl -aq. NaOH, six varieties of starch give $(\text{CH}_2\text{Ph})_2$ ethers; the m.p. varies between 165° and 175° and $[\alpha]_D$ is +117.1° to +120.8° in $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{OH}$. F. N. W.

Hemicellulose-A from English oak wood.—See this vol., 421.

Osmometric investigations of dilute solutions of polymeric carbohydrates. VII. Molecular size of technical cellulose acetates [cellite]. M. ULMANN (*Ber.*, 1935, 68, [B], 134—145; cf. this vol., 201).—Technical cellulose acetate is fractionated by step-wise addition of H_2O to a solution in COMe_2 and intermediate highly-viscous (I) and less viscous (II) fractions are used for determining osmotic pressure in AcOH. (I) and (II) can be dispersed to mols. of the size of a biose anhydride, the process occurring more readily with (II) and the difference being probably most marked at the higher concn. (I), (II), limit dextrin acetate I (III) and II (IV) are dispersed according to concn. to particles which are even multiples of 2C_6 . The stages vary between 32C_6 and 2C_6 . All preps. are similar in the final stage of dispersion, show characteristic differences in the concn. at which the different stages of dispersion appear. In respect close relationships exist between (I) and (IV) and between (II) and (III). The stage $(\text{C}_6)_4$ missing in (I) and (IV) is observed in (II) and (III). Further, a complication in the state of solution occurs with (II) and (III), since at very great dilution the observed osmotic pressures are > those expected and change continuously. Comparison of the properties (I) with those of (IV) shows that viscosity and

ability to form films are not directly related to the mol. wt. of a substance. H. W.

Structure of cellulose dinitrate.—See this vol., 286.

Significance of measurements of dielectric constants in aqueous solution.—See this vol., 294.

Preparation and properties of some cupri-tetra-chlorides and -bromides.—See this vol., 312.

Betaines. I. Racemisation of ethyl propiobetainate chloride [ethyl α -trimethylammonio-propionate chloride]. II. Preparation of *N*-alkylalanine esters and betaine esters. E. BILMANN and N. BERG. III. Ethyl α -ethyl-propiobetainate iodide [ethyl α -trimethylammonio- α -methyl-*n*-butyrate iodide] and similar compounds. E. BILMANN, K. A. JENSEN, and H. B. JENSEN (*Bull. Soc. chim.*, 1934, [v], 1, 1645—1653, 1653—1661, 1661—1670).—I. $l\text{-CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{NMe}_3\text{Cl}$ (I), $[\alpha]_D^{20}$ -25° in dry EtOH, is racemised by NMe_3 , NEt_3 , NPr_3 , NBu_3 , and $\text{NEt}_2 \cdot \text{CH}_2\text{Ph}$ in dry EtOH without replacement of the NMe_3 and k is that of a unimol. reaction. It follows that racemisation (A) is not due to exchange of alkylamino-groups (cf. A., 1912, i, 420). (A) probably occurs by way of the ion of the enolic form, $^+\text{NMe}_3 \cdot \text{C}(\text{C}(\text{OEt}) \cdot \text{O}^-)$, formed under the influence of the base, or, less probably, by feeble ionisation to $^+\text{NMe}_3 \cdot ^-\text{CMe} \cdot \text{CO}_2\text{Et}$ and recombination of this ion with H^+ derived from $^+\text{NHR}_3$. (I) is very rapidly racemised by NaOEt. A nomenclature is proposed, based on the names Et betainate bromide or Et trimethylbetainate bromide for $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NMe}_3\text{Br}$, Et propiobetainate ion for $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{NMe}_3^+$, Et α -ethylpropiotriethylbetainate bromide for $\text{CO}_2\text{Et} \cdot \text{CMeEt} \cdot \text{NEt}_3\text{Br}$, etc.

II. Compounds of the type, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{NRR}'\text{R}''\text{X}$, in which the alkyls are Me or Et, are readily prepared, except that in which $\text{R}=\text{R}'=\text{R}''=\text{Et}$, which could not be obtained. Alanine, aq. *N*-NaOH, MeOH, and MeI give at room temp. a solution, from which *l*-propiobetainate, $^+\text{NMe}_3 \cdot \text{CHMe} \cdot \text{CO}_2^-$, hygroscopic, $[\alpha]_D^{20}$ -18.3° in EtOH, is obtained; this with HCl -EtOH gives *Et l*-propiobetainate chloride (I), hygroscopic, $[\alpha]_D^{20}$ -25.2° in EtOH (corresponding bromide, a syrup). $\text{CHMeBr} \cdot \text{CO}_2\text{Et}$ and dry NHEt_2 at 50—60° give *Et N*-diethylaminopropionate, b.p. 74—75°/13 mm., which with MeI at room temp. gives the methiodide, cryst., hygroscopic, but does not react with cold EtI and with hot EtI gives NEt_4I . $\text{NEt}_2 \cdot \text{CHMe} \cdot \text{CN}$ (modified prep.) does not react with MeI or EtI (cf. lit.). However, $\text{NMe}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ with EtI at 100° gives the ethiodide, m.p. 79.5—80.5°, hygroscopic, and $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ at 100° gives the ethiodide, m.p. 125—126° (lit. 123—125°).

III. Formylation of $\alpha\text{-NH}_2$ -acids is best effected by HCO_2Ac . *l*- $\text{NH}_2 \cdot \text{CMeEt} \cdot \text{CO}_2\text{H}$ (prepared by way of the formyl derivative and brucine salt) affords α -ethyl-propiobetainate, $^+\text{NMe}_3 \cdot \text{CMeEt} \cdot \text{CO}_2^-$, m.p. 133—134° (decomp.), deliquescent (hydrochloride), which is not affected by HCl -EtOH or CH_2N_2 , but with EtI-EtOH at 100° gives *Et* α -ethylpropiobetainate (α -trimethylammonio- α -methyl-*n*-butyrate) iodide (II), m.p. 144—145°. This method also gives a good yield of

the iodide, m.p. 97—98°, corresponding with (I), and of nearly pure $\text{NMe}_3\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 173—175°; similarly EtBr affords *Et betainate bromide*, $\text{NMe}_3\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 152—153°, but MeCl reacts only very slowly. (II) is not racemised by *tert.*-amines, nor is the corresponding chloride (III) (not isolated); since (II) contains no H attached to the α -C, the explanation given above for the racemisation of (II) is supported. (II), (III), and solutions of the hydroxide have the same $[\alpha]$, indicating complete ionisation of these substances in solution. (II) is slowly hydrolysed by amines and more rapidly by NaOEt . d - p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ is rapidly racemised by NaOEt .
R. S. C.

Reactions between sugars and amino-acids.

IV. Crystalline dipeptide-glucosides and the influence of hydrogen-ion concentration on their fission. K. MAURER and B. SCHIEDT (Z. physiol. Chem., 1935, 231, 1—9; cf. A., 1933, 263).—Glycylglycine ester (I) and acetobromoglucose in CHCl_3 afford *glycylglycine ester glucoside tetra-acetate* (II), m.p. 140°, $[\alpha]_D^{20}$ -2.0° in CHCl_3 . With NH_3 in MeOH , (II) gives *glycylglycinamide glucoside* (III), m.p. 118° (decomp.), $[\alpha]_D^{20}$ -6.06° in H_2O . With acetobromocellobiose, (I) yields *glycylglycine ester cellobioside hepta-acetate*, m.p. 105°. With $\text{C}_5\text{H}_5\text{N}\cdot\text{Ac}_2\text{O}$, (III) gives *glycylglycinamidoglucoside penta-acetate*, m.p. 146°, $[\alpha]_D^{20}$ $+7.56^\circ$ in CHCl_3 . Hydrolysis of sarcosine ester glucoside tetra-acetate with NaOEt in EtOH gives in non-cryst. but pure form the *sarcosineglucoside Na salt*, m.p. 110—120°, $[\alpha]_D^{20}$ $+19.32^\circ$ in H_2O , $+17.42^\circ$ in MeOH . Methylation of sarcosineglucoside with CH_3N_2 and treatment of the ester with NH_3 in MeOH yields *sarcosinamidoglucoside* (IV). Na salts of *l*-phenyl-, sinters 125°, m.p. 133° (decomp.), $[\alpha]_D^{20}$ -31.25° in MeOH , -33.0° in H_2O , *sarcosyl*-, sinters 145°, decomp. 160°, $[\alpha]_D^{20}$ $+17.5^\circ$ in MeOH , $+15.32^\circ$ in H_2O , and *glycyl-glycineglucoside*, decomp. 110—115°, $[\alpha]_D^{20}$ $+7.14^\circ$ in MeOH , $+7.32^\circ$ in H_2O , were similarly obtained. Phenylglycine (V) [*r*- or *l*-form] and $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in 2*N*- NaOH afford *r*-chloroacetylphenylglycine (VI), m.p. 128° (or *l*-chloroacetylphenylglycine, m.p. 127—128°, $[\alpha]_D^{20}$ -178.60° in EtOH). With aq. NH_3 , (VI) gives *glycylphenylglycine*, m.p. 248° (*Et* ester hydrochloride, m.p. 189°, hydrobromide, m.p. 170°), *l*-(VI) gives *glycyl-l*-phenylglycine, m.p. 248°, $[\alpha]_D^{20}$ -187.27° in 0.1*N*- HCl [*Et* ester (VII), $[\alpha]_D^{20}$ -120.3° in EtOH (hydrochloride, m.p. 201°, $[\alpha]_D^{20}$ -113.54° in H_2O ; hydrobromide, m.p. 180°, $[\alpha]_D^{20}$ -113.86° in H_2O)]. On keeping, the esters give the *dl*-, m.p. 235°, and *l*-anhydride, m.p. 228°, $[\alpha]_D^{20}$ -84.03° in AcOH , respectively. With acetobromoglucose, (VII) gives *glycyl-l*-phenylglycine *Et* ester glucoside tetra-acetate, m.p. 141°, $[\alpha]_D^{20}$ -65.85° in CHCl_3 , which with NH_3 in MeOH yields *glycyl-l*-phenylglycinamidoglucoside, m.p. from 115°, decomp. 135°, $[\alpha]_D^{20}$ -46.06° in H_2O . (IV) is immediately decomposed by 0.1*N*- HCl , (III) in 3 hr. at p_H 4.5; both are slowly hydrolysed. In 0.1*N*- NaOH , (III) is stable but (IV) is slowly hydrolysed. (III) is hydrolysed by emulsin but not by aminodi- or aminopoly-peptidase.
J. H. B.

Determination of cystine and cysteine in butyl alcohol extracts. W. C. HESS and M. X. SULLIVAN

(J. Biol. Chem., 1935, 108, 195—199).—Data are given for the partition of cystine (I) and cysteine (II) between *N*- HCl and BuOH . (II) is much more readily extracted from *N*- HCl solution by BuOH than (I). The Sullivan, Okuda, and Folin-Marenzi methods for the determination of (I) and (II) can be successfully applied to both aq. and solvent layers if purified BuOH has been used (cf. A., 1933, 1179). Both (I) and (II) can be extracted quantitatively from BuOH by 0.1*N*- NaOH .
A. E. O.

Calcium cyanamide. III. Preparation of nitroguanidine nitrate. Y. KATO, K. SUGINO, and K. KORDZUMI (J. Electrochem. Assoc. Japan, 1934, 2, 187—191; cf. B., 1933, 748).—Cyanoguanidine NH_4 nitrate (I), m.p. 116°, on heating affords, according to the conditions, guanidine, its nitrate (II), or biguanidine. (II) can be dehydrated to nitroguanidine nitrate (III) with fuming HNO_3 (IV); (III) is also produced directly from (I) and (IV).
CH. ABS. (r)

Addition of hydrogen sulphite to thiocarbimides. H. J. BACKER, H. MULDER, and W. FROENTJES (Rec. trav. chim., 1935, 54, 57—61).—The following thiocarbimides are prepared in 60—70% yield by Kaluza's method: *Et* (I), *Me*, m.p. 35°, b.p. 118°, *Pr*^a, b.p. 153°, *Pr*^b, b.p. 137°, *Bu*^a, b.p. 168°, *Bu*^b, b.p. 162°, *Bu*^r (II), b.p. 142°, and CH_2Ph , b.p. 143°/20 mm. (9% yield). These [except (II)] add KHSO_3 in 50% aq. EtOH at 100° to form cryst. *K alkyl-aminothiomethanesulphonates* (III), $\text{NHR}\cdot\text{CS}\cdot\text{SO}_3\text{K}$. (II) is decomposed by KHSO_3 , and PhCNS gives $\text{CS}(\text{NHPh})_2$. The structure of (III) is proved by their failure to give reactions for $\text{S}_2\text{O}_3^{2-}$ and SH^- and by the non-reactivity of $\text{CS}(\text{NMe}_2)_2$ with KHSO_3 . (I) is unaffected by cold H_2SO_4 , but gives SO , when heated with this acid. It can be crystallised from Ac_2O , but is decomposed therein by a drop of H_2SO_4 . Seven nitriles and two carbylamines failed to react with KHSO_3 .
R. S. C.

Ruthenium- and osmium-specific group in organic sulphur compounds. B. STEIGER (Mikrochem., 1935, 16, 193—202).—Ru compounds give sensitive colorations (blue to red) with *N*-alkyl- or -aryl-thiocarbamides, but not isothiocarbamides. The colour is changed by addition of NH_3 ; that from ditolylthiocarbamide only is sol. in Et_2O . Os reacts with $\text{CS}(\text{NH}_2)_2$ only. $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$ gives with Ru a red coloration, destroyed by NH_3 , and turning green in air (limit 1.4×10^{-7} g.). Os gives a blue colour in NH_3 , fading in air. Phenyl-, 1:4-diphenyl- (limit 0.025×10^{-6} g. per c.c.), 2:4-diphenyl- (limit 0.017×10^{-6} g. per c.c.), and α -diphenyl-thiosemicarbazides in HCl or AcOH give violet colorations with Ru, sol. in Et_2O . Os gives insensitive green or brown ppts. $\text{CS}(\text{NH}\cdot\text{NH}_2)_2$ gives a deep red colour, unaffected by NH_3 , with Ru in acid solution (limit 0.6×10^{-6} g. per c.c.), whilst Os gives a pink colour in NH_3 , decolorised by HCl . Dithiourazole gives an intense red with Ru in NH_4 . (limit 0.8×10^{-6} g. per c.c.).
J. S. A.

Formation and decomposition of diazo-ketones and of the so-called diazo-anhydrides from the viewpoint of the electronic theory.

B. EISTERT (Ber., 1935, 68, [B], 208—216).—Theoretical. H. W.

Halogenoalkylarsinic acids. H. J. BACKER and C. C. BOLT (Rec. trav. chim., 1935, 54, 68—72).—The following are prepared in poor yield by King's method (A., 1928, 1231): β -chloropropene-, b.p. 80—84°/14 mm., and γ -chlorobutane-, b.p. 120—125°/14 mm., α -dichloroarsine; β -chloropropene-, m.p. 164.5—165°, γ -chlorobutane- (I), m.p. 167—167.5°, γ -chloro-*n*-pentane- (II), m.p. 159—159.5°, and γ -chloro-*n*-hexane- α -arsinic acid (III), m.p. 144.5—145°. By means of quinine (IV) are obtained the 1-forms of (I), (II), and (III), $[M]_D$ -28° , -12.4° , and -6.8° , respectively [(IV) salts, $+2H_2O$; Ba salts, $[M]_D$ -21.4° , -5.7° , and -4.3° , respectively]. The acids are monobasic to Me-red. R. S. C.

Aliphatic diarsinic acids. H. J. BACKER and C. C. BOLT (Rec. trav. chim., 1935, 54, 47—51).— $(CH_2Br)_2$ and alkaline Na_3AsO_3 give, according to the conditions, C_2H_4 (75%) and impure $Ba_2 \alpha\beta$ -ethanedithiolate, or C_2H_3Br . Other appropriate dibromoparaffins give $\alpha\gamma$ -propane- (36.8%), $+2H_2O$, m.p. 178—180° [reduced by Na_2PO_3 to ? arsenobistrimethyl-encarsinic acid, $[AsO_3H_2(CH_3)_3As]_2$, amorphous, α -butane- (37%), $+2H_2O$, m.p. about 220—225° (decomp.) (reduced probably to the unstable arseno-compound), and α -pentane-diarsinic acid, $+2H_2O$, decomp. about 230° (not reduced to the arseno-compound). The Ca_2 and Ba_2 salts are less sol. in hot than in cold H_2O . The acids are dibasic to Me-red and tribasic to thymolphthalein, but the salts are those of tetrabasic acids. $(CH_2CH_2OH)_2$, from $(CH_2CO_2Et)_2$ and $Na-EtOH$ (55% yield), has b.p. 111—112°/4 mm. R. S. C.

Fission of hexachlorodisiloxan by acetylacetone. H. RHEINBOLDT and W. WISFELD (J. pr. Chem., 1935, [ii], 142, 23—25).— $(SiCl_3)_2O$ and CH_3CO , in $CHCl_3$ give triacetyl-silicon chloride hydrochloride (isolable as the ferrichloride) (Dilthey, A., 1903, i, 405) and a gel-like "silicone." Reaction occurs thus: $(SiCl_3)_2O + 5CH_3CO \longrightarrow 4HCl + (R^-)_2Si \begin{smallmatrix} O \\ \diagup \diagdown \end{smallmatrix} Si(R^-)_2 + [Cl, HCl]^- \longrightarrow [Si(R^-)_3]^+ [Cl, HCl]^- + 1/n [O:Si(R^-)_2]_n$; $R = O-CMe_2CH-CMe_2O^-$. H. B.

Secondary reactions in the preparation of zinc ethyl. R. F. McCLEARY and E. F. DEGERING (Proc. Indiana Acad. Sci., 1934, 43, 127—131).—An improved apparatus for the prep. and manipulation $ZnEt_2$ is described. Secondary reactions lead to γ -diol, C_2H_6 , and C_2H_4 ; there is no indication of the formation of H_2 or of CH_3EtCH_2 . CH. ABS. (r)

Physical properties of alkyl compounds of mercury, tin, and lead. W. J. JONES, D. P. EVANS, GULWELL, and D. C. GRIFFITHS (J.C.S., 1935, cf. A., 1930, 1019; 1931, 609, 1404; 1932, 1933, 663).—By the interaction of the appropriate Grignard reagent with $HgBr_2$, $SnCl_4$, $PbCl_4$, SnR_3Br , or PbR_2Cl_2 the following are prepared: *di-n*-amyl, b.p. 106°/0.5 mm., 133°/10 mm.; *n*-amyl iodide and thiocyanate, m.p. 108°; *Hg* *di-n*-amyl, b.p. 93°/1 mm.; *Hg* *di-n*-amyl bromide, p. 119°, iodide, m.p. 128°, and sulphate, m.p. 180°

(decomp.); *Hg* *di-n*-hexyl, b.p. 110°/0.5 mm., 158°/10 mm.; *Hg* *n*-hexyl bromide; $SnBu_4$, b.p. 145°/10 mm.; $SnBu_3$ bromide, b.p. 163°/12 mm., and iodide, b.p. 172°/10 mm.; Sn *tetra-n*-amyl, b.p. 181°/10 mm.; Sn *tri-n*-amyl bromide, b.p. 189°/13 mm., and iodide, b.p. 198°/15 mm.; Sn *tetra-dl*-amyl, b.p. 174°/10 mm.; Sn *tetra-n*-hexyl, b.p. 209°/10 mm.; Sn *tetra-n*-heptyl, b.p. 239°/10 mm.; Sn *tetra-n*-octyl, b.p. 268°/10 mm.; Sn *tetra-β*-phenylethyl, b.p. 288°/12 mm.; $SnPr_2Br_2$, m.p. 53°; $SnMePr_3$, b.p. 93°/10 mm.; $SnPr_3Bu$, b.p. 121°/10 mm.; $SnMeBu_3$, b.p. 121°/10 mm.; $SnEtBu_3$, b.p. 129°/10 mm.; $SnPr$ *tri-n*-amyl, b.p. 163°/10 mm.; $PbBu_2Cl_2$, decomp. 108°; $PbMe_2Bu_2$, b.p. 96.5°/5 mm., 108°/10 mm.; $PbEt_2Bu_2$, b.p. 90°/1 mm.; $PbPr_2Bu_2$, b.p. 120°/1 mm.; $PbBu_2Bu_2$, b.p. 135°/1 mm.; $PbBu_2$ *diiso*-amyl, b.p. 135°/0.5 mm.; $PbBu_2$ *di-dl*-amyl, b.p. 135°/0.5 mm.; Pb *di-n*-amyl dichloride, decomp. 123—125°, dibromide, sinters 89°, and sulphate, sinters 177°; $PbMe_2$ *di-n*-amyl, b.p. 113°/4 mm., 121°/5 mm., 135°/10 mm.; $PbMe$ *di-n*-amyl chloride, decomp. 121—122°; $PbEt_2$ *di-n*-amyl, b.p. 116—118°/0.5 mm., 157—158°/10 mm. (decomp.); $PbPr_2$ *di-n*-amyl, b.p. 150°/1 mm.; $PbBu_2$ *di-n*-amyl, b.p. 170°/1 mm.; $PbBu_2$ *di-n*-amyl, b.p. 140°/0.5 mm.; Pb *tetra-n*-amyl, b.p. 170°/1 mm.; Pb *di-n*-amyl dinitrate and dinitrate dihydrate, sinters 96—98°; Pb *di-n*-amyl *diiso*-amyl, b.p. 160°/1 mm.; Pb *di-n*-amyl *di-dl*-amyl, b.p. 160°/1 mm.; Pb *di-n*-amyl *di-n*-hexyl, b.p. 180°/0.5 mm.; Pb *di-dl*-amyl dichloride, m.p. 67° (decomp.); Pb *tetra-dl*-amyl, b.p. 150°/0.5 mm.; Cd *di-n*-amyl, b.p. 105°/2 mm.; Cd *di-dl*-amyl, b.p. 94°/2 mm. PbR_4 with conc. HNO_3 gives $PbR_2(NO_3)_2 \cdot 2H_2O$ and HR in agreement with Polis (A., 1887, 572; 1888, 283) and contrary to Calingaert (Chem. Reviews, 1926, 2, 50). $PbBu_2$ dinitrate dihydrate, sinters 116—117°, and $PbPr_2$ dinitrate dihydrate, m.p. 87—89° were obtained. $PbMe_2R_2$ with conc. HNO_3 gives $PbR_2(NO_3)_2 \cdot 2H_2O$; Me is removed in preference to Bu^i or *n*-amyl. The vals. of b.p. d , mol. vol., $[r_L]$, and heats of formation and combustion are given for the above and other HgR_2 , SnR_4 , PbR_4 compounds, $SnEt_2Bu^iBr$, $SnEt_2Br_2$, and $SnBr_4$. Equations are given for the gradation of b.p. with composition and pressure and of mol. vol. with composition. All b.p. and m.p. are corr. $[r_L]$ for Hg, Sn, and Pb are calc. Methods are given for determining Hg, Pb, and Cd in their alkyl compounds. F. R. G.

Spatial configuration of cyclohexane and its derivatives. R. D. DESAI (J. Univ. Bombay, 1934, 3, No. 2, 219—225).—A review of the lit. leads to the conclusion that, despite the hypothetical existence of two multiplanar forms of cyclohexane and its derivatives, the overwhelming chemical evidence is in favour of the uniplanar configuration although it is admitted that evidence is gradually accumulating to support the other view. H. W.

Preparation of gem-dimethylcyclohexane and its behaviour towards noble metal catalysts. N. D. ZELINSKI, K. PACKENDORFF, and E. G. CHOCHLOVA (Ber., 1935, 68, [B], 98—101).—Dimethyldihydroresorcinol in EtOH or H_2O absorbs H_2 very slowly in presence of Pt-C, but rapidly after addition

of H_2SO_4 and with production of 3:3-dimethylcyclohexanol (I), b.p. $183^\circ/742$ mm. (I) is also obtained by catalytic reduction of 3-chloro-5-keto-1:1-dimethyl- Δ^3 -cyclohexene in HCl provided that the concn. of acid is $\geq 12\%$. (I) is transformed by KHSO_4 into 1:1-dimethylcyclohexene, b.p. $118.5\text{--}120^\circ/752$ mm., hydrogenated (Pt-C) to 1:1-dimethylcyclohexane (II), b.p. $119.2\text{--}119.7^\circ/752.8$ mm. (II), alone or mixed with CO_2 , is unchanged by passage over Pt-C at 300° or 330° or by passage over Pt-C or Pd-clay in presence of H_2 at $305\text{--}330^\circ$. H. W.

Reaction of sulphur with benzene in presence of aluminium chloride. G. DOUGHERTY and P. D. HAMMOND (J. Amer. Chem. Soc., 1935, 57, 117—118).—In agreement with Böeseken (A., 1905, i, 583), thianthrene (I), Ph_2S (II), and H_2S are formed from C_6H_6 , S, and AlCl_3 . With C_6H_6 (250 c.c.) and S (32 g.), a max. yield (0.183 mol.) of (I) is obtained with 0.25 mol. of AlCl_3 at 80° . Addition of the S to $\text{C}_6\text{H}_6 + 0.5\text{--}1$ mol. of AlCl_3 gives (II) only. (I) is best prepared by heating a mixture of C_6H_6 (40 g.), CS_2 (200 c.c.), S (32 g.), and AlCl_3 (33.5 g.) for 12 hr. (II) or Ph_2S_2 heated with S and AlCl_3 in light petroleum affords 95—100% of (I). H. B.

Catalytic hydrogenation of toluene by combined hydrogen. N. I. SCHUIKIN and E. A. FEDER (J. Appl. Chem. Russ., 1934, 7, 1192—1196).—Methylcyclohexane is obtained in 26% yield by passing 9:1 EtOH-PhMe mixtures over Ni- Al_2O_3 or Pd-asbestos at $180\text{--}190^\circ$; the reaction is $3\text{EtOH} + \text{PhMe} \rightarrow 3\text{MeCHO} + \text{C}_6\text{H}_{11}\text{Me}$. R. T.

Preparation of mesitylene. E. SUCHARDA and H. KUZYŃSKI (Rocz. Chem., 1934, 14, 1182—1187).—Ipatiev's synthesis of mesitylene (I) (A., 1931, 207) can be effected at lower pressures than those recommended by him. At 195° 47% of the COMe , present in mixtures containing 8% of HCl is converted into (I) after 48 hr.; the reaction velocity with HBr is $>$ with HCl, the yield of (I) is the same, but that of higher polymerides (II) is increased. When the oxide of (I) is heated with HCl, the product consists chiefly of (II), indicating that the oxide is not an intermediate product. R. T.

Relations between acidity and tautomerism. III. The nitro-group and the nitronic esters. F. ARNDT and J. D. ROSE (J.C.S., 1935, 1—10; cf. A., 1933, 146; 1934, 770).— $\text{CH}_2\text{R}\cdot\text{NO}_2$ ($\text{R}=\text{Ph}$, $p\text{-C}_6\text{H}_4\text{Br}$) and CH_2N_2 (I) in Et_2O react slowly, whilst the *aci*-forms $\text{CHR}\cdot\text{NO}_2\text{H}$ react vigorously to give the Me ether of *aci*-phenylnitromethane (II) (cf. v. Auwers and Ottens, A., 1924, i, 516), and the Me ether of *aci*-*p*-bromophenylnitromethane (III), m.p. 65° . (II) at 85° gives CH_2O and PhCHO . (II) with boiling dil. HCl gives 3:5-diphenyl-1:2:4-oxadiazole. (III) at 80° yields CH_2O and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CH}\cdot\text{NOH}$ and with boiling dil. HCl is converted into 3:5-di-*p*-bromophenyl-1:2:4-oxadiazole, m.p. 181° . Prolonged heating of (III) with HCl gives $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$. $\text{NO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (IV) and Et furoxandicarboxylate (V) [not Et bisanhydronitroacetate, as stated by Bouveault and Wahl (A., 1904, i, 796)] are formed from $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ and fuming HNO_3 in Ac_2O . (V) and conc. aq. NH_3 give a substance, m.p. 233° ,

probably furoxandicarboxylamide (cf. Wieland and Gmelin, A., 1909, i, 610). (IV) and (I) in Et_2O give the nitronic Me ester of Et nitroacetate, $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{NO}\cdot\text{OMe}$ (VI), which explodes at 90° to give CH_2O , and decomposes at $65^\circ/0.01$ mm. giving Et oximinooacetate. (VI) and conc. HCl give Et chloroximinooacetate, which with H_2O yields (V), not $\text{H}_2\text{C}_2\text{O}_4$ and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (cf. Propper, A., 1883, 573). Successive treatment of (VI) with 2*N*-NaOH, HCl, and conc. aq. NH_3 yields a substance, m.p. $120\text{--}121^\circ$ (decomp.), regarded as the bisanhydronitroacetamide of Scholl and Schoffer (A., 1901, i, 359). $\text{NO}_2\cdot\text{CH}(\text{CO}_2\text{Me})_2$ (improved prep.) and (I) in Et_2O give the nitronic Me ester of Me nitromalonate, $(\text{CO}_2\text{Me})_2\text{C}\cdot\text{NO}\cdot\text{OMe}$, m.p. 68° , which decomposes at 80° to CH_2O , and with 2*N*-NaOH gives fulminic acid. The product from *p*-thiolyacetone or ω -(*p*-thioly)acetophenone (VII) and Et nitrate (VIII) in EtOH-NaOEt is oxidised (H_2O_2 , AcOH) to *p*-toluenesulphonylnitromethane (IX), m.p. 116° . More gentle treatment of (VIII) and (VII) in EtOH-NaOEt yields ω -nitro- ω -(*p*-thioly)acetophenone, m.p. 78° . (IX) and (I) in Et_2O gives the nitronic Me ester of (IX), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}\cdot\text{NO}\cdot\text{OMe}$, which decomposes at 95° giving CO_2 and *p*-tolylthiocarbimide. $\text{COPh}\cdot\text{CH}_2\cdot\text{NO}_2$ and (I) in Et_2O yield 65% of nitronic Me ester and 35% of enolic Me ether. Contrary to Kuhn and Albrecht (A., 1927, 749) the nitronic acids are formulated $\text{CHR}\cdot\text{N}(\text{OH})\rightarrow\text{O}$, the acidity associated with the NO_2 being attributed to the enolising tendencies of its doubly bound O as in CO and differing from the acidifying properties of the SO_2 .

F. R. G.
1:2-Dimethylnaphthalene of coal tar. O. KRUBER and W. SCHADE (Ber., 1935, 68, [B], 11—16).—A neutral, heavy oil fraction, b.p. about $266\text{--}270^\circ$, is freed by repeated cooling and centrifuging as far as possible from solid components and cautiously treated with 90% and 96% H_2SO_4 to remove acenaphthene and resinifying materials. Treatment of the product with picric acid in EtOH leads to the isolation of 1:2- $\text{C}_{10}\text{H}_8\text{Me}_2$ (I), b.p. $266\text{--}267^\circ/760$ mm. Oxidation of (I) with CrO_3 in AcOH affords 1:2-dimethyl- α -naphthoquinone, m.p. 125° , oxidised by KMnO_4 to 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$. Oxidation of (I) to $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ could not be effected by $\text{K}_3\text{FeC}_6\text{N}_6$ in alkaline solution; the transformation is effected by converting (I) into $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{CO}_2\text{H}$ by dil. HNO_3 and completion of the change by $\text{K}_3\text{Fe}(\text{CN})_6\cdot\text{KOH}$. (I) is converted by 98—100% H_2SO_4 at > 0 into mixtures of non-cryst. sulphonic acids. (I) and 90% H_2SO_4 at 50° afford cryst. 1:2-dimethylnaphthalene-4-sulphonic acid (II) (corresponding amide, m.p. 183°), converted by Na-Hg into 1:2- $\text{C}_{10}\text{H}_6\text{Me}_2$. The Na salt of (II) is transformed by molten KOH into 1:2-dimethyl-4-naphthol, b.p. $205\text{--}210^\circ/15$ mm., m.p. $114\text{--}115^\circ$, which affords the compound $\text{C}_{18}\text{H}_{16}\text{ON}_2$, m.p. 112° , with PhN_2Cl . H. W.

Homologues of naphthacene. II. 2-Methyl- and 2:7-dimethyl-naphthacene: synthetic applications of 2:6- and 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene. E. A. COULSON (J.C.S., 1935, 77—83; cf. A., 1934, 1211).—3:6:2- $\text{C}_{10}\text{H}_5\text{Me}_2\cdot\text{OH}$ (I) with $(\text{NH}_4)_2\text{SO}_3$ and conc. aq.

gives 3:6-dimethyl- β -naphthylamine, m.p. 139° [hydrochloride, m.p. 283° (decomp.); Ac derivative, m.p. 207°], whence (Sandmeyer) 3:6-dimethyl-2-naphthonitrile, m.p. 145°, hydrolysed (EtOH, KOH) to 3:6-dimethyl-2-naphthoic acid (II), m.p. 224° (anilide, m.p. 207—208°). The chloride, b.p. 160°/3 mm., m.p. 70°, of (II) yields with PhMe and FeCl₃ at 90° 2-p-toluoxy-3:6-dimethylnaphthalene, m.p. 112°, which at 400° gives 2:7-dimethylnaphthacene (III), m.p. 362° (9:10-quinone, m.p. 233°), which does not depress the m.p. of 2:6-dimethylnaphthacene (IV). Diphenylcarbonyl chloride (V), tetrahydronaphthalene (VI), and AlCl₃ in CS₂ give 1:2:3:4-tetrahydro-6-naphthodiphenylamide, m.p. 87—88°, hydrolysed (75% H₂SO₄) to the acid (anilide, m.p. 147°), the chloride of which with *m*-xylene and AlCl₃ in CS₂ yields 6-2':4'-dimethylbenzoyl-1:2:3:4-tetrahydronaphthalene [also prepared from 2:4-C₆H₃Me₂-COCl (VI), and AlCl₃], which when heated to 400—420° gives 7-methyl-1:2-benzanthracene, 7-methyl-1:2:3:4-tetrahydronaphthacene, and 2-methylnaphthacene (VII), m.p. 350°. (VII) is oxidised (K₂Cr₂O₇, AcOH) to a resinous substance. 2:6-C₁₀H₆Me₂ is reduced (H₂, C-MoO₃-S, 400°/100 atm.) to 2:6-dimethyl-1:2:3:4-tetrahydronaphthalene (VIII), b.p. 237—239°, m.p. 14—17°, and -decahydronaphthalene, b.p. 216—217°. 2:7-C₁₀H₆Me₂ similarly gives 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene (IX), b.p. 237—238°, and -decahydronaphthalene, b.p. 216—218°. (V), (VIII), and AlCl₃ in CS₂ give a diphenylamide, hydrolysed (75% H₂SO₄) to 2:6-dimethyl-1:2:3:4-tetrahydro-7-naphthoic acid, m.p. 183°, dehydrogenated (Se at 250—300°) to 2:6:3-C₁₀H₅Me₂-CO₂H. Similarly (V), (IX), and AlCl₃ in CS₂ give 2:7-dimethyl-1:2:3:4-tetrahydro-6-naphthoic acid, m.p. 187°, dehydrogenated to (II). (VIII) and H₂SO₄ give a sulphonic acid, the Na salt (X) of which with PCl₅ yields the sulphonyl chloride, which with conc. aq. NH₃ gives 2:6-dimethyl-1:2:3:4-tetrahydronaphthalene-7-sulphonamide, m.p. 166—167°. (X) with fused KOH gives 2:6-dimethyl-1:2:3:4-tetrahydro-7-naphthol, m.p. 116°, having good "wetting power" (cf. Morgan *al.*, B., 1933, 504). This with Se at 240° gives 2:6:7-C₁₀H₅Me₂-OH. Similarly (IX) gives a Na sulphonate (XI) and 2:7-dimethyl-1:2:3:4-tetrahydronaphthalene-6-sulphonamide, m.p. 145.5°. (XI) with fused KOH gives 2:7-dimethyl-1:2:3:4-tetrahydro-6-naphthol, m.p. 87°, and (I). (VIII) or (IX) with the appropriate RCOCl (R=Ph, *p*-C₆H₄Me) and AlCl₃ in CS₂ give 6-benzoyl-2:7- (XII), b.p. 199°/3 mm., 202°/4 mm., 6-*p*-toluoxy-2:7- (XIII), b.p. 199°/mm., or 7-*p*-toluoxy-2:6-dimethyl-1:2:3:4-tetrahydronaphthalene (XIV), m.p. 95°. (XII), (XIII), and (XIV) boil with loss of H₂O and some H₂ to give, respectively, (VII) and 2-methyl- (XV), m.p. 203°; (III) and 2'-dimethyl- (XVI), m.p. 210°; (IV) and 2:6-dimethyl-1:2:3:4-tetrahydronaphthacene (XVII), m.p. 214°. (XV), (XVI), and (XVII) with Se at 40° give (VII), (III), and (IV), respectively. 3:6:2-C₁₀H₅Me₂-COCl and C₆H₆ or PhMe (Friedel-Crafts) give resinous products which are avoided by the above tetrahydronaphthalene derivatives. F. R. G.

Structure of hydrocarbons related to the sterols.—See this vol., 286.

Identity of 3'-methyl-1:2-cyclopentenophenanthrene with Diels' hydrocarbon, C₁₈H₁₆. H. HILLEMANN (Ber., 1935, 68, [B], 102—105; cf. A., 1933, 1154).—Improved methods are given for the conversion of 2-acetylphenanthrene into Me β -2-phenanthrylcrotonate, m.p. 147—148° (corresponding Et ester, m.p. 116—117°), for hydrogenation of the latter to Me β -2-phenanthrylbutyrate, and for reduction of the ketone obtained after ring-closure. Identity of the 3'-methyl-1:2-cyclopentenophenanthrene (I), m.p. 125—126°, with Diels' hydrocarbon is established by the identity of the product, C₁₈H₁₃O₂N, m.p. 232—233°, obtained from each by the action of N₂O₃. The constitution of (I) follows from its oxidation to mellophanic acid. β -2-Phenanthrylcrotonic acid has m.p. 227—228°. H. W.

[Diradical formula of rubene.] A. SCHONBERG (Ber., 1935, 68, [B], 162; cf. A., 1934, 643).—A reply to Dufraisse (A., 1934, 882; this vol., 205).

H. W.

Action of sodium and potassium on compounds containing the NH group. S. V. SHAH and D. G. PISHAVIKAR (J. Univ. Bombay, 1934, 3, No. 2, 106—108).—By use of methods described previously (A., 1933, 153), the *K* and *Na* derivatives of *m*-C₆H₄Me-NHAc, NHMeAc, NHAc₂, CO(NHPh)₂, and (CO-NHPh)₂ have been obtained as micro-cryst. powders quantitatively decomposed by boiling H₂O into KOH (NaOH) and the initial material. *m*-C₆H₄Me-NKAc has m.p. 146°. Compounds could not be obtained similarly from NHPh₂, NHPhMe, NHPhEt, NH₂-CH₂Ph, carbazole, or indole. H. W.

Benzylation of amines. IV. Rate of reaction of benzyl bromide with nitrobenzylaniline and some derivatives. D. H. PEACOCK (J.C.S., 1935, 16—18; cf. A., 1926, 691).—The vals. of 10³*k* for the interaction of CH₂PhBr with various bases at 45° in COMe₂ are given in parentheses: *m*- (7.45, 3.7 at 35°; *E*=13,750 g.-cal.) and *p*-C₆H₄(NO₂)-NH₂ (0.73, 0.36 at 35°; *E*=13,600 g.-cal.), *m*-nitrobenzylaniline (17.2, 9.9 at 35°), *p*- (1.7) and *m*-toluidine (1.17), *p*- (0.18) and *m*-chloroaniline (0.14); *p*-nitrobenzylaniline (14.0, 7.0 at 35°), *p*-toluidine (1—2), and *p*-chloroaniline, m.p. 99.5° (0.28). 3-Chloro-4'-nitrobenzylaniline has m.p. 66°. The results are briefly discussed and it is concluded that the factor most influencing reactivity is the electron availability at the N. J. W. B.

Arylamides of β -arylaminoacrotic acids. II. J. K. THOMSON and F. J. WILSON (J.C.S., 1935, 111—114; cf. A., 1933, 1157).—True β -arylaminoacrotic arylamides are prepared in good yields by two methods: (1) CH₃Ac-CO-NHR+NH₂R \rightarrow NHR-CMe-CH-CO-NHR (I) +H₂O, in presence of a little 2*N*-HCl in an inert solvent (PhMe, PhCl, etc.) immiscible with H₂O, and giving a homogeneous solution at its (relatively low) b.p., or (2) NH₂-CMe-CH-CO-NHR+NH₂R \rightarrow (I)+NH₃, in a similar solvent; (2) gives a better product in all cases except with C₆H₄(NO₂)-NH₂. Thus are prepared β -*m*-nitroanilinocrotono-*m*-nitroanilide, m.p. 152—153°, β -*p*-nitroanilinocrotono-*p*-nitroanilide, m.p. 220—221° (monohydrate, shrinks at 200°), β -*p*-anisidino-

crotono-p-anisidide, m.p. 116—117°; β -*p*-aminocrotono-*p*-phenetidine, m.p. 123—124° (from *acetoacet-p*-phenetidine, m.p. 104—105°), -*m*-4-*xy*lidide, m.p. 124—125°, -*p*-*xy*lidide, m.p. 136—137° (from *acetoacet-p*-*xy*lidide, m.p. 98—99°), and -*m*-chloroanilide, m.p. 81—82°; β -*p*-phenetidino-crotono-*p*-phenetidine, m.p. 105—106°, β -*m*-4-*xy*lidino-crotono-*m*-4-*xy*lidide, m.p. 126—127°, β -*p*-*xy*lidino-crotono-*p*-*xy*lidide, m.p. 107—108°, β -*o*-chloroanilino-crotono-*o*-chloroanilide, m.p. 99—100°, β -*m*-chloroanilino-crotono-*m*-chloroanilide, m.p. 86—87° [only by (2)], and β -*p*-chloroanilino-crotono-*p*-chloroanilide, m.p. 123—124°. J. W. B.

Reaction of aromatic carbimides with organic acids. II. Isolation of carbamic-carboxylic anhydrides. C. NAEGELI and A. TYABJI (Helv. Chim. Acta, 1935, 18, 142—160).—3 : 5-Dinitrophenylcarbimide and AcOH in well-cooled PhMe afford *acetic* 3 : 5-dinitrophenylcarbamic anhydride, decomp. 78°, which passes at 130° into CO₂, Ac₂O, and tetranitrocarbanilide; it decomposes slowly at room temp. *Lauric* 3 : 5-dinitrophenylcarbamic anhydride at 70—80° and finally at 130° behaves similarly; in presence of NH₂Ph it gives CO₂, (NO₂)₂C₆H₃NH₂, lauranilide, m.p. 78°, lauric acid, and 3 : 5-dinitrocarbanilide, m.p. 216° (*laur*-3 : 5-dinitroanilide, m.p. 86—87°). *Phenylpropionic* 3-nitrophenylcarbamic anhydride (I) at 75—90° affords CO₂, 3 : 3'-dinitrocarbanilide (II), and (CH₂Ph·CH₂·CO)₂O, whereas at 160—170°, *phenylpropion-m-nitroanilide*, m.p. 111°, is produced. In absence of solvent (I) and NH₂Ph yield CO₂, CH₂Ph·CH₂·CO·NHPh, CH₂Ph·CH₂·CO₂H, *m*-nitrocarbanilide, and *m*-NO₂·C₆H₄·NH₂; the similar decomp. in warm C₆H₆ is described. In EtOH (I) appears to be transformed mainly into urethane and acid; with CH₂Ph·OH, *benzyl m-nitrophenylcarbamate*, m.p. 116—117°, is formed. *Cinnamic m-nitrophenylcarbamic anhydride* (?) decomposes when heated into CO₂, (CHPh·CH·CO)₂O and (II). The anhydride nature of the product from BzOH and *m*-NO₂·C₆H₄·NCO could not be demonstrated at room temp. *Lauric m-nitrophenylcarbamic anhydride* very readily suffers disproportionation into anhydride and carbamide derivative; *phenylpropionic p-nitrophenylcarbamic anhydride* behaves similarly. A definite anhydride could not be obtained from PhNCO and AcOH and the compound from PhNCO and CHPh·CH·CO₂H is not characterised as a mixed anhydride at room temp. Phenylacetic phenylcarbamic anhydride slowly passes at room temp. into CO₂ and CH₂Ph·CH₂·CO·NHPh. Phenylpropionic phenylcarbamic anhydride is described. Benzoic phenylcarbamic anhydride appears to decompose when heated either into CO₂ and NHBzPh or into CO₂ and CO(NHPh)₂; the direction of decomp. could not be controlled. *Phenylpropionic o-nitrophenylcarbamic anhydride* could not be obtained solid; with NH₂Ph it affords CO₂, CH₂Ph·CH₂·CO₂H, *o*-nitrocarbanilide, CH₂Ph·CH₂·CO·NHPh, and *o*-NO₂·C₆H₄·NH₂.

H. W.

Aminobenzenesulphonates of bivalent elements. V. ČUPR and J. ŠIRUČEK (J. pr. Chem., 1935, [ii], 142, 6—10).—The following are described: *Mg* (+6H₂O), *Zn* (+4H₂O), *Cd* (+4H₂O), *Ca*, *Sr* (+H₂O), *Ba* (lit. +2H₂O), *Cu*, *Mn*, *Ni* (+4H₂O), and

Co (+4H₂O) *o*-aminobenzenesulphonates; *Mg* (+6H₂O), *Zn* (+4H₂O), *Cd*, *Ca* (anhyd. and +6H₂O), *Sr* (+6H₂O), *Ba* (+5H₂O) (lit. +5 and 6H₂O), *Mn* (+6H₂O), *Ni* (+4H₂O), and *Co* (+6H₂O) *m*-aminobenzenesulphonates; *Cu* (+4H₂O), *Mn* (+2H₂O), *Ni* (+4H₂O), and *Co* (+6H₂O) *p*-aminobenzenesulphonates. A relationship between Be and Mg and the sub-group Zn and Cd is not demonstrable from the co-ordination no. of the hydrates (cf. A., 1934, 398).

H. B.

Preparation of N-substituted imines of aliphatic ketones. J. HOCH (Compt. rend., 1934, 199, 1428—1430).—CPr₂(OEt)₂ and the appropriate base at 180—200° afford the *imines*, CPr₂NR, in which R=CH₂Ph, b.p. 150°/17 mm., CH₂Ph·CH₂·, b.p. 155°/16 mm., and CH₂Ph·CH₂·CH₂·, b.p. 168—170°/17 mm., in 29, 10, and 26% yield, respectively. These imines are all unstable and are hydrolysed by cold H₂O. Other acetals did not react similarly with aliphatic bases. By heating CR'R''(OEt)₂ with the appropriate base, first at 120° and then at 200°, 65—98% yields (very low at 100°) of *imines*, CR'R''NR''', are obtained, in which (a) R''=Ph, and R'=R''=Et, b.p. 117—118°/25 mm., *Pr*, b.p. 130—131°/17 mm., R'=Me, R''=nonyl, b.p. 195—197°/24 mm., and R'=Me, R''=Ph, b.p. 175—177°/17 mm., m.p. 41°, (b) R'=R''=Pr, and R'''=o-, b.p. 139—140°/18 mm., *m*-, b.p. 143—145°/20 mm., and *p*-C₆H₄Me, b.p. 143—144°/17 mm., and *o*-, b.p. 150—151°/15 mm., and *p*-C₆H₄·OMe, b.p. 164—165°/17 mm., (c) R'=Me, R''=nonyl, R'''=p-C₆H₄Me, b.p. 205—207°/24 mm., (d) R'=Me, R''=Ph, and R'''=p-C₆H₄·OMe, b.p. 209—211°/15 mm., m.p. 86°, and cyclohexanone-, b.p. 157°/30 mm., and methylcyclohexanone-anil, b.p. 149—150°/18 mm. Secondary products, usually yellow solids, are also formed in small amounts.

R. S. C.

1-Benzoyl- β -naphthylamine. K. DZIEWOŃSKI, L. KWIECIŃSKI, and L. STERNBACH (Bull. Acad. Polonaise, 1934, A, 329—337; cf. A., 1934, 419).— β -C₁₀H₇·NH₂ and BzCl at 185° with anhyd. ZnCl₂ yield 1-benzoyl-2-benzamidonaphthalene, m.p. 155.5—156.5°, which on hydrolysis gives 1-benzoyl- β -naphthylamine (I), m.p. 167.5—168.5° [picrate, m.p. 156—157°; Ac derivative, m.p. 136—137°; N-benzyl derivative, m.p. 129—130°; 2'-hydroxy-3'-naphthoyl derivative (II), m.p. 257—258°]; this, on diazotising and coupling (a) with β -C₁₀H₇·OH, yields 1-benzoyl-2-naphthalene-azo- β -naphthol, m.p. 184—185°, and (b) with 2-hydroxy-3-naphthoic acid, yields 1-(1'-benzoyl-2'-naphthaleneazo)-2-hydroxy-3-naphthoic acid, m.p. 270° (decomp.). (II) on coupling with the requisite diazo-compound gives 1-benzeneazo-2-hydroxy-3-naphthyl-1-benzoyl-2'-naphthylamide, m.p. 247—249°, and the 1-*p*-nitrobenzeneazo-derivative, m.p. 295—298°. (I) with Ac₂O and NaOAc for 8 hr. at 180° affords 2-hydroxy-4-phenyl-5 : 6-benzoquinoline, m.p. 306—307° (picrate, m.p. 226°). (I) heated in EtOH with S and CS₂ on a water-bath for 10 hr. affords bis-(1-benzoyl-2-naphthyl)thiocarbamide, m.p. 184—193° (according to rate of heating). (I) with EtOH, KOH, and CS₂ at the b.p. during 8 hr. gives tris-(1-benzoyl-2-naphthyl)guanidine, m.p. 285°. (I) in CHCl₃ with COCl₂ in PhMe at 60° during 2 days, gives bis-(1-

benzoyl-2-naphthyl)carbamide, m.p. 230°, and with CPhMe and ZnCl₂ at 210° gives 2:4-diphenyl-5:6-benzoquinoline, m.p. 146° (picrate, m.p. 233°; hydrochloride, softens at 147°, resolidifies and melts at 260°, forms a double salt, m.p. 224°, with HgCl₂).

H. G. M.

β-Phenylethylamines. IV. Preparation of β-aminophenylethylamines. K. H. SLOTTA and G. SZYSZKA [with, in part, H. HELLER] (Ber., 1935, 68, [B], 184—192; cf. A., 1933, 819).—β-o-Benzamidophenylpropionic acid is converted by successive treatment with SOCl₂ and conc. NH₃ into the corresponding amide, m.p. 176°, degraded (Hofmann) exclusively to dihydrocarbostyryl, m.p. 165°. *m*-Nitrocinnamic acid, m.p. 207°, is reduced (Na₂S and NaOH) to *m*-aminocinnamic acid, m.p. 180—181° (hydrochloride, decomp. 281°), reduced at a Hg cathode to β-*m*-aminophenylpropionic acid (I) (hydrochloride, m.p. 199°). (I) is transformed into the corresponding chloride, which when treated with NaN₃ and then heated evolves about 65% of the calc. amount of N₂, leaving a product hydrolysed by conc. HCl to brown resins; similar results are obtained from *m*-NHAc·C₆H₄·CH₂·CH₂·COCl. Treatment of (I) in conc. H₂SO₄ with HN₃ in CHCl₃ and of the product with NaOH leads to β-*m*-aminophenylethylamine (II) in 44% yield. Alternatively *m*-NO₂·C₆H₄·CHO is condensed with MeNO₂ in KOH-MeOH or in presence of Na₂CO₃ and NH₃MeCl to *m*-ω-dinitrostyrene, m.p. 125°, electrolytically reduced to (II), b.p. 180°/14 mm. [dihydrochloride, m.p. 310°; picrate, m.p. 204°; compound with 1:2:4-C₆H₃Cl(NO₂)₂, m.p. 197°]. 3-Amino-4-methoxycinnamic acid is reduced electrolytically (yield 78%) or by Na-Hg (yield 56%) to β-3-amino-4-methoxyphenylpropionic acid hydrochloride, m.p. 223°. β-3-Benzamido-4-methoxyphenylpropionic acid, m.p. 140°, is converted (SOCl₂ in CHCl₃ and conc. NH₃) into the corresponding amide, m.p. 161°, which gives unidentified products when degraded (Hofmann). 3-ω-Dinitro-4-methoxystyrene is electrolytically reduced (yield 47.2%) to β-3-amino-4-methoxyphenylethylamine, b.p. 192°/15 mm. [hygroscopic hydrochloride, m.p. 254°; picrate, m.p. 208°; compound with 1:2:4-C₆H₃Cl(NO₂)₂, m.p. 190°]. 3-Nitro-3:4-dimethoxybenzaldehyde (III) and CH₂(CO₂H)₂ in C₅H₅N containing piperidine yield 5-nitro-3:4-dimethoxycinnamic acid, m.p. 164°, reduced (Na₂S) to ill-defined substances. 5-ω-Dinitro-3:4-dimethoxystyrene, m.p. 186° [from (III) and MeNO₂ in presence of KOH-H₂O-MeOH or of Na₂CO₃ and ¹⁸H₂MeCl in abs. EtOH at 15—20°], is electrolytically reduced (yield 49.2%) to β-5-amino-3:4-dimethoxyphenylethylamine, b.p. 202°/14 mm. [dihydrochloride, m.p. 249°; picrate, m.p. 184°; compound with 1:2:4-C₆H₃Cl(NO₂)₂, m.p. 122°].

H. W.

Alkylethylenediamine derivatives. I. NN'-Dibenzylethylenediamine. J. VAN ALPHEN (Rec. trav. chim., 1935, 54, 93—96).—PhCHO (2 mols.) and (·CH₂·NH₂)₂ at 120° give (CHPh·N·CH₂)₂, solid, which with 8% Na-Hg and dry EtOH gives NN'-dibenzylethylenediamine, m.p. 25—26°, b.p. 222°/18 mm. (u. lit.) [hydrochloride, cryst.; (NO)₂, anhyd., m.p. 1, and ? + H₂O (hydrolysed by hot HCl), Ac₂, m.p. 1, Bz., m.p. 183°, and di(phenylcarbamido)-deriv-

ative, m.p. 182°], which with PhCHO affords 2-phenyl-1:3-dibenzyltetrahydroglyoxaline, m.p. 100°.

R. S. C.

Preparation of benzidine bases. V. O. LUKASHEVITSCH (Anilinokras. Prom., 1934, 4, 605—609).—*o*-C₆H₄Cl·NO₂ is converted into 2:2'-dichloroazoxybenzene (I) by reduction with Zn in 50% aq. NaOH at 80°, and (I) is further reduced in more dil. solution at 65—70° to 2:2'-dichlorohydrazobenzene, which is washed with 30—40% H₂SO₄, and converted by 50% H₂SO₄ at 10—40° into 2:2'-dichlorobenzidine (74% yield). *o*-NO₂·C₆H₄·OEt is similarly reduced (in xylene) to the hydrazo-compound, and this is converted into *o*-diphenetidine by 25% H₂SO₄ at 5—20°.

R. T.

Action of nitrous acid on tertiary amines: influence of acidity. C. DONALD and T. H. READE (J.C.S., 1935, 53—58).—The relative amounts (mol. fractions of products in parentheses) of 3:3'-dinitro-4:4'-di(dimethylamino)- (I) (nuclear nitration) and 4:4'-di(nitrosomethylamino)- (II) (nitrosoamine formation by loss of alkyl groups)-diphenylmethane and *p*-NO₂·C₆H₄·NMe₂ (III) (fission accompanied by nitration) produced from CH₂(C₆H₄·NMe₂)₂ (IV) by the action of NaNO₂ in presence of varying [HCl] (0.663—9.035*N*) at 0°, have been determined, in general, by isolation of the products. With 4 mols. of NaNO₂ to 1 mol. of (IV) the yields of (I) and (III) remain const. (0.5) up to 2*N*-HCl, then that of (I) increases up to 3.8*N*-HCl (0.7) and then slowly falls to 9*N*-HCl (with an 8/1 ratio the increase continues more slowly until at 9*N*-HCl it is almost the sole product), whereas that of (III) diminishes rapidly to 0 at 3.8*N*-HCl. The yield of (II) increases (from 0) to a true max. (0.2) at 3.8*N*-HCl and thereafter decreases to 0 at 9*N*-HCl. No action occurs if NaNO₂ completely replaces NaNO₂ at 0°, but with NaNO₃-NaNO₂ full yields of (I) and diminished yields of (II) (α the mol. fraction of NaNO₂) are obtained. With NaNO₂ the amount of NO evolved at 19.3°, with varying [HCl] approx. α the sum of the yields of (I) and (II) at 0°, and in 3.0—6.0*N*-HCl the velocity of evolution of total gases (NO+N₂) is approx. const., but diminishes slightly at lower [HCl]. The Et₂ analogue of (IV) behaves similarly, but CO(C₆H₄·NMe₂)₂ gives only the mono- (0.8 at 0.6*N*-HCl, decreasing to 0 at 7*N*-HCl) and di-nitrosoamines (max. 0.56 at approx. 3*N*-HCl). These results are discussed and are explained by the scheme: [NHRMe₂]Cl + HNO₂ → [NO·NRMe]Cl (IV) ⇌ OMe·NCl·NRMe + HNO₂ → OMe·NO(NO)·NRMe → (+2HNO₂) 2NO + H₂O + OMe·NO(NO₂)·NRMe → NO·NRMe + MeO·NO₂: (IV) + 2HNO₂ → 2NO + H₂O + [NO₂·NRMe₂]Cl (high acidity) → [NO₂·R'·NHMe₂]Cl, analogous to that for the diazonium-diazo system. 4:4'-Di(nitrosoethylamino)diphenylmethane, m.p. 83° [(?) 3:3'-(NO₂)₂-derivative, m.p. 39—40°], is new.

J. W. B.

The two *p*-aminoazoxybenzoic acids. D. BIGIARI and C. ALBANESE (Gazzetta, 1934, 64, 897—909).—AcO₂H oxidises *p*-aminoazobenzene to a mixture which after hydrolysis contains α- and β-*p*-aminoazoxybenzenes, Ph·NO·N·C₆H₄·NH₂ (I), m.p. 134—136°, and NPh·NO·C₆H₄·NH₂ (II), m.p. 133° (mixed

m.p. 113–120°), also the α - and β -*p*-NO₂-compounds. (I) and (II) yield the following derivatives. By diazotisation: α - and β -*p*-hydroxyazoxybenzenes, and, coupling with PhOH, *p*-phenolazoazoxybenzenes, Ph·N₂O·C₆H₄·N·N·C₆H₄·OH, α -, m.p. 203° (known), and β -, m.p. 176° (new?); with PhCHO, *p*-benzylideneaminoazoxybenzenes, α -, m.p. 104–105°, and β -, m.p. 132°; with PhNO, *p*-(benzeneazo)azoxybenzenes, α -, m.p. 135–141°, β -, m.p. 135–136.5°; with Ac₂O, the *Ac* derivatives of (I) and (II), m.p. 151° and 171–172°; with KCNO, *p*-carbamidoazoxybenzenes, α -, m.p. 206°, β -, m.p. 204–206°; with PhNCO, *p*-phenylcarbamidoazoxybenzenes, α -, m.p. 213–214.5°, β -, m.p. 200–210° (decomp.). Oxidation (KMnO₄) of (I) and (II) gives compounds, m.p. 229–231°, and 133–134° [(II) unaltered?]. E. W. W.

Relation between absorption spectra and chemical constitution of dyes. VII. Separation of chromophores in symmetrical bisazo-dyes. J. D. PIPER and W. R. BRODE (J. Amer. Chem. Soc., 1935, 57, 135–138; cf. A., 1934, 1344).—The absorption spectra of 6 mono- and 9 bis-azo-dyes, *p*-NAr·N·R·N·NAr·*p* (I) [R = C₆H₄·, C₆H₄·C₆H₄·, C₆H₄·CH₂·C₆H₄· (A), C₆H₄·CH₂·CH₂·C₆H₄· (B), C₆H₄·CH·CH·C₆H₄·], are determined in EtOH, 3% NaOH, and dil. and conc. HCl as previously described (cf. A., 1928, 1171). With sufficient separation [as (A) and (B)] the 2 chromophores in (I) are independent. Conjugated or closely linked (I) show marked deviations from the theoretical additive absorption of the two components. The deviation is probably influenced by solvent, by bulky substituents (which in NAr·NAr' cause a shift of the bands to lower frequencies), and by the conjugated coupling of the N·N groups to form a single chromophore. H. B.

Nitro-compounds as oxidising agents. W. A. FLETCHER and R. E. LYONS (Proc. Indiana Acad. Sci., 1934, 43, 107–113; cf. A., 1933, 817).—The reaction of CH₃Ph·ONa (I) with a no. of aromatic NO₂-compounds is described. 3 : 3'-Dinitrohydrazobenzene, m.p. 239–241°, is obtained from (I) and *m*-C₆H₄(NO₂)₂; reduction yields 3 : 3'-diaminohydrazobenzene.

CH. ABS. (r)

Metal salts of diazoaminobenzene. G. W. WATT and W. C. FERNELIUS (Z. anorg. Chem., 1934, 221, 187–192).—Methods of prep., analysis, and some physical properties of the Ag, Cu^I, Cu^{II}, and Hg^{II} salts are given. F. L. U.

Products of the reaction of diazomesitylenesulphonic acid with glycerol. (Synthesis of new foam-promoting compounds.) W. JAROSZEWICZ and E. SUCHARDA (Rocz. Chem., 1934, 14, 1188–1194).—Diazomesitylenesulphonic acid and glycerol heated at 100° yield a variety of products, of which the compounds OR·CH₂·CH(OH)·CH₂·OR' and the anhydride, m.p. 114° (decomp.), of OR'·CH₂·CH(OR)·CH·OR' (R = SO₂·C₆HMe₃·OH; R' = C₆HMe₃·SO₃H) have been identified. These compounds are readily hydrolysed by aq. NaOH, with liberation of mesitylenesulphonic acid. R. T.

Character of the diazonium group. Preparation of benzaldehyde-*p*-diazonium sulphate and its condensation with benzene to form triphenyl-

methane derivatives. H. A. J. SCHOUTISSEN (Rec. trav. chim., 1935, 54, 97–100).—*p*-NH₂·C₆H₄·CHO (I) is diazotised by NO·HSO₄ in H₂SO₄–AcOH or H₂SO₄–89% H₃PO₄ and converted into *p*-C₆H₄I·CHO and *p*-OH·C₆H₄·CHO. By diazotisation of (I) and treatment with C₆H₆–H₂SO₄ in AcOH or H₃PO₄ at 10–15° a triphenylmethane-*p*-diazonium salt is obtained, which yields *p*-hydroxy- and *p*-iodo-triphenylmethane, m.p. 82°. This ready condensation is in accord with the strong “negative” character of the diazonium group. R. S. C.

Aliphatic diazo-compounds. Preparation and rearrangement of diazo- $\beta\beta\beta$ -triphenylethane. L. HELLERMAN and R. L. GARNER (J. Amer. Chem. Soc., 1935, 57, 139–143; cf. A., 1928, 878).—Et $\beta\beta\beta$ -triphenylethylcarbamate, m.p. 94° [from CPh₂·CH₂·NH₂ (I) and ClCO₂Et in aq. Na₂CO₃], and N₂O₃ in Et₂O + anhyd. Na₂SO₄ give the *N*-NO-derivative, decomp. 114° (corr.), converted by NaOEt in Et₂O at –15° into diazo- $\beta\beta\beta$ -triphenylethane (II), decomp. 78–80° (corr.). (II) is decomposed by a little Cu-bronze or I in Et₂O or by 25% H₂SO₄ to CPh₂·CHPh (III); decomp. with H₂O at 70–100° gives (III) and a little triphenylacetaldehyde, m.p. > 300°. Decomp. of (II) with AcOH also affords (III); with AcOH in Et₂O or light petroleum, (III) and $\alpha\beta$ -triphenylethyl acetate, m.p. 175.5° (corr.) [corresponding benzoate, m.p. 179.5° (corr.), similarly formed using BzOH], are produced. An electronic mechanism explaining the formation of these products is discussed. (I) and (II) with N₂O₃ in Et₂O + Na₂SO₄ give a complex product from which a little CPh₂·CPh·NO₂ is isolable. H. B.

Conditions of formation of phenol by fusion of sodium benzenesulphonate with sodium hydroxide.—See B., 1935, 91, 137.

Electrochemical reduction of phenols. T. BAHR (Ges. Abh. Kenntn. Kohle, 1934, 11, 246–249; Chem. Zentr., 1934, ii, 876).—By reduction of PhOH with a Pb cathode in acid solution pyrocatechol, quinol, and probably quinone are formed. With a Pt cathode (optimum temp. 70–80°) cyclohexanol (I) is formed. Reduction of (I) under the same conditions gave no cyclonexane or C₆H₆. Reduction of *o*-4-xylenol yielded dimethylcyclohexanol. H. J. E.

[Attempted] synthesis of phenyl sulphates. I. Oxidation of mixtures of phenols with mineral compounds of sulphur in alkaline media. (MLLE.) Y. GARREAU (Bull. Soc. chim., 1934, [v], 1, 1563–1570).—The action of air on solutions of phenols in a mixture (I) of (NH₄)₂SO₃ and aq. NH₃ and in a mixture (II) of (I) with Cu(OH)₂ is slow. PhOH and (II) afford a phenolsulphonate and possibly PhO·SO₃H. *o*-C₆H₄(OH)₂ yields a monosulphonate with (I) and a disulphonate with (II). Guaiacol (III) and (II) give the monosulphonate. The products from *m*-C₆H₄(OH)₂ were not identified. Quinol with (I) affords NH₄ quinoldisulphonate and with (II) NH₄ 2 : 5-diaminobenzquinonedisulphonate is obtained. Phenyl sulphates were not obtained either by treating PhOH in (I) with oxidising agents or by using mixtures of phenols and Na₂S. J. G. A. G.

Action of bromine on *p*-methoxysulphonic acids. M. S. SHAH, C. T. BHATT, and D. D. KANGA

(J. Univ. Bombay, 1934, 3, No. 2, 153—154).—Passage of Br through 3:1:6-OMe·C₆H₃Me·SO₃H in H₂O affords 6-bromo-3-methoxytoluene, b.p. 236—237°, also obtained from Br and *m*-C₆H₄Me·OMe in AcOH. Similarly, 6:3:1-SO₃H·C₆H₃(OMe)·CO₂H yields 6-bromo-3-methoxybenzoic acid, m.p. 162°, also prepared from *m*-OMe·C₆H₄·CO₂H and Br in AcOH or by oxidation of 6:1:3-C₆H₃BrMe·OMe with alkaline KMnO₄. Replacement of SO₃H by Br occurs only when it is *para* to OMe. H. W.

Methylation of sulpho- and nitro-derivatives of cresols and hydroxybenzoic acids. M. S. SHAH, C. T. BHATT, and D. D. KANGA (J. Univ. Bombay, 1934, 3, No. 2, 155—158).—The customary method is applicable to the methylation of *o*-cresol-4- and *p*-cresol-2-sulphonic acid, 4- and 5-sulphosalicylic acid, and 4- and 5-sulpho-*m*-hydroxybenzoic acid, but fails in the cases of 3- (I) and 5- (II) -nitro-*o*-cresol, 2- (III), 4- (IV), and 5- (V) -nitro-*m*-cresol, 2-nitro-*p*-cresol (VI), 3- (VII) and 5- (VIII) -nitrosalicylic acid, and 2-sulphosalicylic acid (IX). Treatment with Me₂SO₄ and anhyd. K₂CO₃ in xylene (Haworth *et al.*, J.C.S., 1923, 123, 2982) yields satisfactory results with (I)—(VII), but fails entirely in the cases of (VIII) and (IX). H. W.

Condensation of *p*-bromophenol and bromocresols with benzoyl chloride and *m*- and *p*-nitrobenzoyl chlorides. G. V. JADHAV and Y. I. RANGWALA (J. Univ. Bombay, 1934, 3, No. 2, 161—162).—Mol. proportions of the acid chloride and bromophenol are heated until evolution of HCl ceases. The following compounds are new: 4-bromo-*o*-tolyl, m.p. 63—64°, 2:6-dibromo-*p*-tolyl, m.p. 94—95°, and 2:3:6-tribromo-*p*-tolyl, m.p. 120°, benzoates; *p*-bromophenyl *m*-nitrobenzoate, m.p. 121—122°; 4-bromophenyl, m.p. 180—181°, 4-bromo-*o*-tolyl, m.p. 184°, 4-bromo-*m*-tolyl, m.p. 144—145°, 4:6-dibromo-*o*-tolyl, m.p. 136—137°, 2:4-dibromo-*p*-tolyl, m.p. 141—142°, and 2:3:6-tribromo-*p*-tolyl, m.p. 159—160° after softening at 156°, *p*-nitrobenzoates. H. W.

Derivatives of -phenetidine. M. PASSERINI, G. RAGNI [in part with W. MARESCO and L. PICIACCI] (Gazzetta, 1934, 64, 909—918).—*p*-Phenetidine (I) and CHCl₃ give *p*-phenetylcarbylamine (II), m.p. 49—50°, and *di-p*-phenetylformamidine, m.p. 111—112°. (II) with COMe₂+AcOH forms the α -acetoxyisobutyryl, m.p. 133—134° (hydrolysed to the α -hydroxyisobutyryl, m.p. 149—150°), with *p*-nitrobenzaldehyde (III) and BzOH the *O*-benzoyl-*p*-nitromandelyl, m.p. 174—176°, and with (III) and salicylic acid the *O*-salicyl-*p*-nitromandelyl, m.p. 174—176°, derivatives of (I). With chlorethane, (I) gives α -*p*-phenetylaminoisobutyrylphenetidine, m.p. 132—133° (hydrochloride, m.p. 240°), and β -*p*-phenetylaminoisobutyric acid, m.p. 192—194° (NO-derivative, m.p. 90—95°); with AcCO₂Na (I) forms α -*p*-phenetylminopropionic acid, which in boiling EtOH condenses to 6-ethoxy-2-methylquinoline-4-carboxylic acid, m.p. 242—244°. E. W. W.

of nitric acid on *p*-hydroxyphenyltrimethylammonium iodide. K. C. ROBERTS (J.C.S.,

1935, 116).—Boiling 2*N*-HNO₃ converts *p*-OH·C₆H₄·NMe₃I into 5(?)-iodo-3-nitro-4-hydroxyphenyltrimethylammonium nitrate, decomp. > 210°, converted by aq. KI into the corresponding iodide, decomp. > 225°. J. W. B.

Purification of α -[2:4-]dinitrophenol. J. C. BIRD, Z. PANCIERA, and E. G. E. SHAFFER (Amer. J. Pharm., 1934, 106, 462—466).—A method of purification of 2:4-dinitrophenol and its Na salt (H₂O of crystallisation completely lost only at 170°), qual. tests for purity, and details of analysis are described. R. S. C.

Cyclic ethers of pyrocatechol with ketones. J. BOESEKEN and G. SLOOFF (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 584—590).—The equilibrium ($K=0.001$) of the pyrocatechol (I)-COMe₂ condensation (A., 1932, 860) is situated largely in favour of the free components, although the H₃BO₃ complex of (I) shows a large conductivity increase. The conclusion that COMe₂ equilibrium and H₃BO₃ conductivity increase do not run parallel with aromatic diols is explained sterically; conditions are less favourable to ring closure with COMe₂ than with H₃BO₃. The two K salts obtained from Et 4-nitroisopropylidenedioxybenzene- ω -carboxylate (A., 1933, 511) and EtOH-KOH are *cis-trans* isomerides of the enol NO₂·C₆H₃(OK)·O·CMe·CH·CO₂Et (Ac derivatives, m.p. 59° and m.p. 67°, respectively) and with CH₂N₂ give two corresponding *Me* ethers, m.p. 120° and m.p. 106°, respectively, both of which are converted by H₂SO₄ into 4-nitropyrocatechol 1-Me ether. Similar *cis-trans* isomerism occurs in the spiran formed by condensation of (I) with 4-methylcyclohexanone, nitration affording two isomeric 5-NO₂-derivatives. No experimental data are given.

J. W. B.
Nitration of 4:4'-dimethoxydiphenylmethane. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 128—129).—4:4'-Dimethoxydiphenylmethane, m.p. 51—52° (modified prep.), and fuming HNO₃ in AcOH at > 30° give the 5:5'-(NO₂)₂-derivative (I), m.p. 164.5—165.5°, oxidised (CrO₃, AcOH) to 5:5'-*di*-nitro-4:4'-dimethoxybenzophenone, m.p. 193°. The dinitro-4:4'-dihydroxydiphenylmethane (II) of Staedel (A., 1895, i, 232) is methylated (Na₂ salt with Me₂SO₄ in PhMe) to (I). Reduction (SnCl₂, AcOH—conc. HCl) of (II) affords 5:5'-*di*amino-4:4'-dihydroxydiphenylmethane, m.p. 220—222° (decomp.) (previous darkening) (dihydrochloride, m.p. > 305°). Distillation of 5:5'-tetra-acetyldiamino-4:4'-diacetoxydiphenylmethane, m.p. 142—143°, gives *di*-(2-methyl-5-benzoxazolyl)methane, m.p. 103—105°.

H. B.
Reactions of organic disulphides and oxidation of organic compounds in presence of disulphides. A. SCHONBERG (Ber., 1935, 68, [B], 163—164).—Bz₂S₂ and tetramethylthiuram disulphide are transformed by PPh₃ in boiling C₆H₆ into Bz₂S and tetramethylthiuram sulphide, respectively, PPh₃S being also formed. Many disulphides such as (CH₂Ph)₂S₂ are very stable towards PPh₃, whereas the dissociable (α -C₁₀H₇·CS)₂S₂ reacts readily. Ph₂S₂ and PPh₃ in presence of H₂O give PPh₃O and PhSH; if O₂ is also present, PhSH passes back into Ph₂S₂,

which therefore does not appear to participate in the change. H. W.

Properties of some optically active sulphonylthiolethanes. F. B. KIPPING (J.C.S., 1935, 18—21).— α -*p*-Carbethoxybenzenesulphonylethyl ketone (A., 1934, 71) and Ph_2 disulphoxide (I) afford *dl*- α -*p*-carboxybenzenesulphonyl- α -phenylthiolethane (II), m.p. 167—168° (*Me* ester, m.p. 72°), resolved by quinine into *d*. (III), m.p. 164—165°, $[\alpha]_{5461}^{20} +134^\circ$ in CHCl_3 (quinine salt, m.p. 136—138°, $[\alpha]_{5461}^{20} +97^\circ$ in CHCl_3 ; *Me* ester, m.p. 73—74°, $[\alpha]_{5461}^{20} +145^\circ$ in CHCl_3), and (through the *l*-menthylamine salt of the mother-liquor) *l*-acid, $[\alpha]_{5461}^{20} -134^\circ$ (*Me* ester, m.p. 73—74°, $[\alpha]_{5461}^{20} -145^\circ$). Oxidation of (II) with $\text{AcOH-H}_2\text{O}_2$ on a water-bath gives α -*p*-carboxybenzenesulphonyl- α -benzenesulphonylethane, m.p. 244° (*Me* ester, m.p. 128—129°). α -*p*-Carbethoxybenzenesulphonyl- α -*p*-toluenesulphonylethane (IV) (*loc. cit.*), NaOEt-EtOH , and (I) give the *Et* ester, m.p. 173°, of α -*p*-carboxybenzenesulphonyl- α -*p*-toluenesulphonyl- α -phenylthiolethane (V), + AcOH , m.p. 145—147°, and solvent-free, m.p. 186—190° (decomp.), the acid being obtained by hydrolysis with the theoretical amount of alkali [excess of alkali regenerates the acid of (IV)]. (V) is resolved through its brucine salt into the *l*-, m.p. 192—205° (decomp., according to the rate of heating), $[\alpha]_{5461}^{20} -16.1^\circ$ in COMe_2 (brucine salt + H_2O , m.p. 171—172°, $[\alpha]_{5461}^{20} +14.1^\circ$ in CHCl_3 ; *Et* ester, m.p. 148° $[\alpha]_{5461}^{20} -3.2^\circ$ in CHCl_3), and *d*-acid, $[\alpha]_{5461}^{20} +15.5^\circ$ in COMe_2 (*l*-menthylamine salt, m.p. 220°; *Et* ester, $[\alpha]_{5461}^{20} +4.24^\circ$ in CHCl_3). No racemisation of (III) occurs in NaOH-aq. EtOH up to 1 equiv. of alkali, but further increase causes a rapid increase in the velocity of racemisation. The *d*- and *l*-*Me* esters undergo rapid racemisation in presence of NaOMe-MeOH . Since the active forms of (V) are not racemised by alkali it is suggested that racemisation occurs by formation of a salt $\cdot\text{S}\cdot\text{CMe}\cdot\text{SO}(\text{ONa})\cdot$, the optical stability of (V) being due to the absence of H on the α -ethane C. J. W. B.

Preparation of the pure diastereoisomeric forms of $\alpha\beta$ -diphenyl-*n*-propyl and -butyl alcohols. F. KAYSER (Compt. rend., 1934, 199, 1424—1426).—Stilbene oxide (I) and MgMeBr give the α -form (liquid) of $\text{CHPhMe}\cdot\text{CHPh}\cdot\text{OH}$; the β -form (obtained from $\text{CHPhMe}\cdot\text{COPh}$) has now been obtained cryst., m.p. 48°. $\text{CHPhEt}\cdot\text{CHO}$ and MgPhBr give the α -form (II) of $\alpha\beta$ -diphenylbutan- α -ol, b.p. 182—184°/18 mm. (phenylurethane, m.p. 118°), the β -form (III), m.p. 82° (phenylurethane, m.p. 124°), of which is obtained by hydrogenation of $\text{CHPhEt}\cdot\text{COPh}$ (IV) or, remarkably, from (I) and MgEtBr . Both (II) and (III) are oxidised to (IV) by $\text{CrO}_3\text{-AcOH}$. R. S. C.

Plant pigments. LXIII. Products of the oxidation of carotenes. Carotenoid of *Thiocystis* bacteria. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1935, 18, 25—27).— α -Semicarotenone affords an oxime $\text{C}_{40}\text{H}_{57}\text{O}_2\text{N}$, m.p. 132°. Oxidation of β -carotene in $\text{C}_6\text{H}_6\text{-AcOH}$ with 0.1*N*- CrO_3 (=10) gives (irregularly) *neo*- β -hydroxycarotene, $\text{C}_{40}\text{H}_{56}\text{O}_2$, m.p. 143°. Lycopene appears to be the sole carotenoid present in the carotenoid fraction from *Thiocystis* bacteria. H. W.

Configuration of alicyclic alcohols. I. Configuration of 2-ethylcyclopentanols. W. HÜCKEL and W. GELMROTH (Annalen, 1934, 514, 233—251).—2-Ketocyclopentylacetic acid (I), m.p. 54° (lit. 50—51°), is reduced (1% Na-Hg , dil. Na_2CO_3 or H_2 , PtO_2 , Et_2O) to (mainly) *trans*-2-hydroxycyclopentylacetic acid (II), m.p. 52.5—53.5°, and a little *cis*-2-hydroxycyclopentylacetic acid lactone (III), b.p. 123°/16 mm., m.p. -17.5° (lit. -70°). Reduction (H_2 , PtO_2 , Et_2O) of the *Me* ester of (I) and subsequent hydrolysis (10% KOH) gives (II) (63%) and (III) (35%) (best method of prep.). Reduction (Na , EtOH) of the *Me* ester, b.p. 125°/14 mm., of (II) affords *trans*-2- β -hydroxyethylcyclopentanol (IV), b.p. 100—105°/0.3—0.4 mm. [*di*(phenylcarbamate), m.p. 97.5—98.5° and 107.5—108° (stable); $(\text{CPh}_3)_2$ ether, m.p. 57—69°], converted by HI at 100° into the cyclic ether, b.p. 144—145°/760 mm. (III) is similarly reduced to *cis*-2- β -hydroxyethylcyclopentanol (V), b.p. 110—115°/0.5 mm., m.p. 36° [*di*(phenylcarbamate), m.p. 129°], whilst valerolactone gives 30% of pentane- α -diol (VI) [*di*(α -naphthylcarbamate), m.p. 128.5—129.5°], and 45% of high-boiling condensation product. (VI) is reduced [HI (*d* 1.96) at 100° followed by Zn and AcOH] to γ -amylene oxide and pentan- β -ol (*H* phthalate, m.p. 63—64°; α -naphthylcarbamate, m.p. 72°). Successive treatment of (V) with CPh_3Cl and BzCl in $\text{C}_6\text{H}_5\text{N}$ affords *cis*-2- β -triphenylmethoxyethylcyclopentyl benzoate, m.p. 120.5°, converted by PBr_5 into the β -bromoethyl ester, which is reduced (Zn dust, 80% AcOH , little H_2PtCl_6) to *cis*-2-ethylcyclopentanol (VII), b.p. 163—165° (phenylcarbamate, m.p. 87°; *H* phthalate, m.p. 90—91°); (IV) could not be similarly converted into (IX) (below) (a substance, b.p. 177—178°, is produced). (VII) is obtained as the main product by reduction (H_2 , Pt-black , AcOH-HCl) of 2-ethylcyclopentanone (VIII) [semicarbazone, m.p. 182° (decomp.)], which is reduced (Na , EtOH) to *trans*-2-ethylcyclopentanol (IX), b.p. 165—166° (*p*-nitrobenzoate, m.p. 48.5—49°; phenylcarbamate, m.p. 76.5°). Mixtures of varying amounts of (VII) and (IX) are produced by catalytic reduction (various conditions) of (VIII). H. B.

Vinyl and hydrobenzoin dehydration of cyclic α -glycols. Extension of the hydrobenzoin type of migration to the cyclic series. M. TIFFENEAU and (MLLE.) B. TCHOUBAR (Compt. rend., 1934, 199, 1624—1626).—Dehydration of *cis*-cyclohexane-1:2-diol by passing its vapour over Al_2O_3 at 250—300° gives cyclohexanone almost exclusively, only traces of cyclopentylformaldehyde (I) being detected, but the *trans*-compound affords only (I). Similarly *cis*-1-methylcyclohexane-1:2-diol gives (90% yield) 2-methylcyclohexanone (II) and only a trace of 1-methylcyclopentylformaldehyde (III), but the *trans*-compound gives a 45% yield of a mixture of 70% of (II) and 30% of (III). Thus the *cis*-forms undergo vinyl dehydration, whereas in the *trans*-forms a hydrobenzoin type of change (C migration) occurs.

Condensation of aromatic ketones with formaldehyde. J. MANTA (J. pr. Chem., 1935, [ii], 142, 11—12).— COPhEt and 40% CH_2O (4 mols.) in boiling EtOH-KOH give α -phenyl- $\beta\beta$ -di(hydroxy-

methylpropyl alcohol, m.p. 96—97°, COPhPr^s similarly affords a 2 : 1 compound, m.p. 81—82°, of α -phenyl- β -hydroxymethylisobutyl alcohol and α -phenyl- β -methyl- β -hydroxymethylbutane- α -diol.

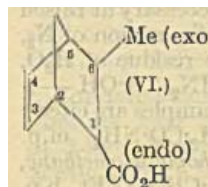
H. B.

Pinacolin and retropinacolin rearrangements in the phenanthrene group. J. SUSZKO and R. SCHILLAK (Rocz. Chem., 1934, 14, 1216—1225).—Bis-diphenylenepinacolin (I) is converted into the β -isomeride (II) [hydrazone (III), m.p. 189°; *phenylhydrazone*, m.p. 222° (decomp.)] by boiling with a mixture of AcOH and 70% H_2SO_4 . 9 : 9-Diphenylene-9 : 10-dihydrophenanthrene (IV), m.p. 195°, is obtained from (II) or (III) by heating with N_2H_4 at 200° for 8 hr. (IV) affords *tetrabenzocyclodecane-1 : 6-dione* (V), m.p. 267°, when boiled for 33 hr. with $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH . Tetrabenzonaphthalene (VI), obtained by boiling (II) for 16 hr. with Zn-Hg and HCl in EtOH , affords (V) on oxidation with $\text{Na}_2\text{Cr}_2\text{O}_7$. 9-Hydroxy-10 : 10-diphenylene-9 : 10-dihydrophenanthrene, m.p. 174—175°, prepared by reducing (II) with Zn and boiling EtOH-NH_3 , yields (VI) when boiled with EtOH-HCl , and (V) when oxidised. (V) is reduced to (VI) by heating at 170° for 5 hr. with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; with MgMeI it affords *tetrabenzo-1 : 6-dihydroxy-1 : 6-dimethylcyclodecane*, m.p. 204°. *Tetrabenzo-9 : 10-dihydroxy-9 : 10-dihydronaphthalene*, m.p. 232°, obtained by boiling (V) with Na and MgI_2 in xylene, is converted into (II) by boiling with 1 : 1 $\text{AcOH-70\% H}_2\text{SO}_4$ for 40 min. The above results confirm the views that (II) is 10 : 10-diphenylenophenanthrene, that (I) is bisdiphenylenoethylene oxide, and that a retropinacolin rearrangement takes place during reduction of (II). R. T.

alloPregnandiol, a new alcohol from the urine of pregnancy. M. HARTMANN and F. LOCHER (Helv. Chim. Acta, 1935, 18, 160—165).—The extracts of the urine are freed from solvent and treated with aq. alkaline-earth hydroxides; the hormone and its hydrate are converted into metallic salts sol. in H_2O , whilst the insol. portion (I) consists of neutral substances (II) and insol. salts of acidic impurities. (II) are removed from (I) by boiling C_6H_6 , and the portion remaining after removal of solvent is treated successively with cold COMe_2 and norit in EtOH , thus giving a mixture consisting of about 5/6 pregnandiol (III) and 1/6 *allopregnandiol* (IV). Separation of (III) and (IV) is best effected through the acetates. *alloPregnandiol diacetate*, m.p. 141.5—142.5° (corr.), $[\alpha]_D^{25} +18.8^\circ$, is hydrolysed to (IV), m.p. 248—248.5° (corr.). Oxidation of (IV) by CrO_3 in cold 90% AcOH leads to the diketone $\text{C}_{21}\text{H}_{32}\text{O}_2$, m.p. 204—204.5°, identical with that obtained by analogous treatment of the OH- α -ketone from the corpus luteum. In (III) the rings A and B are united in the *cis*-position, in (IV) in the *trans*-position (dihydrocholesterol series). H. W.

Steric course of addition and substitution reactions. II. Stereochemistry of diene syn-
 II. K. ALDER and G. STEIN [with M. LIEBMAN and E. ROLLAND] (Annalen, 1934, 514, 1—211; cf. this vol., 211).—2 : 5-*endo*Methylene-tetrahydrobenzoic acid (*endo*) (I), m.p. 39° [from cyclopentadiene (II) and $\text{CH}_2\text{:CH-CO}_2\text{H}$ at $\approx 40^\circ$] (cf. *ibid.*, 1928, 1018), is reduced (H_2 , colloidal Pd, aq. O_2) to 2 : 5-*endomethylene*hexahydrobenzoic acid

(*endo*) (III), b.p. 141—142°/23 mm., m.p. 65—66° (cf. *loc. cit.*) (chloride, b.p. 84°/12 mm.; *anilide*, m.p. 151—152°), and is converted by cold 50% H_2SO_4 into the lactone, m.p. 155—156°, of 3-hydroxy-2 : 5-*endo*-methylenehexahydrobenzoic acid. Crude 2 : 5-*endo*-methylene- Δ^3 -tetrahydrobenzaldehyde (IV) [from (II) and $\text{CH}_2\text{:CH-CHO}$] (cf. *loc. cit.*) is reduced (H_2 , colloidal Pd, MeOH) to the hexahydro-derivative, which is oxidised (method : von Braun and Keller, A., 1933, 259) to (III). (I) and (IV) are, therefore, *endo*-derivatives [cf. (VI) (below)]; they are the main products in the above additive reactions. Hydrolysis (aq. Na_2CO_3) of the product from (II) and fumaryl chloride (V) in Et_2O at -10° gives *trans*-3 : 6-*endo*-methylene- Δ^4 -tetrahydrophthalic acid; direct addition of (V) to (II) occurs. (II) and *trans*-crotonyl chloride similarly afford *trans*-6-methyl(*exo*)-2 : 5-*endomethylene*- Δ^3 -tetrahydrobenzoic acid (*endo*) (VI), m.p. 95—96°, reduced (H_2 , Pd, aq. Na_2CO_3) to the hexahydro-acid (VII), m.p. 69° (A., 1929, 819), and converted by 50% H_2SO_4 into the lactone, m.p. 70—71°, of 3-hydroxy-6-methyl(*exo*)-2 : 5-*endomethylene*hexahydrobenzoic acid (*endo*). (VI) and (VII) are regenerated when their Me esters are heated with conc. MeOH-NaOMe . The *trans*-6-methyl-2 : 5-*endomethylene*- Δ^3 -tetrahydrobenzaldehyde previously described (*loc. cit.*) is (VI) with $\text{CO}_2\text{H=CHO}$, since successive reduction and oxidation gives (VII); it is formed (cf. *loc. cit.*) by direct addition of *trans*-crotonaldehyde to (II).



H. B.

Preparation of acid chlorides by thionyl chloride. P. CARRÉ and D. LIBERMANN (Compt. rend., 1934, 199, 1422—1423).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$, $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, and $\text{Bu}^t\text{CO}_2\text{H}$ with SOCl_2 at or slightly above room temp. give excellent yields of the acid chlorides in the presence of $\text{C}_5\text{H}_5\text{N}$, but not in its absence. R. S. C.

4-Bromo-*o*-toluic acid. K. J. KEUNING and N. EVENHUIS (Rec. trav. chim., 1935, 54, 73—75).— $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ and Br give 4-bromo-*o*-toluic acid, m.p. 170° (lit. 167°) (*Me* ester, m.p. 45°, b.p. 264.5°). 4-Bromo-*o*-xylene and HNO_3 (*d* 1.08) give 5-bromo-*o*-toluic acid, m.p. 181—182° (*Me* ester, b.p. 265°) (cf. *lit.*). R. S. C.

2-Chloro-3 : 5-dinitro-4-chloromethyl- and 2 : 4 : 6-tribromo-3-bromomethylbenzoic acids and attempts to resolve them. A. WEISSBERGER, H. BACH, and E. STRASSER (J.C.S., 1935, 68—71).—2-Chloro-4-chloromethylbenzonitrile (I) [prep. from 3-chloro-*p*-toluidine \rightarrow 3-chloro-*p*-toluonitrile (II) + $\text{PCl}_5 \rightarrow$ (I)] is converted by conc. $\text{H}_2\text{SO}_4\text{-HNO}_3$ (*d* 1.52) at 100° into 2-chloro-3 : 5-dinitro-4-chloromethylbenzoic acid (III), m.p. 198—200°. 2 : 4 : 6-Tribromo-*m*-toluidine is converted (Sandmeyer) into 2 : 4 : 6-tribromo-*m*-toluonitrile, m.p. 123—124°, hydrolysed by 66% aq. HBr at 160—180° to the *amide*, m.p. 202—203°, converted by HNO_2 into the acid (IV) (polymorphous), sinters at 160°, m.p. 190.5—191.5°. With $\text{Br-CHCl}_3\text{-NaHCO}_3$ (IV) affords 2 : 4 : 6-tribromo-3-bromomethylbenzoic acid (V) (polymorphous), sinters at 160°, m.p. 183.5—184.5°. In (III) and (V) the

possibility of enantiomorphism arising from restricted rotation of the CH_2Hal by the two bulky *o*-substituents was anticipated, but attempts to resolve these acids with brucine, strychnine, quinine, or quinaldine failed, even the alkaloid salts exhibiting no difference in rotation from those of 3-chloro-2:6-dinitro-*p*-toluic acid [from (II) by hot $\text{H}_2\text{SO}_4\text{--HNO}_3$]. All m.p. are corr.

J. W. B.

Conversion of carboxylic acids into higher homologues or their derivatives. F. ARNDT and B. EISTERT (Ber., 1935, 68, [B], 200—208).—The acid is converted into its chloride, which is transformed by excess of CH_3N_2 into the diazo-ketone (I) accompanied by a little Cl-ketone: $\text{R}\cdot\text{COCl} + 2\text{CH}_3\text{N}_2 = \text{R}\cdot\text{CO}\cdot\text{CHN}_2 + \text{MeCl} + \text{N}_2$. Treatment of (I) with H_2O , alcohols, NH_3 , primary or *sec.*-amines in presence of finely-divided Ag, Pt, or Cu as catalyst, if necessary at raised temp. and under pressure, leads to elimination of N_2 , wandering of R, and addition to the residue of H_2O , alcohol, amine, etc., thus: $\text{R}\cdot\text{CO}\cdot\text{CHN}_2 + \text{H}\cdot\text{OH} \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{N}_2$. The following examples are cited: *o*- $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{COCl}$ to *o*- $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 160—161°; 1- $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$ to α -naphthoyldiazomethane, m.p. 54—55°, and thence to 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b.p. 175—178°/11 mm., 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 131°, 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_2$, m.p. 180°, and 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{NHPh}$, m.p. 156°: veratric acid to veratroyldiazomethane, m.p. 75°, and thence to homoveratroylamide, m.p. 146°; BzOH to $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}_2$ and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NHPh}$; anthraquinone-2-carboxylic acid to anthraquinonyl-2-acetanilide, m.p. 267—268°; 1-chloroanthraquinone-2-carboxylic acid to 1-chloro-2- ω -diazoacetoanthraquinone, m.p. 148—150° (decomp.), and thence to 1-chloroanthraquinonyl-2-acetanilide, m.p. 285—286°; 1-nitroanthraquinone-2-carboxylic acid to 1-nitro-2- ω -diazoacetoanthraquinone, m.p. 200° (decomp.), and thence to 1-nitroanthraquinonyl-2-acetanilide, decomp. 256°. H. W.

Syntheses in the aromatic-aliphatic series. Phenylacetic acids with the *tert.*-butyl radical in the ring. R. BERG (Rocz. Chem., 1934, 14, 1249—1261).— $p\text{-C}_6\text{H}_4\text{Bu}^\vee\text{CH}_2\text{Cl}$ and aq. $\text{EtOH}\text{--NaCN}$ afford *p*-*tert.*-butylphenylacetone nitrile, b.p. 141—142°, yielding the corresponding acid, m.p. 78—79°, on hydrolysis with aq. $\text{H}_2\text{SO}_4\text{--AcOH}$. 1-Methyl-4-*tert.*-butyl-2(?)*-benzyl chloride*, b.p. 146—147°/26 mm., prepared from $p\text{-C}_6\text{H}_4\text{MeBu}^\vee$, $(\text{CH}_2\text{O})_x$, and HCl in presence of ZnCl_2 , yields similarly the corresponding nitrile, b.p. 145—147°/11 mm., and acid, m.p. 72—73.5°. 1-Ethyl-4-*tert.*-butyl-2(?)*-benzyl chloride*, b.p. 146—147°/18 mm., prepared analogously from $p\text{-C}_6\text{H}_4\text{EtBu}^\vee$, b.p. 207—208°/751 mm. [2:6-(NO_2)₂-derivative, m.p. 94—95°], affords the corresponding nitrile, b.p. 158—159°/12 mm., and acid, m.p. 70.5—72°. R. T.

Esters of thionaphthoic acid. L. SZPERL and J. HERSZAFT (Rocz. Chem., 1934, 14, 1238—1242).—*Me*, b.p. 168.5—170°/10 mm., *Ph*, m.p. 61.6—62.1°, and $\alpha\text{-C}_{10}\text{H}_7$, m.p. 125—126.2°, α -thionaphthoates have been prepared by Taboury's method (Ann. Chim., 1908, 15, 5). The above esters have similar properties to those of other known thio-acids. R. T.

Synthesis of a methyl*tert.*-butyl-naphthalene and -naphthoic acid. G. DARZENS and A. LEVY

(Compt. rend., 1934, 199, 1426—1428).—*p*-*tert.*-Butylbenzyl chloride (prepared in 70% yield), b.p. 115°/16 mm., m.p. —18°, with Et_2 allylsodiummalonate in PhMe gives *Et*, *p*-*tert.*-butylbenzylallylmalonate (75% yield), b.p. 180—181°/3 mm., converted by $\text{KOH}\text{--EtOH}$ and subsequent heating into a mixture of α -*p*-*tert.*-butylbenzyl- Δ^7 -butenoic acid (I), m.p. 68°, and the γ -lactone (II),



b.p. 152°/2 mm. With $\text{H}_2\text{SO}_4\text{,H}_2\text{O}$ (I) gives slowly 20% of (II) and 80% of 4-methyl-6-*tert.*-butyl-1:2:3:4-tetrahydro-2-naphthoic acid, which with S affords 4-methyl-6-*tert.*-butyl-2-naphthoic acid, converted by distillation with CaO in vac. into 1-methyl-7-*tert.*-butyl-naphthalene, b.p. 151—152°/14 mm. [picrate, m.p. 95.5°; styphnate, m.p. 129°; (NO)₂-derivative, m.p. 131°]. R. S. C.

Vegetable heart poisons. V. Aetioallocholanolic acid and its identification with the acid obtained by degradation of azarigenin. R. TSCHESCHE (Ber., 1935, 68, [B], 7—9; cf. A., 1934, 1354).—The identity of the acid $\text{C}_{20}\text{H}_{32}\text{O}_2$ (I) obtained from uzarigenin (*loc. cit.*) with aetioallocholanolic acid is established by comparison of the acids and their Me esters. The genins (II) of the heart poisons have therefore the same C skeleton as the sterols and bile acids. The acid $\text{C}_{19}\text{H}_{30}\text{O}_4$ derived from (I) is aetioallobilanic acid. It is not certain that (II) belong to the *allo*-series. H. W.

Ethyl cyclopentanone-2-carboxylate and *cis*- and *trans*-2-ethylcyclopentanols. G. VAVON and A. HOREAU (Bull. Soc. chim., 1934, [v], 1, 1703—1713).—Et sodiocyclopentanone-2-carboxylate reacts 3—4 times as fast with alkyl iodides as with the bromides and 60—70 times as fast with the latter as with the chlorides. For this alkylation aq. NaOH can advantageously replace the NaOEt usually used. The relative rates of reaction of CH_2PhCl , *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Cl}$, and $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ are 1:5:10:5, whilst 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\text{Br}$ reacts 100 times as fast as CH_3PhBr . The following *Et* 2-alkylcyclopentanone-2-carboxylates are described: *Et* (I), b.p. 11—12 mm.; *Pr*, b.p. 117—119°/9 mm.; *Bu*, b.p. 125—127°/8 mm. (I) with about 20% HCl gives an 80% yield of 2-ethylcyclopentanone (II) and with 20% $\text{NaOEt}\text{--EtOH}$ an 86% yield of α -ethyladipic acid, m.p. 51° (lit. 49°), also obtained without isolation of (I) by use of a deficiency of EtI in the prep. of (I). This acid with Ba(OH)_2 at 160—180° gives an 85% yield of (II), b.p. 157—158° [semicarbazone, m.p. 187° (decomp.)]; this is reduced by $\text{Na}\text{--EtOH}$ to a mixture containing mostly *trans*-2-ethylcyclohexanol (III) (*H* phthalate, m.p. 54.5—55°; phenylurethane, m.p. 73—74°), whereas hydrogenation (Pt-black) in $\text{AcOH}\text{--HCl}$ gives mainly the *cis*-alcohol (IV) (*H* phthalate, m.p. 54.5—55°; phenylurethane, m.p. 86—86.5°). (IV) has a higher *d* than (III), is less readily obtained from the *H* phthalate, and is more readily dehydrated by 3% $\text{H}_2\text{SO}_4\text{--Bu}_2\text{O}$. Both forms have about the same *n*. R. S. C.

Derivatives of salicylic acid. VI. Reaction of thionyl chloride on esters of hydroxybenzoic acids in presence of finely-divided copper. I. Synthesis and constitution of 4:4'-dihydroxy-

3:3'-dicarboxydiphenyl sulphide and related compounds. N. W. HIRWE, G. V. JADHAV, and Y. M. CHAKRADEB (J. Amer. Chem. Soc., 1935, 57, 101—103).—*o*-OH·C₆H₄·CO₂Me (I), SOCl₂, and Cu dust give 4:4'-dihydroxy-3:3'-dicarbomethoxydiphenyl sulphide (II), m.p. 147—148° (diacetate, m.p. 94°; dibenzoate, m.p. 117°; 5:5'-Br₂-derivative, m.p. 133°); reaction does not occur in absence of Cu. (II) is also obtained from (I), SCl₂, and a little Cu; S₂Cl₂ similarly gives (II) and S (also formed in the above reaction; cf. below). Evidence is given to show that the following reactions are intermediary: $4\text{SOCl}_2 + 3\text{Cu} \longrightarrow 3\text{CuCl}_2 + 2\text{SO}_2 + \text{S}_2\text{Cl}_2$; $2\text{CuCl}_2 + \text{SO}_2 \longrightarrow \text{Cu}_2\text{Cl}_2 + \text{SO}_2\text{Cl}_2$; $2\text{SOCl}_2 + \text{Cu}_2\text{Cl}_2 \longrightarrow \text{CuCl}_2 + \text{SO}_2 + \text{S}_2\text{Cl}_2$. (II) is hydrolysed (10% NaOH) to 4:4'-dihydroxy-3:3'-dicarboxydiphenyl sulphide (III), m.p. 269—270° [Na₂ (+H₂O), K₂ (+2H₂O), Ca (+4H₂O), and Ba (+4H₂O), salts; diamide, m.p. 272—273° (decomp.), from (II) and conc. aq. NH₃; diacetate, m.p. 164°; dibenzoate, m.p. 129°; Me₂ ether, m.p. 157°; 5:5'-Br₂-derivative (IV), m.p. 274—275° (decomp.)], converted by warm 6.5% and conc. HNO₃ into 5-nitrosalicylic and picric acid (V), respectively. (III) and Br at 100° give 3:5-dibromosalicylic acid, whilst (IV) is converted by warm 13%, 32.5%, and conc. HNO₃ into 3-bromo-5-nitrosalicylic acid, 2-bromo-4:6-dinitrophenol, and (V), respectively. *o*-OH·C₆H₄·CO₂Et, SOCl₂, and Cu afford 4:4'-dihydroxy-3:3'-dicarbomethoxydiphenyl sulphide, m.p. 110° (diacetate, m.p. 92°), also prepared by esterification of (III); *o*-OH·C₆H₄·CO₂Ph similarly gives 4:4'-dihydroxy-3:3'-dicarbophenoxydiphenyl sulphide, m.p. 158° (diacetate, m.p. 144°). H. B.

Spontaneous hydrolysis of salolphosphoric and phenylphosphosalicylic acids. J. ARAI (J. Biochem. Japan, 1934, 20, 465—480).—Me salicylate with OPh·POCl₂ at 220° followed by treatment with NaOH yields phenylphosphosalicylic acid (I), *o*-CO₂H·C₆H₄·O·PO(OH)·OPh (Ba salt). Max. hydrolysis of 0.002*M*-phosphosalicylic and -salolphosphoric (salol-*O*-phosphinic; A., 1899, 53) acid (II) and (I) occurs at *p*_H 5.5, H₃PO₄ and salicylic acid (III) being liberated in approx. equiv. amounts with each acid. With (II) at *p*_H 5.5 for 3 hr., approx. 14% of H₃PO₄ and of (III) are liberated, whilst the liberation of PhOH is complete; at such a stage the hydrolysate yields the Na salt of salicylic anhydride phosphoric ester, [NaO·PO(OH)·O·C₆H₄·CO]₂O, which dephosphorylates in H₂O with a *p*_H optimum of 5.5 (20% after 3 hr.). F. O. H.

Compounds of tervalent vanadium.—See this vol., 313.

Inversion of α -substituted hydroxyhydrindeneacetic acids. D. H. PEACOCK and B. K. MENON (J.C.S., 1935, 15—16).—Condensation of CH₃Ph·CH₂·CHAc·CO₂Et with 2-bromo-1-hydroxyhydrindene and EtOH·NaOEt, and hydrolysis (KOH·EtOH) of the product, affords trans- γ -phenyl- α -1-hydroxyhydrindene-2 butyric acid, m.p. 131°, converted by boiling HBr·AcOH into the *a*-form, m.p. 94°, of the *cis*-lactone, converted (by inversion about C₆) by boiling *N*-NaOH·EtOH into the *b*-form, m.p. 88°, more slowly and less completely than in case of the corresponding CH₃Ph derivative (A., 1934, 1217).

Similarly is obtained trans- β -*p*-bromophenyl- α -1-hydroxyhydrindene-2-propionic acid, m.p. 175° (Ac derivative, m.p. 171°), converted into the *a*-form, m.p. 134°, and the *b*-form, m.p. 110°, of the *cis*-lactone.

J. W. B.

Preparation of tetraiodophthalic anhydride. G. W. PERKINS and G. P. QUIMBA (Amer. J. Pharm., 1934, 106, 467—473).—Prep. of this compound in 80—99.9% yield by I and fuming H₂SO₄ (50% SO₃) and determination of I therein by fusion with Na₂CO₃—Na₂O₂ are described. R. S. C.

Preparation of methyl caffeate [3:4-dihydroxycinnamate]. F. MAUTHNER (J. pr. Chem., 1935, [ii], 142, 33—34).—Successive treatment of the dicarbomethoxy-derivative of 3:4-dihydroxycinnamic acid (I) [from 3:4-(OH)₂C₆H₃·CHO and CH₂(CO₂H)₂ in AcOH at 100° (bath)] with MeOH·Et₂O·CH₂N₂ and cold aq. EtOH·NaOH (in H₂) gives the Me ester, m.p. 152—153°, of (I). H. B.

Condensation of acetonedicarboxylic acid with phenols and phenolic ethers. II. Formation of 3-keto-7-methoxy-4-methylhydrindenyldeneacetic acid. D. B. LIMAYE and G. R. GOGATE (J. Univ. Bombay, 1934, 3 No. 2, 135—140; cf. A., 1931, 1055).—Condensation of CO(CH₂CO₂H)₂ with *p*-C₆H₄Me·OMe in H₂SO₄ at 25—28° affords 3-keto-7-methoxy-4-methylhydrindenyldeneacetic acid (I), m.p. 218° (decomp.), and 6-methylcoumarin-4-acetic acid (II), m.p. 180° (decomp.), whereas at 0—5° β -2-methoxy- γ -methylphenylglutaconic acid (III), m.p. 169° (decomp.), (II), and an acid, C₂₁H₂₂O₅, m.p. 252° [Et ester, m.p. 122°; semicarbazone, m.p. 272° (decomp.); phenylhydrazone, m.p. 205° (decomp.)], which is converted by conc. H₂SO₄ at 70—80° into (I) result. (III) is transformed into (I) by H₂SO₄. Oxidation of (I) with HNO₃ (*d* 1.2) gives 3-methoxy-6-methyl-*o*-phthalic anhydride, m.p. 186° (Ag and Ba salts and Et H ester, m.p. 94°, of the corresponding acid). From (III) are obtained the anhydride, m.p. 117°, Et₂ ester, b.p. 207°/5 mm., Et H ester, m.p. 82°, semianilide, m.p. 148°, anil., m.p. 225°, 2-methoxy-5-methylisopropenylbenzene, b.p. 205°, 2:6-dihydroxy-3:2'-methoxy-5'-methylphenylpyridine, m.p. 200°, and its Bz₂ derivative, m.p. 134°. (I) yields an Et ester, m.p. 158° [semicarbazone, m.p. 234° (decomp.); oximino-, m.p. 216° (decomp.), and benzylidene, m.p. 143°, derivatives], a semicarbazone, m.p. 252° (decomp.), and a phenylhydrazone, m.p. 213° (decomp.); it is decarboxylated to a product C₁₂H₁₀O₂, m.p. 83°. H. W.

Synthesis of homosyringic [4-hydroxy-3:5-dimethoxyphenylacetic] acid. F. MAUTHNER (J. pr. Chem., 1935, [ii], 142, 26—32).—Syringic acid [from 3:4:5-(OMe)₃C₆H₂·CO₂H and conc. H₂SO₄ at 50°] is converted (method: Lepsius, A., 1914, i, 1072) into the *O*-CO₂Me derivative and thence by PCl₅ in CHCl₃ into the acid chloride. This is reduced (method: Rosenmund, A., 1918, i, 300) to 4-carbomethoxyoxy-3:5-dimethoxybenzaldehyde, m.p. 98—99°, hydrolysed (aq. EtOH·NaOH in H₂) to syringaldehyde (the cyanohydrin of which could not be converted into the mandelic acid). Oxidation (O₃ in EtOAc) of the benzoate, m.p. 77°, of 4-hydroxy-3:5-dimethoxyallylbenzene (A., 1921, i, 726) gives 4-

benzoyloxy-3:5-dimethoxyphenyl-acetaldehyde [oxime (I), m.p. 118—119°] and -acetic acid (II), m.p. 149—150° [nitrile (III), m.p. 127—128°, from (I) and Ac_2O]. Hydrolysis of (II) with 10% NaOH and (III) with aq. EtOH-KOH gives *homosyringic acid*, m.p. 130—131°. H. B.

Perkin synthesis. II. E. MÜLLER, H. GAWLICK, and W. KREUTZMANN (Annalen, 1935, 515, 97—112; cf. A., 1932, 56).—The Na enolate (I) of homophthalic anhydride (*loc. cit.*) reacts with ArCHO (yield of product dependent on reactivity of CO) other than PhCHO. Thus, $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{o-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ give 83 and 55% of β -hydroxy- β -*o*-nitrophenyl- and β -*o*-anisyl- α -*o*-carboxyphenylpropionolactones, $\text{o-C}_6\text{H}_4\langle\text{CH}(\text{CO}_2\text{H})\text{O}\rangle\text{CH}\cdot\text{C}_6\text{H}_4\text{R}$, m.p. 178° and 186.5° (decomp.), respectively (*Me* esters, m.p. 163.5° and 104.5°, respectively). Prolonged interaction of (I) and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and subsequent acidification (dil. H_2SO_4) gives 17% of a resinous product, converted by CH_2N_2 into the substance, $? \text{C}_6\text{H}_4\langle\text{CH}(\text{CO}_2\text{Me})\text{O}\rangle\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{SO}_2\text{Me}$, m.p. 228° (becoming red). Succinic anhydride and NaCPh_3 in C_6H_6 afford a *Na enolate*, which with PhCHO at room temp. for 3 weeks gives dibenzylidenesuccinic acid (*Me* ester, m.p. 116°). The enolates from EtOAc and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Me}$ react with PhCHO in Et_2O to give (after hydrolysis) $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and $\text{CHPh}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$ (*Me* ester, m.p. 76—77°), respectively. NaCPh_3 and $\text{CH}_2\text{Ph}\cdot\text{CN}$ (II) in Et_2O afford the "enolate" $[\text{CHPh}\cdot\text{C}\cdot\text{N}]\text{Na}^+$, which is hydrolysed (dil. AcOH) to (II) and reacts with AcCl and PhCHO giving $\text{CHAcPh}\cdot\text{CN}$ and $\text{CHPh}\cdot\text{CPh}\cdot\text{CN}$, respectively. Reaction products could not be obtained from PhCHO and the enolates from $\text{CHPh}_2\cdot\text{CO}_2\text{Et}$, $\text{CHPh}_2\cdot\text{CHO}$, $\text{CHPh}_2\cdot\text{CN}$, $\text{Pr}^i\text{CO}_2\text{Et}$ (III), Pr^iCHO , and $(\text{Pr}^i\text{CO})_2\text{O}$ (IV) (*Na*, dienolate). The production of $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}(\text{Et})$ from (IV), $\text{Pr}^i\text{CO}_2\text{Na}$, and PhCHO (Fittig *et al.*, A., 1883, 471; 1885, 663) or from (III), PhCHO, and EtOH-NaOEt (Scheibler and Friese, A., 1925, i, 1417) could not be confirmed. The Na enolate of $\text{CH}_2(\text{CO}_2\text{Et})_2$ does not condense with PhCHO in C_6H_6 or in Et_2O containing small amounts of piperidine, NEt_3 , or NaOAc.

The first stage in the Perkin reaction is the formation of an enol or enolate which subsequently condenses with a reactive CO (of the second component).

H. B.

Action of aromatic aldehydes on benzene and toluene in presence of aluminium chloride. D. H. HEY (J.C.S., 1935, 72—75).—Contrary to Gattermann (A., 1906, i, 589) PhCHO and anthracene (I) are formed when dry $\text{CO} + \text{HCl}$ is passed into $\text{C}_6\text{H}_6 + \text{AlCl}_3$ at 45°. C_6H_6 reacts with *m*- or *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{CHO}$, or with $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ to give, in each case, (I), CHPh_3 , and, respectively, PhMe and *m*-xylene or PhCl. The last-named products indicate the reversibility of the reaction $\text{PhCHO} + \text{C}_6\text{H}_6 + \text{CO}$. In agreement with this view PhCHO and AlCl_3 afford CO, and $\text{CO} + \text{HCl}$ with boiling $\text{PhMe}\cdot\text{AlCl}_3$ give a mixture (II) of 2:6- and 2:7-dimethylantracene (identified by oxidation to the quinones), and a mixture of tritolyldmethanes. The same (II) is obtained

by the action of either PhCHO or furfuraldehyde on $\text{PhMe}\cdot\text{AlCl}_3$ at 60°. It is therefore concluded that the hydrocarbon nuclei alone go to form the two end rings in (I) and the three rings in CHAr_3 , the aldehyde supplying only the *meso*-C in the former, and the methane-C in the latter. J. W. B.

Action of halogens on the arylhydrazones of unsaturated aldehydes. F. D. CHATTAWAY and H. IRVING (J.C.S., 1935, 90—92).—The action of excess of Br in AcOH on the appropriate phenylhydrazone of $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ is probably

$$\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh} \longrightarrow 2:4\text{-C}_6\text{H}_3\text{Br}_2\cdot\text{NH}\cdot\text{NBr}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CHBrPh} \longrightarrow 2:4\text{-C}_6\text{H}_3\text{Br}_2\cdot\text{NH}\cdot\text{N}\cdot\text{CBr}\cdot\text{CHBr}\cdot\text{CHBrPh}$$

although a NO_2 in the N:NHPh residue prevents further nuclear substitution. By such methods are obtained $\omega\alpha\beta$ -tri-bromo- β -phenylpropaldehyde-2:4-di-, m.p. 180°, and -2:4:6-tri-bromo-, m.p. 173°, -*p*-nitro-, m.p. 193°, and -2-bromo-4-nitro-, m.p. 199°, -phenylhydrazone, and $\alpha\beta$ -dibromo- β -phenylpropaldehyde-2-bromo-4-nitro-phenylhydrazone. Similar action of Cl_2 gives $\omega\alpha\beta$ -trichloro- β -phenylpropaldehyde-2:4-di-, m.p. 158°, and 2:4:6-tri-chloro-, m.p. 111°, and -2-chloro-4-nitro-, m.p. 190°, -phenylhydrazone. Reduction (SO_2 -aq. NH_3) of the diazonium compound from 2-bromo-4-nitroaniline affords 2-bromo-4-nitrophenylhydrazine, m.p. 142°, the corresponding 2-Cl-derivative, m.p. 142°, being similarly obtained. The following are also new: cinnamaldehyde-2:4-di-, labile and stable form, m.p. 164°, and -2:4:6-tri-bromo-, m.p. 125°, -2-bromo-4-nitro-, m.p. 148°, and -2-chloro-4-nitro-, m.p. 157°, -phenylhydrazone. J. W. B.

Oxidation of 2- and 4-nitro-4'-methylidiphenyl with chromyl chloride. W. S. H. GRIEVE and D. H. HEY (J.C.S., 1935, 114—115).—2- and 4-Nitro-4'-methylidiphenyl are, respectively, converted by $\text{CrOCl}_2\text{-CCl}_4$ and subsequent treatment with SO_2 into 2-, m.p. 101°, and 4-nitrodiphenyl-4'-aldehyde, m.p. 127° (together with the corresponding acid), identical, respectively, with the corresponding products obtained by nitration of diphenyl-4-aldehyde (A., 1933, 1051). J. W. B.

Determination of lignin at low temperatures and the complete hydrolysis of straw. R. S. HILPERT and E. LITTMANN (Ber., 1935, 68, [B], 16—18).—The production of ppts. by the action of H_2SO_4 on carbohydrates (A., 1934, 1205) diminishes greatly with fall of temp. and is generally very slight at 6°. At 0°, straw gives 16% of its wt. of ppt. At $> -10^\circ$, straw dissolves in 72% H_2SO_4 to a clear solution except for a slight residue of ash. Dilution causes pptn. of varying amounts of material, $2\text{C}_6\text{H}_{10}\text{O}_5\text{-H}_2\text{O}$, which is doubtless a carbohydrate and either represents an intermediate product or a component particularly stable to acid. Apart therefrom (8—20%), the solutions are transparent and when neutralised and conc. leave a pale yellow product which reduces Fehling's solution. Straw cannot therefore contain appreciable amounts of substances with the properties of lignin. The unusual sensitiveness of straw to H_2SO_4 indicates the presence of an unknown carbohydrate unless a peculiar linking of the polyose enhances the reactivity of the sugar. H. W.

Cyclic ketones. IV. R. POGGI [in part with (Miss) M. GOTTLIEB] (Gazzetta, 1934, 64, 852—857).—Anisaldehyde (I) and 4-methylcyclohexanone condense (KOH) to form 2-anisylidene- (II), m.p. 91·5—93° [semicarbazone, m.p. 205—208° (decomp.); oxime, m.p. 122—124°], and 2:6-dianisylidene-4-methylcyclohexanone (III), new m.p. 144—145°. (II) and (I) yield (III); (II) and PhCHO, the 6-benzylidene-2-anisylidene compound, m.p. 108—112·5°. Br converts (III) into the compound, $C_{23}H_{23}O_3Br_6$ (?), decomp. 179°. All the above are photo-sensitive. E. W. W.

Structure of metal ketyls. IV. Nature of intermediate product in reaction with alkyl halides. C. B. WOOSTER and J. G. DEAN (J. Amer. Chem. Soc., 1935, 57, 112—114; cf. this vol., 84).—The red solution of Na (I) or K (II) ethoxydiphenylmethyl obtained from $CPh_2(OEt)_2$ and Na or K (2 equivs.) in liquid NH_3 is decolorised by dry O_2 ; benzpinacol Et_2 ether, m.p. 162·5° (converted by HI into $COPh \cdot CPh_3$ and EtI), and ethoxydiphenylmethyl peroxide, m.p. 138° (converted by HI into $COPh_2$ and EtI), are produced. (I) is accompanied by some $CNa_2Ph_2 \cdot CPh_2(OEt)_2 + 4Na \rightarrow CNa_2Ph_2 + 2NaOEt$. (II) is also prepared from $CHPh_2 \cdot OEt$ and KNH_3 in liquid NH_3 . Determinations of OEt show that (I) and (II) do not undergo any appreciable rearrangement during several hr. The ketyl (A) from $COPh_2$ and Na (or K) in liquid NH_3 with $EtBr$ gives products containing 2—3·8% OEt only; (I) [or (II)] is not, therefore, an intermediate. The radical $C_{15}H_{15}O$ (loc. cit.), formed during the reaction between (A) and $EtBr$, is considered to be $CPh_2Et \cdot O \cdot$; (A) thus reacts as $CPh_2Na \cdot O \cdot$. The Na can be removed from (A) by CPh_3 ; $COPh_2$ (about 39%) and $NaCPh_3$ are produced. The reactions and electrolytic properties of metal ketyls are consistent with the equilibrium $CR_2Na \cdot O \rightleftharpoons \cdot CR_2 \cdot ONa$. H. B.

Reactions of p-dimethylaminobenzophenone and the Beckmann transformation of p-dimethylaminobenzophenoneoxime. R. C. SHAH and M. B. ICHAPORIA (J. Univ. Bombay, 1934, 3, No. 2, 172—175).— $p-NMe_2 \cdot C_6H_4 \cdot COPh$ (I) is converted by an excess of MeI in boiling $MeOH$ into the methiodide, m.p. 188—190° (decomp.), from which (I) is regenerated at 190°/3 mm. (I) and Br in $CHCl_3$ afford 3-bromo-4-dimethylaminobenzophenone, m.p. 78—80°. 3:3:5'-Trinitro-4-dimethylaminobenzophenone, m.p. 130°, is obtained from (I) and conc. HNO_3 in $AcOH$ at room temp. or from (I) and HNO_3 (conc. or 1:1). p-Dimethylaminobenzophenoneoxime (II), m.p. 154—155°, is transformed by PCl_5 in Et_2O into p-benzamidodimethylaniline, m.p. 226—228°, thus establishing the anti-configuration of (II). H. W.

General method of preparing α -amino-ketones. I. P. W. NEBER and G. HUH (Annalen, 1935, 515, 283—296; cf. A., 1932, 404).—The formation of the ethyleneimine from ketoxime esters is dependent on the attachment of the SO_2Ar residue to O of the αOH group and does not occur when its place is taken by Ac, Bz, or $CHPh \cdot CH \cdot CO$. Reaction appears independent of the configuration of the oxime and is

generally applicable except in the cases of certain ketonic acids or their esters and ether-ketones such as $NO_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CMe \cdot N \cdot OH$.

2:4-Dinitrodeoxybenzoinoxime (I) is transformed by $PhSO_2Cl$ or $p-C_6H_4Me \cdot SO_2Cl$ in C_5H_5N at 0° into the "ethyleneimine" base, $(NO_2)_2C_6H_3 \cdot CH \cdot \begin{smallmatrix} CPh \\ N \end{smallmatrix}$, m.p. 100°, converted by 50% H_2SO_4 - $EtOH$ at room temp. into α -amino- β -keto- β -phenyl- α -2:4-dinitrophenylethane sulphate, decomp. 156°. Acid hydrolysis of the acetate, m.p. 92°, benzoate, m.p. 136°, and cinnamate, m.p. 117°, of (I) leads to 2:4-dinitrodeoxybenzoin. Transformation of (I) by PCl_5 in Et_2O -dioxan affords 2:4-dinitrophenylacetanilide, m.p. 183°. β -o-Nitrobenzyl Me ketoxime and $p-C_6H_4Me \cdot SO_2Cl$ in C_5H_5N at 0° give the corresponding p-toluenesulphonate, m.p. 124°, hydrolysed with accompanying transformation by 20% H_2SO_4 to o- $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NHMe$, m.p. 145°, and converted by $KOEt$ - $EtOH$ at 0° through α -amino- β -keto- α -o-nitrophenylpropane into 3:6-di-o-nitrophenyl-2:5-dimethyl-3:6-dihydro-1:4-diazine, m.p. 186°. Deoxybenzoinoxime affords an unstable p-toluenesulphonate, m.p. 81°, converted by $KOEt$ - $EtOH$ into desylamine. Propiophenoneoxime p-toluenesulphonate, m.p. 65°, cannot readily be obtained in C_5H_5N by reason of the ease with which it suffers the Beckmann transformation by $C_5H_5N \cdot HCl$. It is obtained in 2N-NaOH and converted by $KOEt$ - $EtOH$ at room temp. into ω -aminopropiophenone, whence 3:6-diphenyl-2:5-dimethyl-1:4-diazine, m.p. 125°. Acetophenoneoxime p-toluenesulphonate, m.p. 79° (decomp.), is converted by $EtOH$ at room temp. into NH_3Ph p-toluenesulphonate, decomp. 233°, and by $KOEt$ into $CH_2Bz \cdot NH_2$ (Bz derivative, m.p. 126°). Acetoxime p-toluenesulphonate, m.p. 88° (decomp.), yields aminopropanone. o-Nitrophenylpyruvic acid oxime, m.p. 172°, is transformed by $p-C_6H_4Me \cdot SO_2Cl$ and C_5H_5N at 0° into o- $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CN$, m.p. 87°. The prep. of Et o-nitrophenylpyruvate oxime, m.p. 124°, and its p-toluenesulphonate, m.p. 120°, is described. o-Nitrophenoxycetoxime, m.p. 134° (lit. m.p. 102°), yields a p-toluenesulphonate, m.p. 104°, remarkably stable towards $EtOH$. 2:4-Dinitrophenoxycetone, m.p. 94°, from 2:4-(NO_2) $_2C_6H_3 \cdot OAg$ and CH_2AcI in boiling C_6H_6 , affords an oxime, m.p. 154°, and its p-toluenesulphonate, m.p. 123°. H. W.

Condensation of styryl methyl ketone with nitrobenzaldehydes. W. KRASZEWSKI (Rocz. Chem., 1934, 14, 1354—1357). Styryl Me ketone and o-, m-, and p- $NO_2 \cdot C_6H_4 \cdot CHO$ in $EtOH$ -NaOH afford styryl o- (I), m.p. 104° (tetrabromide, m.p. 170—171°; semicarbazone, m.p. 195°), m-, m.p. 140° (tetrabromide, m.p. 174—175°; phenylhydrazone, m.p. 176°), and p-nitrostyryl ketone, m.p. 176° (dibromide, m.p. 166—167°; tetrabromide, m.p. 195—196°; phenylhydrazone, m.p. 180—181°). In presence of H_2O , styryl β -hydroxy- β -o-nitrophenylethyl ketone, m.p. 74° (benzoate, m.p. 130°; dibromide, m.p. 104°; semicarbazone, m.p. 179—180°), is obtained in place of (I). R. T.

Dioximes. CIV. G. PONZIO and F. BIGLIETTI (Gazzetta, 1934, 64, 861—868).—Action of N_2O_4 on

$\alpha\zeta$ -dioximino- $\alpha\zeta$ -diphenylhexane (I) [new m.p. 227—228° (cf. A., 1913, i, 171); Ac_2 derivative, m.p. 89°] gives, not the expected peroxide with 10-membered ring, but a mixture of $\alpha\alpha\zeta\zeta$ -tetranitro- (II) with $\alpha\zeta$ -dinitro- $\alpha\zeta$ -diphenylhexane (III), m.p. 83°. (II) is obtained in an α -form, blue, becoming white at 120°, m.p. 137—138°, with isomerisation into the β -form, white, m.p. 141—142°, also obtained by action of HNO_3 on (I). (II) is reduced ($SnCl_2$) to (I) and the diketone. $\alpha\kappa$ -Dioximino- $\alpha\kappa$ -diphenyldecane [new m.p. 125—126° (cf. A., 1912, i, 23); Ac_2 derivative, m.p. 92°] yields with N_2O_4 $\alpha\alpha\kappa\kappa$ -tetranitro- $\alpha\kappa$ -diphenyldecane, α -form, blue, becoming white at 100°, and isomerising at m.p. 130° to the β -form, m.p. 137—138°.

E. W. W.

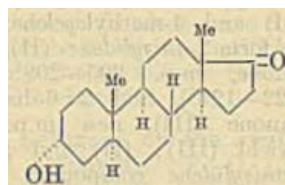
Sexual hormones. III. Elucidation of the constitution of androsterone. L. RUZICKA, M. W. GOLDBERG, and H. WIRZ. IV. Derivatives of synthetic androsterone and one of its isomerides. L. RUZICKA, M. W. GOLDBERG, and J. MEYER (Helv. Chim. Acta, 1935, 18, 61—68, 210—218).—III (cf. A., 1934, 1221). Mainly a reply to criticisms. Examination of a variety of compounds shows that the occurrence of colour and its variations in the Liebermann reaction throw little light on the nature of the C skeleton. Oxidation of cholestane with CrO_3 in $AcOH$ at 85—90° gives α -tioallocholan-17-one, $C_{19}H_{30}O$, m.p. 121—122° (corr.) [semicarbazone, m.p. about 270° (corr., decomp.) after softening], and allocholan acid, m.p. 169—170°.

IV. The only marked difference between the physiological action of synthetic androsterone (I) (A., 1934, 1221) and its acetate (II) lies in the rather longer period required for development of max. action with (II). Dihydrocholesterol benzoate, m.p. 135° to a cryst. liquid phase which becomes transparent at 155°, is oxidised by CrO_3 (=100) in $AcOH$ at 90—95° to 3-hydroxy α -tioallocholanone benzoate, m.p. 210—212° (corr.) [semicarbazone, m.p. 251—253° (decomp.)]. (I) is transformed by $(CH_2CO)_2O$ in C_5H_5N at 80—90° into the *H* succinate, m.p. 184—185° (corr.), and by $BzCl$ in C_5H_5N at 80—90° into the benzoate, m.p. 178—178.5°. Catalytic reduction (PtO_2) of (I) in acid solution ($AcOH-H_2SO_4$) yields a diol (III) $C_{19}H_{32}O_2$, m.p. 223° (corr.) [diacetate (IV), m.p. 162—163°], whereas in neutral or alkaline medium (III) is accompanied by relatively large amounts of the other stereoisomeride (the isolation of a probably non-homogeneous product, m.p. about 205° after softening, is described). Reduction of (II) ($PtO_2-EtOH-H_2SO_4$) affords 3-epiacetoxy α -tioallocholan-17-ol (V), m.p. 183°. (III), (IV), and (V) are about 3 times as active as (I) and (II) physiologically. The oxidation of (I) to 3:17-diketeto α -tioallocholane, m.p. 132°, is described.

H. W.

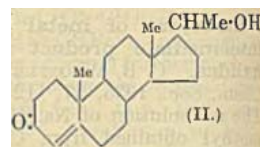
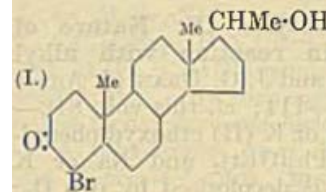
Artificial preparation of male sexual hormone. L. RUZICKA (Naturwiss., 1935, 23, 44—49).— CrO_3 oxidation of dihydro- and epidihydro-cholesterol (I), coprosterol, and epicoprosterol acetates followed by neutralisation, pptn. of the semicarbazones, and hydrolysis yields the hydroxyketones, $C_{19}H_{30}O_2$, that from (I) being identical chemically and biologically with Butenandt's "androsterone" (A.,

1932, 96, 971), which probably has the space formula:



F. O. H.

Δ^4 -Pregnen-20-ol-3-one. Specificity of corpus luteum activity. A. BUTENANDT and J. SCHMIDT (Ber., 1934, 67, [B], 2092—2094).—Pregnanol-3-one



is transformed by $Br-AcOH$ into the substance (I), which loses HBr in boiling C_5H_5N yielding Δ^4 -pregnen-20-ol-3-one (II), m.p. 159°, $[\alpha]_D^{25} +89.7^\circ$ in abs. $EtOH$ [acetate (III), m.p. 138.5°, also obtained by loss of HBr from bromopregnan-20-ol-3-one acetate, m.p. 167.5°]. (II) and (III) appear physiologically inactive.

H. W.

Constitution of astacin. P. KARRER, L. LOEW, and H. HUBNER (Helv. Chim. Acta, 1935, 18, 96—100; cf. A., 1934, 896).—The isolation of α -dimethylsuccinic acid from the products of the oxidation of the diphenazine derivative of astacin (I) shows the latter substance to be 5:6:5':6'-tetraketo- β -carotene. Treatment of the protein-free ligroin extract of lobster shell with I gives a ppt. of the iodide of astacin palmitate, which gives non-cryst. astacin palmitate (astacein), readily hydrolysed by KOH to (I) and palmitic acid.

H. W.

Catalytic hydrogenation of diphenyl triketone. I. L. A. BIGELOW, H. G. RULE, and W. A. P. BLACK (J.C.S., 1935, 83—85).—The course of the catalytic reduction of $COBz_2$ (I) is affected by the proportion and character of the catalyst. With 1 mol. of H_2 - $Pt-PtO_2$ at 15°/2—5 atm. in C_6H_6 , (I) affords dibenzoylcarbinol (II) ($\alpha\gamma$ -diketo- $\alpha\gamma$ -diphenylpropan- α -ol), m.p. 110—111.5° (kept at 106—107°, it undergoes a series of changes to a mixture of isomerides, m.p. 96—98°), further reduced ($2H_2$) to $\alpha\gamma$ -diphenylglycerol (III), m.p. 84.5—85°, $+H_2O$, m.p. 97—99° (Ac_3 derivative, m.p. 84—85°). With less catalyst and $1H_2$ (II) affords (III) and $\alpha\beta$ -dihydroxy- γ -keto- $\alpha\gamma$ -diphenylpropane, m.p. 87—89° (or an isomeride), also obtained by direct reduction of (I), and further reduced to (III).

J. W. B.

Oxidation of 2:7-diacetylfluorene. K. DZIEWOŃSKI, S. KUZDRAŁ, and J. MAYER (Bull. Acad. Polonaise, 1934, A, 348—353).—2:7-Diacetylfluorene (A., 1931, 622) [the formation of an isomeride, m.p. 188—190° (A., 1932, 1251), has not been confirmed] is oxidised by $Na_2Cr_2O_7$ in $AcOH$ at the b.p. to 2:7-diacetylfluorenone, m.p. 252—253°, and 2-acetylfluorenone-7-carboxylic acid, m.p. 307° (decomp.) [*Me* ester, m.p. 225°; diphenylhydrazone, m.p. 265°; amide, m.p. 298° (decomp.)]; sparingly sol.

Na salt]. More prolonged oxidation affords *fluorenone-2:7-dicarboxylic acid*, m.p. 407° (decomp.) (Me_2 ester, m.p. 218°; *phenylhydrazone*, m.p. 332°; *di-amide*, m.p. 337—338°). H. G. M.

Dyeing properties of dicinnamoylmethane derivatives. W. LAMPE and J. TACZANOWSKA (Rocz. Chem., 1934, 14, 1226—1230; cf. A., 1929, 1069).— p - $C_6H_4(CO\cdot CH\cdot CHR)_2$ [$R = \cdot C_6H_5\cdot O_2CH_2$ and $\cdot C_6H_5(OH)\cdot OMe$] are obtained by heating piperonal or vanillin with p - $C_6H_4(CO\cdot CH_2\cdot CO_2Et)_2$ with alcoholic HCl at 100° for 2 hr. The dyeing properties of these substances are compared with those of the dicinnamoylmethane series. Only those substances having a OH group or able to develop one by enolisation are substantive dyes for cotton. R. T.

Quinones from homologues of orcinol and their bromo-substituted products. F. FUZIKAWA (Ber., 1935, 68, [B], 72—76).—Oxidation of divarin Me_2 ether by $Na_2Cr_2O_7$ in AcOH at 100° affords 6-methoxy-2-propyl-*p*-benzoquinone, m.p. 78°. Similarly, *olivetol* Me_2 ether, b.p. 130°/3 mm., gives 6-methoxy-2-*n*-amyl-*p*-benzoquinone, m.p. 63°, and *sphaerophorol* Me_2 ether, b.p. 175—180°/22 mm., yields 6-methoxy-2-*n*-heptyl-*p*-benzoquinone, m.p. 67°. Deoxyhyposalazinol Me_3 ether is converted into 6-methoxy-2:5-dimethyl-*p*-benzoquinone, m.p. 64°, also obtained from β -orcinol Me ether. Me *p*-orsellinate Me_2 ether and Br in AcOH give Me bromo-*p*-orsellinate Me_2 ether, m.p. 80°; the corresponding acid, m.p. 180°, is decarboxylated by Cu chromite in quinoline at 185—190° to 2-bromo-3:5-dimethoxytoluene (I), m.p. 57°. Me dibromo-*p*-orsellinate Me_2 ether, m.p. 84°, yields successively the corresponding acid, m.p. 126°, and 2:6-dibromo-3:5-dimethoxytoluene, m.p. 168°. Oxidation of (I) by $Na_2Cr_2O_7$ in AcOH leads to 3-bromo-6-methoxy-2-methyl-*p*-benzoquinone, m.p. 149°, also obtained by the oxidation of tribromoalectol Me_3 ether. Divarin is methylated (Me_2SO_4 , NaOH) and the crude ether is oxidised to 3-bromo-6-methoxy-2-*n*-propyl-*p*-benzoquinone, m.p. 110°. Similar treatment of *olivetol* leads to 3-bromo-6-methoxy-2-*n*-amyl-*p*-benzoquinone, m.p. 114°. H. W.

Absorption spectra of hydroxynaphthaquinones and of the colouring matter of *Drosera Whittakeri*. A. B. BECK, A. K. MACBETH, and F. L. WINZOR (Austral. J. Exp. Biol., 1934, 12, 203—211).— α - and β -Naphthaquinones differ in absorption spectra only in the absence of free OH. Hydroxydroserone triacetate is of the α -quinone type. P. G. M.

Oxidation of acenaphthene to acenaphthenequinone. A. I. KIPRIANOV and M. M. DASCHEVSKI (J. Appl. Chem. Russ., 1934, 7, 944—949).—The products of oxidation of acenaphthene by $K_2Cr_2O_7$ in AcOH are acenaphthenequinone (I) and naphthalic anhydride (II), sol. in aq. Na_2CO_3 , and an insol. residue (III), consisting of mixed crystals of (I) and (II); the relative yield of (III) increases with duration of oxidation. (I) can be extracted from (III) by prolonged heating with $NaHSO_3$ or Na_2CO_3 dissolved in H_2O or suspended in $PhNO_2$. R. T.

Colouring matters of fungi. XI. Boletol, the colouring matter of the blue-coated *Boletus*.

XII. Synthesis of boletol and isoboletol. F. KÖGL and W. B. DEJES (Annalen, 1934, 515, 10—23, 23—33).—XI. Boletol (I), $C_{15}H_8O_7$, red, chars 275—280° [purified through its Ac_3 derivative (II), m.p. > 300° (becoming red)], is extracted [method essentially that of Bertrand (A., 1902, i, 220; ii, 166)] from *Boletus satanas*, Lenz., *B. luridus*, Schäff., and *B. badius*, Fr. (II), Ac_2O — $NaOAc$, and Zn dust give pentaacetyl-leucoboletol, m.p. 246°, whilst methylation (Et_2O — CH_2N_2) of (I) and subsequent reductive acetylation affords diacetyltrimethyl-leucoboletol (III), m.p. 213°. Distillation of (II) with “electrolytic” Zn dust (prep. described) gives anthracene. (I), which contains a CO_2H group, is decarboxylated (soda-lime) to 1:2:4-trihydroxyanthraquinone and oxidised (30% H_2O_2 , 0.1N-NaOH) to 1:2:3- $C_6H_3(CO_2H)_3$. (I) is, therefore, 1:2:4- or 1:3:4-trihydroxyanthraquinone-8-carboxylic acid. Oxidation [$Pb(OAc)_4$, $AcOH$] of (I) gives 2- or 3-hydroxyanthra-1:4:9:10-diquinone-8-carboxylic acid, m.p. > 300°, which dissolves in conc. Na_2CO_3 to a bright blue solution [(I) similarly gives a red solution], and is spectroscopically identical with the blue pigment in the expressed juice of fresh *Boletus*.

XII. Successive treatment of the product from hemimellitic anhydride (IV), 1:2:4- $C_6H_3(OMe)_3$, and $AlCl_3$ in CS_2 with 20% oleum at 100° (bath), CH_2N_2 , 1% $MeOH$ — $NaOH$ at room temp., and Zn dust+ Ac_2O gives a mixture, m.p. 193—196°, of 9:10-diacetoxy-1:2:4-trimethoxyanthracene-5- and -8-carboxylic acids; one acid (V), m.p. 210—211° (*Me* ester, m.p. 170°), is separated by alternate crystallisation from $AcOH$ and $MeOH$. (V) is identical with (III) (above). Attempted demethylation of (V) causes deep-seated decomp. Quinol, (IV), and $AlCl_3$ — $NaCl$ at 180—190° give 1:4-dihydroxyanthraquinone-5-carboxylic acid, decomp. about 250°. Oxidation of this with $Pb(OAc)_4$ in $AcOH$, treatment of the resulting diquinone (freed from $AcOH$ but not from Pb) with Ac_2O —conc. H_2SO_4 , and subsequent hydrolysis (5% $EtOH$ — KOH) affords a mixture of 1:2:4- and 1:3:4-trihydroxyanthraquinone-8-carboxylic acids [one of which is (I) and the other isoboletol (VI)], separated by adsorption (from $EtOH$ solution) on Al_2O_3 . Reductive acetylation of (VI) gives pentaacetyl-leucoisoboletol, m.p. 235°. Spectroscopic data for (I) (natural and synthetic) and (VI) are given.

Attempted condensation of triacetylnaphthopurpurin and β -vinylacrylic acid (VII) in $EtOH$ at 100° or C_6H_6 results in the polymerisation of (VII). 3-Chlorophthalic anhydride, 1:2:4- $C_6H_3(OMe)_3$, and $AlCl_3$ — $NaCl$ at 200—220° give a mixture, m.p. 185—194°, of 5- and 8-chlorotrimethylpurpurin; Cl could not be replaced by CN (method: G.P. 484,633).

H. B.

Condensation of diketo-compounds with nitromethane. I. Condensation of α -diketones. A. J. JAKUBOVITSCH (J. pr. Chem., 1935, [ii], 142, 37—48).—Phenanthraquinone (I) and $MeNO_2$ (II) in $MeOH$ or $MeOH$ — KOH (varying amounts) give 10-hydroxy-9-keto-10-nitromethyl-9:10-dihydrophenanthrene, m.p. 148—148.5° (sinters at 145—148°) (*K* salt), which when heated above the m.p. decomposes to (I). Benzil and (II) (2 mols.) in $MeOH$ — KOH (2 mols.) at room temp. afford $COPh\cdot CH_2\cdot NO_2$ (III),

PhCHO, MeOBz, CH₂Ph·OH, BzOH, and α , δ -dinitro- β - γ -diphenylbutane, m.p. 238.5—239.5° (decomp.); the following reactions probably occur: Bz₂+MeNO₂→COPh·CPh(OH)·CH₂·NO₂→

COPh·CH₂·NO₂+PhCHO; Bz₂+KOMe→COPh·CPh(OMe)·OK→PhCHO+MeOBz. (III) is hydrolysed slowly by boiling 4% H₂SO₄ to BzOH; with aq. EtOH-HCl, COPh·CCl₂·N·OH (Claisen and Manasse, A., 1893, i, 464) results. Ac₂ heated with an excess of (II) and a little K₂CO₃ gives α -nitro- β -hydroxy- β -methylbutan- γ -one, b.p. 125°/11 mm. [*semicarbazone*, m.p. 214—215° (partial decomp.)]; with an excess of Ac₂, some δ -nitro- γ - ϵ -dihydroxy- γ - ϵ -dimethylheptane- β , ζ -dione, b.p. 127—128°/11 mm., is obtained. H. B.

9 : 10-Dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydrophenanthrene and 2 : 2'-di-*n*-valeryl-diphenyl. T. W. JEZERSKI and M. SPOTOWSKA (Rocz. Chem., 1934, 14, 1243—1248).—Phenanthraquinone and MgBu·I afford 9 : 10-dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydrophenanthrene (I), m.p. 135—135.5°, together with the corresponding 9 : 10-dibutylene-derivative, b.p. 239—240.5°/7 mm. (I) is converted by boiling with CrO₃ in AcOH into 2 : 2'-di-*n*-valeryl-diphenyl, b.p. 197.5—199.5°/6 mm. R. T.

Oxidative degradation of violanthrone and 2 : 2'-dibenzanthronyl to 2 : 2'-dianthraquinonyl-1 : 1'-dicarboxylic acid. Synthesis of this acid from 2-bromo-1-cyanoanthraquinone and its conversion into 1 : 2 : 7 : 8-diphthaloylphenanthridone. R. SCHOLL, E. J. MULLER, and O. BOTTGER (Ber., 1935, 68, [B], 45—49).—2-Bromo-1-cyanoanthraquinone is transformed by Cu powder in boiling PhNO₂ into 1 : 1'-dicyano-2 : 2'-dianthraquinonyl, which darkens without melting at 500° and is hydrolysed by H₂SO₄ to 2 : 2'-dianthraquinonyl-1 : 1'-dicarboxylic acid (I) (corresponding chloride), converted by BzCl in boiling PhNO₂ into 2 : 2'-dianthraquinonyl-1 : 1'-dicarboxylic anhydride (II), decomp. about 375—380°. Oxidation of violanthrone in dil. H₂SO₄ by CrO₃ affords (I), also obtained from 2 : 2'-dibenzanthronyl. Successive treatment of (II) in conc. NH₃ with Na₂S₂O₄ and air leads to the semiamide of (I) [NH₄ and Na salts], converted by Br-NaOH into 1'-amino-2 : 2'-dianthraquinonyl-1-carboxylic acid (Na salt), which in boiling AcOH passes into 1 : 2 : 7 : 8-diphthaloylphenanthridone, m.p. about 480° (decomp.) after darkening at 400° and softening at about 450°. H. W.

Saponins. I. Cyclamin and cyclamiretin. II. Spinatsaponin and [spinat]sopogenin. O. DAFERT [with F. BAUER, M. BAUER, V. CAFESIUS, and S. GREIFINGER] (Sci. Pharm., 1934, 5, 49—56, 61—65; Chem. Zentr., 1934, ii, 1785—1786).—I. The formulae C₆₃H₁₁₀O₃₂ for cyclamin (I) and C₃₅H₅₆O₅ for cyclamiretin (II) previously advanced (A., 1926, 1146) must be replaced by C₅₆H₉₆O₂₉ and C₂₈H₄₆O₄, respectively. The isolation of (I) from cyclamen tubers is described, the content being highest in autumn. (I) is not stable to heating in aq. solution, the hæmolytic index falling rapidly. An ash-free sample of (I) has m.p. 250°, hæmolytic index 1 : 650,000; other biological characteristics

are described. (II) has m.p. 204° (*diacetate*, m.p. 207°; *monobenzoate*, m.p. 209°; *semicarbazone*, m.p. 277°). Reduction of (I) (Na-EtOH) yields *tetrahydrocyclamiretin* (?), C₂₈H₅₀O₄, m.p. 215° (*triacetate*, m.p. 135°). (II) with NaOEt affords a *compound*, C₃₀H₅₂O₅, m.p. 280°; with Br-EtOH, a *compound*, C₂₈H₄₅O₄Br, m.p. 220—223°; and with Br-CCl₄, an impure *compound*, C₂₈H₄₂O₄Br₆ (?).

II. *Spinatsaponin*, C₅₉H₉₀O₂₇, is isolated from spinach roots; it has a hæmolytic index of 1 : 40,000 and many other biological characteristics are recorded. Acid hydrolysis yields *spinatsapogenin* (III), C₃₂H₅₀O₅, m.p. 300°, which gives the Liebermann cholesterol reaction, is acidic (equiv. $\frac{1}{2}$ mol. wt.), and appears to contain 2 OH; no CO or double linking could be detected. The following derivatives of (III) are described: *monoacetate*, m.p. 256°; *Et ester* (?), m.p. 295°; and a *compound*, C₃₀H₄₈O₄, m.p. 219°, formed during esterification. The partial formula C₃₀H₄₈·(CO₂H)(OH)·OAc is advanced for (III). H. N. R.

Crystalline principles from Indian species of *Artemisia*.—See this vol., 268.

Preparation of ketonic terpenes. R. DULOV (Bull. Inst. Pin, 1934, 173—177).—Prep. of the following is described: pinocamphone, b.p. 95°/22 mm. (*semicarbazone*, m.p. 227—228°), from hyssop essence; nopinone and Na nopinate from nopinene and KMnO₄; fenchone from fenchyl alcohol; pulegone, b.p. 105°/18 mm., from peppermint essence; tetrahydrocarvone, dihydrocarveol (and thence dihydrocarvone), and carvotanacetone from carvone.

R. S. C.

Action of hydrogen sulphide on ketonic terpenes. R. DULOV (Bull. Inst. Pin, 1934, 205—209).—The H₂S compound, m.p. 210—211°, of carvone is unaffected by semicarbazide and shows 1.8 OH by MgEtBr. Harries' formula is, therefore, considered correct. Piperitone and verbenone give oily H₂S compounds. 3-Methyl-5-isopropenyl- Δ^2 -cyclohexenone gives crystals, stable at -10°, but decomp. at 0°. Benzylidene- and hydroxymethylencamphor do not react with H₂S. Reaction is considered to be due to hydration of the CO group.

R. S. C.

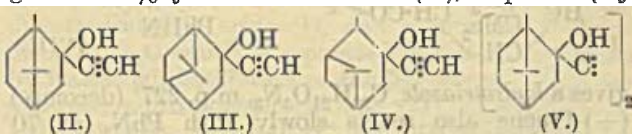
Configuration of derivatives of camphane, isocamphane, etc. J. BOESEKEN (Rec. trav. chim., 1935, 54, 101—106).—The spatial proximity of C1, C2, and C6 in Bredt's formula for camphor (I) accounts (for details see original) for the optical stability of (I), the properties of the OH of borneol and isoborneol, the transformation of camphene (II) into bornyl and isobornyl acetate, of bornyl chloride (III) into (II) and tricyclene, and of 2 : 2-dichlorocamphane (IV), the oxidation of camphorhydrazone by HgO, and the instability of diazocamphane. The bornyl radical [formed by ionisation of (III)] after rupture of the C1—C6 linking and formation of the C2—C6 linking is said to be in the "proto(iso)camphanic" state. Transformation of *d*-(I) by way of (IV) into derivatives of *l*-(I) is due to re-formation of the skeleton by a different path, and not to a true inversion of the mol. Transformations in the fenchene series are similarly explained. R. S. C.

Functional exchange between Grignard compounds and α -bromocamphor. H. WUYTS (Compt. rend., 1934, 199, 1317—1319; cf. A., 1934, 640).—Excess of MgMeI with bromocamphor (I) gives an approx. equimol. mixture of CH_4 and C_2H_6 , camphor (II), and some camphorpinacol. Similarly, with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$, (I) gives PhMe and $(\cdot\text{CH}_2\text{Ph})_2$. (I) with the Mg derivatives of PhBr and $1\text{-C}_{10}\text{H}_7\text{Br}$ gives mainly (II), and with MgPhI or MgPhCl , a considerable amount of PhBr , which indicates that MgI is exchanged for Br . J. L. D.

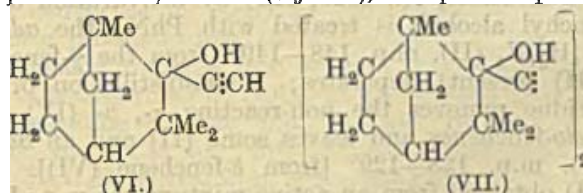
Rupture of the four-carbon ring of pinene glycol. K. SŁAWINSKI and W. ZACHAREWICZ (Rocz. Chem., 1934, 14, 1320—1329).— HBr and pinene glycol in AcOH yield a mixture of products, of which the following have been isolated: a saturated glycol, $\text{C}_{10}\text{H}_{18}\text{O}_2$, m.p. 193—194°; an unsaturated glycol, $\text{OH}\cdot\text{CMe}\langle\text{CH}(\text{OH})\cdot\text{CH}_2\text{CH}_2\rangle\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, m.p. 179—180° (diacetate, b.p. 147—148°/4 mm.); an unsaturated alcohol, $\text{CMe}\langle\text{H}(\text{OH})\cdot\text{CH}_2\text{CH}_2\rangle\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$, b.p. 68—69°/1 mm., 217°/747 mm.; disobrerol; dipinol. R. T.

Stereoisomerism in the pinocampheol and menthol series. H. SCHMIDT and L. SCHULZ (Ber. Schimmel, 1934, 97—100; Chem. Zentr., 1934, ii, 2077; cf. A., 1930, 217, 921).—There are 8 possible optically active pinocampheols. Hydrogenation of *l*-pinocarveol yields a *l*-pinocampheol (I), m.p. 57°; oxidation affords a *d*-pinocampheol, reduced ($\text{Na}\cdot\text{EtOH}$) to a *d*-pinocampheol (II), m.p. 67° [the optical antipode of that described by Gildemeister and Kohler (A., 1910, i, 180)]. (I) and (II) are *cis* and *trans*, respectively, with regard to the Me and the cyclobutane ring. *cis*-*d*-Pinocampheol is obtained by hydrogenation of *d*-pinocarveol (from autoxidised β -pinene). (I) and (II) can be interconverted by heating with alkali metals. Oxidation yields the corresponding pinocampheones. The following are described: *cis*-*l*-pinocampheol (I), m.p. 57°, b.p. 219°, $[\alpha]_D -36^\circ$ (naphthylurethane, m.p. 88°; phthalate, m.p. 126°); *cis*-*d*-pinocampheol, m.p. 57°, b.p. 219°, $[\alpha]_D +37^\circ$ (phthalate, m.p. 126°); *cis*-*dl*-pinocampheol, m.p. 42°, b.p. 219°; *trans*-*l*-pinocampheol, m.p. 67°, b.p. 217°, $[\alpha]_D -55^\circ$ (phenylurethane, m.p. 77°; naphthylurethane, m.p. 91°; phthalate, m.p. 107°); *trans*-*d*-pinocampheol (II), m.p. 67°, b.p. 217°, $[\alpha]_D +55^\circ$ (phenylurethane, m.p. 77°); *trans*-*dl*-pinocampheol, m.p. 36°, b.p. 217° (phenylurethane, m.p. 99°; phthalate, m.p. 113°); *cis*-*l*-pinocampheone, b.p. 212°, $[\alpha]_D -17^\circ$; *cis*-*d*-pinocampheone, m.p. about -35°; b.p. 212°, $[\alpha]_D +17.9^\circ$ (semicarbazone, m.p. 219°); *cis*-*dl*-pinocampheone (oxime, m.p. 88°); *trans*-*l*-pinocampheone, m.p. about -20°; b.p. 211°, $[\alpha]_D -22.8^\circ$ (semicarbazone, m.p. 211°, $[\alpha]_D +22.5^\circ$; *trans*-*dl* inocampheone (oxime, m.p. 89°). *d*-Neoisomenthol, b.p. 214—215°, $\alpha_D -0^\circ$ 20' (naphthylurethane, m.p. 105—106°; phthalate, m.p. -86°; acetate, b.p. 228°, $\alpha_D -19^\circ$ 20'), is obtained catalytic hydrogenation of *d*-isomenthone (III), or (with some inversion) by means of $\text{Al}(\text{OEt})_3$, oxidation with CrO_3 yields (III). H. N. R.

Action of acetylene and its dimagnesium derivatives on ketonic terpenes. R. DULOV (Bull. Inst. Pin, 1934, 164—165, 178—182, 197—204).— C_2H_2 with the Na derivative of camphor (I) gives a 20% yield of the alcohol (II), m.p. 85° (Ag



salt). Nopinene gives similarly the alcohol (III), b.p. 109—112°/20 mm. (Ag salt), and pinocampheone



the alcohol (IV), b.p. 122°/20 mm. (Ag salt). These alcohols show an exaltation of R_f of 0.3—0.6. (I) and $(\text{MgBr}\cdot\text{C})_2$ give slowly the glycol (V), m.p. 203°, the yield being poor partly owing to enolisation; fenchone gives first the alcohol (VI), m.p. 16—18°, and when heated the glycol (VII), m.p. 106° (a second form was obtained impure); camphenilone (VIII) affords the glycol (IX), α -, m.p. 127—128°, and β -form, m.p. 113—114°, giving only (VIII) with KMnO_4 . R. S. C.

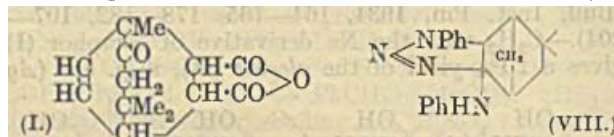
Application of the Friedel-Crafts method to the preparation of bornyltoluene. L. KAMIENSKI and P. LEWISÓWNA (Rocz. Chem., 1934, 14, 1348—1353).—Bornyl chloride, PhMe , and AlCl_3 are kept at 10°/15 mm. for 4 hr., and then at 40°/15 mm. for 3 hr., when *m*- and *p*-, b.p. 163—164°/11 mm., -bornyltoluene are obtained in good yield. The products of nitration of the mixture, and of the reduction of the NO_2 -products, are described.

R. T.

***dl*-Fenchyl alcohol.** G. KOMPPA and S. BECKMANN (Ber., 1935, 68, [B], 10—11).—The alcohol obtained by Zeitschel *et al.* (A., 1932, 619) from American pine oil is identified as *dl*-fenchol (I). The *p*-nitrobenzoate and naphthylurethane of (I) have m.p. 94—95° and 148.5—149.5°, respectively. The non-cryst. cinnamate, b.p. 204°/8 mm. of (I) does not add Br . H. W.

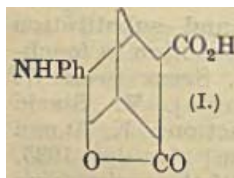
Steric course of addition and substitution reactions. IV. Phenyl azide reaction in fenchene series. K. ALDER and G. STEIN [with W. FRIEDRICHSEN and K. A. HORNUNG]. V. Steric course of the phenyl azide reaction. K. ALDER and G. STEIN [with S. SCHNEIDER] (Annalen, 1935, 515, 165—184, 185—200).—IV. Of the various ring systems now and previously (A., 1931, 489; 1933, 384) investigated, only 1:2:2-dicycloheptene adds PhN_3 readily; 2:2:3-dicyclononenes react slowly at 100°. Thus, 3:6-endopropylene- Δ^4 -tetrahydrophthalic anhydride gives an adduct, $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3$, decomp. 219°. Similarly, the adduct (I), m.p. 165—

166° (from eucaryone and maleic anhydride at 150°), with PhN_3 in EtOAc at 100° (sealed tube) for 6 days



gives a *hydrotriazole*, $\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}_3$, m.p. 227° (decomp.). (+)-Pinene also reacts slowly with PhN_3 at 70° (8 days) to give an *adduct*, $\text{C}_{16}\text{H}_{21}\text{N}_3$, m.p. 77°. When the mixture of fenchenes obtained (cf. Komppa and Roschier, A., 1929, 821) by dehydration of *dl*-fenchyl alcohol, is treated with PhN_3 , the *adduct*, $\text{C}_{16}\text{H}_{21}\text{N}_3$ (II), m.p. 148—149° [from the γ -fenchene (III) present], separates; steam-distillation of the residue removes the non-reacting α -, β - (IV), and *cyclo*-fenchenes and leaves some (II) and an *adduct* (V), m.p. 128—129° [from δ -fenchene (VI)]. The (II) obtained from an active mixture has m.p. 177°; this is also formed when a mixture of active (III) + (IV) [prepared from methyl- β -fenchocamphorol by Komppa and Roschier's method (A., 1918, i, 445)] is treated with PhN_3 [the presence of unaltered (IV) is shown by oxidation]. (V) and an *isomeride* (VII), m.p. 122°, are obtained from PhN_3 and (VI) [prepared from *dl*-isofenchyl alcohol by Nametkin's method (A., 1924, i, 754)]; (V) and (VII) differ in the arrangement of the triazole ring, since thermal decomp. gives the same phenylimine. The results with (VI) differ from those of Komppa and Beckmann (A., 1933, 830). *iso*Fenchoneanil and PhN_3 at 100° for 3 weeks afford the *anilino*triazole (VIII), m.p. 232—233°, converted by $\text{H}_2\text{C}_2\text{O}_4$ in EtOAc into a compound, $\text{C}_{16}\text{H}_{19}\text{ON}$, m.p. 134°. β -Fenchocamphoroneanil similarly gives an *anilino*triazole, m.p. 230° convertible ($\text{H}_2\text{C}_2\text{O}_4$) into 2-*anilino*-5:5-dimethyl-3:6-endomethylenecyclohexanone, m.p. 125—126°. Fenchoneanil (which cannot rearrange to the enamine form) and α -fenchocamphoroneanil (which contains the *endo*- CMe_2 group) do not react with PhN_3 .

V. Addition of PhN_3 to *endo*-*cis*-, *trans*-, and *exo*-*cis*-3:6-endomethylene- Δ^4 -tetrahydrophthalic acid (using ester or anhydride) (details in A., 1933, 384, 942) occurs in the same manner and is independent of the configuration of the CO_2H groups. This is established as follows. Me *trans*-4:5-phenylimino-3:6-endomethylenehexahydrophthalate (obtained by thermal decomp. of the original adduct) is hydrolysed (acid) to the Me ester, m.p. 122—123°, of the *anilino*-lactonic acid (I), m.p. 210°; (I) is also obtained by the

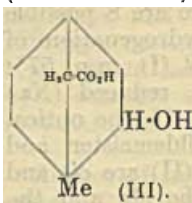


action of EtOH - NaOEt on the *endo*-*cis*- and *exo*-*cis*-phenylimino-esters (rearrangement occurs in both cases). Addition of PhN_3 to dicycloheptene derivatives containing the *endo*- CMe_2 group is probably inhibited owing to interference (with *exo*-addition) by one of the Me. The different behaviour (this vol., 211) of dimeric Me cyclopentadiene-1-carboxylate and Me cyclopentadiene-1-carboxylate-maleic anhydride (which does not add PhN_3) is probably due to the different configuration of the *endo*- $\text{C-CO}_2\text{Me}$ in the two adducts. A small amount of an adduct has been ob-

tained from bornylene and PhN_3 after 5 years at room temp. The heat of activation for the non-retarded (and retarded) reaction is small. H. B.

Identity of darwinol with α -myrtenol. A. R. PENFOLD, G. R. RAMAGE, and J. L. SIMONSEN (J. Proc. Roy. Soc. New South Wales, 1934, 68, 36—38).—“Darwinol” (A., 1924, i, 1328) is identical with α -myrtenol (phenylurethane, m.p. 58—59°; α -naphthylurethane, m.p. 92—93°). It is oxidised (CrO_3) to α -myrtenal [semicarbazone, m.p. 220—221°; phenylsemicarbazone, m.p. 180° (decomp.)]. F. N. W.

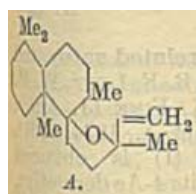
Teresantalic acid and isoteresantalic acid. Y. ASAHINA, M. ISHIDATE, and T. MOMOSE (Ber., 1935, 68, [B], 83—91).—*iso*Ketopinic acid (I) is transformed by successive treatment with HCO_2NH_4 at 220—230° and KOH - EtOH into *trans*- π -2-amino-apocamphane-7-carboxylic acid hydrochloride (II), decomp. about 318° (formyl derivative, m.p. 244°). Treatment of (II) with amyl nitrite in AcOH at 50—60° yields an acid, $\text{C}_{10}\text{H}_{14}\text{O}_2$, b.p. 160°/24 mm., m.p. 144°, which is stable towards KMnO_4 in COMe_2 , but decolorises it slowly in H_2O . *iso*Ketopinohydroazone, decomp. > 350° (from the acid and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 100°), is oxidised by HgO to teresantalic acid, m.p. 158°, $[\alpha]_D^{25} -74.2^\circ$ in C_6H_6 , oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 to santenone, m.p. 46—47°, $\alpha_D \pm 0^\circ$ in EtOH (semicarbazone, m.p. 224°). (I) is converted by Na and EtOH into *trans*- π -apoborneol-7-carboxylic acid (III), m.p. 273°, $[\alpha]_D^{25} +4.2^\circ$ in abs. EtOH [Me ester (IV), b.p. 140—141°/14 mm., m.p. 54°, $[\alpha]_D^{25} +3.6^\circ$ in EtOH]. (IV) and PBr_5 in light petroleum afford Me 2-bromo-*trans*- π -apocamphane-7-carboxylate, a non-distillable oil, which



passes when heated with NH_2Ph into Me apocamphenecarboxylate, b.p. 86—87°/8 mm., hydrolysed to apocamphenecarboxylic acid (V), m.p. 142°, $[\alpha]_D^{25} -70.8^\circ$ in C_6H_6 , which does not depress the m.p. of isoteresantalic acid. Oxidation of (V) with KMnO_4 yields small amounts of an acid not identical with teresantalic acid, whereas $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 convert it into santenone. (V) with AcOH -50% H_2SO_4 at 50—60° gives the lactone (VI), $\text{C}_{10}\text{H}_{14}\text{O}_2$, m.p. 191—192°, of Semmler and Bartelt, oxidised by KMnO_4 in alkaline solution to *l*-*cis*- π -apocamphor-7-carboxylic acid, m.p. 269—270°, $[\alpha]_D^{25} -60.2^\circ$ in EtOH (semicarbazone, m.p. 205°), and *trans*- π -apoisoacetylborneol-7-carboxylic acid, m.p. 122°, whence *trans*- π -apoiso-borneol-7-carboxylic acid (VII), m.p. 288°, $[\alpha]_D^{25} -47.3^\circ$ in abs. EtOH . Oxidation of (VII) with $\text{Na}_2\text{Cr}_2\text{O}_7$ and AcOH gives an acid, m.p. 250°, which does not depress the m.p. of (I) and is transformed through its semicarbazone into π -apocamphane-7-carboxylic acid, m.p. 230°, $[\alpha]_D^{25} -19.0^\circ$ in abs. EtOH . Saturation of Me teresantalic acid, b.p. 92—94°/18 mm. (from the synthetic acid and CH_2N_2), with HBr gives Me hydrobromoteresantate, which is converted by NH_2Ph at 200° followed by hydrolysis into an acid very closely similar to isoteresantalic acid in m.p., solubility, and $[\alpha]_D^{25}$; since teresantalic acid in small amount is obtained when its aqueous solution is oxidised with KMnO_4 , the product is not homogeneous (cf. Rupe *et al.*, A., 1917, i, 138). Hydration of it

affords (VI), m.p. 190—191°, and (VII), m.p. 288° [α]_D²⁵ —47.5° in abs. EtOH. H. W.

Diterpene oxides of the resin of *Dacrydium Colensoi*. II. Manoyl oxide. J. R. HOSKING and C. W. BRANDT (Ber., 1935, 68, [B], 37—45; cf. A., 1934, 897).—Dehydrogenation of manoyl oxide (I) by Se at 240—340° affords 1 : 2 : 5- (1 : 5 : 6-) C₁₀H₅Me₃ (II) (picrate, m.p. 138—139°; styphnate, m.p. 139°) and 1 : 2 : 8- (1 : 7 : 8-) trimethylphenanthrene (III), m.p. 144° [picrate, m.p. (indef.), 160°; corresponding quinone, m.p. 194—195°, and its quinoxaline derivative, m.p. 131—132°]. (I) is converted by 98% HCO₂H at 120—125° into isomanoene, b.p. 139—140°/0.2 mm., hydrogenated (PtO₂) in AcOH at 40° to dihydroisomanoene, which gives an intense colour with C(NO₂)₄, does not further absorb H₂, and is dehydrogenated by Se to (II) and (III). Dihydromanoyl oxide (IV) and 98% HCO₂H afford β -dihydromanoene, C₂₀H₃₄, b.p. 123—124°/0.2 mm., which absorbs 1H₂ (PtO₂ in EtOAc) yielding a substance, b.p. 145°/0.1 mm. (I) in Et₂O at 0° is transformed by HCl into manoene trihydrochloride, m.p. 118—120°, which does not give a Cl-free product when heated with NH₂Ph at 100° and then distilled repeatedly over Na or boiled with KOH-MeOH. Similar treatment of (IV) results in dihydromanoene dihydrochloride, m.p. 120—122°, converted by NH₂Ph into α -dihydromanoene (V), C₂₀H₃₄, b.p. 149—150°/0.3 mm., which absorbs 2H₂ (PtO₂-AcOH). Agitation of (V) with boiling 99% HCO₂H leads to tricyclic dihydroisomanoene, b.p. 124°/0.2 mm. Dihydromanoene dihydrobromide, m.p. 97°, is converted by repeated treatment with Ag₂O or with boiling H₂O into (V). Ozonisation of (I) in CCl₄ and decomp. of the ozonide by boiling H₂O yields CH₂O in considerable amount. Oxidation of (I) with KMnO₄



in COMe, at $\geq 12^\circ$ gives a monocarboxylic acid, C₁₉H₃₂O₃, m.p. 74—75°, converted by HCl in anhyd. Et₂O into the dihydrochloride C₁₉H₃₂O₂Cl₂, m.p. 133—134°. Treatment of sclareol (VI) and its H₂-derivative with HCl affords compounds identical with

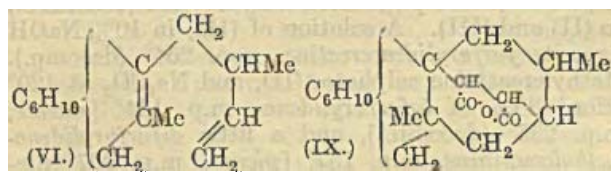
those described above. The C skeleton of (I) is therefore identical with that of (VI) (cf. Ruzicka *et al.*, A., 1931, 737) and of agathidicarboxylic acid (A., 1931, 31). (I) is probably A. H. W.

Biogenesis of some terpenes. J. WALKER (Chem. and Ind., 1935, 55—56).—An intramol. polymerisation of the type involved in the conversion of linalool into α -terpineol would explain the formation of α - and β -eudesmol from nerolidol, and of α -pinene from limonene (I). The bioconversion of (I) into carvone (II) possibly then occurs by direct oxidation of the CH₂ in position 6 to CO, thus giving a (II) of the same rotational sign as (I), as actually occurs in nature, whereas in the conversion of (I) into (II) through the nitrosochloride the CO is formed in position 2 giving a (II) of opposite sign. J. W. B.

Polyterpenes and polyterpenoids. XCII. Caryophyllenic acid and norcaryophyllenic acid. Additive product of maleic anhydride and caryophyllene. L. RUZICKA and W. ZIMMERMANN

R B

(Helv. Chim. Acta, 1935, 18, 219—230; cf. A., 1934, 1215).—The acidic products of the fission of caryophyllene ozonide (cf. A., 1931, 735) are oxidised with HNO₃, thereby giving H₂C₂O₄ (·CH₂·CO₂H)₂, as-dimethylsuccinic acids (I), and a mixture of acids insol. in H₂O which is separated into its components by fractional distillation of the Me esters. Thus are obtained norcaryophyllenic acid (II), C₈H₁₂O₄, m.p. 123.5—124.5°, [α]_D²⁵ +118° in CHCl₃, and caryophyllenic acid (III), m.p. 81—82°, [α]_D²⁵ +28.2° in C₆H₆. (II) gives a Me₂ ester (III), b.p. 107°/12 mm.; it is converted by Ac₂O at 220° (AcCl gives non-uniform products) into the anhydride, m.p. 38—39°, transformed by H₂O into an acid, m.p. 149—150°. (II) is transformed by SOCl₂ at room temp. into the corresponding chloride, b.p. 99—100°/12 mm., converted by Br at 100° into dibromonorcaryophyllenic acid (V), C₈H₁₀O₄Br₂, m.p. 202°; the residues from the prep. of (V) give dehydronorcaryophyllenic acid, C₈H₁₀O₄, m.p. 194° [which absorbs Br and is oxidised to (I) by CrO₃ in AcOH], when boiled with aq. NaOH. (IV) and MgPhBr afford the corresponding Ph₄ glycol, C₃₂H₃₂O₂, m.p. about 194°, oxidised to COPh₂ and (I). (III) yields a Me₂ ester, b.p. 119—119.5°/12 mm., [α]_D²⁵ +47.9°. Caryophyllenyl chloride, b.p. 86—88°/0.2 mm., from (III) and SOCl₂ at room temp., and Br at 100° yield dibromocaryophyllenic acid, C₈H₁₂O₄Br₂, m.p. 198°, transformed by treatment with KOH and subsequent oxidation into (I) in small amount; with less halogen bromocaryophyllenic acid, m.p. 167°, results, converted by the successive action of aq. Ba(OH)₂ and CH₂N₂ into non-homogeneous Me₂ hydroxycaryophyllenate. Caryophyllene (VI) is converted by maleic anhydride (VII) in boiling C₆H₆ to the extent of > 70% into an adduct of which an amount equiv. to 50% of the hydrocarbon is cryst. and the remainder amorphous. 30% of (VI) does not react after repeated treatment with (VII). The adduct (VIII), C₁₉H₂₆O₃, m.p. 98°, is hydrolysed to a dicarboxylic acid (IX), C₁₉H₂₆O₄, m.p. 208° [Me₂ (X), m.p. 156°, and Et₂ (XI), m.p. 113°, esters]. The mol. refractions of (X) and (XI) indicate the absence of a double linking, and the indifference of (VIII) and (IX) towards O₃, BzO₂H, and alkaline KMnO₄ establishes complete saturation, thus leading to the following structures for (VI) and (IX)



H. W.

Synthesis and reactions of $\alpha\delta$ -hydroxyketones. Derivatives of α -hydroxyhexan- β -one and 2 : 5-dimethyl-4 : 5-dihydrofuran. G. POJARLIEFF (J. Amer. Chem. Soc., 1934, 56, 2685—2687).— δ -Chloro- α -acetyl- γ -valerolactone (Traube and Lehmann, A., 1901, i, 501) and MeOH-HCl (0.5%) at room temp. give (after removal of HCl with Ag₂CO₃) Me 2-methoxy-2-methyl-5-chloromethyltetrahydrofuran-3-carboxylate (I), b.p. 97°/1 mm., which when heated with HCl at 120—130° and then distilled affords Me 2-methyl-5-chloromethyl-4 : 5-dihydrofuran-3-carboxyl-

ate (II), b.p. 127°/14 mm. [free acid (III), m.p. 110° (corr.)]. (II) heated with MeOH gives (I). (III) and boiling 0.2*N*-H₂SO₄ afford impure α -chloro- β -hydroxyhexan- ϵ -one, b.p. 95°/3 mm. {acetate, b.p. 117°/5 mm. [semicarbazone, m.p. 131° (corr.)]}, converted by MeOH-HCl into 2-methoxy-2-methyl-5-chloromethyltetrahydrofuran, b.p. 73.5°/13 mm. (II) and α -C₆H₃(OH)₃ in boiling 0.2*N*-HCl give a compound, C₁₃H₁₃O₅Cl, m.p. 250° (corr.), which is either a coumarin or a chromone. δ -Methoxy- α -acetyl- γ -valerolactone, b.p. 134°/4 mm. [from γ -methoxy- α - β -oxidopropane (modified prep.; cf. Blanchard, A., 1927, 853) and CH₂Ac·CO₂Et in EtOH-NaOEt], is converted (as above) into *Me* 2-methoxy-5-methoxy-methyl-4 : 5-dihydrofuran-3-carboxylate, b.p. 126°/15 mm. [free acid (IV), m.p. 82°]. β -Hydroxy- α -methoxyhexan- ϵ -one (V) [from (IV) and dil. H₂SO₄] loses H₂O when heated at atm. pressure and passes into 2-methyl-5-methoxymethyl-4 : 5-dihydrofuran, b.p. 47—48°/11 mm. Oxidation (K₂Cr₂O₇, dil. H₂SO₄) of (V), prepared by Levene and Walti's method (A., 1931, 68), gives α -methoxyhexane- β - ϵ -dione (VI), b.p. 68—70°/0.6 mm. [*di*-*p*-nitrophenylhydrazones, m.p. 175° (corr.)], and lactic acid. (VI) is obtained similarly from 2-methoxy-2-methyl-5-methoxymethyl-tetrahydrofuran, b.p. 72°/14 mm. [from (V) and MeOH-HCl]. α - β -Dihydroxyhexan- ϵ -one and MeOH-HCl afford (mainly) 5-methoxy-5-methyltetrahydrofurfuryl alcohol (cf. Levene and Walti, *loc. cit.*).

H. B.

New synthesis of hydrocarbons of C_nH_{2n+2} series. N. A. ORLOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 286—288).—Hydrogenation (MoS₃) of furfuraldehyde at 220—320°/150 atm. gives *n*-C₅H₁₂ and traces of 2-methylfuran and *n*-C₅H₁₁·OH. Furfurylideneacetaldehyde (?) similarly gives *n*-C₇H₁₆, whilst furethylcarbinol with MoS₃-NiO catalyst at 300—315°/100 atm. gives (1) in larger yield.

F. N. W.

Creatinine derivatives. I. W. R. CORNTHWAITE and E. JORDAN (J. Amer. Chem. Soc., 1934, 56, 2733—2734).—Creatinine (I) and furfuraldehyde (II) (excess) at 140° give 63% of 5-furfurylidene-creatinine (III), m.p. 273° (decomp.) [hydrochloride, m.p. 257° (decomp.)]; picrate, m.p. 244° (decomp.)], and some difurfurylidene-creatinine, m.p. 243° [picrate, m.p. 205° (decomp.)], which is hydrolysed (conc. HCl) to (II) and (III). A solution of (III) in 10% NaOH deposits furfurylidene-creatinine, m.p. 254° (decomp.). Methylcreatinine sulphate, (II), and Na₂CO₃ at 120° afford 30% of 5-furfurylidene-, m.p. 134° [picrate, m.p. 235° (decomp.)], and a little difurfurylidene-methylcreatinine, m.p. 137° [picrate, m.p. 207° (decomp.)]. Furfurylideneacetaldehyde (slight excess) and (I) at 140° give 41% of di(furfurylideneacrylidene)-creatinine, m.p. 268° (picrate, decomp. about 200°). 5-Salicylidene- (83%), m.p. 232° (decomp.) [picrate, m.p. 269° (decomp.)], and 5-cinnamylidene- (17%), m.p. 280° (decomp.) [picrate, m.p. 261° (decomp.)], and dicinnamylidene-creatinine (19%), m.p. 220° (decomp.) [picrate, m.p. 193° (decomp.)], are similarly prepared.

H. B.

Di-*p*-bromophenylfurans and α -diketones. R. E. LUTZ and W. M. EISNER (J. Amer. Chem. Soc.,

1934, 56, 2698—2701).—2 : 5-Di-*p*-bromophenylfuran (I) and HNO₃-AcOH at 70° give *trans*- α - β -di-*p*-bromobenzoyl-ethylene (II), converted by exposure to sunlight (in C₆H₆) into the *cis*-form (III), m.p. 124.5—125° (corr.); (III) is converted into (II) by HNO₃-AcOH at 70° or by exposure of a solution in CHCl₃+I to sunlight. α - β -Di-*p*-bromobenzoyl-ethane (IV) [which with Ac₂O-conc. H₂SO₄ gives (I)], (I), and (CHBz)₂, with PBr₅ afford 3 : 4-dibromo-2 : 5-di-*p*-bromophenylfuran (V); (II) similarly gives *meso*- α - β -dibromo- α - β -di-*p*-bromobenzoyl-ethane, which is unaffected by Ac₂O-conc. H₂SO₄. *cis*- α - β -Dibromo- α - β -di-*p*-bromobenzoyl-ethylene (VI), m.p. 112.5° [from (V) and HNO₃-AcOH at 70°], is converted (solution in CHCl₃+I in sunlight) into the *trans*-form (VII), m.p. 235.5°, also prepared from dibromofumaryl chloride, PhBr, and AlCl₃ in CS₂; (VI) and (VII) are both reduced (Zn dust, AcOH) to (IV). *dl*- α - β -Dichloro- α - β -di-*p*-bromobenzoyl-ethane and Ac₂O-conc. H₂SO₄ give 3 : 4-dichloro-2 : 5-di-*p*-bromophenylfuran, m.p. 166° [also prepared from the following compounds and PCl₅ at 100—150° : (I), (II), (IV), *p*-C₆H₄Br·CO·CH·C(OR)·CO·C₆H₄Br-*p* (R=H and Me), 3-methoxy- and 3-chloro-2 : 5-di-*p*-bromophenylfuran, m.p. 120° (from α - β -di-*p*-bromobenzoyl-ethylene and AlCl₃-conc. H₂SO₄)], which with HNO₃-AcOH at 70° affords *cis*- α - β -dichloro- α - β -di-*p*-bromobenzoyl-ethylene, m.p. 111° [reduced (Zn dust, AcOH) to (IV)], convertible [as for (VI)] into the *trans*-form, m.p. 206° (corr.). The chloride, b.p. 107—108°/12 mm., of *Me H* dibromofumarate, m.p. 75° [obtained by partial hydrolysis (MeOH-KOH) of the Me₂ ester], with PhBr and AlCl₃ in CS₂ gives *Me trans*- α - β -dibromo- β -*p*-bromobenzoylacrylate, m.p. 102°, attempted hydrolysis (NaOH in 80% EtOH at room temp.) of which affords *p*-C₆H₄Br·CO₂H; *Me trans*- α - β -dibromo- β -benzoylacrylate (hydrolysed to BzOH) is similarly prepared using C₆H₆.

H. B.

2 : 3 : 5-Triphenylfurans and related saturated and unsaturated α -diketones. R. E. LUTZ, W. R. TYSON, A. G. SANDERS, and C. K. FINK (J. Amer. Chem. Soc., 1934, 56, 2679—2682; cf. A., 1934, 1361).—4-Chloro-2 : 3 : 5-triphenylfuran (I) is obtained from 2 : 3 : 5-triphenylfuran (II) or its 4-Ac derivative, and α - β -dibenzoyl- α -phenyl-ethylene (III) or -ethane (IV) and PCl₅ at 100°; (I) is also prepared from (III) and EtOH-HCl or AlCl₃-conc. H₂SO₄. The above compounds [except (IV)] and PBr₅ at 60° give 4-bromo-3-phenyl-2 : 5-di-*p*-bromophenylfuran (V) (+H₂O), m.p. 203.5° (corr.) [oxidised (HNO₃ followed by KMnO₄) to *p*-C₆H₄Br·CO₂H (1.89 equivs.)], whilst (II) and PBr₅ at 25° afford 4-bromo-2 : 3 : 5-triphenylfuran (VI), convertible into (V). The furan ring in (II) is thus more reactive than any of the Ph groups. (II) and HNO₃ (d 1.42) in AcOH at 50° give *cis*-(III); use of more HNO₃ at 100° gives β -nitro- α - β -dibenzoyl- α -phenylethylene (VII) (cf. Japp and Klingemann, J.C.S., 1890, 57, 674), which is reduced (Zn dust, AcOH) to (IV). (IV) and HNO₃-AcOH similarly afford (VII) [probably by way of (II)], whilst (VI) gives *cis*- β -bromo- α - β -dibenzoyl- α -phenylethylene, m.p. 63 [reduced (Zn dust, AcOH) to (II) and a little (IV)]; Br must be eliminated before ring-closure, since (VI) is stable under these conditions]. 3-Phenyl-2 : α -di-*p*-bromophenylfuran (VIII), m.p. 114° (corr.) [from α - β -di-

p-bromobenzoyl- α -phenylethane (IX) and Ac_2O -conc. H_2SO_4 at 60°], with HNO_3 - AcOH affords *cis*- β -bromo- $\alpha\beta$ -di-*p*-bromobenzoyl- α -phenylethylene (X), m.p. 142° (corr.). Reduction (Zn dust, AcOH) of $\alpha\beta$ -di-*p*-bromobenzoyl- α -phenylethylene involves 1:6-addition of H_2 (cf. A., 1929, 1459) and gives (VIII) and (IX) (stable under the same conditions); (X) similarly affords (VIII) as the sole product (this is ascribed to the catalytic effect of the ZnBr_2 formed during reduction). (VIII) and PBr_5 give (V). H. B.

Condensation of aldehydes with malonic acid in presence of organic bases. I. In presence of pyridine alone. P. N. KURIEN, K. C. PANDYA, and V. R. SURANGE (J. Indian Chem. Soc., 1934, 11, 823—826).—The yields of condensation products obtained from $\text{CH}_2(\text{CO}_2\text{H})_2$ (I) and a large no. of aromatic aldehydes in presence of $\text{C}_5\text{H}_5\text{N}$ are recorded. $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ condenses with (I) only when a trace of $\text{C}_5\text{H}_5\text{N}$ is used, a 51% yield of coumarincarboxylic acid (not *o*-coumaric acid as in lit.) being obtained.

J. W. B.

[Attempted] synthesis of 2:2'-dihydroxydicinnamoylmethane. W. LAMPE and M. TRENNK-
NERÓWNA (Rocz. Chem., 1934, 14, 1231—1237).—The Cu salt (I), m.p. $241\text{--}242^\circ$, of Et β -3-coumarinyl-3-ketopropionate when boiled in CHCl_3 with the chloride, m.p. $136\text{--}137^\circ$, of coumarin-3-carboxylic acid (II) yields Et di(coumarinyl-3-carbonyl)acetate (III), m.p. $210\text{--}212^\circ$, which on autoclaving affords di(coumarino- α -carbonyl)methane (IV), m.p. $276\text{--}278^\circ$. Attempts to prepare 2:2'-dihydroxydicinnamoylmethane by hydrolysis of (IV) with 5% aq. or alcoholic NaOH, or with POCl_3 in PCl_5 , were unsuccessful, the products with NaOH being (II) and acetyl- α -coumarin, whilst POCl_3 had no action. Et (coumarin- α -carbonyl)-cinnamoylacetate, m.p. $220\text{--}222^\circ$ (decomp.), is obtained analogously to (III) from (I) and cinnamoyl chloride. R. T.

Condensation of phenols and phenolic ethers with acetonedicarboxylic acid. (A) Syntheses of $\beta\beta$ -substituted glutaric acids. (B) Anhydrides of β -2-hydroxyphenylglutaconic acids. V. M. DIXIT and G. N. GOKHALE (J. Univ. Bombay, 1934, 3, No. 2, 80—94, 95—105).—(A) Condensation of $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ with PhOH in 75% H_2SO_4 gives $\beta\beta$ -2:2'-dihydroxydiphenylglutaric acid (I), m.p. 234° (decomp.) [Pb and Cu ($+2\text{H}_2\text{O}$) salts], also obtained starting from citric acid. The constitution of (I) follows from the following observations. It is converted by conc. H_2SO_4 at $50\text{--}60^\circ$ into PhOH and coumarin-4-acetic acid. When oxidised with alkaline KMnO_4 or CrO_3 it affords PhOH and 4-methylcoumarin. With cold, conc. HNO_3 - H_2SO_4 it yields $\beta\beta$ -5:5'-dinitro-2:2'-dihydroxydiphenylglutaric acid, m.p. 204° (decomp.), which passes when heated with fuming HNO_3 into a little picric acid and much $\beta\beta'$ -dinitroxanthone, m.p. 261° , also obtained directly from (I). Moist KOH at 180° transforms it into 2:2'-dihydroxybenzophenone. The acid or its esters do not condense with $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$. The Me_2 ester, m.p. 189° [Ac_2 , m.p. 107° ; Bz_2 , m.p. 152° ; Me_2 , m.p. 85° , and 3:3':5:5'- Br_4 , m.p. 180° (decomp.) derivatives], condenses with $\text{Me}_2\text{C}_2\text{O}_4$ in presence of NaOMe to Me_2 4:5-diketo-2:2-di-*o*-

hydroxyphenylcyclopentane-1:3-dicarboxylate (diphenylhydrazone, m.p. 128°) and with $o\text{-C}_6\text{H}_4(\text{CO}_2\text{Me})_2$ to Me_2 4:7-diketo-3:3-di-*o*-hydroxyphenyl-5:6-benzocycloheptane-1:3-dicarboxylate, m.p. 148° (diphenylhydrazone, m.p. 199°). The following compounds are incidentally described: $\beta\beta$ -2:2'-dihydroxydiphenylglutaric anhydride (II), m.p. 80° , from the acid at 239° (Ac_2 , m.p. 203° , and Bz_2 , m.p. 167° , derivatives), converted by NH_3 at 150° into the corresponding imide (III), b.p. $135^\circ/40$ mm. (Bz_2 derivative, m.p. 61°); $\beta\beta$ -2:2'-dibenzoyloxydiphenylglutaric acid, m.p. 223° (decomp.); $\beta\beta$ -2:2'-dimethoxydiphenylglutaric acid, m.p. 154° (decomp.) (Ag salt), from (I), MeI, and NaOMe, and its anhydride, m.p. 160° ; Et $\beta\beta$ -2:2'-dihydroxydiphenylglutarate, m.p. 145° ; $\beta\beta$ -5:5'-dibromo-, m.p. 180° (decomp.), and $\beta\beta$ -3:3':5:5'-tetrabromo-, m.p. 210° (decomp.), -2:2'-dihydrodiphenylglutaric acid, from (I) and Br in AcOH and H_2O , respectively; the semianilide (IV), m.p. 120° (decomp.) (Ag salt), from (I) and NH_2Ph at 110° , anil, m.p. 220° , from (I) and NH_2Ph at $130\text{--}140^\circ$, from (II) and NH_2Ph in boiling EtOH, or from (IV) by heating at its m.p., and the dianilide, m.p. 298° , from (IV) and NH_2Ph at $160\text{--}180^\circ$, of (I); the NH_4 H salt of (I), converted by distillation/20 mm. into (III). $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ and *o*-cresol in 75% H_2SO_4 afford $\beta\beta$ -2:2'-dihydroxy-3:3'-dimethyldiphenylglutaric acid, m.p. 203° (decomp.) [Cu ($+2\text{H}_2\text{O}$) salt], transformed by conc. H_2SO_4 into 8-methylcoumarin-4-acetic acid, m.p. 184° (decomp.), and *o*-cresol. Similarly, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ gives $\beta\beta$ -2:2'-dimethoxy-5:5'-dimethyldiphenylglutaric acid, m.p. 164° [Cu ($+2\text{H}_2\text{O}$) salt], transformed by conc. H_2SO_4 into 6-methylcoumarin-4-acetic acid, m.p. 183° (decomp.), and 2-methoxy-5-methylphenylglutaconic acid, m.p. 82° . *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ gives $\beta\beta$ -2:2':4:5'-tetrahydroxydiphenylglutaric acid, m.p. $242\text{--}243^\circ$ (decomp.) [Cu ($+2\text{H}_2\text{O}$) salt], converted by conc. H_2SO_4 into 6-hydroxycoumarin-4-acetic acid, m.p. 165° .

(B) Citric acid is heated with conc. H_2SO_4 at $60\text{--}70^\circ$ until evolution of CO ceases, and the solution is treated with PhOH, thus giving coumarin-4-acetic acid (I), m.p. 168° (decomp.), which does not react with Ac_2O , AcCl , or BzCl , passes at its m.p. into 4-methylcoumarin (II), affords an Et ester, m.p. 116° , which condenses with $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ to give the corresponding dicoumaryl, m.p. 246° (Dey *et al.*, A., 1924, i, 538). In addition, β -2-hydroxyphenylglutaconic anhydride (III), m.p. 188° (decomp.), is produced. (I) is transformed into (III) by contact with 100% H_2SO_4 and (III) into (I) by hydrolysis with boiling 20% NaOH. (III) is oxidised to $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ by CrO_3 in AcOH containing a little H_2SO_4 , loses CO_2 at $188^\circ/20$ mm., with formation of a phenolic substance, m.p. 82° , which depresses the m.p. of (II), gives a Bz_2 derivative, m.p. 252° , and a cryst. compound with Ac_2O -NaOAc. The following compounds are obtained similarly. 7-Methylcoumarin-4-acetic acid (IV), m.p. 168° (decomp.), from *m*-cresol (whence 4:7-dimethylcoumarin, m.p. 132° , and Et 7-methylcoumarin-4-acetate, m.p. 131 , converted by $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ into 7-methyl-4:5-dicoumaryl, m.p. 247°) and β -2-hydroxy-4-methylphenylglutaconic anhydride (V), m.p. 212° (decomp.),

which loses CO_2 when heated with formation of a substance, m.p. 110° , and is converted by NaOH into (IV); it is formed in 90% yield from (IV) and anhyd. H_2SO_4 . (V) is oxidised to 2-hydroxy-*p*-toluic acid, m.p. 173° , and yields a Bz_2 derivative, m.p. 275° , hydrolysed by boiling alkali to (IV). 6-Methylcoumarin-4-acetic acid (VI), m.p. 173° (decomp.), from *p*-cresol (whence 4:6-dimethylcoumarin, m.p. 148°) and β -2-hydroxy-5-methylphenylglutaconic anhydride (VII), m.p. 192° (decomp.), which loses CO_2 with formation of a phenolic substance, m.p. 155° , and is oxidised to 5-methylsalicylic acid, m.p. 148° ; the Bz_2 derivative, m.p. 310° , is hydrolysed by boiling alkali to (VI). The interconversion of (VI) and (VII) is described. 8-Methylcoumarin-4-acetic acid (VIII), m.p. 182° (decomp.), from *o*-cresol, which passes at its m.p. into 4:8-dimethylcoumarin, m.p. 118° , and β -2-hydroxy-3-methylphenylglutaconic anhydride (IX), m.p. 188° (decomp.), which loses CO_2 under reduced pressure yielding a phenolic sublimate, m.p. 120° , and is oxidised to 3-methylsalicylic acid, m.p. 158° ; the Bz_2 derivative, m.p. 288° , is hydrolysed by boiling alkali to (VIII). (VIII) and (IX) are interconvertible.

H. W.

Reactions of *o*-hydroxybenzylidenediacetophenones. II. Conversion into pyrylium and benzopyrylium salts. D. W. HILL. III. Formation of a 4-phenacylideneflavene during the preparation of 4'-methoxyflavylium chloride. D. W. HILL and R. R. MELHUIS (J.C.S., 1935, 85—88, 88—89).—II. *o*-Hydroxybenzylidenediacetophenone (I) under different conditions condenses to give flavylium ferrichloride, m.p. 140° , also obtained from 4-phenacylflavene. Elimination of 4-phenacyl group on condensation ($\text{HCl}-\text{TeCl}_3$) does not take place in the phenacylidene series: 4-phenacylflavylium, m.p. $156-157^\circ$, 7-methoxy-4-phenacylflavylium, m.p. 168° , 2:6-diphenyl-4-(2':4'-dimethoxyphenyl)pyrylium, m.p. $190-191^\circ$, 2:6-diphenyl-4-(*o*-acetoxyphenyl)pyrylium, m.p. 181° , 2:6-diphenyl-4-(2'-acetoxy-4'-methoxyphenyl)pyrylium, m.p. 162° , and 2:6-diphenyl-4-(2'-acetoxy-5'-methoxyphenyl)pyrylium ferrichloride, m.p. $225-226^\circ$. The significance of the results in the structure given to benzopyrylium salts is considered.

III. (I) and HCl in Et_2O condense to a flavylium ferrichloride, m.p. $159-161^\circ$, which contains some 4-phenacylflavylium ferrichloride. Condensation of *p*-methoxyacetophenone and salicylaldehyde in Et_2O affords 4'-methoxy-4-(*p*-methoxyphenacylidene)flavene (II), m.p. $167-168^\circ$, and in $\text{EtOH}-\text{NaOH}$ gives *o*-hydroxybenzylidenedi-(*p*-methoxyacetophenone) (III), m.p. 167° , which with AcOH forms 4'-methoxy-4-(*p*-methoxyphenacyl)flavene, m.p. 122° . (III) and boiling AcOH yield (II), converted by HCl into 4'-methoxy-4-(*p*-methoxyphenyl)flavylium chloride, m.p. 120° (decomp.), from which the ferrichloride may be obtained.

F. R. S.

3-Amino- and 3-hydroxy- β -naphthapyrones. B. B. DEY and A. K. LAKSHMINARAYANAN (J. Indian Chem. Soc., 1934, 11, 827—833).—When heated together with $\text{NaOAc}-\text{Ac}_2\text{O}$ at 100° , 2-hydroxy-1-naphthaldehyde (I) and $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ afford the Ac derivative of (I), $\beta\alpha$ -5:6-naphthapyrone, and the

Bz derivative (II), m.p. 230° , of 3-amino- $\beta\alpha$ -5:6-naphthapyrone (III), m.p. 169° (hydrochloride, m.p. 201° ; sulphate), which is obtained by debenzoylation with $\text{AcOH}-\text{HBr}$. The Ac derivative, m.p. 245° , of (III) is obtained by similar condensation of (I) and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ with $\text{NaOAc}-\text{Ac}_2\text{O}$ at 140° . Hydrolysis of (II) with $2N\text{-KOH}$ affords (?) trans- α -benz-amido- β -2-hydroxy-1-naphthylacrylic acid, m.p. 206° (decomp.), whereas with $N\text{-KOH}$ (III) gives cis- α -hydroxy- β -2-hydroxy-1-naphthylacrylic acid, sinters 120° , m.p. 136° (decomp. and resolidification to a solid, m.p. $215-220^\circ$), converted by heating at 160° into 3-hydroxy- $\beta\alpha$ -5:6-naphthapyrone (IV), m.p. 230° (Ac derivative, m.p. 162°), also obtained by the action of HNO_2 on (III). (IV) is not converted by alkali into 2-hydroxynaphthyl-1-acetaldehyde (cf. A., 1934, 1008).

J. W. B.

A simple γ -pyran, 2:4:4:6-tetraphenyl- γ -pyran. A. P. DE CARVALHO (Compt. rend., 1934, 199, 1430—1432).— $\text{CPh}_2(\text{CH}_2\text{Bz})_2$ is dehydrated to 2:4:4:6-tetraphenyl- γ -pyran (I), m.p. $157-158^\circ$, very readily hydrolysed by H_2O . The 3:5- Br_2 -derivative, obtained from Br and (I), but not by dehydration of $\text{CPh}_2(\text{CHBrBz})_2$, resists hydrolysis.

R. S. C.

Manufacture of bases derived from benzdi-oxan.—See B., 1935, 124.

Thiophen series. XXVIII. Bromo-derivatives of 3-thiophene [3-methylthiophen]. W. STEINKOPF and H. JACOB (Annalen, 1935, 515, 273—283; cf. A., 1934, 1365).—3-Methylthiophen (I) is converted by $\text{Br}-\text{H}_2\text{O}$ into 2-bromo-3-methylthiophen (II), b.p. $173-176^\circ$, the constitution of which follows from the production of a single 5-HgCl compound, m.p. 251° , and its conversion into 2-bromo-3-methylthiophen-5-sulphonic acid (corresponding amide, m.p. 142°). (II) is converted by successive action of $\text{Mg}-\text{Et}_2\text{O}$ and CO_2 into 3-methylthiophen-2-carboxylic acid, m.p. 148° , whilst 3-bromo-2-methylthiophen, $\text{Mg}+\text{MgMeBr}$, and Et_2O followed by CO_2 afford 2-methylthiophen-3-carboxylic acid, m.p. $115-117^\circ$. (II), AcCl , and AlCl_3 in light petroleum yield 2-bromo-*o*-acetyl-3-methylthiophen, m.p. $67-68^\circ$. 2-Bromo-5-iodo-3-methylthiophen, b.p. $131-135^\circ/14\text{ mm.}$, m.p. -3° to -2° , is obtained from (II), I, and yellow HgO in C_6H_6 , and 2-iodo-3-methylthiophen, b.p. $86-88^\circ/13\text{ mm.}$, is obtained similarly from (I). More intense bromination of (I) with $\text{Br}-\text{H}_2\text{O}$ affords (I) and 2:5-dibromo-3-methylthiophen (III), b.p. $226-230^\circ$. Grignard degradation of (III) in presence of MeBr gives mainly (II) accompanied by a small amount of 5-bromo-3-methylthiophen (mercurichloride, m.p. $217-220^\circ$). 2:4:5-Tribromo-3-methylthiophen (IV), m.p. 33° , is debrominated to bromomethylthiophenes and (mainly) 4:5-dibromo-3-methylthiophen (V), b.p. $232-233^\circ$ (2-mercurichloride, m.p. $240-241^\circ$). Successive treatment of (V) with $\text{Mg}-\text{MgMeBr}$ and CO_2 in Et_2O leads to 4-bromo-3-methylthiophen-*o*-carboxylic acid, m.p. 195° , reduced by $\text{Na}-\text{Hg}$ to 3-methylthiophen-5-carboxylic acid, m.p. $88-90^\circ$. 4-Bromo-3-methylthiophen, b.p. $180-182^\circ$, gives a di-, blackens at $310-315^\circ$, and a mono-, unchanged $>330^\circ$, mercurichloride. (IV) is converted by an excess of Br in sunlight into 2:4:5-tribromo-3-bromomethyl-

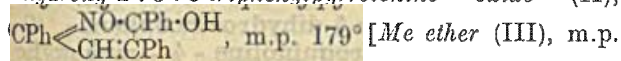
thiophen, m.p. 63—67°, and by AcCl and AlCl_3 in light petroleum into 4 : 5-dibromo-2-acetyl-3-methylthiophen, m.p. 126—127°. (I), BzCl , and AlCl_3 in light petroleum afford 5-benzoyl-3-methylthiophen, m.p. 91—93°, and 2-benzoyl-3-methylthiophen, transformed by Br into 4 : 5-dibromo-2-benzoyl-3-methylthiophen, m.p. 77—79°, also obtained from (V). 2 : 5-Dimethylthiophen, I, and yellow HgO give 3 : 4-di-iodo-2 : 5-dimethylthiophen, m.p. 83°. 2 : 5-Dibromo-3-acetylthiophen, m.p. 55°, is described.

H. W.

Constitution of pyrrolines. A. SONN [with R. PODSCHUS, K. SCHÜTZLER, and G. STEPHANI] (Ber., 1935, 68, [B], 148—151).—Ph vinyl ketone condenses with MeNO_2 in presence of NaOMe-MeOH to Ph γ -nitro-n-propyl ketone, m.p. 102° (decomp.), reduced by Zn and AcOH at 100° to 2-phenyl- Δ^2 -pyrroline [picrate, m.p. 198° (decomp.)], which gives γ -benzamidopropiophenone, m.p. 126°, with BzCl and excess of NaOH . γ -Nitro- β -phenyl-n-propyl Me ketone similarly affords 4-phenyl-2-methyl- Δ^2 -pyrroline (I), b.p. 135°/15 mm. [picrate (II), m.p. 149—150°], whence γ -benzamido- β -phenyl-n-propyl Me ketone (III), m.p. 124°. Reduction of 4-phenyl-2-methylpyrrole with Zn and conc. HCl in Et_2O affords a base shown to be identical with (I) by means of (II) and (III); addition of H_2 occurs therefore in the 4 : 5 position instead of in the expected 2 : 5 position. Ph γ -nitro- β -phenyl-n-propyl ketone yields 2 : 4-diphenyl- Δ^2 -pyrroline, m.p. 48—49° (picrate, m.p. 155—156°), whence Ph γ -benzamido- β -phenyl-n-propyl ketone, m.p. 180—181°.

H. W.

Reaction between $\alpha\beta$ -dibenzoyl- α -phenylethylene and hydroxylamine hydrochloride. A cyclic hydroxynitrone. A. H. BLATT (J. Amer. Chem. Soc., 1934, 56, 2774—2779).—*cis*- $\alpha\beta$ -Dibenzoyl- α -phenylethylene (I) in EtOH and aq. $\text{NH}_2\text{OH}\cdot\text{HCl}$ give 2-hydroxy-2 : 3 : 5-triphenylpyrrolenine oxide (II),



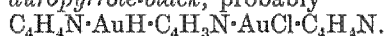
briefly. (II) and MeOH-NaOMe give a Na salt, $\text{C}_{22}\text{H}_{16}\text{O}_6\text{NNa}$.

H. B.

Reaction of amides with magnesylypyrroles. A. SANNA (Gazzetta, 1934, 64, 857—860).—The Mg-EtBr derivatives of pyrrole and NH_2Ac interact to form α -amino- α -2-pyrroylethanol, b. p. 76°.

E. W. W.

An autopyrrole black. G. GIULIANI (Gazzetta, 1934, 64, 894—896).— AuCl_3 oxidises pyrrole to an autopyrrole-black, probably



E. W. W.

Bases obtained from acetophenone, formaldehyde, and ammonium chloride. C. MANNICH and S. M. ABDULLAH (Ber., 1935, 68, [B], 113—120; cf. Schafer *et al.*, A., 1906, i, 574).—The interaction of COPhMe , 33% CH_2O , and NH_4Cl at 100° gives tri- β -benzoyl-ethylamine hydrochloride (I), m.p. 145°, whence tri- β -benzoyl-ethylamine (II), m.p. 67° [picrate, m.p. 140—142°; platinichloride; aurichloride, m.p. 168°; methiodide (III), m.p. 147—148°]. In boiling EtOH (II) passes into Schafer's base (IV), now regarded as 4-hydroxy-5-benzoyl-4-phenyl-1- β -benzoyl-ethylpiperidine, m.p. 150° [hydrochloride (V), m.p. 199—200°; platinichloride, m.p. 207—208°; picrate, m.p. 154°; methiodide, identical with (III)]. (I) with excess of BzCl at 75—80° leads to (V). (V) is unchanged by BzCl in $\text{C}_6\text{H}_5\text{N}$ at 100°, but is converted by BzCl at 155—160° into NBz_3 . Treatment of (II) with Ac_2O at 100° yields aceti- β -benzoyl-ethylamine (VI), m.p. 110°, and an oil smelling of Ph vinyl ketone (VII) which deposits crystals, m.p. 55—57°, (?) β -benzoyl-ethyl acetate (VIII). (VI) gives a dioxime (IX), m.p. 210°, disemicarbazone, m.p. 210—212°, and di- p -nitrophenylhydrazones, m.p. 207—208°. (IV) is transformed by short treatment with Ac_2O at 100° into 4-hydroxy-5-benzoyl-1-acetyl-4-phenylpiperidine (X) [which does not give derivatives with $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ or $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ and with NH_2OH yields (IX)], accompanied by (VII) and (VIII), and on more protracted heating gives (VI). 4-Chloro-5-benzoyl-1-acetyl-4-phenylpiperidine, m.p. 165°, from (X) and SOCl_2 at $\geq 15\text{--}20^\circ$, is converted by NaOH into 5-benzoyl-1-acetyl-4-phenyltetrahydropyridine, m.p. 143°, hydrogenated (Pt-C-EtOH) to 5-benzoyl-1-acetyl-4-phenylpiperidine, m.p. 168°. Distillation of (I) or (V) with steam gives (VII) and di- β -benzoyl-ethylamine hydrochloride (XI), m.p. 175° (corresponding platinichloride, m.p. 194—195°, and aurichloride, m.p. 120°). The corresponding base readily becomes disproportionated into NH_3 and the *tert*.-base, but its *sec*. character is established by its conversion into (VI), its *Bz* derivative, m.p. 105—106°, *NO*-derivative, m.p. 114—115° (decomp.), and carbamide compound, m.p. 187° (decomp.). (XI) with superheated steam slowly gives (VII) and β -benzoyl-ethylamine hydrochloride, m.p. 125° [corresponding platinichloride, m.p. 227—228° (decomp.), and picrate, m.p. 160°]. When preserved, the free base yields NH_3 and (II).

H. W.

Additive products of halogenyl amides with pyridine. J. A. SPRAGGE (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 103—106).—The m.-p. curves of *N*-bromobenzamide, *N*-bromo- and *N*-chloro-phthalimide in $\text{C}_5\text{H}_5\text{N}$ afford evidence of compound form-

ation. The m.p. is a max. at 45–50 mol.-% halogen compound. Solutions more conc. than 55 mol.-% are unstable at room temp. J. L. D.

Optical investigation of the antineuritic vitamin(-B₁).—See this vol., 261.

Optical activity in the indole group. A. McKENZIE and P. A. STEWART (J.C.S., 1935, 104–111).—Reduction of *r*-o-nitromandelic acid (I) with FeSO₄·Ba(OH)₂ gives *r*-o-aminomandelic acid, m.p. 144° (decomp.), which with HCl yields *r*-dioxindole [*r*-o-benzamido-, m.p. 140°, and *r*-o-β-naphtholazo-mandelic acid, m.p. 205–206° (decomp.)]. *r*-o-Nitroacetylmandelic acid, m.p. 102–103°, could not be reduced. *r*-o-Nitrophenylmethoxyacetic acid, m.p. 81–82°, and *Et* *r*-o-nitrobenzoylmandelate, m.p. 76–77°, are described. (I) is resolved with brucine into (–)-o- and (+)-o-nitromandelic acids, m.p. 100–101°, [α]_D²⁰₄₆₁ ±594° in COMe₂. (+)-o-Nitroacetylmandelic acid has m.p. 95–96°, [α]_D²⁰₄₆₁ +367° in COMe₂, and *Et* (+)-o-nitromandelate has b.p. 165–166°/4 mm., [α]_D²⁰₄₆₁ +384° in COMe₂. Reduction of the active NO₂-acids leads to (–)-o- and (+)-o-aminomandelic acids, m.p. 159° (decomp.), [α]_D²⁰₄₆₁ ∓195° in *N*-NaOH [(–)-o-acetamido-, m.p. 160°, [α]_D²⁰₄₆₁ –227° in COMe₂, and (–)-o-β-naphtholazo-mandelic acid, m.p. 190–191° (decomp.)]. (–)-o-Aminomandelic acid is converted with H₂SO₄ into (+)-dioxindole, m.p. 167–168°, [α]_D²⁰₄₆₁ +40° in COMe₂, giving with NHPh·NH₂ an inactive isatin-β-phenylhydrazone and with KOH·EtOH isatide. Other reagents also yield inactive products. (+)-o-Nitromandelic acid, aq. NH₃, NH₄Cl, and Zn give (–)-N-hydroxydioxindole [(–)-trioxindole], m.p. 159° (decomp.), [α]_D²⁰₆₁ –59° in COMe₂, and (+)-N-hydroxydioxindole is similarly obtained. Na (–)-o-aminomandelate and HNO₂ afford (–)-o-hydroxy-mandelic acid, an oil, [α]_D²⁰₄₆₁ –76·6° in COMe₂.

F. R. S.

Ferrohalides of pyridine and quinoline. F. S. TAYLOR (J.C.S., 1935, 115–116).—The following salts are described: *pyridinium ferrochloride*, (C₅H₅NH)₂FeCl₄, yellow, m.p. 127–128°; *quinolinium ferrochloride dihydrate*, (C₉H₇NH)₂FeCl₄·2H₂O, yellow, m.p. 97°; *pyridinium ferrobromide*, (C₅H₅NH)₂FeBr₄, green; *quinolinium ferrobromide dihydrate*, (C₉H₇NH)₂FeBr₄·2H₂O, yellow, m.p. 89°.

F. R. G.

Action of cyanogen iodide on quinolines. O. MUMM and C. BRUHN (Ber., 1935, 68, [B], 176–183).—Addition of CNI to the requisite quinoline in Et₂O in presence or absence of HCN leads to pptn. of the following *iodocyanides*: quinoline, m.p. 104°; *p*-, m.p. 107–108°, and *o*-, m.p. 98°, -toluquinoline; 2-methylquinoline, m.p. 98°; β-naphthaquinoline (I), m.p. 116–117°. The compounds are treated with so much cold, conc. HCl as is necessary for complete dissolution; from the yellow solutions the following *dichloriodides* (II) RH[ICl₂] separate in about 80% yield, their formulation resting on the complete analogy of their properties with those of the compounds derived by addition of ICl to alkali halides: *quinolinium*, m.p. 118–120°; *o*-toluquinolinium, m.p. 146–148°; 2-methylquinolinium, m.p. 112–113°. (II) pass at 100° into the *trichloriodides* (RH)₃[ICl₃], re-converted into the original materials by recrystallisation

from dil. HCl, the following being described: *quinolinium*, m.p. 123°; 2-methylquinolinium, m.p. 148–149°; α-naphthaquinolinium, m.p. 194–195°, transformed by EtOH–H₂O into the corresponding *dichloriodide*, m.p. 166°. Treatment of (II) with H₂O–BaCO₃, saturated NaHCO₃, or H₂O leads to products identical with those obtained by addition of ICl to quinolines. At 130°, (I) suddenly evolves I and acid vapours and passes into a *compound*, m.p. 118–120°, transformed by successive treatment with boiling 2*N*-NaOH and 50% AcOH into β-naphthaquinoline-α-carboxylic acid, m.p. 188–190° [*hydrochloride*, m.p. 220–221° (decomp.)]. The action of CNI therefore differs essentially from that of CNBr (this vol., 92).

H. W.

Synthesis of substituted cinchonic acids with use of weak bases as condensing agents. K. M. PANDALAI (Annalen, 1935, 515, 302–306).—The *cis*-forms of 3-acylideneoxindoles are converted by weak bases into substituted cinchonic acids, although this reaction does not occur with the corresponding *trans*-derivatives (cf. Braude, A., 1933, 282; Lindwall *et al.*, *ibenda*, 164). The mechanism of the reaction differs from that of the Pfitzinger synthesis (A., 1898, i, 207). 3-Acetylideneoxindole (I) is isomerised by irradiation in abs. EtOH with ultra-violet light and then transformed by 33% K₂CO₃ into 2-methylquinoline-4-carboxylic acid, m.p. 242°, also obtained by protracted ebullition of 3-hydroxy-3-acetyloxindole with KOH. (I) is transformed by boiling KOH into dark, resinous material and by irradiation with sunlight in alkaline or EtOH solution into a dark mass from which a definite product could not be isolated. *cis*-3-Phenacylideneoxindole, m.p. 193°, is similarly converted into 2-phenylquinoline-4-carboxylic acid, m.p. 210°. The behaviour of phenacyloxindoles towards conc. alkali and sunlight resembles that of the corresponding Me compounds.

H. W.

Synthesis of 1:4-dihydrocincophens [2-phenyl-1:4-dihydroquinoline-4-carboxylic acids] from 3-phenacyloxindoles. R. N. DUPUIS and H. G. LINDWALL (J. Amer. Chem. Soc., 1934, 56, 2716–2719).—3-Phenacyloxindole (+a little AcOH) and boiling aq. HCl give the *hydrochloride*, m.p. 213–217° (decomp.), of 2-phenyl-1:4-dihydroquinoline-4-carboxylic acid (I), m.p. 165° [*Ag* salt; sulphate, m.p. 198–200° (decomp.)], oxidised (boiling PhNO₂) to 2-phenylquinoline-4-carboxylic acid (II); with aq. EtOH–HCl, (I) and (II) result. The 4'-Cl-, m.p. 145°, 4'-Br-, m.p. 153–155°, and 4'-Me, m.p. 150° (*Ag* salt), derivatives of (I) are similarly prepared and oxidised to the 4'-substituted (II). (I) contains 2 active H, could not be reduced (Na+amyl alcohol or metal+acid), and could not be acylated or alkylated. Isatin and benzphenacylamide in EtOH–piperidine or –NH₂Et₂ at room temp. give 3-hydroxy-3-α-benzamidophenacyloxindole (III), m.p. 144–147°; in the hot, 3-α-benzamidophenacylideneoxindole (IV), m.p. 252–253° [also formed from (III) and EtOH–HCl], results. (IV) is reduced (Zn dust, AcOH) to 3-α-benzamidophenacyloxindole, m.p. 209–211°, converted by aq. EtOH–HCl at 110–120° (bath) into (II); deamination thus occurs at some stage in the reaction.

H. B.

Preparation of quinoline derivatives. VI. K. DZIEWOŃSKI and J. MAYER [with L. MARCZEWSKI, K. PIOTROWSKA, and A. SMORAWINSKA] (Bull. Acad. Polonaise, 1934, A, 338—347, and Roczn. Chem., 1934, 14, 1157—1165; cf. this vol., 222).— p - C_6H_4Cl -COMe (I) heated with $CS(NHPh)_2$ at 180—260° for 4 hr. yields 4-anilino-2- p -chlorophenylquinoline (II), m.p. 159° [hydrochloride, m.p. 170° (decomp.); picrate, m.p. 275° (decomp.); 4-N-NO-, m.p. 200° (decomp.), 4-N-Ac derivatives, m.p. 171°]. Similarly COPhMe and $(p-C_6H_4Cl-NH)_2CS$ afford 6-chloro-4- p -chloroanilino-2-phenylquinoline (III), m.p. 221° [hydrochloride, m.p. 335° (decomp.); picrate, m.p. 245° (decomp.); 4-N-NO-, m.p. 201° (decomp.), 4-N-Ac, m.p. 170°, and (?) NO_2 -derivatives, m.p. 191° (decomp.)], and (I) and $(p-C_6H_4Me-NH)_2CS$ afford 4- p -tolylamino-2- p -chlorophenyl-6-methylquinoline (IV), m.p. 278° [hydrochloride, m.p. 305° (decomp.); nitrate, m.p. 145° (decomp.); acetate, m.p. 305°; picrate, m.p. 243° (decomp.); 4-N-NO-, m.p. 157° (decomp.), and 4-N-Ac derivatives, m.p. 306—307°].

(II) with KOH and EtOH at 200° under pressure yields 4-hydroxy-2- p -hydroxyphenylquinoline, m.p. 216°. Similarly, 4:6-dihydroxy-2-phenylquinoline, m.p. 251—252° (Me_2 ether, m.p. 118°), is obtained from (III), and 4-hydroxy-2- p -hydroxyphenyl-6-methylquinoline, m.p. 274°, from (IV). H. G. M.

Syntheses and transformations of new compounds derived from 2-phenylquinoline. K. DZIEWOŃSKI and J. MOSZEW [with W. JASTRZEBSKA, R. KOCHANŃSKI, J. MAKSYMOWICZ, P. STACHOWICZ, I. STRASIKÓWNA, and P. TRZESIŃSKI] (Roczn. Chem., 1934, 14, 1123—1135).—COPhMe and di- m -tolylthiocarbamide heated at 180—205° for 10 hr. yield 4- m -toluidino-2-phenyl-5-methylquinoline, m.p. 134—135° [hydrochloride, m.p. 173—175° (decomp.); picrate, m.p. 245—246°; N-Ac, m.p. 149—150°, and N-NO-derivative, m.p. 144°], which affords 4-hydroxy-2-phenyl-5-methylquinoline, m.p. 281°, on hydrolysis with EtOH-KOH at 200° for 6 hr. CH_2BzPh (I) and $CS(NHPh)_2$ heated at 190—210° for 6 hr. afford 4-anilino-2:3-diphenylquinoline (II), m.p. 196—197° [hydrochloride, m.p. 279°; nitrate, m.p. 185° (decomp.); picrate, m.p. 259—260°; N-NO-derivative, m.p. 153—154° (decomp.)], which yields on hydrolysis 4-hydroxy-2:3-diphenylquinoline, converted by $POCl_3$ into 4-chloro-2:3-diphenylquinoline, m.p. 121°. (I) and di- p -tolylthiocarbamide when heated at 190° for 3 hr., and then at 210—220° for 3 hr., yield 4- p -toluidino-2:3-diphenyl-6-methylquinoline, m.p. 176° (picrate, m.p. 236°). 2- $C_{10}H_7$ -N:CPhMe, m.p. 65—67°, b.p. 215—220°/13 mm. (from β - $C_{10}H$ -NH₂ and COPhMe with $ZnCl_2$ at 170—220°), with PhNCS at 200° (1 hr.) and then at 280° (30 min.) yields 4-anilino-2-phenyl-5:6-benzoquinoline (III), m.p. 193—194° [picrate, m.p. 238—239° (decomp.); hydrochloride, m.p. 328°], hydrolysed to 4-hydroxy-2-phenyl-5:6-benzoquinoline, m.p. 280—281° (picrate, m.p. 234—235°). The methiodide, m.p. 236—238°, and ethiodide, m.p. 269° (decomp.), of 4-anilino-2-phenylquinoline (2:1 compound with CH_2Br_2 , m.p. 268—270°; 1:1 compound with $BzCl$, m.p. 258—260°) yield 4-phenylmethyl-, m.p. 153—154°, and 4-phenylethyl-, m.p. 164—165°, -amino-2-phenyl-

quinoline, when hydrolysed with EtOH-KOH. The methiodide, m.p. 240° (decomp.), and ethiodide, m.p. 256° (decomp.), of 4- p -toluidino-2-phenyl-6-methylquinoline yield similarly 4- p -tolylmethyl-, m.p. 205—206°, and 4- p -tolylethyl-, m.p. 136°, -amino-2-phenyl-6-methylquinoline. The methiodide, m.p. 246°, and ethiodide, m.p. 253° (decomp.), of (II) afford 4-phenylmethyl-, m.p. 207°, and 4-phenylethyl-, m.p. 174°, -amino-2:3-diphenylquinoline, and 4-phenylmethyl-amino-2-phenyl-5:6-benzoquinoline, m.p. 190—191°, similarly prepared from the methiodide, m.p. 284—285°, of (III). R. T.

Sulphonation of aminoquinolines. K. CYBULSKI, E. SUCHARDA, C. TROSZKIEWICZÓWNA, and W. TURSKA (Roczn. Chem., 1934, 14, 1172—1181).— α -Aminoquinoline-6-, +0.5H₂O, m.p. 280—305° (decomp.), and -8-sulphonic acid (I), +H₂O, m.p. 290—310° (decomp.), and -6:8-disulphonic acid, +1.5H₂O, m.p. >230° (decomp.), are obtained by heating 5-aminoquinoline hydrochloride for different periods with 25—40% oleum; (I) is also obtained from 5-hydroxyquinoline-8-sulphonic acid and aq. NH₃ at 140°. The following acids are prepared analogously: 6-aminoquinoline-5- (II), decomp. at >230°, 7-aminoquinoline-8-; 8-aminoquinoline-5-sulphonic acid (III), m.p. >260° (decomp.); -5:7-disulphonic acid, +H₂O. The products of diazotation of (I), (II), and (III) are described. R. T.

β -Hydroxyphenylethylamines and their transformations. III. Synthesis of benzylisoquinolines under physiological conditions. G. HAHN and O. SCHALES (Ber., 1935, 68, [B], 24—29; cf. A., 1934, 647, 1220).—Study of the action of (1) homopiperonylamine (I) and homopiperonal (II), (2) 3:4-methylenedioxyphenylpyruvic acid (III) and (I), (3) 3:4-methylenedioxyphenylalanine (IV) and (II), (4) (III) and (IV) shows that all β -hydroxyphenylethylamines (V) with substituted OH are suitable for the synthesis of tetrahydroisoquinolines, although condensation is less rapid than with (V) with free OH. The preliminary stage of the ring closure (formation of N -substituted aldehyde-ammonia or of Schiff's base) depends greatly on the p_H of the solution, the rate being maximal at p_H 5. (II) (prep. from safrole described) condenses with the hydrochloride of (I) in H₂O at 25° and p_H 5 to give 6:7:3':4'-dimethylenedioxybenzyl-1:2:3:4-tetrahydroisoquinoline, m.p. 98° (hydrochloride, m.p. 235°). H. W.

Nitrogen compounds in petroleum distillates. VIII. Degradation of the naphthenic base, $C_{16}H_{25}N$, to the lower homologue, $C_{16}H_{25}N$. R. W. LACKEY and J. R. BAILEY (J. Amer. Chem. Soc., 1934, 56, 2741—2743).—The base $C_{16}H_{25}N$ (I), m.p. 23—24.3° (cf. A., 1933, 1305), and Br give (cf. A., 1931, 631) a Br -derivative (II), m.p. 55.7° [picrate, m.p. 194.2° (softens slightly at 192°)], which could not be oxidised (HNO_3 or $KMnO_4$), is reduced (Zn dust, $AcOH$; not Adams) to (I), and does not react with Na at 250°, aq. or EtOH-KOH, $AgOAc$, or Mg . (II) probably contains CH_2Br attached to a neo-C atom. The additive compound, m.p. 80—100°, from (I) and $CNBr$ decomposes at 260°/4 mm. The product from (I) and 37% CH_2O at 190° is oxidised (HNO_3) to

a dicarboxylic acid, $C_{14}H_{19}N(CO_2H)_2$, m.p. about 100° (softens at 85°), decarboxylated at $235\text{--}240^\circ/30$ mm. to an acid, $C_{14}H_{20}N\cdot CO_2H$, m.p. $218\text{--}220^\circ$. Distillation of this with soda-lime gives a base, $C_{14}H_{21}N$, b.p. $266.4^\circ/746$ mm. (picrate, m.p. 146.2°), which could not be brominated or reduced (Adams).

(I) thus resembles 2:4-dimethylquinoline in its reaction with CH_2O . Structure (A) is now assigned to (I).

H. B.

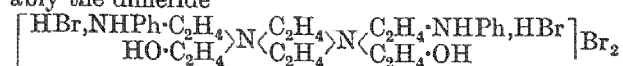
Chemiluminescence of dimethyldiacridylum salts.—See this vol., 281.

Manufacture of compounds of acridinium series.—See B., 1935, 124.

Oxidation of uracil *in vitro*. C. R. SCHWOB and L. R. CERECEDO (J. Amer. Chem. Soc., 1934, **56**, 2771—2772).—Uracil (I) is oxidised [aq. H_2O_2 in presence of C (Nuchar W) at $95\text{--}98^\circ$] to small amounts of isobarbituric (II) and isodialuric (III) acid, $H_2C_2O_4$ (IV), and $CO(NH_2)_2$ (V); in absence of C, a trace of (V) only is isolable. (II) is similarly oxidised [much more readily than (I)] to (III), (IV), and (V). (III) is actually isolated as K dialurate; treatment of (III) with aq. KOH causes isomerisation. Oxaluric acid (a probable intermediate) could not be isolated [probably owing to its ready hydrolysis to (IV) and (V)].

H. B.

Derivatives of *N*-phenylpiperazine. V. PRELOG and Z. BLAZEK (Coll. Czech. Chem. Comm., 1934, **6**, 549—560).—*N*-Phenylpiperazine (I) (A., 1934, 196, improved prep.) and $(\cdot CH_2)_2O$ in boiling MeOH give its *N'*- β -hydroxyethyl derivative (II), m.p. 91° [mono-, m.p. 162° , and di-hydrobromide, m.p. 226° ; dipicrate, m.p. 169° (decomp.); hydrochloride of *O*-Ac derivative, m.p. $206\text{--}207^\circ$; *O*-Bz, m.p. 87° (hydrochloride, m.p. 214°), and *O*-*p*-nitrobenzoyl, m.p. 105° , reduced (Sn-HCl) to the *O*-*p*-aminobenzoyl, m.p. 144.5° , derivatives]. With 66.5% HBr at 170° (II) affords the dihydrobromide, m.p. 256° , of *N'*- β -bromoethyl-, converted by NH_2Ph in boiling Bu^oOH into the trihydrobromide, decomp. $228\text{--}229^\circ$, of *N'*- β -anilinoethyl-, converted by $BzCl$ in C_6H_6 into the monohydrochloride, m.p. 195° , of *N'*- β -benzanilidoethyl-*N*-phenylpiperazine. With 40% CH_2O (I) gives *N*-bis-(*N'*-phenylpiperazyl)methane, CH_2R_2 ($R = \cdot N \langle \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix} \rangle NPh$), m.p. 133° (tetrahydrobromide, m.p. $239\text{--}241^\circ$), and (I) with $COCl_2$ in PhMe affords carbo-*N'*-phenylpiperazide COR_2 , m.p. 183° . Similarly (I) with $CH_2Br\cdot CO_2Et\cdot PhMe$ gives Et *N'*-phenylpiperazine-*N*-acetate, isolated as its mono-, m.p. 166° , and di-hydrobromide, m.p. 210° (decomp.) (hydrobromide, decomp. 257° , of free acid); with CH_2PhCl and 2:4- $C_6H_3Cl(NO_2)_2$ are obtained, respectively, *N*-phenyl-*N'*-benzyl-, m.p. 59° (monohydrochloride, m.p. 228°), and -*N'*-2:4-dinitrophenyl-, m.p. 156° , -piperazine. The compound $C_{12}H_{20}ON_2Br_2$, previously obtained from NH_2Ph and $OH\cdot CH_2\cdot CH_2\cdot N(CH_2\cdot CH_2Br)_2$ (this vol., 71), is probably the dimeride



(dihydrochloride, m.p. 183°), converted by boiling Ac_2O into the compound $[NPh(C_2H_5)_2N(CH_2)_2]Br_2$.

J. W. B.

Condensation of *o*-phenylenediamine with benzaldehyde. S. WEIL and H. MARCINKOWSKA (Rocz. Chem., 1934, **14**, 1312—1319).— $o\text{-}C_6H_4(NH_2)_2$ (I) (1 mol.) and $PhCHO$ (3 mols.) yield phenylbenzylbenziminazole and a compound, m.p. 159° , probably

$C_6H_4 \langle \begin{smallmatrix} N\cdot CPh \\ N\cdot CPh \end{smallmatrix} \rangle CHPh$. $CHPhBz_2$ or $CPhBz_3$ and (I) yield phenylbenziminazole (hydrochloride, decomp. at 200°) when heated at $170\text{--}180^\circ$. 1:2 Compounds of the benziminazole type are obtained from (I) and piperonal, m.p. 175° , and from (I) and vanillin, m.p. 224° ; $o\text{-}OH\cdot C_6H_4\cdot CHO$ and (I) yield $C_6H_4(N\cdot CH\cdot C_6H_4\cdot OH)_2$.

R. T.

Pyrimidines. CXLIII. Preparation of derivatives of uracil. L. R. BUEGER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, **56**, 2754—2755; cf. A., 1933, 1307).— $OEt\cdot CH\cdot CAc\cdot CO_2Et$ and $NH_2\cdot CO\cdot NHMe$ at 140° give *Et* methylcarbamidomethyleneacetate, m.p. $133\text{--}134^\circ$, converted by aq. 5% KOH at 75° followed by acidification (AcOH) into 5-acetyl-1-methyluracil, m.p. 197° . 5-Acetyl-1-phenyluracil, m.p. 228° , and 1-phenyluracil-5-carboxylic acid (I), m.p. 239° (decomp.), are similarly prepared from *Et* phenylcarbamidomethylene-acetate, m.p. 141° , and -malonate, m.p. $170\text{--}171^\circ$, respectively [from $PhNCO$ and $NH_2\cdot CH\cdot CAc\cdot CO_2Et$ and $NH_2\cdot CH\cdot C(CO_2Et)_2$, respectively, in xylene- C_5H_5N]. 1-Phenyluracil, m.p. 247° , is obtained when (I) is boiled with conc. HCl and the solution then evaporated to dryness.

H. B.

Pyrimidines. Molecular rearrangement of 2-ethylmercapto-6-thiocyano-5-ethylpyrimidine. Y. F. CHI and Y. L. T'EN (J. Amer. Chem. Soc., 1935, **57**, 215—217).— $Pr\cdot CO_2Et$, HCO_2Et , and Na in Et_2O give the Na derivative of *Et* formyl-*n*-butyrate, which with ψ -ethylthiocarbamide hydrobromide and aq. KOH at 0° gives 2-ethylthiol-5-ethyluracil, m.p. $119\text{--}120^\circ$, converted by hot $POCl_3$ into 6-chloro-2-ethylthiol-5-ethylpyrimidine, b.p. $160\text{--}162^\circ/22$ mm., which with KCNS in hot $EtOH$, C_6H_6 , or $COMe$, affords a little 2-ethylthiol-6-thioethylurethano-5-ethylpyrimidine, m.p. $77\text{--}78^\circ$, and much 2-ethylthiol-6-thiocyano-5-ethylpyrimidine (I), m.p. $46\text{--}47^\circ$. The structure of (I) is proved by its stability to conc. aq. NH₃ and hot $EtOH$, and its reaction with hot $SH\cdot CH_2\cdot CO_2H$ to form 2-ethylthiol-6-acetyldithiourethano-5-ethylpyrimidine, m.p. $116\text{--}117^\circ$. Although (I) is stable to heat alone and can be distilled unchanged at $158\text{--}160^\circ/5$ mm., it is rearranged by boiling PhMe (6 hr.) or $EtOH$ (2 hr.) to the 6-thiocarbimido-compound, b.p. $146\text{--}149^\circ/8$ mm., which with the appropriate reagents affords 2-ethylthiol-6-thiocarbamido-, m.p. $143\text{--}144^\circ$, -6-phenylthiocarbamido-, m.p. $108\text{--}109^\circ$, and -6-thioethylurethano-5-ethyl-pyrimidine, m.p. $77\text{--}78^\circ$.

R. S. C.

6:7-Dimethyl-9-l-araboflavin. R. KUHN and F. WEYGAND (Ber., 1935, **68**, [B], 166—169).—[α] of synthetic 6:7-dimethyl-l-araboflavin (I) (measured with the Ac_4 derivative) is identical with that of natural lactoflavin within the limits of experimental

error. Definite conclusions cannot be based thereon until the effect of individual OH on the $[\alpha]$ and growth-promoting action of the corresponding flavins is ascertained. Assuming the sign of $[\alpha]$ to be governed by OH proximate to the chromophore, *l*-arabinose, *d*-xylose, *l*-yxose, and, particularly, *d*-ribose must be considered, whereas *d*-arabinose is excluded. (I) shows little ability to couple with the colloid carrier of the yellow ferment of Warburg and Christian. The slight effect produced is not sp. and the expected catalytic actions do not occur. The possibility is considered that the "active group" of the ferment is a lacto-flavinphosphoric acid. Theorell's view that the active group is a "nucleotide" containing 6:7-dimethylalloxazine is regarded as erroneous, since spectroscopic evidence leaves no doubt that the coloured parent material is 6:7-dimethylisalloxazine. H. W.

Optical activity of lactoflavin. R. KUHN and H. RUDY (Ber., 1935, 68, [B], 169—170).—The following vals. of $[\alpha]_D^{20}$ are recorded for lactoflavin (I): $\pm 3^\circ$ in 2*N*-H₂SO₄; $\pm 5^\circ$ in H₂O or 0.01*N*-NaCl; -114° in *N*/75-NaOH; -115° in 0.1*N*-NaOH, -110.5° in 0.2*N*-NaOH; -78° in 1.4*N*-NaOH; -123.5° in 0.04*N*-NaOH-H₄MoO₅; $+350^\circ$ in 0.04*N*-NaOH-Na₂B₄O₇; -59° in AcOH. These vals. are approx. twice as great as those for the red Cd line. There appears to be a relationship between the optical activity and sensitiveness to light of alkaline solutions of (I). H. W.

Natural and synthetic lumilactoflavin. R. KUHN, H. RUDY, and K. REINEMUND (Ber., 1935, 68, [B], 170—172).—The differences observed between synthetic 6:7:9-trimethylflavin (I) and preps. of the pigment C₁₃H₁₂O₂N₄ from natural sources are due to impurities in the latter which are removed only with difficulty by purification through the Ag salt and repeated crystallisation from AcOH. (II) as used in degradation experiments contains 6:7-dimethylalloxazine (formerly α -lumilactoflavin) and β -lumilactoflavin completely identical with (I). H. W.

[Flavins.] P. KARRER (Ber., 1934, 67, [B], 2061—2063).—Mainly a question of priority against Kuhn *et al.* H. W.

[Flavins.] R. KUHN (Ber., 1935, 68, [B], 172—176).—A reply to Karrer *et al.* H. W.

Syntheses of flavins. P. KARRER, K. SCHOPP, F. BENZ, and K. PFAEHLER (Ber., 1935, 68, [B], 216—219).—Reductive condensation of *N*-monoacyl-*o*-phenylenediamines with sugars affords excellent yields of *o*-acetamidophenylamino-pentitols and -hexitols which with alloxan give the corresponding isoalloxazine compounds. The following isoalloxazines are thus obtained: 6:7-dimethyl-9-*l*-1'-arabo- (I), m.p. 298° , $[\alpha]_D -78^\circ$ ($\pm 10^\circ$) in 0.05*N*-NaOH; 7-methyl-9-*l*-1'-arabo-, m.p. 284—285°; 9-*l*-1'-arabo-, m.p. 292°; $[\alpha]_D -108^\circ$ ($\pm 10^\circ$) in 0.05*N*-NaOH; 7-methyl-9-*d*-1'-m.p. about 268—269°; non-cryst. 7-methyl-9-*d*-1'-sorbo-. The compounds resemble lactoflavin (II) in behaviour towards light. (I) differs in m.p. from (II). Change in m.p. above 286° could not be effected by crystallisation of (II), whereas the operation causes divisions into fractions of differing $[\alpha]_D$.

(I) may be identical with the least sol. fraction obtained from (II). H. W.

Syntheses of flavins. III. P. KARRER, K. SCHÖPP, F. BENZ, and K. PFAEHLER (Helv. Chim. Acta, 1935, 18, 69—77; cf. preceding abstract).—A detailed account of work already reported. The following intermediate compounds are described. Et 2-aminophenylcarbamate, m.p. 86° , obtained by reduction (H₂-Pt-EtOH) of Et 2-nitrophenylcarbamate, m.p. 58° (from *o*-NO₂-C₆H₄-NH₂ and ClCO₂Et in boiling CHCl₃). Et 2-amino-4:5-dimethylphenylcarbamate, m.p. 111° . 2-Acetamido-5-methylphenyl-*d*-glucosamine, m.p. 184—185°, $[\alpha]_D -3.0^\circ$ ($\pm 3.0^\circ$) in H₂O, by hydrogenation at 120—135°/15—20 atm. of 2-acetamido-5-methylaniline and glucose in 90% MeOH in presence of Ni [whence 2:6-dimethyl-1-*d*-sorbitylbenzimidazole, m.p. 226° , $[\alpha]_D^{20} -46.4^\circ$ ($\pm 5^\circ$) in H₂O]. 2-Acetamido-5-methylphenyl-*d*-xylosamine, m.p. 156—157°, $[\alpha]_D^{20} -31.5^\circ$ ($\pm 3^\circ$) in H₂O; 2-acetamido-5-methylphenyl-1-arabinosamine, m.p. 159° , $[\alpha]_D +29.4^\circ$ ($\pm 3.0^\circ$) in H₂O; 2:6-dimethyl-1-*l*-arabitylbenzimidazole, m.p. 235—236°, $[\alpha]_D^{20} +56.3^\circ$ ($\pm 2^\circ$); 2-carbethoxyaminophenyl-1-arabinosamine, m.p. 161° , apparently feebly dextrorotatory in H₂O; 2-carbethoxyamino-4:5-dimethylphenyl-1-arabinosamine, m.p. 175° , probably very feebly levorotatory in H₂O. H. W.

Synthesis of "ancient purple." W. ROTTIG (J. pr. Chem., 1935, [ii], 142, 35—36).—6:6'-Dibromindigotin (ancient purple) is prepared by Sachs and Sichel's method (A., 1904, i, 593) from 4-bromo-2-nitrobenzaldehyde [obtained by hydrolysis (conc. HCl) of its oxime, which is prepared from 4-bromo-2-nitrotoluene and EtO-NO in EtOH-NaOEt]. H. B.

Complex salts of 2:2'-dipyridyl with zinc and cadmium.—See this vol., 312.

Triazolium salts. III. Triazolium salts from azimides and ψ -azimides. F. KROLL-PFEIFFER, A. ROSENBERG, and C. MÜHLHAUSEN (Annalen, 1935, 515, 113—130; cf. A., 1934, 182, 785).—Methylation (Me₂SO₄, 2*N*-NaOH) of $\alpha\beta$ -naphtha-1:2:3-triazole (I) gives a mixture of the 1-Me (II), m.p. $86-87^\circ$ (picrate, m.p. $163-164^\circ$), 2-Me (III), m.p. 74.5° (picrate, m.p. $131-132^\circ$), and 3-Me (IV), m.p. $109-110^\circ$, derivatives; the Na derivative of (I) is, therefore, best represented as [C₁₀H₆ $\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$]-Na.⁺ 3-Ethyl- $\alpha\beta$ -naphtha-1:2:3-triazole, m.p. $74-75^\circ$ [prepared by the method of Morgan *et al.* (A., 1922, i, 181, 380)], and EtI at 100° (sealed tube) afford 1-methyl-3-ethyl- $\alpha\beta$ -naphtha-1:2:3-triazolium iodide, decomp. $197-198^\circ$ (picrate, m.p. $166-167^\circ$; periodide, m.p. $125-126^\circ$), also obtained from (II) and EtI. 3-Methyl-1-ethyl-, decomp. 205° (picrate, m.p. $185-186^\circ$; periodide, m.p. $130-131^\circ$), and 1:3-dimethyl- (V), decomp. $208-209^\circ$ (picrate, m.p. $185-186^\circ$), $\alpha\beta$ -naphtha-1:2:3-triazolium iodides are similarly prepared from (IV) and EtI and MeI, respectively. (III) and Me₂SO₄ at 100° give 2:3-dimethyl- $\alpha\beta$ -naphtha-1:2:3-triazolium methosulphate, decomp. $198-199^\circ$ (previous sintering), converted by conc. aq. KI into the iodide (VI), decomp. 168° , which is also formed (very slowly)

from (III) and an excess of MeI at room temp. Prolonged interaction of (III) and MeI at 100° affords (V); (VI) and MeI at 100° give (V) and a little (III). 2-Phenyl- α - β -naphtha-1 : 2 : 3-triazole (VII) (which does not react with MeI) and Me₂SO₄ similarly afford 2-phenyl-3-methyl- α - β -naphtha-1 : 2 : 3-triazolium methosulphate, decomp. 206—207° (previous sintering), which is reduced (alkaline Na₂S₂O₄) to 1-benzene-azo-*N*-methyl- β -naphthylamine. Oxidation (amyl nitrite, AcOH) of 1-benzene-azo-*N*-ethyl- β -naphthylamine and subsequent treatment with picric acid gives 2-phenyl-3-ethyl- α - β -naphtha-1 : 2 : 3-triazolium picrate, m.p. 181—182° [the corresponding ethosulphate is obtained from (VII) and Et₂SO₄]; the corresponding chloride, decomp. 100°, is reduced [(NH₄)₂S] to (VII) and undergoes thermal decomp. to (VII) and EtCl. Thermal decomp. of (V) and (VI) affords (I), (II), and (III).

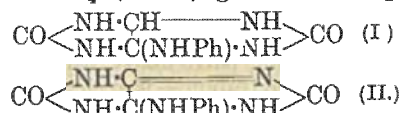
Methylation (Me₂SO₄, 2*N*-NaOH, or MeOH-MeI) of 1 : 2 : 3-benzotriazole (VIII) gives 55% of the 1-Me (IX), m.p. 65°, and 33% of the 2-Me (X), b.p. 103.5—104°/15 mm.; ethylation (EtBr, EtOH-NaOEt) affords a mixture of the 1-Et, b.p. 149.5°/12 mm., and 2-Et (XI), b.p. 108.5°/14 mm., derivatives. (VIII) and CH₂Cl·CO₂H in 2*N*-Na₂CO₃ give (cf. Reissert, A., 1914, i, 432) 1- and 2-benzotriazolylacetic acids, m.p. 212—213° and 223—224°, respectively, which when distilled afford (IX) and (X), respectively. (IX) and MeI at room temp. or 100° give 1 : 3-dimethyl-1 : 2 : 3-benzotriazolium iodide, decomp. 185° (picrate, m.p. 167—168°), also formed by prolonged interaction of (X) and MeI at 100°, which undergoes thermal decomp. to (mainly) (IX) and (X). 1 : 2-Dimethyl-1 : 2 : 3-benzotriazolium methosulphate (XII), m.p. 156—157° [from (X) and Me₂SO₄], is converted into the corresponding picrate, m.p. 121—122°, and iodide (XIII), decomp. 160° [a trace of which is obtained by prolonged interaction of (X) and MeI at room temp.]. Thermal decomp. of (XIII) also gives (mainly) (IX) and (X). Reduction (Na₂S₂O₄, 2*N*-NaOH) of (XII) in absence of air affords *o*-methylazomethylaniline, b.p. 99—102°/3 mm. 1-Methyl-2-ethyl-, m.p. 116—117°, and 2-methyl-1-ethyl-, m.p. 124—125°, 1 : 2 : 3-benzotriazolium picrates are prepared by the action of Me₂SO₄ etc. on (XI) and Et₂SO₄ etc. on (X), respectively. H. B.

Synthesis of 1 : 3 : 5-tripyrindylbenzene. W. JAROSZEWICZ and E. SUCHARDA (Rocz. Chem., 1934, 14, 1195—1197).—3-Pyridyl Me ketone and HCl at 180—185° (9 hr.) yield *s*-tripyrindylbenzene, m.p. 226°, not undergoing sulphonation or nitration even with the most conc. acids at high temp. R. T.

Colorimetric micro-determination of caffeine. G. DENIGÈS (Compt. rend., 1934, 199, 1622—1623).—Caffeine (I) (0.001—0.02 g.) may be determined by evaporation of its CHCl₃ solution, addition of 6 drops of Br-H₂O (saturated in the cold) and *N*-HCl to the residue, gentle evaporation to dryness and heating until a red colour is produced, addition of 10 c.c. of H₂O and 1 drop of 5% aq. Hg(OAc)₂-AcOH, and colorimetric comparison with a standard similarly prepared from pure (I). J. W. B.

Mechanism of autoxidation of uric acid. M. FRÉRETJACQUE (Compt. rend., 1934, 199, 1432—1434).

—Autoxidation (MnO₂ is a catalyst) of alkaline solutions of "isoallantoylaniline" (I) or oxidation by alkaline KMnO₄ (not I) gives the compound (II),



decomp. about 145°, only slowly affected by dil. alkali, but with cold, dil. mineral acids giving rapidly and quantitatively H₂C₂O₄, carbamide, and NH₂Ph. Autoxidation of uric acid (III) in presence of MnO₂ and NH₂Ph affords no (I), the formation of which, in absence of MnO₂, takes place to a greater extent the faster the oxidation proceeds. Addition of NH₂Ph to solutions of (III), freshly autoxidised in presence of MnO₂, does not afford (I). It is concluded that (I) is not formed from (III) and NH₂Ph without oxidation (cf. A., 1933, 427) and that the primary product of autoxidation of (III) is a dioxide, which is decomposed by certain catalysts to a ureide. This ureide can unite with amines, but the products are stable only in strongly alkaline solution, and in neutral or slightly alkaline solution lose CO₂ to give isoallantoin derivatives; the ureide rapidly isomerises to a second ureide, which undergoes the classical degradation. R. S. C.

Attempts to synthesise uric acid from nine-membered cycloids. P. C. GUHA and M. N. RAMASWAMI (J. Indian Chem. Soc., 1934, 11, 811—822).—Hydrolysis of (·CO·NH·CO₂Et)₂ (I) (improved prep.) with boiling dil. HCl gives carbethoxyoxamic acid CO₂H·CO·NH·CO₂Et + 3H₂O, m.p. 133—134°. Condensation of (I) with 1 mol. of CO(NH₂)₂ (II) at 120—125° affords Et allophanate (III), carbethoxyoxamide, m.p. 155—156°, carboxalylldicarbamide, CO<NH·CO·NH·CO<NH·CO·NH·CO, m.p. > 300°, dicarbamyloxalylldiurethane, [·CO·N(CO₂Et)·CO·NH₂], m.p. 230°, and a substance, not melting at 330°. With > 2 mols. of (II) at 135—140° is obtained oxalylldiuret (·CO·NH·CO·NH·CO·NH₂)₂, m.p. 185—186°. With aq. NH₃ (I) gives oxalylbiuret, m.p. 235°, and oxalylldicarbamide, m.p. > 350°; and CO₂Et·NH·CH₂·CO₂Et affords an amide, m.p. 105°, probably CO₂Et·NH·CH₂·CO·NH₂. When heated with Ph₂CO₃ at 170—180°, NH₂·CO·NH·CH₂·COR (IV, R=NH₂) affords glycolylbiuret (V), m.p. 220—221°, similar condensation of the ester (R=OEt) with (II) giving (V) and glycolylldicarbamide, m.p. 236°, also obtained from either (IV) or hydantoin and (II). Condensation of CO(NH·CO₂Et)₂ with C₂H₄(NH₂)₂ affords (III) and carbethylenedicarbamide, CO<NH·CO·NH·CH<NH·CO·NH·CO, m.p. 275—276°, converted by hot conc. HCl into (?) deoxyuric acid, CO<NH·CH₂·C·NH<NH·CH₂·C·NH, not melting at 340°. J. W. B.

Action of chlorine on methylated and acetylated uric acids. H. BILTZ and H. PARDON (Annalen, 1935, 515, 201—252; cf. A., 1932, 1044).—The reactions have been studied with particular reference to the role of the solvent. Uric acid (I) is unaffected by Cl₂ in CHCl₃ or anhyd. AcOH; in aq. AcOH [H₂O : (I) = 1 : 1], 5-chloro- ψ -uric acid

results, whereas fission to alloxan and $\text{CO}(\text{NH}_2)_2$ occurs when $(\text{I}) : \text{H}_2\text{O} = 1 : 5$. Chlorination in Ac_2O leads to 4-chloro-5-acetoxy-9-acetyldihydrouic acid, also obtained from 9-acetylluric acid, whereas the 7-Ac-acid gives 5-chloro-7-acetylisouric acid. 1-Methyluric acid (II) and Cl_2 in CHCl_3 afford 5-chloro-1-methyl- ψ -uric acid (+AcOH), converted by MeOH and EtOH, respectively, into the 5-alkoxy-acid, m.p. 192° and 216° (decomp.). In Ac_2O containing anhyd. AcOH (II) is transformed into 4-chloro-5-acetoxy-9-acetyl-1-methyldihydrouic acid (III), decomp. $>290^\circ$ [reduced by KI to (II)], which reacts violently with boiling H_2O giving methylalloxan, whereas at room temp. a substance, $\text{C}_{10}\text{H}_{12}\text{O}_7\text{N}_4$, m.p. $205\text{--}208^\circ$ (slight decomp.) [reduced to (II)], is produced. With cold or boiling MeOH or EtOH (III) yields 9-acetyl-4-methoxy-, m.p. 212° (slight decomp.), and 9-acetyl-4-ethoxy-, m.p. 228° (decomp.), 5-acetoxy-1-methyldihydrouic acid. Treatment of (III) with $\text{KI-H}_2\text{O}$ gives 9-acetyl-1-methyluric acid, darkening $>320^\circ$, converted by uncontrolled action of CH_2N_2 into 8-methoxycaffeine and by CH_2N_2 in cooled Et_2O into 9-acetyl-6:8-dihydroxy-2-methoxy-1:7-dimethylpurine, m.p. 162° (decomp.). 7-Acetyl-8-acetoxy-1-methylxanthine and Cl_2 in Ac_2O , CHCl_3 , or AcOH afford 5-chloro-7-acetyl-1-methyl- $\Delta^4:9$ -isouric acid (IV), m.p. 201° (decomp.), transformed by short treatment with warm MeOH into 7-acetyl-1-methyluric acid glycol Me_2 ether, m.p. 176° (slightly decomp.) (which yields the corresponding Me_1 ether, m.p. 196° , with 50% AcOH), and by boiling EtOH in 5-ethoxy-1-methyl- ψ -uric acid, m.p. 216° (decomp.). (IV) and hot H_2O yield 1-acetyl-7-methylcaffolide (V), m.p. 192° , transformed by pure CH_2N_2 into 1-acetylisapocaffeine, m.p. 113° , and by $\text{CH}_2\text{N}_2\text{-MeOH}$ into 1:3:7-trimethylcaffolide (VI), m.p. 204° . Hydrolysis of (V) with EtOH-HCl leads to 7-methylcaffolide, m.p. $193\text{--}194^\circ$, which yields (VI) with CH_2N_2 . 3-Methyluric acid and Cl_2 in AcOH- Ac_2O , CHCl_3 , or Ac_2O afford 5-chloro-3-methylisouric acid, m.p. $175\text{--}180^\circ$ (decomp.) after becoming discoloured at 150° . 5-Chloro-7-acetyl-3-methyl- $\Delta^4:9$ -isouric acid, m.p. (indef.) 195° (decomp.), from Cl_2 and 7-acetyl-3-methyluric acid in Ac_2O , AcOH, or CHCl_3 , gives 3-methyluric acid glycol Et_1 ether, m.p. 203° (decomp.), with EtOH and methylalloxan and $\text{CO}(\text{NH}_2)_2$ with H_2O . 5-Chloro-7-methyl- $\Delta^4:9$ -isouric acid, decomp. $>300^\circ$ after darkening $>200^\circ$ [transformed by MeOH into 7-methyluric acid glycol Me_2 ether, m.p. 211° (decomp.)], is the sole product of the chlorination of 7-methyluric acid or its Ac derivative. 9-Methyluric acid and Cl_2 in anhyd. AcOH give 5-chloro-9-methyl- ψ -uric acid, decomp. 210° , whereas (?) 9-methyluric acid 4:5-dichloride (VII), gradual decomp. $>300^\circ$, is formed in CHCl_3 and 4(5)-chloro-5(4)-acetoxy-9-methyldihydrouic acid (VIII) is produced in Ac_2O . On exposure to moist air (VIII) becomes transformed into 9-methyluric acid glycol, m.p. 208° (decomp.), whilst with EtOH it gives 5-ethoxy-9-methyl- ψ -uric acid, m.p. 222° (decomp.); when its solution in Ac_2O is exposed to air it gives 5-chloro-9-methyl- ψ -uric acid, m.p. 208° (decomp.). 7-Acetyl-9-methyluric acid in CHCl_3 appears to give a mixture of (VII) and its Ac derivative; in Ac_2O or, preferably, AcOH + H_2O , 4-chloro-7-acetyl-5-hydroxy-9-methyldihydrouic

acid, m.p. 198° (decomp.), is produced, converted by boiling EtOH into 4-chloro-5-hydroxy-9-methyldihydrouic acid, m.p. 212° (decomp.).

1:3-Dimethyluric acid in AcOH- H_2O gives 5-chloro-1:3-dimethyl- ψ -uric acid, whereas in CHCl_3 , Ac_2O , or anhyd. AcOH 5-chloro-1:3-dimethyl- $\Delta^4:9$ -isouric acid (IX), m.p. 225° (decomp.), converted by H_2O or alcohols into 1:3-dimethyluric acid glycol or its ethers, results. 7-Acetyl-1:3-dimethyluric acid in Ac_2O or anhyd. AcOH yields 5-chloro-7-acetyl-1:3-dimethyl- $\Delta^4:9$ -isouric acid, m.p. 162° (decomp.), whereas (IX) results in CHCl_3 . 1:7-Dimethyluric acid (X) in AcOH, Ac_2O , or AcOH- Ac_2O gives 5-chloro-1:7-dimethyl- $\Delta^4:9$ -isouric acid, m.p. 161° (decomp.) after softening at about 130° , transformed by HCl in AcOH into 4:5-dichloro-1:7-dimethyl-4:5-dihydrouic acid, m.p. 163° (decomp.), converted by H_2O into apocaffeine and by MeOH into 1:7-dimethyluric acid glycol Me_2 ether, m.p. 171° . (X) and Cl_2 in AcOH containing 3% of H_2O give 5-chloro-4-hydroxy-1:7-dimethyl-4:5-dihydrouic acid, m.p. 130° (slight decomp.). 8-Acetoxy-1:7-dimethylxanthine in Ac_2O , AcOH, or CHCl_3 affords 5-chloro-1:7-dimethyl- $\Delta^3:4$ -isouric acid, m.p. 175° (decomp.). 1:9-Dimethyluric acid (improved prep.) yields 4-chloro-1:9-dimethyl- $\Delta^5:7$ -isouric acid (XI), m.p. 198° (decomp.), in Ac_2O , AcOH, or (+1CHCl₃) in CHCl_3 . 7-Acetyl-1:9-dimethyluric acid and Cl_2 in CHCl_3 give (XI), whereas in Ac_2O or AcOH 5-chloro-7-acetyl-1:9-dimethyl- $\Delta^3:4$ -isouric acid, m.p. 168° (slight decomp.), results, which does not react with boiling EtOH. 5-Chloro-3:7-dimethylisouric acid, m.p. 168° (decomp.), arises from 3:7-dimethyluric acid in Ac_2O as in CHCl_3 . 4(5)-Chloro-5(4)-acetoxy-7:9-dimethyldihydrouic acid, m.p. 132° (decomp.), is obtained in Ac_2O ; similarly, 5-chloro-1:3:7-trimethylisouric acid, m.p. 158° (decomp.), is obtained from 1:3:7-trimethyluric acid. In AcOH 1:3:9-trimethyluric acid gives 4-chloro-1:3:9-trimethylisouric acid, whilst in CHCl_3 4:5-dichloro-1:3:9-trimethyldihydrouic acid, m.p. about 171° (decomp.), results (converted by alcohols into 5-alkoxy-1:3:9-trimethyl- ψ -uric acids) and in AcOH 4(5)-chloro-5(4)-acetoxy-1:3:9-trimethyldihydrouic acid, m.p. 126° (decomp.), is formed (converted by alcohols into 1:3:9-trimethyluric acid glycol alkyl₁ ethers). 7-Acetyl-1:3:9-trimethyluric acid (XII) in CHCl_3 gives 4:5-dichloro-7-acetyl-1:3:9-trimethyldihydrouic acid, m.p. 168° (slight decomp.), converted by cold MeOH or EtOH into 4-hydroxy-5-methoxy- (XIII), m.p. 215° , and 4-hydroxy-5-ethoxy- (XIV), m.p. 205° , 7-acetyl-1:3:9-trimethyldihydrouic acid. In Ac_2O or anhyd. AcOH (XII) yields 4-chloro-5-acetoxy-7-acetyl-1:3:9-trimethyldihydrouic acid, m.p. 185° (decomp.), transformed by warm H_2O into 1-acetylisapocaffeine, by the requisite boiling alcohol into (XIII) and (XIV), respectively, and by NH_3 - or $\text{NH}_2\text{Me-EtOH}$ into 4-amino-, m.p. 165° , and 4-methylamino-, m.p. 201° (slight decomp.), 5-hydroxy-7-acetyl-1:3:9-trimethyl-4:5-dihydrouic acid, respectively, which do not form salts with HClO_4 , H_2PtCl_6 , HAuCl_4 , or picric acid. Solid products could not be obtained from Cl_2 and 1:7:9-trimethyluric acid in CHCl_3 or Ac_2O , whereas in AcOH allocaffeine (XV) is formed. When very small amounts of solvent

are used, 3:7:9-trimethyluric acid in CHCl_3 gives 4:5-dichloro-3:7:9-trimethyl-4:5-dihydrouric acid, m.p. 138° (decomp.) [yielding 3:7:9-trimethyluric acid glycol and (XV) with H_2O], in Ac_2O 4-chloro-5-acetoxy-3:7:9-trimethyldihydrouric acid, m.p. 125—130° (decomp.), and in 90% AcOH 4(5)-chloro-5(4)-hydroxy-3:7:9-trimethyldihydrouric acid, m.p. 132° (decomp.). Similarly, by use of regulated amounts of solvent 1:3:7:9-tetramethyluric acid affords in CHCl_3 4:5-dichloro-1:3:7:9-tetramethyldihydrouric acid, m.p. 132° (decomp.), in Ac_2O 4-chloro-5-acetoxy-1:3:7:9-tetramethyldihydrouric acid, m.p. 134° (decomp.), and in AcOH a substance which may be a Cl-OH- or a Cl_2 -compound (+ AcOH). H. W.

Fractionation and purification of organic substances by chromatographic adsorption. III. Is there a chlorophyll *c*? A. WINTERSTEIN and K. SCHON (Z. physiol. Chem., 1934, 230, 139—145).—Contrary to Zscheile (A., 1934, 1115), a third chlorophyll does not exist; the use of talcum as an adsorbent (cf. *loc. cit.*) causes the formation of decomp. products. Previous work (*ibid.*, 91) on chlorophyll, using sucrose as adsorbent, is confirmed. Improved apparatus for separation of relatively large amounts of substances is described. H. B.

Chlorophyll. LI. Partial synthesis of ethylchlorophyllide *b*; 10-ethoxymethylphæophorbide *b*. H. FISCHER and G. SPIELBERGER. LII. Constitution of colouring matter of purple bacteria; 9-hydroxydeoxophæoporphyrin *a*₅. H. FISCHER and J. HASENKAMP (Annalen, 1935, 515, 130—148, 148—164).—LI. Ethylphæophorbide *b* is converted into ethylchlorophyllide *b* by the method previously described (A., 1934, 785) for the *a* compound. Methylchlorophyllide *a*+*b* and benzoquinone (I) in EtOH and N_2 give 10-ethoxymethylphæophorbide *a*, $\text{C}_{38}\text{H}_{40}\text{O}_6\text{N}_4$, m.p. > 320°, and 10-ethoxymethylphæophorbide *b* (II), $\text{C}_{38}\text{H}_{40}\text{O}_7\text{N}_4$, m.p. > 320°, separable by fractionation from Et_2O with HCl . (II) is converted by HI-AcOH at 65° into a little 10-ethoxyphæoporphyrin *b*₆ *Me*₂ ester, $\text{C}_{38}\text{H}_{40}\text{O}_7\text{N}_4$, m.p. 275°, also obtained (details to be published) from phæoporphyrin *b*₆ and EtOH-I . Reduction (H_2 , Pd-black , AcOH) of ethylchlorophyllide *a* (III) (modified prep.; cf. *loc. cit.*) results in the absorption of about 6 H; reoxidation affords phæoporphyrin *a*₅ *Et* ester, m.p. 269°. Allomerisation of (III) with (I) in EtOH , subsequent reduction, and re-oxidation gives mainly 10-ethoxyphæoporphyrin *a*₅ *Et* ester, m.p. 288°. Reduction (H_2 , Pd , dioxan or COMe_2) of (III) results in the uptake of approx. 2 H only; the resulting non-cryst. dihydro-derivative gives a positive phase test, is decomposed by HCl to dihydrophæophorbide *a* (IV), and with (I) in EtOH affords 10-hydroxydihydroethylphæophorbide *a*, $\text{C}_{37}\text{H}_{42}\text{O}_6\text{N}_4$, m.p. about 260°. Reduction (H_2 , Pd , COMe_2) of methylphæophorbide *a* (V) (oxime) and re-oxidation of the leuco-compound in neutral solution gives (IV); re-oxidation occurs more slowly in AcOH-HCl and affords (IV) and phæoporphyrin *a*₅. The leuco-compound formed during neutral reduction of (V) or the *Et* analogue probably undergoes partial rearrangement into the leuco-porphyrin. Phæophorbide *a* (oxime) and $\text{Et}_2\text{O-CH}_2\text{N}_2$ in COMe_2 give (V);

(IV) (in $\text{C}_5\text{H}_5\text{N}$) affords dihydromethylphæophorbide *a*, m.p. 219° (sinters at 215°) (oxime, m.p. 215°) (cf. A., 1933, 1308).

LII. Bacteriochlorophyll (I), obtained by extraction (80% COMe_2) of *Thiocystis* or *Rhodovibrio*, is converted by 10% HCl into bacteriophæophytin *a* (II), which with MeOH-HCl gives bacteriomethylphæophorbide *a* (III), $\text{C}_{36}\text{H}_{38}\text{O}_6\text{N}_4$, m.p. 260°. The Et_2O mother-liquors from (II) and (III) contain a small amount of a phorbide-like compound (? *b* series) (III) gives an oxime, is converted by $\text{Et}_2\text{O-CH}_2\text{N}_2$ in $\text{MeOH-C}_5\text{H}_5\text{N}$ into bacteriochlorin *Me*₂ ester, $\text{C}_{37}\text{H}_{40}\text{O}_7\text{N}_4$, m.p. 205° (which can be oximated), and with HI (d 1.96) in AcOH at 65° affords oxophæoporphyrin *a*₅ and an unidentified porphyrin. A structure is suggested for (III). The bacteriochlorophyll of Noack and Schneider (A., 1934, 112, 1265) is considered to be identical with (I) and not to be related to the *b* series.

Oxochloroporphyrin *e*₅ and $\text{Et}_2\text{O-CH}_2\text{N}_2$ in $\text{COMe}_2\text{-C}_5\text{H}_5\text{N}$ give a *Me*₂ ester, m.p. 279°, which differs from that (m.p. 288°) obtained using MeOH-HCl ; structures analogous to those for the *Me*₂ esters of chloroporphyrin *e*₅ (A., 1933, 402) are assigned. Reduction (H_2 , Pd , HCO_2H) of phæoporphyrin *a*₅ (IV) affords 9-hydroxydeoxophæoporphyrin *a*₆, $\text{C}_{36}\text{H}_{40}\text{O}_6\text{N}_4$, m.p. 281°, which is oxidised ($\text{CrO}_3\text{-AcOH}$) to (IV); short treatment with *S* in oleum gives (IV) and some phæoporphyrin *a*₇. H. B.

Porphyrins. XXXI. Synthesis of tetramethyltetrapropylbilirubinooids, tetramethyltetraethylporphyrin I, II, and IV, tetramethyltetraisobutylporphyrin I, and di-(β-carboxyethyl)tetramethyldipropylporphyrin. XIII. H. FISCHER and M. BERTL. XXXII. Amino- and vinyl-porphyrin and some derivatives. H. FISCHER and E. HAARER. XXXIII. Synthesis of 2:3:6:7-tetra-(αβ-dicarboxyethyl)-1:4:5:8-tetramethylporphyrin. isoUroporphyrin I. H. FISCHER and E. VON HOLT (Z. physiol. Chem., 1934, 229, 37—54, 55—70, 93—102; cf. A., 1934, 1371).—XXXI. With AgOAc or NaOMe , 5-bromo-4:3':5'-trimethyl-3:4'-dipropylpyrromethene hydrobromide gives 5-hydroxy-4:3':5'-trimethyl-3:4'-dipropylpyrromethene (I), m.p. 202°. Bromination of (I) affords a mixture of a dihydrobromide (Gmelin negative) of a base, $\text{C}_{35}\text{H}_{46}\text{O}_3\text{N}_4$, m.p. 280—282° (decomp.), and a trihydrobromide (Gmelin positive) of a 1:10-dihydroxy-2:4:7:9-tetramethyl-3:5:6:8-tetrapropyltetrapyrro-11:14:18-triene. 5-Carbethoxy-2:4-dimethylpyrrole (II) with PrCOCl and AlCl_3 gives 5-carbethoxy-3-butyl-2:4-dimethylpyrrole, m.p. 117°, yielding the carboxylic acid (III), m.p. 182°, on hydrolysis. Decarboxylation of (III) by heating affords 3-butyl-2:4-dimethylpyrrole (IV), m.p. 76°. With $\text{HCO}_2\text{H-HBr}$, (IV) gives cryst. 4:4'-dibutyl-3:5:3':5'-tetramethylpyrromethene hydrobromide, with $\text{MeOH-CH}_2\text{O}$ the corresponding methane, m.p. 184°. With HCN , (IV) yields 5-formyl-3-butyl-2:4-dimethylpyrrole, m.p. 161°. Wolff-Kishner reduction of (IV) affords 2:4-dimethyl-3-butylpyrrole (V), b.p. 100—120°/12 mm. (picrate, m.p. 141°). With HCN , (V) gives 5-formyl-2:4-dimethyl-3-butylpyrrole, m.p. 85°. Bromination of (V) in AcOH-

CCl_4 gives a cryst. mixture (VI) of 5-bromo-3':4:5'-trimethyl- and 5-bromo-3':4-dimethyl-5'-bromomethyl-3:4'-dibutylpyrromethene hydrobromides, which on fusion with succinic acid at $170\text{--}180^\circ$ affords 1:3:5:7-tetramethyl-2:4:6:8-tetrabutylporphyrin, m.p. 229° [*Fe* (hæmin), m.p. 289° , *Cu*, m.p. 277° , complex salts]. By Grignard reaction and ClCO.Et , (V) gives 5-carbomethoxy-2:4-dimethyl-3-butylpyrrole, m.p. 99° , brominated to 5-carbomethoxy-4-methyl-2-bromomethyl-3-butylpyrrole (VII), m.p. 131° . When heated with MeOH , (VII) gives 5:5'-dicarbomethoxy-4:4'-dimethyl-3:3'-dibutylpyrromethane, m.p. 107° , yielding the dicarboxylic acid (VIII), which with Br-AcOH affords 5:5'-dibromo-4:4'-dimethyl-3:3'-dibutylpyrromethene hydrobromide (IX) (free base, m.p. 113°). With HCO.H-HBr , (V) gives 3:3':5:5'-tetramethyl-4:4'-dibutylpyrromethene hydrobromide (X) [free base, m.p. 210° (decomp.)]. Fusion of (IX) and (X) at 180° in methylsuccinic acid gives 1:4:6:7-tetramethyl-2:3:5:8-tetrabutylporphyrin (XI), m.p. $217\text{--}218^\circ$ (hæmin, m.p. 243° ; *Cu* complex salt, m.p. 230°), in poor yield. Bromination of (X) in AcOH at 100° gives 3:3'-dimethyl-5:5'-dibromomethyl-4:4'-dibutylpyrromethene hydrobromide, which on fusion with (IX) gives (XI) in good yield. (VIII), mixed with HCO_2H and aerated at $30\text{--}35^\circ$, or better, in boiling AcOH affords 1:4:5:8-tetramethyl-2:3:6:7-tetrabutylporphyrin, m.p. 284° [hæmin, m.p. 259° , *Cu* complex salt, m.p. $313\text{--}315^\circ$ (decomp.)]. By similar methods (II) yields successively 5-carbomethoxy-3-isobutyl-2:4-dimethylpyrrole, m.p. 108° , 2:4-dimethyl-3-isobutylpyrrole, b.p. $98\text{--}108^\circ/12\text{ mm.}$ (picrate, m.p. 131°), pyrromethene mixture, 1:3:5:7-tetramethyl-2:4:6:8-tetraisobutylporphyrin, m.p. $209\text{--}210^\circ$. Fusion of 3:3'-dimethyl-5:5'-dibromomethyl-4:4'-dipropylpyrromethene hydrobromide with 5:5'-dibromo-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)-pyrromethene in succinic acid at $200\text{--}210^\circ$ yields 2:3:5:8-tetramethyl-6:7-di-(β -carboxyethyl)-1:4-dipropylporphyrin, m.p. $< 300^\circ$, HCl no. 3 [*Cu* salt, m.p. 312° ; hæmin, m.p. $< 420^\circ$; Me_2 ester, m.p. 216° (*Cu* salt, m.p. 260° ; hæmin, m.p. 228°)].

XXXII. 1:3:5:8-Tetramethyl-2:4-diethyl-7- β -carboxyethylporphyrin (pyrroporphyrin XV Me ester) with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in MeOH at 135° yields the hydrazide (I), m.p. 273° (*Cu* salt, m.p. 360°), which with HNO_2 gives the azide (II). In boiling C_6H_6 , (II) affords the β -isocyanic acid, m.p. 252° , in MeOH the methylurethane (III), m.p. 231° , and with NH_4Ph the β -phenylcarbamide. With 10% HCl at $130\text{--}140^\circ$, (III) gives the hydrochloride, m.p. $< 360^\circ$, of α -aminoethyl-1:3:5:8-tetramethyl-2:4-diethylporphyrin (IV), m.p. 194° [NH_2 substitution derivatives: Br , m.p. 301° (*Cu* salt, m.p. 304°); Ac , m.p. 276° (*Cu* salt, m.p. 251°); $\text{Me}_2\text{-MeSO}_4$ (V), m.p. $> 320^\circ$]. Heated with KOH-MeOH , (V) yields 1:3:5:8-tetramethyl-2:4-diethyl-7-vinylporphyrin (VI), m.p. 269° (*Cu* salt, m.p. $229\text{--}230^\circ$), reduced (HI-AcOH) to pyrroetioporphyrin. (VI) adds Et diazoacetate at the double linking. With Br-AcOH in CHCl_3 , (VI) gives 6:7-dibromo-1:3:5:8-tetramethyl-2:4-diethylporphyrin, m.p. $< 360^\circ$, and a substance, decomp. 193° . (VI) adds HBr , but the product is hydrolysed to 1:3:5:8-tetramethyl-2:4-diethyl-7- α -hydroxyethylporphyrin, m.p. 246 , from which H_2SO_4 or heating at 120°

in vac. removes H_2O , regenerating (VI). KMnO_4 (1 mol.) eliminates N from (I) and closes the γ -methine bridge yielding pyrrohodin.

XXIII. Treatment of 5-bromo-4:3':5'-trimethyl-3:4'-di-(β -dicarbomethoxyethyl)pyrromethene hydrobromide with HBr and esterification of the product with MeOH-HCl gives 1:3:5:7-tetramethyl-2:4:6:8-tetra-(β -dicarbomethoxyethyl)porphyrin (I) (isouroporphyrin Me_2 ester), m.p. 284° [*Cu*, m.p. 289° , *Ni*, m.p. 272° , *Ag*, m.p. 290° , *Fe* (hæmin), m.p. 256° , salts]. (I) on hydrolysis yields the free octacarboxylic acid [*Fe* salt (halogen-free internal anhydride)]. With Br in Et_2O , 5-carbomethoxy-2:4-dimethyl-3- α -dicarboxyethylpyrrole (II) (A., 1932, 626) affords the 2-bromomethyl derivative, m.p. $157\text{--}158^\circ$ (decomp.), which in H_2O at 100° gives bis-(5-carbomethoxy-4-methyl-3- α -dicarboxyethylpyrrol)-2-methane, m.p. 138° (decomp.) [Na_2 salt (III) of hexa-acid]. In a current of air, (III) in HCO_2H at $40\text{--}45^\circ$ gives 1:4:5:8-tetramethyl-2:3:6:7-tetra-(α - β -dicarboxyethyl)porphyrin [Me_2 ester (IV), m.p. $317\text{--}318^\circ$ (*Cu*, m.p. $< 290^\circ$, *Fe* salts)]. With 1% HCl at $180\text{--}188^\circ$, (IV) yields an Et_2O -sol. porphyrin identical with coproporphyrin II ester. Hydrolysis of (II) with 5% aq. NaOH affords 5-carboxy-2:4-dimethyl-3- α -dicarboxyethylpyrrole (V), m.p. 198° (decomp.), which is unstable and is readily decarboxylated to 2:4-dimethyl-3- α -dicarboxyethylpyrrole (VI), m.p. $173\text{--}174^\circ$. The main product of the action of HI-AcOH on (V) is (probably) tri-iodo-2:4-dimethyl-3- α -dicarboxyethylpyrrole, m.p. $188\text{--}189^\circ$ (decomp.). With $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$ and HClO_4 , (VI) affords 2:4-dimethyl-3- α -dicarboxyethylpyrro-p-dimethylaminophenylmethene perchlorate, m.p. $199\text{--}200^\circ$. Oxidation of (II) with CrO_3 in aq. H_2SO_4 gives a product $\text{C}_9\text{H}_9\text{O}_6\text{N}$, m.p. $184\text{--}185^\circ$, probably a carb-oxylated hæmatic acid. J. H. B.

Bile pigments. XIV. Synthesis of methoxy-pyrromethenes and bilirubinoid pigments. H. FISCHER and J. ASCHENBRENNER (Z. physiol. Chem., 1934, 229, 71—92; cf. A., 1934, 1234).—Hydrolysis of 5:5'-dicarbomethoxy-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)pyrromethane with 10% aq. NaOH for 15 min. yields a mixture (I), m.p. $186\text{--}187^\circ$, of tri- and tetra-carboxylic acids, consisting mainly of the 5'- CO_2H product. With Br-AcOH , (I) gives the hydrobromides (II) of 5:5'-dibromo- (III) and 5-bromo-5'-carbomethoxy-pyrromethenes. Crystallisation from HCO_2H eliminates Et_2O and gives a mixture, m.p. 210° (decomp.). With MeOH-HCl , (II) affords as the hydrochloride, m.p. 200° (decomp.), 5:5'-dibromo-4:4'-dimethyl-3:3'-di-(β -carbomethoxyethyl)pyrromethene, m.p. 136° , and 5-hydroxy-5'-carboxy-4:4'-dimethyl-3:3'-di-(β -carbomethoxyethyl)pyrromethene (IV), m.p. 231° [*Me* ether *Me* ester (V), m.p. 94°]. With KOH-MeOH , (III) yields 5'-bromo-5-methoxy-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)pyrromethene (VI) [Me_2 ester, m.p. 93° {hydrochloride, m.p. 130° (darkens), decomp. 174°)]. With KOH in MeOH , (II) gives a mixture of the K salt of (VI), 5-bromo-5'-carboxy- (VII) (Me_2 ester, m.p. 130°) and 5'-carboxy-5-methoxy-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)pyrromethene (VIII) (decomp. $210\text{--}218^\circ$). (VI) and (VIII) are separated in the form of the Me_2 esters. With NH_2Ph in MeOH or EtOH ,

(II) gives 5-anilino-5'-carboxy-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)pyrromethene, m.p. 213° (decomp.) (Me_3 ester, m.p. 130°). (VIII) yields Me_2 (dicarbomethoxyethyl), m.p. 167°, and Me_3 [identical with (V)] esters. With CH_2O-HCl , (VIII) gives di-[5-methoxy-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)pyrromethene]methane (IX) (dimethoxycoprobilirubin), m.p. 253° (decomp.) [Me_4 ester (with CH_2N_2), m.p. 152—153°]. (IX) with $MeOH-HCl$ gives a mixture of $(OH)_2$ - and $(OMe)_2$ -esters, which with $FeCl_3$ affords a ferrobilin, m.p. 160°. Decarboxylation of (IV) at 230—240°/vac. gives 5-hydroxy-4:4'-dimethyl-3:3'-di-(β -carbomethoxyethyl)pyrromethene, m.p. 172°, yielding the methane, m.p. 190° (decomp.) (ferrobilin, m.p. 160°). Prolonged hydrolysis of the dicarbomethoxy-compound with $NaOH$ in aq. $EtOH$ gives 5:5'-dicarboxy-4:4'-dimethyl-3:3'-diethylpyrromethane (X) (A., 1927, 1206). Shorter hydrolysis gives a mixture of (X) and the 5'-carbomethoxy-5-carboxylic acid, which with $Br-AcOH$ gives 5-bromo-5'-carbomethoxy- (XI) and 5:5'-dibromo-4:4'-dimethyl-3:3'-diethylpyrromethene (XII) hydrobromides. With $KOH-MeOH$, (XII) yields the 5'-bromo-5-methoxy-derivative, m.p. 107°; the pyrromethene mixture also gives the 5-carboxy-5'-methoxy-product (XIII), m.p. 191° (decomp.), isolated as Me ester, m.p. 93°. With NH_2Ph , (XII) affords 5:5'-dianilino-4:4'-dimethyl-3:3'-diethylpyrromethene (XIV), m.p. 165°, isolated as the hydrobromide, decomp. 260—265°. The (XI) and (XII) mixture also gives 5-anilino-5'-carboxy-4:4'-dimethyl-3:3'-diethylpyrromethene, m.p. 226° (decomp.) (Me ester, m.p. 147°). With 40% CH_2O and conc. HCl , (XIII) gives, as hydrochloride, darkens 160°, m.p. 247° [di-(5-methoxy-4:4'-dimethyl-3:3'-diethylpyrromethene)]methane (XV) (Me_2 ether of isoxetibilirubin), m.p. 181° (decomp.) (ferrobilin, m.p. 265°). With $NaOMe$ at 180—185°, (XIII) gives the 5- OH -compound, m.p. < 230° (decomp.) (ferrobilin, m.p. 265°), corresponding with (XV); with $KOH-PrOH$, (XIII) yields 5-hydroxy-4:4'-dimethyl-3:3'-diethylpyrromethene (XVI), m.p. 200°, which with CH_2O-HCl affords the bilirubinoid, m.p. 265° (decomp.). With $MeOH-HCl$, (XIII) gives 5-hydroxy-5'-carboxy-4:4'-dimethyl-3:3'-diethylpyrromethene, m.p. 234° (decomp.). Fusion of (XIII) in resorcinol yields a product, m.p. 197°. Esterification of 5:5'-dibromo-3:3'-dimethyl-4:4'-di-(β -carboxyethyl)pyrromethene (XVII) with $MeOH-HCl$, but not with CH_2N_2 , gives as the hydrochloride, m.p. 202° (decomp.), the Me_2 ester, m.p. 158°. With $KOH-MeOH$, (XVII) affords 5'-bromo-5-methoxy-3:3'-dimethyl-4:4'-di-(β -carboxyethyl)pyrromethene [Me_2 ester, m.p. 131° (hydrochloride, m.p. 175°)]. J. H. B.

Compounds with condensed pyrrole nuclei, having behaviour analogous to urobilin. G. ILLARI (Gazzetta, 1934, 64, 883—893).—Pyrrole treated with SO_2 in H_2O polymerises slowly to two dark substances, $(C_{18}H_{35}O_{15}N_5S_3)_n$ (I), sol. in $MeOH$, and $(C_8H_{14}O_4N_2S)_m$ (II), insol. (I) and (II) do not melt; the action of diazotised anthranilic acid on either in aq. solution yields the substance, $C_{78}H_{67}O_{20}N_{15}S_2$, no m.p. Both resemble urobilin in giving the Ehrlich reaction, and in absorption bands with mean at 496 $m\mu$. Structures are suggested. E. W. W.

Preparation of 1-thiolbenzthiazole. R. F. DUNBROOK and M. H. ZIMMERMANN (J. Amer. Chem. Soc., 1934, 56, 2734—2736).—1-Thiolbenzthiazole is obtained in about 90% yield from $o-C_6H_4ClNO_2$ (1 mol.), aq. Na_2S_3 (3 mols.), and CS_2 at 85—90° for 3 hr. The following changes probably occur: $2o-C_6H_4ClNO_2 \rightarrow (o-NO_2 \cdot C_6H_4)_2S_2 \rightarrow (o-NH_2 \cdot C_6H_4)_2S_2$ or $2o-NO_2 \cdot C_6H_4 \cdot SH \rightarrow 2o-NH_2 \cdot C_6H_4 \cdot SH \xrightarrow{CS_2} 2C_6H_4 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > C \cdot SH$. H B.

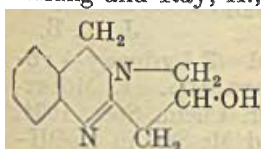
Directive effect of cyano- and iodo-substituents on the thiazole cyclisation of *pp*-disubstituted thiocarbanilides by bromine. M. O. FAROOQ and R. F. HUNTER (Rec. trav. chim., 1935, 54, 122—128).—The following condensations are in agreement with anticipations from the *m*-directing effect of CN and the relative dipole moments of PhI , $PhBr$, and $PhCl$. $p-CN \cdot C_6H_4 \cdot NH_2$ (I), m.p. 88°, and $CSCl_2$ in H_2O give $p-CN \cdot C_6H_4 \cdot NCS$, m.p. 122° (cf. lit.), which with $p-C_6H_4Me \cdot NH_2$ gives *s-p*-cyanophenyl-*p*-tolylthiocarbamide (*p*-cyano-*p*-methylthiocarbamide), m.p. 170° [hydroperbromide, m.p. 156° (decomp.)]. This with Br in $CHCl_3$ gives 1-*p*-cyanoanilino-5-methylbenzthiazole, m.p. 222—223°, also obtained from 1-chloro-5-methylbenzthiazole and (I). Similarly are obtained *s-p*-cyanophenyl-*p*-bromo-, m.p. 180°, -chloro-, m.p. 174—175° [hydroperbromide, m.p. 165° (decomp.)], and iodo-phenylthiocarbamide, m.p. 182° [hydroperbromide, m.p. 173° (decomp.)], *s-p*-iodophenyl-*p*-tolylthiocarbamide, m.p. 186° (hydroperbromide), and *s-p*-nitro-, m.p. 189—190° [hydroperbromide, m.p. 156° (decomp.)], -chloro-, m.p. 190° (hydroperbromide), and -bromo-phenyl-*p*-iodophenylthiocarbamide, m.p. 190°, and 5-bromo-, m.p. 271—272°, -chloro-, m.p. 273—274°, and -iodo-1-*p*-cyanoanilinobenzthiazole, m.p. 275°, 1-*p*-iodoanilino-5-methylbenzthiazole, m.p. 202°, 5-iodo-1-nitro-, m.p. 271—272°, -*p*-chloro-, m.p. 194°, and -*p*-bromo-anilinobenzthiazole, m.p. 202°. 5-Chloro-, m.p. 182°, and -bromo-1-*p*-iodoanilinobenzthiazole, m.p. 198°, are obtained from 1:5-dichlorobenzthiazole and $p-C_6H_4I \cdot NH_2$, and 1-chloro-5-iodobenzthiazole (II) and $p-C_6H_4Br \cdot NH_2$, respectively; they do not depress the m.p. of their position isomeride described above. $p-C_6H_4I \cdot NCS$ and Br in $CHCl_3$ give 5-iodo-1-aminobenzthiazole, m.p. 222° (lit. 210°) which (diazo-reaction) affords (II), m.p. 136°.

R. S. C.

Condensation of thiocarbamides with chloroacetic acid and the conversion of arylformamid inethiolacetic acids into ψ -thiohydantoin derivatives. R. D. DESAI, R. F. HUNTER, and L. G. KOPPAR (Rec. trav. chim., 1935, 54, 118—121).— $CS(NH_2)_2$ and $CH_2Cl \cdot CO_2H$ in H_2O at room temp give formamidinethiolacetic acid, m.p. 234° (decomp.) whilst in $COMe_2$ at room temp. the hydrochloride m.p. 222° (decomp.) (hydrolysed by cold H_2O), is obtained. The acid in hot $AcOH$ yields 2-imino-4-ketotetrahydrothiazole, m.p. 200°. Substituted thiocarbamides in $COMe_2$ lead similarly to arylformamid inethiolacetic acids, $NH_2 \cdot C \cdot (NR) \cdot S \cdot CH_2 \cdot CO_2H$, in which $R=Ph$, m.p. 184° (decomp.) [m.p. 206° (decomp.)], *o*-, m.p. 168° (decomp.) [m.p. 211° (decomp.)], *m*-, m.p. 145° (decomp.) [m.p. 222° (decomp.)], and *p*- C_6H_4Me , m.p. 189° (decomp.) [m.p. 214° (decomp.)], α -, m.p. 190° (decomp.) [m.p. 223°

(decomp.), and β - $C_{10}H_7$, m.p. 214° (decomp.) [m.p. 214° (decomp.)], the m.p. in brackets being those of the hydrochlorides, and thence to 2-arylimino-4-keto-tetrahydrothiazoles, in which the substituent is Ph, m.p. 178°, o-, m.p. 144—145°, m-, m.p. 165°, and p- C_6H_4Me , m.p. 183°, α -, m.p. 213—214° (decomp.), and β - $C_{10}H_7$, m.p. 220—221°. NPhMe·CS·NH₂ gives phenylmethylformamidinethiolacetic acid, m.p. 188° (decomp.) [hydrochloride, m.p. 199° (decomp.)]. CS(NHPh)₂ does not react in cold COMe₂, but in hot EtOH gives 2-phenylimino-3-phenyl-4-ketotetrahydrothiazole. R. S. C.

Constitution of vasicine. W. E. HANFORD, P. LIANG, and R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 2780—2783).—o-Aminobenzylallylamine [by reduction (Fe, H₂O) of the o-NO₂-derivative hydrochloride] [as hydrochloride, m.p. 119—120°], HCO₂Na, and anhyd. HCO₂H give 3-allyl-3 : 4-dihydroquinazoline (I) [picrate, m.p. 180—181° (lit. 172—173°); H oxalate, m.p. 173—174.5° (lit. 172°)], also prepared by Paal and Stollberg's method (A., 1894, i, 210), reduced (H₂, PtO₂, EtOH) to a dihydro-derivative, an oil (picrate, m.p. 180.5—182°). Anthranilallylamine, m.p. 94° [from isatoic anhydride (II) and allylamine in 95% EtOH], evaporated with 85% HCO₂H gives formylanthranilallylamine, m.p. 82—82.5°; when the crude reaction product is heated at 190—210°, 4-keto-3-allyl-3 : 4-dihydroquinazoline (III), b.p. 156—157°/4 mm., m.p. 66—67°, results. Reduction (Na, amyl alcohol) of (III) or (I) affords 3-allyl-1 : 2 : 3 : 4-tetrahydroquinazoline (IV), b.p. 105—110°/3 mm. Reduction (H₂, PtO₂, EtOH) of (III) gives 4-keto-3-n-propyl-3 : 4-dihydroquinazoline, m.p. 96—98° (lit. 82°), also prepared by the successive action of EtOH·NH₂Pr and boiling HCO₂H on (II). 2(? 3)-Allylquinazolinium bromide, m.p. 130—131.5° (from quinazoline and allyl bromide), is hydrolysed (alkali) to, and also prepared by the action of MeOH·conc. HBr on, the corresponding hydroxide (Reynolds and Robinson, A., 1934, 1014). The non-identity of (I) with deoxyvasicine (V) (Ghose, A., 1927, 785) [oxalate, m.p. 235—236° (Maquenne block); picrate, m.p. 205—206° (Maquenne)] and of (IV) with dihydrodeoxyvasicine (VI), m.p. 69—70° [picrate, m.p. 185° (Maquenne)], shows that vasicine (VII) cannot be 4-hydroxy-3-allyl-3 : 4-dihydroquinazoline (Spath and Nikawitz, A., 1934, 310) or 4-hydroxy-2-allyl-1 : 2- or -3 : 4-dihydroquinazoline (Ghose *et al.*, A., 1933, 77; Narang and Ray, A., 1934, 1014). (VI) is prepared by Spath and Nikawitz's method (*loc. cit.*) of obtaining dihydrodeoxypeganine (VIII) (the deoxytetrahydropeganine of these authors). (VI) and (VIII) have the same



(A.)

m.p.; the view (Spath and Kuffner, A., 1934, 787) that (VII) and peganine are identical is thus supported. (V) and (VII) (as hydrochloride) could not be reduced (various catalytic methods). Structure (A) is preferred for (VII).

H. B.

Alkaloids of Senecio. I. Retrorsine. G. BARGER, T. R. SESHADRI, H. E. WATT, and T. TABUTA (J.C.S., 1935, 11—15).—Retrorsine (I),

obtained from *S. retrorsus*, D.C., has m.p. 212°, [α]_D²⁵ −17.6° in EtOH, and gives a monophenylcarbamate, m.p. 200—202°, and a nitrate (+0.5EtOH), m.p. 145°. It is hydrolysed (NaOH) to retronecine (II) and retronecic acid, C₁₀H₁₆O₆, m.p. 177°, [α]_D²⁵ −11.36° in EtOH, and the work of Manske (A., 1932, 286) is confirmed. (II) forms a Ac₂ derivative (picrate, m.p. 146°; methiodide, m.p. 118—120°) and is reduced (PtO₂·H₂) to retronecanol (III) (picrate, m.p. 208°), also obtained by reduction (4H) and subsequent hydrolysis of (I). Diacetylretronecine is reduced to acetylretronecanol (picrate, m.p. 176°; methiodide, m.p. 207—208°). (III) is oxidised (K₂CrO₄) to an amphoteric substance, which gives an Et ester, forming a methiodide, C₉H₁₂O₂NI, m.p. 292—295°. The constitution of the compounds is discussed; retronecane is probably identical with piperolidine, C₈H₁₅N. F. R. S.

Alkaloids of Ulex europaeus. I. G. R. CLEMO and R. RAPER (J.C.S., 1935, 10—11).—Young shoots of *U. europaeus* contain anagryrine, isolated as the picrate, m.p. 242° (picronolate, decomp. 254°), and a small quantity of a base, C₁₅H₂₀O₅N, m.p. 170°. The occurrence is seasonal. F. R. S.

Alkaloids of Holarrhena antidysenterica. III. Action of cyanogen bromide on conessine and its N-demethylation to isoconessimine and conimine. S. SIDDIQUI and R. H. SIDDIQUI (J. Indian Chem. Soc., 1934, 11, 787—795).—Conessine R(NH)·NMe₂ (I) (R=C₂₁H₃₁) [monohydrobromide, m.p. 310—311° (decomp.)] with 1 mol. of BrCN in Et₂O affords its dimethobromide, m.p. 321—322° (decomp.), and cyanoisoconessimine R(NMe)·NMe·CN (II), m.p. 182—183° [hydrochloride, m.p. 289—290° (decomp.); platinichloride, m.p. 210—211° (decomp.); picrate, m.p. 139—140°; methobromide (III), m.p. 255°]. The second tert.-NH₂ group in (I) is more resistant to BrCN, but with 2 mols. of this reagent (I) gives, in addition, some dicyanconimine R[NMe(CN)]₂·N·CN (IV), m.p. 159—160°, obtained, with (III), by the action of 2 mols. of BrCN in EtOAc on (II). (II) with 20% KOH·EtOH affords isoconessimine, R(NMe)·NHMe (Bz, m.p. 159—160° [hydrochloride, m.p. 325—326° (decomp.)]; platinichloride, m.p. 264—265° (decomp.)], Ac, m.p. 127—128° [hydrochloride, m.p. 325—326° (decomp.)]; platinichloride, shrinks at 246°, m.p. 265—266° (decomp.), and NO-, m.p. 163—164° [hydrochloride, m.p. 248—251° (decomp.)]; picrate, m.p. 190—194° derivatives), identical with a specimen from *H. antidysenterica*. Similar hydrolysis of (IV) affords conimine, R(NH)·NHMe (Bz₂, m.p. 250°, Ac₂, m.p. 139—140°, and (NO)₂, m.p. 206—207°, derivatives). On the basis of these results the above partial formulæ are suggested. J. W. B.

Formation of an isomeride of corynanthine by esterification of its product of alkaline hydrolysis. RAYMOND-HAMET (Compt. rend., 1934, 199, 1658—1659).—With KOH·EtOH at 70° corynanthine (I), [α] −73°, gives a substance C₂₀H₂₄O₃N₂ corresponding with the anhydride of corynanthic acid. This with MeOH-gaseous HCl gives a d-hydrochloride (II) of a Me ester (III), [α] +107.2°, liberated from (II) by NaHCO₃. Similarly an Et ester, [α] +95.9°, is ob-

tained. (III) is thus a ψ -corynanthine. Similarly treated yohimbine gives a Me ester identical with the original alcohol. Rotations are in C_5H_5N .

J. W. B.

Alkaloids of *Mitragyna stipulosa*, O. Kuntze. RAYMOND-HAMET and L. MILLAT (J. Pharm. Chim., 1934, [viii], 20, 577—584).—The alkaloid (I), m.p. 215—216° (m.p. depends on mode of heating), isolated from *M. stipulosa* (II) is identical with mitrinermine (III) isolated from *M. inermis*, O. Kuntze. (I) and (III) have the same m.p. (and mixed m.p.), empirical formula $C_{22}H_{18}O_4N_2$, and $[\alpha]$. Both have 2 OMe and give the same reactions with Frohde's and Mandelin's reagents. Mitraphylline, isolated from (II) by Larrieu (Diss., Paris, 1930), can be further purified by crystallisation and is then identical with (I) and (III).

H. G. M.

Simple separation of the *Cinchona* alkaloids from their dihydro-bases. H. THRON and W. DIASCHERL (Annalen, 1935, 515, 252—260).—The mixture, dissolved in 10% H_2SO_4 , is warmed at 40—50° with a 10% solution of $Hg(OAc)_2$ in 5% AcOH, whereby the vinyl bases (I) are transformed into compounds (III) $R\cdot CH(HgOH)\cdot CH_2\cdot OH$ and the Et bases (II) remain unchanged. After cooling and addition of NH_3 which dissolves (III), (II) are collected or extracted with Et_2O . The residual aq. solution is acidified with H_2SO_4 and boiled with H_3PO_3 , whereby Hg is pptd. and (II) are liberated. The separation is nearly quant. A similar separation cannot be effected with $CuCl_2$ in a single operation (cf. Buttle *et al.*, A., 1934, 681). Quinidine, m.p. 172°, is converted by boiling 60% H_2SO_4 into apo-quinidine (IV), m.p. 165—175°, $[\alpha]^{13}_D +100^\circ$ in EtOH, whereas the technical alkaloid, containing about 30% of hydroquinidine, gives (IV) and hydrocupreidine when similarly treated (cf. Ludwiczakwona *et al.*, A., 1933, 1312).

H. W.

Preparation and properties of aurothiosulphates of quinine, ammonium, and calcium. M. PICON (J. Pharm. Chim., 1935, [viii], 21, 101—118).—The prep. of quinine aurothiosulphate, the corresponding NH_4 compound, and Ca salt are described. The properties and the structure of the compounds are discussed.

H. T.

Anomalous properties of chloroformyl derivatives of quinine alkaloids. J. SZUSZKO and F. SZELAG (Rocz. Chem., 1934, 14, 1202—1215).—The Cl atoms of *O*-chloroformyl-cinchonidine (I) [methiodide, m.p. 181° (decomp.)] and -quinine (II) [methiodide, m.p. 208° (decomp.)] are extremely inactive, not being replaced by prolonged boiling with KOAc in EtOH or with NH_2Ph in C_5H_5N . *O*-Carbethoxycinchonidine (III), m.p. 85°, $[\alpha]^{15}_D -17.87^\circ$, is obtained readily from $ClCO_2Et$ and cinchonidine (IV), but not from (I) and EtOH. (I) is 10 times as resistant as (III) to hydrolysis with alcoholic NaOH. Dicinchonidine carbonate is obtained readily from (III) and $COCl_2$, but not from (I) and (IV). *iso*Propyldieneglyceryl quininecarboxylate [methiodide, m.p. 216—218° (decomp.); dimethiodide, m.p. 138° (decomp.)] cannot be obtained from (II) and *iso*propyldieneglycerol, as stated in G.P. 346,889 (Bayer u. Co.). The methiodide, m.p. 226°,

+1.5 H_2O , m.p. 102—103°, $[\alpha]_D -119^\circ$, and dimethiodide, m.p. 90°, of *O*-carbethoxyquinine are described. α -Dibromocinchonidine and $COCl_2$ in PhMe yield α -dibromo-*O*-chloroformylcinchonidine, m.p. 180—181°, $[\alpha]^{15}_D -134.4^\circ$; the corresponding β -dibromo-compound (V), m.p. 173—174°, $[\alpha]^{15}_D -162.9^\circ$, is obtained analogously. (I) and Br in AcOH yield (V), whence it follows that the inactivity of the Cl of (I) is not due to internal rearrangement, with entrance of the Cl into the vinyl group of quinine. (I) and (II) do not afford dimethiodides even with great excess of MeI: the methiodides formed are readily hydrolysed by cold alcoholic NaOH.

R. T.

Photo-oxidation of 2-benzylpyridine and papaverine. A. MULLER and M. DORFMAN (J. Amer. Chem. Soc., 1934, 56, 2787—2788).—Exposure of 2-benzylpyridine (I) (in glass) to light from a quartz-Hg lamp gives a brown product from which a little 2-benzoylpyridine (II) is isolable. Exposure of a C_6H_6 solution of papaverine (III) in quartz to sunlight for 3 days affords approx. 10% of papaveraldine (IV). (I), (II), and (IV) (in C_6H_6) in dry O_2 show no absorption at 115° in the dark (pronounced absorption occurs in Hg light at lower temp.); (III) (in C_6H_6) similarly absorbs O_2 (but is unchanged in air at 60°). (I) and (III) are unaffected by Hg light in a vac.; (II) and (IV) undergo some change. (I)—(IV) are not affected by light of wave-length > 405 m μ .

H. B.

Cotarnine series. I. Action of phenyl-carbimide and -thiocarbimide on cotarnine. B. B. DEY and (Miss) P. L. KANTAM (J. Indian Chem. Soc., 1934, 11, 835—842).—Cotarnine (I) reacts with PhNCO (II) in C_6H_6 to give a carbamide derivative (III), m.p. 137°, which must possess the structure $CHO\cdot R\cdot [CH_2]_2\cdot NMe\cdot CO\cdot NHPh$ [$R=CH_2O_2\cdot C_6H(OMe)$], since it gives an oxime, m.p. 152° (decomp.) (*O*-Ac, m.p. 139°, and *O*-Bz, m.p. 142°, derivatives), converted by further action of (II) into its phenylurethane, $NHPh\cdot CO\cdot O\cdot N\cdot CH\cdot R\cdot [CH_2]_2\cdot NMe\cdot CO\cdot NHPh$, m.p. 151°, also obtained from (II) and the oxime of (I). Similar action of PhNCS on (I) gives the corresponding thiocarbamide derivative, m.p. 132° [oxime, m.p. 142° (*Ac*, m.p. 147°, and *Bz*, m.p. 153°, derivatives), and *anil*, m.p. 146°]. (III) condenses with *o*-, *m*-, and *p*-toluidine to give, respectively, its *o*-, m.p. 196°, *m*-, m.p. 168°, and *p*-toluidil, m.p. 168°, but with NH_2Ph only $CO(NHPh)_2$ is obtained. These results favour the structure $CHO\cdot R\cdot [CH_2]_2\cdot NHMe$ for (I).

J. W. B.

Preparation of morphenol (3-hydroxy-4:5-oxidophenanthrene) from morphine. E. MOSETTIG and E. MEITZNER (J. Amer. Chem. Soc., 1934, 56, 2738—2740).—Morphine and Me_2SO_4 in MeOH-NaOMe give codeine methosulphate (+2 H_2O), degraded (aq. NaOH) (cf. Knorr, A., 1894, i, 430) to α -methylmorphimethine [methosulphate (I) (+COMe $_2$)], which is rearranged [method: Knorr and Smiles, A., 1902, i, 817] to β -methylmorphimethine [methosulphate (II)]. (II) is hydrolysed (20% H_2SO_4 , subsequently removed as $BaSO_4$) to the methohydroxide, which when dried at 100—105°/15 mm. and then treated with H_2O gives methylmorphenol (III) (65% yield). (III) is also obtained in 60—70% yield from (I) or (II) and Na

cyclohexyloxyde in cyclohexanol at 120–140°; with Na amyloxyde in boiling amyl alcohol the yield is only 20%. (III) is demethylated (48% HBr in AcOH) to morphenol (yield nearly quant.). H. B.

Amide of norcodeine-N-carboxylic acid. S. WEIL and S. ROZENBLUMÓWNA (Rocz. Chem., 1934, 14, 1309–1311).—The amides of norcodeine-, m.p. 195–197°, and of normorphine-N-carboxylic acid are less toxic and less therapeutically active than are the parent alkaloids. R. T.

Strychnos alkaloids. LXXXIII. Perhydrogenation of strychnidine and tetrahydrostrychnine to isomeric bases. H. LEUCHS and H. GRUNOW. LXXXIV. Isomerism of the strychninolines. H. LEUCHS, W. DIELS, and A. DORNOW (Ber., 1935, 68, [B], 91–97, 106–113; cf. A., 1933, 170, 841).—LXXXIII. Hydrogenation of tetrahydrostrychnine (PtO₂-N-HCl) leads to a mixture of dodecahydrostrychnines, C₂₁H₃₁O₂N₂, m.p. 248–250° (vac.), [α]_D²⁰ -6.3°/d in abs. EtOH, and m.p. 153°, [α]_D⁰ -14.3°/d in abs. EtOH. The last-named base is transformed by POCl₃ at 100° into the substance C₂₁H₃₃ON₂HCl, m.p. 286°; it resinifies under the influence of Ac₂O and NaOAc. Strychnidine affords the H₈-bases C₂₁H₃₂ON₂, m.p. 109–110°, [α]_D²⁰ +5.4°/d in abs. EtOH {diperchlorate, [α]_D²⁰ +16.2°/d; dimethiodide (I), [α]_D²⁰ +11.5° to +12°}, and m.p. 110–112° (vac.), [α]_D⁰ 0° to +2° in abs. EtOH (diperchlorate, [α]_D²⁰ +6.4°/d). Decahydrostrychnidine I (II) yields the salt C₂₁H₃₄ON₂ZnCl₂·2HCl, [α]_D²⁰ +23.6°/d in H₂O, and an analogous compound, [α]_D²⁰ +22.6°, with ZnBr₂. O-Acetyldodecahydrostrychnidine I is readily isolated from the crude mixture of bases and affords (II) when hydrolysed; the corresponding base II does not appear to react with Ac₂O. The salts C₂₁H₃₂N₂ZnCl₂·2HCl, [α]_D²⁰ -10.6°/d, and C₂₁H₃₄N₂ZnCl₂·2HCl, [α]_D²⁰ 0° to -2.7° in H₂O, are derived from anhydrodecahydrostrychnidine I and octahydrostrychnoline, respectively. (I) is transformed in the first stage of the Hofmann degradation into a mixture of doubly and singly unsaturated bases from which a perchlorate C₂₃H₂₇ON₂·ClO₄·HClO₄, [α]_D²⁰ -25.7°, is isolated; it appears to contain 1 C:C linking.

LXXXIV. Reduction of strychninonic acid (Na-Hg-4H) affords 10–15% of neutral material from which a substance C₁₉H₂₀O₃N₂, m.p. > 295°, [α]_D⁰ -155° in AcOH (apparently a H₂-derivative of isostrychninolone), is obtained. Hydrogenation (PtO₂-AcOH) of strychninolone a (I) yields the compound C₁₉H₂₀O₃N₂, m.p. 263–268°, [α]_D²⁰ -12.2° in AcOH; analogous treatment of acetylstrychninolone a (II) leads to the substance C₂₁H₂₂O₄N₂, m.p. 256–258° (slight decomp.), [α]_D²⁰ -57.2° in AcOH, identical with the by-product which remains when crude (II) is oxidised with KMnO₄. Strychninolone b (+H₂O) is hydrogenated to the compound C₁₉H₂₀O₃N₂, m.p. 205–208°, [α]_D¹⁵ -62.1°, and (?) dihydrostrychninolone c. Acetylstrychninolone b yields acetyldihydrostrychninolone a and a substance C₂₁H₂₀O₄N₂ or C₂₁H₂₂O₄N₂, m.p. 233–235°, [α]_D²⁰ -35° to -36° in AcOH. Strychninolone c and its Ac derivative yield the compounds C₁₉H₂₀O₃N₂, m.p. 227–229°, [α]_D²⁰ -88° in AcOH, and C₂₁H₂₀O₄N₂, m.p. 265°

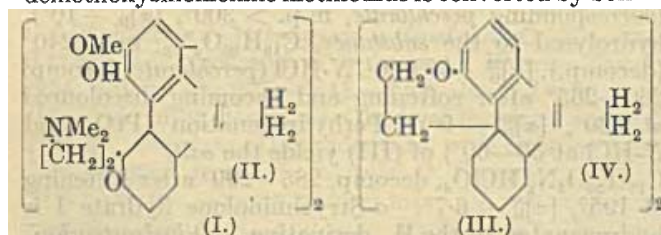
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(slight decomp.), [α]_D²⁰ -124°. Treatment of (I) with 12N-HCl at 100° and esterification of the product with MeOH-HCl gives the ester hydrochloride (III) C₂₀H₂₂O₄N₂·HCl, m.p. 305–310° (decomp.), [α]_D²⁰ +12° (corresponding perchlorate, m.p. > 300°, [α]_D²⁰ +10°), hydrolysed to the substance, C₁₉H₂₀O₄N₂, m.p. 240° (decomp.), [α]_D²⁰ -7° in 0.1N-HCl (perchlorate, decomp. 260–265° after softening and becoming discoloured at 230°, [α]_D²⁰ -9°). Perhydrogenation (PtO₂ and N-HCl at 50–60°) of (III) yields the salt, C₁₉H₂₆O₄N₂·HClO₄, decomp. 285–290° after softening at 195°, [α]_D²⁰ +6.7°. α-Strychninolone hydrate I is hydrogenated to the H₈ derivative. Dihydrostrychninolone a hydrate perchlorate, C₁₉H₂₂O₄N₂·HClO₄, m.p. 180°, [α]_D¹⁵ +46.6° in H₂O, is described. Strychninolone b hydrate (+4H₂O), m.p. 240° (Na salt; perchlorate, C₁₉H₂₀O₄N₂·HClO₄, m.p. about 245° (decomp.), [α]_D²⁰ +24° in H₂O), is obtained from the b form and 12N-HCl or from the resin remaining after hydrolysis of the α-variety. It gives a Me ester perchlorate, C₁₉H₂₂O₄N₂·HClO₄, m.p. about 255° (decomp.), [α]_D²⁰ +26.7° in H₂O, and is hydrogenated (=2H) to a substance C₁₉H₂₂O₄N₂ [perchlorate (IV), m.p. about 200° after softening and frothing at 150°, [α]_D¹⁵ +17.5°]; the perhydrogenated product could not be caused to crystallise and did not give cryst. salts. (IV) is hydrogenated (=8H) to the compound, C₁₀H₃₀O₄N₂·HClO₄, [α]_D²⁰ +29°. H. W.

Strychnine and brucine. Catalytic decomposition of quaternary brucine salts. O. ACHMA-POWICZ and B. BOCHWIC (Rocz. Chem., 1934, 14, 1330–1341).—Benzylbrucinium chloride yields dihydrobrucine and PhMe on hydrogenation (Pd-C); similarly benzylstrychninium chloride yields dihydrostrychnine and PhMe. Methylbrucinium chloride gives methyl-dihydrobrucinium chloride and N₆-methylchanodihydrobrucine, C₂₄H₃₀O₄N₂, m.p. 147–148° (methiodide, m.p. 263–265°; methochloride, m.p. 214–216°; picrate, m.p. 147–150°), from which the H₆-derivative, m.p. 143–144° (methiodide, m.p. 218–222°; Ac₂ derivative, m.p. 108–110°), is obtained by electro-reduction. The above results support the view that brucine and strychnine contain the allyl-amine group. R. T.

Yohimbine. III. J. P. WIBAUT and (FRL.) A. J. P. VAN GASTEL (Rec. trav. chim., 1935, 54, 85–92; cf. A., 1931, 369).—The yohimbine (I) used previously (*loc. cit.*) for dehydrogenation contained much isoyohimbine (II), which constituted the major portion of other commercial samples. Pure (I) gives, however, the same dehydrogenation products, but less ketoyohyrine. The formula C₁₉H₁₈N₂ for yohyrine (III), m.p. 217–218°, is confirmed (cf. A., 1934, 89). The substance C₁₉H₂₀N₂, previously called dihydro-yohyrine, is thus tetrahydroyohyrine (IV). Pure (II) cannot be hydrogenated (PtO₂). Hydrogenation of (III) gives decahydroyohyrine, C₁₉H₂₆N₂, m.p. 228–229° (picrate, m.p. 195–196°), that of (IV) gives slowly octahydroyohyrine, C₁₉H₂₄N₂, m.p. 177–178° (picrate, m.p. 220–221°). Isoyohimboic acid (Et ester, +H₂O, m.p. 202–204°) retains 1H₂O tenaciously and is racemised by C₅H₅N. The 7-ring of (I) is not strained in models. R. S. C.

Sinomenine. XL. (—) and (+)-Bis-1:1'-thebenone. H. GOTO, H. MICHINAKA, and H. SHISHIDO (Annalen, 1935, 515, 297—302).—Bis-1:1'-demethoxysinomenine methiodide is converted by boil-



ing 25% KOH into bis-1:1'-demethoxyde-N-methyl-dihydrosinomenine (I), m.p. 252°, $[\alpha]_D^{25} +45.10^\circ$ in CHCl_3 . Bis-1:1'-de-N-methyl-dihydrothebainone, m.p. 252°, $[\alpha]_D^{25} -45.15^\circ$ in CHCl_3 , is obtained similarly. The corresponding r-compound, m.p. 240—243°, is prepared from equal wts. of the d- and l-forms. The amorphous methiodide of (I) is converted by 25% KOH into (—)-bis-1:1'-dehydrothebenone (III), m.p. 208—212° after softening at 185°, $[\alpha]_D^{25} -201.93^\circ$ in CHCl_3 ; (+)-, m.p. 205—212° after softening at 195°, $[\alpha]_D^{25} +201.54^\circ$ in CHCl_3 , and dl-, m.p. 202—205°, -bis-1:1'-dehydrothebenone are described. Hydrogenation (Pd-C) of (I) leads to bis-1:1'-demethoxyde-N-methyl-dihydrosinomenine (II), decomp. 248—249°, $[\alpha]_D^{25} +33.16^\circ$ in CHCl_3 ; bis-1:1'-de-N-methyl-tetrahydrothebainone, decomp. 249—250°, $[\alpha]_D^{25} -32.52^\circ$ in CHCl_3 , and the corresponding dl-compound, m.p. 245—248° (decomp.), are described. (—)-Bis-1:1'-thebenone (IV), m.p. 230—233° after softening at 225°, $[\alpha]_D^{25} -163.27^\circ$ in CHCl_3 -MeOH, is obtained by catalytic hydrogenation of (III) or by degradation of the amorphous methiodide of (II). (+)- and dl-Bis-1:1'-thebenone have m.p. 233° after softening at 190°, $[\alpha]_D^{25} +163.09^\circ$ in CHCl_3 -MeOH, and m.p. 250—254° after softening at 243°, respectively. H. W.

Tetravalent compounds of platinum with tertiary arsines. G. J. BURROWS and R. H. PARKER (J. Proc. Roy. Soc. New South Wales, 1934, 68, 39—46).—(AsPh₂Me)₂PtCl₂ (I), m.p. 214°, is obtained from AsPh₂Me (II) and H₂PtCl₆ (III); (AsPh₂Me)₂PtBr₂ (IV), m.p. 167°, from (II) and H₂PtBr₆; and (AsPhMe₂)₂PtCl₂ (V), m.p. 193°, from AsPhMe₂ and (III). When freshly prepared, (I), (IV), and (V) are sol. in PhMe, but on heating to their m.p. or keeping at room temp. for 11 months, isomerides insol. in PhMe result, with m.p. 218° (I), 165° (IV), and 196° (V). (I) [or (IV)] with moist Ag₂O affords a base reconverted into (I) [or (IV)] by HCl. F. N. W.

α-Naphthylmethylarsine derivatives. A. SPORZYNSKI (Rocz. Chem., 1934, 14, 1293—1308).—AsRMe₃ (R=α-C₁₀H₇) and Cl₂ in CCl₄ yield AsRMe₂Cl₂, m.p. 127.5—130° (decomp.), which on dry distillation gives AsRMeCl (I), b.p. 165—166°/6 mm., m.p. 62.2—62.7° (HgCl₂ salt, m.p. 105—107°). (I) affords (AsRMe)₂O (II), m.p. 57.5—59°, when boiled with KOH in 50% aq. MeOH. The following compounds are prepared from (II) and the appropriate halogen acid in the cold, or by the action of the appropriate halide on (I): AsRMeF, b.p. 139.5—140°/6 mm., $d_4^{25} 1.4402$, $n_D^{25} 1.6500$; AsRMeBr, m.p.

74—74.6° [dibromide, m.p. 105—106° (decomp.)]; AsRMeI, m.p. 101.8—102.6°; AsRMeCN, m.p. 84—85°, b.p. 190—191°/6 mm.; AsRMeCNS, m.p. 49.5—50.5°. (II) is oxidised by H₂O₂ to RMeAsO₂OH, m.p. 187—188°. The above-described compounds react with HCl or HBr at 100° to yield AsMeCl₂ or AsMeBr, and C₁₀H₈. R. T.

Mercury compounds of nitro-o-cresols.—See B., 1935, 175.

Mercury derivatives of substitution products of diphenylphenolphthalein.—See B., 1934, 175.

Phosphoro-pyridine compounds. E. PŁAZEK and Z. ŚASYK (Rocz. Chem., 1934, 14, 1198—1201).—2-Dimethylaminopyridine (I) and PCl₃ are heated at 100° for 8 hr., excess of PCl₃ is distilled off, aq. NaOH added to an alkaline reaction, excess of (I) removed by Et₂O extraction, the aq. solution evaporated, the residue dissolved in EtOH, and 2-dimethylaminopyridine-5(?) phosphinous acid (II), m.p. 250—252° (decomp.), prepared from the Na salt crystallising from the EtOH solution. The analogous phosphinic acid, decomp. at > 300°, is obtained by oxidising (II) with EtOH-HgCl₂. R. T.

New class of betaines. P. PFEIFFER and K. SCHNEIDER (Ber., 1935, 68, [B], 50—60).—The prep. of betaines containing the group SbCl₆ o- and p- to NMe₃⁺ affords further evidence that betaines are not cyclic compounds but dipole-like substances of the type, ⁺NMe₃·R·CO₂[−], ⁺NMe₃·R·O[−], ⁺NMe₃·R·SO₃[−].

The action of SbCl₃ on C₅H₅N in anhyd. Et₂O leads to the compound, 2SbCl₃·3C₅H₅N, m.p. (indef.) 185°, which passes in vac. over P₂O₅ at 90° into the substance (I) SbCl₃·C₅H₅N. Treatment of (I) with fuming HCl gives the substance [SbCl₄]H·C₅H₅N, m.p. 175°, also obtained from Sb₂O₃ and C₅H₅N in fuming HCl. The compound [SbCl₄]H·R (R=quinoline), m.p. 190° (decomp.), is similarly obtained.

[SbPhCl₂]H·C₅H₅N and [SbPhCl₂]H·R, m.p. 111°, are prepared from SbPhO. Sb p-tolyl dichloride and the appropriate base in AcOH-fuming HCl afford the salts [p-C₆H₄Me·SbCl₂]H·C₅H₅N, m.p. 132°, and [p-C₆H₄Me·SbCl₂]H·R, m.p. 129°. The compounds [p-OMe·C₆H₄·SbCl₂]H·C₅H₅N, decomp. 230°, and [p-OMe·C₆H₄·SbCl₂]H·R, m.p. 125° after softening at 110°, are derived from p-methoxyphenylstibinic acid. Sb m-aminophenyl dichloride hydrochloride, m.p. 218°, in MeOH-fuming HCl is converted by the requisite base into the compounds

[m-HCl·NH₂·C₆H₄·SbCl₂]H·C₅H₅N, m.p. 216°, and [m-HCl·NH₂·C₆H₄·SbCl₂]H·R, m.p. 211°. The salt, m-NH₂·C₆H₄·NMe₃Cl·HCl, decomp. 190—200°, is diazotised and transformed by Sb₂O₃ in fuming HCl into the diazonium compound

m-SbCl₄·N₂·C₆H₄·NMe₃Cl·1.5H₂O, decomp. 124°, which is converted by protracted heating with fuming HCl at 100° into the betaine ⁺NMe₃·C₆H₄·SbCl₅[−], decomp. 224° after blackening at 210°, which yields NMe₃ when warmed with NaOH and gives a yellow turbidity when treated with H₂S in COMe₂-conc. HCl; hydrolysis of it in COMe₂-H₂O and treatment with 70% HClO₄ leads to the perchlorate m-ClO₄·NMe₃·C₆H₄·SbO₃H₂, which darkens at 250°. p-Chlorophenyltrimethylammonium chloride, shrinks at 245°, and SbCl₃ yield the double salt

$m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NMe}_3\cdot\text{SbCl}_4$, m.p. 134° , isomeric with the betaine, from which it is distinguished by giving an immediate ppt. of Sb_2S_3 with H_2S in $\text{COMe}_2\text{-HCl}$ and vigorously evolving HCl when treated with conc. H_2SO_4 . *p*-Aminophenyltrimethylammonium chloride, m.p. 219° , is diazotised and converted into the compound, $p\text{-NMe}_3\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{N}_3\cdot\text{SbCl}_4$, transformed by hot, fuming HCl into the *p*-chlorobetaine $^+\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_6^-$, m.p. $> 250^\circ$ after darkening at 200° , from which the perchlorate, $\text{SbO}_3\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3[\text{ClO}_4]$ is derived. H. W.

Rapid method for dialysing large quantities of protein solution. G. C. H. STONE (Ind. Eng. Chem. [Anal.], 1935, 7, 8).—Protein solutions (10 litres) containing 10% of $(\text{NH}_4)_2\text{SO}_4$ are freed from the salt in 24 hr. by dialysis against tap- H_2O and then distilled H_2O which circulate through collodion sacs arranged in series. J. L. D.

Occurrence of hydroxyvaline as a constituent of proteins. E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1934, 229, 236—240).—No hydroxyvaline could be detected in the hydrolysis products of zein. Dipeptides containing tyrosine and proline (I), leucine (II) and (I), and (II) and glutamic acid were present. J. H. B.

Specific rotation of crystalline edestin. M. FREEMAN (Austral. J. Exp. Biol., 1934, 12, 187—191).—Cryst. edestin rapidly prepared has $[\alpha]_{5461} -50^\circ$ to -53° . Edestin prepared by EtOH -pptn. or dialysis has $[\alpha]_{5461} -56^\circ$ to -58° , due to the presence of some denaturation product. Treatment with alkali, acid, or heat also yields a product with higher rotation. P. G. M.

Action of ultra-violet rays on solutions of peptone and protein. F. LIEBEN and H. JESSERER (Biochem. Z., 1935, 275, 367—372; cf. A., 1933, 1063).—The irradiation (I) produces a skin (II) on the surface of aq. Witte's peptone (with 2.5—3.0% solutions optimum yield at p_{H} 5.5), but not on aq. peptone from caseinogen or silk. Sunlight, diffuse daylight, or sensitizers have no effect. (II) does not give the biuret reaction and contains no tryptophan, whilst the tyrosine content is reduced and the histidine content probably greatly diminished. Since the NH_2 content of (II) is reduced, production of plasteins possibly occurs. The NH_3 or new NH_2R liberated during (I) of proteins (III) probably comes not from the breaking of heterocyclic rings, but from that of peptide linkings which, in (III), are less resistant than in peptones and peptides. In addition to arginine other NH_2 -acids give more new NH_2R when irradiated in a distinctly alkaline than when irradiated in a neutral or acid medium. W. M. C.

Clupein. II. Electrometric titration. K. E. RASMUSSEN and K. LINDERSTROM-LANG (Compt. rend. Lab. Carlsberg, 1935, 20, No. 10, 36 pp.).—Titration curves obtained resemble those for aliphatic NH_2 -acids and their peptides. Logarithmic quantities corresponding with the dissociation consts. are calc., and evidence is given that a clupein prep. is a mixture. The basic structure seems to be a polypeptide with one terminal CO_2H and N. Calc. mol. wts. give

the no. of arginine and NH_2 -acid residues in the protein. H. T.

Organic micro-analysis. K. LINDENFELD (Mikrochem., 1935, 16, 153—170).—By the use of Flaschenträger absorption tubes, with low resistance to the gas stream, the pressure-regulating Mariotte bottle may be dispensed with in Pregl C-H determinations. Evaporation of liquids over a gas flame can cause high results in S determinations. J. S. A.

Rapid determination of carbon in organic compounds. C. B. POLLARD and W. T. FORSEE (Ind. Eng. Chem. [Anal.], 1935, 7, 77).—A wet oxidation method which can be completed in 1—2 hr. is described. J. L. D.

Quantitative micro-analysis of organic compounds. K. LINDENFELD (Rocz. Chem., 1934, 14, 1425—1435).—A no. of modifications of Pregl's methods are proposed. CO_2 is best absorbed by ascarit-soda-lime mixtures. Air-free CO_2 for N determination is obtained by adding 20% H_2SO_4 to Na_2CO_3 in a special apparatus. In S determinations, the solutions should not be evaporated on gas-heated H_2O -baths, owing to absorption of SO_2 from the combustion gases; the error due to this source may attain +1—2%. R. T.

Technique of the Kuttner-Lichtenstein method for the determination of organic phosphorus. D. GLICK (J. Lab. Clin. Med., 1934, 19, 1012—1013; Chem. Zentr., 1934, ii, 1814).—A more rapid method (A., 1932, 531) is described. H. N. R.

Detection and determination of germanium in organic matter. W. GEILMANN and K. BRUNGER (Biochem. Z., 1935, 275, 375—386).—Org. matter is destroyed with hot conc. H_2SO_4 and HNO_3 , and the Ge is separated, after addition of HCl , by distillation as GeCl_4 and pptn. with H_2S . Amounts of Ge > 0.05 mg. are then determined spectroscopically. When the amount is 0.05—0.5 mg., a colorimetric method similar to that used for H_3PO_4 determination (cf. Bell *et al.*, A., 1920, ii, 769), and when it is > 0.5 mg. a gravimetric method (Grosscup, A., 1931, 322) is employed. W. McC.

Rapid determination of hydroxyl by acetyl chloride and pyridine. D. M. SMITH and W. M. D. BRYANT (J. Amer. Chem. Soc., 1935, 57, 61—65).—Modified procedure, applicable to monohydric primary and sec. aliphatic and aromatic alcohols, phenols, and those polyhydroxy-compounds that are appreciably sol. in the reagent, is recommended. The mean accuracy is about $\pm 0.5\%$. The effects of certain interfering substances are discussed. E. S. H.

Physico-chemical methods of analysis of esterification mixtures. J. SALCEWICZ (Rocz. Chem., 1934, 14, 722—738).—The H_2O , EtOH , and EtOAc contents of mixtures containing 6% of AcOH are determined by adding 6% aq. AcOH until the solutions become turbid, and applying the result to the phase diagram of the given system. The error is $> 0.15\%$. R. T.

Reactions and reagents for the detection of organic compounds. III. E. E. EEGRIWE (Z. anal. Chem., 1935, 100, 31—36; cf. A., 1934, 171).—

Colour and fluorescence reactions are described for the detection of glycerol, allyl alcohol, glyoxylic acid, and $\text{H}_2\text{C}_2\text{O}_4$. The behaviour of numerous related substances is recorded. R. S.

Hydroxylamine method for the determination of aldehydes and ketones. Displacement of oxime equilibria by means of pyridine. W. M. D. BRYANT and D. M. SMITH (J. Amer. Chem. Soc., 1935, 57, 57—61).—Modified procedure, using $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $\text{C}_5\text{H}_5\text{N}$ as reagents, is recommended. Determinations of the relative reaction velocities of certain ketones suggest that steric hindrance of CO is responsible for wide variations in the rate. Addition of $\text{C}_5\text{H}_5\text{N}$ displaces the oxime synthesis equilibrium in the direction of completion. E. S. H.

Action of Nessler's reagent on ketonic alcohols and acids. G. SCHUSTER (J. Pharm. Chim., 1935, [viii], 21, 32—43).— α -Hydroxyketones of the form $\text{R}\cdot\text{CO}\cdot\text{CHR}'\cdot\text{OH}$ are oxidised by Nessler's reagent (I) and may be determined under the following conditions: if $\text{R}=\text{R}'=\text{Me}$ or Ph , 2I is rapidly taken up at room temp. to yield the corresponding diketone (Ac. being only slowly oxidised at room temp., but rapidly at 100°); if $\text{R}=\text{R}'=\text{Et}$, Pr^a , Pr^b , or Bu^a , the oxidation is slow at room temp. but rapid at 100° , 4I being absorbed to yield 2 mols. of $\text{R}\cdot\text{CO}_2\text{H}$; if $\text{R}=\text{Me}$ or Ph , and $\text{R}'=\text{H}$, 8I is absorbed at room temp. β - and γ -Hydroxyketones and α -ketonic acids are not oxidised by (I). A. E. O.

Colour reactions of amino-acids with phenols and hypochlorites; new tests for tryptophan and phenylalanine. F. M. MILLER and R. E. LYONS (Proc. Indiana Acad. Sci., 1934, 43, 132—135).—A blue colour develops on treating 2 c.c. of 0.02 molar NH_2 -acid with 8 drops of 5% PhOH and 2 c.c. of 2% aq. NaOCl . The test is not given by tyrosine, tryptophan (I), phenylalanine (II), histidine, and aspartic acid. (I) gives a rose or pink colour with 0.5—0.01% aq. NaOCl and 0.5—0.002% NaOH . Indole and skatole do not interfere. (II) with 0.9—0.2% aq. NaOCl and 0.25—0.003% NaOH gives a white turbidity, which is sp. CH. ABS. (e)

Determination of furfuraldehyde by means of diphenylthiobarbituric acid. V. E. TISCHTSCHENKO and N. V. KOSCHKIN (J. Appl. Chem. Russ., 1934, 7, 1307—1315).—Diphenylthiobarbituric acid (I) is prepared in 80—85% yield by boiling a mixture of $\text{CH}_2(\text{CO}_2\text{H})_2$, $\text{CS}(\text{NHPh})_2$, and AcCl in CHCl_3 for 8 hr. Furfuraldehyde (II) is determined by adding

excess of 1% (I) solution [prepared by dissolving (I) in feebly acid 4% aq. NH_4OAc] to (II) (9—70 mg.) in 12% HCl , and, after 15—20 hr., collecting, washing, drying, and weighing the ppt. of $\text{C}_5\text{H}_4\text{O}\cdot\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2\cdot 5\text{H}_2\text{O}$. The compounds of (I) with other aldehydes are sol. in acids, whilst ketones do not condense with (I).

R. T.

New colour reaction for quinine, quinidine, and cupreine and its application to the determination of quinine. J. A. SANCHEZ (J. Pharm. Chim., 1935, [viii], 21, 24—32).—Quinine (I) is demethylated by boiling H_2SO_4 to cupreine (II), which with diazotised $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ gives a stable orange-red colour or ppt. Quinidine, but not cinchonine, cinchonidine, or cinchonamine, behaves similarly. The reaction is applied to the determination of (I) in cinchona bark, tincture, and fluid extract. (II) may be detected directly, before demethylation, by the same method. A. E. O.

Electrodialysis as method of separation and determination of bases in biological fluids. I. Electrodialysis of aqueous solutions of carnosine, creatine, and creatinine. S. E. SEVERIN (Z. physiol. Chem., 1934, 230, 109—113).—Electrodialysis [using a modified Pauli apparatus with (usually) collodion membranes (Bjerrum and Manegold, A., 1927, 727)] of acidic solutions of carnosine (I), creatinine (II), and creatine (III) causes migration (the velocity decreases in the order quoted) to the cathode (IV); (I)—(III) are thus readily separated from colloidal substances. With solutions of $p\text{H}$ 10—12, little or no (I) passes to (IV); (II) and (III) migrate with a somewhat smaller velocity. Electrodialysis of (II) and (III) occurs very slowly in H_2O alone; (I) migrates to (IV) much more rapidly.

H. B.

Diazo-reaction of histidine. G. BARAC (Compt. rend. Soc. Biol., 1935, 118, 198—200).—Histidine can be determined in pure aq. solution (I), and in blood or urine to which (I) has been added, by the diazo-reactions with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ in alkaline solution, under the same conditions as the determination of PhOH , the colour produced being weaker than with PhOH . R. N. C.

Determination of glycine in proteins. A. R. PATTON (J. Biol. Chem., 1934, 108, 267—272).—The prep. of a protein for the colorimetric determination of glycine is discussed; the colorimetric test is standardised and simplified. H. T.

Biochemistry.

Rare gases not essential to life. A. L. BARACH (Science, 1934, 80, 593—594; cf. A., 1930, 941; 1933, 409).—Mice kept in an atm. of 21% O_2 and 79% N_2 provided no evidence for the view that the inert gases are necessary for normal biological activity. The cause of death in O_2 poisoning is probably not related to any dilution by rare gases which might occur. L. S. T.

Oxygen consumption of immature rats. J. E. DAVIS and A. B. HASTINGS (Amer. J. Physiol., 1934,

109, 683—687).—The mean O_2 consumption of normal rats decreased with age up to the 4th month, and over this period showed no variation between the sexes. Direct measurement of O_2 consumption made possible a distinction between the quiet states of dozing and sleeping. R. N. C.

Prolonged residence in high-oxygen atmospheres. Effects on normal individuals and on patients with chronic cardiac and pulmonary insufficiency. D. W. RICHARDS, jun., and A. L.

BARACHI (Quart. J. Med. [N.S.], 1934, 3, 437—466).—Arterial O_2 saturation was raised to or exceeded normal in 24 hr. Blood- CO_2 increased progressively for several days. Urinary Cl' frequently increased.

CH. ABS. (p)

Influence of an oxygen atmosphere on the blood of *Helix pomatia*. A. RAFFY and P. H. FISCHER (Compt. rend. Soc. Biol., 1935, 118, 15—17).—The p_H and the alkaline reserve of the blood of snails placed in O_2 increases; Cl' , however, remains unchanged.

A. L.

Respiration of certain tropical fresh-water fishes. E. N. WILLMER (J. Exp. Biol., 1934, 11, 293—306).—Fish blood has p_H 6.7. The CO_2 -combining power is < that of other animals. Carbonic anhydrase occurred in all species.

CH. ABS. (p)

Biology of *Calanus finmarchicus*. VI. Oxygen consumption in relation to environmental conditions. S. M. MARSHALL, A. G. NICHOLLS, and A. P. ORR (J. Marine Biol. Assoc., 1935, 20, 1—27).—The respiratory rate increases from 0° to 20° for both males and females at p_H 7.4—8.5. Variations of 100% may occur with light variation. Increase in O_2 content (I) of the H_2O has little effect on respiration, but it is reduced where (I) is < 3 ml. per litre.

P. G. M.

Respiratory gas exchange in *Termopsis nevadensis*. S. F. COOK (Biol. Bull., 1932, 63, 246—257).—There is no decline in O_2 consumption with falling O_2 tension until a concn. of approx. 2% is reached. At lower vals. all gas is consumed. The organism respire anaerobically for 2 days without injury, and can also exist and respire normally in 20% CO_2 . The R.Q. is approx. 1.

CH. ABS. (p)

Oxygen and carbon dioxide content of the blood of insects with the open-trachea system. M. FLORKIN (Compt. rend. Soc. Biol., 1934, 117, 1224—1226).—The O_2 content and partial pressure of the blood of open-trachea insects are practically zero. The CO_2 content varies from 9 to 89 vol.-%.

R. N. C.

Oxygen content of the blood of the brain veins. P. BAMBERGER and H. E. NEVER (Pflüger's Archiv, 1934, 234, 675—679).—The blood of human brain veins contains less O_2 and more CO_2 than that of other veins.

R. N. C.

Continuous measurement of oxygen content of blood flowing through intact vessels. K. KRAMER (Z. Biol., 1935, 96, 61—75).—The artery or vein is inserted in a bakelite holder between a H_2O -cooled micro-lamp and a red-sensitive Se photo-cell and the absorption of a definite wave-length band is determined from the galvanometric response which is calibrated from vals. given by the Van Slyke method.

F. O. H.

Arterialisation of blood. I. Oxygen saturation of blood and respiration during narcosis. II. Equilibrium of oxygen tension between alveoli and blood. III. Gaseous exchange in the lungs during the respiratory pauses. K. KRAMER and H. SARRE (Z. Biol., 1935, 96, 76—88, 89—100, 101—114).—I. Continuous determinations (cf. preceding abstract) of the O_2 saturation (I)

(common carotid and femoral arteries) and respiratory vol. in narcotised dogs (II) indicate a fall in (I) together with variations due to disturbances in the transfer of O_2 from alveoli to blood ("pneumonosis") and in the mechanism of respiration (III). Each pause in the retarded (III) is accompanied by a fall in the alveolar O_2 tension (IV) and in arterial (I) due to the inflow of venous blood. The resulting influence on (III) and the effect of disease are discussed.

II. With (II), the difference between (I) and (IV) is normal (approx. 20 mm. Hg), varies according to Krogh's diffusion theory, and is diminished by increase in respiratory vol. That between (IV) and the O_2 tension of the inflowing venous blood influences depth of (III), O_2 content of the venous blood, changes in the alveolar capillaries, etc.

III. With decreasing O_2 tension, that of alveolar air is always > that of arterial blood. The bearing of the data on oxygenation of the blood, especially during the pauses in (III), is discussed.

F. O. H.

Respiratory adaptation to anoxæmia. A. HURTADO, N. KALTREIDER, and W. S. MCCANN (Amer. J. Physiol., 1934, 109, 626—637).—Exposure to low pressure causes, in arterial blood, increases in red cell count, hæmoglobin, and viscosity, a moderate decrease in CO_2 , and a marked decrease in O_2 content and saturation. In the alveolar air both CO_2 and O_2 tensions are reduced. The respiratory response to anoxæmia includes structural changes in the lungs that favour a more efficient exchange of CO_2 and O_2 .

R. N. C.

Respiratory effect of prolonged anoxæmia in normal dogs before and after denervation of the carotid sinuses. C. L. GEMMILL, E. M. K. GEILING, and D. L. REEVES (Amer. J. Physiol., 1934, 109, 709—713).—The respiratory response to pure N_2 is abolished by denervation, and rate of breathing in O_2 -poor mixtures is increased without an increase in depth of breathing.

R. N. C.

Cardiac output in man. Adaptation of the katharometer for the rapid determination of ethyl iodide in estimations of cardiac output by the ethyl iodide method. Effect of posture on cardiac output and other circulatory and respiratory measurements. J. S. DONAL, jun., C. J. GAMBLE, and R. SHAW (Amer. J. Physiol., 1934, 109, 666—682).

R. N. C.

Factors affecting the oxygen capacity of hæmoglobin. I. Influence of p_H on the oxygen-combining ability of red blood-corpuscles. II. Critical temperature causing heat-injury to gas-carrying ability of hæmoglobin. III. Velocity of heat-injury sustained by hæmoglobin on its oxygen capacity. T. IWATA (Acta Schol. Med. Univ. Tokyo, 1934, 17, 56—62, 63—80, 81—87).—I. The O_2 capacity (I) of red corpuscles in isotonic buffer solutions varies with p_H and reaches max. at 7.0 (25°). The % decrease in (I) for a given change in p_H is independent of the O_2 tension at all vals. > 35 mm. Hg.

II. Hæmoglobin of mammalian blood heated beyond physiological temp. (40 — 47°) undergoes irreversible

denaturation causing a decrease in (I). The CO_2 -carrying ability of the blood is unchanged.

III. Heat-injury to hæmoglobin affecting (I) is in accord with a unimol. reaction, except in the last stages which correspond with a bimol. reaction.

CH. ABS. (p)

Combination of coagulated protein particles with anions. M. MAIZELS (Biochem. J., 1934, 28, 2133—2140).—Coagulated hæmoglobin particles (I) adsorb more anion at p_H 5.2 than at p_H 7.2. If (I) are suspended in a solution containing both a hydrophobic (II) and a hydrophilic (III) ion, the former is preferentially bound, and at p_H 5.2 the latter is practically excluded from combination. Assuming that the bulk of the H_2O in a (I) sediment is free, it follows that practically no (III) ion, and but little (II) ion, is bound at p_H 7.2. The ions strongly adsorbed by (I) are all readily sol. in org. solvents. The anion ratio in (I) exposed to a solution containing Cl' and another ion at p_H 5.2 depends on the relative adsorption of the ions by the protein, but with erythrocytes the controlling factor is the solubility of the anions in the lipid of the membrane (cf. A., 1934, 429).

A. E. O.

Reactions of hæmoglobiniferous cells to acid and basic dyes under varying conditions of hydrogen-ion activity. J. E. KINDRED (Stain Tech., 1935, 10, 7—20).—The substances in Russel bodies and in the cytoplasm of the plasma-cells are probably not hæmoglobiniferous (I) because they do not react as do substances in known (I) cells in respect to the isoelectric point of hæmoglobin.

H. W. D.

Exchange of hydrogen carbonate and chloride ions between blood-serum and red corpuscles at different carbon dioxide tensions. T. IWATA (Acta Schol. Med. Univ. Kyoto, 1934, 17, 88—92).—Serum under high CO_2 tension (I) contains more CO_2 and less Cl than that under low tension. If the two sera are brought into equilibrium under the same (I) the difference of CO_2 contents diminishes somewhat. This difference remains const. and independent of (I).

CH. ABS. (p)

Composition of the hæmocyanin and hæmoerythrin of *Sipunculus nudus*. J. ROCHE (Skand. Arch. Physiol., 1934, 69, 87—96; Chem. Zentr., 1934, ii, 1940).—Hæmocyanins from blood or lymph of various molluscs and Crustaceæ yielded cryst. substances, the N, S, and (notably) Cu contents of which were characteristic of the class of organism. Analysis of hæmoerythrin from *S. nudus* is recorded.

A. G. P.

Spectroscopic studies of hæmoglobin derivatives. L. WACHHOLZ, W. BARANOWSKI, and H. KACZY (Deut. Z. ges. gerichtl. Med., 1934, 23, 83—88; Chem. Zentr., 1934, ii, 1135).—Neutral methæmoglobin has only one absorption band in the red portion of the spectrum.

H. N. R.

Combination between methæmoglobin and peroxides: hydrogen peroxide and ethyl hydroperoxide. D. KEILIN and E. F. HARTREE (Proc. Roy. Soc., 1935, B, 117, 1—15).—Methæmoglobin (I) in solution free from catalase (III) at p_H 5.8—6.5 is converted by the addition of H_2O_2 into methæmo-

globin- H_2O_2 (II) compound with diffuse absorption bands at 589 and 545 m μ . The min. amount of H_2O_2 required to transform (I) into (II) corresponds with 1 mol. of H_2O_2 per Fe atom. (II) is unstable and rapidly decomposes to yield up to 87% of (I). The H_2O_2 disappears without formation of mol. O_2 , so that it seems to be used up in oxidising the 13% of (I) which does not reappear. The decomp. of (II) is not accelerated by (III), but is accelerated by certain easily oxidisable compounds such as $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ or $p\text{-(C}_6\text{H}_4\text{NH}_2)_2$ with reappearance of (I). EtO_3H reacts with (I) to give a compound very similar to (II) both in absorption bands and other properties. EtO_3H and [in the absence of (III)] H_2O_2 oxidise hæmoglobin to yield (I).

W. O. K.

Blood and its components. I. Physico-chemical investigation of their magnetic properties. H. KUDO (Acta Med. Scand., 1934, 81, 511—520; Chem. Zentr., 1934, ii, 1152).—Human and animal bloods are diamagnetic; κ is slightly > for H_2O , and in fever, starvation, and menstruation falls to 6.30×10^{-7} . X-Ray irradiation of rabbits' bodies raises blood- κ . Vals. are given for κ of 14% aq. hæmoglobin, and for 2% and 1.5% serum-albumin, solutions.

R. N. C.

Determination of sodium in human red blood-cells. F. W. OBERST (J. Biol. Chem., 1935, 108, 153—160).—The cells should first be washed with Na-free, dialysed serum made isotonic with KCl and KHCO_3 , and equilibrated with approx. 40 mm. of CO_2 .

A. E. O.

Suspension stability of erythrocytes in solutions of gum acacia. S. P. LUCIA and J. W. BROWN (Proc. Soc. Exp. Biol. Med., 1934, 32, 189—192).—The factors responsible for changes in the suspension stability (I) of erythrocytes (II) are independent of (II). (I) is reduced by solutions of gum acacia, max. instability being produced by a 3—4% solution. Rapidity of formation and size of agglutinated (II) masses increase with (II) concn. The sedimentation curve for rapidly sedimenting bloods is not linear.

R. N. C.

Comparison of the centrifugation with the electrical conductivity method for the determination of the volume of blood-corpuscles. A. SLAWINSKI (Bull. Soc. Chim. biol., 1934, 16, 1575—1577).—The determination by electrical conductivity measurement is more accurate than the method of centrifuging.

A. L.

Changes in the blood of animals according to age. I. Changes in the blood of rodents (*Mus musculus*, L., and *Citellus pygmaeus*, Pall) and birds (*Passer montanus*, L., and *Larus nidibundus*, L.) during the period of growth. N. KALABUKHOV and V. RODIONOV (Folia Hæmatol., 1934, 52, 145—157).—Changes in H_2O content, acidity, glucose content, and size of erythrocytes (I) are recorded. In birds the increase in hæmoglobin (II) results from an increase in (I). In mammals the increase in (II) is preceded by a period of decrease associated with the intake of Fe in the mother's milk.

CH. ABS. (p)

Conditions of determination of lactacidæmia and its variations. F. KAYSER and N. MASIVS

(Compt. rend. Soc. Biol., 1934, 117, 1171—1173).—Vals. for blood-lactic acid in man are untrustworthy unless the subject has been in a state of complete repose for 1 hr. before the blood is drawn. In this condition a series of determinations over a period of several hr. gives concordant results. R. N. C.

Sources of error in the Hagedorn-Jensen method for blood-sugar. G. FREY (Klin. Woch., 1934, 13, 1400).—No glycolysis occurs within 4 hr. when blood is added to aq. $\text{ZnSO}_4 + \text{NaOH}$ before heating to coagulate. NUTR. ABS. (m)

Determination of blood-sugar. Bound sugar of blood. H. BRAUN (Biochem. Z., 1935, 275, 433—447).—The reducing material liberated in blood-serum (I) by acidic or alkaline hydrolysis is "bound sugar" (II). Most of (II) is united to protein (chiefly globulin). Glucose (III) in concns. similar to those found in blood can be accurately determined spectroscopically and the degradation of (III) by alkali may be observed thus. The method should be applicable to the determination of (II) in deproteinised (I) if suitable deproteinising agents are used and the selective absorption of the filtrate does not interfere. (II) but not free sugar is increased in carcinoma. W. McC.

Diurnal variation in blood-sugar level of the rat. M. C. HRUBETZ (Proc. Soc. Exp. Biol. Med., 1934, 32, 217).—Very small variations occur. R. N. C.

Blood-sugar of the snail (*Helix pomatia*, L.). K. SCHWARZ (Biochem. Z., 1935, 275, 262—269).—The blood-sugar of *H. pomatia* is 10—30 mg. per 100 c.c. and remains fairly const. throughout the year both with and without food. The vals. are unchanged on injecting either insulin (I) or adrenaline (II). (I) is not, but (II) is, toxic. P. W. C.

Effect of halogenated acids on the glycolysis of blood *in vitro*. J. LABARRE and P. RIOPEL (Canad. Chem. Met., 1934, 18, 219).—The anti-glycolytic powers of $\text{CH}_3\text{Cl}\cdot\text{CO}_2\text{H}$, $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{H}$, and $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ at a concn. of 1 : 250 are equiv. H. G. R.

Disappearance of fatty acids in presence of serum-protein. Z. GRUZEWSKA and M. G. ROUSSEL (Ann. Physiol. Physicochim. biol., 8, 806—838; Chem Zentr., 1934, ii, 1480).—Ovalbumin in 0.9% NaCl adsorbs PrCO_2H only in traces and AcOH not at all. Adsorption of fatty acids (I) by serum-proteins (II) depends on the concn. of (I). With 0.0025—0.005N-(I) the limit of adsorption is reached in approx. 1 hr. Adsorption is most efficient with the glyceryl esters of (I). The adsorption val. is the same for all (I) at the same mol. concn. R. N. C.

Role of serum-lipins. I. Physico-chemical study. S. WENT and A. VON KUTHY (Z. Immunitat., 1934, 82, 392—398).—Serum-proteins are freed from lipins by coagulation of the serum (I) with EtOH and extraction with Et_2O , and the euglobulin (II) and pseudoglobulins I and II separated by fractional pptn. from aq. solution with Na_2SO_4 . The ppt. corresponding with (II) is > the corresponding ppt. native (I). Addition of aq. lecithin or ecithin-cholesterol emulsion does not affect the

pptn.; hence the splitting of the protein-lipin linking in the (I) complex by EtOH is irreversible. The lipin-free (II) fraction dissociates less readily than (II) in (I). R. N. C.

Cholesterol and phosphatide content of the blood of dairy cows. A. DOULKIN and S. HELMAN (Le Lait, 1934, 14, 797—808).—There is a negative correlation ($r = -0.87 \pm 0.087$) between serum-cholesterol (I) and milk yield and a positive correlation ($r = 0.85 \pm 0.124$) between serum-lipin-P (II) and the % of fat in the milk. The level of (I) is in winter > in summer, and is lowered by feeding seaweed to the cows, turning them out to pasture, or ionisation of the air in the byres. There is apparently no direct correlation between (I) and (II), although there is a positive correlation ($r = 0.84$) between the ratio (I) : (II) and (I). NUTR. ABS. (b)

Adenine-nucleotide content of human blood. I. Determination and content. M. V. BUELL (J. Biol. Chem., 1934, 108, 273—283).—The method for the determination of purine nucleotides in blood has been revised, and data of their content in normal human blood collected. The nucleotide content of whole blood in males is > that of females, but in the red corpuscles the val. is the same. Menstruation seems to have no effect on the vals. A normal person appears to have a characteristic val. for the corpuscular purine-nucleotide content. H. T.

Distribution of the precursors of ammonia in sheep's blood. J. HELLER and A. J. KLISIECKI (Biochem. Z., 1935, 275, 362—366; cf. A., 1932, 1272).—Sheep's blood (I) contains two substances which decompose spontaneously *in vitro* giving NH_3 . One is equally distributed between serum and corpuscles (II) and is removed from (II) by washing with physiological aq. NaCl (III). Alkaline aq. borate does not inhibit the decomp. of this substance. The other (IV) is present in (II) only, is stable in intact (II) undergoing decomp. only after haemolysis, and is not removed from (II) by washing with (III). The enzyme which accelerates the decomp. of (IV) is also not removed by washing with (III). 100 c.c. of (I) contain the equiv. of 0.4—0.6 mg. of $\text{NH}_3\text{-N}$ of the first and of 0.5—0.85 mg. of $\text{NH}_3\text{-N}$ of the second substance. (IV) is probably adenylic acid. W. McC.

"True creatinine" of blood. G. FERRO-LUZZI (Biochem. Z., 1935, 275, 422—429; cf. Behre *et al.*, A., 1922, i, 789).—Since treatment of blood-filtrate (I) with hot aq. NaOH produces degradation products which give the reaction (II) of Jaffe, and since treatment of (I) with kaolin after deproteinisation by the method of Somogyi inhibits (II), whilst hot aq. CH_2O inhibits (II) in (I) exactly as in creatinine (III) solutions, it is concluded that normal blood contains (III) in amount which \propto the intensity of (II). The term "true creatine" should not be used. W. McC.

Origin of blood-indoxyl. B. A. HOUSSAY, P. MAZZOCCO, and D. POTICK (Compt. rend. Soc. Biol., 1934, 117, 1235—1237).—Indoxyl originates in the intestine, and is stored in the blood and excreted by the kidneys. Blood-indoxyl (I) is not affected by extirpation of the thyroid or pituitary. It is modified

slightly and irregularly by extirpation of the intestine; urinary indoxyl falls, but rises again later. Nephrectomy produces a rapid and intense increase of (I), which is reduced to a small val. by extirpation of the intestine. R. N. C.

Role of organs in the elimination of blood-indoxyl. B. A. HOUSSAY, P. MAZZOCCO, and D. POTICK (Compt. rend. Soc. Biol., 1934, 117, 1237—1238).—Injection of urinary indican in dogs produces an increase in blood-indoxyl, which falls rapidly, except after extirpation of the kidneys, by which it is normally excreted. Extirpation of the liver or gastro-intestinal tract does not affect the excretion. R. N. C.

Determination of the tyrosine index of serum-polypeptides. R. GOIFFON and J. SPACY (Bull. Soc. Chim. biol., 1934, 16, 1675—1685).—The serum is freed from protein by phosphotungstic acid on the one hand and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ on the other. The Folin-Denis phenol reagent is added to the filtrates, the difference in depth of colour being measured and expressed as polypeptide-tyrosine. A. L.

Photometric study of the effect of natural waters on human serum *in vitro*. P. PONTIUS (Arch. Phys. biol. Chim.-Phys. Corps org., 1933, 10, 318—326; Chem. Zentr., 1934, ii, 1152).—The turbidity produced on adding the H_2O (I) to the serum, due to pptd. globulins, is governed by the salts present in (I), and hence is a direct indication of its characteristics. R. N. C.

Osmotic pressure and molecular weight of serum-globulins. A. ROCHE and J. BRACCO (Bull. Soc. Chim. biol., 1934, 16, 1479—1497).—Fresh serum-globulin (I) of the horse, (I) aged for several weeks at 0° , (I) heated for a similar period at 37° , and old antidiphtheritic serum had at p_H 7.4 mol. wt. 150,000, 136,000, 225,000, and 225,000, respectively, as determined by osmotic pressure measurements. Horse-serum euglobulin and pseudoglobulin had mol. wt. 152,000 and 110,000, respectively. A. L.

Gelification of human serum by acids. W. KOPACZEWSKI (Compt. rend., 1935, 200, 266—268).—The concn. of acids necessary to produce gelatinisation of blood-serum (A., 1934, 547) is always slightly < that required to cause coagulation. The gelatinising power (I) of various org. acids is most marked in monobasic acids. (I) is not completely dependent on $[\text{H}^+]$, is decreased by the introduction of OH or by increase in the basicity of the acid, but is increased by increasing the no. of CH_2 groups. No differentiation between the dl- and active forms of an acid is observed. (Cf. this vol., 300.) J. W. B.

Determination of blood-protein. L. SERVANTIE and G. DEMENIER (Bull. Soc. Pharm. Bordeaux, 1934, 72, 96—105; Chem. Zentr., 1934, ii, 2109).—The proteins are pptd. and separated and their N content is determined by a modified Kjeldahl process, the NH_4^+ being determined with Nessler's solution. H. N. R.

Determination of serum-protein by measurement of volume of precipitate. F. W. HAYNES (J. Lab. Clin. Med., 1934, 19, 1320—1323).—The vol. of the ppt. obtained by adding phosphotungstic acid

to the dil. (1:50) serum is measured in Shevly-Stafford tubes and compared with standard preps. of caseinogen. CH. ABS. (p)

Blood-protein of hens and egg-laying. M. ROCHLINA (Bull. Soc. Chim. biol., 1934, 16, 1645—1651).—The protein content (I) of the blood of fowls varies according to age, sex, the time of egg-laying, and the breed. The average (I) in chickens, cocks, and hens (II) is 3.5—4.0, 5.5, and 5.6%, respectively; in (II), the min. (I) coincides with the time of laying. A. L.

Composition of hens' blood in relation to egg-laying. M. ROCHLINA (Bull. Soc. Chim. biol., 1934, 16, 1652—1662).—The composition of cocks' blood varies < that of hens' blood, although the differences between individual animals are considerable. Whilst there is a marked change in the Ca and protein content of the blood connected with egg-laying, the Cl⁻ and the dry extract content remain unchanged. A. L.

Phosphorus partition in blood-serum of laying hens. R. R. ROEPKE and J. S. HUGHES (J. Biol. Chem., 1935, 108, 79—83).—The total P (I) of the serum of cocks and non-laying hens is accounted for by the lipid (II) and acid-sol. (III) fractions, whilst in laying hens (I) is > (II)+(III). The P remaining in the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ ppt. after extraction with 10% $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and hot $\text{Et}_2\text{O}-\text{EtOH}$ accounts for the difference; this fraction has the properties of vitellin. H. D.

Phosphorus compounds in the blood-plasma of the laying hen. M. LASKOWSKI (Biochem. Z., 1935, 275, 293—300).—A phosphoprotein is detected in the plasma of the laying but not in that of the non-laying hen. P. W. C.

Calcium distribution in chicken blood. H. PAUL (Proc. Oklahoma Acad. Sci., 1934, 14, 32—34).—Serum-Ca occurs as ionic 20%, protein-bound (I) 30%, and adsorbable Ca (II) 50% of the total. The egg-laying period is marked by an increase, notably of (I) and total (II), and a decline in filterable (II). Non-filterable (II) is associated with shell formation. CH. ABS. (p)

State of calcium in fluids of the body. I. Conditions affecting ionisation of calcium. F. C. MCLEAN and A. B. HASTINGS (J. Biol. Chem., 1934, 108, 285—322).—With total Ca and total protein known, Ca may be calc. Certain variables influence ionisation of Ca in body-fluids, but the individual and combined effects are of slight practical importance compared with the Ca-protein relationship except in the rabbit and possibly other herbivora where citrate has a significant effect. H. T.

Phosphorus of blood. II. Partition of phosphorus in blood in relation to the corpuscle volume. E. WARWEG and G. STEARNS (J. Clin. Invest., 1934, 13, 411—418).—Changes in corpuscle vol. affected the lipin- and ester-P (I). (I) is not const. in human corpuscles. CH. ABS. (p)

Distribution of chloride between plasma and blood-corpuscles in normal and laked blood. S. RASZEJA and A. SLAWINSKI (Bull. Soc. Chim. biol., 1934, 16, 1692—1707).—In normal human and

equine blood (I) the $[Cl']$ in the serum and in the cytoplasm is the same; in (I) treated with citrate or small quantities of Cl' , however, the Cl' does not pass freely from the corpuscles, although in (I) treated with oxalate and F' or with considerable quantities of Cl' , the Cl' passes freely. Variations in the thickness of the corpuscular membranes have a great influence on the amount of free H_2O as determined by the ratio Cl' in corpuscles/serum- Cl' . A. L.

Determination of bromine in blood. R. INDOVINA (Biochem. Z., 1935, 275, 286—292).—A method is described depending on the reaction of Br liberated from ashed blood with fuchsin- SO_2 reagent, the colour developed being compared with standards. The method gives good results down to 6×10^{-6} g.

P. W. C.

Inhibition of blood-clotting by metals *in vitro*. H. HAUSLER and H. SCHNETZ (Biochem. Z., 1935, 275, 187—203).—Cu, Zn, Fe, Cd, Co, Ni, and Pb salts inhibit blood-coagulation *in vitro* in equiv. concn. to about the same extent, the inhibition being complete with concns. $> 0.003M$. Inhibition occurs with both inorg. and org. salts, the anions having only a slight modifying effect. Salts of Ba, Sr, and Ca accelerate clotting, whilst those of Mg and Mn occupy a mean position. As buffer solutions in these experiments, PO_4''' mixture is avoided and acetate-veronal buffer preferred.

P. W. C.

Nucleic acid-caseinogen compounds. Effect of nucleic acid on fibrinogen coagulation. T. KITAJIMA (J. Biochem. Japan, 1935, 21, 123—139).—Nucleic acid (I) combines stoichiometrically with caseinogen (II), the isoelectric point (III) of the compounds formed being diminished by increase in the (I):(II) ratio. Deaminated forms of (II) yield compounds with (I) having (III) of p_H approx. 3.5. (I) retards the coagulation of fibrinogen by thrombin, the retardation being inhibited by Ca^{++} , which combines with (I) to form a compound of low dissociation.

F. O. H.

Clotting of plasma in absence of lipin. H. WU (Proc. Soc. Exp. Biol. Med., 1934, 32, 97—98).—Fat-free plasma coagulates on addition of fat-free serum, or of Ca and lipin, but not with Ca or lipin alone. It is concluded that lipin is necessary for the activation of thrombin, but not for the actual coagulation.

R. N. C.

Coagulating action of the juice of embryonic guinea-pig tissues. P. MENDELEEFF (Compt. rend. Soc. Biol., 1934, 117, 1219—1222).—The coagulating action on plasma of the juice of the embryonic thymus is $>$ that of any other tissue or of the entire embryo. Coagulation is more rapid for the plasma of a pregnant animal.

R. N. C.

Specificity of the coagulating power of embryonic guinea-pig tissues. P. MENDELEEFF (Compt. rend. Soc. Biol., 1934, 117, 1222—1224).—The tissue-juice has little or no coagulant action on plasma of species other than the guinea-pig. For mixtures there is a min. concn. of guinea-pig plasma to produce coagulation.

R. N. C.

Antigenic properties of lipins. K. KIMIZUKA (Biochem. Japan, 1935, 21, 141—152).—Impure

lipin preps. (I) from egg-yolk show only slight antigenic activity (II) when injected with pig's serum into rabbits; phospholipin purified by $CdCl_2$ in EtOH is without (II), whilst hydrogenation or partial oxidation of (I), but not of pure lipin, increases (II). A H_2O -sol. fraction showing (II) can be separated from hydrogenated (I).

F. O. H.

Effect of X-rays on the formation of complement-binding substances in blood. I. P. MISCHT-SCHENKO and M. M. FOMENKO (Strahlenther., 1934, 50, 167—178; Chem. Zentr., 1934, ii, 1637—1638).—X-Irradiation of blood decomposes antibody-albumins, producing substances resembling antigens in appearance.

R. N. C.

Studies on cell structure by the freezing-drying method. V. Chemical basis of the organisation of the cell. VI. Preparation and properties of mitochondria. R. R. BENSLEY and N. L. HOERR (Anat. Rec., 1934, 60, 251—266, 449—455).—V. The globulins, glycogen, and mitochondria (I) of frozen-dried sections (II) of liver of *Amblystoma* remain sol. for 1—2 weeks at room temp., and for 4 months in the cold. Their removal with 0.9% NaCl does not affect the integrity or structure of the cells. In guinea-pig or rabbit liver, (I) are insol., whether the extraction is made from (II) or an emulsion of the tissue (III); the extraction removes large quantities of dissolved proteins, but the cells still retain their integrity. (I) are sol. in 0.005N- NH_4 , which dissolves also the nuclear chromatin and causes the cells to swell and cohere to a gel, further quantities of protein being removed; the characteristic cell structure is still recognisable in stained sections of the gel. The gel is sol. in 0.1N- NH_3 or N-NaOH; from solution, after centrifuging from insol. debris, the NaCl-insol. cell-material is pptd. with AcOH, purified by repeated pptn., washed, and dried over P_2O_5 . Successive extraction with EtOH, Et_2O , and $CHCl_3$ removes fatty material (IV) equiv. to 30% of the dried wt., of which 3.84% is insol. in $COMe_2$. The residual protein, termed *ellipsin*, is the structural protein and the basis of org. continuity of the cell body.

VI. (I) are extracted from (III) by repeatedly centrifuging at low speeds to remove cell debris, followed by high speed to separate (I), washing with 0.9% NaCl and dil. AcOH, and drying over P_2O_5 . (I) contain about 43.6% of (IV) sol. in EtOH, Et_2O , and $CHCl_3$, none of which is lecithin or kephalin. (IV) is partly or wholly unsaturated, and reduces OsO_4 . Fresh (I) are sol. in 0.0005N- NH_3 , and two proteins are pptd. isoelectrically from the solution at p_H 6.6 and an undetermined point further on the acid side.

R. N. C.

Interaction of proteins and nucleic acid. T. CASPERSSON, E. HAMMARSTEN, and H. HAMMARSTEN (Trans. Faraday Soc., 1935, 31, 367—389).—Experiments have been made with a view of devising suitable methods for demonstrating the existence or otherwise of a protein structure in cell nuclei, especially chromosomes. The reaction between La-malonic acid reagent, nucleic acid, and protein has been studied, and also the action of proteolytic enzymes on mixtures of Na nucleinate and proteins. When mitotic cells

are digested with a suitable mixture of activated trypsin and La acetate the chromosomes are rendered visible under the microscope in ordinary light.

M. S. B.
Kinochromatins. G. VAN CAMP (Protoplasma, 1934, 22, 128—136).—A review.
A. G. P.

Polarisation studies in tissue models. M. SPIEGEL-ADOLF and E. A. SPIEGEL (Proc. Soc. Exp. Biol. Med., 1934, 32, 139—141).—The conductance difference (I) between the max. and min. frequencies of an alternating current, produced by a membrane of parchment, collodion, hardened gelatin, or gelatin containing pseudoglobulin, placed between the electrodes in KCl solution, is $\approx 0.4\%$. Membranes of gelatin containing lipins (II) give similar vals., but collodion-lipin membranes (III) have a (I) of 2—5%; hence lipins can imitate the polarisation phenomena observed in animal tissues. In (III) the lipins are homogeneously distributed, whilst in (II) they appear in doubly-refracting lumps, irregularly distributed. Polarisation is increased in (III) by 0.05N-HCl, and decreased by 0.05N-NaOH; it is destroyed irreversibly by 95% EtOH, which extracts the lipins. (I) in brain tissue is decreased by hypotonic solutions, alkali, and other agents that produce swelling of the tissue.
R. N. C.

Origin of uric acid in the hibernating eggs of the silkworm. C. MANUNTA (Atti R. Accad. Lincei, 1934, [vi], 20, 283—286).—This acid is derived largely, not from embryonal metabolism, but from the maternal blood.
T. H. P.

Nucleic acid of the eggs of *Arbacia punctulata*. K. C. BLANCHARD (J. Biol. Chem., 1934, 108, 251—256).—From the unfertilised eggs of the sea-urchin have been isolated in equal amounts a nucleic acid of the $C_{39}H_{51}O_{25}N_{15}P_4$ type and a pentose derivative which may also be of nucleic acid type.
H. T.

Effect of variations in ionic strength on the apparent isoelectric point of ovalbumin.—See this vol., 301.

Kephalin from human brain. V. Oxygen uptake of phosphatides and their acids in presence of catalysts. I. H. PAGE and M. BULOW (Z. physiol. Chem., 1935, 231, 10—18; cf. A., 1932, 533).—Of the salts of Fe, Cu, Co, and Mn, only Fe shows strong activity as catalyst of the oxidation of lecithin (I) and kephalin (II) and the acid mixture resulting from their hydrolysis. (II) is more affected than (I). Cu is slightly active, also Co, for (II) acids. NH_2 -acids are inactive as catalysts. (II) always shows greater uptake than (I) even using phosphatide of the same I val. The phosphatides and acids of the same I val. show no difference.
J. H. B.

Acetylcholine content of nerves, brain, and spinal cord. H. KWIATKOWSKI (Arch. exp. Path. Pharm., 1935, 177, 154—158).—The vagus and ischiadic nerves, brain, and spinal cord of dogs, cats, oxen, guinea-pigs, and men contain acetylcholine ($0.2\text{--}5 \times 10^{-6}$ g. per g.).
F. O. H.

Urea content of the frog's kidney. R. HOBER (Pflüger's Archiv, 1934, 234, 716—721).—The urea content of a frog's kidney dried by heat is $<$ that of a fresh triturated kidney from the same frog. Per-

fusion of the isolated kidney through the aorta and portal vein (I), or through (I) only, with NaCl solution containing urea, produces a deposition of urea in the kidney.
R. N. C.

Lipins in the renal tubule of the cat. W. MODEL (Anat. Rec., 1933, 57, 13—28).—Location of lipins in adult and young cats and in the foetus is recorded.
CH. ABS. (p)

Cystine content of sheep's wool as affected by the protein content of the diet. J. E. LONG, V. G. HELLER, and A. E. DARLOW (Proc. Okla. Acad. Sci., 1933, 13, 12—16).—Variations in diet, within normal limits, do not affect the cystine (I) content of wool. Analytical methods for (I) are compared.
CH. ABS. (p)

Origin of sulphur in wool. II. Cuprous mercaptide method for the determination of cystine or cysteine. S. D. ROSSOUW and T. J. WILKEN-JORDEN (Biochem. J., 1935, 29, 219—224).—After hydrolysis of dried material by 40% H_2SO_4 , and pptn. of colouring matter (I) by adjustment to p_H 4.5, cystine and cysteine are pptd. as cysteine Cu^I mercaptide by addition of Cu_2Cl_2 . Excess of Cu and further (I) are removed from the ppt. by treatment with KCNS and C_5H_5N , and cystine is then determined by the modified Sullivan method (A., 1934, 1021). Cysteine can be regenerated as such only if a large excess of Zn dust is added to the mercaptide in dil. HCl. Twice the normal colour intensity is then obtained in the modified Sullivan method.
A. E. O.

Polarographic studies with the dropping mercury cathode. XLIII. Specific effects of amino-acids. J. SLADEK and M. LIPSCHUTZ (Coll. Czech. Chem. Comm., 1934, 6, 487—497).—Remedies for pernicious anaemia, containing proteolytic products from liver, inhibit the polarographic cysteine test. Among NH_2 -compounds examined to trace the origin of this inhibition, tryptophan, arginine, histidine, β -phenyl- α - and β -alanine suppressed the cysteine effect.
E. S. H.

Proteins of liver. C. ACHARD and M. PIETTRE (Compt. rend., 1935, 200, 363—366).—New apparatus, the histoclast, disintegrates tissue by projecting pulp at high pressure through screens and jets, on to a polished surface at -30° . The cells and even their nuclei are thus broken down. Ox-liver tissue so treated yields an extract containing much NH_2 -acid, and a phosphoprotein of globulin type, but no serum-protein.
E. W. W.

Non-protein-carbon and -nitrogen of muscle and post-mortem changes. II. T. INOUE (Tohoku J. Exp. Med., 1934, 23, 241—254).—Post-mortem increases in non-protein-C and -N in leg muscles of rabbits were parallel.
CH. ABS. (p)

α - β Intramolecular transformation of myosin. W. T. ASTBURY and S. DICKINSON (Nature, 1935, 135, 95).—In air-dried myosin (I) films the mol. chains lie approx. parallel to the surface. On moistening and stretching these chains are pulled approx. parallel to the direction of stretching, and give rise to an X-ray pattern resembling that of muscle or

α -keratin. Further stretching gives a pattern resembling that of β -keratin. Exposure to steam fixes the β pattern at the expense of the α , as in the case of stretched hair. (I) films can usually be stretched in cold H₂O to approx. three times their original length, and like keratin fibres, show well-marked long-range reversible elasticity, the β pattern disappearing on contraction when the film has not been kept stretched in the dry state. Unstretched (I) film like keratin in the labile state contracts by about 20% when exposed to steam. L. S. T.

Sex differences from viewpoint of biochemistry. III. T. TADOKORO (J. Fac. Sci. Hokkaido Imp. Univ., 1934, 2, 13—58).—Myosin (I) and myogen (II) were obtained from muscle by extraction with aq. NaCl and pptn. with (NH₄)₂SO₄, and separated into α and β fractions by pptn. from aq. solution with AcOH. The isoelectric point (III) of β was more acid than that of α . β contained less NH₂-, arginine-, and lysine-N and more histidine- and cystine-N than α . Female (I) and (II) were similar to the β fractions of male (I) and (II). Ovovitellin is separated into α and β fractions by fractional pptn. with AcOH. The (III) of β was more acid than that of α . β contained less (NH₂)₂-, arginine-, cystine-, and lysine-N and more NH₂- and histidine-N than α . H. D.

Potassium [of muscle]. A. LEULIER and A. BERNARD (Bull. Soc. Chim. biol., 1934, 16, 1663—1674).—In the dog, pigeon, cat, and rabbit, the K content of involuntary and voluntary muscle (I) increases from birth with age. The young guinea-pig has the same K content of (I) as the adult animal. Injections of pilocarpine increase the K content of the cardiac muscle, whilst eserine increases that of the skeletal muscles. Gastrocnemius muscle of the frog loses nearly all its K⁺ on immersion in distilled H₂O, but in Ringer's solution with or without addition of K⁺ the diffusion is much less. A. L.

Cataphoresis of normal and pathological crystallin. S. KREIMER and J. NORDMANN (Compt. rend. Soc. Biol., 1935, 118, 83—85).—Crystallin from ox, rabbit (I), and man (II) has 3 isoelectric points at p_H 3.5—4, 5.2—6.8, and 8.0—9.5. With spontaneous cataract in (II) and that caused by C₁₀H₈ in (I), the second isoelectric point is displaced to 6.2—8.0. A. L.

Composition of flesh of domestic fowl. R. HOLCOMB and W. A. MAW (Canad. J. Res., 1934, 11, 613—621).—The % of H₂O, fat, ash, protein, and N in the combined skin, fat, and flesh of chickens are given. E. C. S.

Cholesterol and lecithin in teeth and saliva. F. KRASNOW (J. Dent. Res., 1934, 14, 226—227).—In saliva, lipin-P (I) ranges from 0.1 to 0.4 mg. and cholesterol from 2.0 to 9.0 mg. per 100 ml. In enamel and dentine (I) ranges from 0.5 to 2.8 mg. and from 0.1 to 1.7 mg. per 100 mg., respectively. NUTR. ABS. (m)

Determination of iron in dental enamel. L. L. ENGEL (J. Dent. Res., 1934, 14, 273—276).—Enamel is treated with HNO₃ and the mixture evaporated and ignited. After re-evaporation with HCl the residue is extracted with dil. HCl. Fe is determined colori-

metrically with 2 : 2'-dipyridyl after adjusting the p_H of the solution to avoid pptn. of Ca₃(PO₄)₂.

CH. ABS. (p)

Spark-spectrographic detection of iron in animal tissues. R. MEYER (Protoplasma, 1934, 22, 34—43).—Appropriate apparatus is described and its application to the examination of pigmented cells in the liver of *Salamandra maculosa* recorded. A. G. P.

Copper and "inorganic" iron contents of human tissues. S. L. TOMPSETT (Biochem. J., 1935, 29, 480—486).—The Cu of tissues such as liver (I), kidney, brain (II), pancreas (III), and spleen (IV) is completely extracted with CCl₃·CO₂H and is determined directly in the extract with Na diethyl-dithiocarbamate (V) (A., 1932, 1182). Cu is determined in bone and milk by dissolving the ash in aq. HCl, adding Na citrate, aq. NH₃ until alkaline, and aq. (V), and extracting the complex with Et₂O. The residue after removal of Et₂O is ashed with HClO₄ and H₂SO₄ and Cu is determined in the ash. "Inorg." Fe is determined by adding Na₄P₂O₇ to the ground tissue followed by CCl₃·CO₂H. To an aliquot of the filtrate thioacetic acid and aq. NH₃ are added and the colour is compared with a standard. (I) and (IV) have the greatest, and (II) and (III) the least, [inorg. Fe]. Vertebrae and ribs have fairly high and equal [Fe]. H. D.

Iodine content of oysters. E. J. COULSON (U.S. Dept. Comm., Bur. Fisher. Invest. Rept., 1934, 18, 2—10).—Analytical data are given. Differences in I and Fe contents of samples from various sources may be characteristic of locality of growth. CH. ABS. (p)

Biochemistry of invertebrates of the sea. P. S. GALTISOFF (Ecol. Monog., 1934, 4, 481—490).—Distribution of inorg. matter in invertebrates is discussed with special reference to the Zn, I, Cu, and Fe in oysters. CH. ABS. (p)

Iodine content of the human pituitary. G. F. KOPPENHOFER (Z. ges. exp. Med., 1934, 94, 57—62).—The pituitary (I) of the normal adult contains I; in males there is slightly > in females. In all conditions leading to cachexia the I content is reduced. In liver disease (cirrhosis and toxic atrophy) and in pregnancy no I is found. No correlation is evident between the I content of (I) and thyroid histology. The thyrotropic hormone of the anterior (I) contains no I. NUTR. ABS. (m)

Salts of young bone. C. M. BURNS and N. HENDERSON (J. Physiol., 1934, 82, 7p).—The H₂O content of the cartilaginous epiphyses and ossifying bones of young kittens (1 day to 12 weeks old) decreases with increasing age. From the vals. obtained for Ca, P, and CO₃ of different parts of the bones, bone salts are probably not deposited as a compound of Ca₃(PO₄)₂ and CaCO₃, but rather as a mixture of the two. Furthermore, the composition of the bone gives no indication of the changes occurring under different conditions, unless changes in size and modelling are also considered. NUTR. ABS. (b)

Composition of bones : the femur of the horse. L. SILBERSTEIN (Compt. rend., 1935, 200, 421—

423).—The S, P, Ca, Mg, Na, K, Fe, Al, CO_2 , Cl, F, and total ash contents of the femur of the horse, dried at 105° , have been determined. The principal inorg. constituent is $[\text{Ca}_3(\text{PO}_4)_2]_2\text{CaCO}_3$. Small quantities of $\text{Ca}(\text{OH})_2$ and salts of other metals are also present.

J. W. S.

"Vital reduction" of silver salts by certain arthropodal organs. H. KOCH (Ann. Soc. Sci. Bruxelles, 1934, 54, B, 346—361).—The deposition occurring on certain organs of arthropoda immersed in 0.05–0.1% aq. AgNO_3 is due to selective ("vital") adsorption of Ag^+ followed by a reduction which also occurs, but to a smaller extent, in dead tissue.

F. O. H.

Methylene-blue and acid fuchsin for subcutaneous tissue spreads. T. T. BAIRD (Stain Tech., 1935, 10, 35).—Subcutaneous tissue from the groin of an animal the tissues of which have been stained *in vivo* with trypan-blue is fixed in 5% neutral CH_2O , washed, stained with 1% aq. methylene-blue, washed, counterstained in 1% aq. acid fuchsin, washed, dehydrated in CO_2 , differentiated in EtOH , cleared in xylene, and mounted in Canada balsam.

H. W. D.

Trichloroethylene as a solvent in histological technique. R. E. OLTMAN (Stain Tech., 1935, 10, 23—24).— $\text{CHCl}_3\text{CCl}_2$ is a satisfactory substitute for xylene.

H. W. D.

"Glychrogel" mounting solution. R. M. WOTTON and R. L. ZWEMER (Stain Tech., 1935, 10, 21—22).—0.2 g. of $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ is dissolved in 30 c.c. of warm H_2O and added to a hot solution of 3 g. of gelatin in 50 c.c. of H_2O with which 20 c.c. of glycerol have been mixed. The liquid is then filtered and stored with a crystal of camphor as preservative.

H. W. D.

Effect of diets low or high in chloride on the sodium chloride content of tears. D. MICHAIL and L. RUSV (Compt. rend. Soc. Biol., 1934, 116, 1091—1093).—A diet devoid of Cl⁻ produces sometimes a rise in the NaCl content, sometimes a fall. These results are interpreted in the light of the previous demonstration that the NaCl content of tears depends directly on the tonus of the sympathetic nervous system. A diet containing an excess of Cl⁻ caused a rise in the lachrymal NaCl, which returns to normal in 24 hr.

NUTR. ABS. (m)

Excretory function of the saliva. J. K. MAYR (Klin. Woch., 1934, 13, 1270—1272).—The salivary glands (I) take an active part in the excretion of various substances, and the salivary excretion (II) of such substances as Au, Br, Bi, and neosalvarsan coincides with their accumulation in the tissue-fluids, e.g., in the fluid of a blister raised by cantharides. The apparent (II) is due merely to permeation of (I), as of all tissues, with the substance in question.

NUTR. ABS. (m)

Action of snake venoms on surface films. A. HUGHES (Biochem. J., 1935, 29, 437—444).—The venoms (I) of *Pseudechis porphyriacus*, *Denisonia superba*, *Notechis scutatus*, *Naia naia* (II), and *Vipera elegans* decrease the surface potential of lecithin (III) spread on aq. NaCl to vals. rather > those of

lysolecithin; the discrepancy is due to the presence of protein associated with (I). (I) have no effect on films of cholesterol (IV) or of protein, and cause no hydrolysis of tripalmitin, triolein, cerebrin, or sphingomyelin. (IV) has no sp. inhibiting power on the reaction. The influence of (I) is inhibited at p_H 10.8 and < 4.8; the optimal p_H is approx. 7.3. (I) are stable at p_H 1 but not at p_H 13. Compression of the film of (III) decreases the rate of hydrolysis. At concns. of (I) > 1 p.p.m. the reaction is of zero order and is complete in 5 min., whilst at lower concns. the reaction rate diminishes rapidly with concn. of (I). The heat-stability of (I) depends on the p_H of the medium, being least at p_H > 7.0. There is a direct relation between hæmolytic and lecithinase activities in (I). The (I) of (II) differs from the others examined in that at concns. > 0.5 p.p.m. hydrolysis of (III) is inhibited.

H. D.

Bile acid of snake's bile. V. DEULOFEU (Z. physiol. Chem., 1934, 229, 157—158).—The only bile acid isolated from *Crotalus terrificus* and *Bothrops alternata* was cholic acid. A little cholesterol was obtained.

J. H. B.

Sulphur content of pancreatic blood and thoracic lymph. III. Sulphur content of thoracic lymph after pancreatectomy. IV. Sulphur content of thoracic lymph after ligation of the pancreas and after injection of secretin in dogs. S. KUMAMI (J. Biochem. Japan, 1934, 20, 431—440, 441—450; cf. A., 1933, 965; 1934, 1379).—III. Pancreatectomy in dogs gradually increases the thoracic lymph-S (I), an effect not appreciably influenced by stimulation of the vagus. Injection of glucose or 10% NaCl causes a slight decrease, the level returning to the normal (i.e., increased) val. within 3—4 hr. The influence of pancreatic activity on (I) is discussed.

IV. With dogs in which the ligatured pancreas has atrophied, injection of glucose or vagal stimulation produces a definite but transient rise in (I); intravenous injection of secretin is without effect. Of the increase in (I), > 50% is probably due to increased secretion of insulin.

F. O. H.

Sugar content of human amniotic fluid and the occurrence of fructose. M. ICHIJÔ (Japan J. Med. Sci., II, Biochem., 1934, 2, 359—368).—Reducing fermentable sugars in amniotic fluid decrease towards the time of parturition. Approx. 10% of the total sugar is fructose and the remainder probably glucose.

CH. ABS. (p)

Inorganic constituents of gastric juice and their relationships to each other. G. KATSCH, F. BALTZER, and J. BRINCK (Arch. Verdauungskr., 1934, 56, 1—34).—The human gastric glands secrete HCl. There is also a neutral diluting secretion and an alkaline secretion in the stomach.

NUTR. ABS. (m)

Acid-base balance of gastric juice, blood, and urine before and after stimulation of the gastric juice by histamine. L. MARTIN (Bull. Johns Hopkins Hosp., 1934, 55, 57—80).—In normal subjects the changes observed indicate a relative alkalosis as a result of gastric secretion. In achlorhydric

patients, the differences are usually similar in kind but less in degree.

NUTR. ABS. (m)

Formation of crop-milk of pigeons, its composition and importance for the growth of squabs. W. DABROWSKA (Mem. Inst. Nat. Polon. econ. rurale Pulawy, 1932, 13, 276—295).—The val. of crop-milk (I) for early growth of squabs is due to its high protein and fat contents. Secretion of (I) depends on sex hormones.

CH. ABS. (p).

Calculating composition of milk from fat test alone. J. C. MARQUARDT (Food Ind., 1934, 6, 261).—The formulæ, total solids = $7.627 + 1.346 \times \text{fat}$ and protein content = $1.597 + 0.446 \times \text{fat}$ give results correct to within 0.1%.

CH. ABS. (p)

Composition of the milk of an anthropoid ape. H. M. SCHUMACHER (Z. Kinderheilk., 1934, 56, 415).—100 ml. of milk from a 9-year-old orang-outang which had been lactating for 2 years contained: total solids 11.47, fat 3.5, total protein 1.43, caseinogen 1.06, albumin 0.37, non-protein-N 0.026, sugar 6.02, ash 0.24; Cl 0.09%.

NUTR. ABS. (m)

Seasonal variations in the composition of ewe's milk. T. M. B. (Riv. Zootec., 1934, 11, 357—358). The density of the milk and the whey, the cryoscopic const., the lactose and ash contents show max. vals. early in the year, fall steadily until Sept. and Oct. [end of lactation (I)], and rise in Nov. and Dec. at the beginning of the new (I). The fat and total solids vary inversely to the above. The proteins are approx. const.

NUTR. ABS. (m)

Relation between milk yield, absolute fat production, and percentage fat content of milk in relation to the coefficient of Ezekiel. J. KŘÍŽENECKÝ (Vestn. Česk. Akad. Zemed., 1934, 10, 6—8).—Earlier results and conclusions (A., 1934, 678) are confirmed.

NUTR. ABS. (m)

Passage of vegetable or animal material into the milk. M. LAGRANGE-FRANCES (Le Lait, 1934, 14, 811—817).—Lists of plants which give a particular colour or flavour to milk, or facilitate or retard its coagulation, are given. On feeding 100 g. of cod-liver oil each day to a cow giving 11 litres of milk per day, there was a rise in the % of fat after 15 days and a deeper colour in the butter. A similar effect was obtained by feeding 1.5 kg. of red carrots for one month.

NUTR. ABS. (m)

Human milk. XVI. Vitamin-D potency as influenced by supplementing the diet of the mother, during pregnancy and lactation, with cow's milk fortified with a concentrate of cod-liver oil (test on rachitic infants and rats). D. J. BARNES, F. COPE, H. A. HUNSCHER, and I. G. MACY (J. Nutrition, 1934, 8, 646—657).—Direct administration of vitamin-D to infants gives more effective correction of rickets than indirect methods using breast milk.

A. G. P.

Influence of physical properties of milk on its rate of digestion *in vivo*. C. Y. CANNON and E. (Rept. Agric. Res. Iowa Agric. Exp. Sta., 1933, 25—26).—Curd tension (I) of milk (II) was reduced by pasteurisation at 61°, and still more by oung. Heating at 116° for 15 min. destroys (I).

The rates of digestion by calves of pasteurised, boiled, and autoclaved (II) were similar and > that for raw (II), the difference being most marked after the first 6 hr. of digestion.

CH. ABS. (p)

Composition of intestinal secretions. E. J. DE BEER, C. G. JOHNSTON, and D. W. WILSON (J. Biol. Chem., 1935, 108, 113—120).—The intestinal juices of unanæsthetised dogs having isolated loops at various levels of the intestine were examined. The rates of secretion in the jejunal and ileal were > in the colonic loops. The concns. of Na⁺, K⁺, and Ca⁺⁺ were relatively const. in all secretions (I), but [HCO₃⁻] varied inversely with [Cl⁻], being higher in ileal and colonic than in the less alkaline jejunal (I). Intravenous injection of NaCl, but not of Na₂CO₃, caused an increase in the concn. of the injected anion in the jejunal and ileal (I).

A. E. O.

Composition of mixed duodenal secretions. C. M. WILHELMJ, L. C. HENRICH, and F. C. HILL (Proc. Soc. Exp. Biol. Med., 1934, 31, 969—973).—The average alkalinity, in dogs, of the pancreatic juice, succus entericus, and bile was 0.04N and [Cl] 307 mg. per 100 c.c.

CH. ABS. (p)

Protein and nitrogen content of duodenal juice. J. KRAUSE (Arch. Verdauungskr., 1934, 56, 141—148).—Coagulable protein is normally absent from the duodenal secretion and the bile, but appears when the liver parenchyma is damaged and when the biliary channels are inflamed. Total N is correspondingly increased.

NUTR. ABS. (m)

Method of Terwen for the determination of urobilin. M. ROYER (Compt. rend. Soc. Biol., 1934, 117, 1240—1242).—The method is modified. Urobilin (I) is reduced in absence of air with FeSO₄. (NH₄)₂SO₄, and NaOH; urobilinogen is then oxidised with I in acid solution and (I) determined by the fluorescence method.

R. N. C.

Detection and determination of urinary porphyrin. W. THIEL (Klin. Woch., 1934, 13, 700—703; Chem. Zentr., 1934, ii, 2109).—The porphyrin is extracted and then detected, or determined colorimetrically, by the red colour developed in HCl solution.

H. N. R.

Isolation of glycochamine from urine. C. J. WEBER (Proc. Soc. Exp. Biol. Med., 1934, 32, 172—174).—Details of the extraction of glycochamine (I) from acidified urine with Lloyd's reagent are given. The urine of patients with pseudohypertrophic muscular dystrophy (II) contains more (I) than normal urine. (I) is not produced during the isolation process from creatine, creatinine, or glycine and urea. The isolated (I) represents 23% of the substances (III) in the urine giving a positive Sakaguchi reaction. Glycine fed to a patient with (II) increases (III) in the urine by approx. 60%.

R. N. C.

Colorimetric determination of the tyrosine index of urinary polypeptides. R. GOFFON (Bull. Soc. Chim. biol., 1934, 16, 1686—1691).—The urine is heated with aq. CCl₃·CO₂H, the clear liquid being pptd. with the Folin phosphotungstic reagent (I). The washed ppt. is divided into two equal parts, one of which is treated with the Folin-Wu phenol

reagent, and the other with (I). The difference in optical density \propto the tyrosine content. A. L.

alloPregnandiol, an alcohol from urine of pregnancy.—See this vol., 341.

Diet and reaction of urine. L. M. MODEL, M. G. KUZIN, and Z. V. ANSHMID (J. Physiol. U.S.S.R., 1934, 17, 100—111).—The NH_3 content and p_{H} of urine cannot be predicted from the nature of the mineral matter of the diet alone. High-fat or potato diet increases $[\text{NH}_3]$ and p_{H} in urine. Vitamin deficiency increases $[\text{NH}_3]$. Increased urinary NH_3 is not necessarily accompanied by greater alkalinity.

CH. ABS. (p)

Daily fluctuations in urinary p_{H} . F. KENYON, C. A. WILSON, and I. G. MACY (Arch. Pediat., 1934, 51, 490—500).—The vals. for children (I) range from 4.8 to 8.4 (average 6.0) and for women (II) from 5.0 to 7.9. Alkaline trends are seen after meals and definite alkaline tides appear in (I) in the afternoon following the heavy midday meal, and in (II) after breakfast. (I) show extensive individual variations throughout the day, and widely different positions in the p_{H} range from day to day. No correlations are found between urinary p_{H} , vol., and sp. gr., emotional excitability, or incidence of dental caries.

NUTR. ABS. (m)

Concentration and dilution of urine. E. FREY (Arch. exp. Path. Pharm., 1935, 177, 134—141).—Direct observation of the injected (with blood or Indian ink suspension) vessels of rabbits' kidney indicates that with diuresis due to aq. Na_2SO_4 the greater pressure is in the glomeruli, whilst with that due to H_2O it is in the capillaries and afferent vessels. Hence the concn. or dilution of the urine is dependent on the direction of blood-flow, a phenomenon in agreement with the arrangement of the renal vessels.

F. O. H.

Ultra-filtration in the glomeruli. J. MOSONYI and L. VOITH (Arch. exp. Path. Pharm., 1935, 177, 177—182).—Addition of electrolyte-free horse serum-albumin diminishes the Cl' content (Volhard) and osmotic pressure (I) of 0.85% aq. NaCl . Ultra-filtration of serum gives a residual fluid (II) of increased protein content and diminished $[\text{Cl}']$ and (I). Addition of erythrocytes to (II) increases its (I) and contents of Cl' and protein. The bearing of the results on glomerular filtration is discussed and the conclusions of Wearn and Richards (A., 1926, 195) are criticised.

F. O. H.

Determination of magnesium in urine without preliminary removal of calcium. S. I. YOSHIMATSU and M. HASEGAWA (Tohoku J. Exp. Med., 1934, 22, 463—466).—Mg is pptd. directly from urine by 8-hydroxyquinoline in hot $\text{NH}_4\text{Cl}-\text{NH}_3$ solution. The ppt. is removed by centrifuging, washed with NH_4OAc solution, dissolved in HCl , and treated with excess of Na_2CO_3 and the Folin-Denis reagent for phenols. The colour is compared with that of standard solutions. CH. ABS. (p)

Neutral sulphur of urine. Criticism of the iodometric titration of ethyl sulphide. G. MEDES, K. EVANGELIDES, and K. SHINOHARA (Proc. Soc. Exp. Biol. Med., 1934, 32, 156—157).—The amount

of I taken up at const. temp. by $\text{Et}_2\text{S} \propto$ the amount of Et_2S added, and also $[\text{I}]$, $[\text{I}']$, and p_{H} , the removal of I from solution being due probably to its solubility in Et_2S . Hence the iodometric method for determining Et_2S in urine, based on the apparent formation of Et_2SI_2 (cf. A., 1933, 850), is untrustworthy.

R. N. C.

Determination of digestibility of protein in the mixed excreta of fowls. N. I. CHLEBNIKOV, A. S. SOLUN, and A. K. DANILOVA (Trans. Poultry Res. Inst. Moscow, U.S.S.R., 1934, 1, No. 4, 20—28).—The mixed excreta are boiled with abs. EtOH for 2½—3 min. and filtered. The urea, creatine, and creatinine pass into the filtrate as oxalates, leaving $(\text{NH}_4)_2\text{C}_2\text{O}_4$, uric acid, and indigestible protein as an insol. residue.

NUTR. ABS. (m)

Excretion by the colon. H. SALOMON (Rev. Soc. Argentin. Biol., 1933, 9, 223).—The H_2O -sol. ash (I) in faeces (II) represents the portion excreted by the intestine. The insol. portion is derived from unabsorbed food. With diets rich in cellulose there is an increase in (I), lipins, and cholesterol in (II). Absorption bands of carotene and xanthophyll are observed in (II) after 9 days of diet lacking these pigments.

CH. ABS. (p)

Physico-chemical character of the faeces of normal infants and children with special reference to the character of the faeces on apple and banana diet. T. BAUMANN (Monatsschr. Kinderheilk., 1934, 60, 81—135).—The p_{H} vals. of 24-hr. samples of faeces of infants and children on various diets were: meconium (I), 6.0—6.4; breast milk (II), 4.86—6.1; cow's milk (III), 5.15—8.45; butter-milk (IV), 7.8—8.35; mixed diet (V), 6.4—8.15; apple diet (VI), 5.3—7.95; banana diet (VII), 7.5—8.25. There was no relationship between the p_{H} and the Ca or PO_4''' concns. or ratios. The p_{H} of the deposit was generally > that of the supernatant fluid, the difference being attributed to insol. PO_4''' . The content of free non-volatile org. acids, which were more abundant in (II), (VI), and (VII) faeces than in the others, had a marked influence on the p_{H} . The H_2O and volatile acid contents of the faeces or the reaction and Ca and PO_4''' of the diet bore no const. relation to the p_{H} . Ca and PO_4''' were high and their ratios low in (II), (VI), and (VII) faeces and *vice versa* in the others. The buffering powers of the faeces were in the order: (III), (IV), and (V) > (II) > (I), (VI), and (VII). Buffering power was not related to the p_{H} or Ca : PO_4''' ratio of the faeces. Buffering depended on the total Ca and PO_4''' of the faeces (and consequently of the diet) and on the free org. acids and their salts in the faeces. According to the reaction faecal Ca exists as $\text{Ca}_3(\text{PO}_4)_2$, CaHPO_4 , or $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

NUTR. ABS. (b)

Colloid chemistry, homœopathy, and medicine. A. KUHN (Chem.-Ztg., 1935, 59, 85—86, 106—108).—A review.

Role of copper in hæmoglobin regeneration. H. L. KEIL and V. E. NELSON (Proc. Iowa Acad. Sci., 1932, 39, 163—167).—Among salts of a no. of metals examined only those of Cu induced regeneration of hæmoglobin (I) in anæmic rats. FeCl_3

added to market milk (II) increased (I) owing to the Cu content of (II). The effect of FeCl_3 in this case was increased by simultaneous additions of Mn, As, and Ni.
CH. ABS. (p)

Protective action of copper and spleen extract in *Bartonella* anaemia in rats. G. PANDO (Z. Immunitat., 1934, 82, 63—65; Chem. Zentr., 1934, ii, 1152).—Neither injection of $\text{Cu}(\text{OAc})_2$ and feeding with CuSO_4 nor treatment with lipins extracted from the spleen has any effect on *Bartonella* anaemia.
R. N. C.

Significance of the serum-iron in anaemia. J. F. McINTOSH (J. Clin. Invest., 1934, 13, 714).—In dogs after bleeding the serum-Fe (I) falls and remains low until haemoglobin (II) regeneration is complete. In cases of hypochromic anaemia during Fe medication (II) tends to rise first, (I) later; narrow fluctuations in (II) are accompanied by wide changes in (I). In an untreated case of pernicious anaemia (I) was high; during reticulocytosis produced by liver extract it fell and rose gradually as treatment was continued. (I) appears to represent a balance between (II) synthesis and Fe available from food and Fe depots.
NUTR. ABS. (m)

Characteristics of the synovial fluid in various types of arthritis. C. S. KEEFER, W. K. MYERS, and W. F. HOLMES, jun. (Arch. Int. Med., 1934, 54, 872—887).—The corresponding bacteria could be cultured from the synovial fluid (I) from cases of gonococcal, haemolytic streptococcal, and tuberculous arthritis (II), (I) from other types of (II) being sterile. Gonococcus complement fixation and Wassermann tests agreed with those given by the blood. The total cell count is increased in all types of (II), being highest for infected (I). The non-protein-N content is the same in infected or sterile (I) and in blood. The total protein is > normal.
C. G. A.

Characteristics of synovial fluid in gonococcal arthritis. W. K. MYERS, C. S. KEEFER, and W. F. HOLMES (J. Clin. Invest., 1934, 13, 767—776).—Total protein and cell contents of the fluid characterise it as an exudate. The non-protein-N was identical with that of blood (I) and the sugar varied with the level of (I)-sugar and nos. of leucocytes and bacteria.
CH. ABS. (p)

Glutathione content of the blood in chronic arthritis and rheumatoid conditions. B. D. SENTURIA (J. Lab. Clin. Med., 1934, 19, 1151—1155).—Vals. are not appreciably different from normal.
CH. ABS. (p)

(A) **Technique for showing the presence of a principle acting on the adrenal cortex in urine cancer.** (B) **Gonadostimulin in urine of cancer.** M. ARON (Compt. rend. Soc. Biol., 1935, 118, 85—88, 88—90; cf. A., 1934, 206).—(A) Examination of the adrenal cortex of rabbits before and after injection of the animals with the COMe_2 ppt. from urine of cancer indicates that (I) contains a principle which causes a large excretion of lipins. (B) (I) causes, on injection into rabbits, a dilatation of the ovarian follicles.
A. L.

Spontaneous precipitation of cholesterol in a [cancerous] plasma. C. SANNIE and R. TRUHAUT

(Compt. rend. Soc. Biol., 1934, 117, 1188—1190).—The cryst. substance pptd. on keeping from a sample of plasma from a case of ovarian cancer had the solubility and colour reactions of cholesterol (I). The (I) of the entire sample was 4.2 g. per litre. In later samples from the same subject, pptn. did not occur when (I) was 3.1 and 2.0 g., but an unidentified ppt. was obtained in a sample with 4.5 g. per litre. Analysis of the sample with 3.1 g. showed that the (I)-solubilisers (bile salts, soaps, etc.) were more or less increased, the (I)/lipin ratio being decreased.
R. N. C.

Distribution of arginine in Jensen rat sarcoma. E. ANNAU and B. GOZSY (Z. Krebsforsch., 1934, 40, 572—576; Chem. Zentr., 1934, ii, 1804).—The average arginine (I) content of the sarcoma is 0.0385 mg. of extracted (I) per g. of fresh tissue, and 4.46% of the total (I), referred to the dried substance. Under the same conditions, rat liver contains 0.00—0.0047 mg. of extracted (I) per g. of tissue, and 3.16% of total (I). The high (I) content of the sarcoma is due to the presence of a histone containing 13.94% (I) and 18.38% N.
R. N. C.

Malignant growth in relation to enzyme activity. M. COPISAROW (Protoplasma, 1934, 22, 137—144).—A review.
A. G. P.

Typical chemical change of plasma-albumins in carcinoma. P. F. MERZBACH (Klin. Woch., 11, 1984—1985; Chem. Zentr., 1934, ii, 1491).— $\text{NH}_2\text{-N}$ is high in patients with malignant tumours; in normal persons it is never > 8% of the total N.
R. N. C.

Cyanosis from compressions of the mediastinum. F. C. ARRILLAGA and A. C. TAQUINI (Compt. rend. Soc. Biol., 1934, 117, 1238—1239).—In three patients with mediastinal tumours, compression of the vena cava, and cyanosis there was an intense alveolar hyperventilation, the CO_2 of the alveolar air being low and the O_2 high. The arterial blood of the cyanosed area was perfectly oxygenated, the haemoglobin being 94% saturated. The venous blood showed very low O_2 and high CO_2 , and the alkaline reserve was low. Cyanosis was due to the slowing-down of the local circulation, with consequent increased yield of O_2 to the tissues, and the passage into the tissues of an O_2 -poor capillary blood.
R. N. C.

Effect of vitamin-C on the growth of experimental mouse cancer. E. FODOR and S. KUNOS (Z. Krebsforsch., 1934, 40, 567—571; Chem. Zentr., 1934, ii, 1801).—Subcutaneous administration of ascorbic acid (I) increases very considerably the rate of growth (II) of Ehrlich mouse cancer; the increase is greater when (I) is given with the food. (II) increases \propto the size of the tumour.
R. N. C.

Effect of heavy water on viability of mouse sarcoma and rat carcinoma. K. SUGIURA and L. C. CHESLEY (Proc. Soc. Exp. Biol. Med., 1934, 31, 1108—1111).—In both cases proliferation was unaffected by immersion in 94% H_2O (I) containing isotonic amounts of Locke-Ringer solution. Destruction of growth capacity in hypotonic solution was influenced by (I).
CH. ABS. (p)

Effect of deuterium oxide on rat sarcoma R-39. C. E. REA and S. YUSTER (Proc. Soc. Exp. Biol. Med., 1934, 31, 1058—1060).—Multiple injections of H_2O in the neighbourhood of the tumour stimulated the growth in some cases.

CH. ABS. (p)

Carcinogenicity of chrysene and oleic acid. A. C. BOTTOMLEY and C. C. TWORT (Amer. J. Cancer, 1934, 21, 781—788).—The carcinogenic action (I) of chrysene (III) is increased by dissolution in oleic acid (II). Solutions in C_6H_6 have no (I), but cause tumours if small amounts of (II) are added. Solutions in lard are inactive. The (I) of (III) and of a synthetic pinene tar increases with the concn. used. The action resembles that of 1:2:5:6-dibenz-anthracene.

CH. ABS. (p)

Properties of the causative agent of a chicken tumour. IX. Effects of aqueous extracts of chicken tumour on yeast-nucleic acid. D. A. MACFAYDEN (J. Exp. Med., 1934, 60, 361—373).—Extracts contain a polynucleotidase (I) and a phosphatase, distinguished by reactions to H_2O , pH , and rates of activity. (I) is adsorbed by $Al(OH)_3$.

CH. ABS. (p)

Occurrence of calcareous disease. I. Disease caused by fodder containing calcium compounds. T. SAIKI and K. FUJIMOTO (J. Agric. Chem. Soc. Japan, 1934, 10, 619—620).—Disease appeared in rats receiving a complete diet with 3.9% Ca as lactate, carbonate, or as calcite, but not in those receiving Ca phosphate.

CH. ABS. (p)

Biochemical aspect of dental caries. C. T. GROVE and C. J. GROVE (Dental Cosmos, 1934, 76, 1029—1036).—Salivary mucin and dental plaques are sol. in NH_3 , and high salivary NH_3 (I) is a factor in immunity to caries. An alkaline diet influences caries by increasing (I).

CH. ABS. (p)

Susceptibility of rats to dental caries. IV. Etiology of fissure caries. T. ROSEBURY, M. KARSHAN, and G. FOLEY (J. Amer. Dental Assoc., 1934, 21, 1599—1611).—The caries (I)-inducing ingredient of deficient rations is the cereal particle and not the sp. carbohydrate. Addition of Ca, P, and cod-liver oil to such diets did not prevent (I). Incidence of (I) was unrelated to the degree of calcification of teeth and bones or to the blood-Ca or -P.

CH. ABS. (p)

Factors predisposing to immunity to dental caries. Vitamins. J. D. KING (Brit. Dental J., 1934, 57, 233—239).—A review.

CH. ABS. (p)

Diet and its relation to dental disease. J. LENNOX (J. Amer. Dental Assoc., 1933, 20, 2203—2210).—Caries is induced by P-deficient diets. Changes occur in saliva whereby its inhibitory action on activities of *Lactobacilli* is lowered and P is leached from the crowns of teeth.

CH. ABS. (p)

Diet and nerve supply to dental tissues. M. MELLANBY and J. D. KING (Brit. Dental J., 1934, 56, 538—549).—Vitamin-A is an important factor in the maintenance of healthy tissues.

CH. ABS. (p)

Residual nitrogen and its fractions in the liver in experimental diabetes. H. ELIAS, H. KAUNITZ, and R. LAUB (Z. ges. exp. Med., 1934, 94, 182—198).—

In dogs starved for 4 days the residual N of the liver was reduced. After total pancreatectomy the residual N and urea- and polypeptide-N were markedly increased, whilst the NH_2 -N was reduced. After partial pancreatectomy the vals. approached those found in normal and fasting animals. When insulin was given to dogs after complete pancreatectomy the vals. were within normal limits.

NUTR. ABS. (b)

Fasting blood-carotene level in normal and diabetic individuals. H. BRANDALEONE and E. P. RALLI (Proc. Soc. Exp. Biol. Med., 1934, 32, 200—201).—Blood-carotene in diabetics is raised > 100%, and cholesterol approx. 30%, > normal.

R. N. C.

Blood-cholesterol in diabetic children. P. NOBÉCOURT and P. DUCAS (Arch. Med. Enfants, 1934, 37, 522—526).—There is no apparent correlation between the cholesterol content of the blood and level of blood-sugar, carbohydrate tolerance, or general health. The hypercholesterolaemia indicates a disturbance of lipin metabolism probably due to the diabetes.

NUTR. ABS. (m)

Pathophysiology of fat metabolism in diabetes. S. LEITES, E. SORKIN, and A. AGALETZKAJA (Klin. Woch., 1934, 13, 1272—1276).—In man, the character of the changes of blood-neutral fat (I) and -ketones (II) depends on the amount of fat ingested and to a greater extent on the initial level of (I) and (II). In diabetes this autoregulation is disturbed, the initial, max., and min. lipaemic and ketonaemic thresholds being increased. The degree of disturbance measures the severity of the disease. When (II) val. exceeds the initial threshold, administration of butter has an antiketogenic effect.

NUTR. ABS. (m)

Lipins of the skin in experimental diabetes. V. J. MATTHEWS, J. K. NEWTON, and W. R. BLOOR (J. Biol. Chem., 1935, 108, 145—151).—Experimental diabetes in the cat results in a mobilisation of neutral fat from the skin and muscles to the liver, the cholesterol (I) content of which decreases, and an increase in the phospholipin and (I) content of the skin.

A. E. O.

Synthetic production of β -hydroxybutyric and acetoacetic acids in fasting and in diabetes. J. MONGUIO (Klin. Woch., 1934, 13, 1116—1120).—Intravenous injection of 8 g. of NaOAc is followed, in fasting dogs, by a rise in the ketones of the blood. A more marked rise is produced by simultaneous administration of adrenaline. The same holds for human subjects on a diet poor in carbohydrate. After oral administration of 25 g. of NaOAc the ketone content of the urine of human diabetics increases considerably. AcOH may be a source of ketones when the liver contains little or no glycogen.

NUTR. ABS. (m)

Factors determining the effect of exercise on blood-sugar in the diabetic. R. RICHARDSON (J. Clin. Invest., 1934, 13, 699).—When the fasting blood-sugar (I) is < 175 mg. per 100 ml. it is reduced during exercise; when between 175 and 300 mg. it is unchanged, when > 300 mg. it is increased. Intravenous injection of 0.1 unit of insulin (II) causes a fall in (I) during exercise in the last group. Exercise after (II) or food is accompanied by a fall in (I)

in patients in whom it is unchanged or increased during exercise in the fasting state. In diabetics this effect of an intravenous injection of 0.5 unit of (II) lasts for half an hr. NUTR. ABS. (m)

Glucose excretion after exercise in experimental diabetes. W. H. CHAMBERS, H. E. HILM-WICH, and M. E. KENNARD (J. Biol. Chem., 1934, 108, 217—225).—No increase in urinary glucose (I) or N occurs during exercise. In recovery (I) and N excretion together increase and the (I) rise is succeeded by a fall. A similar rise and fall in D:N ratio is found after injecting adrenaline. The source of the extra (I) may be muscle-glycogen. H. T.

Physiology of the surviving mammalian heart. VIII. Consumption of sugars by surviving hearts of diabetic cats. R. VON POMOTHY (Biochem. Z., 1935, 275, 448—454; cf. A., 1933, 630).—The glucose consumption by the hearts is < that of normal hearts (I), whilst the mannose, fructose, and galactose consumptions are about half those of (I), the extent of consumption decreasing as the severity of the disease increases. Lactose and maltose are not consumed. W. MCC.

Influence of the pancreas and the liver on the glucose tolerance curve. S. SOSKIN, M. D. ALLWEISS, and O. J. COHN (Amer. J. Physiol., 1934, 109, 155—165).—The liver is essential to the normal curve. The pancreas is not essential if blood (I) contains sufficient insulin to maintain (I)-sugar const. CH. ABS. (p)

Physiological disturbances during experimental diphtheritic intoxication. IV. Blood-electrolyte and -haemoglobin concentrations. D. C. DARROW, H. YANNET, and M. K. CAREY (J. Clin. Invest., 1934, 13, 553—560).—After injection of diphtheria toxin rabbits' blood showed increased haemoglobin and serum-inorg. P and decreased Na⁺ and Cl⁻ concns. CH. ABS. (p)

Pathogenesis of renal dwarfism. A. LOESCHKE (Jahrb. Kinderheilk., 1934, 143, 11—35).—The growth deficiency is not \propto the impairment in renal function (I) and appears before (I) is at all marked. After administration of Na₂HPO₄ the blood-P reaches a level > in normal or rachitic children. The rise in blood-sugar after ingestion of glucose or subcutaneous injection of adrenaline is also greater in the renal dwarfs; this is attributed to acidosis. Urinary diastase is not increased. Dwarfism and renal changes are manifestations of a general congenital abnormality, and the development of rickets in renal dwarfs is probably due to lack of Ca and chronic acidosis. NUTR. ABS. (m)

Treatment of muscular dystrophy with glycine. D. P. CUTHBERTSON and T. K. MACLACHLAN (Quart. Med. [N.S.], 1934, 3, 411—435).—High muscular incapacity is associated with high creatinuria (I). Administration of glycine increased (I) for a period, with a subsequent return to normal or < normal levels. CH. ABS. (p)

Glycine deficiency and glycine therapy of progressive muscular dystrophy. W. LINNEWEH F. LINNEWEH (Deut. Arch. klin. Med., 1934, 166, 526—531).—In muscular dystrophy (2 cases)

there was no deficiency in glycine (I) stores or power to produce (I). The beneficial action of (I) is confirmed; its mode of action is not clear, but it is not a substitution therapy. When large amounts of BzOH were given to a patient on a diet poor in (I) there was no diminution in the excretion of creatine (II); hence direct formation of (II) from (I) seems not to occur. NUTR. ABS. (m)

Effect of gelatin feeding on cases of pseudo-hypertrophic progressive muscular dystrophy. P. KISNER, E. S. WEST, and J. A. KEY (Proc. Soc. Exp. Biol. Med., 1934, 32, 143—145).—The cases were temporarily improved by gelatin (I) feeding. The creatinine coeffs. were reduced during the feeding period, creatine excretion (II) being slightly increased. Feeding with glycine (III) increased (II), but the increased val. suggested that other constituents of (I) besides (III) were responsible. Ephedrine did not affect (II) excretion. (I) and (III) appeared to afford similar degrees of stimulation to the cases. R. N. C.

Creatine metabolism in muscle disease. A. T. MILHORAT and H. G. WOLFF (J. Clin. Invest., 1934, 13, 723).—Patients with muscle disease are classified as (1) those with marked creatinuria (I) and deficient creatine tolerance (II) exaggerated by administration of glycine, and (2) those with slight (I) and only slightly deficient (II) not exaggerated by glycine. The second group may have advanced atrophy in certain muscle groups. Creatine output and (II) appear to be an expression of the total mass of improperly functioning muscle and not an index of the amount of atrophied muscle or of the primary site of the disease. NUTR. ABS. (m)

Photosensitisation of animals in S. Africa. VII. Nature of the photosensitising agent in Geeldikkop. C. RIMINGTON and J. I. QUIN (Onderstepoort J. Vet. Sci., 1934, 3, 137—157).—The pigment responsible for the photosensitivity in Geeldikkop (a naturally occurring disease among sheep in S. Africa) and in experimental icterus produced in sheep by ligation of the bile duct is phylloerythrin (I). In a bile-fistula sheep on a chlorophyll-free diet there was no evidence of photosensitivity and (I) was not found in the bile, serum, or faeces. Probably (I) is produced in the fore-stomachs. NUTR. ABS. (m)

Respiratory exchange during exercise in heart disease. III. M. CAMPBELL (Quart. J. Med. [N.S.], 1934, 3, 369—380).—The CO₂ in expired air was < normal but O₂ utilisation was not much altered. CH. ABS. (p)

Iodine and cholesterol content of the blood as related to essential hypertension. M. BURGER and W. MOBIUS (Klin. Woch., 1934, 13, 1349—1352).—Blood-I (I) was determined by Pfeiffer's wet ashing method, which gave results 3—4 times > that of Fellenberg. (I) varies with age; from the 5th decade it rises to reach a max. in the 8th decade. Essential hypertensive subjects, without signs of renal failure, exhibited, in the main, an increased (I), and many had an increased basal metabolic rate (II). There was no general correspondence between (I), (II), and blood-pressure. Blood-cholesterol was not

increased; the occasional coincidence of high cholesterol with hypertension (III) is not of significance in the pathogenesis of essential (III). There is probably a causal connexion between increased thyroid activity and essential (III).
NUTR. ABS. (b)

Glycogenetic function of the liver in experimental hyperthyroidism. M. V. BUELL and M. B. STRAUSS (Bull. Johns Hopkins Hosp., 1934, 55, 220—228).—In severe experimental hyperthyroidism in rats (produced by repeated intramuscular injections of thyroxine) oral administration of *d*-lactic acid (I) produces, as compared with normal lactate-fed controls, a higher blood-(I) and a lower liver-glycogen. The blood-sugar rise is the same. This supports the view that in such hyperthyroidism gluconeogenesis from (I) is retarded, rather than that glycogenolysis is accelerated.
NUTR. ABS. (b)

Basal metabolism and specific dynamic action in cardiac disease and hyperthyroidism. A. BERLAND and T. DONSKOWA (Arch. Mal. Cœur, 1934, 27, 494—516).—In 31 cases of cardiovascular disease the basal metabolic rate (I) was > normal in 22 and < normal in 9 cases (Krogh's method). The increase in (I) is attributed to a disturbance in the resynthesis of glycogen from lactic acid, an anaerobic process which may be affected by the low O₂ tension and possibly acidosis. In these patients an absence of sp. dynamic action (II) was attributed to disturbance of cell metabolism. (II) is high in hyperthyroidism.
NUTR. ABS. (b)

Bile in thyroid diseases. Bile-stone formation. L. M. GOLBER (Arch. exp. Path. Pharm., 1935, 177, 159—166).—Increase of thyroid gland activity (I) (e.g., Basedow's disease) increases the cholesterol (II) content of the liver-bile and diminishes the bile acid (III) level of the bile in the gall-bladder (IV). The ratio (III)/(II) thus falls and whilst it rises with decreased (I), the concn. function of (IV) is depressed with both types. The bearing of the data on bile-stone formation is discussed. F. O. H.
NUTR. ABS. (b)

Importance of relative iodine deficiencies in certain forms of goitre. D. MARINE (J. Amer. Dietetic Assoc., 1934, 9, 1—5).—Goitre produced by the action of org. cyanides in cabbage on thyroid secretion is prevented by excess of I and by a factor occurring in fruits, possibly a hexuronic acid.
CH. ABS. (p)

Calcium metabolism in hyperparathyroidism. H. C. OLSEN (Diss., Nord. Insulinlab. Copenhagen, 1934, 195 pp.).—In the white rat urinary Ca increases, in general, with the degree of diuresis and is also greater when the previous diet is meat, containing 5—6 mg. of Ca per 100 g., than after a prediet of cereals and milk products, with 770 mg. of Ca per 100 g. Administration of paroidin (I) (Parke Davis) causes an increased output of Ca with corresponding hypercalcaemia and increased Ca content of liver and kidneys. This extra Ca possibly comes from the bones. (I) administration or hyperparathyroidism fixes the Ca in the blood, so rendering it useless to the organism and causing the liberation of more and more Ca to preserve the ratio mobile Ca : fixed Ca.
NUTR. ABS. (m)

Effect of dietary deficiency or infestation of chickens with the nematode, *Heterakis gallinae*. P. A. CLAPHAM (J. Helminthol., 1934, 12, 123—126).—Deficiency of Ca and P in the diet induces lowered resistance to infestation.
CH. ABS. (p)

Resistance of chickens to parasitism. J. E. ACKERT (Kansas Agric. Exp. Sta. 6th Biennial Rept., 1932, 112—113).—Resistance to infection by the nematode *A. lineata* was increased by vitamin-A (cod-liver oil) and -B (yeast) and by feeding of skim milk.
CH. ABS. (p)

Prophylactic effect of vitamin-A and -D on prevention of common cold and influenza. H. H. BEARD (J. Amer. Dietetic Assoc., 1934, 10, 193—199).—Daily administration of cod-liver oil reduced the no. and severity of colds, but did not affect influenza.
CH. ABS. (p)

Progressive obstructive jaundice. Changes in certain elements of the blood and their relation to coagulation. J. L. CARR and F. S. FOOTE (Arch. Surgery, 1934, 29, 277—296).—In obstructive jaundice clots are abnormal owing to accumulation of incompletely metabolised products of proteins in blood [S compounds, probably cysteine (I) or related mercaptans]. PhBr reduces the amount of (I) in circulation and reduces bleeding.
CH. ABS. (p)

Hydrogen-ion concentration of bile in relation to gallstone formation. H. BRONNER (Arch. klin. Chirurg., 1934, 180, 597—599).—In man, the reaction of the bile in hepatic ducts depends on the nature of the diet. Mainly vegetable food makes the bile alkaline, mainly animal food makes the bile acid. In an acid bile (I) the Ca content is high, whilst in an alkaline bile (II) the cholesterol (III), bile salt, and fatty acid contents are high. In mice, by alteration of the diet, it is possible to ppt. in the bile either Ca salts or (III), the Ca salts being pptd. in the (II), the (III) salts in (I). Thus sudden changes in the diet may lead to the typical gallstone with alternating concentric rings of Ca salts and (III).
NUTR. ABS. (b)

Fibrinolytic activity of haemolytic streptococci on blood of cases of recurrent tropical lymphangitis. P. MORALES-OTERO and A. POMALES-LEBRON (Proc. Soc. Exp. Biol. Med., 1934, 32, 110—113).—Vals. are given for the fibrinolytic activity (I) of 33 strains of *Str. haemolyticus* isolated from different conditions. The plasma clot derived from cases of recurrent tropical lymphangitis apparently develops a definite resistance to (I).
R. N. C.

Phosphatides. X. Nature of the phosphatides of the spleen in Niemann-Pick disease. E. KLENK (Z. physiol. Chem., 1934, 229, 151—156; cf. A., 1934, 1245).—The chief phosphatide constituent of a Niemann-Pick spleen was sphingomyelin (I). Lecithin and kephalin were also present. The fatty acids obtained from hydrolysis of (I) were lignoceric, and probably palmitic, stearic, and nervonic acids.
J. H. B.

Character of the gaseous distension in mechanical obstruction of the small intestine. J. S. HIBBARD and O. W. WANGENSTEEN (Proc. Soc. Exp. Biol. Med., 1934, 31, 1063—1066).—Following ob-

struction near the ilio-cæcal junction, gas accumulations comprised N_2 70%, CO_2 6—12%, O_2 10—12%, CH_4 , H_2 , NH_3 , NH_2Me , in small amounts, and in some cases H_2S 1—14%, increasing after death. Of the total, 68% was swallowed air; of the remainder, 70% diffused from blood, and 30% was due to decomp. of food. CH. ABS. (p)

Chemical and physical relation between blood-serum and body-fluids. I. Nature of cedema fluids and evidence regarding the mechanism of cedema formation. D. R. GILLIGAN, M. C. VOLK, and H. L. BLUMGART (J. Clin. Invest., 1934, 13, 365—381).—Differences in concn. of electrolytes are governed by differences in protein concn. Fluid is a simple dialysate in equilibrium with serum in accordance with the Donnan law. CH. ABS. (p)

Effect of posture (standing) on serum-protein concentration and colloid osmotic pressure of blood from the foot in relation to formation of cedema. J. B. YOUNG, H. S. WELLS, D. DONLEY, D. G. MILLER, and H. FRANK (J. Clin. Invest., 1934, 13, 447—450).—Standing increased serum-protein and colloid osmotic pressure. Albumin and globulin were equally affected. CH. ABS. (p)

Differentiation of the flocculation and "super-flocculation" in the serum of paludism. F. TRENSZ (Compt. rend. Soc. Biol., 1935, 118, 11—12).—Henry's reaction for paludism should be carried out in 0.3% aq. NH_4Cl in order to prevent the "super-flocculation" caused by H_2O alone. A. L.

Acid-base equilibrium and acidity of urine in peptic ulcer. F. B. LEWIN and A. M. BALZWINIK (Arch. Verdauungskr., 1934, 56, 81—93).—In patients (I) with ulceration, the urine during starvation is usually more acid, and the titratable acidity and urinary NH_3 are usually greater, than in the patients (II) with non-ulcerative gastro-intestinal affections. Intravenous injection of 50 ml. of 4% aq. Na_2CO_3 rarely produces alkaline urine in (I), whilst in (II) alkalisation is the rule. NUTR. ABS. (m)

Porphyria excretion in normal pregnancy and its relationship to blood-pigment metabolism. C. CARRIE and L. HEROLD (Arch. Gynakol., 1934, 158, 54—59).—The average daily excretion of porphyrin (I) in normal pregnancy fell from about 20 to about 10×10^{-6} g. at the end of pregnancy, with a rapid rise to normal after parturition. Since the rate of red cell destruction is increased towards the end of pregnancy, the fall of (I) excretion may indicate passage of the liberated (I) into the foetus for use in foetal blood formation. NUTR. ABS. (b)

Sugar and calcium partition in blood of normal and diseased animals. A. C. GONZAGA (Univ. Philippines Nat. Appl. Sci. Bull., 1934, 1, 4, 1—40).—Methods for determining sugar partition are compared. *Post-partum* vals. for total sugars increase during the first day, decline on the second, and increase again on the third. Animals in pregnancy show increased diffusible (I) and non-diffusible Ca (II) followed by a return to normal at parturition. Hyperglycaemia during milk-fever is from increased true sugar only. Hypo-

calcaemia is due to reduction of (I) and (II), (I) undergoing the greater change. CH. ABS. (p)

Blood-ammonia in eclampsia. J. B. LLUSIA (Zentr. Gynakol., 1934, 58, 1754—1771).—The slightly raised blood- NH_3 (I) of pregnancy is further increased in pre-eclampsia (II), still more so in eclampsia (III), and reaches its max. val. simultaneously with the onset of fits; the acidosis of pregnancy is similarly increased in (III). NH_3 precursors in the blood are diminished in (II) and (III), their place being taken almost entirely by free NH_3 . Eclamptic fits may be related to the high (I), but not so other symptoms. NUTR. ABS. (m)

Ketone content of the blood in labour and pre-eclamptic toxæmia. D. F. ANDERSON (J. Obstetr. Gynaecol. Brit. Empire, 1934, 41, 261—266).—Blood-COME₂ and -CH₂Ac-CO₂H vals. in cases of normal labour and cases of pre-eclamptic toxæmia were 1.1—3.2 mg. per 100 ml. in the former and 1.1—5.8 in the latter group, all > normal. NUTR. ABS. (p)

Variations in serum-magnesium and in partition of serum-calcium in normal parturition and in milk-fever. W. GODDEN and J. DUCKWORTH (Biochem. J., 1935, 29, 445—455).—In two out of three cows calving normally, raised serum-Mg (I) was observed at parturition (II); in milk-fever (III) a rise in (I) occurred at (II) which persisted for the duration of (III). The fall of serum-Ca following (II) was steeper in those animals in which (III) subsequently developed, corresponding with a greater depression in the Ca complexes adsorbable and non-adsorbable on $BaSO_4$. H. D.

Surface tension of urine during the menstrual cycle. C. F. SELOUS and P. W. PERRYMAN (Nature, 1935, 135, 233—234).—Variations in γ of urine during the menstrual cycle are recorded. The curve shows a min. during menstruation and a max. at the probable time of ovulation. L. S. T.

Sucrose in the urine in a case of pancreatic disease. T. BARANOWSKI and W. MOZOŁOWSKI (Klin. Woch., 1934, 13, 955—956; Chem. Zentr., 1934, ii, 1480).—Sucrose has been isolated and identified in the urine in a case of pancreatic lithiasis. R. N. C.

Physico-chemical changes in the blood following pneumothorax and section of the phrenic nerve. A. RISI (Arch. exp. Path. Pharm., 1935, 177, 119—126).—Following hypotensive pneumothorax (I) in dogs, the osmotic pressure (II) of blood and serum is diminished for approx. 48 hr., a min. val. occurring $\frac{1}{2}$ hr. after (I). Unilateral phrenectomy (III) has the opposite effect. With (I), but not (III), the alkaline reserve (IV) and pH of the blood are increased. The combined effect of (I) and (III) in normal or pregnant dogs is an increase in (IV), (II) being unchanged. F. O. H.

State of calcium in the blood of rickets. E. L. COMPERE, F. C. McLEAN, and A. B. HASTINGS (J. Clin. Invest., 1934, 13, 687—688).—Concns. of total Ca and ionic Ca (determined and calc.) were within or very near the normal range in children with rickets (I). No correlation was found with the severity of the (I) as judged by the inorg. P concn. of the serum or by the clinical evidence. NUTR. ABS. (b)

Glycolysis in the tissues of rachitic animals. G. POPOVICIU and G. BENETATO (Compt. rend. Soc. Biol., 1934, **116**, 1098—1100).—Anaerobic glycolysis is much diminished in the surviving kidney and liver of rachitic, as compared with normal, rats.

NUTR. ABS. (m)

Viosterol in the prophylaxis of rickets in premature infants. Clinical, chemical, and rontgenologic observations. L. T. DAVIDSON and K. K. MERITT (Amer. J. Dis. Children, 1934, **48**, 281—308).—The Ca and inorg. P of the serum are substantially the same for full-term and premature infants, and do not vary in the first 5 months even in severe clinical and rontgenologic rickets. Low vals. for Ca occur in osteoporosis. In doses of 20 drops daily viosterol, 250D, is inadequate for protection.

CH. ABS. (p)

Experimental scurvy. XXIII. Blood-ketones in guinea-pigs fed on a vitamin-C-free diet. J. SHIMADA (J. Biochem. Japan, 1934, **20**, 395—404).—The blood-COME₂ of guinea-pigs (normal average, 0.0018%) tends to increase during scurvy. The effect is more marked with the CH₃Ac·CO₂H and, to an even greater extent, with the β-hydroxy-butyric acid levels (normal averages, 0.0113 and 0.0073%, respectively). Inanition finally causes a decrease in the total blood-ketones, the disturbance in which is not associated with a disturbance of the carbohydrate metabolism.

F. O. H.

Experimental scurvy in relation to the character of the basal diet. M. F. GLAZUNOV and K. L. POVOLOTZKAYA (Bull. Appl. Bot. Genetics, U.S.S.R. [Suppl.], 1934, **67**, 217—224).—The Bezsonov diet even with addition of orange juice does not prevent scurvy in guinea-pigs. Addition of autoclaved hay affords protection.

CH. ABS. (p)

Experimental silicosis: quartz, sericite, and irritating gases. W. D. ROBSON, D. A. IRWIN, and E. J. KING (Canad. Med. Assoc. J., 1934, **31**, 237—245).—Sericite did not increase irritation by N₂O and SO₂, but SiO₂ dust induced pulmonary silicosis in 3 weeks.

CH. ABS. (p)

Detection of mineral particles in sputum in silicosis. H. E. BURKE (J. Ind. Hygiene, 1935, **17**, 27—29).—Sputum is conc. by evaporation, and treated with aqua regia. Solid matter is removed by centrifuging and incinerated on a slide, leaving any SiO₂ in the form of birefringent particles. SiO₂ was present in sputum from silicosis.

J. S. A.

Production of adrenaline in shock, and its role in defensive vaso-constriction against hypotension. F. D. ALSINA (Compt. rend. Soc. Biol., 1934, **117**, 1251—1252).—Increased adrenaline secretion (I) occurs during severe hæmorrhage. In continued bleeding, (I) increases progressively until death.

R. N. C.

Magnesium in calves. I. Tetany produced by ration of milk or milk with various supplements. C. W. DUNCAN, C. F. HUFFMAN, and C. S. ROBINSON (J. Biol. Chem., 1935, **108**, 35—44).—Calves fed on a whole-milk diet with a Mg intake of 8—13 mg. per kg. of body-wt. exhibited tetany (I) with normal blood-Ca and -P. In all cases the

blood-Mg (II) was low. Supplementing the diet with cod-liver oil, parathormone, or linseed oil was without influence on (I) or (II).

H. D.

General metabolism of nitrogenous substances in tuberculosis. I. BALANESCU, D. ZAMFIR, S. OERIU, and I. STANESCU (Wien. klin. Woch., 1934, **47**, 1023—1024).—The NH₂-acid content of the blood (I) decreased in severe cases of tuberculosis and rose to normal when clinical improvement occurred. (I)-creatinine was raised only when there was disturbance of renal function. Uric acid in (I) was low only in severe cases and rose with clinical improvement. The non-protein-N of (I) was usually low in severe cases, but in mild cases it was liable to rise with any exacerbation of the disease.

NUTR. ABS. (b)

Carbohydrate metabolism in tuberculosis. R. J. DRABKINA (Beitr. klin. Tuberk., 1934, **85**, 295—301).—An increased post-prandial hyperglycæmia was observed in tuberculosis (I). In severe cases the hyperglycæmic effect of adrenaline was small. The effect of insulin was small in some cases and protracted in others. Insufficiency of both the adrenal and insular systems in severe (I) is deduced.

NUTR. ABS. (b)

Proliferative and exudative tuberculosis with reference to their relationship to the various fractions derived from the tubercle bacillus. F. M. POTTINGER (Ann. Int. Med., 1934, **8**, 123—128).—Phosphatides stimulate monocytes and young connective tissue to produce epitheloid and giant cells. Lipins build up structural defence. Waxes cause proliferation of fibroblasts, and COME₂-sol. fats, that of all connective tissue cells and cells of blood vessels. Polysaccharides are toxic to leucocytes and damage the adrenals. Proteins are responsible for fever, cause proliferation of plasma cells, and produce allergic sensitisation.

CH. ABS. (p)

Determination of the proteins of blood-serum and its value in tuberculosis. W. PAGEL and L. B. STORT (Tubercle, 1934, **15**, 454—459).—The test is based on the ability of bile to keep proteins in solution after heating the serum. The test fails in cases of albuminuria or loss of albumin by other means.

CH. ABS. (p)

Action of intravenously-administered lecithin in pulmonary tuberculosis. G. SCORPATI (Rass. Clin. Terap., 1934, **33**, 143—150; Chem. Zentr., 1934, ii, 1491—1492).—Injection of an emulsion of lecithin and cholesterol produced an improvement in blood-constitution, increased white-cell content, fall of temp., and improved general condition.

Role of mineral metabolism in incipient infantile tuberculosis. G. POPOVICIU (Compt. rend. Soc. Biol., 1934, **116**, 1101—1104).—A rise in Ca×P occurs in the blood of infants with fresh tuberculous infection.

NUTR. ABS. (m)

Oxalic acid metabolism. A. ATHANASIOU and H. REINWEIN (Deut. Arch. klin. Med., 1934, **176**, 475—479).—In tuberculous and diabetic patients, elimination of H₂C₂O₄ was not closely related to the amount present in blood (I). Vals. for (I) were >

normal. There was little change in the $\text{H}_2\text{C}_2\text{O}_4$ content of dog's (I) after 7 days' fasting.

A. G. P.

Ammonia content of brain during uræmia. J. ŠTEFL and H. KUNZOVA (Arch. exp. Path. Pharm., 1935, 177, 313—316).—Injection of normally non-toxic doses of soya-bean urease into animals in which nephritis (I) has been induced by $\text{UO}_2(\text{NO}_3)_2$ hastens the appearance of uramic convulsions (II) and death. (II) are probably due to the increased NH_3 content of the brain which accompanies (I).

F. O. H.

Basal metabolism of European women in south India and the effect of change of climate on European and south Indian women. E. D. MASON (J. Nutrition, 1934, 8, 695—713).

A. G. P.

Basal (standard) metabolism of the Australian merino sheep. II. Factors concerned. A. W. PERCE (Counc. Sci. Ind. Res. Australia Bull., 1934, No. 84, 22 pp.).—Data for lambs of various ages are given, and effects of differences in pasture, of shearing, and of sex are considered.

A. G. P.

Gas metabolism of tissue *in vitro*. VII. Kidney tissue. 2. Tissue respiration under various carbon dioxide concentrations. T. OKABE and S. KODAMA (Tohoku J. Exp. Med., 1934, 23, 273—278).—At p_{H} 6.72—7.68, the O_2 consumption and CO_2 output of liver, cortex, and medulla of rabbit kidney increased with p_{H} .

CH. ABS. (p)

Anomalous respiratory quotients of hibernating animals. L. DONTCHOFF and C. KAYSER (Compt. rend. Soc. Biol., 1935, 118, 81—83).—The R.Q. of dormice recovering from CO_2 anaesthesia have vals. such as 2.2, 3.4, and even ∞ . These are explained by the ability of the anaesthetised animals to retain quantities of CO_2 and by the rise in the body temp. on revival. Analogous conditions occur during the awakening after seasonal hibernation.

A. L.

Gaseous metabolism of prolonged voluntary contraction of skeletal muscle. H. REIN and J. H. TALBOTT (Z. Biol., 1935, 96, 15—27).—Continuous records of the O_2 consumption, expired CO_2 , etc. (A., 1933, 1064) in men during periods of rest and physical exercise indicate that the gaseous metabolism of the recovery process occurs mainly in tissues other than contracted muscle, where, however, an increased elimination of catabolic products occurs.

F. O. H.

Nature and physiological function of muscle ammoniogenesis, and the co-ordination of chemical processes in muscle. J. K. PARNAS, P. OSTERN, and T. MANN (Rocz. Chem., 1934, 14, 1358—1376).—Adenosinetriphosphoric acid (I) does not undergo deamination in muscle, but adenylic acid (II) arising from (I) may be resynthesised to (I), or be deaminated to inosic acid (III). The chief processes taking place during contraction are: (I) + (glycogen) + $\text{H}_2\text{O} \rightarrow$ (II) Harden-Young ester (II) + phosphocreatine (V) \rightarrow (I) + creatine (VI); (VI) + (IV) \rightarrow (V) + $2\text{OH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$; when the reaction of glycolysis is completed, the reaction

(II) + $\text{H}_2\text{O} \rightarrow$ (III) + NH_3 takes place. During the resting stage resynthesis of (II) from (III) is possible.

R. T.

Non-utilisation of alcohol during muscular work by the rat. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 118, 62—64).—No difference is observed in the amount of EtOH (I) oxidised by resting and exercised rats injected with aq. EtOH. The energy obtained from (I) is therefore not used for muscular work.

A. L.

Micro-technique for the study of alcohol oxidation by tissue *in vitro*. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 118, 64—67).—The technique is described. The rate of oxidation of EtOH is increased by substitution of O_2 for air, the presence of methylene-blue and deproteinised blood.

A. L.

Chemical reactions in muscle. III. Phosphate transport by pyruvic acid. J. K. PARNAS, P. OSTERN, and T. MANN. **IV. Specificity of phosphoglyceric acid as phosphate donator.** C. MANN-LUTWAK (Biochem. Z., 1935, 275, 163—166, 167—168; cf. A., 1934, 1027).—III. Addition of AcCO_2H to muscle pulp (I) containing NaF inhibits NH_3 formation and leads to resynthesis of adenosinetriphosphoric acid (II) providing PO_4''' is present. AcCO_2H probably first forms a phosphoric ester which then passes its PO_4''' to adenylic acid.

IV. Diphosphoglyceric acid has no effect on the formation of NH_3 , and the degradation of phosphocreatine and (II) in (I) and the action of phosphoglyceric acid in these reactions (A., 1934, 1027) appear to be highly sp.

P. W. C.

Connexion between muscle metabolism and weather. II. O. RIESSER, G. KUNZE, and K. GALLE (Biochem. Z., 1935, 275, 169—186).—The P_2O_5 exchange of rabbit's muscle varies from day to day according to climatic conditions, cold dry air tending to give high, and warm moist air to give low, P_2O_5 contents. This relationship is especially marked using directly determined P_2O_5 vals. (inorg. + phosphagen- P_2O_5), but is not so marked with either phosphagen or pyrophosphate vals. (cf. A., 1934, 1253).

P. W. C.

Demonstration of polar localised phosphoric acid liberation by directly stimulated muscle of cold-blooded animals. S. S. ROBBINS and M. L. WILHELM (Pflüger's Archiv, 1934, 234, 707—715).—Prolonged passage of electric current in either direction through frog's muscle in Ringer's solution, or a series of shocks, causes localised H_3PO_4 liberation at the anode, independent of the type of physical effect of the current on the muscle. The amount of H_3PO_4 liberated \propto the quantity of electricity passed. The effect is due either to anodic breakdown of labile H_3PO_4 compounds or increase of permeability. An antagonistic effect occurs at the cathode.

R. N. C.

Role of potassium in the electrolytic system of muscle. H. NETTER (Pflüger's Archiv, 1934, 234, 680—695).—A muscle (I) perfused with Ringer's solution containing K^+ takes up about 1/5 of the quantity of K already present. Injection of adrenaline in frogs produces an accumulation of (I)-K, whilst $\text{CH}_3\text{I} \cdot \text{CO}_2\text{H}$ produces a decrease. The O_2

consumption of (I) in Ringer's solution is raised by increasing [K], which augments glycolysis and acid formation. The K taken up by perfused (I) is distributed between (I) and the perfusing solution in the ratio of its previous concns. in them. In the same way NH_4 is distributed according to the fall of concn. in (I). R. N. C.

Membrane potential of the muscle as a determining factor of excitability. I. Influence of chlorides on membrane potential and on excitability of the frog sartorius muscle. II. Action of hypertonic Ringer's fluid. III. Action of carbon dioxide on the muscle. IV. Effect of fatigue due to prolonged stimulation of the muscle. V. Effect of glucose-Ringer's fluid and highly hypertonic Ringer's fluid on the muscle. VI. Action of calcium chloride on the muscle. VII. Action of sodium thiocyanate on the muscle. S. OKABE (Japan J. Med. Sci., III, Biophys., 1934, 3, 1—15, 17—23, 25—34, 35—40, 41—44, 45—48, 49—54).—I. In small concns. all chlorides (K, Mg, Ba, Sr) increase membrane potential (I) and excitability (II); at higher concns. ($>10^{-2}$) there is a depressive effect on (I) and (II).

II. Hypertonic Ringer's solution decreases injury potential and (II).

III. CO_2 decreases (I) and (II), but not proportionally.

IV, V. In hypertonic solutions injury potential and (II) decrease in inverse proportion to the altered rheobase.

VI. In concns. from 4.3×10^{-3} to 1.7×10^{-2} in Ringer's solution CaCl_2 decreases injury potential in inverse proportion to alterations in rheobase.

VII. NaCNS increases (I) and (II). CH. ABS. (p)

Transparency and action metabolism of muscle. II. A. VON MURALT (Pflüger's Archiv, 1934, 234, 653—664).—The breakdown of creatine-phosphoric acid (I) in muscle subjected to a short tetanus always causes a decrease in the extinction (II) produced in light transmitted through the muscle. The resynthesis of (I) on recovery under aerobic conditions is parallel with the return of (II) to its original val. In more prolonged anaerobic stimulation (II) falls to an equilibrium point, where further falls are balanced by equal rises on recovery. Inhibition of (I) resynthesis with $\text{CH}_2\text{I}-\text{CO}_2\text{H}$ results in a small decrease of (II) with each tetanus, parallel with the amount of (I) destroyed. Lactic acid (III) formation does not affect primarily the optical properties of muscle, but in the isotonic aq. solution (IV) there is a slow increase of (II), the extent of which is associated with the amount of (III) formed and the amount of available ions (particularly Ca^{++}) in (IV). R. N. C.

Relative nutritional values of proteins. E. LESNÉ and R. CLÉMENT (Compt. rend. Soc. Biol., 1934, 116, 1311—1313).—Young rats grow well on diets containing caseinogen, meat peptone, and ovalbumin, less satisfactorily on diets containing proteins from soya bean and sunflower, and very poorly (death ensues) on a diet containing gelatin.

NUTR. ABS. (m)

Effect of heating caseinogen on [growth] gains in rats. W. D. SALMON (Ann. Rept. Alabama Agric. Exp. Sta., 1932, 20).—When used as sole source of protein in diets supplied with vitamin- B_1 (I) and - B_2 (II), caseinogen, after heating to 130° for 48 hr., failed to produce growth in rats. Subnormal growth followed supplementary feeding of extracted yeast (III) residues. Unheated caseinogen after thorough extraction with acidified H_2O produced normal growth when (I) and (II) were supplied as protein-free extracts of (III). CH. ABS. (p)

Derivation of factors for computing the gaseous exchange and heat production in the metabolism of caseinogen by the albino rat. M. KRISS and R. C. MILLER (J. Nutrition, 1934, 8, 669—674).—Of the total calories of caseinogen ingested 96.6% were digested and 80.8% were metabolisable. For computing gaseous exchange and heat production the factors given are: 1 g. urinary N=6.67 litres of respiratory O_2 , 5.47 litres of CO_2 and 30.59 g.-cal.

A. G. P.

Effect of the protein level of the ration on certain blood-constituents of the hen. W. C. RUSSELL and A. L. WEBER (Poultry Sci., 1934, 13, 376—378).—Blood-creatinine was higher on a low- than on a high-protein diet. The non-protein-N, uric acid, urea, and sugar contents were less affected.

A. G. P.

Influence of protein on the growth of ducks. W. L. HAMLYN, H. O. BRANION, and J. R. CAVERS (Poultry Sci., 1934, 13, 333—337).—Ducklings (I) utilise proteins more efficiently than do chicks. The optimum level for (I) is approx. 18%. A single protein supplement is as satisfactory as a mixture.

A. G. P.

Passage of native proteins through the normal gastro-intestinal wall. B. RATNER and H. L. GRUEHL (J. Clin. Invest., 1934, 13, 517—532).—Undecomposed protein may pass unchanged through the walls of the intestinal tract. CH. ABS. (p)

Effect of fat on the utilisation of protein. F. MAIGNON (Bull. Soc. Chim. biol., 1934, 16, 1410—1450).—White rats fed on ovalbumin (I), fat (II), and vitamins (III) survived longer and had a greater period of fixed wt. than animals receiving (I), carbohydrate (IV), and (III) in equiv. calorific val., a result apparently contrary to the view that (IV) administration exerts a sparing effect on protein-N. The difference in the N balance (V) in animals fed on the alternative diets was therefore examined over the const. wt. period. With diets having the ratio (I)/(II) as 1/2 and (I)/(IV) as 1/4.7, (V) was the same in both cases, but with a greater proportion of protein, the diet containing the (II) caused a less negative (V). The results support the view of Falta and Gignon (A., 1908, ii, 961) that a min. amount of (IV) is necessary for life, this being derived from protein during starvation, (II) being incapable of providing it. A. L.

Nitrogen catabolism in invertebrates. II. Correlation between uricotelic metabolism and habitat in the phylum Mollusca. J. NEEDHAM. III. Arginase in the invertebrates; new method for its determination. E. BALDWIN (Biochem. J.,

1935, 29, 238—251, 252—262).—II. Data are given for the uric acid content of the nephridia and other tissues of a large no. of molluscs.

III. The tissue containing arginase (I) is allowed to act on an excess of arginine (concn. 2%) for 30 min. only, at 28° and at p_H 9.5, controlled by means of a glycine buffer. The amount of urea produced then \propto (I) concn. under standard conditions. (I) is widely distributed among invertebrates. Among gastropod molluscs (II), (I) occurs only in fresh- H_2O and terrestrial species, the hepatopancreases of many of which contain (I) in concn. comparable with that in mammalian livers. (I) is probably concerned in the production of both urea and uric acid by (II). The (I) content of a tissue tends to disappear in starvation. A. E. O.

Biochemistry of allantoin. IV. Injection of adrenaline and allantoin excretion. V. Administration of yeast-nucleic acid and exogenous allantoin excretion. T. MIYAHARA (J. Biochem. Japan, 1934, 20, 383—386, 387—393).—IV. Injection of adrenaline into rabbits (I) fed on a diet poor in purines increases the urinary excretion of total N, allantoin (II), and uric acid (III), whilst the uricolytic index (IV) is somewhat decreased.

V. Intravenous or oral administration of yeast-nucleic acid (as Na salt) into (I) markedly increases the excretion of (II) and (III), whilst (IV) is slightly diminished. F. O. H.

Metabolism of glyoxaline. P. LELU (Compt. rend., 1935, 200, 353—355).—Glyoxaline excretion (I) in the rabbit, dog, pig, and rat increases with increasing protein in the diet or during inanition, whilst in each case the proportions of (I) to total N or to total metabolic products excreted decreases. H. D.

Blood and urine chemistry during the specific dynamic action of glycine in normal subjects and in schizophrenics. C. REID (J. Mental Sci., 1934, 80, 379—396).—No significant differences in the distribution of blood- and urinary N of normal and schizophrenic patients followed oral administration of glycine. CH. ABS. (p)

Relationship between nutrition and wool production of Merino sheep. I. Technique employed for determining the utilisation of food-stuffs and the wool produced over short periods. II. Effect of the administration of cystine, cysteine, sulphur, and of methionine on the growth of wool of a merino ewe on a protein-poor ration. H. R. MARSTON (J. Agric. Sci., 1935, 25, 103—112, 113—131).—I. Wool growth was calc. from vals. obtained by shaving marked areas on the shoulders at short intervals.

II. Wool production was increased by addition of *l*-cystine to the diet. Approx. 80% of the additional S was absorbed and about 50% was excreted in urine. Subcutaneous injection of *l*-cystine produced somewhat larger increases in wool growth and higher S retention. Injection of methionine produced a small increase, and the feeding of S was without effect. A. G. P.

Partition of excreted sulphur in relation to metabolism. E. F. TERROINE and R. RAZAFI-

MAHERY (Compt. rend., 1935, 200, 350—352).—Replacing a carbohydrate- by a protein-rich diet (I) in the pig, or fasting a rabbit after maintaining it on a min. diet, decreases the proportion of neutral to total $SO_4^{''}$ excreted. Ethereal $SO_4^{''}$ persists in the urine on a protein-free diet, increases slightly on (I), and greatly during total inanition. H. D.

Physiological availability of pentocystine and homomethionine. H. M. DYER and V. DU VIGNEAUD (J. Biol. Chem., 1935, 108, 73—78).—Pentocystine and homomethionine, administered to rats on a cystine-deficient diet (A., 1933, 1149), produced no alteration in their growth curves. H. D.

Hole of glutathione in living tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1935, 231, 39—46).—The dilution factor shown by kidney tissue is, like that of liver extracts, due to cysteine (I). (I) arises from glutathione (II), fission of which is a function of both time and temp. The production of (I) is favoured by interruption of respiration. (II) is neither an oxidising nor reducing system of tissue, but an inactive store of thiol substance. (II) yields active thiols when heavy metals and (I) are present to form a complex salt specifically catalysing the oxidation of (II). J. H. B.

Passage of ovoglobulins through the shell membrane. E. McNALLY (Proc. Soc. Exp. Biol. Med., 1934, 31, 946—947).—The increased wt. of the mature as compared with the immature egg is due to higher content of thin albumin. CH. ABS. (p)

Behaviour of enzymes in hen's eggs during incubation. R. AMMON and E. SCHÜTTE (Biochem. Z., 1935, 275, 216—233).—The considerable increase in esterase content of hen's eggs during incubation is investigated, the enzymes being differentiated in terms of substrate into tributyrinase, methylbutyrase, and choline-esterase. P. W. C.

Effect of administration of carbohydrate, protein, or fat on the blood-sugar of children. A. PANOFF (Monatsschr. Kinderheilk., 1934, 60, 194—204).—In children (I) of 8—14 years, suffering from non-metabolic diseases, 50 g. of sucrose or 100 g. of white bread always cause an increase in the fasting blood-sugar, lasting for 2 hr. Butter (50 g.) causes a slight fall in blood-sugar (II) in (I) and in diabetics (III). After 50 g. of pure, cooked protein a delayed rise occurs in (II) in about 2 hr., except in some (III). NUTR. ABS. (m)

Glucose and non-glucose portions of "blood-sugar" in the hepatic and portal veins of the decapitate cat at different sugar levels. J. M. D. OLMSTED and L. S. READ (Amer. J. Physiol., 1934, 109, 303—306).—In the decapitate cat, without food since the previous night, the glucose portion (determined after pptn. with Zn salts) of the "blood-sugar" (I) (determined after pptn. with tungstate) is significantly higher in hepatic (II) than in portal vein blood (III). The average difference, 28 mg. per 100 ml. when the liver is supplied with (III) only, is relatively const. over a considerable range of (I) level. Since glycogen (IV) is deposited meanwhile in the liver it is unlikely that liver-(IV) can be

formed from blood-glucose. There is no difference between (II) and (III) with respect to the concn. of the non-glucose fraction of (I), which is slightly increased immediately after decapitation and after asphyxia. NUTR. ABS. (m)

Carbohydrate tolerance during carbohydrate starvation. N. I. NISSEN (Hospitallstidende, 1934, 77, 241—252).—In young persons with normal carbohydrate metabolism, a few days on low-carbohydrate (I) diet causes a fall in fasting blood-sugar, an abnormally high and protracted hyperglycæmia following oral or intravenous administration of glucose, with similar results following oral but not intravenous administration of galactose. The degree of disturbance is not dependent on the degree of acidosis and is greater on a low than on a high calorie diet. The results are attributed to decreased or delayed glycogen production and possibly to reduced (I) utilisation. NUTR. ABS. (m)

Bile acids and carbohydrate metabolism. XXXIII. **Liver-glycogenesis due to administration of constituents of hens' eggs and cholic acid.** T. FUKASE (J. Biochem. Japan, 1935, 21, 111—117; cf. this vol., 111).—The liver-glycogenesis (I) due to ingestion of egg-white by starved rabbits is increased by administration of Na cholate or of extracts of egg-yolk; large amounts of the latter, however, depress (I). F. O. H.

Relative nutritional values of carbohydrates. E. LESNÉ and R. CLÉMENT (Compt. rend. Soc. Biol., 1934, 116, 1313—1315).—In young rats, fed on adequate diets in which the source of carbohydrate is varied, the best growth occurs with wheat, oats, rice, or barley. Rye and maize flours are inferior. Sunflower, soya, and peanut flours, which contain less carbohydrate, are worst. When sugar or starch is used as 50% of the ration, the growth is poor, and when the proportion reaches 70%, the rats die. NUTR. ABS. (m)

Oxalic acid metabolism. A. ATHANASIOU and H. REINWEIN (Deut. Arch. klin. Med., 1934, 176, 475—479).— $\text{H}_2\text{C}_2\text{O}_4$ in blood (I) is determined by a new method. In dogs starved for a week there is little change in the (I) level. Normal human (I) contains 3—4 mg. per 100 ml. In tuberculosis and diabetes the (I) level is somewhat higher (mean vals. 4.76 and 4.52 mg., respectively), there being no apparent relation between the (I) level and either the severity of the disease or the urinary $\text{H}_2\text{C}_2\text{O}_4$ excretion. NUTR. ABS. (b)

Variations in fat and water content of the carp. M. STANGENBERG (Polish Agric. Forest. Ann., 1934, 32, 87—103).—The chemical composition of the carp is affected by the nature of the food, especially in the first three years; e.g., rye increases fat and lupins increase protein contents. CH. ABS. (p)

Fat tolerance tests. H. BLOTNER and R. FITZ (J. Clin. Invest., 1934, 13, 707).—In the normal subject the blood-cholesterol remains unchanged after 500 ml. of 20% fat. In obesity or diabetes insipidus there is a progressive rise which can be sharply inhibited by injection of posterior pituitary

extract. Insulin (I) causes a rise in normal individuals receiving (I) therapy for gain in wt.

NUTR. ABS. (b)

Absorption of soluble, volatile fatty acids. R. H. HUGHES and E. J. WIMMER (J. Biol. Chem., 1935, 108, 141—144).—In the dog, there is no increase in sol., volatile fatty acids (I) present in the thoracic lymph as glycerides during the process of digestion of fats containing tributyrin. The (I) are probably absorbed by the blood, and thus escape glyceride synthesis. A. E. O.

Fat metabolism. V. Degradation of unsaturated fatty acids in the living organism. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 590—597).—Following administration of triundecenoin (15 and 25 g.), male urine contained sebacic acid indicating a rupture of undecenoic acid at the double linking. With olive and rape oils, no decomp. products of oleic or erucic acid occurred in the urine. The conclusions of Smith (A., 1934, 210) are criticised and the degradation of fatty acids is discussed. F. O. H.

Liver and fat metabolism. F. X. AYLWARD, H. J. CHANNON, and H. WILKINSON (Biochem. J., 1935, 29, 169—178).—The changes in the liver-lipins of rats were studied over a period of 13 hr. following a meal of sucrose, caseinogen, fat (40%), and cholesterol (I) (2%), both with and without choline chloride (II) (2%). (II) partly prevented the fall in phosphatide content, occurring from the 4th to the 7th hr. The neutral fat (III) content rapidly increased from the 4th to the 10th hr., then returned to normal at the end of 13 hr. (II) lowered the (III) content uniformly. The I vals. of the total fatty acids decreased during the first 10 hr. both with and without (II). The free (I) content showed no change, but a striking linear increase in (I) esters [not affected by (II)] occurred from the 7th hr. onwards, evidently the first stage in the production of the (I)-fatty liver by (I)-feeding. The results are discussed in relation to the role of the liver in fat metabolism. A. E. O.

Automatic regulation of fat metabolism in man. S. LEITES (Klin. Woch., 1934, 13, 1056—1060).—On administration of butter to normal men, changes in the blood-fat (I) and -ketone (II) contents depend, during the first 9 hr., on the amount of fat fed, but in the subsequent period on the initial level of (I) and (II). If the latter is normal or low, the administration has a ketogenic, but if high an anti-ketogenic, action. The normal lipæmia and ketonæmia thresholds, respectively, of 60—90 and 6—9 mg. per 100 ml. are increased to 130 and 14 mg. A second administration of butter 3 hr. after the first leads to a decrease of hyper-lipæmia and -ketonæmia. Changes of R.Q. are also recorded. NUTR. ABS. (m)

Effect of hydrogenated fat on abnormal carbohydrate respiratory quotients of rats on a fat-deficient diet. L. G. WESSON and F. C. MURRELL (Proc. Soc. Exp. Biol. Med., 1934, 31, 1118—1121).—Partial hydrogenation of the EtOH-sol. fraction of lard did not diminish the effectiveness of this fraction in lowering abnormally high R.Q. CH. ABS. (p)

Effect of prunes and the water extract of prunes on the plasma-carbon dioxide-combining capacity and composition of the urine when included in acid, neutral, and uncontrolled diets. E. MRAK, C. SMITH, J. FESSLER, H. LAMBERT, and T. HARPER (J. Nutrition, 1934, 8, 633—646).—Addition of prunes to acid or neutral diets caused, in most cases, increased excretion of org. acids and a decrease in NH_3 , total acids, and urinary p_{H} . Effects were small in uncontrolled diets. The CO_2 -combining power (I) of the plasma was unchanged by feeding prunes. Changes in (I) under varying conditions are examined. A. G. P.

Proteins of mottled gram bean (*Phaseolus mungo*, L. var.). T. Y. Lo (Dept. Agric. Chem. Peiping, Nutrit. Bull., 1934, B, No. 1, 1—12).—Mottled gram beans (I) contain 20.27% of crude protein [18.06% true protein (II)]. Of (II) 38.07% is H_2O -sol., 14.03% sol. in 10% aq. NaCl, 2.36% in 73% EtOH, and 2.14% in 0.2% aq. NaOH. The protein of (I), when fed as the sole protein, is incapable of supporting normal growth in rats.

NUTR. ABS. (m)

Mineral content of mottled gram bean. T. Y. Lo (Dept. Agric. Chem. Peiping, Nutrit. Bull., 1934, B, No. 1, 27—39).—Mottled gram beans (I) contain Ca 0.117, P 0.260, Fe 0.0073, Cl 0.0256, total ash 3.28%. Of the latter about 65% is sol. in H_2O and 93% in acid. For rats, on a diet of (I), caseinogen, maize starch, lard, yeast, and cod-liver oil, the main deficiencies are of P, Na, and Cl. NUTR. ABS. (m)

Vitamin content of the mottled gram bean. T. Y. Lo (Dept. Agric. Chem. Peiping, Nutrit. Bull., 1934, B, No. 1, 13—26).—The bean (I) is a fairly good source of vitamin-A (II), 20% in the ration being sufficient to support normal growth when no other source of (II) is present. In a diet otherwise deficient in the vitamin-B complex, 14% of (I) permits normal growth and development in young rats. A moderate amount of vitamin-D is present, but no -C.

NUTR. ABS. (m)

Nutritive value of locusts. ANON. (Farming in S. Africa, 1934, 9, 232).—Redwing locusts before they reached the flying stage contained H_2O 10.5, protein 46.1, fat 9.6, fibre 12.5, ash 5.0, P_2O_5 1.2%. Locust meal can be fed to stock at a 10% level.

NUTR. ABS. (b)

Nutritive value of quinoa. P. MAZZOCCO (Compt. rend. Soc. Biol., 1934, 117, 1245—1246).—Quinoa alone is not a complete diet. The protein, mineral matter, and carbohydrate contents are sufficient, and it also contains vitamin-B, but the other vitamins are absent.

R. N. C.

Chemical composition of quinoa. P. MAZZOCCO (Compt. rend. Soc. Biol., 1934, 117, 1244—1245).—Quinoa resembles the cereals, but contains slightly more protein, fat, ash, and Ca. A complete analysis is given, and also analyses of the ash and proteins.

R. N. C.

Nutritional value of Chinese oatmeal. T. Y. Lo (Dept. Agric. Chem. Peiping, Nutrit. Bull., 1934, No. 1, 47—56).—The protein of the meal is satisfactory in quality and quantity, but there is deficiency

of mineral elements and of vitamin-D, although an appreciable amount of vitamin-A and of the vitamin-B complex is present.

NUTR. ABS. (m)

Turkey nutrition investigations. H. M. SCOTT and J. S. HUGHES (Kansas Agric. Exp. Sta. 6th Biennial Rept., 1932, 78—79).—Vitamin-A requirements of poults (I) are > those of chicks. (I) are sensitive to deficiencies of vitamin-D, which cause decline in Ca and inorg. P in blood. CH. ABS. (p)

Metabolism of silkworms. III. Reducing power of the hæmolymph of *Bombyx mori*. L. S. DEMJANOVSKI and E. PROKOVJEVA (Biochem. Z., 1935, 275, 455—463; cf. A., 1933, 631).—In the caterpillar (I) the reducing power (II) of the hæmolymph (III) decreases as the age increases, but exhibits increases at each shedding of skin, lowest vals. being reached half-way between sheddings. 100 c.c. of (III) contain the equiv. of 50—80 mg. of glucose. In the pupæ the val. is 140—190 mg.; it increases as the age increases. (II) of the blood of the moth falls rapidly as the age increases, especially in the female (IV) (from the time of laying onwards). At all stages of growth (II) of (III) in (IV) is > in the male. (II) of (III) in (I) increases after feeding and remains at the increased level, no matter what the amount or quality of the food, for extended periods. In diseased (I), (II) of (III) is greatly reduced, since (II) is greatly dependent on the health of (I). W. McC.

An often wrongly-interpreted character of the internal medium of *Ascidia*. M. FLORKIN (Compt. rend. Soc. Biol., 1934, 117, 1226—1228).—The CO_2 content of the internal medium (I) of *Ciona intestinalis* is < that of sea- H_2O (II) in equilibrium with the atm. (III), and is unchanged when (I) is brought into equilibrium with (III). Hence CO_2 partial pressures in (I) and (II) are in equilibrium. In an aquarium there is a rapid fall of CO_2 in (I). The CO_2 contents in (II) entering the buccal siphon and expelled by the cloacal siphon are identical. Hence the alkaline reserve of (I) is low, suggesting that the species does not utilise the CO_2 in (II).

R. N. C.

Passage of fluid and certain dissolved substances through the intestinal mucosa as influenced by changes in hydrostatic pressure. E. S. NASSET and A. A. PARRY (Amer. J. Physiol., 1934, 109, 614—625).—Absorption of glucose in aq. solution by the intestinal mucosa is independent of intra-intestinal pressure (I) between 50 and 250 mm. of solution below atm. pressure. Secretion of NaCl and enzymes increases linearly as (I) decreases. Increase of colloid osmotic pressure (II) in the lumen relative to that of blood-serum does not affect absorption of H_2O ; hence (II) of the lacteal lymph is inadequate to account for such absorption. In dogs with intestinal transplants, apparent absorption is increased by anaesthesia, which may result from inhibition of secretion. The temp. of the intestine influences fluid exchange within it.

R. N. C.

Effect of p_{H} on the absorption of sugars. E. GELLHORN and L. F. MOLDAVSKY (Amer. J. Physiol., 1934, 109, 638—644).—In a prep. in which the intestine is perfused with isotonic glucose solution and simultaneously the blood-vessels supplying it are

perfused with PO_4''' -buffered Ringer's solution, the circulatory rate being kept const., alteration of p_{H} in the blood-vessel perfusate (I) in either direction produces a reversible increase in glucose absorption, the min. sensitivities being $+0.2$ and -0.1 . Increased acidity of (I) due to CO_2 also increases absorption, the sensitivity being as above. If the intestinal perfusate (II) is buffered with PO_4''' , small changes of its p_{H} produce changes in p_{H} in (I), with consequent increased absorption; if (II) is unbuffered, large p_{H} changes cause only slight changes in absorption, the p_{H} of (I) being unchanged. Xylose is absorbed in the same way under similar conditions; hence alterations in intestine permeability by p_{H} changes are not due to interference with intermediary chemical processes involved in the glucose absorption.

R. N. C.

Influence of various sugars on growth of cultures of fibroblasts *in vitro*: morphological changes produced by such sugars. II. (A) Hexoses. (B) Disaccharides and polysaccharides. Y. HUANG (Folia Pharmacol. Japan, 1934, 18, 122—133, 134—142).—(A) Growth of fibroblasts is favoured by *d*-glucose (I), *d*-galactose, *d*-fructose, and *d*-mannose (II) in small concns., but is inhibited by larger amounts. (I) is the least and (II) the most toxic.

(B) Maltose (III), sucrose (IV), and glycogen stimulate or retard growth according to concn. (IV) was more toxic than (III).

CH. ABS. (p)

Influence of various sodium salts on growth and on morphology of cultures of fibroblasts *in vitro*. II. Sodium nitrate, nitrite, bromate, iodate, sulphate, thiosulphate, and phosphate. K. KIRASHIMA (Folia Pharmacol. Japan, 1934, 18, 163—180).—All salts examined decrease growth of fibroblasts, and in high concn. destroy the tissue. Greatest effects are produced by NaBrO_3 and least by Na_2SO_4 .

CH. ABS. (p)

Growth of human fibroblasts in media containing copper. J. P. M. YOGELAAR and E. ER-
LICHMAN (Amer. J. Cancer, 1934, 22, 66—75).—Adult thyroid tissue grows actively in media containing 0.0075 mg. of Cu per c.c., but 0.0112 mg. is toxic.

CH. ABS. (p)

Influence of arsenic compounds on growth of cultures of fibroblasts *in vitro*; morphological changes produced. H. OKADA (Folia Pharmacol. Japan, 1934, 18, 208—223).— H_3AsO_3 (I), Na_3AsO_3 , H_3AsO_4 , Na_3AsO_4 , Na cacodylate, and atoxyl (II) produce identical changes in the tissue. Growth is favoured by low concns., but larger amounts cause rapid degeneration. (I) is the most and (II) the least active.

CH. ABS. (p)

Effect of glucose on the maintenance of acid-base equilibrium. G. LINO (Riv. Patol. sper., 1934, 13, 169—172).—The lowering of the alkali reserve caused by injection of 1% HCl in rabbits does not occur when glucose is injected simultaneously.

NUTR. ABS. (m)

Organic acids and the acid-base relationship: oxalic acid. E. F. KOHMAN (J. Amer. Dietetic Assoc., 1934, 10, 100—106).—A review.

CH. ABS. (p)

Effect of alkaline and acid diet on oxidative processes in the body. K. E. BOHNDORF (Z. ges. exp. Med., 1934, 94, 300—304).—Acid diet (I) produced a fall in the C : N and vacat O_2 : N ratios of the urine of rats, whilst alkaline diet (II) caused an increase. The vacat O_2 : C ratio was not significantly changed. Hence (I) increases, and (II) decreases, oxidation.

NUTR. ABS. (b)

Inorganic salts in nutrition. IX. Correlation between suppressed growth and the development of polycythæmia induced by feeding a ration poor in salts. P. P. SWANSON and A. H. SMITH (J. Nutrition, 1934, 8, 659—667).—Unless growth is repressed by feeding a salt-poor ration with caseinogen, a polycythæmia is not produced.

A. G. P.

Factors influencing mineral metabolism of dairy animals. H. W. CAVE, W. H. RIDDELL, J. S. HUGHES, C. H. WHITNAH, and H. F. LIENHARDT (Kansas Agric. Exp. Sta., 6th Biennial Rept., 1932, 63—65).—Calves receiving an all-milk diet showed deficient hæmoglobin (V) and subnormal growth after 3 months. Ingestion of glucose (I) increased the blood-sugar (II) in lactating cows. Milk (III) drawn at the period of max. increase of (II) had higher concn. of lactose (IV) than that drawn on preceding or following days. Increase in (IV) was not \propto the increase in (II). Fermentable sugars in (III) [calc. as (I)] increased over a period of 24 hr. after dosage with (I). The (V) content of blood was not affected by breed, age, or fasting. Silage is deficient in vitamin-C.

CH. ABS. (p)

Determination of changes in body-fluids. P. H. LAVIETES (J. Clin. Invest., 1934, 13, 718).—Assuming that the concn. of $\text{Na} + \text{K}$ in serum- H_2O is approx. equal to and varies with that in body- H_2O as a whole, and that practically all the Na and Cl of the body is restricted to interstitial fluids with concns. approx. those in serum- H_2O , changes in interstitial fluid (I) vol. may be deduced from the metabolism of Na or Cl. The (I) exchange calc. independently from Na and Cl changes usually shows remarkable agreement. The determination of total H_2O exchange from $\text{Na} + \text{K}$ metabolism in many instances gives more reasonable vals. than those obtained by Newburgh's method.

NUTR. ABS. (m)

Importance of cations in the energy metabolism of warm-blooded cells, especially tumour cells. A. LASNITZKI (Protoplasma, 1934, 22, 274—298).—The antagonistic effects of K^+ and Ca^{++} on the respiration and development of embryonic and mature tissues are examined.

A. G. P.

Metabolism of copper and iron in splenectomised rats free from *Bartonella muris* infection. M. SANDBERG and D. PERLA (J. Exp. Med., 1934, 60, 395—402).—Splenectomy (I) is followed after 2 weeks by increased Cu in faeces associated with a negative Cu balance. Fe retention increases during 4—6 weeks after (I) and subsequently returns to normal. Creatine and creatinine metabolism is unchanged and the amount of uric acid unaffected. N retention increases. The spleen is essential for the utilisation of Cu in the body.

CH. ABS. (p)

Copper metabolism in man. T. P. CHOU and W. H. ADOLPH (Biochem. J., 1935, 29, 476—479).—From Cu balance determinations in man the min. necessary Cu intake is 2 mg. daily. The total Cu in the adult body is 100—150 mg. H. D.

Influence of calcium and iodine on growing rats. J. THOMPSON (Endocrinol., 1933, 17, 537—549).—Low-I diets induce symptoms of exophthalmic goitre. Addition of Ca intensifies the effect, causes enlargement of thyroid and degeneration of parathyroid gland, lowers blood-I, and also the % of Ca and ash in bones. CH. ABS. (p)

Calcium requirement of laying hens. L. C. NORRIS, G. F. HEUSER, A. T. RINGROSE, and H. S. WILGUS, jun. (Poultry Sci., 1934, 13, 308—309p).—For white Leghorn pullets a diet containing 1.65—1.80% of Ca and 0.50—0.75% of P is optimum for egg production. NUTR. ABS. (m)

Calcium and phosphorus assimilation by dairy cows. J. P. LA MASTER, E. C. ELTING, and J. H. MITCHELL (Ann. Rept. S. Carolina Agric. Exp. Sta., 1933, 62).—Heavily milking cows show negative Ca and P balances on legume hay—grain rations. Addition to the ration of maize silage effected a return to positive balances. Addition of marl to an oat-hay ration increased Ca assimilation, but had no effect in the case of soya-bean hay, grain, and silage with moderately heavy milking cows. CH. ABS. (p)

Effect of acid, neutral, and basic diets on the calcium and phosphorus metabolism of dogs. A. F. MORGAN, E. A. GARRISON, H. HOUSEHOLDER, A. M. HANSEN, M. V. SEBERGER, J. T. WATENPAUGH, A. FELSHER, and M. L. LONG (Univ. Calif. Pub. Physiol., 1934, 8, 61—106).—Greatest growth was obtained on base-forming (Na_2CO_3) rations (I). Inorg. P of whole blood was lowest on acid-forming (NH_4Cl) rations (II) without cod-liver oil (III), and highest on neutral ration (IV) with or without (III). Total serum-Ca (V) was decreased by (II) with or without (III). Diffusible serum-Ca remained approx. 50% of (V), and was only slightly increased by (II). The $\text{Ca} \times \text{P}$ product was lowest on (II) without (III) and highest on (IV). Storage of both Ca and P was greatest with (IV) or (I) whether supplemented or not with vitamin-D (VI). The ash content of bones and teeth was decreased by absence of (VI) on a low-Ca ration (VII) or (II). The Ca of bone ash was decreased by (VII) and the P decreased by an acid (VII). CH. ABS. (p)

Bone tests in pigs. V. HORN (Bied. Zentr. [Tierernähr.], 1934, B, 6, 213—226).—Addition of vitamin-D (I) to a low-Ca ration improved bone composition, but had no effect when the ration already contained adequate supplies of Ca and P. Bones from animals which, from the beginning, had received no supplement of Ca, P, or (I) had the same composition as those receiving these supplements throughout. A. G. P.

Calcium, phosphorus, and vitamin-D requirements of swine. G. DUNLOP (J. Agric. Res., 1935, 22, 49).—The effect of varying the Ca:P ratio of the diet on the general condition and blood

picture in pigs is examined. Under ordinary conditions the optimum level of dietary Ca is 0.45% of the dry matter with a (I) of 1:1.3. The P requirement is probably influenced by the proportion of phytin supplied. Blood-phosphatase reaches a min. with (I) at 1:2. A. G. P.

Calcium and phosphoric acid in nutritional physiology. O. LOEW (Deut. med. Woch., 1934, 60, 1242; Chem. Zentr., 1934, ii, 1944).—In rabbits, guinea-pigs, and mice the no. and wt. of the young were increased by additional Ca feeding. A. G. P.

Assimilation of phosphorus from di- and tricalcium phosphate, bone dicalcium phosphate, and cooked bone meal. K. V. ROTTENSTEN and L. A. MAYNARD (J. Nutrition, 1934, 8, 715—730).—Differences in the effectiveness of the phosphates were small, but indicated a slight superiority of secondary compounds. A. G. P.

Creeper fowl. VIII. Effect of bone extract on skeletal growth and the phosphatase content of the bones. W. LANDAUER, E. UPHAM, and F. RUBIN (J. Biol. Chem., 1935, 108, 121—126).—Aq. bone extract injected during the first 8 weeks of life was without effect on bone growth of normal or creeper chicks, the bones of each showing the same decline of phosphatase activity after the 3rd week. A. E. O.

Growth and calcification of bones. M. YOSHITOMI (J. Biochem. Japan, 1935, 21, 37—53).—With chick embryos grown *in vitro* (A., 1929, 1197; 1931, 259), optimal growth and calcification of the femur occur at p_{H} 7.2—7.4. Growth is inhibited by co-enzyme (I) from pig's heart-muscle (A., 1932, 775) + Na hexose diphosphate (II), and direct ultra-violet irradiation (III), enhanced by glucose, sucrose, lactic acid, dipeptide phosphate (IV) (A., 1933, 1062), lecithin, and (III) of the culture medium, whilst fructose, AcCO_2H , (II), caseinogen, tryptophan, cystine, and cod-liver oil (V) have little or no effect. Calcification is inhibited by glucose and fructose, enhanced by (II), (III), (V), and lecithin, whilst lactic acid, AcCO_2H , (I), (I)+(II), (IV), caseinogen, tryptophan, and cystine have little or no effect. F. O. H.

Development of calcifying mechanism in the long bones of the rabbit. J. S. F. NIVEN and R. ROBISON (Biochem. J., 1934, 28, 2237—2242).—The activity of the calcifying mechanism (I) in normal rabbit tissue is > that in the hypertrophic cartilage (II) of rachitic animals. (II) and the osteoid tissue become calcified *in vivo* soon after their formation, and (I) is present before the deposition of Ca occurs. The inorg. mechanism and the phosphatase are not destroyed by COMe_2 treatment or desiccation of the tissue. A. L.

Development of the calcifying mechanism in avian cartilage and osteoid tissue. H. B. FELL and R. ROBISON (Biochem. J., 1934, 28, 2243—2253).—Whilst uncalcified normal osteoid tissue in its early stages could not be calcified *in vitro*, at a later stage, immediately before calcification (I) *in vivo* took place, this was possible. Fowl cartilage (II) in the long bones begins to hypertrophy at an

early stage in embryonic life, but (I) begins about the 15th day of incubation, and is never complete. Whilst the early hypertrophic (II) contains phosphatase, it cannot be artificially calcified, but at later stages this is partly possible. Cultures of fibrous tissue from the periosteum were uncalcified under conditions suitable for the (I) of osteoid tissue. A. L.

Distribution of therapeutic and other substances in the organism. G. HECHT (Angew. Chem., 1935, 48, 14—17).—The distribution, accumulation, and excretion of drugs administered by various routes are discussed. The urinary, but not the biliary, excretion of dyes can be correlated with their permeability through artificial (*e.g.*, Cellophane) membranes. The excretion of acidic dyes depends on the degree of dispersivity. Thus with 1—3 SO_3H groups, finely dispersed dyes are excreted by the kidney (I) and liver (II) (*i.e.*, into urine and bile) and coarsely dispersed dyes by (II) alone, whilst with > 3 SO_3H groups the former are excreted by (I) alone and the latter not at all. The differences are probably due to the hydrophilic character of SO_3H . F. O. H.

Biological detection of abietic acid and parent substances. Sulphite-cellulose effluent. R. DANNEEL (Arch. exp. Path. Pharm., 1935, 177, 248—259).—The toxicity of colophony, abietic acid, and pine-resin (dissolved in aq. Na_2CO_3 or emulsified in H_2O) to fish is not diminished by aeration, is doubled by a rise of temp. of 10° (over a range of 5 — 21°), and is due to the effect on the nervous system. That of sulphite-cellulose effluents (I) is diminished by dilution with H_2O or addition of NaOH and is due to saponifiable constituents which are sol. in light petroleum and damage the respiratory (branchial) system. The bearing of the data on the toxicity of (I) (at Königsberg) is discussed. F. O. H.

Activity of substances from croton oil. R. BÖHM, B. FLASCHENTRÄGER, and L. LENDLE (Arch. exp. Path. Pharm., 1935, 177, 212—220).—Croton resin (I), $[\alpha]_D$ approx. $+70^\circ$ in CHCl_3 (A., 1895, i, 680), loses its toxicity on treatment with alkali, whilst with CS_2 it yields an inactive cryst. resin, $[\alpha]_D^{25} +167^\circ$ in CHCl_3 . (I) also affords inactive phorbol (II), $\text{C}_{20}\text{H}_{28}$ or 30O_6 , a tricyclic substance with five OH, one $\cdot\text{O}\cdot$, and three double linkings. The toxicity of the Ac_4 derivative (III) of (II) equals that of (I); the Bz derivative is inactive. Loss of H_2O from (II) gives the ketone, crotophorbolone. A prep., $[\alpha]_D +20^\circ$ in CHCl_3 , of the toxic principle can be obtained by physical methods; hydrolysis by EtOH —alkali affords (I) and (II). The pharmacology of (III), a stimulant of the central nervous system, is described. F. O. H.

[Active principles of] *Gleditsia triacanthos* (Linné). Y. T. OESTER (J. Amer. Pharm. Assoc., 1934, 23, 1198—1200).—Aq. extracts (which are free from alkaloids and glucosides) of *G. triacanthos* (honey locust) contain an oxytocic principle ("hypoxysin") and a second constituent of marked depressor action. F. O. H.

Detection and distribution of narcotics in the brain. R. FISCHER and A. HAUSCHILD (Pharmaz. Mh., 1934, 15, 64—68; Chem. Zentr., 1934, ii, 1814).—

Established methods for the identification of narcotics fail in the case of brain materials. The narcotic is extracted with Et_2O , purified by means of NaOH , H_2SO_4 , and KMnO_4 , and finally identified by micro-methods. In man and dogs, veronal (I) and luminal (II) are found principally in the cerebrum and, to a smaller extent, in the paleo-encephalon; (II) is never found in the cerebellum, but may be detected in the spinal cord; the converse is true of (I). H. N. R.

Action of anaesthetics on living protoplasm. L. V. HEILBRUNN (Proc. Amer. Phil. Soc., 1934, 74, 159—165).—Stimulation causes gelation of protoplasm comparable with blood-clotting. Et_2O prevents this effect in sea-urchin eggs when $[\text{Ca}^{++}]$ is minimal. CH. ABS. (p)

Determination of chloral hydrate in blood and urine. M. M. FRIEDMAN and F. A. CALDERONE (J. Lab. Clin. Med., 1934, 19, 1332—1333).—The blood-filtrate is treated with $\text{C}_5\text{H}_5\text{N}$ and NaOH and chloral vals. are obtained colorimetrically. CH. ABS. (p)

Avertin and liver function. T. KOBAYASHI (J. Biochem. Japan, 1934, 20, 405—421).—Rectal administration (I) of avertin (0.3 g. per kg.) to dogs (II), but not rabbits (III), increases the secretion of bile, whilst the relative and abs. concns. of bilirubin and bile acids markedly decrease. The effect is not appreciably influenced by the degree of narcosis or by the simultaneous action of insulin, adrenaline (IV), atropine, ingested glucose, or blocking of the reticulo-endothelial system. (I) of avertin produces a prolonged hyperglycemia (V) in (III), but not (II), whilst with (II), the (V) due to (IV) is inhibited and that due to ingested glucose is enhanced. These facts together with the resulting diminution of liver-glycogen in (III) indicate that avertin damages the liver. F. O. H.

Benzene and hydrocarbon therapy. J. KAJRIUKSTIS (Münch. med. Woch., 1934, 81, 493; Chem. Zentr., 1934, ii, 2098).—Physiological effects of the aliphatic hydrocarbons (I) in benzene are most marked in the case of C_7H_{16} . C_6H_6 has the action of a blood poison but xylene and $\text{C}_6\text{H}_4\text{MeEt}$ produce effects resembling those of (I). A. G. P.

Action of various compounds of the thymol and carvacrol series on respiration and blood-pressure and their antagonistic action to adrenaline in its raising of blood-pressure. T. MAEDA (Folia Pharmacol. Japan, 1934, 18, No. 2—3, 79—94).—The thymol nucleus accentuates the action of these compounds in lowering blood-pressure. CH. ABS. (p)

Action of induced fever on lachrymal elimination of sodium chloride. D. MICHAIL and P. VANCEA (Compt. rend. Soc. Biol., 1934, 117, 1273—1274).—The rise of temp. induced in man by intramuscular injection of sterile milk is accompanied by an increase in lachrymal NaCl , both reaching their max. at the same time. The parallelism becomes less evident in the later phases, the NaCl tending to remain high. Plasma- NaCl falls as lachrymal NaCl rises. R. N. C.

Substances causing fever, particularly dinitrophenol. J. DADLEZ and W. KOSKOWSKI (Compt.

rend. Soc. Biol., 1935, 118, 97—99).—The fever (I) caused by administration of dinitrophenol, like that caused by methylene-blue, PH_3 , and dinitro- α -naphthol, is due to an increase in the rate of metabolism, and is of peripheral origin (II). (I) caused by neutral-red, Me-orange, peptone, and gelatin is of central origin (III). (I) caused by tetrahydro- β -naphthylamine involves both (II) and (III). A. L.

Effect of 2:4-dinitrophenol on cellular respiration. R. H. DE MEIO and E. S. G. BARRON (Proc. Soc. Exp. Biol. Med., 1934, 32, 36—39).—2:4-Dinitrophenol (I) increases considerably the respiration of cells and tissues, but is without effect if respiration has been inhibited by CO or KCN. It does not oxidise lactate activated by α -hydroxy-oxidase, and has no action on the respiration of gonococci. R. N. C.

Cellular oxidative mechanism involved in dinitrophenol stimulation of respiration. M. E. KRAHL and G. H. A. CLOWES (Proc. Soc. Exp. Biol. Med., 1934, 32, 226—228).—4:6-Dinitro-*o*-cresol (I) accelerates the reduction of cytochrome (II) in normal yeast in the presence of many substrates, but only with glucose is the reducing ability of the combination equal to the sum of those of the individual agents. (I) is equally efficient with or without pyruvate and lactate. In yeast poisoned with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$, (II) reduction is not accelerated, even when lactate or glucose is present. The reactivity of tissues to (I) stimulation is inhibited to a limited degree by non-sp. dehydrase poisons such as $\text{Na}_4\text{P}_2\text{O}_7$ and narcotics. It is probable that (I) stimulates cellular respiration by accelerating the oxidation by (II) of a substrate previously or simultaneously acted on by cellular anaerobic dehydrases. R. N. C.

Relationship between blood-cholesterol and increased metabolism from dinitrophenol and thyroid. W. C. CUTTING, D. A. RYTAND, and M. L. TAINTER (J. Clin. Invest., 1934, 13, 547—552).—Changes in blood-cholesterol in thyroid disease are not related to the metabolic rate (I), but to other actions of the thyroid secretion. Dinitrophenol stimulates both a low and a normal (I).

CH. ABS. (p)

Variations in creatininuria during experimental fever. F. KAYSER (Bull. Soc. Chim. biol., 1934, 16, 1498—1517).—The changes in the amount of creatinine (I) excreted by man during malarial fever, and by rabbits during fever caused by injection of 2:4-dinitrophenol, tetrahydro- β -naphthylamine, and yeast are compared with the variations in body-temp. (II). In all cases, although considerable variations in (I) occurred, no relationship of these with (II) could be established. A. L.

Effect of certain physical factors on the *in vitro* testing of anthelmintics. P. D. HARWOOD (Proc. Soc. Exp. Biol. Med., 1934, 32, 131—133).—The anthelmintic effect of solutions of alkylresorcinols (I) in 0.9% NaCl *in vitro* is max. when there is an undissolved excess present in the liquid state, the optimum temp. being 37°. For (I) that are solid at 1, $n\text{-C}_6\text{H}_{14}$ can be used as a solvent, as it is non-toxic to ascarides and scarcely affects (I). R. N. C.

Pharmacological action of tannic acid. II. Drugs modifying the coagulant action of tannic acid on the proteins of ovalbumin. U. SAMMARINO (Arch. Farm. sperim., 1935, 59, 1—28).—The coagulant action of tannic acid (I) on ovalbumin (II) is greatly increased by addition of HCl. With a const. (I) concn., the extent of pptn. increases progressively with addition of HCl; if [HCl] is kept const., the viscosity curve (III) rises rapidly to infinity, then falls sharply to a subnormal val. If (I) and HCl are increased together in the same proportion, (III) shows two infinity breaks, indicating that (I) in presence of HCl retains its power of pptg. (II) fractionally (cf. A., 1934, 1397). The p_H of the mixture is not altered at the pptn. points. The action of (I) is decreased by addition of NaOH. Increasing (I) concn. with const. NaOH does not affect the viscosity, and p_H falls steadily. The action of (I) is not affected by addition of NaCl with const. (I) concn. Increase of (I) concn. with const. [NaCl] gives a (III) with two small breaks corresponding with the first and second fractions of (II) proteins; p_H falls steadily as for NaOH. Glucose has a similar action to NaCl with const. (I) concn. (III) shows breaks indicating that glucose does not affect pptn. of the first fraction, but for the second and third fractions its action is similar to that of NaCl, but stronger. The p_H of the mixture falls steadily until the pptn. of the second fraction, when it falls sharply. R. N. C.

Nitrogen metabolism. II. Production of glycine during benzoic acid poisoning. U. LOMBRISO, C. ZUMMO, and M. STASSI (Arch. internat. Physiol., 1934, 39, 1—23).—Guinea-pigs progressively lose 30—40% of their wt. when NH_4OBz or NaOBz is added to a diet previously proved adequate for wt. maintenance. About 80—90% of the NH_4OBz is eliminated in the urine as hippuric acid (I). The further addition of gelatin reduces the loss of wt., but neither NH_4 citrate nor NH_4 glycocholate gives protection. Na salts of org. acids (citric, tartaric, or glycocholic) not only prevent loss of wt., but cause a significant augmentation and reduce the amount of BzOH appearing as (I) to 60—65%. The fate of the remaining BzOH is unknown. (I)-N cannot be derived from NH_4 salts. NUTR. ABS. (m)

Amino-esters of naphthoic acid. M. E. BJERREGAARD and B. HOUSTON (Proc. Oklahoma Acad. Sci., 1934, 14, 77).—The local anæsthetic activity of the hydrochlorides of γ -diethylaminopropyl and β -diethylaminoethyl α -naphthoate (from $\alpha\text{-C}_{10}\text{H}_7\text{COCl}$ and the alcohol) was comparable with that of cocaine, but the toxicity was less. CH. ABS. (p)

Action of quinoline derivatives on the gametocytes of *Plasmodium præcox*. I. L. KRITSCHESKI and A. I. PINES (Klin. Woch., 1934, 13, 807—809; Chem. Zentr., 1934, ii, 1160).—Plasmoquin (I) in concn. 1:1000, and plasmocid (8- γ -diethylaminopropylamino-6-methoxyquinoline) (II), in concn. 1:1500, introduced into the *Spinus spinus* at the height of infection with *Plasmodium præcox* are able to destroy the power of the gametocytes to infect the *Culex pipiens*, 12—24 hr. after the treatment. Neither (I) nor (II) is effective in concns. 1:4000 or 1:8000. R. N. C.

Toxic effect of phenylquinolinecarboxylic acids. A. RISI (Arch. int. Pharmacodyn. Thé., 42, 117—127; Chem. Zentr., 1934, ii, 1491).—The min. lethal doses for dogs, guinea-pigs, and rabbits, and the histological effects on peroral administration, of 2-phenylquinoline-4-carboxylic acid are given.

R. N. C.

Depressor action of extracts of organs, particularly kidney extract. J. DADLEZ and W. KOSKOWSKI (Compt. rend. Soc. Biol., 1935, 118, 95—97).—The depressor action of extracts of the following organs on the rabbit injected with atropine and under urethane anaesthesia decreases in the order: striped muscle, heart, kidney, spleen, uterus, liver, testicle, mammary gland. Extracts of brain, lung, and bone marrow have a hypertensive action.

A. L.

Depressor extracts of human tissues. H. N. HARKINS and P. H. HARMON (Proc. Soc. Exp. Biol. Med., 1934, 32, 23—26).—Neither toxic thyroid nor carcinomatous tissue extract contains any unusual amount of depressor substance. The depressor resembles Chang and Gaddum's "*P* substance."

R. N. C.

Cardiac depressor (acetylcholine ?) released by dorsal nerve-root stimulation. O. W. TIEGS (Austral. J. Exp. Biol., 1934, 12, 161—167).—The depressor effect obtained on the isolated frog's heart by dorsal nerve root stimulation is not due to a change of p_H of the perfusing fluid; it is augmented by eserine and inhibited by atropine, properties in common with acetylcholine.

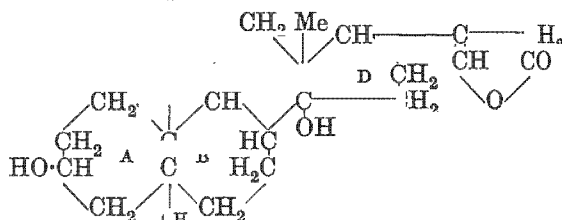
P. G. M.

Biological assay of cardiac stimulants. Toxicity of a national standard for digitalis powder compared with the international standard. J. LEVY and K. OTTERSTROM (Bull. Soc. Chim. biol., 1934, 16, 1518—1530).—A comparison is made of the toxicities of the international and the French national digitalis standard preps. using the min. lethal dose (slow perfusion) method with dogs and guinea-pigs, and the method of % mortality following injection of increasing doses into frogs and guinea-pigs. The former (accuracy about 15%) is considered preferable.

A. L.

Plant cardiac poisons. III. Degradation of a genin of the cardiac poisons to a bile-acid derivative. R. TSCHESCHE. **IV. Constitution of trianhydrostrophanthidin.** R. TSCHESCHE and H. KNICK (Z. physiol. Chem., 1934, 229, 219—232, 233—235; cf. A., 1934, 193).—III. Oxidation of the α_1 -lactone from uzarigenin with CrO_3 in AcOH gives a dicarboxylic acid, $\text{C}_{20}\text{H}_{36}\text{O}_4$, m.p. 245° (decomp.). [Me_2 ester (I), m.p. 160 — 162° , $[\alpha]_D^{25} +4.9^\circ$ in CHCl_3]. (I) is converted (Grignard) into the *ditert*-carbinol, which with CrO_3 in AcOH affords the acid (II), $\text{C}_{20}\text{H}_{32}\text{O}_2$, m.p. 228 — 230° [Me ester (III), m.p. 140 — 142° , $[\alpha]_D^{25} +48.3^\circ$ in CHCl_3]. The α_2 -lactone similarly gives a dicarboxylic acid, $\text{C}_{23}\text{H}_{36}\text{O}_4$ (Me_2 ester, m.p. 106 — 107° , $[\alpha]_D^{25} +1.0^\circ$ in CHCl_3), which yields (II) on oxidation of the *ditert*-carbinol obtained by Grignard reaction. Oxidation of the *tert*-carbinol obtained from (III) affords an acid, $\text{C}_{19}\text{H}_{30}\text{O}_4$, decomp. 265° (anhydride, m.p. 186°), indicating that the lactone side-chain of the cardiac poisons is attached

directly to a ring. (II) is probably identical with *ætioallocholanolic acid*, m.p. 230° (Me ester, m.p. 140°), obtained by a method similar to that described by Wieland *et al.* (A., 1927, 247) for *ætiocholanolic acid*. The constitution of the cardiac poisons is discussed. Strophanthidin is probably



IV. Oxidation of trianhydrostrophanthidin (VI) with HNO_3 affords $1:2:3:4\text{-C}_6\text{H}_2(\text{CO}_2\text{H})_4$. Ring B of (V) has probably become benzenoid in (VI) with transference of the CHO from C_{10} to C_1 . J. H. B.

Calcium salts in the detoxication of gossypol. W. D. GALLUP and R. REDER (Proc. Oklahoma Acad. Sci., 1934, 14, 74—75).—Gossypol (I) inhibits hydrolysis of olive oil by lipase, the effect being most pronounced in presence of Ca. Detoxication of (I) in cottonseed meal is attained by feeding high-Ca diets. Na is nearly as effective in rats. Mixtures of NaHCO_3 and CaCO_3 give best results.

CH. ABS. (p)

Lack of vitamin-A not the chief cause of cottonseed meal injury in pigs. W. L. ROBISON (Ann. Rept. Ohio Agric. Exp. Sta., 1934, 70).—Vitamin-A deficiency is not the cause, but is related to cottonseed injury.

CH. ABS. (p)

Toxic substance occurring in certain samples of plant foodstuffs. III. Hæmoglobin levels in white rats which were fed with toxic wheat. K. W. FRANKE and V. R. POTTER. **IV. Effect of proteins on yeast fermentation.** K. W. FRANKE and A. L. MOXON (J. Nutrition, 1934, 8, 615—624, 625—631).—III. In many cases affected rats had low hæmoglobin levels.

IV. Protein (I) from healthy grain increased and that from "affected" grain did not materially affect the rate of fermentation of yeast (II). The stimulatory action of (I) is greater for wheat than for maize, and varies with the proportion of (I) to (II).

A. G. P.

Surface activity of alkaloids. T. SUZUKI (J. Biochem. Japan, 1935, 21, 153—171).—The σ of 0.002—0.01M solutions of 26 alkaloids in PO_4^{3-} buffer at p_H 7.48 containing ovalbumin was determined. The data are correlated with their action as protoplasmic poisons, anaesthetics, etc., and, as far as possible, with their structure.

F. O. H.

Preparation of simaruba bark as an abortive. F. W. FREISE (Sci. Pharmaceutica, 1934, 5, 65—67; Chem. Zentr., 1934, ii, 2100).—The principal constituents are: a cryst. alkaloid, anthelmintic and refractive; a "bitter substance," antidiarrhoeic; a soft resin, strongly emetic; an essential oil, therapeutically inactive; and tannin. The tannin content diminishes on keeping through phlobaphen formation. On animals, the drug acts as an abortive

in small quantities, larger quantities producing fatal irritation of the mucosa and vomiting. R. N. C.

Comparison of the utero-adrenalinolytic activity of corynanthine, yohimbine, and ergotamine. E. ROTHLIN and R. HAMET (Compt. rend. Soc. Biol., 1935, 118, 33—36).—Previous results showing that the utero-adrenalinolytic activity of corynanthine was twice that of yohimbine by direct comparison are confirmed using ergotamine as standard. A. L.

Influence of sympathetic nerve poisons on the glycosuria of splenectomised rabbits. C. TATEISHI (J. Biochem. Japan, 1935, 21, 101—110).—Splenectomy enhances alimentary glycosuria (I) in rabbits. Administration of atropine or ergotamine partly or totally inhibits this increase, but has no effect on the (I) of normal rabbits. F. O. H.

Preservation of the physiological activity of cocaine hydrochloride solution. J. RÉGNIER and R. DAVID (Bull. Sci. pharmacol., 1934, 41, 321—328; Chem. Zentr., 1934, ii, 2100).—The activity of cocaine hydrochloride solution is stable to heat and storage only at p_H 4. A Na_2HPO_4 buffer is without effect, but a solution buffered with AcOH and NaOAc at p_H 4.2 retains its activity when heated, if the p_H is unchanged, and loses only 20% of its activity after 6½ months. R. N. C.

Action of protein-organic base compounds on warm- and cold-blooded animals. H. LEONTJEV and V. ALEXANDROVSKI (Z. Biol., 1935, 96, 146—152).—Subcutaneous injection of an aq. prep. of nicotine (5—20 mg. per kg. in pigeons, mice, rats, guinea-pigs, rabbits, dogs, and cats and 150 mg. per kg. in frogs and axolotls) with an "equiv." amount (approx. 8 times by wt.) of caseinogen produces only mild symptoms of toxicity. The mechanism of the detoxication is discussed. F. O. H.

Colorimetric determination of morphine in biological fluids by the iodoxybenzoate method. G. A. EMERSON (Proc. Soc. Exp. Biol. Med., 1934, 31, 1004—1006).—Leake's method gives results accurate to $\pm 3\%$. CH. ABS. (p)

Morphine hyperglycæmia. P. T. SHEN (J. Biochem. Japan, 1935, 21, 173—195).—Injection of morphine into rabbits produces a hyperglycæmia (I) which decreases with continued administration. Section of the splanchnic nerves and administration of ergotamine or luminal depress (I), whilst adrenalectomy and decerebration (but not decortication) totally inhibit (I). F. O. H.

Metabolism during chronic morphine action. v. **Pathology of morphine.** G. ANTON and E. BERK (Arch. exp. Path. Pharm., 1935, 177, 226—234).—The abnormally high hyperglycæmia (I) following ingestion of glucose by human morphine (II) diets (HI) (A., 1931, 1329) also occurs in dogs habituated to (II); with fructose (I) is normal. With (II)-habituated but not excessively weakened dogs, the loss in body-wt. due to (II) is prevented or reversed by administration of insulin, the tolerance of which of (III) and the extent of the preliminary (I) injection are probably due to the liver damage caused by (II). O. H.

Saliva tests. II. Heroin. J. C. MUNCH (J. Amer. Pharm. Assoc., 1934, 23, 1185—1187).—Mice respond to subcutaneously injected heroin by tail reactions (I) similar to those given by morphine (A., 1934, 1256), but at the lower threshold of 0.5 mg. per kg. body-wt. Following injection of heroin into horses, the saliva contains a substance giving positive (I) in mice. F. O. H.

Strychnine hyperglycæmia. P. T. SHEN (J. Biochem. Japan, 1934, 20, 481—490).—Section of the splanchnic nerves, administration of ergotamine, or adrenalectomy markedly inhibits the hyperglycæmia (I) due to injection of strychnine nitrate (II) into rabbits. (I) is not related to the convulsions due to (II). F. O. H.

Determination of caffeine in biological fluids and tissues. A. F. KUNZ (Biochem. Z., 1935, 275, 270—285).—A method is described for the determination of caffeine (I) in urine, blood, faeces, organs, and coffee which gives trustworthy results with 0.05—20 mg. of (I). For identification of (I) C and N determinations are used. A modification of the prep. of the (I)- $AuCl_3$ complex is described which permits the detection of 0.00125% of (I). P. W. C.

Relationship between the constitution of some amino-ethers and their pharmacological action. J. LEVY, D. KOHLER, and L. JUSTIN-BESANÇON (Compt. rend., 1935, 200, 259—261).—Of 16 NH_2 -ethers administered (dose 0.02 g. per kg.) to dogs previously given an intravenous injection of ephedrine hydrochloride (I) (0.005 g. per kg.) one group, containing aromatic derivatives of the type $ArO\cdot CH_2\cdot CH_2\cdot N$, are adrenolytic, causing recession of the exophthalmia, the second group are non-adrenolytic, those of the type $CH_2R\cdot O\cdot CH_2\cdot N$ (R=Me or a ring) remove mydriasis but not the exophthalmia, whereas when R=an aliphatic C_3 chain, they sensitise the eye to the action of (I). J. W. B.

Creatinuria in adolescent males. II. Effects of oral administration of ephedrine sulphate. A. B. LIGHT and C. R. WARREN (J. Amer. Med. Assoc., 1934, 103, 410—411).—Ephedrine sulphate (25 mg. orally) administered 3 or 4 times to healthy boys (12—17 years) known to be excreting creatine (I) raises the blood-pressure and pulse rate, but has no appreciable effect on the vol. of urine or the daily output of preformed creatinine. Creatinuria is markedly reduced on the day of administration, and in half of the subjects on the next day also, but to a smaller extent, the others then having an output of (I) > on the pre-control day. NUTR. ABS. (m)

Action of hydroxyephedrine on the oxygen consumption of the white mouse. S. AHNSTRÖM and R. ÖEHNELL (Skand. Arch. Physiol., 1934, 68, 181—186; Chem. Zentr., 1934, ii, 1157).—Metabolism was stimulated by small doses of adrenaline (I) and a no. of $(OH)_1$ - (II) and 3:4- $(OH)_2$ -derivatives (III) of ephedrine and norephedrine. The activities of (I) and (III) were > those of (II), which decreased in the order $m > p > o$ -(II). R. N. C.

Importance of chemical constitution, especially of a methoxy-group in the *m*- or *p*-position in the side-chain, for the pharmacological action

of phenoxyethylamine and phenoxyethylpiperidine derivatives. III. Action on blood-pressure. Y. FUGIMOTO (*Folia Pharmacol. Japan*, 1934, 17, No. 2, 31—44).—Removal of OMe lowered blood-pressure and, if in the *p*-position, depressed peripheral effect and enhanced central vaso-constrictor action > if in the *m*-position. CH. ABS. (*p*)

Vasomotor effect of phenoxyethylamine and phenoxyethylpiperidine derivatives from the viewpoint of the pharmacological importance of a methoxy-group in the *m*- or *p*-position in the side-chain. Y. FUGIMOTO (*Folia Pharmacol. Japan*, 1934, 18, No. 2—3, 100—105).—Compounds free from OMe dilated, and those having OMe constricted, the vessels of the rabbit's ear. The significance of the N side-chain is considered. CH. ABS. (*p*)

Variations in alkaline reserve during ophidian intoxication. J. VELLARD and M. MIGUELOTE-VIANNA (*Ann. Acad. Brasil Sci.*, 1934, 6, 201—206).—The alkaline reserve (*A*) in the blood of dogs injected with the venom from *Crotalus terrificus* (I), *Lachesis atrox* (II), and *Naja tripudians* decreases slightly in the early stages of the poisoning; and more markedly [particularly in cases (I) and (II)] just before death. The final decrease in *A* seems to be associated only with the mechanism of the death, asphyxia being the principal controlling influence. E. L.

Influence of spleen extracts and bile acids on the sugar excretion threshold in rabbits with biliary fistulæ. C. TATEISHI (*J. Biochem. Japan*, 1935, 21, 55—62).—Withdrawal of bile increases the sugar excretion threshold, which returns to approx. normal levels on subcutaneous injection of Na cholate and/or spleen extract. F. O. H.

Influence of (a) liver and spleen extracts and (b) sympathetic nerve poisons on the sugar excretion threshold of splenectomised rabbits. C. TATEISHI (*J. Biochem. Japan*, 1935, 21, 63—76, 89—100).—(a) The increased sugar excretion threshold (I) of splenectomised rabbits (II) is diminished to normal vals. by administration of small amounts of liver extract (III), whilst large amounts further increase (I). Administration of small amounts of (III) + spleen extract decreases (I) to subnormal vals.

(b) The increased (I) of (II) falls to normal or subnormal vals. on administration of atropine or, to a smaller extent, of ergotamine. F. O. H.

Influence of liver-extract fractions on the sugar excretion threshold. C. TATEISHI (*J. Biochem. Japan*, 1935, 21, 77—88).—The increased threshold (I) due to splenectomy in rabbits (II) is further increased by the basic fraction [pptd. by phosphotungstic acid (III)] of the liver of (II) and diminished by the NH_2 -acid fraction [not pptd. by (III)]. Neither fraction influences the (I) of normal (II). F. O. H.

Blood changes in "mustard-gas" poisoning as an aid in diagnosis. O. MUNTSCHE (Klin. Woch., 1934, 13, 482—485; *Chem. Zentr.*, 1934, ii, 2099).—Poisoning with $(\text{C}_2\text{H}_5\text{Cl})_2\text{S}$ produces lowering of the red cell count and hæmoglobin (I), pronounced

neutropenia, lymphocytosis, and granule formation. Recovery is attended by increases in lymphocytes and eosinophiles; rate of decrease of red cells is raised after 3—4 hr., the val. remaining at the limit of normality. The progress of lung oedema can be studied from blood-(I). R. N. C.

Effect of some toxic gases on cell metabolism. J. JANY and C. SELLEI (*Biochem. Z.*, 1935, 275, 234—241).—The effect on respiration (I) and glycolysis (II) of suspensions of *B. coli* of HCN (III), CNBr (IV), acetaldehyde, AsEtCl_2 (V), AsPh_2CN (VI), and $(\text{C}_2\text{H}_5\text{Cl})_2\text{S}$ (VII) is investigated and compared with the effect of (VII) on the metabolism of animal tissue. All the substances exert considerable influence on both (I) and (II), but no relationship exists between this and other physiological effects. Thus (III) and (IV) have similar, but (V) and (VI) opposite, effects. In presence of substances inhibiting (I), aerobic (II) is increased more strongly or decreased less markedly than is anaerobic (II). P. W. C.

Delayed detection of carbon monoxide in the corpse. P. HEILMANN (*Deut. Z. ges. gerichtl. Med.*, 1934, 23, 215—217; *Chem. Zentr.*, 1934, ii, 1659).—CO poisoning could be detected 144 days after death by both chemical and spectroscopic tests. The tannin test was the best chemical method. H. J. E.

Sodium nitrite as antidote for hydrogen sulphide poisoning. V. KARASSIK and V. CHELOKHANOVA (*Compt. rend. Soc. Biol.*, 1935, 118, 23—25).—Aq. NaNO_2 injected into mice and rabbits before or after H_2S intoxication serves as an antidote. A. L.

Sodium tetrathionate as an antidote to hydrocyanic acid poisoning. A. CHISTONI and B. FORESTI (*Arch. int. Pharmacodyn. Théor.*, 42, 140—172; *Chem. Zentr.*, 1934, ii, 1490—1491).— $\text{Na}_2\text{S}_4\text{O}_6$ in neutral or alkaline solution, injected subcutaneously in ten times the theoretical quantity, decomposes NaCN forming non-toxic products (NaCNS , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$). R. N. C.

Influence of various water-soluble heavy metal salts on blood-glutathione. T. MAEDA (*Folia Pharmacol. Japan*, 1934, 18, No. 2—3, 132—142).—Salts of Bi, Cu, Fe, Hg, and Sb increased the glutathione content of the blood of male rabbits. Heavy doses reversed the effect. Bi salts were the most active, but over long periods and in small dosages Fe salts produced the greatest increase. CH. ABS. (*p*)

Bismuth poisoning. S. SEREFIS (*Med. Klinik*, 1934, 30, 968—971; *Chem. Zentr.*, 1934, ii, 1490).—The org. acids (I) of the gastric juice, particularly lactates, are normally present in too small quantity to form sufficient Bi complex (II) in oral Bi medication; in pathological conditions (II) formation from (I) and polyhydric alcohols (III) is considerable. $\text{Bi}(\text{OH})_3\text{NO}_3$ in the stomach forms BiCl_3 with gastric HCl and chlorides, which unites with (I) and (III) to form sol. (II), in which state Bi is resorbed by the mucous membrane. Resorption is hindered by H_2S , which forms insol. Bi_2S_3 , and by reduction of BiCl_3 complex to Bi by proteins in alkaline solution.

Argyrosis, especially of the eyes. W. GERLACH (Klin. Woch., 1934, 13, 797; Chem. Zentr., 1934, ii, 1645).—Intravenous injection of org. or inorg. Ag preps. causes rapid accumulation of Ag in the eyes and in certain internal organs. A. G. P.

Toxicology of some chromium derivatives. D. BRARD (J. Pharm. Chim., 1934, [viii], 20, 549—576).—The effect of the administration (by the mouth and by injection) of Cr salts and $\text{Cr}_2\text{O}_7^{--}$ to dogs is described. H. G. M.

Toxicity of chromium compounds. D. BRARD (J. Pharm. Chim., 1935, [viii], 21, 5—23).—Acute $\text{K}_2\text{Cr}_2\text{O}_7$ poisoning in the dog is chiefly due to the caustic and emetic properties of the salt, but if $\text{K}_2\text{Cr}_2\text{O}_7$ is slowly absorbed, e.g., after intradermal injection, death is produced by asphyxia due to the toxicity of Cr. In daily small doses, Cr^{+++} is less toxic than $\text{Cr}_2\text{O}_7^{--}$, but produces the same symptoms, including severe anaemia, ultimately fatal. Considerable fixation of Cr takes place in the endocrine glands. A. E. O.

Chronic poisoning by manganese dioxide. L. LYON-CAEN and A. JUDE (Ann. Med. leg. Criminol. Police Sci., 1934, 14, 511—517; Chem. Zentr., 1934, ii, 1647).—Inhalation of MnO_2 dust affected the central nervous system. A. G. P.

Magnesium and liver-glycogen. S. L. SVEINSSON (Arch. exp. Path. Pharm., 1935, 177, 221—225).—Subcutaneous or intramuscular injection of Mg gluconate does not increase the liver-glycogen of growing rats (cf. A., 1934, 553). F. O. H.

Biological action of copper. VON LINDEN (Med. Welt, 1934, 8, 1112—1115; Chem. Zentr., 1934, ii, 2098).—A review. Cu facilitates oxidative processes and stimulates growth through its action on the cell plasma. Excessive amounts inhibit cell activity. A. G. P.

Arsenic habituation by means of cultivated tissue. H. OKADA (Folia Pharmacol. Japan, 1934, 18, 198—207).—Resistance of fibroblasts to As decreases with long-continued culture in As media or in those in which the As content is successively increased. As probably accumulates in the tissue. CH. ABS. (p)

(A) Action of lead and zinc sulphides [on animals]. (B) Solubility in infusions of organs. C. G. SANTESSON (Skand. Arch. Physiol., 1934, 67, 17—195, 196—200; Chem. Zentr., 1934, ii, 1155—1156).—(A) Physiological effects are recorded.

(B) Of the sulphides of Hg^{II} , Bi, Cu, Pb, and Zn in Na_2S solution, only CuS dialysed through a collodion membrane. In presence of infusion of rabbit liver (I) HgS , Bi_2S_3 , and CuS passed through the membrane. Addition of HCl and (I) lowered the solubility of all sulphides except CuS. A. G. P.

Spectrographic determination of lead in urine. OLAK (J. Amer. Chem. Soc., 1935, 57, 104—107).—The acidified (HNO_3) urine is evaporated to dryness, the residue is heated to $> 500^\circ$, and the ash dissolved in HNO_3 . A known amount of Bi solution is added, and the intensities of the spectrum lines (Pb) and 2898-Å. (Bi) are compared. The E E

amount of Pb is found by comparison with standards. Solutions containing 0.01—0.2 mg. of Pb per litre can be analysed. H. B.

Lead content of bones in experimental lead poisoning. Influence of age. M. KASAHARA and S. I. NOSU (Arch. exp. Path. Pharm., 1935, 177, 272—275).—Following administration of the acetate, the deposition of Pb in the bones of young rabbits and goats is markedly $>$ that with adult animals. F. O. II.

Significance of the changes in the red corpuscles in the early diagnosis of lead poisoning. I. M. FLECKEL, I. G. TSCHERNOW, and K. I. TURGEL (Zentr. Gewerbehyg., 1934, 21, 34—41; Chem. Zentr., 1934, ii, 1490).—Reticulocytosis and polychromosia are the earliest and most permanent changes in the red corpuscles in Pb poisoning. The change is lessened by simultaneous administration of I with Pb.

Spasm-alleviating action of octin in lead poisoning. K. KOTZING (Klin. Woch., 1934, 13, 592—593; Chem. Zentr., 1934, ii, 1160).—Octin (octenylmethylamine) is effective without attacking the kidneys. R. N. C.

Effects of fluorine in water on teeth. F. S. MCKAY (Water Works Eng., 1934, 87, 925—928).— H_2O containing 6 p.p.m. caused mottling, whereas 0.5 p.p.m. did not. The crit. val. is approx. 2 p.p.m. CH. ABS. (p)

Presence of fluorine in water supply of Colorado and its relation to occurrence of mottled enamel. C. H. BOISSEvain (Colorado Medicine, 1933, 30, 142—148).—Occurrence of F in H_2O is ascribed to fluorite-bearing granite. Mottled enamel in teeth is associated with the presence of > 1 p.p.m. of F in H_2O . CH. ABS. (p)

Effect of various amounts of sodium fluoride on the teeth of white rats. H. T. DEAN, W. H. SEBRELL, R. P. BREAUX, and E. ELVOVE (U.S. Pub. Health Repts., 1934, 49, 1075—1081).—In amounts of 25 p.p.m. NaF in drinking- H_2O affected rats' teeth. Addition of CaCO_3 to the diet caused no change. CH. ABS. (p)

Fluorine in drinking-water. See this vol., 316.

Effect of fluorine on calcium and phosphorus metabolism in albino rats. E. M. LANTZ and M. C. SMITH (Amer. J. Physiol., 1934, 109, 645—654).—Growing rats fed with a complete diet containing 0.1% of NaF (I) retain less Ca and P than controls (II) on the same diet without NaF. With (I) in the diet the Ca : P retention ratio is $<$ in (II). At 60 days of age Ca and P retention by (II) decrease suddenly, calcification having practically ceased. In (I) administration calcification extends over a longer period, so that in the older animals Ca and P retention is $>$ in (II). (I) animals excrete more Ca and P in the faeces than (II), and the Ca : P excretion ratio is $>$ in (II). F probably interferes with Ca absorption. R. N. C.

Influence of fluorides on the blood-phosphorus and phosphorus metabolism of rabbits. L. REK (Arch. exp. Path. Pharm., 1935, 177, 343—349).—Subcutaneous injection (I) (equiv. to 2.26 mg. F per

kg. in all cases) of NaF affects neither the P metabolism nor the health whilst with oral administration (II), the blood-inorg. P (III) is 40% >, and the total P (IV) is 25% <, the normal val., the resulting P balance (V) being -4%. Following (I) and (II) of KHF_2 , 44.3 and 50% of ingested P are retained, respectively, the blood-P remaining approx. const. With (I) and (II) of NH_4HF_2 , retention of P occurs; transient changes in (III) and (IV) are corr. so that a positive (V) is maintained. (I) of CaF_2 produces an increased urine-P and a (V) of -5.8%; during the succeeding control period, however, (V) falls to -158.75% whilst the urine-P/fæces-P becomes 20:1, changes due to Ca^{++} . (II) of CaF_2 also produces a negative (V), (III) being increased and (IV) diminished.

F. O. H.

Differentiation between photosensitised and ultra-violet effects on frogs. H. F. BLUM and C. R. SPEALMAN (Amer. J. Physiol., 1934, 109, 605—613).—Frogs are photosensitised by injecting with hæmatoporphyrin or dyes of the fluorescein group. In presence of O_2 , irradiation with visible light (I) destroys bacteria, protozoa, and enzymes, inactivates bacteriophage, toxins, and viruses, hæmolyses erythrocytes, stimulates skeletal muscle to contraction, and prevents clotting of blood. The effects are not produced in absence of O_2 , whether replaced by H_2 , N_2 , CO, or a vac. Irradiation of non-sensitised frogs with ultra-violet light produces the above effects in presence or absence of O_2 ; its action therefore differs essentially from that of (I).

R. N. C.

Mitogenetic radiation. A. GURVITCH (Ann. Inst. Pasteur, 1935, 54, 259—267).—A lecture.

Mechanism of action of enzymes. S. J. PRZYŁECKI (Rocz. Chem., 1934, 14, 1377—1388).—The action of enzymes is explicable on the basis of purely chemical reasoning, without introduction of considerations of surface energy.

R. T.

Activity of enzymes in living cells. A. OPARIN (Ergebn. Enzymforsch., 1934, 3, 57—72; Chem. Zentr., 1934, ii, 1633—1634).—Factors concerned in controlling enzymic activity in living cells and causing changes of activity on the death of the cells are discussed.

A. G. P.

Enzyme production in transplanted loop of upper jejunum. H. B. PIERCE, E. S. NASSET, and J. R. MURLIN (J. Biol. Chem., 1934, 108, 239—249).—Variation of enzyme content for different and the same dogs is confirmed. Carbohydrases are the most active enzymes of succus entericus. Lipase and peptidase are present, but no definite proof of the presence of proteinase is found.

H. T.

Enzyme-chemical method. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1934, 229, 241—254).—A discussion. Points stressed are: the influence of the colloidal carrier on inhibition, activation, p_H -activity curve, and determination of enzymes; action of COMe_2 , which produces less alteration than EtOH, action of glycerol, differentiation of lyo- and desmo-enzymes; individual differences in the enzyme content of animal organs.

J. H. B.

Preparation in the pure state of the active grouping of the yellow enzyme. H. THEORELL

(Biochem. Z., 1935, 275, 344—346).—The active group of Warburg's yellow respiration enzyme is a mono-phosphoric ester of a flavin.

P. W. C.

Restriction by phosphate of the rate of reaction in Warburg and Christian's system. H. THEORELL (Biochem. Z., 1935, 275, 416—421; cf. A., 1932, 74).—The rate (I) of uptake of O_2 during the reaction is restricted by inorg. PO_4''' (II); the degree of restriction inversely \propto the concn. of (II). (I) \propto the amount of intermediate enzyme (III) and the amount of co-enzyme (IV) but is independent of the initial concn. of hexose monophosphate (V). (II) affects the reducing but not the oxidising system. (III) is a phosphatase. In any reaction between (IV), (III), and (V), reversible elimination of PO_4''' must occur.

W. McC.

[Base from] co-enzyme preparations. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1935, 275, 464; cf. this vol., 249).—The base $\text{C}_6\text{H}_6\text{ON}_2$ is nicotinamide.

W. McC.

Effect of supersonic rays on enzymes. XLIII. Peroxidase reaction. M. MATSUDAIRA and A. SATO (Tohoku J. Exp. Med., 1934, 22, 412—416).—Irradiation inactivates milk peroxidase, and also the catalases in blood and taka-diastrase when greatly diluted.

CH. ABS. (p)

Catalase and oxidative processes in animal tissues as possible factors in adaptation. H. S. HOPKINS (Biol. Bull., 1934, 67, 115—125).—In lamellibranchs the catalase content (I) of the muscle was higher in intertidal than in wholly submerged species. The O_2 consumption was approx. parallel to (I).

CH. ABS. (p)

Laccase. VI. Purification by sodium carbonate and ammonium sulphate treatment. VII. By dialysis and adsorption. VIII. By ultrafiltration. IX. By combined methods. General conclusions. P. FLEURY and C. CAMPORA (Bull. Soc. Chim. biol., 1934, 16, 1589—1602, 1603—1607, 1608—1616, 1617—1624).—VI. Defecation of lac juice with an equal vol. of $\text{N-Na}_2\text{CO}_3$ and pptn. of the laccase in the filtrate (I) with saturated aq. $(\text{NH}_4)_2\text{SO}_4$ at p_H 6.1 gives a ppt. (II) which contains 60% of the enzyme activity and only 5% of the Mn in

VII. Dialysis and adsorption on $\text{Al}(\text{OH})_3$ at p_H 4.4 followed by elution at p_H 9.5 is used to concentrate the laccase in (II).

VIII. By ultrafiltration of (II) at p_H 5.2 through collodion membranes the laccase is retained and concn. considerably, the final prep. being three times as active as the original juice and containing 1.2% of ash, 0.0066% of Mn, and no Fe.

IX. A summary.

A. L.

"Intermediate enzyme" from frog's muscle. T. WAGNER-JAUREGG, E. F. MOLLER, and H. RAUEN (Z. physiol. Chem., 1935, 231, 55—61).—The dehydrogenation of *l*-malic acid by methylene-blue (I) in presence of frog-muscle extract (II), flavoprotein, and co-enzyme is only slightly inhibited by KCN. If (I) is replaced by air, the O_2 uptake proceeds at only one fourth the rate. In the dehydrogenation of hexose-phosphoric acid (Neuberg ester) by (I) in presence of

"intermediate enzyme" (III) of Warburg and Christian, (III) may be replaced by (II), although the activity is lowered. KCN does not inhibit the reaction. With O, as H acceptor, in the presence of (III) the reaction proceeds normally, but with (II) practically ceases. When (II) and (III) are both present, the action of (III) is greatly depressed; (II) must therefore contain inhibitors. J. H. B.

Dehydrogenase activities of the gastro-intestinal mucosa. S. SAKISAKA (Fukuoka Ik. Zasshi, 1934, 27, 415—426).—The dehydrogenase oxidises succinic and malic (I) acids, glyceraldehyde, candiolin, histidine (II), and glutamic acid (III). The action on (II) and (III) is accelerated by presence of (I), but retarded by fumaric acid. CH. ABS. (p)

Non-production of acetonedicarboxylic acid from citrate by citricodehydrase. D. MÜLLER (Biochem. Z., 1935, 275, 347—349).—Citricodehydrase from cucumber seeds or from yeast does not convert citric acid into acetonedicarboxylic acid (cf. Langecker, A., 1934, 1251). W. McC.

Xanthine-oxidase. J. TOYAMA (Fukuoka Ik. Zasshi, 1933, 26, 1483—1499).—Xanthine- (I) -oxidase, isolated from milk, hydrolyses (I) and hypoxanthine (II). The optimum of the enzyme is 8.0 and optimum temp. 40°. (I), (II), and aldehyde are oxidised. Inhibitory agents include Et₂O, CHCl₃, PhMe, glycerol, and salts of Ag, Cu, and Hg. Sunlight, ultra-violet, and Ra radiation inactivate the enzyme. CH. ABS. (p)

Reduction of dinitrophenols by redox indicators and enzymes. G. D. GREVILLE and K. G. STERN (Biochem. J., 1935, 29, 487—499).—Reductive titration of 4 : 6-dinitro-*o*-cresol (I) with Na₂S₂O₄ or Pd-H₂, or oxidative titration with K₃Fe(CN)₆, or the mixing of equimol. amounts of 4-nitro-2-amino- (II) and 2 : 4-dinitro-phenol (III), with or without addition of yeast cells, gave no evidence of the reversibility of the systems involved. (I) does not increase the O₂ uptake of erythrocytes. The reduction of (I) was followed by a series of potential indicators (A., 1923, ii, 285) from $E_h + 0.040$ to -0.270 volt; the rate of reduction is not determined solely by the p.d. of the indicator system. Formic dehydrogenase does not reduce (I) or (III) except in presence of benzyl-viologen (IV), Nile-blue, and Janus-green. (II) is isolated as a reduction product of (III). (IV) is first reduced by the dehydrogenase and the reduced (IV) reacts with (I) or (III). Xanthine-oxidase reduces (I) without indicators. Lactic dehydrogenase reduces (I) only in the presence of pyocyanin, toxoflavin, and anthraquinone-2-sulphonate. Succinic dehydrogenase does not reduce (II) in the presence of indicators. Unwashed rat muscle reduces (I) and more rapidly in the presence of (IV). H. D.

Enzymic equilibrium. K. P. JACOBSON and J. TAPADINHAS (Bull. Soc. Chim. biol., 1934, 16, 1637—1644; cf. A., 1934, 693).—Previous results on the influence of glycerol (I) and $(-CH_2 \cdot OH)_2$ (II) on the equilibrium const. for liver fumarase-fumaric-malic systems are confirmed by gravimetric methods. Glucose, like (I) and (II), favours the formation of

Stabilisation of carboxylase solutions. O. VON SCHÖNEBECK and C. NEUBERG (Biochem. Z., 1935, 275, 330—338).—The maceration extract is prepared by grinding together dry yeast with 3 times its wt. of 50% glycerol (I), digesting for 5 hr. at 37°, and clearing the fluid by centrifuging. The solution can then be kept for a month without loss of carboxylase (II), although after 3 days co-enzyme must be added to ferment sugar. (II) cannot be removed from (I) solution by the usual adsorbents. P. W. C.

Emulsin. XVIII. Fission of phenol- β -*d*-glucoside 6-methyl ether by almond emulsin. B. HELFERICH and E. GÜNTHER (Z. physiol. Chem., 1935, 231, 62—64; cf. this vol., 250).—Fusion of β -*d*-glucose 6-Me ether tetra-acetate with PhOH and *p*-C₆H₄MeSO₃H and hydrolysis of the product gave a mixture of phenol- α - and - β -*d*-glucoside 6-Me ether, from which 2 fractions containing respectively about 50% and 70% of the β -compound were obtained. Both fractions were slowly hydrolysed by almond emulsin (I), indicating that methylation of the 6-OH of the β -*d*-glucosides retards but does not prevent fission by (I). J. H. B.

Specificity of amylases. Action of amylases on starch hydroxyethyl ether. W. ZIESE (Z. physiol. Chem., 1934, 229, 213—218).—The ether is attacked by α - but not by β -amylase, even in presence of amylokinase (I). The decrease in viscosity of the solution is used as a measure of the reaction, since the changes in $[\alpha]$ and reducing power are negligible. The degradation of starch by pancreas-amylase (optimum p_H 6.1—6.3) is accelerated by (I).

J. H. B.
Endo enzymes of tissue and glands. V. Amylases of liver and other organs. R. WILLSTÄTTER and M. RONDEWALD (Z. physiol. Chem., 1934, 229, 255—268).—Liver (I), muscle (II), and pancreas (III) contain mixtures of the various lyo- and desmo-amylases. (III) contains mainly lyo-amylase-III with some -I. Amylase-I, -II, -III, and -IV are all found in some samples of (I), although usually one or more is absent. (II) contains amylase-III and -I (with a little -IV in one case). The amylolytic activity does not remain const. On keeping the organ pulp in the cold, there is usually loss of -II and -IV. In the COMe₂-dried preps. -III predominates, whilst -IV decreases in comparison with the fresh material. The desmo-preps. from heart consist of mixtures of -I and -III, from (I) almost exclusively -I. J. H. B.

Mechanism of enzyme action. Role of neutral salts in the action of amylase on starch. E. BAUER (J. Chim. phys., 1934, 31, 535—552).—Theoretical. The consequences of various theories of enzymic action are analysed and discussed in the light of experimental results, particularly those of Trautmann and Ambard (A., 1934, 693). The conclusion reached is that the action consists in (1) establishment of a chemical or adsorption equilibrium between the anions (X') of the added salt and the enzyme (ϕ), (2) progressive diffusion of mols. of the substrate (S) towards the mols. formed in (1), giving a complex $\phi X'S$, and (3) hydrolysis of the complex, liberating ϕ or $\phi X'$. The influence of p_H is best

interpreted by considering that ϕ behaves as an amphoteric ion. F. L. U.

Effect of certain chemicals on amylase activity. R. H. CLARK and H. I. EDWARDS (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 107—125; cf. A., 1932, 427).—The activity of many compounds which act as accelerators or inhibitors, or have little effect, on the enzymic activity of malt diastase in starch solution at p_H 6.4 at 30° is studied. Often concn. is the determining factor, a higher concn. favouring inhibition. KCNS (I), $CH_2Cl \cdot CH_2 \cdot OH$ (II), and glycerol monochlorohydrin may either accelerate or inhibit. Halogen ions have the greatest effect; Cl^- accelerates in low concn., I^- inhibits the reaction (cf. A., 1931, 1455; 1933, 1215). Accelerating org. Cl-compounds probably owe their activity to a slight dissociation into Cl^- . (I) and (II) also break the rest period in plants, which indicates that there may be a relationship between amylase activity and the breaking of dormancy. J. L. D.

Starch-amylase viscosimetry. I. Determination of amylolytic activity applicable to human serum. W. R. THOMPSON, R. TENNANT, and C. H. WIES (J. Biol. Chem., 1935, 108, 85—104).—As a basis for comparison of amylase digestion curves with starch- $CaCl_2$ substrates, determined viscosimetrically, the time, t , such that in the last $\frac{3}{4}$ of this time a 7.5% change in η has occurred is taken. A modified pantograph is used in the determination of t . Enzyme concn. $\propto 1/t$. Introduction of human serum into a pancreatic digestion mixture has a purely additive effect on amylase activity (I). Only small changes in t are produced by variations in $CaCl_2$. The relation between serum (I) and p_H is the same as for pancreatin solutions. H. D.

Validity of iodine and copper reduction methods for amylase. L. C. CHESLEY (Proc. Soc. Exp. Biol. Med., 1934, 31, 1097—1101).—The achromic I method with or without added Cl^- and $PO_4^{''}$ buffer is unsatisfactory. The Cu method gives quant. results. Dextrin and 3 samples of sol. starch were saccharified at the same rate. CH. ABS. (p)

Determination of invertase activity. J. B. SUMNER and S. F. HOWELL (J. Biol. Chem., 1935, 108, 51—54).—Invertase activity is determined by incubation of the solution with sucrose in NaOAc buffer and subsequent addition of NaOH. The invert sugar is determined by the dinitrosalicylic acid method (A., 1925, i, 1491). H. D.

Relationship between p_H and source of different carbohydrases. E. HOFMANN (Biochem. Z., 1935, 275, 320—327).—The p_H optima of preps. of invertase, α - and β -glucosidase, and β -galactosidase obtained from yeasts, bacteria, and moulds are determined and tabulated together with results of other authors. With bacteria the optima are about 7 and with moulds at 4—5. P. W. C.

Biochemistry of carbohydrates. XII. β -Glycuronosidase. G. OSHIMA. XIII. Enzymic decomposition of glucosamine. I. KAWAKAMI (J. Biochem. Japan, 1934, 20, 361—370, 423—429).—XII. The content of β -glycuronosidase (I) (A., 1934, 675), as indicated by hydrolysis of mentholglycuronic

acid, in the skeletal muscle, intestinal mucosa, submaxillary gland, brain, uterus, heart, and pancreas of oxen (II) and dogs (III) is low. The lung, kidney, and liver of (II) have a moderate, and those of (III) a low, content of (I). The endocrine organs and spleen of both (II) and (III) are rich in (I), the action of which appears to be reversible.

XIII. Preps. from rabbit and ox liver or kidney hydrolyse glucosamine (optimum p_H 6.7—7.7) yielding d -lactic acid (I) but not NH_3 or urea. The changes in the reducing val. indicate a fission into $AcCHO$ by "glucosaminase" (this vol., 111) and a subsequent conversion into (I) by glyoxalase. F. O. H.

Glycolysis in brain tissue. C. A. ASHFORD (Biochem. J., 1934, 28, 2229—2236).—The glycolytic rate (I) of sliced rabbit brain (II) is 3 to 4 times that of the chopped tissue, and (I) is reduced when the $NaHCO_3 \cdot CO_2$ (III) buffer is replaced by $PO_4^{''}$ buffer (IV) at the same p_H . Glycolysis of (II) in (III) is lowered by the presence of (IV). Inorg. PO_4 is rapidly liberated from (II) in (III), the rate of liberation being decreased by glucose and remaining unaffected by the concn. of F which inhibits (I). (II) can produce lactic acid from pyruvate and α -glycerophosphate only to a small extent. A. L.

Enzymic degradation of mucoitinsulphuric acid. C. NEUBERG and W. CAHILL (Biochem. Z., 1935, 275, 328—329).—The enzymic prep. from *B. fluorescens non-liquefaciens* which was previously used to degrade chondroitinsulphuric acid (A., 1931, 875, 1089) also attacks mucoitinsulphuric acid, liberating 95% of the $SO_4^{''}$ and yielding a strongly reducing substance. P. W. C.

Phosphatases. V. Separation of the accompanying esterase from the liver-phosphoesterase active in the acidic region. E. BAMANN and K. DIEDERICH (Ber., 1935, 68, [B], 6—7; cf. this vol., 251).—The separation depends on the ready destructibility of the esterase action by N -AcOH, to which the phosphoesterase (activity max. p_H 5.5) is remarkably stable. H. W.

Occurrence of two phosphoesterases differentiated by their optimum p_H in animal organs. E. BAMANN and E. RIEDEL (Z. physiol. Chem., 1934, 229, 125—150).—The phosphoesterase activity shown by autolysates from animal organs has a p_H optimum at 5—6 as well as at 9.5, indicating the probable presence of two distinct enzymes. The effect is shown, although not to an equal extent, with autolysates of pig's kidney and ox and pig liver. The p_H optima are somewhat affected by the degree of purity of the enzymes, but not by change of buffer or addition of Mg^{++} , although the activity at the higher p_H is enhanced by Mg^{++} . The kinetics in both acid and alkaline ranges has been studied. J. H. B.

Anaerobic decomposition of hexosephosphoric acids by animal tissues. I. N. ARIYAMA. II. Production of methylglyoxal from hexosediphosphoric acid by various tissues. S. NAKAMURA (J. Biochem. Japan, 1934, 20, 371—381; 1935, 21, 9—18).—I. Hydrolysis of hexosediphosphoric acid by muscle extracts free from co-enzyme (i.e., heated at 60° for 15 min.) does not produce

lactic acid, > 90% of the dephosphorylated product appearing as AcCHO. The data indicate that such a process is not identical with that occurring during natural glycolysis (I) and that the postulation of AcCHO as the main intermediary in (I) is incorrect.

II. Autolysed tissues (brain, muscle, liver, kidney, spleen, bone, blood, rabbit's sarcoma, rat's carcinoma) produce triosephosphoric acid (especially brain and tumour) and AcCHO (especially muscle) from hexose diphosphate, reactions not related to the formation of lactic acid.

F. O. H.

Decomposition of hexose diphosphate by an enzyme of tobacco leaves. T. BABA (Biochem. Z., 1935, 275, 248—252).—Enzyme preps. from tobacco leaves are able to decompose hexose into triose phosphate.

P. W. C.

Enzymic equilibrium reaction between hexose-diphosphoric acid and dihydroxyacetonephosphoric acid. IV. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1935, 275, 430—432; cf. A., 1934, 1261).—As regards heat of reaction, experimental only agree with calc. results when vals. formerly given are multiplied by 2.4 (cf. Iwasaki, A., 1929, 354; Kobel *et al.*, *ibid.*, 398; Jacobsohn, this vol., 121).

W. McC.

Hydrolysis of adenosinetriphosphoric acid by phosphomonoesterase and pyrophosphatase. T. SATOH (J. Biochem. Japan, 1935, 21, 19—36).—Mono- (I) and pyro-phosphatase (II) with p_H optima for each at 4.0 and 9.0 (A., 1932, 305; 1933, 426) hydrolyse adenosinetri- (adenylpyro-)phosphoric acid (III), indicating that there are present 1 mol. of H_2PO_4 as a mono-ester and 2 mols. as $H_4P_2O_7$ ester. The behaviour of complexes formed by treatment of adenylic acid and $H_4P_2O_7$ and the non-influence of (II)-activator on the dephosphorylation of (III) by (II) indicate the formula $O \leftarrow CH[CH_2 \cdot O \cdot O(OH)_2] \cdot CHP'$ [$P' = \cdot O \cdot PO(OH) \cdot O \cdot PO(OH)_2$] for (III). (II) at p_H 4 dephosphorylates 50% of (III) in approx. 10 hr. at 37°. From such a hydrolysate adenosinediphosphoric acid (Ca salt), containing 2 $-H_2PO_4$ groups and hydrolysed by (I) but not (II), can be isolated. (III) with (I) at p_H 9 and with addition of Mg^{++} yields inosine- and not adenosine-pyrophosphoric acid. Prolonged hydrolysis by (I)+(II) yields adenylic acid. The specificity of enzyme preps. from pig's liver hydrolysing (III) but not glycerol- or pyrophosphoric acid could not be confirmed (A., 1933, 980).

F. O. H.

Behaviour of mono- and di-phosphoglyceric acid with hæmolysed red cells and organ fluids. W. SCHUCHARDT and A. VERCELLONE (Biochem. Z., 1935, 275, 261).—Earlier work (A., 1934, 1242) on the breakdown of mono- (I) and di- (II) -phosphoglyceric acids to $AcCO_2H$ by hæmolysed erythrocytes is extended to the use of tissue juices. Here both (II) and (I) are attacked. Use of PO_4^{---} buffer is undesirable, enzymic activity being inhibited thereby.

P. W. C.

Comparison of the Jenner-Kay and Bodansky methods for determining phosphatase in plasma and serum. L. S. PALMER and J. W. NELSON (Proc.

Soc. Exp. Biol. Med., 1934, 31, 1070—1073).—The two methods had approx. the same accuracy.

CH. ABS. (p)

Determination of serum- and bile-phosphatase activity. E. J. KING and A. R. ARMSTRONG (Canad. Med. Assoc. J., 1934, 31, 376—381).— Ph_3PO_4 (I) is preferable to glyceryl phosphate as a substrate in determining phosphatase activity, since it is hydrolysed more rapidly and $PhOH$ is easily determined. Serum or plasma (0.5 c.c.) is mixed with (I) and barbitol, the mixture is maintained at 37° for 30 min., and proteins pptd. by the Folin-Ciocalteu reagent. After filtration Na_2CO_3 is added to the liquid and the blue colour compared with that of standard preps.

CH. ABS. (p)

Acid-base catalysis and the action of esterase. E. A. SYM (Act. Biol. Exp. Warsaw, 1932, 7, 197—219).—Comparison of the system alcohol-acid-ester- H_2O in the presence of esterase with that in presence of HCl leads to the assumption that H_2O can produce enzymic catalysis at the contact interface.

CH. ABS. (p)

Enzymic esterification. E. A. SYM (Rocz. Chem., 1934, 14, 1418—1424).—The initial velocity, v , of esterification (I) in the system oleic acid- Bu^+OH is expressed by $v = k_E[\text{oleic acid}][Bu^+OH]$ when the reaction is catalysed by pancreatic esterase (II), and by $v = k_H[\text{oleic acid}][Bu^+OH]^2$ in presence of picric acid catalyst. The val. of v for enzymic (I) in a no. of org. solvents (CCl_4 , $CHCl_3$, CH_2Cl_2 , C_6H_6 , $PhMe$, xylene, $PhCl$, $PhNO_2$, NH_2Ph) is inversely \propto the dipole moment of the solvent. The reaction of (I) in presence of highly dehydrated (II) is autocatalytic, owing to activation of (II) by the H_2O produced.

R. T.

Specificity and inhibition characteristics of liver-esterase and pancreas-lipase. H. H. R. WEBER and C. G. KING (J. Biol. Chem., 1935, 108, 131—139).—The inhibitory power (I) of Na salts of n -fatty acids towards lipase (II) is always very small, but their (I) towards esterase (III) increases up to Na laurate and then decreases almost to zero for the palmitate and stearate. Hexyl and octyl alcohols, which produce a greater lowering in surface tension than the corresponding Na soaps, have also a greater (I) than the latter. The (I) of unsaturated acids, both aliphatic and aromatic, is much > that of the corresponding saturated acids. The effect of o -substitution on the (I) of substituted $BzOH$ is $I > OH > Br$, NO_2 , or Cl (cf. A., 1932, 543, 1166). The Bu_1 ether of $(\cdot CH_2 \cdot OH)_2$ (IV) [unlike the Et_1 ethers of (IV) and $OH \cdot [CH_2]_4 \cdot OH$] is fairly active against (III) but not against (II). The max. velocity of hydrolysis of the α -monoglycerides by (III), which occurred at monohexoin both in solution and in emulsions, is > the velocity for simple esters of monohydric alcohols. The less sol. β -monoglycerides are not acted on by (III), but both α - and β -monoglycerides are equally readily hydrolysed by (II).

A. E. O.

Enzyme action. XLIX. Lipase actions of tissues of rachitic rats. K. G. FALK and G. McGUIRE (J. Biol. Chem., 1935, 108, 61—71; cf. A., 1926, 757).—There is no significant difference between the esterase activities of extracts from the livers and kidneys of normal (I) and rachitic rats (II);

lung extracts from (II) hydrolysed butyrates less in relation to their hydrolysis of other esters than did extracts from (I). H. D.

Biological chemistry of zinc. II. Effect of zinc salts on hydrolysis of triacetin by pancreatic lipase. III. Influence of zinc salts on the activity of salivary diastase. M. ANDRETTICHEVA (Bull. Soc. Chim. biol., 1934, 16, 1730—1755, 1756—1760).—II. The inhibitory effect of ZnSO_4 (I) on the hydrolysis of triacetin (II) by pancreatic lipase decreases with decreasing amounts of (I), but the inhibitory effect of $\text{Zn(NO}_3)_2$ (III) is not quite so marked. Whilst $0.1N\text{-Ca(NO}_3)_2$ inhibits (II) hydrolysis, at a concn. of $0.02N$ and $0.01N$ there is an accelerating action.

III. For a given p_H the effect of (III) on the action of salivary diastase (IV) \propto the concn. of (III). At $0.05N$ concn., however, the action of (IV) is completely inhibited at all p_H vals. At neutrality (III) even in small concn. inhibits the (IV) action, but in acid solution small quantities have an accelerating action which reaches a max. at p_H 4.8 with $0.0025N$ (III). A. L.

Acid-alkali equilibrium and acid-base coefficient. I. A. SMORODINCEV and L. A. PHILIPPOVA (J. Biochem. Japan, 1935, 21, 1—7).—The application of A/B , the acid-base coeff. (I) (A., 1933, 253), to biochemical systems is discussed. During autolysis of ox-muscle, B decreases, attaining a min. 24—28 hr. after death, whilst A rapidly increases, attaining a max. 24—48 hr. after death. Both A and B attain approx. const. vals. after 72 hr., (I) reaching a max. after 4 hr., after which it abruptly sinks and attains a const. val. approx. thrice that occurring 1 hr. after death. F. O. H.

Digestion in the plaice (*Pleuronectes platessa*). L. E. BAYLISS (J. Marine Biol. Assoc., 1935, 20, 73—91).—A $0.1N\text{-HCl}$ extract of the mucous membrane of the stomach contains a proteolytic enzyme, optimum p_H 1.5—2.5, probably pepsin. The intestinal mucosa contains trypsin, erepsin, and a polypeptidase with optimum p_H 7.5—8.5; the liver is an even more potent source of trypsin. The liver, gall-bladder, and intestine also contain lipase and amylase, the first being the most potent source. No proteolytic enzyme was demonstrated in the bile even after administration of pilocarpine. Digestion of fats and carbohydrates does not take place in the stomach. P. G. M.

Influence of toluene on the activity of pepsin and trypsin. Y. L. WANG (J. Chinese Chem. Soc., 1934, 2, 340—342).—PhMe decreases the action of pepsin on caseinogen, but has only slight effect on that of trypsin. R. S. C.

Influence of iron compounds on proteolytic and peptolytic processes. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1935, 231, 51—54).— Fe^{++} accelerates the action of crude and inhibits that of purified papain or gelatin (cf. this vol., 122). $\text{K}_4\text{Fe(CN)}_6$ is an immediate activator which does not combine with the concomitant; $\text{K}_3\text{Fe(CN)}_6$ inhibits slightly. Haemoglobin-Fe has a strong activating effect. Similar effects are shown with gelatin-peptone as substrate. J. H. B.

Labile glutamine peptides, and the origin of the ammonia set free during the enzymic digestion of proteins. J. MELVILLE (Biochem. J., 1935, 29, 179—186).—*N*-Benzylcarbonato- α -glutamylglycine Et ester, m.p. 124° [in 47% yield from *N*-benzylcarbonato- α -glutamic anhydride (I) (A., 1932, 935) and glycine Et ester], was converted into the acid chloride (by PCl_5), which, with NH_3 , yielded *N*-benzylcarbonato- α -glutamylglycine Et ester, m.p. 167° , hydrolysed by cold aq. NaOH to *N*-benzylcarbonato- α -glutamylglycine. Catalytic reduction of the latter yielded α -glutamylglycine (II), $[\alpha]_D^{25} +76^\circ$ in H_2O . α -Glutamyl- α -glutamic acid (III), $[\alpha]_D^{25} +15^\circ$ in $N\text{-HCl}$, was similarly prepared from Et_2N -benzylcarbonato- α -glutamyl- α -glutamate (A., 1932, 935), the intermediates being Et_2N -benzylcarbonato- α -glutamyl- α -glutamate, m.p. 181° , and *N*-benzylcarbonato- α -glutamyl- α -glutamic acid. The tripeptide α -glutamylglycylglycine (IV) was also prepared (but not completely purified) starting from glycylglycine Et ester, which with (I) gave *N*-benzylcarbonato- α -glutamylglycylglycine Et ester, m.p. 136° , converted in the usual way into *N*-benzylcarbonato- α -glutamylglycylglycine Et ester, m.p. $150\text{--}152^\circ$, which was then hydrolysed and reduced catalytically. α -isoGlutamine prepared by the method of Bergmann and Zervas (A., 1932, 935) contains some α -glutamine (V), and when the anhydride ring of (I) is opened by NH_3 (and perhaps also by NH_2 -acid esters), both α - and γ -amides are formed (about 17% γ -amide). The peptides (II), (III), and (IV) all exhibit the labile characters of (V). All give abnormally high $\text{NH}_2\text{-N}$ (Van Slyke) and are unstable in aq. solution at 100° . At 37° , and at p_H vals. of 1.8, 7.0, 7.8, and 8.3, rapid hydrolysis of the amide group of (V) takes place, especially at p_H 1.8 when 80% is liberated as NH_3 in 2 days. (III) behaves similarly at p_H 8.3, so that it is probable that NH_3 formed during the digestion of proteins by pepsin, aminopolypeptidase, dipeptidase, and trypsin comes from the spontaneous breakdown of (V) and labile peptides containing (V). During the breakdown the liberated glutamic acid is rapidly transformed into pyrrolidonecarboxylic acid, even at 37° . (II), (III), and (IV) are readily hydrolysed by yeast peptidases. A. E. O.

Technique for study of tryptic-ereptic digestion of proteins. B. SURE, M. C. KIK, and K. S. BUCHANAN (J. Biol. Chem., 1935, 108, 11—18).—The stomach, pancreas (I), small intestine, and liver of the rat are extracted with glycerol and H_2O , the extracts are incubated with caseinogen at p_H 7, and $\text{NH}_2\text{-N}$ is determined from time to time. The rate of tryptic-ereptic digestion increases with increasing concn. of the extracts. Extracts of (I) show considerable tryptic activity. H. D.

Behaviour of oxidising agents towards purified arginase. G. KLEIN and W. ZIESE (Z. physiol. Chem., 1934, 229, 209—212).—Although crude arginase (I) is inhibited by O_2 , pure (I) is quite insensitive to mol. O_2 and is activated by traces of oxidising agents, such as KMnO_4 , H_2O_2 , I-KI , and $\text{K}_2\text{S}_2\text{O}_8$. It is inhibited by SH-compounds which activate crude (I). J. H. B.

Temperature coefficient and apparent energy of activation of the enzymic hydrolysis of arginine; stability of arginase under various conditions. A. HUNTER (Quart. J. Exp. Physiol., 1934, 24, 177—188).—The temp. coeff. of the arginine-arginase reaction decreases with rising p_H . The enzyme is very susceptible to heat in alkaline media, and shows max. stability near to neutrality.

CH. ABS. (p)

Uricase. I, II, III. Resynthesis of uric acid from its cleavage products by uricase. IV. Effect of inanition on the uricolytic activity of liver extract. R. OIKAWA (Sei-i-kwai Med. J., 1933, 52, 1—24, 25—38, 38—42, 43—49).—I. Uricase (I) from rabbit liver has optimum p_H 7.1—7.2, optimum temp. 48°, is destroyed at 70°, is active in O_2 , less in N_2 , and inactive in CO_2 , CO , and H_2 . Autolysis does not affect activity.

II. Factors influencing activity of liver-(I) have no effect on the enzyme *in vitro*. Large dosages of uric acid (II) to the animal increase (I) and (II) in the liver. Allantoin (but not urea) inhibits activity.

III. No evidence of resynthesis was obtained.

IV. Increased activity was observed after prolonged periods of starvation.

CH. ABS. (p)

Influence of viscosity of the medium on the velocity of oxidation of uric acid in presence of insoluble uricase. R. TRUSZKOWSKI and Z. CHAJKINÓWNA (Rocz. Chem., 1934, 14, 1389—1395).—No relationship exists between the viscosity of the medium (aq. glycerol, sucrose, or gelatin) and the velocity of oxidation of uric acid in presence of insol. ox-kidney uricase. At above certain critical concns., % retardation of reaction \propto the concn. of the solutes.

R. T.

Metabolism, respiration, and gaseous exchange in yeast cells during the growth of yeast by the aeration method. H. CLAASSEN (Biochem. Z., 1935, 275, 350—360; cf. A., 1931, 263).—Equations (I) are given for the changes which occur during the process when the nutrient medium contains only sugar, NH_4 compounds, and salts. On the basis of (I) it is found that for the production of 100 parts of yeast (II) 80 parts of O_2 are required and 144 parts of CO_2 are liberated. Most of the O_2 is consumed in oxidising H in degradation products of the sugar and in NH_3 , whilst the greater part of the CO_2 is a fermentation (III) product. Since very dil. solutions are involved, the great production of (II) occurs only because of the very large surface of the (II) cells; this permits diffusion even when differences in concn. are very low. The factors which control the uptake of nutrient material and O_2 at various stages during (III) are discussed.

W. McC.

Respiration of yeast in water containing deuterium oxide. G. W. TAYLOR and E. N. HARVEY (Proc. Soc. Exp. Biol. Med., 1934, 31, 954—957).—The O_2 consumption was decreased by concns. of $H_2O > 20\%$.

CH. ABS. (p)

Factors influencing autolysis of yeast cells. A. BELITZER (Protoplasma, 1934, 22, 17—21).—The sugar content of yeast cells becomes the limiting factor in autolysis. Effects of mechanical injury to

cells are examined in relation to the simultaneous increase in glycogen hydrolysis.

A. G. P.

Respiratory action of nitrophenols. L. PLANTEFOL (Compt. rend. Soc. Biol., 1934, 117, 1167—1169).—Contrary to Genevois and Saric (this vol., 253), 2:4-dinitrophenol increases the respiration of brewer's yeast, the optimum concn. being 0.18—0.36 g. per litre of medium.

R. N. C.

Effect of certain salts on enzyme activity. Effect of sodium selenate, selenite, selenide, tellurite, sulphate, sulphide, arsenite, and vanadate on rate of carbon dioxide production during yeast fermentation. A. L. MOXON and K. W. FRANKE (Ind. Eng. Chem., 1935, 27, 77—81).—The toxicity of the above compounds decreases in the order Se, V, As, Te. The toxicity of SeO_3'' , Se'' , and SeO_4'' decreases in that order. S'' and SO_3'' accelerate fermentation *pari passu* with the H_2S formed thereby. Na_2SO_4 has a slight retarding effect. Na_2S counteracts the toxic effect (T') of Se compounds. S has no accelerating effect and little counteracting effect on T' . Na_2SO_4 , $(NH_4)_2SO_4$, and $Na_2S_2O_3$ do not counteract T' .

E. C. S.

Wildier's bios. W. L. MILLER (Trans. Roy. Soc. Canada, 1934, [iii], 28, III, 185—187).—Bios IIA (purification described), an aminohydroxybutyric acid (I) (cf. A., 1926, 749), when added [0.02 mg. of (I) per c.c. of culture medium] to sugar solution containing excess of inositol and bios IIB and Clark's salts, increases the yeast crop 4—5 times. Some yeasts give no crop under these conditions, but only when tomato or lemon juice is added. This effect is not due to vitamin-C.

J. L. D.

Physiology of micro-organisms, *Fusarium betæ*, *Macrosporium commune*, and *Verticillium lateritium*. O. I. KUPLENSKAJA (Trans. Central Sci. Res. Inst. Sugar Ind. U.S.S.R., 1933, No. 12, 54—63).—*F. betæ* inverts sucrose (I) and utilises the products with the production of EtOH and org. acids. It decomposes pectins, and tolerates p_H 2.5—9.0. It is resistant to antiseptics and is but little affected by low temp. *M. commune* inverts (I) but consumes products more slowly, and is not greatly affected by changes of temp. The p_H range 3.5—8.2 is suitable for growth. *V. lateritium* inverts (I) and is sensitive to changes of temp. and p_H .

CH. ABS. (p)

Phases of the metabolism of *Tricophyton interdigitale*, Priestley. D. R. GODDARD (J. Infec. Dis., 1934, 54, 149—163).—Glucose (I), mannose, fructose, maltose, arabinose, and, to a smaller extent, sucrose favour the growth of *T. interdigitale* (II) and *M. lanosum* (III). Galactose increases growth of (II) but not of (III). Neither species uses lactose. (I) decreases protein hydrolysis in (II) without affecting NH_3 production. Caseinogen supports growth and is hydrolysed finally to NH_3 . During hydrolysis of peptone (IV) the initial increase in NH_3 -acids is followed by decline with simultaneous increase in NH_3 and p_H . The latter changes are not affected by (I). In (I)–(IV) media, curves showing NH_3 and (I) formation and growth rate are of similar forms during the period of exponential growth.

CH. ABS. (p)

Chemistry of sclerotia of *Pachyma hoelen*, Rumph. IV. Comparison of β -pachyman with other related carbohydrates. V. Nutrient value of pachyman. K. TAKEDA (J. Agric. Chem. Soc. Japan, 1934, 10, 679—684, 685—690).—IV. β -Pachyman (I) resembles pectose or pachymose, but differs from fongose (II), callose, or paradextran. (II) from *A. niger* is separable into 2 fractions having $[\alpha]_D +219.33^\circ$ and $+268.0^\circ$, respectively.

V. (I) has low nutritive val. for rats.

CH. ABS. (p)

Identification of a fungal carotenoid. W. H. SCHOPFER (Compt. rend. Soc. Biol., 1935, 118, 3—5).—*Mucor hiemalis* and *Phycomyces blakesleeianus* grown on media containing asparagine or glycine as N source synthesise β -carotene (I) (identified by its absorption spectrum). The presence of 1×10^{-6} g. of vitamin- B_1 per c.c. in the medium inhibits (I) formation, and the synthesis occurs to a greater extent in the mycelium of the (+) sex.

A. L.

Effect of growth-factors on some *Mucorineae*. W. SCHOPFER (Ber. deut. bot. Ges., 1934, 52, 560—563).—Differences between the growth-promoting action of wheat extract and that of vitamin-B on certain fungi are examined.

A. G. P.

Effect of mineral constituents in the medium on acid production by *Aspergillus niger*. W. S. BUTKEVITSCH and A. G. TIMOFEEVA (Biochem. Z., 1935, 275, 405—415).—When growth (I) of the mould is checked by relative lack of (combined) P, S, or N in the nutrient medium accumulation of citric acid (II) occurs, the yield of (II) from sugar being high. With lack of N or P, accumulation of gluconic acid (III) and $H_2C_2O_4$ is restricted but the accumulation of (III) and $H_2C_2O_4$ increases with lack of S. Limitation of (I) due to lack of K or Mg leads to reduction in (II) production and in yield of (II) from sugar. (II) almost disappears when there is simultaneous lack of K and Mg. Lack of Mg causes reduction in accumulation of (III) and $H_2C_2O_4$, but lack of K causes large increase in $H_2C_2O_4$ production and smaller increase in (III) production.

W. McC.

Constitution of carolic and carolinic acids.—See this vol., 327.

Use of developed mycelia in the study of the physiology of moulds. D. BACH (Bull. Soc. Chim. biol., 1934, 16, 1708—1719).—The mycelium is allowed to develop on a suitable liquid medium which is then withdrawn, the culture being washed and placed in the experimental nutrient medium.

A. L.

Photosynthetic organisms. G. R. CLEMO and H. McILWAIN (Chem. and Ind., 1935, 134).—A porphyrin has been obtained from organisms of the chromatium type, and has been found to contain Mg. It also yields a cryst. ester.

P. G. M.

Biochemical processes in deep-sea mud. T. GINSBURG-KARAGITSHEVA and K. RODIONOVA (Biochem. Z., 1935, 275, 396—404).—The org. matter of mud from the floor of the Black Sea (depths 177—1920 m.) contains up to 10% of material (C 75—80, H 10—12, S 5—12, O 2—10%; m.p. 55—78°; average mol. wt. 344—512) sol. in org. solvents and consisting

chiefly of bituminous substances (hydrocarbons). Microflora (I) which reduce SO_4^{--} to H_2S and degrade cellulose, fats, and proteins are present. Those which attack fats and fatty acids decrease the I val. and increase the amount of unsaponifiable matter. The properties of (I) indicate close relationship to (I) of oil-bearing strata in N. Caucasus and in other oil-producing districts of the U.S.S.R.

W. McC.

Distribution and conditions of existence of bacteria in the sea. S. A. WAKSMAN (Ecol. Monog., 1934, 4, 523—529).—Development of marine bacteria depends on the distribution and nature of org. matter and essential nutrients and on the presence of energy sources, e.g., H_2S , S, H_2 , NH_3 , NO_3 , and CH_4 .

CH. ABS. (p)

Marine bacteria and their role in the cycle of life in the sea. II. Bacteria concerned in the nitrogen cycle. S. A. WAKSMAN, M. HOTCHKISS, and C. L. CAREY (Biol. Bull., 1933, 75, 137—167).—Distribution of nitrifying, denitrifying, and N-fixing marine organisms is examined.

CH. ABS. (p)

I. Conditions of life in the ocean. II. Conditions at great depths. A. KROGH (Ecol. Monog., 1934, 4, 421—429, 430—439).—I. Distribution of N, P, and org. matter is discussed in relation to the life of marine micro-organisms.

II. Vertical distribution of total and NH_3 -N and C is examined. The average content of org. N and org. C was approx. const. at all depths.

CH. ABS. (p)

Interrelations between higher plants and micro-organisms. A. ISAKOVA (Bull. Acad. Sci. U.S.S.R., 1934, 7, 993—1006).—The distribution of micro-organisms in soil surrounding plant roots is examined. The decomp. of org. matter is effected by groups of organisms which are characteristic for each plant species.

A. G. P.

Metabolism of purple sulphur bacteria. P. A. ROELOFSEN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 660—669).—The evolution of CO_2 by the bacteria (I) in media containing inorg. salts at 30° and in H_2 or N_2+CO_2 is due to auto-fermentation (II), which can be reduced by 70% by prior keeping in the dark at 35° for 24 hr. and is not increased by addition of org. substances, nor influenced by Na_2SO_4 (cf. A., 1934, 698). In the dark (I) absorb H_2 (the rate of uptake $\propto [CO_2]$ and is increased by light) but do not thrive when H_2+CO_2 is the only assimilable substrate. O_2 is rapidly absorbed (not due to respiration). After keeping in the dark (I) take up CO_2 rapidly for a short time and then slowly during the period of illumination. The supplementing of the H donor (III) from (II) by oxidisable S compounds, but not by glucose, acetate, butyrate, or malate, increases the CO_2 uptake. (I) grown in light of 590 m μ can oxidise $Na_2S_2O_3$. (I) grown in peptone broth produce, in the dark, gas containing 8—30% of H_2 ; with such strains Na malate acts as (III) for the assimilation of CO_2 in the dark. The changes in oxidation-reduction potential of suspensions (IV) of (I) with variations in light, concn. of (III), etc. indicate that (IV) behave as a photo-electric half-cell.

F. O. H.

Metabolism of purple bacteria. II. H. GAFFRON (Biochem. Z., 1935, 275, 301—319).—Purple S

bacteria (I) can utilise the energy of infra-red light. (I) contain catalase and can utilise O_2 . The CO_2 assimilation of (I) during anaerobic growth is investigated in presence of salts of a no. of fatty acids and the increase of assimilation val. with mol. size (cf. A., 1933, 639) confirmed. The brown bacteria which accompany (I) behave very similarly to (I). (I) in an atm. of H_2 can reduce CO_2 , NO_3' , acetate, lactate, pyruvate, and glycollate. P. W. C.

Respiration of acetone bacteria and bacterial autolysis. O. EHRSIMANN (Z. Hyg., 1934, 116, 490—494).—The sp. action of pyocyanin and methylene-blue on the respiration of active bacteria is also produced by a no. of redox (I) indicators. The intensity of the action is related to the (I) potential and solubility of the dye, its constitution (notably the no. of sulpho-groups), and in a smaller degree to the velocity of re-oxidation and the electrolyte content of the medium. The enzyme system of *Gonococcus* occurs in other species of bacteria. A. G. P.

Citric acid fermentation. H. EMDE (Biochem. Z., 1935, 275, 373—374; cf. Apoth.-Ztg., 1932, 47, 1418, 1433).—The production of citric acid (I) from quinic acid (II) by oxidation (Fischer *et al.*, A., 1934, 1222) supports the view that (II) is an intermediate in the fermentative conversion of sugars into (I).

W. McC.

Biochemistry of bacilli of the *coli-aërogenes* group in milk. I. LIPSKA (Lait, 1934, 14, 673—683; Chem. Zentr., 1934, ii, 1861).—Classification of the organisms by chemical activities is examined. Fermentation tests, indole production, and the Voges-Proskauer reaction are the most characteristic.

A. G. P.

Oxidation-reduction studies of growth and differentiation of species of *Brucella*. C. D. TUTTLE and I. F. HUDDLESON (J. Infec. Dis., 1934, 54, 259—272).—Graphite electrodes may be utilised for determining E_h in liquid media under aerobic conditions. Change of E_h during incubation of cultures of different species of *Brucella* are recorded.

CH. ABS. (p)

Oxidation-reduction potentials of toxoflavin. K. G. STERN (Biochem. J., 1935, 29, 500—508).—Toxoflavin (I) (A., 1934, 537) is titrated oxidatively and reductively as previously described (A., 1934, 846). The system is fully reversible and electro-active between p_H 4 and 8; E_h at p_H 7 is -0.049 volt. The E_h - p_H curve reveals two dissociation consts. pK 5.8 and 7.2. Individual titration curves are atypical in that the index p.d. averages 21 mv. between p_H 4.6 and 6.4 and rises to 34 mv. at p_H 8.3. No evidence of semiquinone formation during reduction is obtained. The theoretical treatments of Michaelis (A., 1933, 611) and of Elema (A., 1933, 464) are applied on the basis that a two-stage reduction occurs, and vals., agreeing well, for a const. related to the stability of the intermediate compound are obtained by the two methods. The ultra-violet absorption spectrum of (I) at p_H 6.5 has a steep band at 260 $m\mu$ and a lower band at 405

Keeping at p_H 3 or 11 destroys the sp. absorption. (I) stimulates respiration of mammalian erythrocytes and converts oxy- into met-hæmoglobin.

H. D.

Proteolytic and deaminising enzymes of *Clostridium sporogenes* and *Cl. histolyticum*. O. A. BESSEY and C. G. KING (J. Infect. Dis., 1934, 54, 123—127).—Proteolytic activity in filtrates or suspensions of *Cl. histolyticum* (I) is $>$ that of *Cl. sporogenes*. The two proteases are similar, having optimum p_H 7.5 and producing mainly polypeptides. The deaminising enzyme of (I) is the less active. In both cases there is marked specificity of action in respect of NH_2 -acids.

CH. ABS. (p)

Tubercle bacillus. II. Fractional extraction of lipins from fresh unheated bacilli. M. MACHEBŒUF, J. DIERYCK, and R. STROOP (Ann. Inst. Pasteur, 1935, 54, 71—85).— CO_2 extraction at $\approx 20^\circ$ in vac. yields a fraction (I) (17.2%) containing no P, with no acid-resisting properties, and devoid of "hapten" activity. (I) contains a large proportion of fats and unsaponifiable matter. Further extraction of the residue with cold Et_2O yields a fraction (II) (2.2%) which also contains no P, hapten substances, or acid-resistant material. $EtOH$ affects certain complexes present so that even cold Et_2O will extract phospholipins. Cold $MeOH$ in vac. extracts a fraction (III) (6.13% of dried bacilli) which contains phospholipins (2.05% of dried bacilli), and possesses powerful hapten activity without acid-resisting properties. Further extraction of the residue with boiling $EtOH$ yields a product which can be divided into two fractions (IV) and (V), and finally, boiling C_6H_6 extracts fraction (VI). (IV), (V), and (VI) contain P, whilst only (V) and (VI) contain acid-resisting substances. P. G. M.

(A) Preparation and properties of "acid wax" from human tubercle bacilli. (B) Fatty acids of human tubercle bacilli. F. ULZER and H. GRUBER (Wiss. Mitt. osterr. Heilmittelstelle, 1934, 12, 1—2, 4—6; Chem. Zentr., 1934, ii, 1474, 1475; cf. A., 1930, 1478).—(A) The mixture of Et_2O -sol. lipid constituents obtained by acid hydrolysis of tubercle bacilli is termed "acid wax" (I). H_2SO_4 yields 21% of (I), m.p. 40—41°, acid val. 55—70, esterification no. 112—117, I val. 16.4—18.0.

(B) 10 g. of (I) yield 3.5 g. of mixed fatty acids (54% solid, 46% liquid). The solid contains a cerotic acid, $C_{26}H_{52}O_2$, m.p. 80°, stearic and palmitic acids. The liquid has I val. 27 and probably consists of oleic acid with considerable amounts of saturated acids of high mol. wt. H. N. R.

Sterol content of bacteria, especially tubercle bacillus. Detection of cholesterol. E. HECHT (Z. physiol. Chem., 1935, 231, 29—38).—Sterols were detected in the light petroleum extract of the dried bodies of various acid-fast bacteria (I) grown on sterol-free media. (I) included human tubercle, "Bethge," bovine tubercle, "GA," strain "BCG," and timothy-grass bacilli. J. H. B.

Inhibitory action of sulphur on the growth of tubercle bacilli. G. B. LAWSON (Amer. Rev. Tuberc., 1934, 29, 650—651).—Addition of S in amounts ≤ 3 mg. per 100 c.c. of medium inhibited the growth of the organism. No increase in the p_H of the medium occurred with dosages up to 30 mg.

CH. ABS. (p)

Media suitable for the culture of the tubercle bacillus. A. BERTHELOT, F. VAN DEINSE, and G. AMOUREUX (Bull. Soc. Chim. biol., 1934, **16**, 1571—1574).—The prep. of media containing AcCO_2H suitable for culturing tubercle bacilli is described.

A. L.

Purification of tuberculin. G. A. C. GOUGH (Brit. J. Exp. Path., 1934, **15**, 237—242).

CH. ABS. (p)

Behaviour of blood-cholesterol following injections of tuberculin. K. KATO (Proc. Soc. Exp. Biol. Med., 1934, **32**, 12—13).—Injection of old tuberculin into rabbits produces an immediate increase in blood-cholesterol, followed in some cases by a fall below normal; all cases return to normal within a week.

R. N. C.

Influence of nutritive conditions on acid-fastness of bacteria. D. W. BRUNER (J. Infec. Dis., 1934, **55**, 26—38).—Acid-fastness could not be induced in non-acid-fast (I) organisms by supplying fatty materials in media, but temporary (I) types of acid-fast bacilli were produced by starvation.

CH. ABS. (p)

Application of the Ramon method to the titration of antibacterial sera. N. KOSOVITCH (Compt. rend. Soc. Biol., 1934, **117**, 1162—1165).—The method, applied to a mixture of the filtrate from a culture of anthrax bacilli and the corresponding antiserum, shows a very clear "initial flocculation zone," analogous to that for toxins and antitoxins.

R. N. C.

Anticoagulant action of glucose and sucrose from the point of view of the study of the thermostability of the properties of antispirchaetal sera. G. J. STEFANOPOULO and E. BUDING (Compt. rend. Soc. Biol., 1934, **117**, 1173—1175).—Addition of glucose to antispirchaetal sera stabilises their agglutinating and lytic properties to warming at 90° for considerable periods, the length of which increases with the quantity of glucose added. Sucrose is even more effective, the sera being similarly resistant at 100°.

R. N. C.

Relation of the potential and charge of bacteria to their agglutination. H. A. ABRAMSON (Trans. Electrochem. Soc., 1934, **66**, 335—343).—During coagulation by simple salts the net surface charge of particles is not, in general, decreased; it is rather the surface potential, ζ , which is lowered while the surface charge usually increases. For proteins (cf. A., 1933, 567) the surface density of net charge, σ , frequently seems to depend primarily on the p_H val., and there is, therefore, no max. in the ζ -concn. curve unless the total salt concn. itself also influences σ . The process of bacterial agglutination by salts and immune sera is discussed on the basis of these considerations.

H. J. T. E.

Pigment elaborated by the diphtheria bacillus. M. PAÍO and M. PHILIPPE (Compt. rend., 1935, **200**, 173—175).—A culture of the bacillus at 0° changes in colour from brown to yellow [the bacillus having elaborated a pigment (I) which probably contains the pyrrole group], the original absorption band decreasing in intensity about 70%, although there is no diminution in toxicity. Atoxic diphtheria bacilli

do not elaborate (I), nor do paratyphoid, tetanus, dysentery, and staphylococcal bacilli. (I) is partly dialysable, whereas the toxic element is much more indiffusible.

J. L. D.

Influence of compounds of the moranyl series on the structure of colloids. Influence of compounds of the moranyl series on diphtheria toxin. H. GOLDIE (Compt. rend. Soc. Biol., 1935, **118**, 38—42, 42—45).—1 : 4 : 6 : 8- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_4(\text{SO}_3\text{Na})_3$ (I) in the free state or combined with other groups ppts. serum-globulin at p_H 4—5. Only complexes of (I) such as "moranyl" (II), "inverse moranyl" (III), and "benzoyl-benzoyl" (IV) ppt. $\text{Fe}(\text{OH})_3$ in acid medium. Of these substances only (II) produces a marked fluorescence in alkaline solutions of gonacrine, and only (III) will ppt. colloidal NaCl . (I) has only a slightly reducing action on the activity of diphtheria toxin and its pptn. by acid, and has no action on acid solutions of pig-stomach broth (V) or peptone (VI). (II), (III), and (IV) cause at p_H 4—5 a rapid pptn. of the toxin, the anatoxin, (V), and (VI). The action of (III) and (IV) on the activity of the toxin and the antigen, unlike that of (II), which is considerable, is similar to that of (I), although both reduce greatly the power of flocculation.

A. L.

Influence of cysteine on production of hæmotoxin of *Cl. welchii*. J. H. ORR and G. B. REED (Canad. J. Res., 1934, **11**, 622—627; cf. A., 1929, 474).—Addition of H_2S or of < 0.1% of cysteine (I) to Robertson's chopped-meat media completely inhibits the production of hæmotoxin (II) by *Cl. welchii*. The effect is related to the metabolism of the organism, and not to direct reaction with (II). Addition of these concns. of (I) has little effect on the oxidation-reduction potential of the media, but has a marked effect on that of cultures during the most active period of growth. Beef-muscle media [with low % of cystine (III)] give a good yield of (II); fish-muscle media [with high % of (III)] give a poor yield.

E. C. S.

Growth-stimulating properties of cystine and tryptophan. W. BURROWS (J. Infect. Dis., 1934, **54**, 164—170).—Among 16 NH_2 -acids examined cystine and tryptophan alone exerted a stimulatory action on the growth of *Cl. botulinum* on glucose media containing hydrolysed caseinogen and gelatin.

CH. ABS. (p)

Carbohydrate nature of pantothenic acid (Williams). A. J. SALLE and R. W. DUNN (Proc. Soc. Exp. Biol. Med., 1934, **32**, 168—172; cf. A., 1933, 982).—Rice-bran extract contains a substance (I) which stimulates the growth of *Escherichia coli*, but not of *B. alcaligenes faecalis*. Growth is accompanied by production of acid and gas, as for carbohydrates, but growth does not tend to a max., and p_H falls more rapidly with increasing concn. of (I) than with glucose (II). Stimulation by (I) and (II) together is not cumulative, and the final p_H increases with concn. (I) is therefore not a hexose, and is probably pantothenic acid.

R. N. C.

Solid brilliant-green lactose bile medium for direct plating with results in seventeen hours. R. E. NOBLE and F. O. TONNEY (J. Amer. Water

Works Assoc., 1935, 27, 108—120).—A solid medium described is a trustworthy substitute for liquid brilliant-green lactose bile, although the productivity of both liquid and solid media was about 65% that of standard lactose broth (I). On the other hand, ferrocyanide citrate agar was 15% more productive than (I). The short incubation period required with the new medium gives sp. information on the incidence of *coli-aerogenes* organisms more quickly and accurately than liquid fermentation medium. C. J.

Choice of culture media, natural and synthetic. A. BERTHELOT (Bull. Soc. Chim. biol., 1934, 16, 1553—1557). A. L.

Synthetic media suitable for the study of *B. tumefaciens*. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1934, 16, 1558—1560).—The composition and prep. of three synthetic media are described. A. L.

Culture media containing peptised ground-nut oil-cake. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1934, 16, 1561—1564).—The prep. is described. A. L.

Culture media prepared from peptised soya-bean oil-cake. A. BERTHELOT, G. AMOUREUX, and F. VAN DEINSE (Bull. Soc. Chim. biol., 1934, 16, 1565—1567).—The prep. is described. A. L.

Use of *Stachys* root in the preparation of culture media. A. BERTHELOT, F. VAN DEINSE, and G. AMOUREUX (Bull. Soc. Chim. biol., 1934, 16, 1568—1570).—Advantages of media containing *Stachys* root are described. A. L.

Agar-agar. Physico-chemical properties and influence on the growth of micro-organisms. A. ITANO and Y. TSUGI (Bull. Agric. Chem. Soc. Japan, 1934, 10, 111—112).—Superior grades of agar contain relatively less N and ash and have lower d , osmotic pressure, surface tension, and higher p_H . Micro-organisms grew better on lower grades, possibly because of their I content. CH. ABS. (p)

Centrifuging of bacteriophages. A. GRATIA (Compt. rend. Soc. Biol., 1934, 117, 1228—1230).—The active material after centrifuging is contained in the sediment. R. N. C.

Protein-free suspensions of virus. VI. Purification of vaccine virus by absorption and elution. I. J. KLIGLER (Proc. Soc. Exp. Biol. Med., 1934, 32, 222—225).—Adsorption from a 10% suspension (I) in 0.9% NaCl with kaolin and subsequent elution with aq. NH_3 gives a potent suspension of vaccine virus giving negative Esbach and ninhydrin reactions and containing 1.0—2.7 mg. of non- NH_2 -N per 100 c.c. The severity of the reaction produced by (I) is > that of the same dilution of the purified virus. The eluates in general are active in as high a dilution as (I). R. N. C.

Destructive action of substances dissolved from glass on single-cell cultures. P. S. J. SCHURE (oc. K. Akad. Wetensch. Amsterdam, 1934, 37, 669—674).—With drop-cultures of *Reticularia lycoper-Bull.*, containing few spores, a toxic action (I) (due to SiO_2 ?) arises from the use of cover-slips (II) of quartz, mica, Cu, and cetylamine, but not of collodion,

starch, paraffin wax, zein, or steel. (I) is not related to the electric charge between (II) and H_2O .

F. O. H.

Relation between change of temperature and the viscosity of the bacterial suspension and the thermal death point of bacteria. H. INOUE (Sei-i-kwai Med. J., 1934, 53, 1—31).—Sudden change in the colloidal condition of the proteins determines the death point of bacteria. CH. ABS. (p)

Fungicidal power of phenol derivatives. I. Effect of introducing alkyl groups and halogens. G. J. WOODWARD (J. Lab. Clin. Med., 1934, 19, 1216—1223).—The fungicidal power (I) of alkyl derivatives of phenols (II) for pathogenic yeasts and moulds increases with the no. of C atoms in the side-chain. In dihydric (II) the alkyl may replace H in the ring or OH without appreciably affecting (I). Increased (I) due to halogen substitution is in the order $Cl < Br < I$. Introduction of NO_2 has little effect on (I). The position of the alkyl is, in general, immaterial, although salicylic is more effective than *m*- or *p*-hydroxybenzoic acid. CH. ABS. (p)

Biological problems in chemotherapy. W. YORKE and F. MURGATROYD (Lancet, 1935, 228, 191—193).—A summary of the results obtained in the action of As and Sb compounds on trypanosomes. L. S. T.

Bactericidal action of human blood. W. LEHMANN (Z. Hyg., 1934, 116, 495—506).—The presence of bactericidal matter in the plasma is not confirmed. A. G. P.

Bactericidal effects of X-rays. F. L. MOHLER and L. S. TAYLOR (J. Res. Nat. Bur. Stand., 1934, 13, 677—679).—Effects of X-rays in liquids are localised in columns of ionisation along the path of each high-speed electron. Such an ionisation column (I) must pass through a particular part of the bacillus (II) to cause death, the sectional area of (II) being > that of (I). H. J. E.

Parathyroid hormone. W. R. TWEEDY, W. P. BELL, and C. VICENS-RIOS (J. Biol. Chem., 1935, 108, 105—112; cf. A., 1933, 319).—Inactivation of the hormone (I) by oxidation occurs without deamination by the action of H_2O_2 , and with only 35% deamination when (I) is carefully treated with HNO_3 . (I) is stable to reducing agents including Na-Hg and H_2 -Pt under pressure, and its S content (0.2%) is not due to cystine or other -S-S- groups. A. E. O.

Calcium and phosphorus. VII. Effect of variations in dosage of parathormone, calcium, and phosphorus in the diet on the concentrations of calcium and inorganic phosphorus in serum and on the histology and chemical composition of the bones of rats. D. H. SHELLING, D. E. ASHER, and D. A. JACKSON (Bull. Johns Hopkins Hosp., 1933, 53, 348—389; cf. A., 1933, 1329).—Parathormone (I) injections induce hypercalcaemia and hyperphosphotaemia, the latter depending on the dosage and P intake. Hypercalcification of bone by vitamin-D increases the ratio ash : org. matter and (I) causes a retention or decrease in the ratio. Action of (I) on bones varies with the dosage and with the amounts and ratio of Ca and P in diet. CH. ABS. (p)

Thyroid extract in prostate swelling. H. SMITH (Indian Med. Gaz., 1934, 69, 254—256; Chem. Zentr., 1934, ii, 1637).—Administration of thyroxine produces diminution of the prostate by inhibiting the internal secretion of the testes. R. N. C.

Urinary excretion of iodine. I. Loss of iodine in urine following thyroidectomy. G. M. CURTIS and F. J. PHILLIPS (J. Clin. Invest., 1934, 13, 777—787).—Part of the additional I excreted after thyroidectomy is derived from extra-thyroid sources. Increased urinary I also follows operations to tissues remote from the thyroid. CH. ABS. (p)

Reversal of thyroid activity by iodine. A. LOESER (Klin. Woch., 1934, 13, 533—534; Chem. Zentr., 1934, ii, 2095).—Administration of I causes an inversion of the secretory activity of the anterior pituitary, which secretes more or less thyrotropic hormone according to the quantity of I, resulting in a reversal of thyroid activity. In hypophysectomised animals the thyroid effect of I fails to appear, a proof of the direct action of I on the thyroid. R. N. C.

Extrathyroidal origin of thyroxine-like active iodine compounds. I. ABELIN (Klin. Woch., 1934, 13, 940—942; Chem. Zentr., 1934, ii, 1479—1480).—Hydrolysis of an iodised albumin produces small quantities of a substance rich in I which gives no biuret reaction, is sparingly sol. in acids, and easily sol. in alkalis. From its physiological resemblance to thyroxine (I) it is termed *homothyroxine*. It raises basal metabolism in normal and thyroidectomised rats, affects MeCN-resistance in white mice, and produces decolorisation and albinism in black hens' feathers. The physiological effect of iodoproteins depends on their I content and the nature of its union; overloading with I renders them inactive. The peripheral tissue is probably responsible for the extra-thyroidal origin of (I)-like substances. R. N. C.

Significance of the thyroid for the respiration of tissue sections from warm-blooded animals. H. PAAL (Klin. Woch., 1934, 13, 207—209; Chem. Zentr., 1934, ii, 2094—2095).—The O_2 consumption (I) of liver tissue (II) *in vitro* is not increased by thyroxine (III) or the thyrotropic hormone (IV) alone, but addition to the serum, in which (II) is placed for respiration, of thyroid tissue (V), which is again removed during the actual measurement, produces a considerable increase, which with (IV) is > with (III) and remains const. over some hr., whilst that produced with (III) falls gradually. Hence (V) must secrete a substance that increases (I) in combination with (III) or (IV). Thyronine in quantities of 0.005 mg. or less produces an increase in (I) in 1—2 hr.; di-iodotyrosine has the same effect, but reduces metabolism to a more marked degree than (III). R. N. C.

Relationships between adrenal and thyroid. I. ABELIN (Z. ges. exp. Med., 1934, 94, 353—358).—Removal of both adrenal glands, like over-secretion of the thyroid gland, led in rats to disappearance of glycogen (I) from the liver (II) and muscle (III), together with a diminution in their fat content. Administration of di-iodotyrosine or a special diet containing cod-liver oil, bone marrow, and yeast

extract greatly reduced the loss of (II)-(I) both in adrenalectomised and hyperthyroid animals, although the former always died. The adrenal and thyroid hormones may have antagonistic effects on (II)- and (III)-(I). NUTR. ABS. (b)

Swelling of the muscles of adrenalectomised rats. E. PONDER and R. GAUNT (Proc. Soc. Exp. Biol. Med., 1934, 32, 202—204).—The conclusion of Winter and Hartman that adrenalectomy causes an increase in muscle permeability is not confirmed. The % of H_2O in the muscles is increased. R. N. C.

Inhibition of adrenalineglycogenolysis in frog's liver by metals. H. HAUSLER and H. SCHNETZ (Biochem. Z., 1935, 275, 204—215).—Salts of Cu, Cd, Zn, Mn, Ni, Co, Pb, Hg, Fe^{II} , and Fe^{III} , up to concns. of 10^{-2} millimol. per litre, either do not increase the rate of liberation of sugar from frog's liver or (Cu, Zn, Hg) cause an increase only at a definite concn. The increase of glycogenolysis (I) in frog's liver brought about by adrenaline is completely inhibited only by salts of Cu, Zn, and Cd; Fe (both salts and in colloidal form) increases (I) and Mn, Ni, Co, Pb, and Hg salts are inactive. P. W. C.

Adrenaline and the blood-sugar level. M. C. HRUBETZ (Proc. Soc. Exp. Biol. Med., 1934, 32, 218—219).—Blood-sugar (I) in rabbits reaches a max. $1\frac{1}{2}$ hr. after subcutaneous injection of adrenaline, and has not returned to normal after 4 hr. With doses of 0.05—0.4 mg. per kg. of body-wt., (I) increases with the dose up to 0.2 mg. per kg., when the curve flattens out. The deviations of (I) from the level increase with the time after the injection, and with the dose. R. N. C.

Muscle-glycogenesis in splenectomised rabbits. S. TUZIOKA (J. Biochem. Japan, 1935, 21, 119—122).—The muscle-glycogenesis in rabbits is diminished by splenectomy, whilst subsequent administration of spleen extracts produces a return to normal values. F. O. H.

Hormonal control of the motion of the intestinal villi. II. Villikinin. E. VON KOKAS and G. VON LUDANY (Pflüger's Archiv, 1934, 234, 182—186).—The hormone (villikinin) controlling the motion of the intestinal villi is extracted by HCl from the duodenal mucosa. It is not destroyed by pepsin or trypsin, and hence is not secretin or cholecystokinin. It is not pptd. by saturation with NaCl, nor by $CCl_3\text{-CO}_2\text{H}$. R. N. C.

Villikinin. E. VON KOKAS and G. VON LUDANY (Pflüger's Archiv, 1934, 234, 589—593).—The action of villikinin (I) on the intestinal villi is not affected by atropinisation of the animal. Treatment of the extract of intestinal mucosa with histaminase, animal C, or CH_2O does not influence its (I) activity. The activity of the villi is not influenced by adenosine. Accordingly, (I) is not identical with choline, histamine, or adenosine. NUTR. ABS. (m)

Action of incretin on the glycosuria of depancreatized dogs. J. LA BARRE and J. LEDRUT (Compt. rend. Soc. Biol., 1934, 117, 1210—1212).—Intravenous injection of incretin in depancreatized

dogs causes a decrease in glucose excretion in the urine.

R. N. C.

Crystalline insulin. Nature of free amino-groups in insulin and isolation of phenylalanine and proline from crystalline insulin. H. JENSEN and E. A. EVANS, jun. (J. Biol. Chem., 1935, 108, 1-9).— α -Naphthyl- and phenyl-thiocarbimide (I) give products with insulin (II) containing only 5% of its original activity, unchanged S, and decreased NH_2 -N contents. No NH_3 is liberated on treatment of the products with NaOH , whilst on acid hydrolysis the phenyl- (III) and *naphthyl-hydantoin*, m.p. 161-162°, of phenylalanine are obtained. Proline is also isolated as the aurichloride of its betaine.

H. D.

Action of phenylthiocarbimide on insulin. S. J. HOPKINS and A. WORMALL (Biochem. J., 1934, 28, 2125-2132).—A detailed account of work already noted (A., 1934, 1142).

A. E. O.

Determination of insulin in body-fluids and tissues. O. KAUSCH (Pharm. Ztg., 1935, 80, 33).—A review of methods in which insulin is pptd. with $(\text{NH}_4)_2\text{SO}_4$ or picric acid or determined spectrometrically. The methods of Knoop and Niederhoff (Pharm. Ztg., 1924), Wyss (A., 1925, i, 1220), of Folin and Marenzi, and of Sullivan are inapplicable.

W. McC.

Immediate response of plasma-cholesterol to injection of insulin and of adrenaline in human subjects. M. BRUGER and H. O. MOSENTHAL (J. Clin. Invest., 1934, 13, 399-409).—After injection of insulin in diabetic or non-diabetic subjects, hypoglycaemia (I) is not associated with change in plasma-cholesterol (II). Injection of orange juice or glucose during (I) results in a decline in (II). Adrenaline sufficient to cause hyperglycaemia does not alter (I).

CH. ABS. (p)

Influencing parasympathetic action by insulin. H. TSUDZIMURA (Pflüger's Archiv, 1934, 234, 255-257).—Intravenous injection of insulin in normal and depancreatized cats does not alter the reaction of the blood-pressure to vagus or chorda-tympani stimulation, or to choline; hence it plays no part in parasympathetic action.

R. N. C.

Liver-lipins in completely depancreatized dogs maintained with insulin. A. KAPLAN and I. L. CHAIKOFF (J. Biol. Chem., 1935, 108, 201-216).—The livers of depancreatized dogs (I) maintained with insulin are much larger than normal and contain 17-35 times the normal amount of total lipins (II) consisting chiefly (94%) of neutral fat. Since the proportion of phospholipins is below normal, the liver fatty acids appear relatively to be less unsaturated. In the post-absorptive state, the livers of (I) show a marked increase in cholesteryl ester (III) content, accompanied by the complete disappearance of (III) from the blood, the total (II) content of which is also below normal. The ratio of (III) to free cholesterol is also much > normal. The accumulation of (II) in the livers of (I) is not due to increased rate of transport of (II) to the liver.

A. E. O.

Insulotropic hormone from intestinal mucosa ('duodenin'). II. H. HELLER (Arch. exp. Path.

Pharm., 1935, 177, 127-133).—Subcutaneous injection of "duodenin" (I), the hypoglycaemic principle from duodenal mucosa (A., 1930, 117), lowers the blood-sugar (II) of normal or glucose-fed rabbits (III); (I) is also active when taken orally by men or (III). Pepsin+HCl at p_{H} 4.5 does not destroy (I). With trypsin at p_{H} 8-8.5, slow destruction appears to occur, the product lowering (II) but not influencing the external secretion of the pancreas.

F. O. H.

Melanophoric action of extracts of organs. J. DADLEZ and W. KOSKOWSKI (Compt. rend. Soc. Biol., 1935, 118, 99-101).—The melanophore-dilating effect on frogs of the extracts of the following organs decreases in the order, brain, liver, lung, spleen, and testicles. Extracts of striped muscle, heart, kidney, uterus, mammary gland, and bone marrow are without action.

A. L.

"Fat-metabolism" hormone and hyperglycaemia. B. HARROW, B. NAIMAN, I. M. CHAMELIN, and H. MAZUR (Proc. Soc. Exp. Biol. Med., 1934, 31, 940-942).—Injection into rabbits of an anterior pituitary-like substance (from urine) caused an increase in sugar, COMe_2 , and lactic acid contents of blood and a decrease in CO_2 -combining power.

CH. ABS. (p)

Separate action on liver-glycogen and blood-ketones of the carbohydrate- and fat-controlling hormones of the anterior pituitary. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1934, 13, 1052-1053).—A complete separation of carbohydrate- (I) and fat-controlling (II) hormones of the anterior pituitary has been made by ultrafiltration at different p_{H} . The purified (II) hormone increases the blood-ketones (III) in the rat without alteration in liver-glycogen (IV) and the pure (I) hormone decreases (IV) without changing (III).

NUTR. ABS. (b)

Acetonuria following treatment with the fat metabolism hormone of the anterior pituitary. K. J. ANSELMINO and F. HOFFMANN (Z. ges. exp. Med., 1934, 94, 305-308).—Injection of the fat metabolism hormone of the anterior pituitary produced in dogs and rats a marked increase of ketonuria.

NUTR. ABS. (b)

Pituitary mechanism regulating carbohydrate metabolism and its disturbance in diabetes mellitus. Anterior pituitary hormone regulating carbohydrate metabolism. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1934, 13, 1048-1052).—A substance appears in the blood of healthy persons after carbohydrate feeding, but not after fat or protein feeding or in fasting subjects, which, on injection into rats, lowers liver-glycogen (I). This substance is probably identical with that from the anterior pituitary (II) which similarly diminishes (I). This substance is designated the (II) carbohydrate-controlling hormone and is not identical with any other known (II) hormone. More of this active substance is found in the blood (III) of fasting diabetics than in normal (III). These patients also have more of the fat-controlling hormone, since injection of their fasting serum into rats caused increases in the (III)-ketones.

NUTR. ABS. (b)

Anterior pituitary gland and glycogenolysis. M. FLUCH, H. GREINER, and O. LOEWI (Arch. exp.

Path. Pharm., 1935, 177, 167—176).—Extirpation (I) of the anterior lobe (II) of the pituitary gland in frogs does not influence the glycogen content of the liver. Perfusion with Ringer's solution alone or with small amounts of adrenaline produces in such frogs a glycogenolysis < that of controls, the inhibition being of gradual onset after (I). The influence of (II) on glycogen metabolism is discussed. F. O. H.

Adrenotropic substance of the pituitary as influenced by age, castration, sex, and thyro-parathyroidectomy. F. E. EMERY and C. A. WINTER (Anat. Rec., 1934, 60, 381—390).—Implantation of pituitary (I) in young rats produces an adrenal hypertrophy (II) < that from injection of older rats with (I) extract. (II) in young male rats is > in females, but in mature animals it is approx. the same for both sexes. The female (I) has an adrenotropic potency > that of the male. Castration of the donors does not affect the potency. The adrenotropic hormone has no action in thyro-parathyroidectomised animals.

R. N. C.

Arrest-point of pitressin in the kidney. R. HAUPTFELD (Klin. Woch., 1934, 13, 839—842; Chem. Zentr., 1934, ii, 1942).—Immersion of weighed pieces of rabbits' renal medulla or cortex in NaCl solutions of variable concns. and subsequent weighing is used to determine the isotonic [NaCl] to the kidney cells and canal contents. The osmotic changes from pituglandol (I) are directly the reverse of those from diuresis. It is concluded that the action of (I) on the kidney canals is to increase resorption of H_2O .

R. N. C.

Anterior-pituitary sex-hormone content in the urine of elderly men. A. KUKOS (Klin. Woch., 1934, 13, 943—944; Chem. Zentr., 1934, ii, 1478).—Of 17 healthy men aged 70—85, prolan could be detected in the urine of only six, the ovary reaction being very weak in all cases.

R. N. C.

Effects of avian pituitary glands in salamanders. K. F. STEIN (Proc. Soc. Exp. Biol. Med., 1934, 32, 157—161).—Implantation of fowls' anterior pituitaries, or injection of the powdered gland in NaCl solution, causes ovulation out of season and hypertrophy of the thyroid gland in *Triturus viridescens*, showing that there is no specificity of the hormones causing these effects between birds and amphibians.

R. N. C.

Effect of feeding thyroid on anterior pituitary of the female albino rat. M. CAMPBELL, J. M. WOLFE, and D. PHELPS (Proc. Soc. Exp. Biol. Med., 1934, 32, 205—208).—In female rats fed with desiccated thyroid the œstrus cycle is suppressed to a degree \propto the dose of thyroid, the pituitaries are subnormal in wt., and the anterior lobes exhibit histological changes.

R. N. C.

Interactions of gonad-stimulating hormones in ovarian development. H. L. FEVOLD and F. L. HISAW (Amer. J. Physiol., 1934, 109, 655—665).—The follicle-stimulating (I) and luteinising hormones (II) of the anterior pituitary are extracted from the dried gland with 50% aq. C_5H_5N and partly separated by pptn. with $BzOH$. The sol. fraction is pptd. with 33% $COMe_2$, the ppt. taken up in H_2O , 1% cresol added at p_H 4.1—4.2, and the mixture left in the cold for 24 hr. The separated ppt. is added to

the insol. $COMe_2$ residue, and the solution treated with $Ba(OH)_2$ until neutral to phenolphthalein; the ppt. is removed and the solution again pptd. at p_H 4.1—4.2 with 1% cresol, the ppt. being added to the other insol. fractions. (I) is pptd. from the solution by $EtOH$ or $COMe_2$. (II) is extracted from the combined ppts. with $PO_4^{'''}$ buffer solution at p_H 8.0, and pptd. at p_H 4.1—4.2. (II) combined with (I) in very small quantities produces marked increases in the wt. of the rat's ovary; the increase in wt. is, however, more related to the amount of (I) injected. The action of the gonadotropic hormone (III) of pregnancy urine is augmented by combining with (I), but not with (II). Similarly, the effect of (I) is augmented by small quantities of (III). The existence of Evans' "synergistic" substance (IV) (cf. A., 1933, 1086; 1934, 457) has not been confirmed. (I) and (IV) have not been identified as separate substances; preps. of (IV) exhibit marked luteinising power, and are probably mixtures of (I) and (II).

R. N. C.

Effects of injection of ovarian and pituitary extracts on serum-calcium in normal, ovariectomised, and hypophysectomised toads. H. A. SHAPIRO and H. ZWARENSTEIN (J. Exp. Biol., 1934, 11, 267—272).—Extracts of ovarian tissue without corpus luteum increase serum-Ca (I). Antuitarin acts similarly after hypophysectomy (II). Pituitrin depresses (I) normally, and after ovariectomy and (II).

CH. ABS. (p)

Morphological comparison of anterior pituitaries of normal castrated female rats and those receiving injections of pregnancy urine extracts. J. M. WOLFE (Proc. Soc. Exp. Biol. Med., 1934, 32, 184—186).

R. N. C.

Anterior pituitaries of infantile female rats receiving pregnancy urine extracts. J. M. WOLFE (Proc. Soc. Exp. Biol. Med., 1934, 32, 214—216).

R. N. C.

Response of the gonads of immature pigeons to various gonadotropic hormones. H. M. EVANS and M. E. SIMPSON (Anat. Rec., 1934, 60, 405—421).—The testes of immature pigeons are stimulated by the gonadotropic hormone (I) of the anterior pituitary (II), and also feebly by the equine (I), which has a similar effect on immature pigeon ovaries. Neither prolan (III) from pregnancy or menopause urine, nor urine from a patient with embryonic carcinoma of the testes, has any effect. (II) secretes a "synergist" (IV), which has no sp. gonadotropic action, but activates (III), so that it stimulates the gonads of immature rats, but not those of pigeons. There is evidence that a mixture of (III) and (IV) is not identical with (I).

R. N. C.

Reduction of the thymus by gonadotropic hormone. H. M. EVANS and M. E. SIMPSON (Anat. Rec., 1934, 60, 423—435).—Daily injections of the equine gonadotropic hormone (I) in young rats result in an atrophy of the thymus. The effect is inhibited in both sexes by castration, but is produced in males with cryptorchidism or avitaminosis-E, and also in castrated males injected with œstrin in addition to (I).

R. N. C.

Crystallographic and refractometric researches on α -folliculin. A. NEUNAUS (Z. Krist., 1934, 89, 505—512).—Three forms of the hormone, rhombic (stable), rhombic (metastable), and monoclinic (metastable), exist; goniometric, X-ray, and refractivity data are given. B. W. R.

Rapid hormonal diagnosis of pregnancy in mature mice. A. MANDELSTAMM and E. KAPLUN (Wien. klin. Woch., 1934, 47, 813—814; Chem. Zentr., 1934, ii, 1941).—Grown female mice, injected with 3—4 c.c. of urine over 24 hr., and irradiated with red light before and during the injections, showed blood-points in the ovary within 48—50 hr.

R. N. C.

Effect of oestrin on the mammary rudiments of male mice differing in susceptibility to tumour development. W. M. GARDNER, A. W. DIDDLE, E. ALLEN, and L. C. STRONG (Anat. Rec., 1934, 60, 457—468).—The mammary glands of normal male mice undergo a gradual growth for 60—75 days when injected daily with 3 mouse-units of oestrin.

R. N. C.

Effect of oestrin injections on experimental pancreatic diabetes in the monkey. W. O. NELSON and M. D. OVERHOLSTER (Proc. Soc. Exp. Biol. Med., 1934, 32, 150—151).—Injections of anterior pituitary extract (I) produce hyperglycaemia and glycosuria (II). Injection of oestrin (III) in depancreatised monkeys decreases or suspends (II) entirely; withdrawal or supplementing of (III) with (I) causes reappearance of (II). Blood-sugar in the diabetic animal is also lowered by (III), which probably suppresses the diabetogenic activity of the anterior pituitary.

R. N. C.

Experimental colloid goitre after injection of folliculin. L. KARP and B. KOSTKIEWICZ (Klin. Woch., 1934, 13, 189—190; Chem. Zentr., 1934, ii, 1479).—Injection of folliculin (I) in rabbits produces a goitrous degeneration of the thyroid gland, the lumina of which become filled with colloids (II). The action of (I) is probably due to production of (II) and the prevention of their elimination from gland.

R. N. C.

Absorption of oestrogenic substances of pregnancy urine administered orally to young rats. C. B. FREUDENBERGER and P. M. HOWARD (Anat. Rec., 1934, 60, 267—272).—The oestrogenic hormones in 0.1 c.c. of pregnancy urine diluted 1:15, administered orally thrice daily to young ovariectomised rats, produce premature opening of the vagina in 4—5 days.

R. N. C.

Oestrin and corpus luteum hormones. K. PEDERSEN-BJERGAARD and B. KONSTANTIN-HANSEN (Dansk Tidsskr. Farm., 1935, 9, 29—51).—The biological assay, prep., and constitution of oestrin (I), corpus luteum hormones, and their associated derivatives are discussed. The urinary excretion of (I) by women increases during the intramenstrual period, attaining a max. at approx. the 18th—22nd days.

O. H.

Hitherto unrecognised biological action of the female sex hormone. K. EHRHARDT and K. KUHN (Endokrinol., 1934, 14, 245—256; Chem. Zentr.,

1934, ii, 1796).—Injection of young female carps with the female hormone (I), or its addition to the aquarium H_2O , produces a rapid enlargement of the oviduct. The effect is so sensitive that it can be used to demonstrate (I) in the urine of a normal woman, or to follow (I) metabolism in the menstrual cycle.

R. N. C.

Oestrus in hypophysectomised rats para-biotically connected with castrates. E. WITSCHI and W. T. LEVINE (Proc. Soc. Exp. Biol. Med., 1934, 32, 101—107).—Parabiosis produces const. oestrus due to the increased secretion of follicle-stimulating hormone (I) without luteinising hormone (II) by the anterior pituitary of the castrate. It is concluded that a high level of (I) in the blood-stream suppresses the secretion of (II).

R. N. C.

No anti-hormones against oestrin. F. E. D'AMOUR, C. DUMONT, and R. G. GUSTAVSON (Proc. Soc. Exp. Biol. Med., 1934, 32, 192—194).—The action is not affected by simultaneous injection of serum from male, normal, or ovariectomised animals, either untreated or themselves injected with oestrin for considerable periods.

R. N. C.

Follicular hormone and androkinin in the excreta during the normal menstrual cycle and the administration of folliculin *per os*. SIEBKE (Arch. Gynakol., 1934, 156, 317—320; Chem. Zentr., 1934, ii, 1477).—A healthy woman excretes 10,000 mouse-units of folliculin (I) in the urine (II) and faeces (III) during menstruation. Daily administration of 600 units produces no increase, but with 1500 units an increase is observed, particularly in the middle of the cycle. The (II) curve rises more sharply than the (III) curve. Androkinin (IV) can be demonstrated in (II), often in large quantities. No decrease in (IV) is detected after administration of (I).

R. N. C.

Constitution of androsterone.—See this vol., 346.

Artificial preparation of male sexual hormone.—See this vol., 346.

Androsterone, a crystalline male sexual hormone. I. Isolation from men's urine. II. Chemical characterisation. A. BUTENANDT and K. TSCHERNING. III. Isolation of a physiologically inactive sterol derivative from men's urine, its relation to dehydroandrosterone and androsterone; constitution of androsterone. A. BUTENANDT and H. DANNENBAUM (Z. physiol. Chem., 1934, 229, 167—184, 185—191, 192—208).—I. Impurities are removed from the conc. acidified urine by successive processes as follows: extraction with $CHCl_3$, extraction with KOH, steam distillation, alkaline and acid hydrolysis, and treatment with C_6H_6 -light petroleum. The petroleum phase is extracted with 60% EtOH. The extract yields an *oxime*, m.p. 215—221°, which on hydrolysis with dil. acid gives *androsterone* (I), $C_{19}H_{30}O_2$, m.p. 178°, $[\alpha]_D^{20} +93^\circ$ in EtOH (*semicarbazone*, m.p. 274—276°, *phenylhydrazone*, m.p. 153—154°; *thiosemicarbazone*, m.p. 250—255°). (I) has an activity of 1 unit in $15-20 \times 10^{-5}$ g. when tested by the comb-growth method on capons.

II. (I) forms physiologically active esters on treat-

ment with the appropriate anhydride in C_5H_5N : *acetate*, m.p. 160–161°, $[\alpha]_D^{20} +86.14^\circ$ in EtOH (*oxime*, m.p. 219–220°), *propionate*, m.p. 145°, indicating the presence of OH. (I) is also a ketone and is saturated. It is therefore a saturated tetracyclic OH-ketone. (I) with CrO_3 in AcOH affords *androstanedione*, m.p. 129°, $[\alpha]_D^{20} +104.8^\circ$ in EtOH, with about half the activity of (I). Clemmensen reduction of (I) yields *androstane*, $C_{19}H_{32}$, m.p. 49–50°.

III. The light petroleum fraction rejected in the isolation of (I) gave with semicarbazide a crude mixture, decomp. 240°, yielding a *semicarbazone*, m.p. 275°, giving on hydrolysis a singly unsaturated *chloroketone* (II), $C_{19}H_{27}OCl$, m.p. 157°, $[\alpha]_D^{20} +15.5^\circ$ in $CHCl_3$ (*oxime*, m.p. 168–169°). Catalytic hydrogenation (Pd) gives the *dihydrochloroketone* (III), m.p. 173° (*semicarbazone*, m.p. 285°). With KOBz at 180°, (II) affords the *benzoate*, m.p. 250°, of *dihydroandrosterone*, m.p. 148°, physiological activity about $\frac{1}{3}$ that of (I). Similarly with KOAc (III) yields the *acetate* of (I) and a singly unsaturated *ketone*, $C_{19}H_{28}O$, m.p. 104°, which on hydrogenation (Pd) gives *androstanone*, $C_{19}H_{30}O$, m.p. 122° [*semicarbazone* (IV), m.p. 263–266°]. With NaOEt at 200° (Wolff-Kishner), (IV) affords androstane (V), $C_{19}H_{32}$, m.p. 49–50°. (V) is not identical with *ætiocolane*, m.p. 78–80°, obtained by Wolff-Kishner reduction of *ætiocolanone-17*; hence (I) does not belong to the cholanic acid-pregnandiol series. (I) is chemically and physiologically identical with 3-*epihydroxyætiocolanone* (Ruzicka *et al.*, A., 1934, 1221). J. H. B.

Differences between male hormone extracts from urine and from testes. E. DINGEMANSE, J. FREUD, and E. LAQUEUR (Nature, 1935, 135, 184).—Large differences in the size of the seminal vesicles are produced in rats treated with the male hormone extracted from urine or from testes. L. S. T.

Alleged oestrogenic activity of the male sex hormone. F. L. WARREN (Nature, 1935, 135, 234).—Male hormone (I) (androsterone) prepared from cholesterol has no effect on the female genital tract of mice. The oestrogenic activity of (I) preps. reported by previous investigators must be due to the presence of substances other than (I). (I) may be the precursor of the female hormone. L. S. T.

Vitamins: their specific and non-specific action. P. KARRER (Giorn. Chim. Ind. Appl., 1934, 16, 593–602).—A lecture.

Vitamins in apples. Vitamin-A, -B, and -C contents of the Rome Beauty, Delicious, Stayman, Yellow Newtown, and Winesap. I. A. MANVILLE, A. S. MCMINIS, and F. G. CHUINARD (J. Amer. Dietetic Assoc., 1934, 10, 135–152).—Vitamin contents are recorded. The occurrence in apples of a substance, other than carotene, possessing vitamin-A activity is indicated. Vitamin-A and -C are more closely correlated with gene activity than with chromosome no. CH. ABS. (p)

Vitamins of pears. II. Vitamin-A, -B, and -C in the Winter Nelis, D'Anjou, and Bosc after a short storage period. I. A. MANVILLE and F. G. CHUINARD (J. Amer. Dietetic Assoc., 1934, 10, 217–227). Winter Nelis (I) and D'Anjou (II) pears contain

about 4, and the Bosc about 3, Sherman units of vitamin-A (III) per oz. Two months' storage reduces these vals. by nearly 50%. The vitamin-C (IV) content is 4 Sherman units per oz. for (II), 3 for (I), and 2.5 for Bosc. The (IV) content also falls on storage, and no difference in (III) or (IV) contents of similar varieties grown in different districts is observed. The amount of vitamin-B complex in pears appears to be slight. NUTR. ABS. (m)

Vitamin-A and -C contents of brown algae. L. L. PROZOROVSKAYA and A. N. SHIVRINA (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 65–69).—Vitamin-A occurs in *Fucus* sp. (I). Vitamin-C was not present in *Laminaria digitata* (II). (I) contains more carotene than (II). CH. ABS. (p)

Size and fat and vitamin-A content of the liver of Teleostei. S. SCHMIDT-NIELSEN, A. FLOOD, and J. STENE (Kong. Norske Vid. Selsk. Forhandl., 1933, 6, 146–149; Chem. Zentr., 1934, ii, 1865).—Data for the fat content, Lovibond val., and wt. of the liver for a no. of species are recorded and discussed. H. J. E.

Vitamin-A in animal and plant cells. P. JOYET-LAVERGNE (Compt. rend., 1935, 200, 346–348; cf. this vol., 109).—A blue colour with $SbCl_5$ is obtained in the chromosomes of protozoa during growth and reproduction. H. D.

Absorption spectra characteristic of vitamin-A in animal and vegetable oils. J. B. PHILIPSON and J. W. WOODROW (Proc. Iowa Acad. Sci., 1932, 39, 220).—Absorption bands characteristic of vitamin-A in animal fats are also shown by plant materials containing the growth-promoting factor. CH. ABS. (p)

Purification of biosterol (vitamin-A) and its crystalline derivatives. S. HAMANO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 82–86).—A detailed account of work already noted (this vol., 260). The maleic anhydride adduct, $C_{35}H_{38}O_8$, of the Bz derivative of vitamin-A has m.p. 164°.

Relation between the biological, chemical, and physical methods of vitamin-A determination. K. C. LATHBURY (Biochem. J., 1934, 28, 2254–2264).—Comparison of the vitamin-A content of natural (I) and distilled (II) oils as determined by the Carr-Price colour test (III) and the biological assay indicates that the ratio between the no. of international units per g. and the result of (III) is greater in the case of (I) than of (II). The ratio between the result from (III) and that from the extinction coeff. method (IV) in the case of (II) is $>$ than of (I). Vals. obtained from (IV) may be converted into biological units by multiplying by 1400 and the val. from (III) by multiplying by 40 in the case of (I) and 20 in the case of (II). A. L.

Spectrophotometric determination of vitamin-A. A. CHEVALLIER and P. CHABRE (Bull. Soc. Chim. biol., 1934, 16, 1451–1478).—A comparison of the intensity of absorption at 328 m μ of oils and their biological assay indicates that the spectrophotometric method (II) is trustworthy for vitamin-A (I) determination when the max. (III) in the absorption spectrum of the oil occurs at 328 m μ , and when these are not too greatly coloured and only slightly acid. Oils

badly prepared have (III) displaced due to the presence of (I) decomp. products, and the method is no longer trustworthy. It is possible to differentiate, using (II), between the effects of (I) and those of other carotenoid products. A. L.

Specific effect of vitamin-A on growth. W. D. GALLUP (Proc. Oklahoma Acad. Sci., 1934, 14, 53—56).—Efficiencies of various sources of vitamin-A (I) in correcting ophthalmia in calves are compared. Nutritive requirements of calves and rats differ with respect to (I). CH. ABS. (p)

Transmission of vitamin-A from parents to young in mammals. IV. Effect of the liver reserves of the mother on the transmission of vitamin-A to the fetal and suckling rat. W. J. DANN (Biochem. J., 1934, 28, 2141—2146).—The store of vitamin-A (I) in the young rat up to the time of weaning approx. \propto but is very much $<$ the (I) reserves of the mother, which are not likely to be seriously depleted in the rearing of a litter on a normal diet. A. E. O.

Physiological and therapeutic action of colloidal solutions of pro-vitamin-A when locally applied to the eye. P. A. RATSCHESKI (Klin. Woch., 1934, 13, 918; Chem. Zentr., 1934, ii, 1945).—Colloidal solutions of carotene are prepared by shaking EtOH-Et₂O and COMe₂ solutions with H₂O. Properties are recorded. R. N. C.

Effect of vitamin-A deficiency on the concentration of blood-lipins of albino rats. M. E. SMITH (J. Nutrition, 1934, 8, 675—687).—Relationships between the vitamin-A supply and the cholesterol, fatty acids, and lecithin of the blood are examined. A. G. P.

Extraction of vitamin-B from a fuller's earth adsorbate. W. D. SALMON (Ann. Rept. Alabama Agric. Exp. Sta., 1931, 43—45).—The adsorbate is washed with H₂O followed by 80% EtOH containing 5% AcOH, and extracted repeatedly with a C₆H₅N-AcOH mixture. The extract is conc. and treated in successive stages with increasing amounts of EtOH. The final fraction has 75% of the activity of the original adsorbate. CH. ABS. (p)

Relation of vitamin-B to carbohydrate metabolism. G. A. SCHRADER (Ann. Rept. Alabama Agric. Exp. Sta., 1931, 35—39).—Beri-beri in pigeons is associated with high blood-sugar (I) vals., especially in the later stages. Rats deprived of vitamin-B (II) showed no significant increase in (I). (II)-deficient pigeons could absorb glucose from the digestive tract. Starvation of (II)-deficient rats caused normal depletion of glycogen, which was replenished after feeding with *d*-glucose or lactic acid (half neutralised with NaOH). CH. ABS. (p)

Enzymic efficiency in avitaminosis. I. Influence of vitamin-B deficiency on tryptic and ereptic digestion of caseinogen. II. Influence of vitamin-B deficiency on efficiency of pancreatic lipase and esterase. B. SURE, M. C. KIK, K. S. BUCHANAN (J. Biol. Chem., 1935, 108, 27—33).—I. Vitamin-B deficiency (I) is without influence on the tryptic and ereptic activities of rats pancreatic and intestinal extracts. F. F.

II. (I) produces a decrease in the pancreatic lipase digestion of tributyrin and olive oil, and the esterase digestion of PrCO₂Et. H. D.

Preparation and chemistry of vitamin-B₁. H. KAKEFUDA (Fukuoka Acta med., 1934, 27, 99—100).—Vitamin-B₁ (I) from rice germ is purified by means of the platinichloride or picrolonate, and the salt with AuCl₃. A 0.1% solution gives a strong diazo-reaction, but a 0.01% only a faint yellow colour. Ultra-violet (but not X-)rays destroy the activity of the crystals. The absorption spectrum of the hydrochloride shows a band at 265—280 mμ. The relative proportions of (I) in the germ, bran, and silverskin of rice are as 3 : 2 : 1. NUTR. ABS. (m)

Vitamin-B₁. II. Oryzatoxin. I. A. SIMPSON (Bull. Inst. Med. Res. Fed. Malay States, 1934, No. 1, 24 pp.).—White rice (I), which produced polyneuritis in pigeons when used as the staple article of diet before or after heating to 160—165° for 6 hr., contained a strain of *B. vulgaris* (II). EtOH extracts of (I) or of (I) liquefied by (II) yielded emulsions innocuous to pigeons when administered orally, but fatal subcutaneously; the principal effect is haemolysis, and the symptoms do not resemble those of beri-beri (cf. A., 1930, 827). F. O. H.

Relation between kinds of carbohydrate and vitamin-B₁ deficiency. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1934, 630—639).—The appearance of symptoms of vitamin-B₁ deficiency was not influenced by the kind of starch supplied as sole carbohydrate source in deficient rations. Addition of yeast corr. the toxic action of sucrose on the kidneys. CH. ABS. (p)

Vitamin-B₁ and blue fluorescent compounds. R. A. PETERS (Nature, 1935, 135, 107).—Preps. of vitamin-B₁ (I) are converted by oxidation in aq. solution into substances which give an intense sky-blue fluorescence in ultra-violet light. The bearing of this result on the constitution of (I) is discussed. L. S. T.

Vitamin assay and its application in study of vitamin-B₁ and -B₂ contents of mung beans and grain sorghums. R. REDER (Proc. Oklahoma Acad. Sci., 1934, 14, 50—52).—Vals. for various food products are determined. The % of fat in diets did not affect results of rat tests. CH. ABS. (p)

Isolation of lactoflavin (vitamin-B₂) from hay. R. KUHN and H. KALTSCHMITT (Ber., 1935, 68, [B], 128—131).—Lactoflavin (I) is isolated from dried Californian lucerne as the Ac₄ derivative identical in composition, optical activity, absorption spectrum, and growth-promoting power with that derived from milk. (I) is thus a vegetable pigment which, without chemical change, is stored in the livers of animals and passes into the milk. (I) may be involved in the assimilation of CO₂. H. W.

Concentration of vitamin-B₂ by adsorption and elution from fuller's earth. S. LEPKOVSKY, W. POPPER, jun., and H. M. EVANS (J. Biol. Chem., 1934, 108, 257—265).—Vitamin-B₂ can be adsorbed by fuller's earth and recovered by washing with dil. NH₄Et₂ or NaOH. After a second adsorption the activity of the vitamin is diminished. H. T.

Effect of p_H on stability of vitamin- B_2 . W. D. SALMON (Ann. Rept. Alabama Agric. Exp. Sta., 1931, 30—31).—The growth-promoting action of yeast extracts is destroyed by autoclaving more rapidly in alkaline than in acid media.

CH. ABS. (p)

Effect of process of manufacture on the vitamin- B_2 content of dried skim-milk. H. J. DAVIS and L. C. NORRIS (Poultry Sci., 1934, 13, 305—306p).—There was no measurable loss of vitamin- B_2 activity (determined on hens), whether the milk was dried by spray or roller process, or when the milk was overheated before or during the drying.

NUTR. ABS. (b)

Relation of dermatitis in chicks to lack of vitamin- B_2 and to dietary egg-white. J. G. LEASE and H. T. PARSONS (Biochem. J., 1934, 28, 2109—2115).—The dermatitis produced in chicks fed on a well-supplemented ration rich in egg-white is cured by an extracted liver residue (I) poor in vitamin- B_2 (II), but not by a liver extract rich in (II). A similar dermatitis due to lack of (II) is cured by the extract, but not by (I). The toxic effect of egg-white is not due to its destructive action on (II) during storage, nor is it prevented by addition of yeast to the ration.

A. E. O.

Non-identity of adenine and vitamin- B_1 . C. Y. CHEN (Bull. Agric. Chem. Soc. Japan, 1934, 10, 105—108).—Neither adenine nor adenylothymethyl-pentose possesses vitamin- B_1 activity.

CH. ABS. (p)

Synthesis of vitamin-C by luteal tissue. G. BOURNE (Nature, 1935, 135, 148—149).—The corpus luteum of the guinea-pig can synthesise vitamin-C, and when the foetus is developed it either takes over or supplements the vitaminogenic function of the luteal tissue.

L. S. T.

Fat-soluble vitamins and the synthesis of vitamin-C by the animal organism. P. ROHMER, N. BEZSSONOFF, and E. STOERR (Compt. rend. Soc. Biol., 1935, 118, 56—57).—Suckling infants fed on a diet of acidulated dried milk (I) ceased to eliminate vitamin-C (II) after 4 days. Administration of small quantities of egg-yolk or cod-liver oil with (I) caused reappearance of (II) after 7 days. Synthesis of (II) is therefore closely related to the presence of vitamin-A and/or -B.

A. L.

Influence of non-alimentary factors on the synthesis of vitamin-C. P. ROHMER, N. BEZSSONOFF, and E. STOERR (Compt. rend. Soc. Biol., 1935, 118, 58—59).—The vitamin-C content of cow's milk is very low in winter, but increases rapidly in spring, even before the animals go to pasture.

A. L.

Mannose dehydrogenase and ascorbic acid. B. C. GUHA and A. R. GHOSH (Current Sci., 1934, 3, 251).—Incubation of liver, spleen, and kidney tissue of the rat with mannose at p_H 7.4 yields 0.3—0.35 mg. of ascorbic acid per g. of tissue in 3 hr. These tissues are unable to synthesise the vitamin from glucose, fructose, galactose, xylose, or arabinose, whilst the same tissues from the guinea-pig have no action even on mannose.

P. G. M

Biological formation of ascorbic acid. B. C. GUHA and A. R. GHOSH (Nature, 1935, 135, 234).—The brain, heart-muscle, and leg-muscle tissues of the rat can form ascorbic acid (I) from mannose (II), but to a smaller extent than the spleen, liver, and kidney tissues. The liver tissues of only those animals known to be independent of external sources of (I) can produce it from (II); that of the pigeon converts glucose into (I) (see preceding abstract).

L. S. T.

Vitamin-C and narcotine. N. N. VOROSCHCOV, jun., and A. T. TROSHTZENKO (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 161—164).—The product of demethylation of narcotine (with HCl) has no vitamin-C activity.

CH. ABS. (p)

Antiscorbutic [in-]activity of a preparation of methylnarcotine. K. L. POVOLOTZKAYA (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 165—169).—The preps. are devoid of vitamin-C.

Nature and determination of vitamin-C. G. VIALE (Rev. sudamer. endocrinol., 1934, 17, 547—552).—Iodometric determinations of glutathione include the val. for ascorbic acid (I). (I) prevents the oxidation of adrenaline in air, its reducing action being accentuated by light, especially in the presence of fluorescent substances. (I) is determined in $CCl_3 \cdot CO_2H$ extracts by means of methylene-blue.

CH. ABS. (p)

Therapeutic method of determining vitamin-C. K. L. POVOLOTZKAYA (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 225—232).—Compared with the prophylactic, the therapeutic method with guinea-pigs suffering from scurvy gives sufficiently exact results, wt. increase and macroscopic pathological changes being the criteria. The min. healing and preventive doses are nearly the same.

NUTR. ABS. (m)

Biological method for determining vitamin-C. V. N. BUKIN, K. L. POVOLOTZKAYA, and M. F. GLAZUNOV (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 195—215).—Prophylactic doses of vitamin-C (e.g., orange juice) do not improve the Bezssonov diet. Additions of irradiated cereals, carotene (I), and salts were also ineffective. A diet of autoclaved hay and autoclaved carrots (II) was satisfactory. (I) may replace (II), which serves as a source of -D and improves the -A content.

CH. ABS. (p)

Chemical methods in determining vitamin-C. V. N. BUKIN and K. L. POVOLOTZKAYA (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 179—194).—The Bezssonov reaction and I titration do not measure vitamin-C activity. Tillmans' 2 : 6-dichlorophenol-indophenol reaction is not sp., but serves for preliminary observations. The reagent is reduced by sugars at high temp.

CH. ABS. (p)

Probable presence of ascorbic acid in the vitreous humour of the ox eye. C. DUMAZERT and P. PASSELAIGUE (Compt. rend. Soc. Biol., 1934, 116, 1035—1036).—Vitreous humour (I) has an antiscorbutic action on guinea-pigs. (I) by neutral $Pb(OAc)_2$ treatment yielded a syrup having many of the reactions of ascorbic acid (II). From the 2 : 6-dichlorophenol-indophenol titration, the (II) content of ox-(I) should be 10—15 mg. per 100 c.c.

NUTR. ABS. (b)

Vitamin-C content of dried onions. S. N. MATZKO (Questions of Nutrition, U.S.S.R., 1934, 3, No. 3, 122—124).—Dried onions or leeks contain no vitamin-C. NUTR. ABS. (m)

Fermented cabbage (sauerkraut) as source of the antiscorbutic vitamin. K. L. POVOLOTZKAYA, V. N. BUKIN, L. A. HARDER, and M. M. MAKAROVA (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 103—112).—Cabbage fermented in brine loses 50%, that fermented in pure culture of lactic acid bacilli only 10—20%, of its vitamin-C val. NUTR. ABS. (m)

Presence of the antiscorbutic vitamin in northern varieties of fruits, berries, and vegetables. V. N. BUKIN, K. L. POVOLOTZKAYA, and N. P. ONOKHOVA (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 25—51).—The min. daily dose which prevented scurvy in guinea-pigs was for kohlrabi 1 g., head cabbage 1—4 g., turnip 6 g., potato 6—9 g., beetroot < 12 g., carrot 18 g., apple 5—18 g., apple variety Antonovka 3 g., black currant (var. Lia prolific) 0.25—0.5 g., strawberry (var. Saxon) 1.5 g., and sweet potato 6 g. NUTR. ABS. (b)

Foodstuffs as vitamin-bearers. I. Contents of antiscorbutic factor in huckleberries stored during the winter and in preserve of black-currant juice. B. A. LAVROV, B. I. JANOVSKA, and N. S. JAROUSOVA. **II. Vitamin contents of spinach preserves and of garlic after winter-storage.** N. S. JAROUSOVA and B. I. JANOVSKA (Questions of Nutrition, U.S.S.R., 1934, 3, No. 2, 29—31, 31—33).—I. Stored huckleberries contain only traces of vitamin-C (I), but preserved black-currants are a good source of (I).

II. Preserved spinach is a rich, but stored garlic a very poor, source of (I). NUTR. ABS. (m)

Influence of the cooking of vegetables on the preservation of vitamin-C. V. N. BUKIN, N. A. IZMAILOVA, and A. P. BOGOCHUNAZ (Bull. Appl. Bot. U.S.S.R., 1934, Suppl. 67, 129—142).—On boiling, cabbage and potato lost 50%, swede turnip 30%, and kohlrabi none, of the vitamin-C content. NUTR. ABS. (b)

Ascorbic acid and glutathione content of rapidly growing young tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1935, 231, 47—50).—In brain, with the growth of the animal, the abs. amount of reducing substances (I) decreases, but the glutathione (II) content remains const.; the "X-substance" (III) [mainly ascorbic acid (IV)] decreases. In the liver, the abs. amount of (I) scarcely decreases, the (II) content increases, (III) remains const. (IV) and (II) are not related to growth or increased cell-production in either healthy organs or tumours. J. H. B.

Depigmentising action of l-ascorbic acid. (Hyperpigmentation produced by folliculin and vitamin-C.) W. JADASSOHN and F. SCHAAF (Klin. Woch., 1934, 13, 845—846; Chem. Zentr., 1934, ii, 1801).—Administration of large quantities of vitamin-C does not prevent the hyperpigmentation by folliculin of the mammary areolas of guinea-pigs. R. N. C.

Biological value of vitamin-C. T. MOLL (Deut. med. Woch., 1934, 60, 1197—1200).—A daily dose of

0.25 mg. of ascorbic acid (I) > doubles the survival time of guinea-pigs (II), as compared with controls, but the min. preventive dose for optimal growth and the production of completely normal teeth is 1.5—2.0 mg.; 0.5 mg. of (I) is equiv. to 1.5 ml. of lemon juice. Mice receiving by mouth up to 50 mg. of (I) daily for 12 weeks show no signs of disease, but 100 mg. rapidly cause death. (II) receive 100 mg. daily for 5 weeks without development of pathological signs. The existence of hypervitaminosis-C is considered improbable. NUTR. ABS. (m)

Diagnosis of vitamin-C subnutrition by urine analysis; antiscorbutic value of human milk. L. J. HARRIS and S. N. RAY (Lancet, 1935, 228, 71—77).—Infants suffering from scurvy, or with a history of vitamin-C (I) underfeeding, excrete less (I) in their urine than do well-nourished infants on low-(I) diets. Human milk contains three to four times the amount of (I) in cow's milk. The determination of (I) in urine by micro-titration with 2:6-dichlorophenol-indophenol is described. L. S. T.

Determination of vitamin-D. B. O'BRIEN and K. MORGAREIDGE (Proc. Soc. Exp. Biol. Med., 1934, 32, 113—117).—Improvements of X-ray technique are described. R. N. C.

Determination of vitamin-D. II. Effect of seasonal variation and sex on calcification in rachitic chicks. L. L. LACHAT (Poultry Sci., 1934, 13, 353—357).—The ash content of bones of chicks receiving a rachitogenic diet showed definite seasonal variations. Differences between sexes were insignificant. A. G. P.

Existence of two forms of vitamin-D in fish-liver oils. C. E. BILLS, O. N. MASSENGALE, and M. IMBODEN (Science, 1934, 80, 596).—The vitamin-D of bluefin tuna (*Thunnus thynnus*) liver oil and that of cod-liver oil are different substances or different mixtures of substances. One rat unit of the former has only 15% of the antirachitic effectiveness of one rat unit of the latter for the chicken. The former contains approx. 4×10^4 I.U. per g. L. S. T.

Relative antirachitic values of cod-liver oil, viosterol, and irradiated milk. T. G. H. DRAKE, F. F. TISDALL, and A. BROWN (Canad. Med. Assoc. J., 1934, 71, 368—376).—Irradiated milk and viosterol were more effective than cod-liver oil. CH. ABS. (p)

Effect of equivalent units of vitamin-D in the form of a cod-liver oil concentrate and irradiated ergosterol on the hatchability and vitamin-D content of the egg. R. M. BETHKE, P. R. RECORD, and O. H. M. WILDER (Ann. Rept. Ohio Agric. Exp. Sta., 1934, 74).—Supplementary feeding of vitamin-D (I) as cod-liver oil produced proportional increases in the (I) content of the egg-yolk. The corresponding increases with similar dosages of ergosterol were smaller. The hatchability of the eggs was unaffected. CH. ABS. (p)

Relation between the antirachitic factor and the weight and contents of the gall-bladder of the chicken. W. C. RUSSELL, M. W. TAYLOR, and D. F. CHICHESTER (J. Nutrition, 1934, 8, 689—694).—Gall-bladders of chickens receiving a basal ration without

cod-liver oil (I) contained bile (II) in larger quantities and having a higher % of total ash and lower % of Ca than those of birds receiving a (I) supplement. Retention of (II) is unrelated to the p_H of the duodenal contents. A. G. P.

Hypervitaminosis-D rickets: action of vitamin-D. A. W. HAM and M. D. LEWIS (Brit. J. Exp. Path., 1934, 15, 228—234).—Large dosages of vitamin-D inhibited normal calcification in rat bones. The mechanism of this effect is considered.

CH. ABS. (p)

Unsaponifiable fraction of wheat-germ oil: vitamin-E. J. C. DRUMMOND, E. SINGER, and R. J. MACWALTER (Biochem. J., 1935, 29, 456—471).— C_2HCl_3 extraction of wheat-germ oil gave a product vitamin-E- (I) -active in a dose of 23 mg. daily. The fraction (II) unsaponifiable by EtOH-KOH contained 60% of sterols. (II) after removal of the sterols was divided into five fractions by adsorption from light petroleum on Al_2O_3 . The adsorbed fractions were eluted with MeOH-Et₂O (4:1), and the fractionation was followed by determinations of (I) activity and the ultra-violet absorption spectra (III). The material yielded by the lower zone of the adsorption column was active in doses of > 0.2 mg. daily and showed a band with a max. at 294 $m\mu$ and a min. at 265 $m\mu$. Continued reabsorption of this fraction on Al_2O_3 gave a product (I)-active in a daily dose of 0.1 mg.; the activity of one product was increased by hydrogenation. A parallel between (III) of the various fractions and (I) activity was observed; the ratio of the extinction coeffs. at the max. and min., respectively, and the increase in absorption at the max. are the best indices of concn. of the substance responsible for absorption. Acetylation of the active fractions gave β -amyirin acetate with little absorption and no (I) activity. Ultra-violet irradiation of a product active in a dose of 0.2 mg. daily decreased the activity by 80% and (III) was changed. Hydrogenation of the most active fraction reduced the I val. from 166 to 26 in 5 hr., whilst the (I) activity and (III) were unchanged. Extraction of 1 g. of sterol-free (II) by the method of Girard (A., 1933, 870) gave 10 mg. of a ketonic substance with, however, no change in absorption at 294 $m\mu$. The remaining fractions from the Al_2O_3 adsorption contained, besides sterols, lutein, cryptoxanthin, squalene, a lipochrome, and a hydrocarbon similar to that found in mammalian livers.

H. D.

Surface films of vitamin-E concentrates. F. E. ASKEW (Biochem. J., 1935, 29, 472—475).—A vitamin-E-active oil and a cryst. substance (I) derived from it are spread on dil. HCl and the surface pressure and p.d. plotted against area. The curves obtained are consistent with the presence of a polycyclic substance with a H_2O -attracting group near one end of the mol. The curve of β -amyirin is much steeper and shows a more marked rearrangement to a solid film than that of (I).

H. D.

Growth-deficiency disease, curable by wheat-germ oil. H. BLUMBERG (J. Biol. Chem., 1934, 108, 227—238).—Purified diets containing vitamin-A, -D, and -F check the early and middle growth of rats. Wheat-germ oil and egg-yolk cure any irregularities

in reproduction and growth. The growth factor contained in the oil may be either vitamin-E or another unknown fat-sol. substance.

H. T.

Phototropism of the *Avena* coleoptile and the theory of the light-intensity gradient. H. G. DU BOY (Ber. deut. bot. Ges., 1934, 52, 530—559).—The light gradient in plants controls phototropic curvature. Light response of *Avena* coleoptiles is discussed as the resultant of photochemical changes and in relation to the activity of auxin.

A. G. P.

Growth-promoting substances of the auxin and the bios group. F. KOGL (Ber., 1935, 68, [A], 16—28).—A lecture.

H. W.

Identity of the growth-promoting and root-forming substances of plants. K. V. THIMANN and J. B. KOEPLI (Nature, 1935, 135, 101—102; cf. A., 1934, 1418).—Synthetic 2-indolylacetic acid (I) is fully active in promoting root formation in peas. The growth-promoting and root-forming substances of plants are identical. Indole and certain homologues of (I) are inactive in root formation.

L. S. T.

Activation of cambial growth. R. SNOW and B. LE FANU (Nature, 1935, 135, 149).—Cambium cells from strips of decapitated young sunflower hypocotyls continue to grow and to produce xylem and roots when covered with gelatin containing auxin (I) from the Et₂O-sol. extract of urine. The hormone activating cambial growth may thus be identical with (I).

L. S. T.

Effect of various endocrine preparations on growth of beans. I. S. YUN and W. L. HONG (J. Chosen Med. Assoc., 1934, 24, 568—591).—Thyroglandol stimulated soya-bean sprouts in all concns. Antuitrin, pituitrin, testiglandol, luteoglandol, interenin, epiglandol, spleen and liver extracts, thyroxine, and parathyroidin were inhibitory. Adrenaline (5%) inhibits growth, but not at lower concns. Insulin and ovarian hormone stimulate in 1% solution, but inhibit at 5%.

CH. ABS. (p)

Influence of chemical stimulants on the growth of plants. A. ZLATAROFF (Bull. Soc. Chim. biol., 1934, 16, 1720—1729).—The calorific val. of the plantules of the cotyledons of the seeds of *Cicer arietinum* and *Arachis hypogaea* immersed in 5% aq. $MgSO_4$ and $MnSO_4$ was 8% and 18%, respectively, > those immersed in H_2O . In the same manner barley immersed in aq. $MnSO_4$ and $MgSO_4$ gave a malt having 3% more diastatic activity than that from barley immersed in H_2O .

A. L.

Influence of different concentrations of chlorides on the growth of tomatoes. A. V. JURIEVA (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1065—1072).—The max. amount of NaCl tolerated by tomatoes is 0.2% of the dry wt. of soil. The stimulatory effect of 0.05% of NaCl is attributed to the direct ionic action and not to osmotic phenomena.

A. G. P.

Electrophysiological [plant] growth theory. K. RAMSHORN (Planta, 1934, 22, 737—766).—The potential gradient (I) in various plant organs is examined. Tropic responses in plants are correlated with changes in (I) which, in turn, control the translocation of growth-promoting substance.

A. G. P.

Effect of temperature on the growth and composition of Stayman and Baldwin apple trees. G. T. NIGHTINGALE and M. A. BLAKE (New Jersey Agric. Exp. Sta. Bull., 1934, No. 566, 20 pp.).—At 21°, both varieties grew well, and additions of NO_3' produced increased growth. At 7-2° growth was checked and leaves accumulated sugar (I), starch (II), and anthocyanin pigments (III). Treatment with NO_3' was followed by utilisation of carbohydrates (IV) and formation of org. N compounds, which in Stayman remained largely in the fine roots, but in Baldwin were translocated to aerial organs. At 35°, Baldwin lost (III), but made little growth, probably owing to exhaustion of (IV) and failure to reduce NO_3' . Degradation and translocation of (II) in older roots and stems was insufficient to meet requirements of leaves. Stayman produced more growth and was less unfavourably affected by the high temp. A. G. P.

Effects of temperature on the growth and metabolism of Elberta peach trees and growth responses of other varieties. G. T. NIGHTINGALE and M. A. BLAKE (New Jersey Agric. Exp. Sta. Bull., 1934, No. 567, 20 pp.).—Sand-cultured peach trees, starved of N, were unaffected by transference to greenhouse conditions at 11° and 21°, but at 35° new weakly growth was produced, and stored carbohydrate (I) decreased rapidly, protein breakdown and re-utilisation occurred, respiration increased, but CO_2 intake was low. In a similar series of plants to which NO_3' was given, little growth occurred at 11°. (I) accumulation remained high, respiration rates were low, and photosynthesis was active. NO_3' was absorbed by roots, but assimilation was limited. At 70°, NO_3' additions produced vigorous growth, with rapidly reduced (I) and appearance of org. N throughout the trees. NO_3' was completely assimilated in fine roots. At 35° NO_3' assimilation was very rapid, but growth was weak and leaves became mottled. A. G. P.

Effects of storage temperature on the propagation value of potato tubers. J. O. HARTMAN (Cornell Univ. Agric. Exp. Sta. Mem., 1934, No. 168, 39 pp.).—Tannin (I) vesicles are located at the base of young buds, but slowly disappear with advancing growth. Starch (II) grains appear in the cortex of buds when the latter develop to approx. 0.9 cm. in length. Walls of cells of very young leaves and apical tissue consist mainly of hemicellulose. In longer shoots (II) accumulation at the base is considerable, and (I) and solanine were abundant in and near the tips, green tips containing more than white tips. Microchemical changes in sprouts are related to the size of the sprout. Storage temp. affects the rate, but not the type, of the changes. A. G. P.

Factors affecting the development of the cotyledonary buds of the common bean, *Phaseolus vulgaris*. C. F. MORELAND (Cornell Univ. Agric. Exp. Sta. Mem., 1934, No. 167, 28 pp.).—Failure of lateral buds to develop is associated with a localised deficiency of N and, possibly, of carbohydrates. A. G. P.

Effects of increasing the iodine content of tomato plant on respiration and enzymic activity.

F. L. WYND (Ann. Missouri Bot. Gard., 1934, 21, 367—431).—Addition of KI (1—20 p.p.m.) to nutrient media depressed growth and caused loss of green colour and dropping of leaves. Small concns. increased respiration, peroxidase and invertase activity, which declined when larger proportions were used. With high [KI] catalase activity increased and oxygenase declined to small extents. Peptase was unaffected. CH. ABS. (p)

Internal atmosphere of apples. O. J. DOWD (Proc. Amer. Soc. Hort. Sci., 1933, 30, 162—163).—During growth the vol.-% of CO_2 declines and that of O_2 increases. CH. ABS. (p)

Physiological factors affecting the germination of seed maize. J. L. ROBINSON (Iowa Agric. Exp. Sta. Res. Bull., 1934, No. 176, 67—112).—Differences in the rates of germination and development of seed harvested in different stages of maturity are examined. During preliminary soaking in H_2O seed collected in immature stages absorbed more H_2O and lost more sugars and sol. N than did fully matured seed. In air-dry maize most sugars (I) were non-reducing. After soaking, nearly all (I) in seed and in the solution were reducing (I). Manuring of the crop with superphosphate did not influence the germination of the seed produced. A. G. P.

Distribution of water, dry matter, and nitrogen during the germination of *Impatiens balsamina*. L. H. WELSCH (Protoplasma, 1934, 22, 63—127).—During germination the extent and nature of development of, and the distribution of H_2O in, the seedling are controlled by the imbibitional properties of the protein matter. Translocation of cotyledon-N is limited to the upper portion of the hypocotyl (I) at an early stage, that to the lower portion of (I) and to roots ceasing entirely. Translocation of non-N dry matter proceeds steadily. Development of the lower portion of (I) ceases when the imbibition of the protein reaches a stable limit of approx. 0.1%. A. G. P.

Photodynamic phenomena in green and colourless strains of *Euglena gracilis*. O. JIROVEC and K. VACHA (Protoplasma, 1934, 22, 203—208).—The greater sensitivity to photodynamic influence of green than of colourless cultures is attributed to the O_2 excess due to assimilation. A. G. P.

Stimulation process in *Spirogyra* and *Vaucheria* and potential measurements in plant cells. K. UMRATH (Protoplasma, 1934, 22, 193—202).—In a no. of species examined the cell contents exhibited a negative potential with respect to that of the external medium. A. G. P.

Permeability of plant cells. H. BONTE (Protoplasma, 1934, 22, 209—242).—Substances insol. or sparingly sol. in lipins penetrate cell walls in accordance with their mol. vols. (I). Lipin-sol. or surface-active substances penetrate more rapidly than their (I) suggest. The mechanism of plasmolytic effects is examined. A. G. P.

Capacity of isolated plant protoplasts to be drawn into threads. H. PFELFFER (Kolloid-Z., 1935, 70, 26—31).—A discussion. E. S. H.

Chromosome and aster dimensions of dividing cells in regenerating tissues of *Clymenella*

torquata exposed to thiol and sulphoxide. F. S. HAMMETT (Protoplasma, 1934, 22, 173—178).—Chromosomes increase in thickness under the influence of $\cdot\text{SH}$ (glutathione), and become shorter and thinner under that of Ph_2SO . A. G. P.

Utilisation of nutrients by colonial bent (*Agrostis tenuis*) and Kentucky blue grass (*Poa pratensis*). H. B. SPRAGUE (New Jersey Agric. Exp. Sta. Bull., 1934, No. 570, 16 pp.).—In sand cultures the grasses showed a difference in tolerance of deviations from optimum nutrient composition. $(\text{NH}_4)_2\text{SO}_4$ was the dominant factor controlling growth, which was inversely related to the concn. of $(\text{NH}_4)_2\text{SO}_4$ supplied. The N content of tops and roots increased with the concn. of $(\text{NH}_4)_2\text{SO}_4$, which was probably absorbed in toxic amounts. NH_4Cl produced similar effects. Growth was increased by NaNO_3 , unaffected by Na_2SO_4 , and inhibited by NaCl to extents similar to those produced by NH_4Cl . Response to NaNO_3 at p_{H} 4.5 was $>$ that at 6.5. The $\text{PO}_4^{''}$ of tops and roots increased with that in the nutrient. No definite relationship existed between the $[\text{Ca}^{''}]$ and $[\text{Mg}^{''}]$ of the nutrient and the intake by the grasses. Tolerance of bent to acid conditions is not the result of a low Ca requirement. The ratio roots : tops was greatest in the more acid media. At p_{H} 4.5 NaNO_3 increased the tops without affecting roots, but at 6.5 root growth was much reduced. $(\text{NH}_4)_2\text{SO}_4$ did not affect the ratio at p_{H} 4.5, but decreased roots at 6.5. A. G. P.

Excretion of nitrogenous compounds from the root nodules of leguminous plants. A. I. VIRTANEN and S. VON HAUSEN (Nature, 1935, 135, 184—185).—The excretion of N compounds (mainly NH_2 -acids) from the nodules depends largely on the supply of air to the roots. It is not due to a decomp. of the nodule-proteins or to a mechanical wounding of the root hairs. The N fixation is assumed to occur at the surface of the bacterial cells in the nodule, and the N compounds formed are partly utilised by the host plant and partly diffused into the soil. L. S. T.

Natural regulation of protein metabolism in plants. K. PAECH (Planta, 1934, 22, 794—799).—Decomp. of protein in intact leaves is approx. the same in the presence or absence of O_2 and is paralleled by the consumption of carbohydrates. Synthesis or hydrolysis of protein is controlled by the relative balance of sugars or NH_3 . Breakdown of the cell structure, e.g., after 60—80 hr. in anaerobiosis, is the cause and not the effect of increased proteolysis. A. G. P.

Mechanism of the inter-conversion of hexose sugars in living organisms. K. M. DAQUD and W. TADROS (Biochem. J., 1935, 29, 225—237).—It is suggested that the formation of an intermediate polysaccharide constitutes one stage in the inter-conversion of hexoses in the living organism. Starch, besides being the principal reserve carbohydrate (I) of seeds and the (I) into which other sugar reserves are converted during germination, also plays a direct part in the hexose inter-conversion, for which the intact living seed is necessary. If enzymic extracts of germinated seeds act on (I) reserves *in vitro*, the end-products are identical with those obtained by

acid hydrolysis. The mannogalactan of carob and fenugreek (II) seeds gives rise to starch during germination, later hydrolysed to glucose by an amylase elaborated during germination. The fructosan formed in small quantities during germination of (II) seeds later diminishes or disappears. Possible mechanisms of inter-conversion are discussed. A. E. O.

Relation between the natural order of plants and their chemical composition. P. KLASOW (Svensk Papp. Tidn., 1934, 37, 302—306; Chem. Zentr., 1934, ii, 1938).—Differences in pentose : hexose ratio, type of lignin, and content of AcOH are cited as characteristic of plant families. A. G. P.

Plant reproductive cells. IV. Chemical constituents of the spores of *Aspidium filix mas*. A. KIESEL and G. SCHIPITZINA (Z. physiol. Chem., 1934, 229, 159; cf. A., 1926, 440).—Thymine, arginine, and lysine were identified in the acid hydrolysate of the spores. J. H. B.

Chemical composition of the round-leaved sundew (*Drosera rotundifolia*, L.). W. R. WITANOWSKI (Wiadomosci Farm., 1934, 61, 420—422, 432—433).—Freshly-dried plants contain BzOH , hydroxynaphthoquinones, and a naphthoquinone, droserone , $\text{C}_{11}\text{H}_8\text{O}_3$, m.p. 70—71°, sublimes at 100—110°/3 mm. (*oxime*, m.p. 151°), which on oxidation yields γ -coccinic acid. CH. ABS. (r)

Chinese perilla. Y. F. CHI (J. Chinese Chem. Soc., 1934, 2, 315—325).—The extract (34%) obtained from the leaves of Chinese perilla, *P. Nankinensis*, Deene, by EtOH contains some furfuraldehyde, and 2.5% of a volatile oil; this oil contains no perilla-aldehyde, but 1% of an aldehyde and more of a ketone, $\text{C}_{11}\text{H}_{16}\text{O}$, m.p. 11.5—12°, b.p. 114—116°/22 mm., $[\alpha]_{\text{D}} +1.713^\circ$ (*oxime*, m.p. 67°; *semicarbazone*, m.p. 240°). The non-volatile portion contains much glucose and a resin (I). Extraction of (I) with ligroin gives a mixture, from which, after treatment with $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and hydrolysis, are obtained hentriacontane, ceryl alcohol, a phytosterol, AcOH , PrCO_2H , a mixture of about equal parts of stearic and palmitic acids, and a mixture of oleic, linoleic, linolenic, and isolinolenic acids. Extraction of the ligroin-exhausted (I) with Et_2O yields *perillol*, $\text{C}_{22}\text{H}_{40}\text{O}_2$, $+2\text{H}_2\text{O}$, m.p. 271—272° [*acetate*, m.p. 193.5° (decomp. above 285° after resolidification)]. R. S. C.

Root of *Peucedanum decursivum*, Maxim (*Umbelliferae*). Y. F. CHI and Y. T. WONG (J. Chinese Chem. Soc., 1934, 2, 329—336).—These roots yield to EtOH tannins, glucose, a little AcOH , a substance, $\text{C}_{12}\text{H}_{18}\text{O}_4$ or $\text{C}_{15}\text{H}_{26}\text{O}_5$, m.p. 150—151°, and a resin which by hydrolysis affords a phytosterol (? spongosterol), AcOH , EtCO_2H , PrCO_2H , palmitic, stearic, oleic, and linoleic acids. R. S. C.

Constituents of *Orthosiphon* leaves. A. GOUDSWAARD (Pharm. Tijds. Nederl.-Indie, 1934, 11, 145—152; Chem. Zentr., 1934, ii, 1951).—The leaves of *Orthosiphon stamineus*, Benth., contain a *phytosterol*, m.p. 139°, and an unidentified substance, m.p. 192°. H. N. R.

Roots of *Citrullus colocynthis*, Schrader. R. R. AGARWAL and S. DUTT (Current Sci., 1934, 3, 250—251).— EtOH extraction of the powdered root gave

α -elaterin and hentriacontane. An impure saponin was also obtained. P. G. M.

Hemicelluloses of the wood of English oak.
II. Composition and properties of hemicellulose-A from samples of wood dried under various conditions. M. H. O'DWYER (Biochem. J., 1934, 28, 2116—2124; cf. A., 1932, 202).—The composition of hemicellulose-A (I) of oak wood is not affected by drying below 40°. Sapwood-(I) suffers degradation if the parent wood is dried above 40°, but heartwood-(I) is stable at 100°. Sapwood-(I), but not heartwood-(I), gives a blue colour with I, and the transition from the former to the latter in wood is accompanied by constitutional change in (I), including an increase in the content of methoxyaldobionic acid (II) residues. Both sapwood- and heartwood-(I) contain chiefly anhydroxylose residues combined with uronic acid and with (II) residues, the former acids predominating in sapwood-(I). The (II) residues are much more resistant to hydrolysis than the uronic acids. The insol. residue remaining after acid hydrolysis of (I) contains much less OMe than lignin, and is probably formed from (II). Glucose was not isolated as a product of hydrolysis of sapwood-(I), and the latter still gave a reaction with I after treatment with takadiastase. (I) may be of similar composition in all hardwoods. A. E. O.

Nature, distribution, and development of certain cell-wall constituents of plants. H. W. BUSTON (Biochem. J., 1935, 29, 196—218).—In developing pods of beans and sweet peas, the relative proportion of pectin (I) and hemicellulose (II) remains almost const. throughout the greater part of the growth period, but the (II) content decreases towards the close. In the development of the woody stem of the rose, the increase in lignin (III) runs parallel with increase in (II), but there is no loss of (I), which therefore does not constitute the source of (III) during primary lignification. The (II) content [but not the (I) content] of detached leaves falls when they are starved or slowly dried. (II) is more labile than (I) and may be available for respiration in these circumstances, the loss consisting mainly of hexose units and, to a smaller extent, of pentosan. Rapid growth is conducive to the formation of galactoarabans and (I). The "A" types of (II) in the leaves of the bean and vine consist mainly of galactose units, whilst the corresponding (II) for certain monocotyledon leaves (e.g., grass, maize; but not hyacinth and narcissus) is mainly a xylosan. The relation between (I) and (II) and lignification is discussed. (I) is the precursor of only a limited type of (II) viz., the arabans. A. E. O.

Bog-moss. II. Sphagnum cellulose. M. SHIKATA and M. WATANABE (Proc. Imp. Acad., Tokyo, 1934, 10, 608—611, and Mem. Coll. Agric. Kyoto, 1934, 33, 1—8; cf. A., 1932, 889).—This is best purified by chlorination and gentle boiling with 1% NaOH. It then gives glucose quantitatively and is more resistant to degradation by 17.5% NaOH, but less resistant to oxidation, than other celluloses. R. S. C.

Arbutin content of leaves of *Vaccinium vitis idaea*. R. GAGER and L. ZECHNER (Pharmaz. Mh.,

1934, 15, 93—95; Chem. Zentr., 1934, ii, 1474).—Cranberry leaves contain appreciable amounts of arbutin (I), the min. occurring in June, the period of max. growth. It is concluded that (I) is a reserve material. (I) is found, in smaller amounts, in other parts of the plant. H. N. R.

Formation of diketones from the ingredients of tobacco. C. NEUBERG and M. KOBEL (Biochem. Z., 1935, 275, 339—343).—Dry distillation of citrus pectin gave 0.066%, of tobacco pectic acid 0.069%, and of meso-inositol 0.135% of Ac₂O. Dry distillation of Zn lactate gave 0.425% of AcCOEt. P. W. C.

Saponin from soya bean. R. C. BURRELL and E. D. WALTER (J. Biol. Chem., 1935, 108, 55—60).—Soya beans are extracted with EtOH, and the residue is electro-dialysed and extracted with Et₂O. Crystals of a saponin (I) separate from the EtOH solution of the residue identical with those previously found (A., 1931, 1304). Galactose and possibly rhamnose are present in the hydrolysate from (I), also a *sapogenin*, m.p. 198—200°, C 77.8, H 11.13%, $[\alpha]^{25}_D +73.7^\circ$ in CHCl₃. H. D.

Plant-phosphatides and lecithin. III. Phosphatides of wheat germ. W. DIEMAIR and B. BLEYER (Biochem. Z., 1935, 275, 242—247).—The phosphatide-fatty acids consist chiefly of palmitic and linoleic acids and the bases of choline and colamine. The ratio of saturated to unsaturated acids is 1 : 5. P. W. C.

Biogenesis of some terpenes.—See this vol., 351.

Purification of chlorophyll. H. A. BAKKER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 679—684).—Details of an improved extraction (in dark, or in green light) of chlorophyll (I) (0.5 g., 97% pure by Mg determination) from the dried leaves (75 g.) of *Brassica oleracea*, var. *acephala*, by a combination of the methods of Willstätter *et al.*, Winterstein *et al.* (A., 1934, 91), and Tswett (chromatographic adsorption, A., 1907, ii, 144) are given. No evidence of the presence of a third component of (I) (Zscheile, A., 1934, 1115) was obtained. J. W. B.

Photodecomposition of chlorophyll. B. HUBERT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 684—688).—When the colour curves, obtained by Weigert's method (A., 1916, ii, 545), for chlorophyll (I) (fresh spinach) are plotted at 15 min. intervals, log *E* decreases with time between 590 and 700 m μ but increases between 500 and 590 m μ . In the range 625—680 m μ the decrease is homogeneous, suggesting a decrease in concn., and at 700 m μ an increase in the concn. of some substance (II), produced by photodecomp. of (I), is indicated. The grey zone (confirmed) in Tswett's chromatogram (A., 1907, ii, 144) may correspond with (II). Weigert's colour curve for (I) may be obtained with partly photo-decomposed (I). J. W. B.

Colouring matters of fungi. XI. Boletol, the colouring matter of the blue-coated *Boletus*. XII. Synthesis of boletol and isoboletol.—See this vol., 347.

Flavin-like pigment from linseed. H. WILLSTAEDT (Svensk Kem. Tidskr., 1934, 46, 259—261).—

Aq. NaCl extracts of various materials [eggs, linseed (I), etc.] which produce allergic symptoms in sensitive persons (II) frequently exhibit a yellowish-green fluorescence on ultra-violet irradiation. (III). Aq. ovo- and lacto-flavin, however, are inactive when tested on the skin of (II), by the Schultz-Dale guinea-pig uterus method, or by complement formation. Addition of EtOH (1 vol.) to aq. extracts of (I) gives filtrates (containing both flavin and allergic principle) which, on acidification after, but not before, treatment with 2*N*-NaOH and (III), yield a pigment on extraction with CHCl_3 ; this pigment resembles known flavins in its rapid adsorption on freshly pptd. PbS, but not on fuller's earth, and in its colour reaction with Zn in 10% HCl (A., 1934, 461). F. O. H.

Carotenes from roots and leaves at various stages of development. G. MACKINNEY (J. Biol. Chem., 1935, 108, 45—49).—Carotene (I) was extracted by the method of Smith (A., 1932, 619) modified by saponification of the light petroleum extract with KOH-MeOH before concn. Both components of (I) were obtained from individual carrot roots (II). There was no marked variation with age in the proportions of the components of (I) in (II) and in the leaves of *Hedera helix* and *Sequoia sempervirens*. H. D.

Extraction of carotene from carrot juice. G. ROSENBERG (Bull. Soc. Chim. biol., 1934, 16, 1761).—The carotene (I) is adsorbed by PbO-Pb(OAc)_2 (1 : 3), and eluted with light petroleum. The extract is saponified with KOH in EtOH. The (I) is transferred to CS_2 and pptd. by EtOH. A. L.

Products of oxidation of carotenes. Carotenoid of *Thiocystis* bacteria.—See this vol., 340.

Nitrogen metabolism of the apple fruit. I. Determination of amino-nitrogen by the Van Slyke method in presence of tannin. A. C. HULME (Biochem. J., 1935, 29, 263—271).—Abnormally high vals. obtained for $\text{NH}_2\text{-N}$ in apple extracts (I) by the Van Slyke method are due to the presence of tannin, which can only partly be removed from (I) (although almost completely from pure solution) by pptn. with caseinogen, but is completely removed by pptn. with $\text{K}_2\text{Cr}_2\text{O}_7$, without affecting $\text{NH}_2\text{-}$ or acid-amide groups. A. E. O.

Nicotyrine in tobacco. A. WENUSCH (Biochem. Z., 1935, 275, 361).—Dried Brazilian tobacco (I) contains nicotyrine (II) [isolated as picrate from the distillate obtained on subjecting (I) to steam-distillation in presence of KOH]. Possibly (II) does not occur in the plant, but is produced from nicotine during fermentation because of the absence from the leaves of reducing substances. W. McC.

Protoplasm. V. Nucleic acid and the nucleoproteins of pea embryos. A. KIESEL and A. BELOZERSKY (Z. physiol. Chem., 1934, 229, 160—166).—Pea embryos contain two nucleoproteins differing in $\text{NH}_2\text{-}$ acid content and in solubility, one being sol. in H_2O , the other in alkali. On hydrolysis they yield constituents similar to those of animal nucleic acid. There is no evidence for a basic,

protamine- or histone-like substance in the protein constituent. J. H. B.

Alkaloid of the seeds of *Leonurus sibiricus*, L. C. F. SHU (J. Chinese Chem. Soc., 1934, 2, 337—339).—The seeds contain *leonurinine*, $\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$, m.p. 262—263° (decomp.). R. S. C.

Misconceptions relative to the mineral composition of plants. W. THOMAS (Science, 1934, 80, 587).—A discussion. L. S. T.

Method for bleaching leaves. I. McVEIGH (Stain Tech., 1935, 10, 33—34).—Leaves are bleached in 5% NaOCl after rinsing in 95% EtOH. H. W. D.

Lugol's solution for the Flemming triple stain. L. A. MARGOLENA (Stain Tech., 1935, 10, 35—36).—The application of alcoholic Lugol's solution after safranin and after crystal-violet improves, hastens the differentiation of, and stabilises preps. of botanical material stained by Flemming's method. H. W. D.

Micro-nephelometry and its application to certain irradiated living tissues. W. M. MILLAR (Radiology, 1934, 23, 294—298).—A combination of microscope and photo-electric cell is described. Irradiation did not alter the opacity of ovalbumin, but did affect tadpole tissue. CH. ABS. (p)

Rapid standardisation of protein extracts by determining the nitrogen content. V. L. COHEN (J. Allergy, 1933, 5, 70—73).—The method is based on that of Hubbard and Sly (A., 1933, 1181). CH. ABS. (p)

Determination of glyoxaline compounds in urine, faeces, and sera. M. LOEPER, A. LESURE, and A. THOMAS (Bull. Soc. Chim. biol., 1934, 16, 1385—1409).—A modification of the method of Hanke and Koessler (A., 1919, ii, 67) for the determination of substances containing the glyoxaline group in blood (I), urine (II), and faeces (III) is described. (I) contains ≥ 30 , (II) ≥ 300 , and (III) ≥ 100 mg. per litre. A. L.

Diazo-reaction of histidine.—See this vol., 370.

Determination of very small amounts of thiocyanate in biological fluids. F. HARTNER (Mikrochem., 1935, 16, 141—152).—2 c.c. of liquid are deproteinised with $\text{CdSO}_4 + \text{NaOH}$, glutathione being thereby removed simultaneously. The liquid is acidified with HNO_2 -free HNO_3 , NaCl added, and AgCNS pptd. by 0.5*N*-AgNO₃. The ppt. is converted into AgBr by 0.8 c.c. of 10% NaBr. To the solution, containing CNS', 1 c.c. of 0.0001*N*-KBrO₃ is added and the solution acidified with HCl in a stoppered tube. Na_2HPO_4 is added as a buffer, KI added, and the I liberated by excess of Br titrated with 0.001*N*- $\text{Na}_2\text{S}_2\text{O}_3$. The alternative oxidation of CNS' with 0.001*N*-I⁺-KI in alkaline solution tends to give erratic results. J. S. A.

Modifications of Leusden's method for determining carbon dioxide. T. AKABA (Sei-i-kwai Med. J., 1933, 52, 146—155).—The use of 0.07% Ba(OH)_2 solution containing 4 c.c. of phenolphthalein solution (0.04% in 50% EtOH) per litre, and of a 45-c.c. reservoir is recommended. CH. ABS. (p)

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1935.

General, Physical, and Inorganic Chemistry.

Ground state of H_2 . H. M. JAMES and A. S. COOLIDGE (J. Chem. Physics, 1935, 3, 129—130).—A correction and addition to a recent paper (A., 1934, 23). F. L. U.

The two-quantum Σ -states of the hydrogen molecule. R. D. PRESENT (J. Chem. Physics, 1935, 3, 122—128).—Results of calculations for two of the two-quantum states are given. F. L. U.

Effect of a strong electric field on light emission of para-helium in the extreme ultra-violet. H. BOMKE (Physikal. Z., 1935, 36, 158—161).—A positive-ray tube for the investigation of the Stark effect at very high field strengths is described. An electrical splitting of the para-He series $1S-mP$ could not be observed. Four He lines were ascribed to the new series $1S-mS$ and $1S-mD$. A. J. M.

Intensity modifications of the helium spectral lines emitted by high-frequency excitation. S. MATSUDA (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 2, A, 115—123).—The intensities of lines excited by high-frequency and an ordinary transformer are compared for the range 7300—2400 Å. N. M. B.

Ultra-violet absorption band of Li_2 . J. E. VANCE and J. R. HUFFMAN (Physical Rev., 1935, [ii], 47, 215—216).—Data, assignments, and a vibrational analysis are given for 60 band heads in the range 3100—3500 Å. N. M. B.

Fine structure of the components in the Paschen-Back effect of multiplets. P. JACQUINOT (Compt. rend., 1935, 200, 383—384).—In agreement with theory, the Li 6707 Å. doublet gives Paschen-Back effect components which themselves show fine structure. J. W. S.

Interpretation of band spectroscopic results nitrogen. N. R. TAWDE (J. Univ. Bombay, 1934 3, No. 2, 53—57).—Rydberg's conclusions are tested (cf. A., 1932, 104). D. R. D.

Excitation of band spectra: rotational structure. G. O. LANGSTROTH (Canad. J. Res., 1935, 12, 13).—The contours of three second positive N bands change in shape as the energy of the exciting electrons is varied. The results can be explained when there is a probability that an impinging electron will excite the electronic configuration of a mol. and then interact with the rotation before escaping from a mol. field. E. S. H.

Spectra F III, F II, and F I. B. EDLEN (Z. Physik, 1935, 93, 433—449). A. B. D. C.

Magnetic weakening of the fluorescence of Te. and S.. I. I. AGARBICEANU (Compt. rend., 1935, 200, 385—386).—Theoretical. J. W. S.

Interference measurements in the infra-red arc spectrum of iron. W. F. MEGGERS (J. Res. Nat. Bur. Stand., 1935, 14, 33—40).—Wave-length data are given, relative to Ne standards, for the 91 strongest lines in the range 7164.469—10216.351 Å. characteristic of integrated light from an Fe arc at atm. pressure and measured by the Fabry-Perot interferometer. Deviations from the vals. obtained from the vac. arc are interpreted as pressure and Stark effects. The use of integrated light from an Fe arc at atm. pressure for infra-red sub-standard $\lambda\lambda$ is suggested. J. W. S.

(A) Absolute intensity of the zinc resonance line 3076 Å. and the life period of the 2^3P_1 state of zinc. (B) Isotope displacement effect with the 3076 Å. zinc resonance line. W. BILLETER (Helv. phys. Acta, 1934, 7, 505—513, 524—536; Chem. Zentr., 1934, ii, 2364).—(A) Vals. are recorded. The life period of the 2^3P_1 state of Zn (2.6×10^{-5} sec.) is $>$ that of Cd (2.5×10^{-6} sec.) or Hg (1×10^{-7} sec.). (B) Analysis of the hyperfine structure shows an effect attributed to Zn^{64} , Zn^{66} , and Zn^{68} . H. J. E.

Structure of Br III. K. R. RAO and S. G. KRISHNAMURTY (Nature, 1935, 135, 309).—The spark spectrum of Br has been photographed over the range 450—7000 Å. The structure identified for Br III is analogous to that of Se II. L. S. T.

Zeeman splitting of lines of krypton I, argon I, and xenon I spectra. B. POGANY (Z. Physik, 1935, 93, 364—377). A. B. D. C.

Spectrum of molybdenum I. II. M. A. CATALAN and P. DE MADARIAGA (Anal. Fis. Quím., 1933, 31, 707—734).—644 lines between 2326 and 9767 Å. are classified in quintet and septet levels. Kiess' fundamental limit (a^7S), 59,560, is not satisfactory, but $57,200 \pm 200$ gives vals. analogous to those for the other elements of the same period, except for the 7s term, which is regarded as fictitious. The ionisation potential is 7.06 volts. H. F. G.

Molecular spectrum of cadmium vapour. J. K. ROBERTSON (Nature, 1935, 135, 308—309).—The view that Cd can emit light of λ 2212 Å. is maintained (cf. A., 1934, 1147). L. S. T.

Molecular spectrum of cadmium vapour. J. G. WINANS and S. W. CRAM (Nature, 1935, 135, 344—345).—Evidence is discussed indicating that

the emission max. at 2212 Å. in the Cd arc is due to an impurity. L. S. T.

Nuclear moments of tellurium and selenium isotopes. S. RAFALOWSKI (*Acta Phys. Polon.*, 1933, 2, 119—123).—From hyperfine structure measurements of the arc spectrum of Te and Se, the even isotopes of Te and Se have zero nuclear moments. CH. ABS. (e)

Spectrum of doubly-ionised iodine. J. B. SETH (*Nature*, 1935, 135, 269).—Most of the terms have been identified in the 6s and 6p levels and a few in the *od* level. L. S. T.

Iodine spectra of feeble excitation. G. BALASSE and (MLLE.) GALET (*Bull. Acad. roy. Belg.*, 1935, [v], 21, 87; cf. A., 1930, 830).—A correction. N. M. B.

Nuclear moment of holmium (Ho^{165}). H. SCHULER and T. SCHMIDT (*Naturwiss.*, 1935, 23, 69).—Most of the lines in the range 4000—6500 Å. show a hyperfine structure, the commonest being made up of eight lines with decreasing distances apart and intensities. The nuclear moment is $7/2$. A. J. M.

Hyperfine structure in the hafnium spectrum. E. RASMUSSEN (*Naturwiss.*, 1935, 23, 69—70).—The lines at 5550, 5452, 5373, 5243, and 4655 Å. are very narrow doublets; weaker components are found at greater distances. The strong lines are due to Hf^{178} and Hf^{180} , the weaker components being due to the magnetic separation of Hf^{177} and Hf^{179} . Isotopic displacements are very small; lines 5613, 5552, 4837, and 4000 Å. show none. The nuclear moment is probably $\frac{1}{2}$, and is certainly $\geq 3/2$. A. J. M.

Fine structure of the mercury line 5461 Å. in absorption. H. C. BURGER and P. H. VAN CITTERT (*Physica*, 1935, 2, 87—96).—Measurements by a modification of the Fabry-Perot interferometer giving multiple interference are recorded. H. J. E.

Intensity distributions of spectral lines and emission of the continuous spectra in luminous mercury vapour. M. FUKUDA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, 26, 21—32).—Intensities of Hg lines (I) appearing in the luminous glow have been compared with (I) in the arc (II). The variation of (I) with the distance from (II) has been studied, and the origin of the continuous spectra is attributed to collision of free electrons and ions. R. S.

Absorption by metastable thallium atoms. F. MULLER (*Helv. phys. Acta*, 1934, 7, 488—491; *Chem. Zentr.*, 1934, ii, 2363).—Absorption measurements of $\lambda\lambda$ 5350 and 3530 Å., arising from the metastable $6^2P_{3/2}$ state, are recorded for various temp. and used to calculate the concn. of metastable atoms. H. J. E.

Spectra of Pb IV and Bi V. G. K. SCHOEPFLE (*Physical Rev.*, 1935, [ii], 47, 232—234).—For Pb IV, 34 term vals. and classifications of 79 lines in the region 198—5005 Å., and for Bi V 14 term vals. and classifications of 18 lines in the range 176—1487 Å., are tabulated. Ionisation potentials are 42 and 55.7 volts, respectively. N. M. B.

Quadratic Zeeman effect in the principal series of sodium. E. SEGRÈ (*Nuovo Cim.*, 1934, 11, 304—308; *Chem. Zentr.*, 1934, ii, 2499). H. J. E.

Atmospheric bands in the ultra-violet. F. W. P. GOTZ (*Arch. Sci. phys. nat.*, 1934, [v], 16, 266—268).—A summary and discussion of recent results and their bearing on the distribution of O_3 with altitude. N. M. B.

Ozone and oxygen in planetary atmospheres. R. WILDT (*Nachr. Ges. Wiss. Gottingen*, 1934, [ii], 1, 1—9; *Chem. Zentr.*, 1934, ii, 2176; cf. A., 1933, 587).—The O_3 content of the atm. of Uranus cannot, from spectrographic data, exceed the equiv. of 0.5 cm. under normal conditions. J. S. A.

Comparison of atmospheric extinction in the ultra-violet and visible spectrum. P. ROSSIER (*Arch. Sci. phys. nat.*, 1934, [v], 16, Suppl., 68—72).—A correction must be applied to the usual equations when observations are not made at the zenith. F. L. U.

Light of the night sky. J. KAPLAN (*Nature*, 1935, 135, 229).—The auroral green line has been excited by a rapidly interrupted discharge through $\text{N}_2 + 1\% \text{O}_2$. The conditions indicate a manner of production similar to that in the light of the night sky. L. S. T.

Spectrum of Nova Herculis, 1934. A. BEER and F. J. M. STRATTON (*Nature*, 1935, 135, 346).—Forbidden lines of O I are prominent. L. S. T.

Spectrum and composition of the gaseous nebulae. I. S. BOWEN (*Astrophys. J.*, 1935, 81, 1—16).—H is the most abundant element and He is the next. N, O, Ne, S, and possibly C and A, are present, but much rarer. L. S. T.

Redward shift of spectral lines of nebulae. P. I. WOLD (*Physical Rev.*, 1935, [ii], 47, 217—219).—An explanation is proposed, based on the characteristics of a wave travelling in a medium in which the velocity of light is a function of time. N. M. B.

Absolute wave-length of the aluminium $K\alpha_{1,2}$ line determined by the plane lattice method. E. BACKLIN (*Z. Physik*, 1935, 33, 450—463).—This is given as 8.3395 Å., and leads to the val. 4.805×10^{-8} e.s.u. for the electronic charge. A. B. D. C.

Emission lines and absorption edges in the L series of barium and caesium. G. KELLSTROM and B. B. RAY (*Ark. Mat. Astr. Fysik*, 1934, B, 24, No. 13, 5 pp.; *Chem. Zentr.*, 1934, ii, 2495).—Data are recorded and discussed. H. J. E.

O series of Rontgen spectra. M. SIEGBAHN and T. MAGNUSON (*Ark. Mat. Astr. Fysik*, B, 24, No. 27; *Chem. Zentr.*, 1934, ii, 2174).—A line attributed to the O series has been identified in the Th spectrum. J.

Higher series of Rontgen spectra. M. SIEGBAHN and T. MAGNUSON (*Ark. Mat. Astr. Fysik*, 1934, B, 24, No. 6; *Chem. Zentr.*, 1934, ii, 2174).—Lines attributed to transitions between N and levels are given by the elements from Cs to Eu, not by preceding or following elements. Tl, Pb, ,

Th, and U also give series attributed to transitions $O \rightarrow P$ or $N \rightarrow O$. J. S. A.

Equilibrium emission and activity changes in oxide-coated cathodes. A. J. MADDOCK (Phil. Mag., 1935, [vii], 19, 422—436).—Investigation of cathodes having a mixture of BaO and SrO on a Ni core at various temp. indicate that a layer of Ba exists at the outer oxide surface giving the enhanced emission, and that for any temp., equilibrium is reached when the rate of loss of Ba by temp. evaporation equals the rate of gain by diffusion from the body of the oxide; the higher is the temp. the less is the amount of surface covered. High-temp. treatment alone is sufficient for the ageing process; cathodes after such treatment show high activity. Curves of activation and deactivation at various temp., and data for the loss of emission on flashing at temp. $>$ normal, are given. N. M. B.

Pressure displacement of spectral lines near the series limit. C. REINSBERG (Z. Physik, 1935, 93, 416—426).—Theoretical. If the Ramsauer cross-section for slow electrons has a min. the displacement is towards the red, otherwise towards the violet. A. B. D. C.

Growth of an electron stream and the calculation of the current strength in a gas discharge that is not self-sustaining. N. KAPITZOV (Physikal. Z. Sovietunion, 1934, 6, 82—120). CH. ABS. (e)

Electric moment of an electron. A. LEES (Proc. Camb. Phil. Soc., 1935, 31, 94—98).—The views of Frenkel and Dirac regarding an electron possessing an electric moment in addition to a magnetic moment are analysed. An electron does not possess an electric moment. W. R. A.

Electrical density and electronic radius. E. REICHENBACHER (Physikal. Z., 1935, 36, 173—177).—Theoretical. A. J. M.

Possible physical interpretations of negative energy electrons. H. MANDEL (Z. Physik, 1935, 93, 329—337).—A theory equiv. to that of Dirac is given. A. B. D. C.

Production of positive electrons by β -rays. D. SKOBELZYN and (Miss) E. STEPANOVA (J. Phys. Radium, 1935, [vii], 6, 1—11).—A cloud-track investigation was made of the β -radiation emitted by RaBr_2 . Positrons are produced by the passage of Ra-C β -rays through thin layers of C, celluloid, etc. Velocity distribution analysis shows that the emission intensity is inversely \propto (positron energy)². The effective cross-section of the Pb atom, \propto (at. no.)², is of the order 10^{-22} cm. Results appear to diverge from Dirac's theory of positron production. N. M. B.

Artificially excited positrons. C. RAMSAUER (Z. Physik, 1935, 93, 432; cf. Rupp, this vol., 139). A. B. D. C.

Production of ions in a high vacuum. R. FLANJO (Compt. rend., 1935, 200, 539—540).—A definite velocity and a mol. jet of the substance of which ions are required are all to impinge at right angles in a very high vac. Ions produced by collision of a mol. with one

electron are taken off at right angles to the two beams by a low-intensity electric field before further collisions can occur. J. W. S.

Accommodation coefficient of mercury ions on a mercury surface. R. C. MASON (Physical Rev., 1935, [ii], 47, 241—248).—The anomalously high pressures exerted on a Hg surface to which were attracted Hg positive ions produced in a Hg arc are explained on the hypothesis that each ion sputters a large no. of atoms and the reaction on the surface of these escaping sputtered atoms gives the observed forces. The observed force was a linear function of the energy of the ions. The limits found for 1000-volt ions, where a =accommodation coeff., n =no. of atoms sputtered per ion, and V_s =electron volt equiv. energy of the sputtered atoms, were $100 > n > 7.8$; $0.92 > a > 0$; $0.78 < V_s < 128$. N. M. B.

Molecular scattering by gases. L. F. BROADWAY (Z. Physik, 1935, 93, 395—396).—Knauer's criticism (A., 1934, 1150) of systems lacking cylindrical symmetry is refuted. A. B. D. C.

Molecular scattering in gases. F. KNAUER (Z. Physik, 1935, 93, 397).—A reply to Broadway (cf. preceding abstract). A. B. D. C.

Recent at. wt. determinations [of carbon, nitrogen, and fluorine]. W. CAWOOD (Nature, 1935, 135, 232—233).—Limiting ratios of N_2O , C_2H_4 , CO_2 , and CF_4 with O_2 have been determined using an improved micro-balance. At. wts. obtained are N 14.006(8), C 12.012(2) and 12.010(1) from C_2H_4 and CO_2 , respectively, and F 18.995. Calc. compressibilities at 21° are N_2O 0.00559, C_2H_4 0.00636, CO_2 0.00522, and CF_4 0.00418. The high val. for C is in agreement with other recent determinations and 12.01 is probably the best val. for C. This indicates the presence of approx. 1% of C^{13} . A repetition of the measurements with MeF using the new apparatus confirms the val. 18.995 for F in preference to 19.01 (A., 1931, 1207). L. S. T.

Rare earths. XLIII. I. At. wt. of europium. II. Specific gravity of europium chloride. E. L. MEYERS [with B. S. HOPKINS] (J. Amer. Chem. Soc., 1935, 57, 241—243).—The ratio $\text{EuCl}_3 : \text{Ag}$ gives the at. wt. of Eu 152.30 ± 0.018 (cf. Aston's val., 151.9; A., 1934, 1150). EuCl has d^{35} 4.471. E. S. H.

Radioactivity: old and new. (LORD) RUTHERFORD (Nature, 1935, 135, 289—292).—A lecture. L. S. T.

Investigation of the upper limit of the thorium $\text{C}+\text{C}''$ β -ray spectrum by means of the Wilson cloud chamber. P. C. HO (Proc. Camb. Phil. Soc., 1935, 35, 119—124).—The upper limit of the continuous $\text{Th-C}+\text{C}''$ β -ray spectrum is $9250H_p$, and no β -particles of higher energy were observed. The val. is in good agreement with vals. obtained by Henderson (this vol., 275). W. R. A.

Studies with thorium- C'' . J. ZIRKLER (Z. Physik, 1935, 93, 477—478).— $\text{Th-C}''$ can be used as an indicator despite its short life. A. B. D. C.

Scattering of hard γ -rays and annihilation radiation. E. J. WILLIAMS (*Nature*, 1935, **135**, 266).

L. S. T.

Slowing down of neutrons by collisions with hydrogen nuclei. C. H. WESTCOTT and T. BJERGE (*Proc. Camb. Phil. Soc.*, 1935, **31**, 145—152).—Neutrons are more readily captured by various atoms when their kinetic energies are reduced by hydrogen nuclei (cf. Fermi *et al.*, *A.*, 1934, 1284). The neutron source was surrounded by various thicknesses of H_2O and the no. of neutrons captured by an apparatus consisting of two semi-cylinders of Ag sheet exposed to neutron bombardment for 1 min. determined by Geiger-Müller counter. Collision cross-sections for primary neutrons and for slow neutrons have been determined. The nature of the "gas" of slow neutrons is discussed, but no definite conclusion regarding the energy of the neutrons concerned is reached.

W. R. A.

Attempt to detect spontaneous emission of neutrons photographically. S. PIENKOWSKI and J. STARKIEWICZ (*Acta Phys. Polon.*, 1933, **2**, 105—110).—Swientoslawski and Dorabialska's results (*A.*, 1933, 335) were not confirmed.

CH. ABS. (e)

Selective capture of slow neutrons by certain nuclei. F. PERRIN and W. M. ELSASSER (*Compt. rend.*, 1935, **200**, 450—452).—Neutron energy and effective cross-section of neutrons and nuclei are considered.

N. M. B.

Directed diffusion or canalisation of slow neutrons. F. L. HOPWOOD and T. A. CHALMERS (*Nature*, 1935, **135**, 341—342).—Neutrons are directed or canalised along tubes having walls made of a material such as paraffin wax with high H content. Graphite, but not impure ebonite, gives a small effect.

L. S. T.

Artificial radioactivity. A. I. ALICHANOV, A. I. ALICHANIAN, and B. S. DŽELEPOV (*Z. Physik*, 1935, **93**, 350—363).—The limit of continuous positron radiation is 3.7×10^6 for P and 1.45×10^6 volts for N_2 , and that of electron radiation from Mg is 3.05×10^6 volts.

A. B. D. C.

Artificial radioactivity excited in gold and the complexity of its radiation. L. SOSNOWSKI (*Compt. rend.*, 1935, **200**, 391—393).—Bombardment of Au by neutrons from Be irradiated with Ra γ -rays yields a radioactive material of half-life $2\frac{1}{2}$ days and emitting β -rays. The velocity distribution is the same as with the radioactive Au produced by neutrons from Be bombarded by α -rays (*A.*, 1934, 1284). A γ -radiation of 2.5×10^5 e.v. has been observed, but it is not associated with the main β -radiation, since its half-life period is only 5 hr.

J. W. S.

Radioactivity excited in platinum by neutrons. L. SOSNOWSKI (*Compt. rend.*, 1935, **200**, 446—447).—Investigation by a Geiger-Müller counter and by retardation in Al of the radiation from Pt activated by slow neutrons from a Be source irradiated by Ra γ -radiation indicated the emission of β -particles of energy 1.5×10^6 e.v., due to the isotopic transformation $\text{Pt}^{78} \rightarrow \text{Au}^{79}$.

N. M. B.

Detection of nuclear disintegration in a photographic emulsion. H. J. TAYLOR and M. GOLD-HABER (*Nature*, 1935, **135**, 341; cf. this vol., 277).—Exposure of a photographic plate treated with borax to a Rn-Be neutron source produces numerous short straight tracks of which the equiv. in air is 1.1 ± 0.1 cm. These are due to the disintegration of B by slow neutrons: $\text{B}^{10} + n^1 \rightarrow \text{Li}^7 + \text{He}^4$, which requires a mass of 10.011 ± 0.001 for B^{10} . With Li-impregnated plates, tracks corresponding with the reaction $\text{Li}^6 + n^1 \rightarrow \text{He}^4 + \text{H}^3$ have been obtained. Their lengths represent the sum of the ranges of the two resultant particles, which is 6.9 ± 0.2 cm. in air.

L. S. T.

Range of disintegration particles obtained from lithium and boron by bombardment with protons. S. KIKUCHI, S. NAKAGAWA, and H. AOKI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **26**, 33—35).—The results of Oliphant *et al.* (cf. *A.*, 1933, 1100) have been confirmed. No evidence of additional particle groups could be obtained.

R. S.

Nuclear transformation of nitrogen by fast α -rays. O. HAXEL (*Z. Physik*, 1935, **93**, 400—410).—N gives O^{17} and a radioactive nucleus of half-life 1.2 min.

A. B. D. C.

Nuclear chemistry. K. K. DARROW (*J. Chem. Educ.*, 1935, **12**, 76—82).

L. S. T.

Ionisation by cosmic and radioactive radiation at different gas pressures. Influence of the wall of the vessel. Disintegration of heavy atoms by cosmic rays. J. CLAY (*Physica*, 1935, **2**, 111—124).—Vals. are recorded for the ionisation (I) in A up to 100 atm. A method of separating (I) due to particles originating in the gas from that due to particles emitted by the walls is described. From Fe walls particles of range 1 cm. in 78 atm. of A were observed. With Au or Pb walls other particles, of much higher energy, were emitted. An intermediate photon radiation is indicated.

H. J. E.

Secondary effects of cosmic rays. P. AUGER and A. ROSENBERG (*Compt. rend.*, 1935, **200**, 447—449).—From the effect of Pb screens the mechanism is proposed for the production of electron clusters of two signs from matter subjected to cosmic rays.

N. M. B.

Classification of radiations in the complete system of cosmic rays. H. GEIGER and E. FUNFER (*Z. Physik*, 1935, **93**, 543—555).

A. B. D. C.

Attempt to detect the neutrino. M. E. NAHMAS (*Proc. Camb. Phil. Soc.*, 1935, **31**, 99—107).—The magnetic moment of a neutrino is shown experimentally by different methods to be $< 2 \times 10$ Bohr magneton.

W. R. A.

Ionisation power of a neutrino with magnetic moment. H. A. BETHE (*Proc. Camb. Phil. Soc.*, 1935, **31**, 108—115).—Mathematical. The no. of ions produced by a neutral particle of small mass with a magnetic moment of n Bohr magnetons is $103n^2$ per km. path in air at n.t.p. and is practically independent of the mass and energy of the particle. A large fraction of secondary electrons produced have high energy and may be counted if they are

produced in the wall of the Geiger counter instead of in the counter itself. W. R. A.

Neutrino theory of light. P. JORDAN (Z. Physik, 1935, 93, 464—472).—The light field is assumed to consist of neutrinos the interaction of which with electric charge gives the appearance of light quanta. A. B. D. C.

Nuclear synthesis and stellar radiation. H. J. WALKER (Phil. Mag., 1935, [vii], 19, 341—367; cf. this vol., 7, 275).—A general survey of the relations of annihilation of matter, synthesis of elements, and the nature of cosmic radiation. A complete theory of nuclear synthesis by neutron capture and β -radioactivity is proposed. The neutron is regarded as the fundamental nuclear component; protons and α -particles are formed mainly within nuclei as a result of the β -radioactivity of missing isotopes. N. M. B.

Interaction between matter and the magnetic field. L. DE BROGLIE (Compt. rend., 1935, 200, 361—363).—Theoretical. J. W. S.

Relation between vector and linking Eigenfunction methods for spin degeneracy. R. S. BEAR and H. EYRING (J. Chem. Physics, 1935, 3, 93—106; cf. A., 1934, 7).—Mathematical. F. L. U.

Precision light absorption measurements with a prism mirror spectrometer and thermoelement. H. GUDE (Z. Physik, 1935, 93, 388—394).—Wadsworth and Leiss systems are discussed. A. B. D. C.

Temperature variation method to assist in vibrational analyses of complex molecular spectra. J. H. CLEMENTS (Physical Rev., 1935, [ii], 47, 220—224).—The initial (lower) vibrational levels of the absorption bands of an electronic band system of a polyat. mol. are determined from photometric measurements of the absorption at two temp. not widely separated. The method is restricted to spectra in which the rotation lines are fairly broad compared with the intervals between them, or are very closely spaced. N. M. B.

Measurement of intensity distribution and width of predissociation lines of the AlH molecule. L. FARKAS and S. LEVY (Z. Physik, 1935, 93, 427).—Measurements have been made to determine reflexion coeffs. (cf. A., 1934, 1051). A. B. D. C.

Ultra-violet band spectrum of magnesium hydride and magnesium deuteride. A. GUNTSCHE (Z. Physik, 1935, 93, 534—538).—Predissociation has been detected in both mols. A. B. D. C.

Band spectrum of barium hydride at 10,000 Å. W. WATSON (Physical Rev., 1935, [ii], 47, 213—217; cf. A., 1933, 207).—Frequencies and combination differences for the 10,052 Å. band are tabulated. The state and origin of this and the 8924 Å. band are discussed. N. M. B.

Absorption spectrum of sulphur dioxide. J. CLEMENTS (Physical Rev., 1935, [ii], 47, 224—229).—Complete data for bands in the region 3900—2600 cm^{-1} are tabulated, and assignments and analyses proposed.

Absorption spectra of saturated halides. R. S. SHARMA (Bull. Acad. Sci. Agra and Oudh, 1933, 3, 87—92; Chem. Zentr., 1934, ii, 2179).—The vapours of BCl_3 , BBr_3 , SiCl_4 , SiBr_4 , TiCl_4 , TiBr_4 , SnCl_4 , SnBr_4 , TeCl_4 , TeBr_4 , and PbCl_4 show continuous absorption (I) below a limiting λ , with bands. With TiBr_4 (I) is broken by two regions of transmission; SnCl_4 has one such. Heats of formation from thermochemical data are 2—3 times those calc. from the λ of the absorption limit. J. S. A.

Theory of the co-ordinate linking. V. Absorption spectra of simple salts of the transition elements. M. KARIM and R. SAMUEL (Bull. Acad. Sci. Agra and Oudh, 1934, 3, 157—168; Chem. Zentr., 1934, ii, 2049; cf. A., 1933, 886).—Absorption coeffs. of aq. VCl_3 , Na_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, MnCl_2 , KMnO_4 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, FeCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, YCl_3 , RuCl_3 , $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$, OsCl_4 , IrCl_4 , and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ have been measured. The halogen salts show a correspondence between the absorption max. and term differences. The curves for Na_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ are similar, the chief absorbing ion being probably HCrO_4^- in each case. H. J. E.

Ultra-violet absorption spectra of the stannic halides in various solvents. (MISS) M. I. GRANT (Trans. Faraday Soc., 1935, 31, 433—440).—Solutions of SnI_4 over Sn are stable and obey Beer's law, although Sn(OH)_4 is gradually formed. The absorption curve, with two max. at λ 365 m μ and 285 m μ , in C_6H_{14} is that of undeformed SnI_4 . In EtOH the first max. is suppressed and the second shifted to 295 m μ , owing to deformation of the mol. Greater deformation takes place in MeOH. SnBr_4 in solution over Sn gradually forms SnBr_2 and deposits Sn(OH)_4 . SnBr_2 is insol. in C_6H_{14} but sol. in MeOH; no change of the absorption curve therefore takes place in C_6H_{14} . In MeOH the SnBr_4 curve is gradually replaced by that of SnBr_2 . M. S. B.

Theory of co-ordinate linking. VI. Absorption spectra of some complex salts in different solvents. R. SAMUEL and M. UDDIN (Trans. Faraday Soc., 1935, 31, 423—432).—Absorption spectra in saturated solutions of NaCl, KCl, KBr, K_2CO_3 , Na_2CO_3 , and Na_2SO_4 have been investigated for the following salts: $[\text{Co(NH}_3)_6]\text{Cl}_3$ (I), $[\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2$ (II), $[\text{Co(NH}_3)_5\text{NO}_2]\text{SO}_4$ (III), $\text{Na}_2[\text{Fe(CN)}_5\text{NO}]$ (IV), $\text{Na}_2[\text{RhCl}_6]$ (V), $\text{K}_2[\text{PtCl}_4]$ (VI). Changes in the absorption max. of (I), (II), (III), and (IV), mainly due to a Stark effect as a result of the influence of a foreign ion of opposite charge, are observed. In the presence of CO_3^{2-} new bands appear, indicating the introduction of CO_3^{2-} into the complex ion. The absorption curves of (V) and (VI) in presence of KCl and NaCl show a small shift only, due to the Stark effect; negative ions except Cl^- produce a large displacement. From these and earlier results it is concluded that co-ordinated ions may exhibit quite different types of linking in solution, some being bound by non-electrostatic linkings and others by electrostatic forces only. M. S. B.

Ultra-violet absorption of pyridine, measured with the help of the decomposition of fructose in ultra-violet light. General method for deter-

mining ultra-violet absorption of pure liquids and solutions. R. CANTIENI (Helv. Chim. Acta, 1935, 18, 3—4).—A vertical cylindrical quartz tube of 1 cm. bore, closed at the top and connected at the bottom with a levelling tube, is filled with 10% aq. fructose solution. It is surrounded by a second quartz tube of 2 cm. bore, and the liquid of which the absorption is to be measured is contained in the annular space. After exposure for 1 hr. to light from a quartz-Hg lamp the vol. of CO generated in the fructose solution is measured. This vol. \propto the quantity of ultra-violet light transmitted by the external liquid. Pure C_6H_5N and aq. solutions more conc. than 1% are opaque, and solutions more dil. than 0.001% transparent, to ultra-violet light. F. L. U.

Ultra-violet absorption of the thiocarbimide and thiocyanate groups. M. PESTEMER and B. LITSCHAUER (Monatsh., 1935, 65, 239—244).—By measurements of the ultra-violet absorption of $EtNCS$ and $OMe \cdot CH_2 \cdot NCS$ in C_6H_{14} and $MeOH$ it is shown that the absorption band with its max. at $\nu = 4020 \text{ mm.}^{-1}$ observed by Kremann *et al.* (A., 1933, 885) in $CH_3 \cdot CH \cdot CH_2 \cdot NCS$ must be due to the $\cdot NCS$ group and not to $\cdot C \cdot C \cdot$. S appears to be the absorbing atom, since both $EtNC$ and $EtCN$ have practically no absorption whilst $EtSCN$ and Bu^iSCN both show absorption bands. M. S. B.

Ultra-violet absorption of binary liquid mixtures. VI. System ethyl thiocyanate-hexane. M. PESTEMER and G. SCHMIDT. VII. System aniline-*m*-cresol in ethyl alcohol. (FRL.) P. BERNSTEIN. VIII. System acetone-benzene. M. PESTEMER and B. LITSCHAUER (Monatsh., 1935, 65, 239—244, 245—251, 252—261).—VI. 7 mixtures were examined and no marked shift of the absorption band of $EtSCN$ was noticed.

VII. The extinction coeffs. of NH_2Ph and *m*-cresol are additive.

VIII. Measurements on 7 mixtures indicate considerable deviations from additivity. Since C_6H_6 has practically no dipole moment, dipole association is not necessarily the cause of positive or negative variations of the extinction curves of binary mixtures. M. S. B.

Metachromatism. II. Spectro-photometric study of metachromatic colouring matters. L. LISON (Bull. Acad. roy. Belg., 1934, [v], 20, 1160—1167).—The absorption curves in the visible region of various metachromatic substances have been studied at various concns. It is concluded that only metachromatic substances change in colour in relation to their concn. The modification in structure which produces this characteristic is possible only if one partly substituted NH_2 is present. The phenomenon appears to occur only in presence of H_2O . (Cf. A., 1934, 473.) J. W. S.

Optical absorption of porphyrins. W. HEROLD (Z. physikal. Chem., 1934, 171, 463—464).—Polemical against Stern and Wenderlein (this vol., 10).

Optical absorption of porphyrins. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1934, 171, 465).—A reply to Herold (cf. preceding abstract). R. C.

Effect of temperature on the absorption of crystals in the infra-red. M. BLACKMAN (Nature, 1935, 135, 233).—Consideration of the reasons for the effect. L. S. T.

Rotation-vibration bands of hydrogen cyanide near 10,381 Å. W. SCHIEB and K. HEDFELD (Z. Physik, 1935, 93, 428).—A revised allocation of lines gives moments of inertia 19.7 and $18.93 \times 10^{40} \text{ g. cm.}^2$ (cf. this vol., 10). A. B. D. C.

Infra-red spectrum of fluorine oxide, F_2O . G. HETTNER, R. POHLMAN, and H. J. SCHUMACHER (Naturwiss., 1935, 23, 114—115).—The spectrum of F_2O was investigated over the range 1—27 μ . Strong bands were found at 5.75, 7.6—8.4, 10.8, and 12.0 μ , the first, and last two, being double. The last three are ascribed to ground vibrations, and F_2O thus has a bent structure. There is a close relationship between the spectrum of F_2O and that of Cl_2O , if the band at 14.5 μ , ascribed by Bailey and Cassie to CO_2 (A., 1933, 1228), is due to Cl_2O . A. J. M.

Smekal-Raman effect in inorganic substances. J. WEILER (Naturwiss., 1935, 23, 125—130, 139—144).—A review. A. J. M.

Raman spectrum of phosphine. J. M. DELROSSE (Bull. Acad. roy. Belg., 1934, [v], 20, 1157—1159).—The Raman spectrum of solid PH_3 , near its m.p., excited by 22,938, 24,705, and 24,516 cm.^{-1} lines shows a strong vibration frequency of 2306 cm.^{-1} , corresponding with the 3336 cm.^{-1} frequency of NH_3 . J. W. S.

Raman effect in electrolyte solutions. I. SIMONS (Soc. Sci. fenn., Comm. phys.-math., 1934, 7, No. 9, 24 pp.; Chem. Zentr., 1934, ii, 1898).—Intensity measurements for Raman lines (I) in aq. nitrates of Na, K, NH_4 , Ca, Cd, and Pb, and in aq. $(NH_4)_2SO_4$, $CdSO_4$, HNO_3 , and H_2SO_4 are recorded. For the salts the relative intensities of (I) \propto concn., indicating complete dissociation. Two stages in the ionisation of H_2SO_4 were detected. H. J. E.

Raman effect. XXXVIII. Raman spectrum of organic substances. Isomeric paraffin derivatives. V. K. W. F. KOHLRAUSCH and F. KÖPPL. XXXIX. Polysubstituted benzenes. V. K. W. F. KOHLRAUSCH and A. PONGRATZ (Monatsh., 1935, 65, 185—198, 199—204).—XXXVIII (cf. A., 1934, 239). Data are recorded and discussed for Bu^iOH , NH_2Bu^i , $(\cdot CH_2 \cdot OH)_2$, $(\cdot CH_2 \cdot NH_2)_2$, *n*- $C_6H_{13}I$, 3 isomeric $C_5H_{11}Cl$, 7 CH_2Cl_2 , $\alpha\alpha\alpha$ - and $\alpha\alpha\beta$ - $C_2H_3Cl_3$.

XXXIX. Spectra have been determined for $C_6H_4Cl \cdot X$ ($X = NH_2$, OH, F, CN, Br, or I in *o*-, *m*-, and *p*-positions). The three positions are characterised by the lines 1030, 1000, and 630, respectively; 600 cm.^{-1} is common to all (cf. A., 1934, 346). M. S. B.

Raman effect and dipole moment in relation to free rotation. II. Modes of vibration of ethylene halides. S. MIZUSHIMA and Y. MORINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 26, 1—10; cf. this vol., 13).—Mathematical. It is shown that the Raman lines 653 and 752 cm.^{-1} , previously reported, correspond with the antisym-

metric and the symmetric vibrations, respectively, in the *trans*-state. N. M. B.

Raman effect. XL. Raman spectra of *cis-trans* isomerides. O. PAULSEN (Z. physikal. Chem., 1935, B, 28, 123—134).—Measurement of the Raman spectra and polarisation relations of *cis*- and *trans*-C₂H₂Cl₂ has confirmed Trumpy's results (A., 1934, 1056). Most of the observed lines could be allotted to particular types of vibration of the mol. R. C.

Raman effect of normal nonyl, decyl, and dodecyl nitrates. L. MEDARD and R. ALQUIER (J. Chim. phys., 1935, 32, 63—65).—A large no. of lines and frequencies are tabulated for the three nitrates. The vals. change only slightly amongst the higher members of this homologous series (cf. A., 1934, 716). J. G. A. G.

Investigation of molecular compounds by Raman spectra. I. Saturation of affinity of oxygen in molecular compounds of alcohols, ethers, ketones, and aldehydes. G. BRIEGLEB and W. LAUPPE (Z. physikal. Chem., 1935, B, 28, 154—166).—The Raman spectrum of a solution of HBr in Et₂O at room temp. consists of the superimposed spectra of EtBr and Et₂O, but if the solution is prepared and examined at -40° a different spectrum, that of the mol. compound, appears. The Raman spectrum shows that with formation of SnCl₄.Et₂O considerable changes occur in the SnCl₄ mol. R. C.

Raman spectra of ketonic terpenes. R. DULOV (Bull. Inst. Pin, 1934, 214—219).—As expected from the exaltation of [M]₀, the frequency of the Raman lines due to the ethylenic linking and CO of conjugated ketones is lowered. Examples are given from the carvone, pulegone, and thujone series. R. S. C.

Luminescence in water caused by ultrasonic waves. H. FRENZEL and H. SCHULTES (Z. physikal. Chem., 1934, B, 27, 421—424).—Ultrasonic waves cause luminescence in H₂O, unless the latter is gas-free. This observation supports the theory of electric processes at the interface between expelled air bubbles and H₂O (cf. A., 1933, 473). R. C.

Fluorescence in liquids. J. FRANCK and H. LEVI (Z. physikal. Chem., 1934, B, 27, 409—420).—By analogy with gases it is deduced that the extinction of fluorescence by collisions must occur in liquids in such a way that the electron excitation energy reappears as near as possible in its entirety as electron excitation energy. This may occur either by electron quantum transitions in the other colliding mol. (I) or by chemical reaction between the two. It is a general condition for fluorescence in solution that the excitation energy shall be < the energy necessary for any possible change in (I). Examination of the effect of foreign substances on the fluorescence of chlorophyll in EtOH solution shows that there are cases where photo-oxidation occurs by the acceptor itself taking up energy, thus becoming attackable by O₂ (cf. A., 1933, 1214), not by activation of O₂ (cf. *ibid.*, 1256). The relation between intensity of fluorescence and duration of irradiation has been examined. R. C.

Fluorescence spectra of rubene (tetraphenyl-rubene) in benzene solution and in the solid state. C. DHERE and (MLLE.) A. RAFFY (Compt. rend., 1935, 200, 386—388).—The fluorescence spectrum of a C₆H₆ solution of rubene extends from 6500 to 5400 Å., and consists of two bright bands separated by a region of lower intensity. The spectrum is identical whether excited by a C arc or by monochromatic radiation. The solid shows fluorescence only when irradiated with violet or ultra-violet light. J. W. S.

Yield of fluorescence in aqueous fluorescein solutions on anti-Stokes excitation. A. JABLONSKI (Acta Phys. Polon., 1933, 2, 97—103).—A fall in the yield was observed on exciting with longer waves than that at which the max. in the fluorescence band was observed. CH. ABS. (e)

Lenard phosphors in theory and practice. E. TIEDE (Chem.-Ztg., 1935, 59, 105—106, 127—129).—A review of the general nature of Lenard phosphors, and their methods of prep., structure, and technical applications. A. J. M.

Unsaturated nature of dyes and the photo-voltaic phenomenon. (MLLE.) C. STORA (Compt. rend., 1935, 200, 552—554).—The photopotential (I) of many dyes is determined under standard conditions and is independent of the no. of NH₂ and substituted or unsubstituted groups. Fluorescent dyes have a strongly positive (I), influenced by secondary reactions such as photochemical change and oxidation in air. Auxochromes are not concerned in the phenomenon. J. L. D.

Spectral sensitivity of photo-electric counters. R. AUDUBERT and C. REITHMULLER (Compt. rend., 1935, 200, 389—391).—Photo-electric cathodes of amalgamated Cu, CuI, Cu₂S, Cu₂O, PbO, PbI₂, and black SnO show rapidly increasing sensitivity with decreasing λ between 2700 and 2400 Å. The sensitivity of Mg, Cd, CdS, and anodically oxidised Al and Ta increases from about 3300 Å., with max. between 2200 and 2400 Å. Amalgamated Zn has a max. about 2500 Å. and is still sensitive in the visible region. It is possible with various photo-electric cathodes to cover the whole region of emission during chemical reactions. J. W. S.

Detectors. H. GEISMANN (Physikal. Z., 1935, 36, 132—138).—The properties of crystal detectors are examined. Pure PbS is incapable of acting as a detector unless its surface is covered with an insulating rectifying layer (I), which may be uni- or poly-mol. A detector may consist of the arrangement Pt surface-(I)-Pt point. The Pt may be replaced by other metals, and the nature of (I) is not important. For rectification, one of the electrodes must be a point electrode; provided it conducts, it may be of any material. A. J. M.

Effect of magnetic field on the crystal photo-effect. G. GROETZINGER (Physikal. Z., 1935, 36, 169—173).—The effect on the crystal photo-effect (I) of a magnetic field (II) perpendicular to the direction of the incident light is two-fold: (1) there is a decrease in the e.m.f. produced by (I) in the direction of the light (III); (2) a component of the e.m.f.

perpendicular to (II) and (III) is produced. The latter is quite distinct from the Hall effect.

A. J. M.

Crystal photo-effect with single crystals of cuprite. R. DEAGLIO (*Physikal. Z.*, 1935, 36, 144—146).—The crystal photo-effect was investigated for crystals of cuprite from various sources, in order to verify the author's theory (A., 1933, 554). The effect depends on the purity of the crystal.

A. J. M.

Photo-effect in cuprite crystals. N. I. BARBAUMOV, D. L. SHUTAK, and A. F. ZIVCHINSKI (*Physikal. Z. Sovietunion*, 1934, 5, 666—675).—It is more difficult to establish a barrier-layer photo-effect in cuprite than in a Cu_2O plate. The effect is more a vol. than a layer effect. CH. ABS. (c)

Oxygen content and the electrical properties of valve layers of W, Ta, and Nb. O. MOHR (*Z. Physik*, 1935, 93, 298—314).—Potential variations of capacity (Günther-Schulze and Betz, A., 1931, 1130) were investigated for W, Ta, and Nb, and are ascribed to variations in conductivity due to movement of O in the monocryst. oxide lattice. Structure and variations of valve layers are discussed theoretically.

A. B. D. C.

Rotational state of molecules in liquids. P. DEBYE (*Physikal. Z.*, 1935, 36, 100—101).—The rotation of mols. in liquids cannot be free, but there is a rotational vibration about an axis, of which the orientation gradually changes. Consideration of the dipole moments (I) of a substance in the liquid and vapour states gives the ratio of the mol. polarisations (II), from which the energy required to rotate a mol. 90° out of its position may be calc. In the case of H_2O this is $10kT$. The variation of (I) with the solvent is also explained on this basis. The fact that the Kerr const. (III) for a substance in the liquid state is $<$ that in the gaseous state is connected with the limited rotation of mols. in the liquid state. The effect of the solvent on (III) will be twice as great as that on (II): verified by recent work on PhCl .

A. J. M.

Properties of layers of molecular dipoles. C. E. GUYE (*Arch. Sci. phys. nat.*, 1934, [v], 16, Suppl., 143—145).—Forces due to a single layer and to superposed layers of oriented dipoles are calc.

F. L. U.

Dielectric constants of weakly polar crystals and their variation with temperature. A. EUCKEN and A. BUCHNER (*Z. physikal. Chem.*, 1934, B, 27, 321—349).—Born's theory of the dielectric const., ϵ , of solids is valid only for ionic crystals of extremely high polarity. Even the alkali halides do not entirely fulfil this condition, and the theoretical vals. of ϵ are always $>$ the observed vals., and with less polar substances (I) the discrepancies are much greater, with the temp. coeff. of ϵ sometimes qualitatively incorrect. By means of the curves derived by Kirkwood (A., 1932, 447) and Bartholome (A., 1933, 1227) for the variation of the dipole moment of two oppositely charged atoms with their distance apart, the high observed vals. of ϵ for (I) and the variation of ϵ with temp. are explained. The ϵ of various salts

at room temp. and, for several, between -190° and 100° has been measured.

R. C.

Dielectric constant and conductivity of ionised gases. T. V. IONESCU and C. MIHUL (*J. Phys. Radium*, 1935, [vii], 6, 35—48).—The variations of capacity and conductance of a condenser containing ionised gases are due to free electrons and to others having a characteristic vibration frequency. An applied electric field strongly modifies the variations due to the free electrons; a magnetic field separates the effects of the two types of electrons. The characteristic frequency is explained by electrons attached to the O_2 mols., and having a precession in the magnetic field of the mol., the frequency being equal to the characteristic frequency. Data on the effect of moisture and pressure variation are given.

N. M. B.

Dipole moment of associated molecules and validity of mass law for association. E. HERTEL and E. DUMONT (*Z. physikal. Chem.*, 1935, B, 28, 14—16).—Sakurada's method of determining the dipole moment of associated mols. (A., 1934, 475) is of little val.

R. C.

Dipole moments of chlorine monoxide and chlorine dioxide. D. SUNDHOFF and H. J. SCHUMACHER (*Z. physikal. Chem.*, 1935, B, 28, 17—30).—The vals. 1.69 ± 0.09 and $0.78 \pm 0.08 \times 10^{-18}$ e.s.u. have been obtained for ClO_2 and Cl_2O , respectively. These show the mols. to be bent, which agrees with chemical and spectroscopic data (cf. A., 1933, 557, 1228).

R. C.

Significance of some anomalous dipole moments. E. BERGMANN and (MISS) A. WEIZMANN (*Chem. and Ind.*, 1935, 150—151).—The abnormal dipole moments (I) of *p*-nitrosodialkylanilines, assumed to be due to resonance, may be connected with the abnormal ease of hydrolysis and reaction with MeI and BzCl , which seem to occur by way of $\text{NO}^+ \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2^-$. The relatively slight abnormality in (I) for xanthone (3.07; calc. 1.92) compared with pyrone is in line with the more normal ketonic properties of the former and may be due to its more truly aromatic character.

R. S. C.

Electric moments of phenylethylene and substituted phenylethylenes. M. M. OTTO and H. H. WENZKE (*J. Amer. Chem. Soc.*, 1935, 57, 294—295).—The following electric moments are recorded: $\text{CHPh} \cdot \text{CH}_2$ 0.37, *p*-bromo- 1.35, *p*-chloro- *p*-ethyl-phenylethylene 0.61, *p*-tolylethylene 0.63, all $\times 10^{-18}$.

E. S. H.

Permanent electric moments of some alkyl chlorosulphites. P. TRUNEL (*Compt. rend.*, 1935, 200, 557—559).—The electric moments of $\text{OMe} \cdot \text{SOCl}$ and $\text{OEt} \cdot \text{SOCl}$, calc. from the dielectric const. of dil. solutions in C_6H_6 and the mol. refractions, are 2.30 and 2.63×10^{-18} e.s.u., respectively, at 25° . The vals. for $\text{OPr} \cdot \text{SOCl}$, $\text{OBu} \cdot \text{SOCl}$, and $\text{C}_6\text{H}_{13} \cdot \text{O} \cdot \text{SOCl}$ are each about 2.70×10^{-18} e.s.u. The vals. for 45 are about 0.03×10^{-18} e.s.u. higher in each case. It is concluded that the angles of the linkings are independent of the alkyl radicals, and that they do not vary appreciably with temp.

J. W. S.

Negative results in variation of dielectric constant. J. WEIGLE and R. LUTHI (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 148—150).—The dielectric const. (D) of five polar liquids exposed to ultrasonic waves remained const. to 0.05%. For H_2O and $COMe_2$ in turbulent flow corresponding with a Reynolds no. of 60,000, D is const. within 0.02%.

F. L. U.

Refractive index of thallium vapour near the line λ 5350.46 Å. G. BALIN and S. MANDELSTAM, jun. (Physikal. Z. Sovietunion, 1934, 6, 159—162).—The val. of $n-1$ for Tl vapour at λ 5461 Å. is 300—450 times < McClennan's val., and is compatible with Fermi and Rasetti's val.

CH. ABS. (e)

Refractive indices of p -azoxyphenetole in the state of anisotropic liquid. P. CHATELAIN (Compt. rend., 1935, 200, 412—413).—Using the Newton ring method with plain and half-platinised glass plates and lenses, the ordinary and extraordinary refractive indices of p -azoxyphenetole have been determined at 135—185° and for λ 6500, 5460, 4850, and 4360 Å. Results agree with previous vals.

J. W. S.

Dispersion and rotatory dispersion of simple sugar derivatives. N. A. SÖRENSEN and B. TRUMPY (Z. physikal. Chem., 1935, B, 28, 135—153).—The dispersion (I) and rotatory dispersion (II) of α - and β -methyl-glucoside, -galactoside, and -l-rhamnoside have been measured in the visible. For each (I) is simple, corresponding with a centre of absorption at ~ 830 Å. Except for β -methyl-galactoside (II) is simple, the absorption centre responsible for rotation lying between about 1400 and 1500 Å. The displacement of this relative to the centre for refraction agrees with Kuhn's theory. The consts. of the dispersion formulæ, λ_{OR} , λ_{Oa} , and ϵ_R , are for each β -form > for the α -form, but this is not true for some sugars studied by others. Most of the cases of (II) reported by Hirst *et al.* as complex (cf. A., 1934, 1092) prove to be instances of simple (II) if damping is taken into account.

R. C.

Circular dichroism of optically active β -octyl nitrite in the vapour state. H. B. ELKINS and W. KUHN (J. Amer. Chem. Soc., 1935, 57, 296—299).—The ultra-violet absorption spectra of gaseous Me, isocamyl, and β -octyl nitrite (I) have been examined and compared. No fine structure was observed. Measurements of the circular dichroism (I) have been made at 90°. The inconstancy of the anisotropic factor is a property of the alkyl nitrite mols., and is partly due to the fact that the absorption has to be attributed when various nitrites are compared to two different electronic transitions producing an anisotropy of opposite sign and showing a shift in wave no. of opposite sign.

E. S. H.

Structure of the six-membered rings C_6H_6 and C_6Cl_6 . R. KAISER (Physikal. Z., 1935, 36, 92—99).—The theory of the determination of mol. structure by X-ray interference methods is discussed. For C_6Cl_6 , a new steel cell with mica windows which withstand the action of C_6Cl_6 vapour at 450° is described. The scattering curve of C_6H_6 agrees best with a p.e. model, but no quant. results could be obtained for scattering intensities. The results for

C_6Cl_6 are more satisfactory. The C—C distance in C_6H_6 and C_6Cl_6 is 1.42 ± 0.03 Å.; the Cl—Cl distance in C_6Cl_6 is 3.35 ± 0.05 Å.

A. J. M.

Systematisation of simple inorganic acids. H. ERLÉNMEYER (Z. physikal. Chem., 1934, B, 27, 404—408).—These acids can be regarded as formed by some or all of the four cells in the outer electron shell of the central atom, Si, P, S, or Cl, coming to be occupied by a complete octet, the extra electrons being derived from added atoms or groups, *i.e.*, the two-electron groups in the inert-gas configuration of the ion of the central atom undergo equiv. replacement by octets.

R. C.

Problem of valency. R. C. MENZIES (Chem. and Ind., 1935, 200—202).—Examples are cited in favour of the view that the stability of many compounds may be correlated with the dual tendency of elements to function with an even covalency and to complete the electron systems of the inert gases.

H. W.

Can cobalt have a co-ordination number 8? C. DUVAL (Compt. rend., 1935, 200, 399—401).—Analysis of Co^{III} oxalatopentammine tartrate indicates a formula $[Co(NH_3)_5C_2O_4]_2C_4H_4O_6$ containing no H_2O . This is confirmed by the optical activity being purely a function of the tartrate radical. The salts with other acids are also either anhyd. or lose their H_2O of crystallisation readily. The results are in agreement with co-ordination nos. 6 for Co and 1 for $H_2C_2O_4$.

J. W. S.

Pair linking theory of valency. H. LESSHEIM and R. SAMUEL (Nature, 1935, 135, 230—231).—Theoretical.

L. S. T.

Electronic theory and organic chemistry. I. Valency; polarity; energy. V. RASUMOVSKI (Bull. Soc. chim., 1935, [v], 2, 179—194).—An electronic theory of valency is developed based on dynamical principles. It is assumed that the formation of a chemical linking involves the pairing of electrons, in a neutral zone between the two atoms, but coupled and free valency electrons are all under the influence of the two atoms involved, thus giving rise to charges which cause deformation of the system and oppose an increase of polarity. The difference

between polar (MX) and non-polar compounds is thus only one of relative degrees of polarity, of particular and variable magnitude for each compound. From an analysis of the duration of the period in which electrons are within the sphere of influence of the two atoms it is concluded that no electrons are either completely free or completely paired, and that the degree (I) of coupling is the fundamental criterion of chemical activity. Increase of (I) is accompanied by diminution in normal activity and increase in the co-ordinating activity of their mols. Applications are discussed.

J. W. B.

Association and polarisability. G. BERGER (Z. physikal. Chem., 1935, B, 28, 95—111).—The association of various aromatic hydrocarbons in C_6H_{14} , C_6H_6 , and CCl_4 has been investigated ebullioscopically. Association is, in general, greatest in C_6H_{14} and smallest in C_6H_6 , but the ratio of the vals. in the two depends on the structure of the solute. The results

are interpreted on the basis of London's theory of van der Waals forces, assuming that association \propto the energy of attraction between two dissolved mols. and inversely \propto the square of the energy of attraction between solvent and solute mols. With plate-shaped mols. markedly anisotropic in respect of polarisability, *e.g.*, C_6H_6 and $C_{10}H_8$, on association an orientation parallel to the surface of max. polarisability is assumed. The observed association in CCl_4 is the theory indicates, which is ascribed to the polarising action of the C-Cl dipoles on the double linkings of the solutes. R. C.

Atomic bromine. G. M. SCHWAB (Z. physikal. Chem., 1934, B, 27, 452—459).—Free Br atoms are produced by electric discharge in Br_2 under 0.1 mm. Every collision with the wall, irrespective of the nature of the latter, leads to recombination. R. C.

Spectroscopy and valency. III. Periodic functions of non-hydride di-atoms. C. H. D. CLARK (Proc. Leeds Phil. Soc., 1935, 3, No. 1, 26—41; cf. A., 1934, 476).—The bearing of the occurrence of max. or min. vals. of spectroscopic const. in group X on structural and valency problems is discussed. F. L. U.

Representation of potential curves for diatomic molecules. W. LOTMAR (Z. Physik, 1935, 93, 528—533).—Different potential-nuclear expressions are discussed. A. B. D. C.

Vibrations of symmetrical tetratomic molecules. (MISS) J. E. ROSENTHAL (Physical Rev., 1935, [ii], 47, 235—237).—Mathematical. N. M. B.

The triple linking. (MLLE.) T. AALAM and J. MARTINET (Bull. Soc. chim., 1935, [v], 2, 142—155).—A survey is given of the relation between electronic structure and chemical and physical properties with special reference to compounds of N. J. G. A. G.

Characteristic vibrations of mechanical models of molecules. I. Three mass systems. F. TRENKLER (Physikal. Z., 1935, 36, 162—168).—The work of Kettering *et al.* (A., 1930, 1349) is extended, but limited to plane systems. Models were constructed of steel cylinders and screwed rods, and the form of the vibration was determined by cinematography. The linear symmetrical and asymmetrical and the symmetrical bent and ring forms were investigated. The frequencies, no., and type of the vibrational forms are in qual. and quant. agreement with the valency force system. A. J. M.

New molecular models. H. A. STUART (Z. physikal. Chem., 1934, B, 27, 350—358).—The radius of the sphere of action in the combined state has been calc. for the atoms of various elements from existing data. Mol. models in which the constituent atoms are represented by caps of spheres instead of true spheres give a moderately correct picture of the space-filling in homopolar mols.; spherical models do not (cf. A., 1932, 446). By using transparent material, the disposition of the nuclei can be shown. R. C.

Space-charge in molecular-ray experiments. M. KRATZENSTEIN (Z. Physik, 1935, 93, 279—291).—Space-charge effects appear in mol.-ray observations when the mean free path within the furnace is less than $3/2$ that of the furnace aperture. A. B. D. C.

Molecular diameter of deuterium as determined by viscosity measurements. A. B. VAN CLEAVE and O. MAASS (Canad. J. Res., 1935, 12, 57—62).—Viscosity measurements of H_2^2 over the range 23° to -183° and of the system $H_2^2-H_2$ over the whole concn. range at 22° show that H_2^2 has the same mol. diameter as H_2 . The difference between the mol. vol. of liquid H_2^2O and H_2O is ascribed to a difference in equilibrium between associated and non-associated mols. E. S. H.

Zero point energy and physical properties of H_2O and H_2^2O . J. D. BERNAL and G. TAMM (Nature, 1935, 135, 229—230).—The marked differences in the physical properties of H_2O and H_2^2O must be ascribed to differences in the frequency of angular vibration or libration of the mols. Differences in sp. heat, heats of evaporation and fusion of H_2O and H_2^2O , and the λ shifts in the spectrum of H_2O are accounted for quantitatively. L. S. T.

Changes of matter and their arrest. E. LANGE (Z. Elektrochem., 1935, 41, 107—111).—Physical and chemical changes are considered in a general way, in terms of attractive forces, thermal kinetic energy, and potential thresholds, an example of the last-named being the activation energy of a chemical reaction. R. S. B.

Approximate analytical calculation of exchange energies for Thomas-Fermi atomic systems. P. GOMBAS (Z. Physik, 1935, 93, 378—387).—A method that avoids numerical integration is given, and is applied to RbBr and KCl. A. B. D. C.

Surface tension, density, and molecular constitution of a pure liquid. R. LAUTIE (Bull. Soc. chim., 1935, [v], 2, 155—159).—By means of the equations relating characteristic temp. with surface tension, γ , and the change, Δ , of d between room temp. and T_c , vals. of Δ and γ of a normal liquid over a wide range of temp. are calc. from the sum of the parachors of its constituent atoms and linkings. J. G. A. G.

Parachor and structure of nickel carbonyl. F. W. LAIRD and M. A. SMITH (J. Amer. Chem. Soc., 1935, 57, 266—267).—The surface tension of $Ni(CO)_4$ at 8° , 14° , and 20° is 17.21, 16.55, and 15.88 dynes per cm., respectively. The parachor of $Ni(CO)_4$ is 259.9, indicating the val. 19.9 for P_{Ni} . E. S. H.

Parachors of ethyl orthoformate and triphenylmethane. D. L. HAMMICK and H. F. WILMUT (J.C.S., 1935, 207).—The re-determined parachors of $CH(OEt)_3$ and $CHPh_3$ (367.2 and 586.5, respectively) show no anomaly. There is no evidence that three large groups substituted in the CH_4 molecule produce parachor anomaly (cf. A., 1934, 350). W. S.

Interferometric determinations with X-rays in chlorine, methane, and trimethylamine. RICHTER (Physikal. Z., 1935, 36, 85—91).—1 De

scattering curve of Cl_2 agrees more closely with that based on the Hartree approximation than with the Fermi and Thomas approximation. The NMe_3 mol. is a very flat pyramid. A. J. M.

Simplification of Prins' formula for diffraction of X-rays by a perfect crystal. F. MILLER, jun. (Physical Rev., 1935, [ii], 47, 209—212).—Mathematical. N. M. B.

Theory of anisotropic liquids. XXI. Molecular forces produced by liquid crystals. C. W. OSEEN (Ark. Mat. Astr. Fys., 1934, A., 24, No. 19, 11 pp.; Chem. Zentr., 1934, ii, 1890; cf. A., 1934, 1162).—Difficulties in explaining the structure of cholesterol nematic substances persist on treating the mols. as three-dimensional. H. J. E.

Anisotropy in the velocity of growth of new grains on recrystallisation. M. KORNFIELD (Physikal. Z. Sovietunion, 1934, 6, 170—174).—An anisotropy in the growth of new grains is observed when polycryst. Al is heated at temp. slightly > the recrystallisation temp. The degree of anisotropy depends on the temp. of heating. CH. ABS. (e)

Study of crystal orientation by means of the Weissenberg X-ray goniometer. J. PALACIOS, J. HENGSTENBERG, and J. G. DE LA CUEVA (Anal. Fís. Quím., 1933, 31, 811—821).—The interference diagram obtained on a single plate is used in conjunction with a nomogram to give a diagram showing the orientation of the crystals in a polycryst. material. Typical results for Al wire and foil are described. H. F. G.

Effect of a grain boundary on the deformation of a single crystal of zinc. R. F. MILLER (Amer. Inst. Min. Met. Eng., Inst. Met. Div., 1934, Tech. Pub. No. 576, 9 pp.).—On elongation, the single-crystal section of the specimen became elongated by a single flexural gliding process, and assumed a characteristic shape on encountering the grain boundary. CH. ABS. (e)

Transformation of NH_4Cl at -30° . J. WEIGLE and F. HUBER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 150—152).—Lattice consts. for the two modifications of NH_4Cl are given for the range -75° to 20° . A sudden expansion with rise of temp. occurs at about -30° , and two lattices, the dimensions of which differ by 0.3%, coexist over an interval of 5° . F. L. U.

Transformation of NH_4Br near -40° . J. WEIGLE and H. SAINI (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 147—148).—A preliminary account of X-ray measurements showing that below -40° NH_4Br is no longer cubic. F. L. U.

X-Ray investigation of lattice distortions produced in copper by filing. G. W. BRINDLEY and H. W. SPIERS (Proc. Leeds Phil. Soc., 1935, 3, No. 1, 4—11).—The at. scattering factor for filings from Th and hard-drawn Cu is > that for pptd. Cu. The filing, attributed to lattice distortion caused by the filing, can be explained by assuming a random displacement of the atoms of 0.125 Å. from the points of the undistorted lattice. F. L. U.

X-Ray studies on the hydrous oxides. V. ferric oxide monohydrate. H. B. WEISER and

W. O. MILLIGAN (J. Amer. Chem. Soc., 1935, 57, 238—241).— $\beta\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is formed as a yellowish ppt. by the slow hydrolysis of aq. FeCl_3 . X-Ray data show that the crystals are orthorhombic, having a_0 5.28, b_0 10.24, and c_0 3.34 Å. E. S. H.

X-Ray studies on the hydrous oxides. VII. Ferric oxide. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1935, 39, 25—34).—Ageing under H_2O of the brown gel pptd. by bases from aq. Fe^{III} salts is shown by X-ray analysis to produce $\alpha\text{-Fe}_2\text{O}_3$ (I) in a few weeks or months when cold, or in a few hr. when near b.p. Systematic investigation shows the growth from finely-divided particles to crystals large enough to give sharp diffraction lines. Pptn. near 100° gives immediately a weak X-ray diagram. Contrary to the results of Thiessen *et al.* (A., 1930, 559), dehydration isotherms of the gel formed by slow hydrolysis of $\text{Fe}(\text{OEt})_3$ show no breaks due to definite compounds. Rapid hydrolysis of Fe^{III} salts gives (I), whilst slow hydrolysis gives a yellow ppt. of hydrous $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (II). FeCl_3 is an exception, giving $\beta\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Under certain conditions $\text{Fe}_2(\text{SO}_4)_3$ gives a definite basic sulphate instead of (II). M. S. B.

X-Ray determination of the structure of FeAl_3 . E. F. BAKHMETEV (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 292—293).—The dimensions of the unit cell are $15.48 \times 8.11 \times 11.92$ Å. (24 mols. FeAl_3). CH. ABS. (e)

Crystal structure of LaTi_3 . A. ROSSI (Gazzetta, 1934, 64, 955—957).— LaTi_3 has a hexagonal lattice with a 3.45 Å., c/a 1.60, $d_{\text{obs.}}$ 10.92, 10.89.

O. J. W.
Constitution of lithium nitride. E. ZINTL and G. BRAUER (Z. Elektrochem., 1935, 41, 102—107).— Li_3N has hexagonal co-ordination, and not the cubic mol. lattice of Brill (cf. A., 1928, 108). a 3.658 Å., c/a 1.061; each cell contains one Li_3N . N^{IV} at 000, Li^{I} at $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{3}{2}\frac{3}{2}0$. Each N^{IV} is distant 1.94 Å. from 2 Li^{I} , and 2.11 Å. from 6 Li^{I} . $d_{\text{calc.}}$ 1.28, $d_{\text{obs.}}$ 1.3. By replacing 6 F' by 30" or 2N" in LiF the "anion gap" lattices of Li_2O and Li_3N follow. R. S. B.

Crystal structure of hexachloro-salts. G. ENGEL (Centr. Min. Geol., 1934, A, 285—286).—Vals. are recorded for the a parameters of a series of salts of the $\text{R}^{\text{I}}_2\text{R}^{\text{IV}}\text{Cl}_6$ type ($\text{R}^{\text{I}}=\text{K}, \text{NH}_4, \text{Rb}, \text{Cs}, \text{Tl}$; $\text{R}^{\text{IV}}=\text{Ti}, \text{Se}, \text{Zr}, \text{Sn}, \text{Te}, \text{Pt}, \text{Pb}$). All except K_2TeCl_6 belong to the cubic K_2PtCl_6 type. CH. ABS. (e)

Structure of caesium enneachlorodiarсениte, $\text{Cs}_3\text{As}_2\text{Cl}_9$. J. L. HOARD and L. GOLDSTEIN (J. Chem. Physics, 1935, 3, 117—122).—The hexagonal unit cell, containing 1 mol., has a_0 7.37, c_0 8.91 Å., $d_{\text{calc.}}$ 3.42. The structure is discussed. F. L. U.

Compounds with the perovskite structure. A. HOFFMANN (Z. physikal. Chem., 1935, B, 28, 65—77; cf. A., 1933, 1098; 1934, 615).—The dimensions of the perovskite (I) lattices of SrXO_3 ($\text{X}=\text{Ti}, \text{Sn}, \text{Hf}, \text{Zr}, \text{Ce}$) have been measured. The results agree with the condition that for the (I) structure in compounds YXO_3 the val. of the radius ratio $(R_{\text{Y}}+R_{\text{O}})/\sqrt{2(R_{\text{X}}+R_{\text{O}})}$ must be < 1.1, but < 0.9. The compound BaPrO_3 has been prepared. PbZrO_3 shows the

lines of the (I) structure and of a superlattice, the length of the edge of the unit cell being tripled in at least one direction. R. C.

Crystal structure of arsenical struvite. R. SALVIA (Anal. Fis. Quím., 1933, 31, 822—824).—The rhombic pyramidal crystals have a_0 7.00, b_0 6.14, c_0 11.11 Å.; 2 mols. in the unit cell; space-group C_{2v}^7 . H. F. G.

System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$. I. Preparation of crystalline B_2O_3 and some of its physical properties. S. S. COLE and N. W. TAYLOR. **II. Properties of anhydrous and hydrated metaborates of sodium and potassium.** S. S. COLE, S. R. SCHOLES, and C. R. AMBERG (J. Amer. Ceram. Soc., 1935, 18, 55—58, 58—61).—I. H_3BO_3 was dehydrated in vac. at 200° and then sintered at 225° for 400 hr. X-Ray examination showed the material to be free from glass. Cryst. B_2O_3 was also obtained by the devitrification of the anhyd. glass at 280—290°: n 1.458, d 1.805, m.p. 294° \pm 1°; the cubic unit cell contains 16 mols. a_0 10.035 Å.

II. The prep. and physical properties (including X-ray data) of the salts are recorded. J. A. S.

Crystal structure of cyanuric triazide. I. E. KNAGGS (Nature, 1935, 135, 268).—Hughes' measurements (this vol., 286) are not sufficiently precise to permit his conclusions. L. S. T.

Crystal form of anhydrous citric acid. G. M. BENNETT and J. L. YUILL (J.C.S., 1935, 130).—Anhyd. citric acid is monoclinic with β 99° 7', $a : b : c = 1.935 : 1 : 1.150$; d_4^{25} (vac.) 1.665, m.p. 156—157° (corr.). It has low positive double refraction. The transition point of the anhyd. and monohydrated forms is 36.3°. J. W. S.

Properties of cellulose esters of homologous fatty acids. S. E. SHEPPARD and P. T. NEWSOME (J. Physical Chem., 1935, 39, 143—152).—Physical properties of a series of cellulose tri-esters of homologous aliphatic acids, from AcOH to stearic acid, show that the cellulose character is gradually submerged as the length of the chain increases. The structure of the solids is discussed on the basis of X-ray and wetting and spreading data. M. S. B.

Crystallographic and X-ray investigation of some diphenylamine derivatives. R. G. WOOD, S. H. AYLIFFE, and N. M. CULLINANE (Phil. Mag., 1935, [vii], 19, 405—416).—2 : 4 : 6-Trinitrodiphenylamine exists in two identical forms, reddish-orange prisms and yellowish-orange needles, the former separating from EtOAc, the latter from EtOH. X-Ray measurements gave $a : b : c = 1.49 : 1 : 2.13$, β 115° 33'; 4 mols. per unit cell, d 1.570, space-group C_{2h}^5 ($P2_{1/c}$). 2 : 4 : 6-Trinitro-4'-methyl-diphenylamine exists as deep red needles (stable) from COMe_3 , and yellowish-orange needles from CCl_4 . The former has $a : b : c = 0.737 : 1 : 0.345$, β 103°; the latter, $a : b : c = 2.51 : 2 : 1.74$, β 114° 8'; each has d 1.532, 4 mols. per unit cell, space-group as above. N. M. B.

Crystal structure of ergosterol and cholesterol derivatives. G. E. R. SCHULZE (Z. physikal. Chem., 1934, 171, 436—444).—The compound of ergosteryl acetate (I) with maleic anhydride has the space-

group C_2^2 . Comparison of the dimensions of the unit cells of the two isomerides with those of ergosterol (II) and (I) leads to conclusions as to the position of the double linkings consonant with Windaus' formula for (II) (A., 1934, 768). The dimensions of the unit cells of cholestene dibromide, hydroxy-cholestenone dibromide, cholestanedione, cholesteryl acetate, and acetoxybisanallocholic acid have been determined. R. C.

Structure of cellulose trinitrate. M. MATHIEU (Compt. rend., 1935, 200, 401—403; cf. this vol., 286).—The monoclinic lattice defined by the parameters a 13.9, c 9 Å., β 90°, b (axis of fibre) 25.6 Å. is suggested. J. W. S.

α -Folliculin. See this vol., 413.

X-Ray diffraction studies of built-up films of long-chain compounds. G. L. CLARK, R. R. STRETT, and P. W. LEPPA (J. Amer. Chem. Soc., 1935, 57, 330—331).—Technique for the investigation of reactions in uni- and multi-mol. films is described.

E. S. H.
Diffraction of electron beams by a crystal lattice. T. HAYASI (Sci. Rep. Tōhoku, 1934, 23, 491—522).—Mathematical treatment of the interference bands obtained by scattering of a non-symmetrical spherical wave by a crystal lattice.

W. P. R.
One-dimensional electron diffraction. J. R. TILMAN (Phil. Mag., 1935, [vii], 19, 485—500; cf. Emslie, A., 1934, 243).—Investigation of the one-dimensional diffraction of fast electrons by the (110) face of Zn blende indicates that the electrons often become confined to potential tubes in the crystal surface, which contain whole or parts of both Zn and S ions. Measured vals. of the mean electrostatic potentials inside these tubes are accounted for theoretically. The diameter of the tubes is approx. that of a Zn ion, 1.6 Å. N. M. B.

Surface lattice interference in the passage of cathode rays through galena. S. VON FRIESEN (Ark. Mat. Astr. Fysik, 1934, B, 24, No. 8, 4 pp.; Chem. Zentr., 1934, ii, 1894). H. J. E.

Electron diffraction by aluminium and aluminium oxides. C. MONGAN (Helv. Phys. Acta, 1934, 7, 482—484; Chem. Zentr., 1934, ii, 2169).—The absence of Al_2O_3 lines from electron diffraction photographs of very fine Al powder shows that any Al_2O_3 layer must be $< 10^{-6}$ cm. thick. Results are given for corundum and Al_2O_3 , showing very fine particle size. J. S. A.

Derivation of the free path of metal electrons in bismuth from the electrical resistance of very thin single crystal wires. A. EUCKEN and F. FORSTER (Nachr. Ges. Wiss. Göttingen, 1934, [ii], 1, 43—54; Chem. Zentr., 1934, ii, 2186).—The sp. resistance (I) of very thin wires was given by $\rho_d = \rho_{\infty}[1 + \alpha^2/d]$, α being a measure of the reflexion of electrons from the metal surface. (I) was measured for single Bi crystals of 1.9—24 μ diameter from 20° to 550° abs. The free path, calc. from α , varied as T^{-2} — T^{-3} , in agreement with the classical, but not the Fermi-Sommerfeld, electron theory. J. S. A.

Effect of electric charge on the conductivity of a metal foil. M. PIERUCCI (Nuovo Cim., 1934, 11, 277—287; Chem. Zentr., 1934, ii, 2507; cf. A., 1933, 117).—The conductivity of a W foil increased on giving it a positive or negative charge.

H. J. E.

Variation of the resistance of nickel with temperature at the Curie point. B. SVENSSON (Ann. Physik, 1935, [v], 22, 97—100).—The temp.-resistance curve of Ni shows a change of direction at the Curie point ($362.9 \pm 0.2^\circ$), agreeing with the view that spontaneous magnetisation ceases at this temp.

A. J. M.

Variation of the resistance of metals in a magnetic field. S. TITEICA (Ann. Physik, 1935, [v], 22, 129—161).—Mathematical.

A. J. M.

Electrical resistance of cobalt in longitudinal magnetic fields. M. S. ALAM (Z. Physik, 1935, 93, 556—560).—The resistance increases with increasing magnetic field and reaches a saturation val. with magnetic saturation; hysteresis appears with decreasing magnetic field.

A. B. D. C.

Thermodynamics of magnetisation. E. C. STONER (Phil. Mag., 1935, [vii], 19, 565—588).—Theoretical.

Energetic and magnetic anisotropy in polycrystalline ferromagnetic plates in a magnetic field. A. DRIGO (Nuovo Cim., 1934, 11, 345—356; Chem. Zentr., 1934, ii, 2508).—A theoretical discussion.

H. J. E.

(A) Can the magnetic coupling of spontaneous magnetisation be observed experimentally?
(B) Origin of changes of susceptibility with the frequency. A. PERRIER (Helv. phys. Acta, 1934, 7, 471—472, 474—475; Chem. Zentr., 1934, ii, 2508).

H. J. E.

Dependence of the permeability of iron, nickel, and cobalt on frequency. R. SANGER (Helv. phys. Acta, 1934, 7, 478—480; Chem. Zentr., 1934, ii, 2508—2509).—The origin of the fall in ferromagnetic permeability above a crit. frequency of the magnetic field is discussed.

H. J. E.

Problems on the theory of ferromagnetism. HIRONE (Sci. Rep. Tôhoku, 1934, 23, 523—536).—e Heisenberg theory does not account for the existence of a saturation val. of magnetisation. At liquid H., temp. vals. deviate from an integral no. of one Bohr magneton. An analysis based on consideration of energy levels in each term of an elementary complex with the atoms in their ground state is given, which explains the deviation. The sp. heat of a ferromagnetic substance attains a max. at the temp. of the crit. point. It is shown that the magnetic transformation is an endothermic change which explains the large increase in sp. heat below the change point. The sp. heat due to the magnetic change is calc., and when added to the sp. heat due to thermal vibrations results in a val. in good agreement with experiment.

W. P. R.

Magnetic properties of pure nickel near the point. L. NEEL (J. Phys. Radium, 1935, 10, 1—10).—Using an improved high-precision apparatus, data for the variation of susceptibility

with temp. and magnetic field accurate to 0.005° were obtained for Ni, for the range 50—1000 gauss, from the Curie point (358°) to 368° .

N. M. B.

Tribo- and photo-electric effects for palladium. P. A. MAINSTONE (Phil. Mag., 1935, [vii], 19, 278—290).—The frictional charge is a min. and the photo-sensitivity a max. at moderately low pressures. Reversal of sign of the frictional charge is due to the presence of O_2 . Occluded H_2 increases the photo-sensitivity to a max. at saturation, not diminished by subsequent removal of the H_2 . The form of the low-pressure frictional isotherm is independent of the occlusion of gas.

C. W. G.

Nature of the metallic state. W. C. FERNELIUS and R. F. ROBEY (J. Chem. Educ., 1935, 12, 53—67).—A discussion.

L. S. T.

Dispersion of optical activity of quartz in directions inclined to the optical axis. C. MUNSTER and G. SZIVESSY (Physikal. Z., 1935, 36, 101—106).—When the normal is inclined $56^\circ 10'$ to the optical axis, quartz behaves as if it were inactive to perpendicularly incident parallel light throughout the whole spectral range. Such plates should be used in certain optical instruments.

A. J. M.

Plasticity of rock-salt crystals. E. N. DA C. ANDRADE (Nature, 1935, 135, 310).—Plates of rock-salt can easily be bent under running cold H_2O .

L. S. T.

Deformation slip in single tin crystals. K. BAUSCH (Z. Physik, 1935, 93, 479—506).—Slip was obtained in the new system $[010](100)$. Slip-tension curves were obtained at different rates of deformation and different temp. A theory of crystal plasticity is given.

A. B. D. C.

Allotropy of sulphur. K. NEUMANN (Z. physikal. Chem., 1934, 171, 399—415).—Mol. wt. determinations with the vapour in equilibrium with the solid forms of S at 60—100° show the vapour of S_α and S_β to consist of S_8 mols. The existence of Muthmann's S has been confirmed (cf. A., 1933, 1258). Wigand's reaction velocity method for determining the mol. wt. of insol. S (A., 1908, ii, 676) is valueless. The vapour of this form contains mols. $< S_8$ probably identical with Aten's S_n ; S_n is a polymerisation product of these. The proportion of material sol. in CS_2 in plastic S does not change when the latter is drawn into threads. Meyer and Go's picture of the structure of S threads (A., 1934, 1296) seems to be incorrect; the considerable proportion of amorphous sol. material ($S_\lambda + S_n$) present cannot be disregarded. A thread which has hardened at room temp. recovers in hot H_2O , unless the amorphous part has been previously extracted with CS_2 .

R. C.

Mol. wt. of a pure liquid at its normal b.p. R. LAUTIE (Compt. rend., 1935, 200, 455—456).—The mol. surface energy const. and the effect of polymerisation and the existence of double mols. are considered for liquefied gases and org. and inorg. liquids.

N. M. B.

Diamagnetism of light and heavy water. F. W. GRAY and J. H. CRUICKSHANK (Nature, 1935, 135, 268—269).—The mol. diamagnetism (I) of H_2O

is 12.96—0.02. Mixtures containing 44, 62, and 87% of H₂O show strictly additive susceptibility. H₂O, H₂O, and H¹H²O thus appear to have identical (I). More refined measurements reveal a lag in which appears an observable magnetic difference between H₂O and H₂O. With freshly melted H₂O the susceptibility reaches a max. after 20 min. and then falls slightly to a const. val. This behaviour is interpreted in terms of the state of co-ordination of H₂O. With H₂O, a similar but less pronounced change occurs.

L. S. T.

Magnetochemical investigations. XII. Magnetic behaviour of some volatile fluorides. XIII. Fluorides of copper, nickel, and cobalt. P. HENKEL and W. KLEMM (Z. anorg. Chem., 1935, 222, 70—72, 73—77).—XII. Diamagnetic measurements have been made on GeF₄ and all the known hexafluorides at the temp. of liquid O₂. The results are compared with the vals. calc. by Angus' method (A., 1932, 795). SF₆, SeF₆, and TeF₆ are in good agreement. GeF₄ shows an unexplained deviation. The experimental vals. for MoF₆, WF₆, and UF₆ are considerably < the calc. vals., UF₆ being paramagnetic. The behaviour is compared with that of the O compounds.

XIII. The magnetic susceptibilities χ of CuF₂, NiF₂, CoF₂, and CoF₃ have been measured at -183°, -78°, and 20°. Effective magneton nos. are also given. These are considerably < for salt-like compounds in general, the fluorides apparently standing between chlorides and oxides. For CoF₃ a magnetic moment similar to that of Fe³⁺ is to be expected, i.e., about 5.2, but it is 2.46 only, at 20°. M. S. B.

Paramagnetic properties of bivalent chromium salts. E. LIPS (Helv. Phys. Acta, 1934, 7, 537—583; Chem. Zentr., 1934, ii, 2375).—Measurements of the susceptibility of CrSO₄·6H₂O follow the Curie-Weiss law (I) between 54° and 400° abs. The magneton no. = 4.82 Bohr units. CrCl₂ deviates from (I) throughout the same temp. range. H. J. E.

Influence of physical state on the magnetic properties of some salts of the iron group. A. LALLEMAND (Ann. Physique, 1935, [xi], 3, 97—180).—Variation of magnetic susceptibility with temp. was investigated. The magnetic moments of paramagnetic salts melted in their H₂O of crystallisation can assume vals. varying with the concn., the susceptibility decreasing at high concn. For CoCl₂ the effect at high concn. is not wholly reversible on dilution, and explains the two types of solution previously reported. Magnetic data for gaseous FeCl₃ establish the mol. as Fe₂Cl₆. The ions of Fe^{III} and Mn^{II} salts gave 29.5 and 29.2 magnetons respectively, compared with the quantum val. 29.38. The val. for the anhyd. chlorides deviates from the theoretical 28.7. The magnetic properties of the hydrated chlorides and their solutions were identical. Results in general agreed with Weiss' law. N. M. B.

Thermal expansion of rock-salt and pure NaCl. H. SAINI (Helv. phys. Acta, 1934, 7, 494—500; Chem. Zentr., 1934, ii, 2191).—The thermal expansion of rock-salt and of chemically pure NaCl, determined by X-rays, agree between 0° and 100°, but differ above that temp. J. S. A.

Cryoscopic properties of some terpenes. R. DULOU (Bull. Inst. Pin, 1934, 210—213).—The cryoscopic const. (I) of camphenilone, m.p. 36—37°, is 605 and the heat of fusion 3.2 g.-cal.; it gives good vals. for the mol. wt. of several substances. (I) for camphene is about 270. R. S. C.

Stoicheiometry. I. Heat of fusion of organic compounds. J. TIMMERMANS (Bull. Soc. chim. Belg., 1935, 44, 17—40).—Determinations of the heat (*L*) and mol. heat (*Q*) of fusion of org. compounds (1) by direct measurement, (2) from the cryoscopic const., and (3) from the f.-p. curves of binary mixtures of "normal" substances are discussed and the data tabulated. It is generally possible to predict the order of magnitude of *L* or *Q* from the chemical nature and the structure and shape of the mols., but a few anomalous vals. remain unexplained. F. L. U.

Purification and physical properties of organic compounds. VIII. Thermal study of liquid crystal formation. E. L. SKAU and H. F. MEIER (Trans. Faraday Soc., 1935, 31, 478—480).—A time-temp. curve (cf. A., 1933, 667) has been obtained for *p*-methoxycinnamic acid. The f.p. is 172.1° and the transition point from the liquid-cryst. to the liquid-amorphous state is 187.3°. The ratio of the heat of fusion of the solid to the heat of transition of the liquid crystals is 7:1. M. S. B.

Purification and physical properties of organic compounds. VII. Effect of impurities on the apparent heat of fusion. E. L. SKAU (J. Amer. Chem. Soc., 1935, 57, 243—246; cf. A., 1934, 1085).—Determinations with pure and impure C₆H₆ show that large errors may be involved when the usual method of correcting for the presence of impurities is followed. E. S. H.

Heat of vaporisation of a pure substance from the measurement of temperature at two points and the vertical distance between them. S. C. COLLINS (J. Amer. Chem. Soc., 1935, 57, 330).—Theoretical. E. S. H.

Heats of sublimation of organic molecules. K. L. WOLF and H. G. TRIESCHMANN (Z. physikal. Chem., 1934, B, 27, 376—380).—Measurement of the heat of sublimation, *Q*, of fumaric and maleic acids and their Me esters, and various aromatic substances has indicated a general divergence from Trouton's rule. The relation of *Q* to intramol. forces (cf. A., 1932, 21) is discussed. R. C.

Direct determination of heat of condensation. II. Experiments with intensively dried liquids. A. SMITS and D. CANNegieter (Z. physikal. Chem., 1935, 172, 1—32; cf. A., 1934, 836).—The heat of condensation, *Q*, of the vapour from C₆H₆ dried for a long time over P₂O₅ passes with increasing duration of drying through a min., ~9% < the normal val. (I), but ultimately rises to (I) again. The depression of *Q*, which is observed only if the whole apparatus has previously been heated while a current of dry O₂ passed through, is the greater the more rapid is vaporisation and condensation. With EtBr drying increases *Q*, but with Br the results were inconclusive. These effects are ascribed to the delaying

by drying of the establishment of inner equilibrium. Q may from this cause either rise or fall. Between formation and condensation C_6H_6 vapour approaches inner equilibrium according to the unimol. law. The wall of a highly dried glass apparatus becomes moist again after a time, probably due to diffusion of H_2O to the surface from within. This increases the rate of internal transformation in the vapour phase. For C_6H_6 one pseudo-component is probably a polymeride of the other. R. C.

Anomalous specific heats. B. RUHEMAN and M. RUHEMAN (Physikal. Z. Sovietunion, 1934, 6, 186—188).—It is suggested that all the sp. heat anomalies at transition points (*e.g.*, transition of metals to superconductors) should be interpreted in terms of phase changes in binary systems.

CH. ABS. (e)

Calculations of heat capacities of gases at high pressures and temperatures. I. I. GELPERIN and S. M. RIPS (Khimistoi, 1934, 6, 455—458).—A formula was calc. for the mol. sp. heat of N_2 , H_2 , and CO at 0—600° and 700—1200 atm.

CH. ABS. (e)

Specific heats of light-metal fluorides at high temperatures. A. N. KRESTOVNIKOV and G. A. KARETNIKOV (Legk. Metal, 1934, 3, No. 4, 29—31).—Vals. are recorded for the sp. heats of MgF_2 , BaF_2 , and Na_3AlF_6 (300—1000°) and for NaF (300—800°).

CH. ABS. (e)

Determination of small density differences in water. E. HOFER (Z. physikal. Chem., 1934, B, 27, 467—472).—A combination of the methods of d determination of Gilfillan and Polanyi (A., 1933, 1136) and Lewis and Macdonald (J. Amer. Chem. Soc., 1933, 55, 1297) permits determination of d differences in H_2O with a precision of 5×10^{-7} .

R. C.

Density of water in relation to its thermal history. M. DOLE and B. Z. WIENER (Science, 1933, 81, 45).—Determinations of flotation temp. show that the freezing and melting of H_2O and ice produce no detectable changes in the internal structure of H_2O . Ice H_2O obtained by melting large commercial ice blocks appears to have a larger d than purified H_2O by 2.4 p.p.m. There is no evidence of an enhanced % of $(H_2O)_2$ in ice H_2O as compared with steam H_2O .

L. S. T.

Low-temperature densities of WF_6 and OsF_8 ; C_4F_4 as immersion liquid. P. HENKEL and W.

(Z. anorg. Chem., 1935, 222, 67—69).—Density measurements have been made in CF_4 at -183° , but, as the f.p. of CF_4 is $-183.6 \pm 0.2^\circ$, no CF_4 must be present. For WF_6 d is 4.75 ± 0.02 and for OsF_8 3.87 ± 0.02 . These give 62 and 87 c.c., respectively, for the zero point mol. vols. Neglecting the central ion the increases for F' are, therefore 10.3 and 10.6 c.c., respectively. These are normal vol. 9.5 c.c. The ratios $d_{0^\circ \text{ abs.}}/d_{b.p.}$ for compounds are 1.41 and 1.44, respectively, i.e. normal val. within the limits of experimental error. M. S. B.

of thallos iodide. F. ISHIKAWA and Y. SATO (J. Chem. Soc. Japan, 1934, 55, 930—

934).—Dilatometric data are recorded. The transition temp. was $170-171^\circ$. CH. ABS. (e)

Kinetic-molecular theory and its relation to heat phenomena. J. A. TILM (J. Chem. Educ., 1935, 12, 31—34). L. S. T.

Thermodynamic theory of the equation of state. V. JACYNO, S. DEREJANKIN, A. OBNORSKI, and T. PARFENTJEV (Z. Physik, 1935, 93, 348—349).—The previous theory is extended to bring c_p and c_v into the equation (cf. A., 1934, 1070).

A. B. D. C.

Properties of real gases according to the thermodynamic equation of state. IV. V. JACYNO (Z. Physik, 1935, 93, 338—347).—Formulæ are given for the internal energy, enthalpy, entropy, "max. work," and thermodynamic potential of He (cf. this vol., 22).

A. B. D. C.

Thermodynamic functions of tetramethylmethane. L. S. KASSEL (J. Chem. Physics, 1935, 3, 115—116).—Mathematical. F. L. U.

Thermodynamic properties of dichloromethane. I. S. SUGAWARA (J. Soc. Mech. Eng., Tokyo, 1934, 37, 491—496).—V.-p. measurements are recorded (60° to -20°). The b.p., crit. temp., and crit. pressure were 40.18° , 216° , and 49.7 kg. per sq. cm. respectively.

CH. ABS. (e)

Critical constants of propane. J. A. BEATTIE, N. POFFENBERGER, and C. HADLOCK (J. Chem. Physics, 1935, 3, 96—97; cf. this vol., 438).—Examination of isotherms in the crit. region give t_c $96.81 \pm 0.01^\circ$, p_c 42.01 ± 0.02 normal atm., v_c 4.43 ($\pm 1\%$) c.c. per g.

F. L. U.

Critical temperatures as microchemical test. J. HARAND [with note by F. EMICH] (Monatsh., 1935, 65, 153—184).—A simple micro-method for the determination of crit. temp. (I) is described. (I) of $MeCl$, CH_2Cl_2 , $CHCl_3$, CCl_4 , and Et_2O have been found. From these the crit. temp. of CH_4 has been calc. as 186.6° abs. (I) of *n*-, *iso*-, and technical C_4H_{10} have been determined and it is shown that the method may be used for the identification of substances, gaseous at room temp., which are not otherwise easily distinguishable from one another; it may also be applied to the determination of purity. (I) of C_6H_6 -PhMe and $CHCl_3$ - CCl_4 mixtures have been determined and are in good agreement with the vals. calc. from Pawlewski's formula. M. S. B.

Effect of intensive drying on establishment of inner equilibrium. III. A. SMITS and D. CANNEGIETER (Z. physikal. Chem., 1934, 171, 445—453; cf. A., 1931, 799).—V.-p. measurements cannot be made sufficiently rapidly to demonstrate the effect of intensive drying (I) on inner equilibria in liquids. Measurements of the heat of condensation (II) of vapour formed from the liquid, however, can be made with sufficient rapidity (cf. this vol., 436). The results which have been obtained explain Smith's observations on the effect of (I) on the rate of distillation of MeBr (A., 1932, 329). Baker's results for the effect of (I) on (II) (J.C.S., 1922, 121, 568) are inconclusive. In Manley's experiments (A., 1929, 753) the C_6H_6 was not intensively dried. So

far, the only properties of liquids conclusively shown to be affected by (I) are (II) and rate of condensation.

R. C.

Vapour-pressure measurements with rhombic and monoclinic sulphur below the m.p. K. NEUMANN (Z. physikal. Chem., 1934, 171, 416—420).—V.p. measurements have been made at 60–115°. The calc. mol. heats of vaporisation are $24,080 \pm 70$ and $23,240 \pm 70$ g.-cal. for S_α and S_β , respectively, giving 840 ± 100 g.-cal. for the heat of transition.

R. C.

Vapour pressures of the hexafluorides of selenium and tellurium. P. HENKEL and W. KLEMM (Z. anorg. Chem., 1935, 222, 65–66).—Previous measurements (A., 1932, 905) have been repeated and the vals. for SeF_6 at lower temp. have been corr., giving 5.9₅ instead of 5.6₃ kg.-cal. for the heat of sublimation α . This brings the ratio σ/T_{subl} into line with the vals. for SF_6 and TeF_6 . The results are not in agreement with those of Yost *et al.* (A., 1933, 466).

M. S. B.

Vapour-pressure curve of thallium at very small vapour densities. F. MULLER (Helv. phys. Acta, 1934, 7, 491–492; Chem. Zentr., 1934, ii, 2363).—Vals. between 350° and 500° are deduced from the abs. intensity of absorption of the 3776 Å. Tl line in the vapour.

H. J. E.

Vapour-pressure curve of nitrobenzene. M. T. TOVAL and E. MOLES (Anal. Fís. Quím., 1933, 31, 735–745).—Between 95.8° and 207.9° the v.p. is given by $\log p = 8.172443 - 2552.683/T$; calc. b.p. 209.6°. Latent heat of evaporation is 94.84 g.-cal., and the ebullioscopic const. 49.13. These results were obtained with the thermometer stem immersed in the vapour; results obtained with the thermometer stem emergent, even after correction, show discrepancies.

H. F. G.

Hydrogen sulphide. T. BATUECAS (J. Chim. phys., 1935, 32, 58–62).—Polemical (cf. A., 1934, 355).

J. G. A. G.

Compressibilities and expansion coefficients of gases at low pressures. J. B. M. COPPOCK (Phil. Mag., 1935, [vii], 19, 446–457; cf. A., 1934, 40).—Simplified relations are deduced between compressibilities and expansion coeffs., and results are tabulated and applied for a large no. of gases.

N. M. B.

Compressibility of and equation of state for gaseous ethane. J. A. BEATTIE, C. HADLOCK, and N. POFFENBERGER (J. Chem. Physics, 1935, 3, 93–96).—The compressibility has been measured at intervals of 25° from 25° to 250° for densities 0.5–5.0 mols. per litre. Consts. for the Beattie-Bridgeman equation of state are given. The calc. wt. of a normal litre of C_2H_6 is 0.2%, and the crit. pressure 10%, < observed vals. The v.p. of the liquid measured at 0° is 23.57 and at 25° 41.37 normal atm.

F. L. U.

Changes of state of viscous systems. IX. Viscosity and elasticity. H. UMSTATTER (Kolloid-Z., 1935, 70, 174–180; cf. A., 1933, 569).—A theory of the viscosity-time effect is advanced, which is supported by published results (cf. A., 1927, 309).

E. S. H.

Viscosity of helium I and helium II. E. F. BURTON (Nature, 1935, 135, 265).—The η of He I, which is formed at 4.2° abs., increases as temp. is reduced to 2.3° abs.; at 2.2° abs. the liquid suddenly becomes much less viscous and changes to He II.

L. S. T.

Viscosity, thermal conductivity, and diffusion of gas mixtures. XXX. Viscosity at low temperatures of hydrogen, helium, and neon, and binary mixtures of them down to 90° absolute. M. TRAUTZ and H. ZIMMERMANN (Ann. Physik, 1935, [v], 22, 189–194).—The viscosity of He and Ne was determined at 194.6° abs. and 90° abs., and that of the three binary mixtures of Ne, He, and H_2 at 90° abs. Various consts. for the pure gases and mixtures calc. from the results agree with those already derived theoretically (A., 1934, 136).

A. J. M.

Measurements on the viscosity of oxygen gas at liquid oxygen temperatures. A. VAN ITTERBECK and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 11, and Physica, 1935, 2, 97–103).—The viscosity (η) has been determined by the oscillating-disc method between 79.4° and 90.2° abs. and at different pressures. Combined with the work of others the results show that η decreases linearly with fall of temp. above 140° abs., approx., but more rapidly below. A decrease in η with increase in pressure is indicated.

M. S. B.

Effect of temperature on viscosity of tetrachlorides of elements of fourth group of periodic classification. G. P. LUTSCHINSKY (Z. physikal. Chem., 1934, 171, 348–352).—The variation with temp. of the viscosities, η , of CCl_4 , SiCl_4 , TiCl_4 , and SnCl_4 follows Batschinski's formula $\eta = c/(v - \omega)$, where v is the sp. vol. ω increases with decreasing at. wt. of the central element, and $\omega M \propto$ the linear size of the mol. (M = mol. wt.).

R. C.

Viscosity and molecular association. B. PRASAD (J. Indian Chem. Soc., 1934, 11, 913–918).—In $\log \eta = \alpha + \beta/T$ (η = coeff. of viscosity, T = abs. temp., α, β = const.), β varies with mol. association (I). Comparison of β at two temp. gives the ratio of the mol. wt. at these temp. To obtain abs. vals. of (I), β for the unassociated liquid may be calc. from the approx. relationship, crit. temp. $T_c = 0.7\beta$. Using this, (I) for H_2O decreases from 2.3 at 5° to 1.5 at 65°. A comparison of the results for H_2O , MeOH , PrOH , BuOH , and AcOH with those obtained by the Eötvös-Ramsay method shows qual. agreement, but the viscosity method is preferred.

A. J. M.

Solutions of isopropyl alcohol in benzene, in water, and in benzene and water. A. L. OLSEN and E. R. WASHBURN (J. Amer. Chem. Soc., 1935, 57, 303–305).—Determinations of f.p., solubility, n , d , and η have been made.

E. S. H.

Surface tension of binary liquid mixtures. System aniline-cyclohexane. J. WELLM (Z. physikal. Chem., 1935, B, 28, 119–122).—The surface tension, γ , of mixtures has been measured at 32° and 60°. The temp. coeff. of γ is abnormally small, owing to dissociation of associated NH_2Ph complexes with rising temp. Association of the component with the larger γ lowers the γ of the mixture, whilst associ-

ation of the component with the smaller γ has the reverse effect. R. C.

Heats of reaction and viscosities of ether-chloroform mixtures. D. B. MACLEOD and F. J. WILSON (Trans. Faraday Soc., 1935, 31, 596—603).—The heat evolved on mixing Et_2O and CHCl_3 is a max. for equimol. proportions, at 3°, 15°, and 24°, indicating the formation of a compound. Figures given in an earlier paper (A., 1934, 723) are corrected. F. L. U.

Heat of mixing, heat of vaporisation, and association. K. L. WOLF, H. PAHLKE, and K. WEHAGE (Z. physikal. Chem., 1935, B, 28, 1—13).—Data are recorded for the heats of mixing of aliphatic alcohols (I) with hexane (II) and with C_6H_6 and of C_6H_6 and cyclohexane with (II), and for the heats of vaporisation of (II) and ketones. Steric influences are more prominent in solvation of (I) with C_6H_6 than in association of (I) mols. with each other. With increasing steric shielding of (I) fewer triple and quadruple mols. are formed, but the formation of double mols. is scarcely affected by increasing chain length. C_6H_6 has a strong de-associating action compared with (II). With mols. having freely rotatable polar groups, the rotation of which is prevented by intramol. dispersion or directive effects, dipole moments in C_6H_6 are > in (II). R. C.

Dependence of the internal friction [on the composition] of fused KCl-MgCl_2 mixtures. S. KARPATSCHOV and A. STROMBERG (Z. anorg. Chem., 1935, 222, 78—80).—The coeff. of friction (I) has been determined at 500—750° by the damping of the swings of a Pt sphere. The curves obtained by plotting (I) against mol.-% MgCl_2 have a pronounced max. corresponding with the compound 2KCl.MgCl_2 . M. S. B.

Surface tension sensitivity of viscosity determinations. W. LINKE (Physikal. Z., 1935, 36, 45).—The η -concn. curves of "nekal" solutions differ according as η is determined by an Ostwald or an Engler (I) viscosimeter. In (I) the surface tension affects the result. A. J. M.

Rates of evaporation of chlorine, bromine, and iodine from aqueous solutions. M. J. POLISSAR (J. Chem. Educ., 1935, 12, 89—92).—In open vessels at an average temp. of 24°, the sp. rate of evaporation is the same for Br solutions, I solutions containing < 0.006M-KI, and Cl_2 solutions of concn. > 0.001M. The controlling factor is the rate of diffusion of the solute from the bulk to the surface the solution. L. S. T.

Diffusion gases through metals. T. FRANZINI (Nature, 1935, 135, 308; cf. this vol., 25).—An adsorption threshold on one side and an evaporation pressure on the other side of the metal are presumed. orbs H_2^+ considerably from a mixture of H_2 and H_2^+ , whereas H_2 diffuses very slowly, in comparison with H_2 , through the metal. L. S. T.

Linear crystallisation velocity of ice from ordinary and heavy water. G. TAMMANN and A. (Z. anorg. Chem., 1935, 222, 12—16).—The crystallisation velocity (I) ice has been followed in capillary tubes. Admixture with an insol. H H

substance, such as clay, lowers (I) for a small supercooling but, beyond 6°, produces no effect. This is explained by the character of the crystallisation process. With 12° supercooling (I) for ordinary H_2O is > for H_2O (> 99.5% purity). This is explained by the greater heat of fusion of heavy ice combined with the practically equal sp. heats. The max. (I), which alone can be regarded as characteristic, requires a supercooling of 25—30° and must be > 10 m. per min. M. S. B.

Transitions in the copper-gold alloy. II. Migration of atoms in the copper-gold lattice. III. Effect of strain on the lattice equilibrium. V. S. GORSKY (Physikal. Z. Sovietunion, 1934, 6, 69—76, 77—81; cf. A., 1928, 1078).—The velocity of transition of a 50% Cu-Au alloy to its equilibrium state has been determined by measuring the ratio of the tetragonal and digonal crystal parameters in its dependence on annealing time and temp.

CH. ABS. (e)
Existence of a transformation of exactly the second order. U. DEHLINGER (Z. physikal. Chem., 1935, B, 28, 112—118; cf. this vol., 155).—The continuous transition from an ordered to a random distribution in metallic mixed crystals (A., 1934, 1065) is a transformation of the second order and only as a limiting case, not observable practically, is it a transformation of the third order. A transformation of the second order is probably realisable experimentally in Fe_3Al (cf. *ibid.*, 954). R. C.

Correlation of equilibrium relations in binary aluminium alloys of high purity. W. L. FINK and H. R. FRECHE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., 1934, Tech. Publ. 580, 14 pp.).—A comprehensive review and discussion. CH. ABS. (e)

Aluminium-rich alloys of the ternary system aluminium-tin-manganese. A. SCHUCK (Z. Metallk., 1935, 27, 11—18).—In alloys of Al with Mn 0—6 and Sn 0—20% the only compound present is MnAl_7 , and only the two binary Al eutectics exist. Addition of Sn to the Al-MnAl₇ eutectic lowers the m.p. from 649° to a min. of 620—622° with 20% Sn. In alloys with 73% Mn the primary radial acicular structure prevents segregation of the Sn-rich eutectic. All the alloys tested are soft and easily workable, cannot be hardened by heat-treatment, and are readily oxidised by exposure to air or moisture. Adequate protection against corrosion is, however, afforded by lacquer coatings baked on at < 220°. A. R. P.

ϵ -, γ -, and β -Phases of the system cadmium-silver. P. J. DURRANT (J. Inst. Met., 1935, 56, Advance copy, 437—448).—Thermal and micrographic analysis of the system between 30 and 60% Ag has shown that the liquidus consists of 4 smooth curves intersected by peritectic horizontals at 592° (28—35.5% Ag), 640° (35.5—43.5% Ag), and 736° (56—62% Ag). The ϵ -field extends to 33.5% Ag at 590°, 34.2% Ag at 535—408°, 32.5% Ag at 305°, and 29% Ag at 100°, the ϵ + γ -field to 35.5% Ag at 592°, 37.4% Ag at 510°, and 36% Ag at 100°, and the γ -field to 41.5% Ag at 640—230° and 40% Ag at 100°. In the range 40—60% Ag the system is very complex since the β -phase is stable only at high temp. and

decomposes on cooling first into β' , then into β'' , the transformation points depending on the composition; in $\beta + \gamma$ alloys a peritectic horizontal exists at 470° (41.5–47.8% Ag) with a triple point at 42.5% Ag, and in $\alpha + \beta$ alloys a eutectoid horizontal occurs at 440° (49–57% Ag) with the eutectoid point at 50.5% Ag. The $\beta' \rightarrow \beta''$ transformation occurs at 230° in $\beta' + \gamma$ alloys (41.5–49% Ag) and at 240° in $\alpha + \beta'$ alloys (49–54.5% Ag); the β' -field commences at 45.3% Ag at 230° . The range of pure β'' is about 1% Ag around 49% Ag at 230° and around 47% Ag at 100° . At both the eutectoid points the solid solution decomposes into a characteristic Widmannstatten structure.

A. R. P.

Constitution and properties of cadmium-tin alloys. D. HANSON and W. T. PELL-WALPOLE (J. Inst. Met., 1935, 56, Advance copy, 449–470).—Re-examination of the system by thermal analysis and micrographic examination has shown the eutectic to be at 176° and 33% Cd, and a very small solid solubility to exist at both ends. Above 131° 5–6% Cd is sol. in Sn, but below this temp. two conjugate solid solutions are formed containing at 127° 1.25 (I) and 5% Cd (II), respectively. At 127° in all alloys between 1.25 and 99.5% Cd (II) undergoes a eutectoid transformation, and at 170° there is a slight transition, connected with a change of solubility of Sn in Cd, in alloys with 40–90% Cd. The grain-size of Sn is considerably reduced by addition of Cd, only 1% Cd being sufficient to increase the no. of grains per sq. cm. after rolling to 80% reduction from 1600 to 26,000. After annealing for 1 day at 160° Sn with 5% Cd shows 48,000 grains per sq. cm. The Brinell hardness of alloys quenched from 160° rises to a max. of 34 with 5% Cd, but this val. falls to 21 after storage for 2 months; similarly the tensile strength of the 5% Cd alloy falls from 9 tons per sq. in. immediately after quenching to just > 4 tons per sq. in. in 3 months.

A. R. P.

Electrochemical and X-ray investigation of solid thallium amalgams. A. ÖLANDER (Z. physikal. Chem., 1934, 171, 425–435).—The electrode potentials and their temp. coeffs. for Tl amalgams containing 20–30 at.-% Tl have been measured. The results establish the boundary of the δ phase, which is face-centred cubic, and show that the structure of the alloy of composition Tl_2Hg_5 is not ordered. TlHg_2 possibly corresponds with an ordered structure, but TlHg_3 does not. The belief that the δ phase undergoes a transition a little below its m.p. (A., 1916, ii, 329) is erroneous. X-Ray examination shows the existence of an intermediate phase with a body-centred cubic lattice between 86 and 90 at.-% Tl.

R. C.

Rhodium-copper alloys. O. E. ZVJAGINTSEV and B. K. BRUNOVSKI (Ann. Inst. Platine, 1935, 12, 37–66).—Thermal, microscopic, X-ray, and hardness data afford evidence of the compound Rh_2Cu_2 (transition point 1015° , cubic face-centred structure), and possibly of Rh_3Cu .

R. T.

(A) Platinum-antimony alloys. (B) Platinum-rhodium alloys. V. A. NEMILOV and N. M. VORONOV (Ann. Inst. Platine, 1935, 12, 17–25, 27–35).—(A) F.p., conductivity, hardness, and crystallo-

graphic data confirm the existence of PtSb_2 , but not of Pt_3Sb_2 (Friedrich and Leroux, A., 1909, ii, 96); other possible compounds are Pt_4Sb and PtSb with transition points at 670° and 660° .

(B) The f.p., hardness, conductivity, and micro-structure of Pt-Rh alloys indicate that solid solutions only are formed.

R. T.

Osmiridium. III. X-Ray analysis. O. E. ZVJAGINTSEV and B. K. BRUNOVSKI (Ann. Inst. Platine, 1935, 12, 5–15).—The X-ray diagrams indicate a fibrous structure, with a tendency to recrystallisation.

R. T.

Heusler alloys. S. VALENTINER and G. BECKER (Z. Physik, 1935, 93, 629–633).—Magnetic susceptibility and electric resistance show that MnAlCu_2 is stable up to 300° .

A. B. D. C.

Penetration of a magnetic field into superconductive alloys. J. DE HAAS and J. M. CASIMIR-JONKER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 2–7).—The effect on a cylindrical rod of the alloy of a magnetic field perpendicular to the axis, at temp. below the transition point, has been studied by measuring the resistance of a Bi wire threaded along the axis of the rod. No magnetic disturbance of Bi_5Tl_3 was observed at the b.p. of He with approx. 4000 gauss. The magnetic transition curves of a Pb-Tl (64.8% Tl) alloy are given for 3 temp. $<$ transition point. The increase in resistance of a Bi wire has been plotted against field strength for Bi_5Tl_3 at 4.21° and 3.70° abs., and for Pb-Tl at 4.21° , 3.75° , 2.99° , and 2.01° abs. The lowest field which can penetrate into the superconductive Pb-Tl alloy has been plotted as a function of the temp. and the region of magnetic disturbance of the superconductive state indicated. The connexion with thermal conductivity is discussed.

M. S. B.

X-Ray study of the system ferric oxide-aluminum oxide. R. YOSIMURA, S. KOSOBÉ, and S. ITO (J. Soc. Chem. Ind. Japan, 1935, 38, 22B–25B).— Fe_2O_3 and Al_2O_3 pptd. from FeCl_3 and AlCl_3 mixtures with aq. NH_3 and ignited at 1000° form solid solutions of the same type of crystal structure as either oxide separately but not in all proportions. The solubility of Al_2O_3 in Fe_2O_3 is about 36 mol.-% and that of Fe_2O_3 in Al_2O_3 17–27 mol.-%.

C. I.

Active oxides. LXXXIV. Changes in the magnetic properties of mixtures of beryllium, calcium, copper, cadmium, and lead oxides with chromic oxide during their chemical combination. H. KITTEL (Z. anorg. Chem., 1935, 222, 1–11).—The investigations are similar to those previously made (this vol., 158). For BeO , CuO , and CdO a rise in magnetic susceptibility χ takes place at 600 – 700° , accompanied by changes in colour and an increase in bulk d . The rise for CaO is at 1000° . CaO shows an initial slight fall at about 500° and CdO a more marked fall at 400° . The system $\text{PbO-Cr}_2\text{O}_3$ shows a very marked fall in χ at 400° and subsequently a very small rise above 800° , although the change in bulk d still takes place at the higher temp. Cryst. chromites are formed in all cases and none of the systems has ferromagnetic properties.

Absorption of hydrogen chloride into various organic liquids and calculation of the heat of absorption. I. S. HAMAY (Bull. Chem. Soc. Japan, 1935, 10, 5—16).—The solubility (S) of HCl in CCl_4 , $(\text{CH}_2\text{Cl})_2$, $(\text{CHCl}_2)_2$, and $(\text{CH}_2\text{Br})_2$ has been determined at 15°, 20°, and 25°, and 400—700 mm., and the heats of dissolution have been calc. The influence of electric moment, internal pressure, and bond energy of the solvent on S is discussed. R. S. B.

Semi-quantitative measurements of the solubility of quartz in super-critical steam. C. J. VAN NIEUWENBERG and (MISS) P. M. VAN ZON (Rec. trav. chim., 1935, 54, 129—132).—The solubility (S) of SiO_2 in super-crit. steam has been determined approx. at 300—500 atm. at 380°, 400°, and 425°. S increases with falling temp. (more H_2O is present at the same pressure at a lower temp.), and decreases with decreasing pressure, tending towards zero at the crit. pressure, in analogy with the system Et_2O —anthraquinone (cf. A., 1930, 1521). R. S. B.

Solubility of calcium sulphate in saturated solutions of potassium and sodium chlorides. A. P. PALKIN and N. M. BRIKMAN (Trans. State Inst. Appl. Chem. U.S.S.R., 1932, No. 16, 16—23).—Vals. at 0—175° are recorded. CH. ABS. (e)

Influence of salts on the solubility of double mercuric thiocyanates. B. V. J. CUVELIER (Natuurwetensch. Tijds., 1935, 17, 26—29).—The solubility of $\text{CdHg}(\text{SCN})_4$ and of $\text{ZnHg}(\text{SCN})_4$ in aq. solutions of KSCN has been measured. D. R. D.

Solubility of non-electrolytes. I. Free energy of hydration of some aliphatic alcohols. J. A. V. BUTLER, C. N. RAMCHANDANI, and D. W. THOMSON (J.C.S., 1935, 280—285; cf. A., 1933, 772).—The v.-p. curves of *n*-, *iso*-, *sec*-, *tert*-butyl, *n*-, *iso*-, *sec*-, *tert*-amyl, *n*-hexyl, *n*-heptyl, and *n*-octyl alcohol have been determined. The partial pressures p of the isomeric propyl, butyl, and amyl alcohols over their dil. aq. solutions (mol. fraction N) are given, and the free energy of hydration $F^\circ - F_g^\circ = RT \log (p/N)$ calc. In the normal alcohols, the increment of $RT \log (p/N)$ is 160 g.-cal. per CH_2 , whilst smaller differences occur in the isomeric alcohols, the significance of which is discussed. R. S.

Distribution of (A) saturated fatty acids between water and toluene; (B) triethylamine between water and aromatic hydrocarbons; (C) benzoic acid between water and isobutyl alcohol, (D) dimethylmalonic acid, (E) monochloroacetic acid; (F) dichloroacetic acid between two contiguous liquid phases. N. A. DE KOLOSOVSKI (Chem. Russ., 1934, 4, 1064—1069, 1070—1073—1076, 1077—1080, 1091—1095, 1096—1097).—(A) PONOMAREVA]. See A., 1934, 26

(B) [with S. A. ANDRIUSCHTSCHENKO]. Data are given for NET_3 — H_2O — C_6H_6 and —PhMe at 25°.

A. BEKTUROV]. Data given for 25°.
N. P. PONOMAREVA]. Data are given for $\text{HMe} \cdot \text{CO}_2\text{H}$ — H_2O — $\text{C}_5\text{H}_{11} \cdot \text{OH}$ and — Et_2O at 25°.
[with F. S. KULIKOV]. Data are given for $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$ — H_2O —PhMe, — CHCl_3 , —Ph NO_2 ,

— $\text{Bu}^\text{t}\text{OH}$, —*n*- and —*iso*- $\text{C}_5\text{H}_{11} \cdot \text{OH}$, and for $\text{CHCl} \cdot \text{CO}_2\text{H}$ — H_2O —PhMe, — CHCl_3 , and —Ph NO_2 , at 25°. R. T.

Adsorption of oxygen on charcoal. Calorimetry and kinetics of slow adsorption. A. LENDLE (Z. physikal. Chem., 1935, 172, 77—94).—The mol. integral heat of adsorption, Q , on sugar C has been measured over a wide pressure range. When the amount of O adsorbed is small, $Q=80$ kg.-cal., but this falls with increasing adsorption and tends to a limit of 5500 g.-cal. The temp. coeff. is positive. With rise in the temp. of preliminary outgassing from 550° to 780° Q rises considerably, doubtless due to increase in the no. of adsorbing centres of high potential. The adsorption consists of an almost instantaneous process and a slower process (I) with a much larger Q val. which at higher temp. determines the character of the total reaction. (I) is a chemical process, not merely dissolution. A calorimetric method of measuring the rate of O adsorption is described. R. C.

Absorption of iodine vapour by active carbon and silica gel. P. DEMOUGIN (Compt. rend., 1935, 200, 662—665).—The quantities of I adsorbed by various types of C and SiO_2 gel are approx. the same at 128° (above the m.p. of I) as at 17°, 60°, and 100°. These quantities are also \propto the absorptive powers of the samples for Et_2O vapour near the saturation point, but they are not \propto the absorptive powers for CO_2 or for I from solution. It is inferred that the I film adsorbed from the gas phase is liquid, even at temp. considerably < m.p. J. W. S.

Adsorption of ethylene on active centres of nickel. G. M. SCHWAB (Z. physikal. Chem., 1934, 171, 421—424).—Strassen's data for the catalysed hydrogenation of C_2H_4 (A., 1934, 974) agree with the exponential relation between temp. and kinetically measured adsorption coeff. demanded by the Langmuir—Hinshelwood theory of heterogeneous reaction velocity, and the heat of adsorption of C_2H_4 on Ni so calc. agrees with that determined directly. R. C.

Adsorption of gases by glass walls. XI. Nitric oxide. M. CRESPI (Anal. Fis. Quím., 1933, 31, 825—829).—The adsorption of NO by glass at pressures between 760 and 95 mm. has been determined. The magnitude of the correction for adsorption in v.d. measurements is discussed. H. F. G.

Adsorption isotherm. K. FISCHBECK, H. MAAS, and H. MEISENHEIMER (Z. physikal. Chem., 1934, 171, 385—398).—The equation $x = (Ap + Bp^2)/(C + p)$ has been deduced to express the connexion between the amount of gas sorbed, x , and the pressure, p . This equation requires rise of x with p in the saturation region and agrees with existing experimental data. It also accords with data for swelling, and successfully represents the simultaneous adsorption of two gases even in cases where Langmuir's theory fails (A., 1933, 1241). R. C.

New interpretation of the adsorption isotherm. G. E. CUNNINGHAM (J. Physical Chem., 1935, 39, 69—77).—A new theory of the kinetics of gas adsorption is developed on the assumption that a

gas mol. must not necessarily collide with a surface in order to be adsorbed, but must come within a certain range of attraction of the adsorbing surface. The amount of gas adsorbed on a given kind of elementary surface \propto the pressure, but different kinds of surface are saturated at different pressures. The mathematical formulæ deduced are in better agreement with experimental data than is Langmuir's equation. A discrepancy between the latter and the Langmuir theory is indicated. The relation between Freundlich's equation and the new theory is discussed.

M. S. B.

Relation between adsorption, solubility, and nature of the solvent. IV. N. SATA and S. WATANABE (Kolloid-Z., 1935, 70, 159—165; cf. A., 1934, 140).—The solubility and adsorption by C of *o*-, *m*-, and *p*-OH·C₆H₄·CO₂H and NEt₄I in binary mixtures of H₂O, MeOH, EtOH, BuOH, COMe., C₆H₆, and CCl₄ have been determined. The curves are antibatic in mixtures of polar liquids, especially when one of the components is H₂O.

E. S. H.

Interfacial energy and the molecular structure of organic compounds. III. Effect of organic structure on adsorbability. E. R. LINNER and R. A. GORTNER (J. Physical Chem., 1935, 39, 35—67).—A comparative study of the adsorption of a large no. of org. acids on Norit has been made. The Freundlich adsorption isotherm is valid, except at low concns., and has been used to calculate the areas under the curves for the fatty acids. Ratios of these areas for successive members of homologous series have a constancy $>$ that obtained by Freundlich's method. The Langmuir equation (I) is applicable to the data, low concns. again excepted. The const. β of (I) is equal to the max. adsorption α when the equilibrium concn. is that of a saturated solution. The different acids have been compared at max. adsorption ($\alpha = \beta$) by determining the relative cross-sectional areas of the mols. calc. after certain assumptions have been made. The branched chain has little effect on β . Introduction of more ·CO₂H, ·OH, or ·CO decreases β . CHO·CO₂H·H₂O is more readily adsorbed than AcOH. There is little difference between *cis*- and *trans*-isomerides, but the double linking decreases adsorption. An alternation exists for the vals. of β for odd and even acids of the homologous series of both mono- and di-carboxylic acids. This appears to confirm the view that the lower members of both series are adsorbed in the solid state.

M. S. B.

Models of the superposition and interpenetration of components in gas mixtures adsorbed on thermionic, photo-electric, and catalytic surfaces. I. Principles. M. C. JOHNSON (Proc. Physical Soc., 1935, 47, 287—305).

N. M. B.

Measurement of the interfacial tension at a mercury-mercurous sulphate solution interface by the drop-weight method. K. E. GLIDDEN (J. Amer. Chem. Soc., 1935, 57, 236—237).—Data are recorded for different concns. at 20°. Interfacial tension is a linear function of log concn. down to 0.0001M-Hg₂SO₄.

E. S. H.

Thin films of insoluble substances on liquid surfaces. I. UHARA (J. Chem. Soc. Japan, 1934, 55, 928—929).—By passing H₂S gently over the surface of aq. Pb(NO₃)₂, a film of PbS of thickness 10⁻⁵—10⁻⁶ cm., and with reflecting power comparable with that of Hg, was obtained.

CH. ABS. (e)

Unimolecular films of lecithin and related compounds. A. HUGHES (Biochem. J., 1935, 29, 430—436).—The surface potential (I) of films of tripalmitin, triolein (II), and cholesterol shows no change from p_H 2 to 12, but for lecithin (III) and lysolecithin (IV) (I) decreases from p_H 3 to 6 and 2 to 5, respectively, as the result of ionisation. The area per hydrocarbon chain in the liquid expanded film of (IV) is about twice that for (III). On dil. KMnO₄ solutions, (III) is oxidised more rapidly than (II) or (IV). Homogeneous mixed films are obtainable from ovalbumin (V) and (II), but films of (III) and certain other fats do not appear to be changed by injection of (V) at any p_H .

A. E. O.

Thickness of a surface film of copper. M. L. NICHOLS (J. Amer. Chem. Soc., 1935, 57, 267—269).—A method for determining the least thickness of metal which will give the same e.m.f. as the massive metal is described. The val. for Cu is 0.39 m μ .

E. S. H.

Wetting characteristics of galena. F. E. BARTELL and G. B. HATCH (J. Physical Chem., 1935, 39, 11—23).—Four different methods for the determination of contact angles have been used. The pressure of displacement method gives results for powdered galena (I) which can be duplicated. It is the only method which can be used for powders. The horizontal plate method is not suitable for (I) or for any substance having two different angles of contact—advancing and receding. The vertical rod method gives trustworthy results, provided a smooth clean surface can be obtained. The deposited film method is satisfactory when a film of the pure material can be prepared by sublimation. With a clean surface of (I) the advancing contact angle of H₂O is 90° and the receding 0°. Powdered (I) is less organophilic than freshly cleaved or sublimed (I), but the latter approaches powdered (I) in surface properties when heated, probably due to oxidation. (I) functions as an organophilic or hydrophilic solid depending on whether it is first wetted by an org. liquid or H₂O. This is in contrast to SiO₂ which is hydrophilic only, and to C which is organophilic only. The wetting produces no permanent change since, when dried, (I) behaves like fresh material again. The deposited film method indicates that As₂S₃, Bi, S, Ph₂, and C₁₀H₈ also behave like (I).

M. S. B.

Influence of adsorbed films on the potential difference between solids and aqueous solutions, with special reference to the effect of xanthates on galena. P. A. LINTERN and N. K. ADAM (Trans. Faraday Soc., 1935, 31, 564—574).—K Et (or Bu) xanthate (I) makes the potential of an oxidised surface of galena (II) against aq. KCl up to 0.3 volt negative to that observed in its absence. The potential of reduced (II) is little affected except acid solutions which decompose (I), nor is it changed by (I) when acting as a reversible electrode, as it

does in aq. Na_2S . No significant change in the potential of $\text{Ag}-\text{AgCl}$ electrodes was produced by adding substances likely to be adsorbed. F. L. U.

Capillary systems. XII (3). Sphere-spiral as a structure element in homogeneous and heterogeneous spherical packing. E. MANEGOLD (Kolloid-Z., 1935, 70, 149—159; cf. this vol., 284).—Mathematical. E. S. H.

Determination of the electrophoretic migration velocity of suspended particles, and a process for measuring the charge of hydrophobic sols. O. ENSLIN, G. LINDAU, and R. RHODIUS (Kolloid-Z., 1935, 70, 189—198).—A modified microscopical method of determining the velocity of electrophoresis is described. The cell is disposed vertically, so that observations on an individual particle can be repeated indefinitely. Results with particles of SiO_2 in H_2O and electrolyte solutions are recorded. Repeated observations on the same particle yield different velocities, and the velocities of different particles may differ by 25%, due to variations in the shape of the particles. Variation in the mean vals. of several series of determinations in the same system is about 5%. Observations on the migration of particles, on which are adsorbed the micelles of a hydrophobic sol, are reported. E. S. H.

Indene as a cryoscopic solvent. W. KLATT (Z. physikal. Chem., 1934, 171, 454—462).—Indene (I) has m.p. -1.76° , latent heat of fusion 19.9 g.-cal. per g., and mol. f.-p. depression per 1000 g. 7.28° . Monohydric alcohols and monobasic org. acids are associated in (I) solution. C_{10}H_8 raises the f.p. of (I), indicating complete miscibility in the solid state. R. C.

Solvent action. IX. Rotatory powers of the *l*-menthyl esters of *m*-nitro- and 3:5-dinitrobenzoic acids in relation to the solvent, concentration, temperature, and wave-length of light. A. MCLEAN (J.C.S., 1935, 229—236; cf. A., 1934, 476).—Mol. wt. determinations show that *l*-menthyl *m*-nitrobenzoate and 3:5-dinitrobenzoate are associated in hexane, whilst in C_6H_6 combination with the solvent occurs also, due possibly to hexapolar association (I). In substituted benzenoid solvents, (I) should decrease with increasing dipole moment in agreement with the observed increase in rotatory powers (II). The variation of (II) with concn. and temp. has been measured and the results are discussed in relation to current theories. R. S.

Solutions of electrolytes. A. W. DAVIDSON (J. Chem. Educ., 1935, 12, 24—30).—An introduction to modern views. L. S. T.

-p. elevations of aqueous solutions of strong electrolytes. E. PLAKE (Z. physikal. Chem., 1935, 113—128).—Measurements have been made ternary and bi-bivalent salts at concns. of 0.008—0.3M. The relation between the osmotic coeff. O , and concn. agrees at low concns. and for ionic diameters of 3—5 Å. with the extended Debye 1931, 1127). Comparison with f.-p. data shows the ionic diameters to be practically the temp. The variation of O with temp. indicates that in aq. solutions of some ternary

salts there is association in the sense of Nernst's hypothesis. For partly dissociated solutes O varies with temp. < for completely dissociated salts. R. C.

Theory of diffusion of electrolytes. M. PLANCK (Z. Physik, 1935, 93, 696—697).—Sitte's equation (A., 1934, 1309) represents an alternative approximation of Poisson's general equation.

Theory of diffusion of electrolytes. K. SITTE (Z. Physik, 1935, 93, 698—701).—Sitte's approximation is more appropriate than Planck's.

A. B. D. C.
Diffusion of magnesium and cadmium sulphates. L. W. ÖHOLM (Finska Kem. Medd., 1934, 43, 55—66).—Davies' measurements by the optical method (A., 1933, 347) disagree with those of other workers and may be vitiated by convection effects.

CH. ABS. (e)
Influence of the concentration and nature of the solute on the compressions of aqueous solutions. R. E. GIBSON (J. Amer. Chem. Soc., 1935, 57, 284—293).—The compressions (to 1000 bars) of various solutions of 16 salts (mainly of K) and of AcOH have been determined over a wide concn. range. The effects of the different salts on the compression of H_2O increase with the charge on the solute ions and decrease with the ionic radius, but other factors also probably operate. The effective pressure of the salts in solution $\propto [\text{H}_2\text{O}][\text{salt}]$. The equation for the vol. of a solution as a function of the pressure gives vals. for the compressibility of solutions at 1 bar which are in accord with those obtained from sound velocity measurements, even when the effective pressure is determined at 1000 bars. The bulk compression-concn. curve for AcOH solutions passes through a min. The apparent compression of H_2O in AcOH solutions is a linear function of $\sqrt{(\text{concn.})}$ only at the H_2O end. The relative departures from the simple law of mixtures of the compressions of aq. AcOH and aq. salts vary linearly with the product $[\text{H}_2\text{O}][\text{salt}]$ in the solutions. E. S. H.

Mixture rule for viscosity of aqueous solutions of strong electrolytes, empirical determination of specific ionic viscosities, and repression of hydrolysis by a neutral salt. H. TOLLERT (Z. physikal. Chem., 1935, 172, 129—142).—From measurements of the viscosity, η_M , of binary aq. solutions of strong electrolytes it is found empirically that $\eta_M = \sqrt{(\eta_1\eta_2)[1 + A'\sqrt{(\gamma_1\gamma_2)}]}$, where η_1 and η_2 are the viscosities and γ_1 and γ_2 the concns. of the components and A' is a const. At high dilutions this becomes Falkenhagen's limiting law. The solubilities of K_2SO_4 in $N\text{-HCl}$ and of KHSO_4 in $N\text{-KCl}$ have been measured at 20° . Sp. ionic viscosities have been calc. The repression of the hydrolysis of AlCl_3 by KCl has been determined. R. C.

Molecular arrangement and X-ray diffraction in ionic solutions. J. A. PRINS (J. Chem. Physics, 1935, 3, 72—80; cf. A., 1931, 1218).—X-Ray diffraction patterns of saturated aq. $\text{Th}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$ indicate a more or less regular arrangement of heavy ions in the liquid. The arrangement becomes less regular with dilution. Solutions containing Ag , Pb , or Ba show a "gaseous" distribu-

tion which is attributed to the existence of a large proportion of undissociated mols. A third group comprises the alkali halides, the patterns of which are best explained by interference between scattering from the heavy ion and that from the H_2O mols. around it. F. L. U.

Spectral property of electrolytes in solution. F. VLES (Compt. rend., 1935, 200, 545—547).—It is shown that the dissociation const. and the oxidation-reduction const. of electrolytes in solution (p_K) are related to the λ of absorption bands of these compounds by $\lambda \cdot 21.2/p_K\mu$. The relation is confirmed for $N\text{-NaOAc}$, $\text{Na}_2\text{B}_4\text{O}_7$, $N\text{-CuSO}_4$, and NH_4Cl , all in aq. solution, and H_2O . J. W. S.

Optical absorption and association of cadmium, zinc, and copper halides in aqueous solution. E. DOEHLEMAN and H. FROMHERZ (Z. physikal. Chem., 1934, 171, 353—378).—Absorption curves (I) have been determined in the visible and ultra-violet regions. The tendency to form MX_4^{--} ions increases in the order $\text{Zn} < \text{Cd} < \text{Hg}$ and $\text{Cl} < \text{Br} < \text{I}$. CuCl_2 and CuBr_2 in aq. solution and in presence of an excess of alkali halide up to $[\text{X}'] = 2M$ exhibit absorption bands which must be ascribed to CuX_4^{--} . With $[\text{X}'] > 2M$ there is evidence of the formation of larger, polynuclear complexes. Mixed solutions of Cu^I , Cu^{II} , and alkali halides exhibit in the ultra-violet only the bands of the corresponding Cu^{II} - and Cu^I -halogen complexes, but there is increased absorption in the green, which causes the dark brown colour of the mixed solutions. R. C.

Colour and molecular state of telluric acid and alkali tellurates in aqueous solutions of various $[\text{H}^+]$. C. STÜBER, A. BRAIDA, and G. JANDER (Z. physikal. Chem., 1934, 171, 320—330).—The optical absorption of pure aq. solutions of H_6TeO_6 and solutions containing HClO_4 is shifted further into the ultra-violet compared with that of KHTeO_4 and K_2TeO_4 solutions, yet diffusivity measurements show that both the acid and these salts are present in solution as single mols. at p_H 0—14. The effect of $[\text{H}^+]$ on the absorption is probably due to intramol. change, such as $\text{Te}(\text{OH})_6 \rightleftharpoons \text{H}_2\text{TeO}_4\text{, aq.} \rightleftharpoons \text{H}^+ + (\text{HTeO}_4\text{, aq.})'$, after the manner of an indicator. R. C.

Relation between heat-conductivity and structure in silica aerogel. S. S. KISTLER (J. Physical Chem., 1935, 39, 79—85).—The heat-conductivity of SiO_2 aerogel of d 0.184, filled with air, CO_2 , or CCl_4 , at different pressures, has been measured. From these data, and the mean free path of the gas mols., the average distance separating the elements of structure is calc. to be 5.0×10^{-6} cm. M. S. B.

Coagulation in smokes. R. WHITLAW-GRAY (J.C.S., 1935, —280).—Liversidge lecture. Smokes, as distinct from sols, undergo spontaneous coagulation (I). The mechanism of (I) is described and methods for the determination of n , the no. of particles per c.c., are compared. The $\ln n$ -time curve is linear, but very fine smokes have higher (I) velocities. The theory of (I) is given and the influence of temp. and pressure discussed. R. S.

Sedimentation equilibrium measurements with low-molecular substances in the ultra-centrifuge. K. O. PEDERSEN (Nature, 1935, 135, 304—305).—Using the improved Svedberg ultra-centrifuge working at 120,000 r.p.m. changes in concn. of solutions of NaCl , LiCl , and glycine have been obtained; these are measured optically. The mol. wts. calc. from these data are in fair agreement with known vals. L. S. T.

Viscosity and plasticity of disperse systems. I. Determination of constants of plastic flow of clay suspensions. M. P. VOLAROVITSCH and D. M. TOLSTOR (Kolloid-Z., 1935, 70, 165—174).—Apparatus and procedure for determining the consts. of Bingham's equation for plastic flow are described. Experiments with clay suspensions show that the results are independent of the rate of deformation and the dimensions of the apparatus. E. S. H.

Diffusion of colloids. R. O. HERZOG (Z. physikal. Chem., 1935, 172, 239—241).—With lyophilic sols normal diffusion may be accompanied by pseudo-diffusion due, not to free motion of the particles, but to swelling. This is probably one of the principal causes of anomalous diffusion (cf. this vol., 25). R. C.

Colloidal gallium. E. EINECKE (Naturwiss., 1935, 23, 131).—The a.c. dispersion method at high voltages (about 50,000 volts) yields oxide-containing aqua- and Et_2O -sols, but with lower voltages (about 220 volts) sols containing 75% Ga are formed which are deep brown in colour by reflected and transmitted light. A. J. M.

Reversal of charge of highly purified ferric oxide sols by multivalent electrolytes. W. PAULI and H. NEURATH (Kolloid-Z., 1935, 70, 135—149).—The charge of the sols can be reversed by neutral salts with quadrivalent anions, and by alkali solutions or salts which hydrolyse to give alkali, but not by trivalent anions, such as $\text{Fe}(\text{CN})_6^{--}$. Sols reversed by quadrivalent anions are not flocculated by CO_2 ; their flocculation by acids depends on the H^+ activity. Sols reversed by alkali are flocculated by CO_2 and by equiv. amounts of acids of different strengths. E. S. H.

Influence of the electric field on the viscosity of colloid solutions. I. External electroviscous effect in benzene solutions of smoked sheet caoutchouc. A. PASSYNSKI (Kolloid-Z., 1935, 70, 180—188).—The change of dielectric and mechanical properties of 1—3% caoutchouc solutions in C_6H_6 by the action of a static electric field on the streaming liquid has been determined. The influence of field strength, streaming velocity of the liquid, concn., temp., and the action of an a.c. field has been investigated. The results can be explained in terms of the elastic deformation of the colloid structure under the influence of the electric field. E. S. H.

Coagulation of colloidal cadmium sulphide. W. BIAŁEK (Rocz. Chem., 1934, 14, 1499—1525).— H_2S acts as a peptiser of CdS , yielding negatively-charged particles; the stability of the sol varies exponentially with the $[\text{H}_2\text{S}]$. The coagulating power of cations increases in the series $\text{Li} < \text{Na} < \text{K} < \text{NH}_4 < \text{Rb} < \text{Cs}$, and $\text{Ca} < \text{Sr} < \text{Ba}$; anions are without action.

The process of coagulation by electrolytes proceeds autocatalytically; the temp. coeff. is 2.05 per 10°. The velocity of coagulation is given by $dx/dt = kx(1-x)$, where x is the relative turbidity. R. T.

Liesegang phenomenon applied to banded malachite. R. J. HARTMAN, E. W. KANNING, and F. G. KLEE (J. Chem. Educ., 1934, 11, 346—349).—Liesegang bands closely resembling banded malachite are formed when 0.5–0.8*N*-CuCl₂ or -Cu(NO₃)₂ diffuses downwards into a solution made by mixing equal vols. of aq. Na silicate, *d* 1.06, and 0.5*N*-(NH₄)₂CO₃, or by bubbling CO₂ through aq. Na silicate, *d* 1.03. CH. ABS.

Emulsions. III. Lipin-containing substances as emulsifiers. R. M. WOODMAN (J.S.C.I., 1935, 54, 70—72T; cf. A., 1934, 597).—Aq. dispersions of lipins from various sources and of various ages yield dual emulsions on shaking by hand with fat solvents. For oil-rich phase vol. ratios, both types of emulsions appear to be simultaneously present (possibly as complex emulsion systems), as far as can be judged by drop tests. This may be due to the presence in the lipins of opposite-type emulsifiers, which act independently of each other.

Peptisation of barium sulphate crystals. D. BALAREV (Z. physikal. Chem., 1935, B, 28, 78—80).—Unit crystallites of BaSO₄ of colloidal dimensions but less sol. than macro-crystals have been obtained. It must therefore be supposed that interfacial tension rises in the region of colloidal dimensions (cf. this vol., 16). R. C.

Electric double layer of colloids. V. Supplementary investigation of peptisation by isomorphous ions. VI. Peptisation by foreign ions. H. R. KRUYT and H. A. CROUW (Z. physikal. Chem., 1935, 172, 49—55, 56—63; cf. A., 1934, 253).

AgI sols may be peptised by Cl⁻. If an AgI sol is formed from equiv. amounts of AgNO₃ and KI presence of much Na phosphate or C₂O₄²⁻ the latter has a temporary peptising action because some Ag phosphate or Ag₂C₂O₄ is formed, leaving KI to peptise. Halogen-substituted org. ions do not peptise. Pptd. AgI is directly peptised only by I⁻.

VI. The possibility of peptising sols by ions which can replace isomorphously the lattice anions has been demonstrated with HgS, AgS, and Cu₃[Co(CN)₆]₂ sols. Cu₃[Fe(CN)₆]₂ and Cu₃[Co(CN)₆]₂ are peptised by KCN because CN⁻ is here a potential-determining ion. Szilard's "peptoid" sols (A., 1908, ii, 197) are peptised by their own ions derived from acid formed by hydrolysis. Instances of sol formation on reactants in stoichiometrical proportions detailed and explained. R. C.

Osmotic pressure of cellulose nitrate solutions. (M. L. D.) DOBRY (J. Chim. phys., 1935, 32, 50—57).—The results already noted (A., 1934, 178) are inconsistent with the solvation and swelling pressure hypotheses. J. G. A. G.

Dielectric investigations of cellulose derivatives in organic liquids. III, IV. S. LEE and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 178—180).—The dielectric const. and the polarisability of solutions of cellulose dextrin acetate and of

cellulose triacetate (I) in CHCl₃-C₆H₆ mixtures are unaffected by the thixotropic sol-gel transformation; there is thus no change in solvation or in ease of orientation or rotation.

IV. (I) when swollen in C₆H₆-CHCl₃ possesses orientation polarisation, but this is slightly < when dissolved; the mols. are thus easily deformed when in the swollen state. A. G.

Thixotropy of solutions of cellulose derivatives. I. Chloroform solutions of cellulose triacetates of different degrees of degradation after addition of non-solvents. M. TANIGUCHI, S. LEE, and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 16—18B).—For solidification to occur the concn. of the solute and the proportion of non-solvent must be higher for cellulose dextrin acetate than for the less degraded fibrous cellulose acetate. The gelatinising effects of C₆H₁₄, light petroleum, and PhMe are > those of C₆H₆, CS₂, CCl₄, and COMe₂, and the time required to set after shaking falls with increasing duration of keeping after the addition of the non-solvent. A. G.

Lyophilic colloids; their theory and application. III. M. H. FISCHER and M. O. HOOKER (Kolloid-Beih., 1935, 41, 95—146; this vol., 163).—A review with particular reference to biology. E. S. H.

Application of the Kohlrausch-Weber theory of the moving boundary in mixed electrolytes and colloid solutions. W. HACKER (Kolloid-Beih., 1935, 41, 147—238).—The moving boundary method and the difficulties of applying it to colloids are discussed. Experiments supporting the Kohlrausch-Weber theory are described. E. S. H.

Peptisation analysis of soil colloids. A. T. TRULIN (Kolloid-Z., 1935, 70, 207—211).—Methods, applicable to CO₃²⁻-free soils, for separating (a) electronegative and isoelectric gels, and (b) org. protective colloids from mineral suspensions, are described. E. S. H.

Benzoquinone-gelatin gels. J. BUCHHOLZ (Kolloid-Z., 1935, 70, 200—202).—Irreversible gels are formed at definite temp. and concn., probably through an oxidation process resembling tanning. The gelation time is shorter the higher is the temp. Quinol salts out gelatin. E. S. H.

Gelatin deformed in an electric field. (MLLE.) S. VEIL (Compt. rend., 1935, 200, 550—552; cf. A., 1933, 1005; 1934, 961, 1172; this vol., 178).—When the direction of the current is reversed after a gelatin film has undergone deformation in an electric field, the film recovers for a time its conducting properties, but finally the current decreases and the film again tends to become a dielectric. Repeated reversal of current leads to progressively less recovery of conductivity. Low-frequency a.c. slowly yields alkaline electrode areas, which exude H₂O and correspond with the cathodic areas of d.c. The effect is the less marked the higher is the frequency. J. W. S.

Colloid chemical hydrolysis of albumins. II. S. I. DIJATSKOVSKI and V. A. LIVANSKAJA (Kolloid-Z., 1935, 70, 202—207; A., 1934, 488).—Certain com-

ponents of ovalbumin have the power to emulsify Et_2O . The Et_2O extracts a fraction having polar properties, to an extent inversely \propto the concn. of the albumin.

E. S. H.

Complex coacervation of amylophosphoric acid and proteins and its probable bearing on the problem of amylopectin. P. KOETS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 63—74).—Amylose in solution does not form coacervates with positively-charged proteins, probably owing to the smallness of its negative charge. After esterification with H_3PO_4 , however, the resulting amylophosphoric acid exhibits appreciable anodic migration, and, from its behaviour with gelatin and potato albumin, apparently forms coacervates with proteins. It is suggested that the behaviour of amylopectin is best explained on the assumption that it is a flocculated coacervate of amylophosphoric acid and one or more proteins.

M. S. B.

Elementary displacements in homogeneous chemical equilibria. Variations of concentration. Constant-volume reactions. P. MONTAGNE (Compt. rend., 1935, 200, 452—454; cf. this vol., 301).—Mathematical.

N. M. B.

Thermodynamic equilibria. E. JUSTI and M. VON LAUE (Physikal. Z., 1935, 36, 146).—Eucken's statement (this vol., 155) that the sp. heat-temp. curve must have two max. in the neighbourhood of an equilibrium of the third kind is unacceptable. There is only one max.

A. J. M.

[Thermodynamic equilibria.] A. EUCKEN (Physikal. Z., 1935, 36, 147).—A reply to the above.

A. J. M.

Thermodynamic problem. A. SKRABAL (Z. Elektrochem., 1935, 41, 147—149).—An explanation is offered (cf. this vol., 301).

E. S. H.

Chemical equilibria in low-pressure gas discharges in the neighbourhood of the cathode and in the positive column. P. JOLIBOIS (Compt. rend., 1935, 200, 651—652; cf. A., 1934, 975).—The equilibria for $2\text{CO}_2 + \text{O}_2$ and $2\text{H}_2 + \text{O}_2$ mixtures passed through the positive column of a discharge tube correspond with temp. $>$ those for mixtures passed through the cathode region. The apparent temp. falls in each case at low pressure, this being attributed to loss of kinetic energy by the electrons and positive ions on collision with the walls of the tube.

J. W. S.

Dissociation of sulphur monochloride vapour. R. C. BARTON and D. M. YOST (J. Amer. Chem. Soc., 1935, 57, 307—310).—The v.d. of S_2Cl_2 has been measured at 1 atm. and 272—528°. Decomp. does not occur below 300°/1 atm. The dissociation of S_2Cl_2 vapour at lower pressures and under equilibrium conditions has been investigated at 160—800°. Excess of Cl_2 represses the dissociation. The results indicate that the reaction is S_2Cl_2 (gas) = S_2 (gas) + Cl_2 (gas), but the calc. heat of reaction does not agree with independent thermal data.

E. S. H.

A thermodynamical theory of solutions. F. MICHAUD (J. Chim. phys., 1935, 32, 66—90).—Mathematical. The theory is developed from the

concepts of v.p. and the semipermeable membrane. The true mol. wt. of a solute is that which corresponds with the d of the vapour of the solute in equilibrium with the solution. When the interpretation of data for dil. solutions by the classical theory leads to anomalous results, the present theory permits the true mol. wt. to be deduced.

J. G. A. G.

Specific thermodynamic properties of aqueous solutions of strong electrolytes. E. A. GUGGENHEIM (Phil. Mag., 1935, [vii], 19, 588—643; cf. A., 1932, 338).—Limitations of the Debye-Huckel theory are discussed. A modified theory is developed and applied to data for strong electrolytes.

H. J. E.

Isotopic exchange equilibria. H. C. UREY and L. J. GRIEFF (J. Amer. Chem. Soc., 1935, 57, 321—327).—With the aid of spectroscopic data the equilibrium consts. and enrichment factors of several exchange reactions involving isotopes of the lighter elements have been calc. The results show that there is a theoretical limit to the precision of at. wt. determinations, which has already been reached for several lighter elements. Reactions for the separation of isotopes are suggested.

E. S. H.

Spectrographic method for the study of unstable compounds in equilibrium. R. TSUCHIDA (Bull. Chem. Soc. Japan, 1935, 10, 27—40).—A general method is described for studying equilibria of the type $m\text{A} + n\text{B} \rightleftharpoons \text{A}_m\text{B}_n$ in solution by light absorption measurements when (a) A and B do and do not absorb in the same region as A_mB_n , and (b) the absorption of A or B overlaps that of A_mB_n . KI and I give at 23—25° a max. absorption at wave no. $20 \times 10^3 \text{ cm}^{-1}$ due to I_2 , and at 28 and $34.5 \times 10^3 \text{ cm}^{-1}$ due to the compound. At $22 \times 10^3 \text{ cm}^{-1}$ all solutions have the same absorption. For KI_3 , the equilibrium const. is approx. 5.6×10^3 . The calc. absorption of KI. shows two max. and two min.

R. S. B.

Dissociation constants of some aliphatic arsinic acids. H. J. BACKER and C. C. BOLT (Rec. trav. chim., 1935, 54, 186—194).—The dissociation consts. of the following alkylarsinic acids (I), prepared (a) from the alkyl halide or sulphate and Na_3AsO_3 or (b) by oxidation of RAsCl_2 (Gibson *et al.*, A., 1931, 1434) with 10% H_2O_2 , have been determined by the use of a Pt or glass electrode. The vals. of $k_1 \times 10^4$ and $k_2 \times 10^9$, respectively, are given in parentheses: methane- (2.46, 5.69), ethane- (1.28, 4.47), *n*-propane- α - (0.611, 0.808), *n*-butane- α - (0.587, 1.22), *n*-pentane- α -, m.p. 162° (0.723, 0.859), and *n*-hexane- α -arsinic acid, m.p. 166° (0.693, 0.642) [prepared by (b) through *n*-hexyldichlorophenarsazine, m.p. 89°, and *n*-hexyldichloroarsine, b.p. 106—107°/13 mm.]. (I) are stronger acids than the corresponding CO_2H acids, but are weaker than the chloroalkylarsinic acids (this vol., 333), the dissociation consts. of which are β -chloroethane- (2.08, 4.23), β - (II) (1.73, 4.05) and γ -chloropropane- (2.36, 2.96), γ -chloro-*n*-butane- (1.13, 1.43), *n*-pentane- (1.93, 1.71), and *n*-hexane- (3.09, 4.88), α -arsinic acid. Δ^{β} -Propene- α -arsinic acid as strong as (II).

J. W. B.

Behaviour of thallium halides in iodine solutions. R. LYDÉN (Finska Kem. Medd., 1934, 43,

67—85).—The effect of I on the solubility of TiCl_3 and TiBr_3 in MeOH , EtOH , PrOH , and $\text{EtOH-Et}_2\text{O}$ was studied. Complexes are formed by TiCl_3 and TiBr_3 in the I-alcohol mixtures. LiI with TiI_3 forms the solid phases LiTiI_4 , TiI_3 , and Ti_3I_4 . CH. ABS. (e)

Activity coefficients of water in the solution: sodium hydroxide ($m=0\sim0.9$)-water. Y. KOBAYASHI and H. WANG (J. Sci. Hiroshima Univ., 1934, 5, 71—82).—The e.m.f. (E) of the cell $\text{Hg}|\text{HgO}, \text{NaOH}(m)|\text{H}_2(\text{Pt})$, for $m=0.05\sim0.9$, is given by $E=E^\circ+am+bm^2$ mv., where $a=0.07692$, 0.05792 , and 0.04286 , and $b=0.35236$, 0.36421 , and 0.37217 , respectively, at 22.5° , 25.0° , and 27.5° . The differential free energy and energy of dilution have been calc. $RT \log f$, where f =activity coeff. of H_2O , rises to a max. at m =approx. 0.60. The bearing of these results on vals. of f for the solution $\text{NaOH-MeOH-H}_2\text{O}$ is discussed (cf. following abstract). R. S. B.

Activity coefficients of water in the solution: sodium hydroxide-methyl alcohol-water. Y. KOBAYASHI, N. AKAI, and S. FURUKAWA (J. Sci. Hiroshima Univ., 1934, 5, 57—70).—The activity coeffs. of H_2O in mixtures containing about 10% MeOH and 0.05—0.5 molal NaOH have been determined at 25° by e.m.f. measurements on the cell $\text{Hg}|\text{HgO}, \text{NaOH}(m), \text{MeOH-H}_2\text{O}|\text{H}_2(\text{Pt})$. Vals. of the partial pressure of H_2O calc. from e.m.f. data agree with experiment. R. S. B.

Vapour pressure in a system with ground-up crystals. D. BALAREV (Z. physikal. Chem., 1934, 171, 466—468; cf. this vol., 16).—Theory and experiment show that the grinding up of crystals raises the v.p. for dehydration but lowers it for rehydration. This effect disappears with time and its disappearance is attributed to ageing (cf. A., 1933, 346). R. C.

Transition point of sodium sulphate decahydrate. H. S. TAYLOR (J. Amer. Chem. Soc., 1934, 56, 2643).—The transition point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is 34.48° . E. S. H.

Investigation of hydrate dehydration by emanation method. R. MUMBRAUER (Z. physikal. Chem., 1935, 172, 64—76; cf. this vol., 32).—The emanation method clearly shows the two stages in the isothermal dehydration of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ to the anhyd. salts. Dehydration causes a loosening of the crystal structure and the development of a large internal surface. There is evidence of decrease of the internal surface at 400° . R. C.

Effect of pressure on phase equilibria of sodium tungstate and related thermodynamic properties. R. W. GORANSON and F. C. KRACEK (J. Chem. Physics, 1935, 3, 87—92; cf. A., 1932, 697).

The following equilibrium temp. (1 atm.) have been determined for Na_2WO_4 (I, II, and III): I \rightleftharpoons II, 587.6° ; I \rightleftharpoons liquid, 695.5° ; the effects of pressure on the III \rightleftharpoons I and II \rightleftharpoons III and t_{III} are given by $t=588.8+0.025(p-40)$ respectively, p being in bars. t_{III} is 53 ± 0.01 . The melting curve is given by $t=595.5+0.0219p-1.18 \times 10^{-6}p^2$. Heats of fusion and transformation are given, and other quantities calc. F. L. U.

Thermal dissociation of lithium hydride. C. B. HURD and G. A. MOORE, jun. (J. Amer. Chem. Soc., 1935, 57, 332).—Dissociation pressures have been measured between 782° and 926° . Assuming the reaction to be $2\text{LiH}=2\text{Li}+\text{H}_2$, the heat change is $44,000 \pm 2000$ g.-cal. E. S. H.

Systems NaOH-NaNO_3 and KOH-KNO_3 . N. M. RETORTILLO and E. MOLES (Anal. Fis. Quím., 1933, 31, 830—839).—The m.-p. diagrams indicate the existence of the compounds $2\text{NaOH}, \text{NaNO}_3$, $\text{NaOH}, \text{NaNO}_3$, and $2\text{KOH}, \text{KNO}_3$, which may be formulated as salts of H_3NO_4 . H. F. G.

Thermal decomposition of rhodichlorides. G. GIRE and F. PUCHE (Compt. rend., 1935, 200, 670—672).—The dissociation pressures of $\text{Ba}_3(\text{RhCl}_6)_2$ are < those of RhCl (A., 1926, 138). The $\log p-1/T$ lines cut at 963° , about the m.p. of BaCl_2 . The heats of dissociation calc. from these are 32.9 and 42.5 g.-cal. corresponding with -9.6 g.-cal. per mol. as the heat of fusion of BaCl_2 . J. W. S.

Compounds of sulphur dioxide with various amines. A. E. HILL and T. B. FITZGERALD (J. Amer. Chem. Soc., 1935, 57, 250—254).—V.-p. measurements of the binary systems of SO_2 with *o*-, *m*-, *p*-toluidine, quinoline, *n*-amyl- and *n*-heptyl-amine have been made. The compounds formed show variations in the ratio SO_2 : amine from 1:2 to 2:1, the 1:1 ratio predominating. The approx. heats of formation of the compounds have been calc. E. S. H.

Phase diagrams of low-melting mixtures. I. The system methane-ethylene. M. RUMMAN and A. LIKHTER (Physikal. Z. Sovietunion, 1934, 6, 139—149).—Equilibrium data and sp. heats are recorded for the complete concn. range. There is a eutectic at 84.55° abs. (12.2% of C_2H_4). CH. ABS. (e)

Effect of pressure on eutectic mixtures. H. A. C. MCKAY and B. HIGMAN (Phil. Mag., 1935, [vii], 19, 367—375).—Equations connecting pressure, eutectic temp., and eutectic composition are deduced and are applied to available data for the systems NHPh_3 , C_6H_6 , and C_{10}H_8 -urethane and C_{10}H_8 -*p*-toluidine. N. M. B.

Thermodynamic constants of iodine trichloride. N. P. NIES and D. M. YOST (J. Amer. Chem. Soc., 1935, 57, 306—307).—The pressure and composition of the vapour in equilibrium with solid ICl_3 and a liquid phase have been determined at 25° and 35° . The vals. of $K=P_{\text{ICl}_3}/P_{\text{Cl}_3}$ are 1.09×10^{-3} and 4.36×10^{-3} , respectively, when P is in atm. The free energy and heat content of solid ICl_3 at 25° are -5410 and $-21,150$ g.-cal., respectively. The standard virtual entropy is 41.1 g.-cal. per degree. E. S. H.

System MgO-FeO-SiO_2 . N. L. BOWEN and J. F. SCHAIRER (Amer. J. Sci., 1935, [v], 29, 151—217; cf. A., 1932, 997; 1933, 1120).—The system has been studied by thermal, chemical, and microscopical analysis in the way previously described. $\text{MgO}+\text{FeO}$ and $\text{Mg}_2\text{SiO}_4+\text{Fe}_2\text{SiO}_4$ form complete series of solid solutions, and $\text{MgSiO}_3+\text{FeSiO}_3$ forms a series with > 90 mol.-% of FeSiO_3 . Low liquidus temp. all lie

on the FeO-SiO_2 side of the triangular equilibrium diagram. The m.p. of the olivine series lie between 1890° (Mg) and 1205° (Fe). The metasilicate series is complicated by the occurrence of incongruent melting at the Mg end with separation of olivine and at the Fe end with separation of SiO_2 , and by the formation of two series of mixed crystals, monoclinic stable at high and orthorhombic at low temp. The courses of crystallisation are discussed with reference to natural magmas. The calc. heat of fusion for both Mg and Fe olivines is 14 kg.-cal. per mol. Optical properties of the several phases are given. Application of the results to slags and refractories is indicated.

F. L. U.

Quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$: quaternary system $\text{CaO-2CaO,Al}_2\text{O}_3\text{-5CaO,3Al}_2\text{O}_3\text{-4CaO,Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$. F. M. LEA and T. W. PARKER (Phil. Trans., 1934, A., 234, 1—41).—Phase relations in the following systems have been determined: 2CaO, SiO_2 (A)— $4\text{CaO, Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (B); CaO-A-B ; $\text{A-B-5CaO, 3Al}_2\text{O}_3$ (C); CaO-A-B-C . No new compounds were observed. The compound 3CaO, SiO_2 (D) is stable only between 1900° and 1250° , the latter being a definite transition temp. for D CaO+A . Temp. relations and crystallisation paths in quaternary systems are discussed.

System lime-potash-alumina. L. T. BROWN-MILLER (Amer. J. Sci., 1935, [v], 29, 260—277).—The system has been studied for small % K_2O by means of thermal, optical, and X-ray methods. The system $\text{CaO-K}_2\text{O}$ forms no compound; $\text{K}_2\text{O-Al}_2\text{O}_3$ forms a hygroscopic compound $\text{K}_2\text{O, Al}_2\text{O}_3$ (I), stable at 1650° , crystallising in the isometric system with $n=1.603\pm0.005$ for white light. In the ternary system (I), $3\text{CaO, Al}_2\text{O}_3$ (II), $5\text{CaO, 3Al}_2\text{O}_3$ (III), $\text{CaO, Al}_2\text{O}_3$ (IV), $3\text{CaO, 5Al}_2\text{O}_3$ (V), and the pure components may be in equilibrium with liquid. The quintuple points are: the eutectic for (I), (II), and (III) (+ K_2O) at 48% CaO , 4.8% K_2O , and 47.2% Al_2O_3 , in equilibrium with liquid and vapour at $1425\pm5^\circ$; the eutectic for (I), (III) (+ K_2O), and (IV), at 39% CaO , 5% K_2O , and 56% Al_2O_3 , $1430\pm5^\circ$; and at 48% CaO , 6.5% K_2O , and 44.7% Al_2O_3 , when (I), (II), and CaO coexist with liquid and vapour at $1475\pm5^\circ$. $\beta\text{-Al}_2\text{O}_3$ and corundum crystallise from $\text{Al}_2\text{O}_3+3.5\%$ K_2O heated to 1550° . Data are given for the regions of stability of the system (II)-(III) and portions of the fields of (I)- CaO .

R. S. B.

Action of water vapour on copper fluoride. L. DOMANGE (Compt. rend., 1935, 200, 239—241).—The equilibrium $\text{CuF}_2+\text{H}_2\text{O} \rightleftharpoons \text{CuO}+2\text{HF}$ has been studied at $200\text{--}450^\circ$ by passing H_2O over heated CuF_2 , analysing the resultant vapour, and extrapolating to zero streaming velocity. The heat of reaction, calc. from the temp. variation of the equilibrium const., is $-25,200$ g.-cal.

R. S. B.

Metamorphism in the reciprocal salt pair $(\text{Na}^+, \text{K}^+)(\text{Cl}^-, \text{IO}_3^-)$. T. G. SAHLSTEIN (Bull. comm. geol. Finlande, 1934, No. 104, 104—110).—From 27° to 37° the salts $\text{NaIO}_3\text{-H}_2\text{O}$ and KCl represent the stable pair in contact with aq. solution. From 39.5° to 50° KIO_3 and NaCl are the stable pair.

CH. ABS. (e)

The system diphenyl-dibenzyl-naphthalene. Nearly ideal binary and ternary systems. H. H. LEE and J. C. WARNER (J. Amer. Chem. Soc., 1935, 57, 318—321).—The system Ph_2 (I)— $(\text{CH}_2\text{Ph})_2$ (II) has a simple eutectic at 44.3 mol.-% Ph_2 and 29.5° ; the system (I)— C_{10}H_8 (III) at 55.6 mol.-% (I) and 39.4° ; (II)—(III) at 38.6 mol.-% (III) and 32.7° . The system (I)—(II)—(III) has a simple ternary eutectic at 33.8 mol.-% (I), 39.2 mol.-% (II) and 17.4° . The solubilities, eutectic temp., and eutectic compositions of these systems are in agreement with those calc. for ideal solutions.

E. S. H.

Crystallisation in a ternary system exhibiting a peritectic and a eutectic. System antipyrine-carbamide-urethane. K. HRYNAKOWSKI and F. ADAMANIS (Z. physikal. Chem., 1935, 172, 33—48).—The system shows a peritectic at 59° with 32.5% urethane and 15.0% $\text{CO}(\text{NH}_2)_2$, and a eutectic at 31.0° with 60.0% urethane and 2.5% $\text{CO}(\text{NH}_2)_2$. The theory of crystallisation in such systems is developed.

R. C.

Thermal equilibria in ternary systems. II. Phenacetin-antipyrine-quinine. K. KRYNAKOWSKI and F. ADAMANIS [with K. KAWECKI and Z. POLUBIŃSKI] (Rocz. Chem., 1934, 14, 1488—1498).—The system has one eutectic at 640° , antipyrine 47, quinine 25, and phenacetin 28%.

R. T.

(A) **Equilibria in the system $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$.** N. A. OSOKOREVA, M. A. OPUKHETINA, D. N. SHOIKHET, E. F. PLAKSINA, and A. I. ZASLAVSKI.

(B) **Calculation of the equilibrium in water at high temperatures.** E. I. AKHUMOV and B. B. VASILIEV (Trans. State Inst. Appl. Chem. U.S.S.R., 1932, No. 16, 24—47, 48—59).—Isotherms and polytherms have been determined at $10\text{--}110^\circ$ for $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$, $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$, $\text{KCl-MgCl}_2\text{-H}_2\text{O}$, and NaCl-KCl .

CH. ABS. (e)

Anomalous heat effects of certain minerals and compounds. II. Ice calorimeter measurements. W. SWIENTOSŁAWSKI, A. ZMACZYŃSKI, I. ŻŁOTOWSKI, J. USAKIEWICZ, and J. SALCEWICZ (Rocz. Chem., 1934, 14, 1474—1478).—The heat production of monazite and As_2S_3 , alone, or with salts of La, Y, and Sc, is $\approx 5 \times 10^{-5}$ g.-cal. per kg. per hr.; the anomalous heat effects reported by Dorabalska (A., 1932, 927) are not confirmed.

R. T.

Energies of hydrocarbon molecules. R. SEEBER (J. Chem. Physics, 1935, 3, 81—86).—Energies of formation of 12 hydrocarbons, including saturated, unsaturated, open-chain, and cyclic, have been calc. by applying the Heitler-London-Pauling-Slater theory. The vals. agree with those observed. The validity of a bond additivity rule appears to be fortuitous.

F. L. U.

Heat of formation and stability of chain compounds. H. G. GRIMM and H. WOLFF (Angew. Chem., 1935, 48, 133—137).—The heat of formation from the elements in the normal state (H) of the chain compounds $\text{C}_m\text{H}_{2m+2}$, $\text{Si}_m\text{H}_{2m+2}$, N_mH_{m+2} , O_mH_2 , S_mH_2 , has been calc. assuming additivity. H increases with m for the C series, but decreases in all the other series. The equilibrium consts. at room temp. for the formation of chain compounds have been calc.

using Nernst's theorem. All members of the series are thermodynamically unstable with respect to the first member. H for glucose, cellulose, and $\text{OH}\cdot\text{CH}_2\cdot[\text{O}\cdot\text{CH}_2]_x\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$ has been calc. for formation from the elements and from CH_2O . R. S. B.

Heats of combustion and refractivity data for chloro-substituted fatty acids and esters. Connexion between chemical constitution, heat of combustion, and molecular refraction. E. SCHJANBERG (Z. physikal. Chem., 1935, 172, 197—233).—For both Cl-substituted and unsubstituted esters the heat of combustion, the mol. refraction, R_L , and the mol. dispersion are not the same as for the iso-esters. The energy of breaking, E , of the C-Cl linking is greatest when the Cl is in the α -position to the CO_2H group and smallest when it is in the γ -position. It falls on ascending a homologous series of esters of a given acid but tends to a limit, and the fall is the slower the more remote is the Cl from the CO_2H . The refraction and dispersion of the C-Cl linking on the whole run parallel with E , but remain const. in a homologous series. A bomb lined with AgBr is not suitable for determining heats of combustion of Cl-substituted compounds (cf. Roth, B., 1922, 350). In Berthelot and Matignon's method (A., 1891, 1311) a correction must be applied for Cl in the gas phase. The best method is the quartz-wool method (A., 1931, 1262). R. C.

Specific conductance of dilute solutions at 0° and 25°. C. R. JOHNSON and G. A. HULETT (J. Amer. Chem. Soc., 1935, 57, 256—258).—Results obtained with several aq. sparingly sol. salts show that saturated solutions of such salts are useful for calibrating conductance cells. E. S. H.

Effect of the surface on moving processes in dilute strong electrolytes. S. OKA (Proc. Phys.-Math. Soc. Japan, 1934, 16, 332—339).—The surface effect (I) and relaxation force are calc. on the Debye-Falkenhagen theory. (I) tends to lower the ionic mobility. CH. ABS. (e)

Low-frequency conductivity of mixtures of aqueous solutions of electrolytes. A. DEUBNER

A. DOBENZIG (Physikal. Z., 1935, 36, 139—141).—Increase in the conductivity (I) occurs when solutions of the sulphates of Cu, Zn, Mn, Mg, Ni, Ca, and Cd are mixed with solutions of NaCl the same (I). Other mixtures [e.g., $\text{K}_4\text{Fe}(\text{CN})_6 + \text{NaCl}$] show a decrease in (I). An explanation, based on alteration of the mobility of the ions in NaCl solution, is put forward, but this fails to cover all cases. A. J. M.

Measurement of the conductance of electrolytes. VI. Galvanic polarisation by alternating

Platinisation. G. JONES and S. A. CHRISTIAN (J. Amer. Chem. Soc., 1935, 57, 272—280, 280—284; cf. A., 1933, 676).—VI. A cell for measuring resistance (I) and capacitance (II) due to polarisation with alternating current is described. Results are given, using Ag, Ni, and Pt electrodes. Polarisation (I) is inversely \propto (freq.)⁻¹. Polarisation causes a (II) in series with (I), which decreases with increasing frequency. Polarisation (I) and polarisation (II) depend on the

electrode metal, the electrolyte, and temp., but are independent of c.d. and the separation of the electrodes, and uninfluenced by another superimposed current of a different frequency.

VII. A criterion of the sufficiency of platinisation to eliminate errors due to polarisation is the variation of the apparent or measured resistance with frequency. Addition of $\text{Pb}(\text{OAc})_2$ to the platinising solution is beneficial. E. S. H.

Physico-chemical studies of complex formation involving weak acids. XIII. Reactions of malonic acid with typical metallic bases. H. T. S. BRITTON and M. E. D. JARRETT (J.C.S., 1935, 168—175; cf. A., 1925, ii, 977).—Conductivity data are given for the titration of malonic acid (I) with NaOH , $\text{Mg}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$, $\text{Be}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, and $\text{Cu}(\text{OH})_2$. The reaction of the first 0.5 equiv. of $\text{Mg}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ with (I) is normal, but the p_H is reduced on further addition of base, owing to complex formation. In the case of the weaker bases, the conductivity is due chiefly to the hydrolysed (I), and it is suggested that the feebly ionised products of combination are pseudo-colloidal. R. S.

Conductivity of complex compounds of palladium. A. A. GRINBERG, V. M. SCHULMAN, and S. I. CHORUNSHENKOV (Ann. Inst. Platine, 1935, 12, 119—132).—Measurements of the conductivity of solutions of salts of the types K_2PdX_4 , $[\text{Pd}(\text{NH}_3)_4]\text{X}_2$, *cis*- and *trans*- $\text{Pd}(\text{NH}_3)_2\text{X}_2$ and $-\text{Pd}(\text{NH}_3)_2\text{C}_2\text{O}_4$ ($\text{X} = \text{Cl}, \text{Br}$) give results in accordance with Tscherniaev's *trans*-influence theory for the corresponding Pt salts. The stability of Pd is < that of Pt salts. R. T.

Electrochemical study of the system $\text{AlBr}_3\text{--CuBr}$ in ethyl bromide. V. A. PLOTNIKOV and E. J. GORENBEIN (J. Gen. Chem. Russ., 1934, 4, 1042—1046).—The sp. conductance varies directly with $[\text{CuBr}]$ and inversely with the dilution; Cu is deposited at the cathode. The results obtained with EtBr are analogous to those obtained with C_6H_6 . R. T.

Potential of metals in solutions of other ions. O. ESSIN and M. LOTZMANOVA (J. Gen. Chem. Russ., 1934, 4, 1138—1146).—The e.m.f. of Au electrodes in aq. CuSO_4 , $\text{Cu}(\text{NO}_3)_2$, and AgNO_3 is given by $E_{\text{Au/MX}} = a + bE_{\text{M/MX}}$, where MX is one of the above salts. R. T.

Process of mutual displacement of metals. N. ISGARISCHEV and I. MIRKIN (Korros. Metallschutz, 1934, 10, 109—112; Chem. Zentr., 1934, ii, 2188).—In the displacement of Cu, Cd, Pb, Ni, Fe, and Co by Zn, differences between the order of replacement and the electropotential series are due to the varying overvoltage of H liberated on the metallic couple formed. J. S. A.

Effect of the composition of glass on the interfacial potential: glass-aqueous solutions of electrolytes. K. S. EVSTROPIEV and N. V. SUIKOVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 421—428).—The potential of the glass electrode (I) in contact with solutions of electrolytes has been studied with glasses of different

composition, limited, however, to three components. In the titration of 0.025*N*-HCl with 0.1*N*-NaOH a Na₂O-SiO₂ glass with 80 mol.-% SiO₂ gave a curve agreeing with that obtained with the Pt-H₂ electrode. Three-component glasses fall into two groups: (1) those containing CaO, MgO, BaO, or PbO, and (2) those containing Al₂O₃, ZnO, or B₂O₃. A glass containing BaO behaves in a solution of Ba⁺⁺ as a Ba electrode. A. J. M.

Electrokinetics. XV. Use of inert electrodes in measuring streaming potential. H. B. BULL (J. Amer. Chem. Soc., 1935, 57, 259—260; cf. A., 1934, 143).—The use of a Pt or Au electrode in place of the calomel half cell is recommended. E. S. H.

Over-potential of the hydrogen isotopes. F. P. BOWDEN and H. F. KENYON (Nature, 1935, 135, 105).—The same linear relation between *c.d.* and over-potential holds for both isotopes and the slope of the line is approx. the same. The irreversible potential of H₂ is about 0.13 volt more negative than that of H, and under optimum conditions about 14H₂ for 1H₂ should be liberated at the cathode. The temp. coeff. of the H₂ over-potential is > that for H₂. L. S. T.

Concept of normal acidity potential. G. SCHWARZENBACH (Z. physikal. Chem., 1935, 172, 234—236).—Polemical against Wiberg (this vol., 38). R. C.

Concept of normal acidity potential. E. WIBERG (Z. physikal. Chem., 1935, 172, 237—238).—A reply to Schwarzenbach (cf. preceding abstract). R. C.

Potentiometric titration of non-aqueous solutions applied to amino-acids. A. G. OGSTON and J. F. BROWN (Trans. Faraday Soc., 1935, 31, 574—585).—Dissociation consts. of NH₄OH, CH₂Cl·CO₂H, *o*-NH₂·C₆H₄·CO₂H, and tyrosine have been determined by titration in MeOH solution, and those of tyrosine and glycine in H₂O and 80% and 95% EtOH. The results are in general agreement with those of Neuberger (A., 1934, 638) and support the zwitterion hypothesis. F. L. U.

Mercuric cyanide and mercuric oxycyanide electrodes. O. TOMICEK and R. PRIBIL (Coll. Czech. Chem. Comm., 1935, 7, 10—24; cf. A., 1931, 450).—Reproducible vals. of potential for varying [H⁺] are obtained with the electrodes Hg|Hg(CN)₂ and Hg|Hg(CN)₂,HgO, when [Hg(CN)₂] and [HCN] are const. in acid solutions, and [Hg(CN)₂,HgO] is const. in alkaline solutions. The equiv. point is marked by a single max. of inflexion of the titration curve in the case of weak acids and by the first of two in the case of strong acids. R. S.

Relative oxidation potentials of nitric acid solutions. R. G. MONK and H. J. T. ELLINGHAM (J.C.S., 1935, 125—130; cf. A., 1932, 705).—The potential *e* of the electrode system Pt|HNO₃,HNO₂ = *e*₀' - 0.0296 log [HNO₂] for a given [HNO₃] in solutions up to 12*M*-HNO₃ and 0.1*M*-HNO₂. When [HNO₂] > 0.1*M*, the *e*-log [HNO₂] curve deviates from linearity. The relative oxidation potential *e*₀' is taken as a measure of the oxidising tendency of a given HNO₃ solution. The results are in agree-

ment with the view that *e* is controlled by the equilibrium $\text{HNO}_3 + 2\text{H}^+ + 2\ominus \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$. HNO₂ was determined by interaction with PbO₂ in excess of HNO₃. R. S.

Oxidation potential of the alkaline permanganate-manganese dioxide electrode. L. V. ANDREWS and D. J. BROWN (J. Amer. Chem. Soc., 1935, 57, 254—256).—The val. 0.489 ± 0.001 volt has been determined for the half cell MnO₄' + 2H₂O + 3e ⇌ MnO₂(s) + 4OH'. The oxidation potentials of related electrodes and the corresponding free energies have been calc. E. S. H.

Oxidation-reduction equilibria of oxypurines. (MILE.) S. FILITTI (J. Chim. phys., 1935, 32, 1—45).—Earlier work (A., 1934, 32, 367) has been extended. The data refer to systems of ionic strength, *μ*, 0.03—1.14 at 6.7—8.5 and 25° and 38°. The normal oxidation-reduction potential, *E*, corr. for activity, for the system hypoxanthine + 2H₂O ⇌ uric acid + 2H₂, (I) is 0.068 ± 0.003 volt at 38° and *μ* = 1.0421, leading to Δ*F* = +6300 + 300 g.-cal., and the corresponding vals. for the system xanthine + H₂O ⇌ uric acid + H₂, (II) are *E* 0.123 ± 0.003, Δ*F* 5700 ± 150, from which the vals. for hypoxanthine + H₂O ⇌ xanthine + H₂ are Δ*F* 600 and *E* 0.013. From the temp. coeff. the heats of reaction at const. pressure are: (I) 13,600 at *p*_H 7.36 and *μ* 1.1376 and (II) 6500 at *p*_H 7.7 and *μ* 0.1359. J. G. A. G.

Reduction of dinitrophenols by redox indicators and enzymes.—See this vol., 401.

Oxidation-reduction potentials of toxoflavin. See this vol., 407.

Electrolytic growth of metal crystals. 1. Growth of silver crystals in aqueous solutions. T. ERDEY-GRUZ (Z. physikal. Chem., 1935, 172, 157—187).—The growth of a spherical single crystal of Ag in solutions containing Ag as complex cation or complex anion has been studied. The substances present in solution, independent of their concn. or the *c.d.*, *I*, determine what faces appear on the growing crystal. In some cases some of the faces predicted by the Kossel-Stranski theory are not developed; in others faces not predicted appear. This discrepancy is attributed to adsorption of dissolved mols. or ions. For solutions of AgI + KI and Ag₂O + NH₃, 1/η, where η is the overvoltage, is a linear function of log *I*, indicating that the rate of the two-dimensional formation of nuclei determines the rate of metal deposition, *v* (cf. A., 1932, 24). With solutions of AgBr + NH₃ and AgCl + NH₃ log *I* is a linear function of η, showing that *v* is determined by the rate at which the ions lose their charge. For solutions of AgCN + KCN and others *I* is a uncat function of η, indicating that the rate of supply of ions to the growing points determines *v*. R. C.

Overvoltage theory and simultaneous discharge of several ionic species. O. ESSIN (Z. physikal. Chem., 1934, 171, 341—347; cf. A., 1934, 468).—On the basis of Volmer's overvoltage theory equations have been derived for the partition of current between ionic species which are being discharged simultaneously. They agree with exis-

experimental data and with new data for the discharge of Ni^{++} and H^+ , and Cd^{++} and H^+ . R. C.

Cathodic passivity. K. M. GORBUNOVA and A. T. VAGRAMJAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 443—453).—Study of the electro-deposition of metals has shown that the formation of nuclei takes place at lower potentials when the surfaces of the electrodes have not been previously exposed to air. A. J. M.

Mechanism of explosions and combustion. W. JOST (Z. Elektrochem., 1935, 41, 183—194).—A review.

Spectra and latent energy in flame gases. S. STEELE (Nature, 1935, 135, 268; cf. A., 1934, 1288).—The emission of infra-red radiation during the explosive reactions occurring in a combustion engine suggests that some metastable H_2O and CO_2 mols. may be formed. Knocking may be connected with the proportion of metastable mols. formed during combustion. L. S. T.

Theory of combustion. III. N. SEMENOV (Z. physikal. Chem., 1935, B, 28, 43—53; cf. A., 1928, 847; 1931, 436).—The chain reaction theory of the inflammation limits (I) in gaseous oxidation reactions requires that the position of the limits shall be independent of the no. of initial centres, n , starting the chains. Experiment shows, however, that if n is increased, photochemically, by ionisation, or by admixture of H or O atoms, the lower limit falls and the upper limit rises (A., 1933, 572; this vol., 47). O atoms are particularly effective, and combustion of the mixture $2\text{H}_2 + \text{O}_2$ below a certain pressure may occur at room temp. in presence of a sufficiently high [O], the temp. not rising above 150° . These observations may be accounted for by assuming that when two active centres collide the probability of chain branching increases. The theory that spark ignition is due to the heating effect of the spark is unsatisfactory, since in some cases dilution with an inert gas facilitates inflammation. At the point of sparking a very high concn. of initial centres results, with consequent widening of (I). Le Chatelier's theory of flame propagation is not universally valid; the propagation of a cold flame has been observed, which may be accounted for by diffusion of active centres from the combustion zone into the adjoining region, there interacting to produce an initial concn. sufficient for cold inflammation. R. C.

Theory of degenerate explosions. N. SEMENOV (Z. physikal. Chem., 1935, B, 28, 54—64; cf. A., 1931, 436).—The symmetrical S-shaped curves typical of the kinetics of many processes of the non-stationary type may be derived by the theory of degenerate explosions (I) assuming that the probabilities of chain branching and breaking do not depend on the reactant concns. Taking account of interaction of the chains (preceding abstract), however, a different type of curve results. Reaction now is the more rapid and occurs at a lower temp. the more initial centres are present. The shape of the kinetic curve depends on the branching on interaction of the chains, and may approach that of a zero or first order reaction. This modified theory of (I) explains

existing data for numerous homogeneous gas reactions in which after a short period of induction the velocity assumes a const. val. approx. \propto the initial pressure of reactants. Probably many unimol. reactions are non-stationary processes of the (I) type. R. C.

Correlation of ionisation and radiation in carbon monoxide-oxygen explosions. W. A. KIRKBY (J.C.S., 1935, 165—168).—"Dry" and "moist" $2\text{CO} + \text{O}_2$ mixtures in a glass sphere were ignited at the centre by a spark, and synchronous records were made of visible (0.4 — 0.63μ) and infra-red (0.74 — 1.2μ) radiation emitted and the ionisation current across a central electrode gap. The max. of visible and infra-red emission were slightly later than the three coincident max. of temp., pressure, and ionisation current, and the shapes of the decay portions of the radiation and ionisation curves were markedly different, showing that the "afterglow" in these explosions was due chiefly to some cause other than the recombination of ions, although this cause is operative during approx. the same period as that of ionic recombination. J. G. A. G.

Correlation of flame movement and ionisation current during explosions. W. A. KIRKBY (J.C.S., 1935, 160—165).—Synchronised records of flame movement and development of ionisation current were obtained with $2\text{CO} + \text{O}_2$ mixtures (I) in a cylindrical glass explosion vessel (II) fitted along its length with five equidistant pairs of electrodes (III); at each (III), an ionisation current was recorded as soon as the flame front arrived, and after this had passed, the conductivity \propto the temp. and pressure at the (III). The ionisation persisted for a period which corresponded, approx., with the duration of the "afterglow" at the corresponding positions. The explosions of "moist" (I) were vibratory and those of "dry" (I) were non-vibratory and of lower velocity. The duration of afterglow and persistence of ionisation in "dry" (I) were $>$ in "moist" (I). With a similarly constructed phosphor-bronze cylinder, the corresponding explosion velocities and vals. of the degree of ionisation were $<$ in (II). The "afterglow" is attributed partly to recombination of ions and partly to emission by thermally excited mols. J. G. A. G.

Intensive drying. A. SMITS (Z. physikal. Chem., 1935, B, 28, 31—42).—The difficulties of intensive drying (I) experiments are detailed. Bodenstein's theory of the effect of (I) on gas reactions (A., 1933, 575) is rejected. It seems possible that activated mols. can react with other mols. only when the former are in the field of force of, or in some way combined with, H_2O mols. R. C.

Oxidation of silane. H. J. EMELÉUS and K. STEWART (Nature, 1935, 135, 397).—When mixed with O_2 pure SiH_4 is not explosive at 1 atm. At lower pressures ignition occurs at a well-defined limit which is the higher the higher is the temp. In small concn. CHCl_3 and EtI lower the upper limit and in larger amounts prevent ignition, an effect which can be counteracted by a rise in temp. A mixture containing the higher hydrides of Si can also be rendered non-inflammable by small amounts of these inhibitors.

The lower crit. oxidation pressure of mixtures of SiH_4 and O_2 directly \propto a power of the vessel diameter slightly > 1 . The oxidation of SiH_4 resembles that of PH_3 rather than that of CH_4 . L. S. T.

Explosion of azomethane. A. O. ALLEN and O. K. RICE (J. Amer. Chem. Soc., 1935, 57, 310—317).—The crit. pressures at which explosion of gaseous Me_2N_2 occurs at temp. between 340° and 390° have been determined. The crit. pressure is raised by mixing with He (N_2 has no effect) and by decreasing the size of the reaction vessel. The Semenov theory of thermal explosions, according to which the heat of reaction leads under certain conditions to an explosion, is applicable to the data. E. S. H.

Kinetics of thermal *cis-trans* isomerisation. IV. G. B. KISTIAKOWSKY and W. R. SMITH (J. Amer. Chem. Soc., 1935, 57, 269—271; cf. A., 1934, 493).—The rate of isomerisation of *cis*-Me cinnamate has been studied at 5—500 mm. and 563 — 660° abs. The rate is independent of pressure between 70 and 500 mm., but appears to fall at 5 mm. The reaction appears to be homogeneous. The activation energy is $41,600 \pm 2000$ g.-cal. The rate at higher pressures is given by $k = 3.5 \times 10^{10} e^{-41,600/RT}$. The mechanism of reaction is discussed. E. S. H.

Decomposition of ozone in aqueous solution. III. F. KAWAMURA (J. Chem. Soc. Japan, 1934, 55, 849—857).—The rate of decomp. (I) is the same in aq. KClO_3 and Na_2SO_4 as in H_2O . In H_2SO_4 , H_3PO_4 , and H_3BO_3 , (I) is $<$ in H_2O , especially with a high acid concn. In aq. Na_2HPO_4 , NaHCO_3 , Na_2CO_3 , and $\text{Na}_2\text{B}_4\text{O}_7$, (I) is much $>$ in H_2O , especially with a high salt concn. The reaction is $2\text{O}_3 = 2\text{O}_2 + 2\text{O}$. CH. ABS. (e)

Mechanism of ionic reactions. R. A. OGG, jun., and M. POLANYI (Trans. Faraday Soc., 1935, 31, 604—620; cf. A., 1934, 1185).—A theory of uni- and bi-mol. ionic reactions involving a homopolar mol. is developed from a consideration of potential energy as a function of nuclear separation. The factors contributing to the activation energy of electrolytic dissociation of a homopolar mol. are discussed. Activation energies of reactions between halogen ions and Me halides are calc. and compared with experimental vals. for some chemically related reactions. The results of the comparison support the essential validity of the theory. F. L. U.

Origin of bromine liberated as bromide ion in the interaction of bromoacetic ions with bromoacetic molecules. H. M. DAWSON (Proc. Leeds Phil. Soc., 1935, 3, 22—25; cf. A., 1933, 1125).—The origin of Br' produced in the hydrolysis of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$ by the interaction of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Br}\cdot\text{CO}_2'$ has been investigated by comparing the velocities of the reactions (1) $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et} + \text{AcO}'$ and (2) $\text{CH}_2\text{Br}\cdot\text{CO}_2' + \text{EtOAc}$, in which no acid-base equilibrium subsists. The greatly increased velocity of (1) indicates that the Br' is derived from the mol. rather than the ion. The facts as a whole suggest that Br is liberated from both ions and mols. when they collide with other ions or mols. which are basic. F. L. U.

Reduction velocity of chloric and bromic acids. A. SKRABAL and H. SCHREINER (Monatsh., 1935, 35, 213—231).—The velocity of reduction of ClO_3' and BrO_3' by Cl' , Br' , and I' in acid solution has been determined for dil. solutions. The products were allowed to oxidise As_2O_3 . The reaction \propto the concn. of halide ion, ClO_3' or BrO_3' , and $[\text{H}']^2$. For the $\text{Br}-\text{BrO}_3'$ reaction at higher concn. a secondary reaction, in which the velocity $\propto [\text{Br}']^2$, takes place. The mechanism of the reaction is discussed.

M. S. B.

Inversion of sodium nitrite with nitrogen oxides. A. G. ZHIVOTOVSKI (Khimstroi, 1934, 6, 380—384).—The rate is independent of the decreasing $[\text{NaNO}_2]$ and the increasing $[\text{NaNO}_3]$ in the solution. The optimum temp. is 20 — 40° . The inversion ceases at an acidity of 0.2 — 0.3 mol. per litre. CH. ABS. (e)

Conversion of dissolved sodium chromate into dichromate by carbon dioxide under pressure. G. AGDE and K. E. VETTER (Angew. Chem., 1935, 48, 92—95).—The influence of reaction time, temp., $[\text{Na}_2\text{CrO}_4]$, and pressure of CO_2 has been studied. E. S. H.

Mechanism of substitution at a saturated carbon atom. III. Kinetics of the degradations of sulphonium compounds. J. L. GLEAVE, E. D. HUGHES, and C. K. INGOLD. IV. Constitutional and solvent effects on the mechanism, kinetics, velocity, and orientation of substitution. E. D. HUGHES and C. K. INGOLD. V. Hydrolysis of *tert*-butyl chloride. E. D. HUGHES (J.C.S., 1935, 236—244, 244—255, 255—258).—III. The reaction $\text{Y}' + ^+\text{SAlkR}_2 \longrightarrow \text{AlkY} + \text{SR}_2$ in H_2O , aq. EtOH , and abs. EtOH is, in general, accompanied by the formation of olefines (cf. A., 1934, 152), and follows either a bimol. substitution process (I)

formulated $\text{Y Alk-X} \longrightarrow \text{Y-Alk} + \text{X}$ or a unimol.

process (II) formulated (i) $\text{Alk-X} \longrightarrow \text{Alk} + \text{X}$ and

(ii) $\text{Y}^+ \text{Alk} \longrightarrow \text{Y-Alk}$, where (ii) is a relatively instantaneous change. As Alk ascends the series (III) Me, Et, Pr^i , and Bu^i , and as Y' ascends the series (IV) OH' , OPh' , CO_3'' , Br' , and Cl' , the mechanism changes from (I) to (II), a transition point lying between OPh' and CO_3'' . In series (III), the abs. velocity coeff., k , passes through a min., signifying transition from mechanism (I) to (II) between Et and Pr, and in series (IV) k decreases with decreasing basicity of Y to a const. val., since Y is excluded from the slow stage of (II). The position of the point of transition and the vals. of k vary with solvent and concn. in a manner consistent with the theory.

IV. The theory (A., 1933, 701) is elaborated. The published data for a wide variety of reactions, classified according to the state of electrification of X and Y, are consistent with processes (I) and (II), above, process (II) being favoured by (i) large electron-release from Alk, (ii) strong electron affinity in group X, (iii) sufficiently low nucleophilic activity in reagent Y, and (iv) high ionising capacity of the solvent. Electrophilic substitutions are also considered and the bearing on Walden inversions is discussed.

V. The hydrolysis of Bu^nCl has been investigated in aq. EtOH and aq. COMe_2 at 8–45°. No olefine was formed; the reaction is unimol. and independent of $[\text{KOH}]$. The mechanism conforms to type (II), above, and the activation energy, 23 kg.-cal., calc. from the temp. coeff. is that of the ionisation of the halide.

J. G. A. G.

Interaction of alkyl iodides and sodium *m*-4-xylyloxyde in ethyl alcohol. P. J. HARDWICK (J.C.S., 1935, 141–144).—The rates of reaction of MeI , EtI , Pr^nI , Pr^iI , Bu^nI , Bu^iI , and $n\text{-C}_5\text{H}_{11}\text{I}$ with 1:3:4- $\text{C}_6\text{H}_3\text{Me}_2\text{ONa}$ (I) in EtOH have been determined at 28–66°. The bimol. velocity coeffs., k , increase with decreasing initial concn. Determinations of the degree of dissociation, α , of (I) show that the observed velocities are due almost entirely to xylyloxyde ions, and coeffs., independent of dilution, are given by $k = \alpha k_i$. The reactivities of the *n*-alkyl iodides decrease to a limiting val. with increase of mol. wt. and the reaction velocities are of the same order as those calc. by means of the simple theory of activation by collision. The heats of activation derived from the temp. coeff. are between 19.5 and 23.4 kg.-cal.

J. G. A. G.

Influence of variations in structure on the reactivity of an alcohol with hydrobromic acid. G. M. BENNETT and F. M. REYNOLDS (J.C.S., 1935, 131–141).—The rates of reaction and the occurrence of subsidiary reactions have been investigated in PhOH at 76–97°. The velocity coeffs., k , of the *n*-aliphatic alcohols fall on a smooth curve, the vals. diminishing from MeOH to a const. val. with Pr^nOH and higher members. The activation energy is 26.6 kg.-cal. for MeOH and approx. 30.5 for the other members of the series. The reactivities are: *tert*.-alcohol > Bu^nOH > Pr^nOH > primary alcohol > $\text{CH}_2\text{Pr}^n\text{OH}$ and $\text{OH}\cdot[\text{CH}_2]_3\cdot\text{NO}_2$ > $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NO}_2$, and the importance of polar effects as compared with steric hindrance in esterification is emphasised. The retarding effect of an electron-attracting group and the accelerating influence of an electron-repelling group is shown in the series $\text{C}_6\text{H}_4\text{X}\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{OH}$, where the reactivities are: $-p\text{-Me} > o\text{-Me} > m\text{-Me} > \text{H} > p\text{-Cl}$ and in the series $\text{Ar}\cdot\text{S}\cdot[\text{CH}_2]_2\cdot\text{OH}$ where $\text{Ar} = p\text{-C}_6\text{H}_4\cdot\text{OMe} > \text{Ph} > p\text{-C}_6\text{H}_4\cdot\text{Br} > p\text{-C}_6\text{H}_4\cdot\text{NO}_2$ and $s\text{-C}_6\text{H}_5\text{Cl}_3 > 2:4\text{-H}_3(\text{NO}_2)_2$. The reactivity of the OH of the glycols rises to a max. as the no. of C atoms is increased from 2 to 4 and thereafter decreases to the const. val. of the OH of cetyl alcohol. The reactivities of the series $\text{OPh}\cdot[\text{CH}_2]_n\cdot\text{OH}$ and $\text{OH}\cdot[\text{CH}_2]_n\cdot\text{Cl}$ increase rising vals. of *n*. The results, in conjunction with those previously obtained (A., 1932, 26) with analogous thio-compounds, are consistent with theory.

J. G. A. G.

course of reaction of halogenoacetic acids with cysteine and with thioglycollic acid. H. VON LER (Z. physikal. Chem., 1934, 17, 171–184).—The rate of reaction of (I) with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ (II) or $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ (III) in aq. solution at p_H 7.5 is not affected by a small amount of CuSO_4 . The rate for the reaction velocity of cysteine (IV) with (I) and (III) at const. p_H has been derived and

confirmed experimentally; CuSO_4 has little effect. The velocity coeffs. of the reaction of (IV) with (II) and (III) are 10–15 times those of the reactions of (I).

R. C.

Emission wave theory of periodic reactions. V. Study of periodic reactions by methods of physico-chemical analysis. P. F. MICHALEV and F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1934, 4, 1117–1127).—The equation $\lambda v = hN/M$ (λ = distance between bands, v = velocity of propagation, N = concn. of the external electrolyte, and M its mol. wt.) is verified for a no. of Liesegang systems, and is found to hold the more closely the smaller is the concn. of gelatin. The phenomenon of Liesegang ring formation is analogous to that of emission of stationary waves on the surface of a flowing liquid.

R. T.

Decomposition velocity of [calcium] carbide with water. A. S. FALIKEVICH (Khimstroj, 1934, 6, 442–445).—Between 5° and 50° the reaction rate of coarsely granulated CaC_2 with H_2O increases 1% per 1° rise in temp.

CH. ABS. (e)

Kinetics of the thermal decomposition of calcium azide. K. K. ANDREEV (Physikal. Z. Sovietunion, 1934, 6, 121–138).—There is an induction period during which reaction nuclei are destroyed by impurities. This is followed by a period when the velocity $\propto p^{2/3}$. The last stage of the reaction is of the first order. The crit. increment for nuclei growth increases from 20 g.-cal. at 70° to 34 g.-cal. at 135°. At low temp. CaN or Ca_2N_2 is formed. On rapid heating at high temp. Ca is an additional product. The detonation temp. in vac. and air are 110° and 142°, respectively.

CH. ABS. (e)

Action of chlorine on ferric oxide and other oxides. C. DEL FRESNO and J. F. F. MOYANO (Anal. Fis. Quim., 1934, 32, 128–133).—The rate of reaction (I) of Cl_2 with Fe_2O_3 (e.g., Fe ores) is highly dependent on the particle size. Amongst oxides of any one group of the periodic system, (I) decreases on passing from lower to higher periods.

J. S. A.

Reactivity of carbon. H. L. RILEY and H. E. BLAYDEN (Nature, 1935, 135, 397–398).—Graphite and highly graphitised forms of C are oxidised approx. 20–25 times more rapidly than sugar charcoal by excess of $\text{CrO}_3\text{-H}_3\text{PO}_4$ at 100°. Hard metallurgical coke is oxidised more rapidly than gas and low-temp. cokes.

L. S. T.

"Probability" of corrosion. R. B. MEARS and U. R. EVANS (Trans. Faraday Soc., 1935, 31, 527–542; cf. A., 1934, 1181).—The influence of sixteen external factors on the probability (I) and the conditional velocity of corrosion of different kinds of Fe in contact with aq. KCl solutions has been determined. (I) is depressed by increase of $[\text{O}_2]$, by K_2CO_3 , by the proximity of other corroding points, and by increase in the temp. of pre-exposure to O_2 , and is increased by rise in the temp. of the experiment, by SO_2 (but not CO_2) present in the gas phase, and by increase of $[\text{KCl}]$. In general both the primary air-formed oxide film and the secondary film of corrosion products contribute to protect the metal. The film-substance is porous, and becomes protective

when the pores are small enough to be blocked with corrosion products. F. L. U.

Velocity of dissolution of metals in aqueous salt solutions. IV. Dissolution of tin in aqueous ferric chloride. E. BEKLER, W. ŁUKASZEWICZ, and F. WEJCÓWNA (Rocz. Chem., 1934, 14, 1479—1487).—The dissolution of Sn in aq. FeCl_3 containing HCl involves the reactions: $\text{Sn} + 2\text{FeCl}_3 \longrightarrow \text{SnCl}_2 + 2\text{FeCl}_2$; $\text{SnCl}_2 + 2\text{FeCl}_3 \longrightarrow \text{SnCl}_4 + 2\text{FeCl}_2$; $\text{Sn} + \text{SnCl}_4 \longrightarrow 2\text{SnCl}_2$. The velocity of dissolution is given by $-v \cdot dx/dt = s[k_1(a-x) + k_2x]$, where v is the vol. of the solution, s the Sn surface (sq. cm.), a the initial $[\text{FeCl}_3]$, and x the fraction of FeCl_3 reduced at time t . The temp. coeff. of the const. k_1 is 1.24. R. T.

Action of heat on some metallic camphor-carboxylates. M. PICON (Compt. rend., 1935, 200, 397—399).—The velocity of liberation of CO_2 from Mg, Ca, Na, Mn, Zn, Ce^{III} , UO_2^{II} , Cu^{II} , Bi, Pb, Ag, Hg^{II} , Tl^{I} , and Tl^{II} camphorcarboxylates at 100° generally increases with increasing equiv. wt. of the metal. At higher temp. hydrocarbons and H_2 are formed, of composition depending on the metal. C_2H_2 is not formed in detectable amounts, but ethylenic hydrocarbons are produced, especially at high temp. and from the Ca and Na salts. On maintaining $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{CO}_2\text{Na}$ in a vac. at 175° it yields $\text{C}_{10}\text{H}_{14}(\text{ONa}) \cdot \text{CO}_2\text{Na}$, a white compound, sol. in MeOH and EtOH and with HCl regenerating the acid in theoretical quantity. J. W. S.

Specificity of oxidising agents: comparison of the oxidising action of lead tetra-acetate and periodic acid on polyhydroxy-compounds. R. CRIEGEE (Sitzungsber. Ges. Beförd. ges. Naturwiss. Marburg, 1934, 69, 25—47; Chem. Zentr., 1934, ii, 2515).—Largely a discussion of work already reported (A., 1933, 1272). H_5IO_6 (I) effects oxidative fission of glycols in the same manner as $\text{Pb}(\text{OAc})_4$ (II). There is no direct relationship between the speeds of the two oxidations, except in the case of stereoisomerides. With α -OH-acids and $\text{H}_2\text{C}_2\text{O}_4$, (I) and (II) react in completely different ways. These differences are discussed theoretically, in relation to the mechanism previously advanced, and attributed chiefly to differences in the polar nature of (I) and (II) and to structural differences in the compounds undergoing oxidation. The kinetics of many such oxidations are described in detail. H. N. R.

Theories of catalysis. D. PORRET (Ann. Guehard-Severine, 1934, 10, 392—400).—A lecture.

Catalytic effect of hydrogen on the carbon monoxide flame. W. E. GARNER and F. H. POLLARD (J.C.S., 1935, 144—151).—The discontinuity in the radiation-pressure curves of CO flames

H_2 is interpreted as the pressure, given by $p_0 - k_2/(p_{\text{H}_2} + k_1)$, at which two independent mechanisms producing flames operate at equal speeds. The nature of these mechanisms is discussed. The process which is stable at the higher pressures of H_2 , p_{H_2} , depends mainly on the rate at which H atoms are produced by collision of H_2 with newly formed CO_2 is raised by CO_2 , Br, and CCl_4 (cf. A., 1932, ~), but with Cl, the discontinuity becomes less

well defined. 4—5% of Cl_2 and Br extinguish the flame. Other sp. effects are recorded and the results are interpreted in terms of the deactivation of the H atoms by which the reaction chains are propagated. J. G. A. G.

Catalysis of hydrogen peroxide decomposition by ferrous sulphate and sodium tungstate. B. A. KONOVALOVA (Z. anorg. Chem., 1935, 222, 81—91).— Na_2WO_4 alone has no effect on the decomposition of H_2O_2 in acid solution, but it has a marked accelerating effect on the catalysis of H_2O_2 decomp. by FeSO_4 . This behaviour is due to the formation of Na_2WO_8 , which is normally stable in acid solution but is decomposed in presence of FeSO_4 with evolution of O_2 at a rate $>$ that with FeSO_4 alone. M. S. B.

Electron transfer processes in the mechanism of oxidation-reduction reactions in solution. J. WEISS (Naturwiss., 1935, 23, 64—69).—The conditions affecting the velocity of reactions between ions are reviewed. The mechanisms of the heterogeneous and homogeneous catalytic decomp. of H_2O_2 , the oxidation of Fe^{II} salts by mol. O_2 , and other oxidation reactions are considered. A. J. M.

Aluminium chloride as a catalyst of hydrogen interchange. J. KENNER, M. POLANYI, and P. SZEGO (Nature, 1935, 135, 267—268).— AlCl_3 catalyses the interchange between C_6H_6 and HCl. With ordinary C_6H_6 and HCl containing 13.4% of $\text{H}^2 >$ 90% of the H^2 passes to the C_6H_6 . L. S. T.

Factors in the autoxidation of ether. M. LANDON (Bull. Soc. chim., 1935, [v], 2, 53—57).—Peroxide formation, which is much slower in the dark than in light, is strongly catalysed by traces of MeCHO , but is retarded by H_2O and acids. NaOH prevents the appearance of the oxidation products, and distillation from NaOH is probably the simplest way of removing peroxide and preparing pure Et₂O. J. G. A. G.

Oxidation of iodoform [and carbon tetra-iodide] solutions. R. DUBRISAY and G. EMSCHWILLER (Bull. Soc. chim., 1935, [v], 2, 127—141; cf. A., 1932, 1215; 1934, 261).—Details are given of work previously noted and the results are compared with photochemical data. The "dark" oxidation of CHI_3 is inhibited by the same substances in pure CCl_4 as in C_6H_6 . The temp. coeff. of the "dark" reaction in CCl_4 is 1.7, corresponding with an activation energy of 9500 g.-cal. Added I and acid catalyse the reaction by suppressing retarding agents, since in pure solvents I retards the oxidation and acid has no effect. The photochemical and "dark" oxidation of Cl_2 is very rapid in PhMe, Et_2O , CS_2 , and CHCl_3 , but, unlike that of CHI_3 , is least rapid in CCl_4 and C_6H_6 , unless the last be highly purified. HCl opposes the catalytic effect of I. J. G. A. G.

Catalytic action of inorganic halides. Racemisation by complex formation. K. BODENDORF and H. BÖHME (Annalen, 1935, 516, 1—29).—The catalytic action of certain inorg. halides in the reactions of org. halogeno-compounds has been ascribed to complex formation with consequent increased tendency towards ionisation: $\text{RCl} + \text{MCl} \rightleftharpoons \text{R}[\text{MCl}_2] \rightleftharpoons \text{R}^+ + [\text{MCl}_2]^-$. This hypothesis is ex-

aminated by consideration of the case in which the organic halide is optically active and has the halogen attached to the asymmetric C atom. The carbonium ions would therefore be configuratively labile, since only 3 valencies are saturated and the postulates of the tetrahedron model are absent. Racemisation is therefore to be expected, since in reunion of the ions both antipodes are equally favoured. Racemisation of CHPhMeCl has been observed in the presence of a variety of complex-forming chlorides. The effect cannot be ascribed to Cl', since HgCl₂ under equiv. conditions has a very much more marked action than HCl, LiCl, or NMe₄Cl, which are quantitatively equal to one another. Further, the racemising action of ZnCl₂ is completely nullified by LiCl owing to the production of Li[ZnCl₃]. In presence of HgCl₂ in COMe₂ racemisation of CHPhMeCl follows the unimol. law and is 50 times slower than in MeNO₂ and > 1000 times slower than in Et₂O. There is thus an approx. parallelism between rate of racemisation and dielectric const. of the solvent; in extension of this view it is found that CHPhMeCl is very rapidly racemised in the absence of catalyst in HCO₂H and that addition of HgCl₂ has no influence on the rate of change. In EtOH an inversion of sign is observed, due to the production of optically non-homogeneous CHPhMe·OEt. With ZnCl₂ the rate of reaction depends very greatly on the concn. of catalyst in PhNO₂ and MeNO₂, the activity of the catalyst gradually diminishes. BCl₃ in C₆H₆ or PhNO₂ is more active than HgCl₂ or ZnCl₂ and the dependence of rate on concn. of catalyst is considerably more pronounced. SiCl₄ in C₆H₆ or PhNO₂ is inactive. With TiCl₄ in CHCl₃ the dependence of rate on concn. of catalyst is more marked than with any other chloride. With SnCl₄ racemisation is about 10 times as rapid in C₆H₆ as in PhNO₂, a reversal of the usual relationship between rate and dielectric const. of medium. AsCl₃ in C₆H₆ or PhNO₂ is inactive. The activity of SbCl₅ is so great that the experiments are not exactly reproducible owing to the influence of minute traces of impurity. SbCl₃ has comparatively little effect, and the reaction does not follow the unimol. law. The temp. coeff. of the reaction varies between 2 and 4. H. W.

Enzymic esterification.—See this vol., 403.

Effect of electric waves on heterogeneous catalysis in solutions. E. WILKE and H. GANSER (Kolloid-Z., 1934, 70, 132—135).—Electric waves (90—200 m.) influence the catalytic action of diastase on starch solutions, and of Ag sol and Pt sol, but not I₂ on H₂O₂. The effect seems to be on the catalyst, not the reaction. E. S. H.

Catalytic combustion at high temperatures. N. DAVIES (Phil. Mag., 1935, [vii], 19, 309—325).—Catalytic combustion with air of various proportions of CO and H₂ on Pt and Pd surfaces was investigated up to approx. 1600°. Action, for CO, is entirely suppressed at about 1200°, but at higher temp. the wires recover their activity and action proceeds, at a diminishing rate, up to nearly the m.p. of the wires. A discontinuity is not observed with H₂ except when the wires have been previously used in CO mixtures or have been exposed to air for a long period; in such

cases there is a partial or complete discontinuity at about 1200° for a first heating. N. M. B.

Thermal decomposition of hydrogen peroxide in presence of glass wool and copper sulphate. K. C. BAILEY (Sci. Proc. Roy. Dublin Soc., 1935, 21, 153—164).—The decomp. has been re-investigated at 35° using inhibitor-free H₂O₂ solution which underwent only very slow spontaneous decomp. after being specially filtered. The rate of decomp. in the presence of purified glass wool and small [NaOH] is given by $v = k_2[\text{H}_2\text{O}_2][\text{OH}'] + k_1[\text{H}_2\text{O}_2]$. The p_H of the solution increased during the first 3—10 hr. and then remained const. or fell slowly. v is little affected by the wt. of glass wool, but the negligible reaction in the absence of suitable solid surfaces suggests that both first and second order reactions are heterogeneous. Glass wool with Cu adsorbed from solution catalyses the reaction markedly. The decomp. is of zero order; the velocity coeff. \propto the wt. of Cu adsorbed and falls only at low [H₂O₂]. Cu⁺⁺ in solution has little effect, and the decomp. probably proceeds by way of a Cu peroxide. J. G. A. G.

Influence of solvent on heterogeneous catalysis. Catalysis of hydrogen peroxide in different solvents. I. L. V. PISARSHEVSKI and T. S. GLIKMAN (Bull. Acad. Sci. U.R.S.S., 1934, 1281—1290).—The reaction has been studied in H₂O (I), Et₂O (II), and in (I)–(II) mixtures. The velocity is greatest in (I)–(II), and least in dry (II), but rapidly increases with small additions of (I). It is suggested that the solvent effect is connected with reaction chains in solution. R. S.

X-Ray examination of certain mixed catalysts. G. WAGNER, G. M. SCHWAB, and R. STAEGER (Z. physikal. Chem., 1934, B, 27, 439—451; cf. A., 1934, 850).—Where kinetic measurements indicate that the second component increases the activity by preventing structural changes in the active component at high temp. (CuO–ZnO) or by forming a new kind of active centre (CuO–MgO), the X-ray diagram shows the unchanged lattices of both components. Where the second component has a poisoning action (CuO–Cr₂O₃) or the mixture has considerably increased activity despite increased heat of activation (CuO–Al₂O₃), the X-ray diagram points to compound formation. The increase in the activity of Ni by Cu dissolved in it (*ibid.*, 607) may be due to the distension of the Ni lattice, or to the co-existence of several mixed crystal lattices distended to differing extents, "active lines" occurring at the interfaces. R. C.

Synthesis of ammonia at very high pressures greater than 1000 kg. per sq. cm. and the chemistry of very high pressures. J. BASSER (Bull. Soc. chim., 1935, [v], 2, 108—119).—Full details are given of the apparatus and results already noted (A., 1934, 1082). J. G. A. G.

Catalytic action of Japanese acid earth. X. Mechanisms of the promotion and poisoning of the catalytic action. K. ISHIMURA (Bull. Chem. Soc. Japan, 1935, 10, 1—5).—The promotive power of Al₂O₃–SiO₂ catalyst (I) on C₁₀H₈ is a function of the H₂O retained by (I) at 120°. NH₃, RNH₂, RCN, and C₅H₁₁·NO₂ are strong, HCl and AcOH are weak, poisons. The catalytic activity of (I) is restored after

poisoning with NH_3 by heating at $500^\circ/4$ mm. The adsorption of C_{10}H_8 on (I) is independent of the presence of poison or promoter, and hence the latter affect only the active spots. The surface area of (I) is 1.11×10^5 sq. cm. per g., of which approx. 20% is catalytically active.

R. S. B.

Oxidation of ether in presence of active carbon.

I. DEMOUGIN and LANDON. II. Reactions and determination of oxidised ether. LANDON (Bull. Soc. chim., 1935, [v], 2, 27—34, 34—53).—I. The catalysis, by metallic salts and oxides, of Et_2O (I) formation from Et_2O and subsequent decomp. to H_2O_2 , etc., in presence of air and sunlight has been investigated. Mg^{II} and Zn^{II} afford the highest yields of (I); Fe^{III} , Ni^{II} , Cu^{II} , Co^{II} , SiO_2 , and Al_2O_3 catalyse both processes, whilst active C, in addition, decomposes the H_2O_2 . Cr^{III} gives H_2O_2 , whilst Mn^{II} and PbO inhibit formation of (I). A steam-activated C containing Mn^{II} is recommended for recovering Et_2O from vapours.

II. The pink colour produced by adding KCNS to Et_2O is not due to Fe^{III} , but is probably referable to nitrite content. Titration of Et_2O with KMnO_4 in presence of H_2SO_4 determines the total H_2O_2 but does not distinguish between free H_2O_2 and H_2O_2 present as (I), and includes nitrite. By continuously agitating KI with Et_2O , the I liberated passes through a max. (II). The observed phenomena are attributed to the absorption of I by Et_2O and the equilibrium $\text{MeCHO} + \text{I}_2 \rightleftharpoons \text{CH}_3\text{I} + \text{CHO} + \text{HI}$. When peroxide is present chiefly as free H_2O_2 , (II) is rapidly attained (e.g., after 5 min.), but when much (I) is present, (II) is reached only after shaking for longer periods (e.g., 20 min.).

J. G. A. G.

Catalytic conversion of cyanamide into carbamide. O. T. ROTINI (Chimica e l'Ind., 1935, 17, 14—20).—The relative efficiencies of various catalysts are approx. as follows: hydrated MnO_2 100, $\text{Fe}(\text{OH})_3$ 3, $\text{Al}(\text{OH})_3$ 0.3, $\text{Co}(\text{OH})_2$ 4, $\text{Ni}(\text{OH})_2$ 1, various soils 2—10 (depending mainly on their MnO_2 content, but much > would be expected from their composition). $\text{Fe}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, pyrolusite, TiO_2 , SiO_2 , and humic acids are without catalytic activity. The reaction velocity passes through a max. at p_{H} 9.0 with $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ and at p_{H} 8.6 with $\text{Fe}(\text{OH})_3$. In all cases the log. of the velocity coeff. increases linearly with rise of temp. It is deduced that cyanamide probably has the structure $\text{HN}:\text{C}:\text{NH}$ and not $\text{N}:\text{C}:\text{NH}_2$.

D. R. D.

Action of some catalytic poisons on the hydrogenation of benzene in a liquid medium at room temperature. R. TRUFFAULT (Bull. Soc. chim., 1935, [v], 2, 244—253).—The catalytic action of Ni-black on the hydrogenation of C_6H_6 at room temp. is less affected by the poisoning action of thiophen (I) or halogen derivatives of C_6H_6 than Pt-black. 0.1 g. of (I) is necessary to inhibit the action of 3 g. of Ni. Much greater quantities of (I) are necessary to prevent the hydrogenation of cyclohexene by Ni. H_2O has also a retarding action. Vulcanised rubber has an inhibiting action, but natural rubber, containing no S, has not. The best method for the purification of C_6H_6 from (I) is by Haller and Michel's method of treatment with AlCl_3 .

M. S. B.

Electrolytic separation of diplogen. W. W. SAWYER (Proc. Camb. Phil. Soc., 1935, 31, 116—118).—The theory of Bell and Wolfenden (A., 1934, 154) for H^2 concn. by electrolysis depends on the assumption of a const. val. of γ , where $\gamma = 1 - (dN/dr_0)/(dE_0/dr_0)$, N being the min. possible energy for a neutral atom at distance r from the origin and E_0 the least energy which a nucleus, moving in a steady state at r from the origin, can have. Theoretically γ is const. and independent of the mass of the isotope.

W. R. A.

Electrolysis of solutions of zinc chloride in mixtures of water and ethyl alcohol. C. CHARMETANT (Compt. rend., 1935, 200, 380—381).— H_2O — EtOH solutions of ZnCl_2 (30—40 g. per litre) containing > 300 g. of EtOH per litre yield no free Cl_2 on electrolysis, HCl and MeCHO being formed. The yield of MeCHO is > 50—60% theoretical. With low $[\text{EtOH}]$ a little Cl_2 is evolved. Except with very high $[\text{EtOH}]$ the yield of Zn at a c.d. of 2 amp. per sq. cm. is about 96% after 1 hr. and decreases with time. The yield increases with decreasing c.d. The deposit is the purer, but the less adherent, the higher is the c.d., and the adherence also diminishes with increasing $[\text{EtOH}]$.

J. W. S.

Polarographic studies with the dropping mercury cathode. XLV. Electro-reduction of selenites and tellurites. L. SCHWAER and K. SUCHY (Coll. Czech. Chem. Comm., 1935, 7, 25—32; cf. A., 1934, 1177).—Polarograms of the reduction of selenites (I) and tellurites (II) show three waves due to the steps $\text{TeO}_2 \rightarrow \text{TeO} \rightarrow \text{Te} \rightarrow \text{TeH}_2$. In presence of 0.1N- NH_4Cl and 0.1N- NH_3 (I) are reduced at -1.43 volts and (II) at -0.65 volt (from Hg_2Cl_2 zero) in one step. Cu, Bi, (I), and (II) may be determined separately in presence of Na K tartrate. A sharp max. which increases linearly with $[\text{TeO}_2]$ appears in the polarogram at the limiting current due to electrodeposition of Te.

R. S.

Isolation of gadolinium. F. TROMBE (Compt. rend., 1935, 200, 459—461).—The Gd is obtained as a fusible alloy with 6% Cd by electrolysis with Cd in a C crucible. Separation is then effected by fractional distillation in a Mo crucible under 0.001 mm. pressure at 1230—1240°. Gd 98.4% pure is obtained; it does not decompose boiling H_2O , and oxidises only slowly in air.

N. M. B.

Electrolysis of metals during the simultaneous scraping of the anode and cathode by means of a diamond. J. GILLIS and J. SWENDEN (Rec. trav. chim., 1935, 54, 219—234).—Electrolysis with continuously scraped electrodes of Cu, Ni, and Cd, and between two dropping Hg electrodes, in solutions of the corresponding salts at < certain concns., gives linear current-p.d. curves. With Ni solutions > 0.1M and Cu solutions > 1M the curves are logarithmic, but Cd gives linear curves at 0.0001—1M and at relatively high c.d. and p.d. Unscraped Ni gives a logarithmic curve $\log r = a + b \log c$, where r = polarographic resistance (of the cell during electrolysis), c = concn., and a and b are consts. Similarly $\log r' = a + b \log (r')$ (r' = resistance in absence of electrolysis), depends on the anion according to $\text{CNS}^- > \text{NO}_3^- > \text{SO}_4^{--}$, but the anion does not influence the concn. a

which $f=1$ for the same metal. The addition of gelatin, C_3H_5N , and tartaric acid changes r at 16° and 27° according to $\log r = A + B \log c$, where $c = \text{concn. of added substance}$, and A and B are consts., a relation of the same form as the Freundlich adsorption isotherm. Unless both electrodes are scraped the added substance has no influence. f increases with the degree of polarisation of the electrode, in the order $Cd < Cu < Ni$. On adding gelatin etc. to Cu solutions f rises to approx. the same val. as for Ni . The results can be interpreted according to the theory of Hoekstra (cf. A., 1934, 372). R. S. B.

Use of a modified Haring cell in detecting electrode reactions. J. E. STARECK and R. TAFT (Trans. Electrochem. Soc., 1935, 67, 97—114).—The application of a modified transparent Haring cell to the study of the deposition of Ag from $AgNO_3$ and from cyanide solutions is described. Using Pt for the main and reference electrodes, the anode and cathode current-voltage curves were determined from very low c.d. upwards and the discontinuities therein are discussed. The anode products are Ag peroxide and O_2 . At the cathode $cryst. Ag$, H_2 , and AgH are detected. In the system $Pt[AgNO_3]Pt$ a pronounced break in the cathode curve is attributed to the formation of AgH , further evidence for the existence of which is advanced. The system $Pt[KCN]Pt$ is also examined and the nature of the electrode reactions discussed. The character of the deposits, particularly as regards colour effects and the stability of the coloration, is also discussed. J. W. C.

Voltaic couples and corrosion.—See B., 1935, 231.

Motor-electrolytic current as a factor in corrosion.—See B., 1935, 231.

Rhenium plating.—See B., 1935, 233.

Electrolysis in the glow discharge. V. Special behaviour of polar hydrogen and oxygen in electrolysis of aqueous sulphuric acid. A. KLEMENC and T. KANTOR (Z. physikal. Chem., 1934, B, 27, 359—375; cf. A., 1934, 39).— H_2O_2 and $H_2S_2O_8$ produced in the glow discharge electrolysis (I) aq. H_2SO_4 are formed principally by either polar or apolar at. H produced by decomp. of H_2O vapour in the anode or cathode fall: $2H_2SO_4 + 2H = 2H_2 + H_2S_2O_8$, $2H_2O + 2H = 2H_2 + H_2O_2$. H_2SO_5 is produced by $H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$. H liberated on a solid cathode does not so react, possibly because it dissolves in the electrode. Polar O does not oxidise in (I), therefore oxidation effected by O produced on an electrode must be catalysed by the latter. In (I) or sulphate solutions no $H_2S_2O_8$ is produced, but πO_2 is formed, apparently by $2OH = H_2O_2$ occurring in the solution. Under the influence of the glow zone, which is near the surface of the solution, H_2O mols. decompose: $H_2O = OH + H$, $H_2O = H_2 + O$ (cf. 1929, 1146). At a solid anode the only reaction or OH is $2OH = H_2O + O$. R. C.

Nitrogen peroxide, NO_2 . R. SCHWARZ and ACHENBACH (Ber., 1935, 68, [B], 343—349).—Passage of the glow discharge through a mixture of O_2 (1:20) at 1 mm. and cooling of the products in liquid air in the apparatus described (A.,

1934, 1183) gives a pale blue condensate, apparently a mixture of N_2O_3 and higher oxides. If the condensing tube forms part of the discharge tube a colourless deposit of *nitrogen trioxide*, NO_3 , is obtained. It is stable at $< -142^\circ$, above which it slowly decomposes into NO_2 and O_2 . In aq. media it is relatively stable. The very low temp. of condensation, the spectroscopic behaviour, and the co-ordinatively unsaturated character of the compound indicate the monomeric form and therefore the structure $O:N < \overset{O}{\underset{O}{\text{O}}}$. Hydrolysis in H_2O is not accompanied by

production of H_2O_2 , thus excluding the constitution $NO_2 \cdot O \cdot O \cdot NO_2$ and identity with the dimeric oxide N_2O_6 . In presence of H_2O it is decomposed into O_2 and NO_2 , which yields NO_2' and NO_3' , and hence it does not function as an acid anhydride. H. W.

Influence of light on the combination of hydrogen and oxygen and of hydrogen and nitrogen at various temperatures. M. MIYANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 70—76).—The mixtures $2H_2 + O_2$ (I), $5H_2 + 2NO$ (II), and $3H_2 + N_2$ (III) have been exposed to ultra-violet light from condensed Al and Co sparks at $> 460^\circ$. (III) does not react. (I) gives H_2O and H_2O_2 , whilst (II) gives H_2O and NH_3 or N_2H_4 . The influence of temp. and λ has been studied. R. S.

Exchange reactions of deuterium and methane under the influence of excited mercury. H. S. TAYLOR, K. MORIKAWA, and W. S. BENEDICT (J. Amer. Chem. Soc., 1935, 57, 383).— CH_4 and H_2 react at 40 — 300° in the presence of Hg vapour when illuminated by resonance radiation, the activation energy being about 5 kg.-cal. R. S. C.

Photochemical formation of carbonyl chloride. VIII. Simultaneous formation of carbonyl chloride and hydrogen chloride. M. BODENSTEIN, W. BRENSCHKE, and H. J. SCHUMACHER (Z. physikal. Chem., 1935, B, 28, 81—94; cf. A., 1931, 1137).—Rollefson's data (A., 1934, 496), supposed to show the chain carrier to be Cl_2 , agree equally well with the assumption that it is $COCl$, as postulated by the authors. Repetition of Rollefson's experiments on the photochemical reaction of Cl_2 , CO , and H_2 using more exact methods and over a wider concn. range supports the authors' mechanism. At low $[Cl_2]$ there is appreciable breaking, by $H + COCl_2 = HCl + COCl$ on the wall, of the chains giving HCl . The formation of $COCl_2$ may be accelerated by the simultaneous formation of HCl by $HCO + Cl_2 = COCl_2 + H$ acting as a chain reaction. R. C.

Coloration of calcium sulphide phosphors by light. S. ROTHSCHILD (Z. physikal. Chem., 1935, 172, 188—196).—By ignition of mixtures of S , $Ca(OH)_2$, and Na_2CO_3 or K_2CO_3 brownish-violet phosphors are obtained which, without previously being subjected to one-sided compression, deepen in colour in light, the effect being intensified if Bi is present. Addition of $NaCl$ yields a product originally almost white. The tendency to coloration in light does not depend on the phosphorescing power; the deciding factor is the mechanism whereby the atom

groupings, characteristic of the phosphor and formed by ignition, store up the energy of absorbed radiation.

R. C.

Oxidation of Fe^{++} to Fe^{+++} by irradiation with X-rays of solutions of ferrous sulphate in sulphuric acid. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 60—61; cf. A., 1929, 408).—The reactions taking place are (1) $\text{Fe}^{++} + \text{H}^+ = \text{Fe}^{+++} + \frac{1}{2}\text{H}_2$; (2) $\text{Fe}^{++} + \text{H}^+ + \frac{1}{2}\text{O}_2 = \text{Fe}^{+++} + \frac{1}{2}\text{H}_2\text{O}$; (3) $\text{Fe}^{++} + \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} = \text{Fe}^{+++} + \text{OH}^-$. The quantity of Fe^{++} oxidised per unit dosage of radiation increases with decreasing p_{H} and is independent of $[\text{FeSO}_4]$ and of the pressure of O_2 when this is present.

F. L. U.

Light reaction of alkaline bases on mercuric iodide. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 290—291).—For concns. of alkali below 6*M* the final product is HgO . Below 1.5*M* there is a transitory formation of HgI_2, HgO (I) and the reaction is uninfluenced by light. Above 2*M* the tendency to form the white $3\text{HgI}_2, \text{HgO}, 3\text{KOH}$ from (I) increases with increasing proportion of HgI_2 ; this compound is then decomposed by the action of light, giving HgO and K_2HgI_4 . Above 7*M*- KOH the white compound formed, $\text{HgI}_2, 2$ or $3\text{HgO}, x\text{KOH}$, is practically stable to light while still moist, but turns brown when dry.

M. S. B.

Blackening of photographic plates by ultrasonic waves. N. MARINESCO and M. REGGIANI (Compt. rend., 1935, 200, 548—550; cf. A., 1933, 473).—When ultrasonic waves are passed for 8 min. to 1 hr. through a bath of dil. developer containing an unexposed photographic plate, the latter is blackened in the form of stationary waves. This is attributed to activation by collision between the mols. of Ag salt, in accordance with Perrin's theory.

J. W. S.

Electrolytic development of photographic layers. E. KELLNER and K. BENNEWITZ (Z. wiss. Phot., 1935, 33, 212—224, 225—233).—Anodic bromination of a Ag electrode gave two kinds of AgBr, one being grey and adherent (formed by reaction of Br^- on giving up its charge) and the other yellow and non-adherent (formed by interaction of Ag^+ from anodic polarisation, with neighbouring KBr); the yellow form is more light-sensitive. The formation of Ag nuclei in a photographic emulsion is considered as the result of absorption of a light quantum in places in the AgBr crystal having a natural strain in the crystal lattice; the Ag nuclei form new centres of strain for commencement of development. By wrapping gelatin emulsions on a paper base in close contact with a Zn cathode, or in contact with Hg as cathode, development is obtained on electrolysis of the solution in which it is placed; considerable fogging is always found, due probably to at. H. The effects of varying time of exposure, development, composition of the electrolyte, voltage, c.d., etc. have been determined. The results are compared with those of chemical development.

J. L.

Theory of the ideal colour-sensitivity of photographic negative material. III. J. E. DE LANGHE (Z. wiss. Phot., 1935, 33, 205—211; cf. A., 1934, 610).—The outward form of the equation for the characteristic curve is unchanged, but I_0 is made

dependent on λ . The theory of Arens and Eggert is not in agreement with the results derived mathematically.

J. L.

Distribution of nuclei with solarisation and their removal. LUPPO-CRAMER (Z. wiss. Phot., 1935, 33, 201—204).—Polemical against Arens. The coagulation theory does not afford an explanation of solarisation (cf. A., 1934, 1184; 1933, 577).

J. L.

Primary process of photochemical decomposition of formaldehyde. II. T. LOCKER and F. PATAT (Z. physikal. Chem., 1934, B, 27, 431—438; cf. A., 1934, 740).—In the decomp. in the predissociation region no free H atoms are formed. Decomp. in the fine structure and predissociation regions may occur either by the H atom initially released reacting before it can leave the mol. with the HCO radical to give H_2 and CO (cf. A., 1930, 702), or, more probably, by the vibrating mol. contributing part of the energy of separation by attractive forces between the H atoms helping to break the C-H linking when the mol. is extended to a certain extent. On photodecomp. polymerised CH_2O yields CO and H_2 in the same proportions as normal CH_2O .

R. C.

Biocolorescence of aromatic compounds of the benzene series. W. KAETEL (Standesztg. deut. Apothek., 1934, 3, 30; Chem. Zentr., 1934, ii, 2367—2368).—Solutions of a camphor derivative or synthetic adrenaline coloured by light were decolorised by the presence of photographic layers, the latter being changed.

H. J. E.

Photodecomposition of chlorophyll.—See this vol., 421.

Three new phototropic compounds.—See this vol., 497.

Reciprocal interchange of the hydrogen atoms of the co-ordination space of a complex salt and of water. O. BANKOWSKI (Monatsh., 1935, 65, 262—266).—The following complex salts have been dissolved in H_2O containing 10.8% of H_2O : $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ (I), $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{Cl}$ (II), and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (III). The H_2O was subsequently removed and the determination of d indicated a fall in H_2O content. The no. of H^1 atoms in the salt replaced by H^2 could be calc. The change is complete in 5 min. One atom is exchanged in (I), in agreement with Bronsted's view that the cation is a monobasic acid (A., 1928, 1326). Three atoms are exchanged in (II), probably giving one NH_3 group, and five in (III) giving NH_3 and H_2O of crystallisation. This agrees with the view that, in this case, the H_2O is outside the co-ordination sphere.

M. S. B.

Isotopic fractionation of water by distillation. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 39—40).—Purity was checked by determination of electrical conductivity, and d of samples was studied by means of a SiO_2 buoyancy balance. In a distillation at 1 atm. the most and least volatile fractions differed by 6.3 p.p.m.

R. S. B.

Isotopic fractionation of water due to evaporation and distillation. T. TITANI and M. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 41—42).—

from the mother-liquor of salt obtained by the slow evaporation of sea- H_2O is 5.4 p.p.m., and H_2O from sugar-cane molasses is 2.8 p.p.m., heavier than normal H_2O . R. S. B.

Tribromogold. A. BURAWOY and C. S. GIBSON (J.C.S., 1935, 217—218).—The mol. wt. in boiling Br corresponds with the formula Au_2Br_6 , and evidence in favour of the constitution $Br_2Au \begin{smallmatrix} \nearrow Br \\ \searrow Br \end{smallmatrix} AuBr$.

is adduced, the Au^{III} being 4-covalent as in the analogous org. derivatives (cf. A., 1934, 877). There was no evidence of an OEt -derivative of Au when Au_2Br_6 in Et_2O was mixed with $KOEt$ in $EtOH$, but the filtrate afforded *monopyridinomobromogold* (decomp. $> 120^\circ$) with C_5H_5N . J. G. A. G.

Separation of calcium from rare earths by hydrolysis. G. P. ALEXANDROV (Redk. Met., 1934, 3, No. 4, 52—53).— H_2O vapour was passed over a mixture of chlorides of the rare earths (I) and of Ca and Sr at 500—600°, converting (I) into oxychlorides. The product was digested with hot H_2O , hydroxides of (I) being pptd., whilst the Sr and Ca dissolve. One further pptn. with $H_2C_2O_4$ then suffices to eliminate Ca. The method is applicable with large amounts of Ca. CH. ABS. (e)

Action of alkaline-earth bases and silver oxide on mercuric iodide. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 220—222).—On account of its slight solubility $Ca(OH)_2$ has not much action on HgI_2 , but a small quantity of HgO is formed. $Ba(OH)_2$ and $Sr(OH)_2$ give HgO in the cold, but when hot, at concns. of base above M , white *oxyiodides* of the probable composition $HgI_2 \cdot 2$ or $3HgO \cdot xBa(OH)_2$ [or $Sr(OH)_2$] are formed. These are sensitive to light, sol. in aq. KI, $Na_2S_2O_3$, or KCN, and easily decomposed by H_2O and acids. When HgI_2 and H_2O are shaken together with increasing quantities of Ag_2O for 24 hr. AgI alone is first formed. As the proportion of Ag_2O is increased $HgI_2 \cdot 2AgI$ is obtained in increasing quantity. M. S. B.

Reactions of mercuric iodide. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 373—375).— Hg_2I_2 is formed from HgI_2 by reaction with Na_2SO_3 , $SnCl_2$, and boiling HCO_2Na ; Hg is pptd. by NH_4OH , HCl in presence of KOH , Na hypophosphite in HCl , $NHPh \cdot NH_2$ or Zn in aq. KOH , glucose, fructose, arabinose, and xylose in KOH . Sucrose, mannitol, and inositol give a brown compound which is a mixture of Hg_2I_2 and HgI_2 . Double decomp. takes place with $AgNO_3$, alkali and alkaline-earth chlorides, and chlorides of org. bases. $FeCl_3$ gives I_2 , $HgCl_2$, and I . $Na_2S_2O_3$ dissolves HgI_2 in the cold and ppts. HgS when hot, especially in acid solution. K_2TeO_4 gives a pale yellow $HgTeO_4 \cdot 2HgO$, but K_2SeO_3 and K_2SeO_4 have no action. Veronal forms white crystals of $(CO \begin{smallmatrix} \nearrow NH-CO \\ \searrow C=O \end{smallmatrix} N)_2Hg$. Gardenal and phenylethylbarbituric acid give the same reaction. M. S. B.

Action of cyanogen compounds on HgI_2 . E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 296—297).—The following compounds have been prepared from

HgI_2 with: KCN, $Hg(CN)_2$, $2KCN$; $K_4Fe(CN)_6$ and concn. of the solution, $K_4Fe(CN)_6 \cdot HgI_2 \cdot 2H_2O$, easily decomposed by dil. acids giving HgI_2 ; $K_3Fe(CN)_6$, a dark green solution but no complex; NH_4CNS , white crystals of $NH_4CNS \cdot HgI_2 \cdot 6H_2O$, readily decomposed by H_2O ; $KCNSe$, $KCNSe \cdot HgI_2 \cdot 2H_2O$, very unstable; $KCNO$, fine white needles of $5KCNO \cdot HgI_2 \cdot 4H_2O$, easily decomposed by acids. $Na_2Fe(NO)(CN)_5 \cdot 2H_2O$ has no action on HgI_2 . M. S. B.

Preparation and mode of formation of boron hydrides. III. **Action of anhydrous sodium formate on boron, boron oxide, and boron nitride.** E. WIBERG and W. SUTTERLIN (Ber., 1935, 68, [B], 296—299; cf. this vol., 50).—Contrary to Vournasos (A., 1910, ii, 549, 948), traces of B hydrides are not formed by the action of HCO_2Na on B, B_2O_3 , or BN. The observed reducing action of the gaseous products of the change is attributed to substances (? CO) derived from HCO_2Na and the green colour of the burning gases to traces of solid B compounds carried over. H. W.

Action of substituents on boron halides. IV. **Action of hydrogen and alkyl halides on boron halides.** E. WIBERG and U. HEUBAUM (Z. anorg. Chem., 1935, 222, 98—106; cf. A., 1932, 258).—Br is replaced by Cl, to a very small extent only, when BBr_3 and HCl are kept together for several hr. in a vac. at room temp. MeF and $EtCl$ have no action on BCl_3 at temp. from -60° to 300° . CPh_3Cl reacts immediately with BCl_3 in vac. at room temp. or below 0° and forms an equimol. yellow additive compound, insol. in CCl_4 and decomposed by $MeOH$, $EtOH$, and H_2O . It is decolorised by long exposure to air. When heated to 200° it darkens but does not melt. It is decomposed by distilling in vac. at 80° . CPh_3F also forms a deep yellow additive compound. M. S. B.

Compounds of the type $BCl_{3-n}(OR)_n$. II. **Decomposition [into two compounds of the same series] in the compound $BCl_{3-n}(OMe)_n$.** E. WIBERG and W. SUTTERLIN (Z. anorg. Chem., 1935, 222, 92—97).—The compounds $BCl_{3-n}(OMe)_n$ are stable and show no inclination, when pure, for division into two compounds of the same series containing more and less Cl, respectively. In the presence of a base, however, this division takes place. NMe_3 with $BCl(OMe)_2$ forms an additive compound which, on warming at 100° for 4 hr., gives $BCl_2 \cdot OMe \cdot NMe_3$ and $B(OMe)_3$. With $BCl_2 \cdot OMe$ the behaviour is similar, but requires a temp. of 180° and gives $BCl_3 \cdot NMe_3$ and $B(OMe)_3$. NMe_3 has no action on $B(OMe)_3$. Its action on BCl_3 has been previously described (cf. A., 1932, 258). M. S. B.

Light from [burning] aluminium and aluminium-magnesium [alloy]. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1935, 54, 239—244).—Al burns more slowly in O_2 than does Mg, giving a spectrum very similar to that obtained with the latter. The light yield with 0.3μ Al foil is 26 lumens per watt per mg. Al. The flashing time decreases with increasing Mg content for Mg-Al alloys, and the light yield increases, becoming $>$ for the pure components with 5—10% Mg. The spec-

trum from the alloy is similar to that obtained with the components. With Mg-Al wire wound as a coil and heated with an explosive powder the flash time decreases and the light yield increases considerably as the radius of the coil increases. R. S. B.

Preparation of iron-free solutions of titanous sulphate and titanous sulphate. R. ROSEMAN and W. M. THORNTON, jun. (J. Amer. Chem. Soc., 1935, 57, 328—329).—The purification of $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ is described. $Ti(SO_4)_2$ is prepared therefrom by treatment with H_2SO_4 , and $Ti_2(SO_4)_3$ by electro-reduction of $Ti(SO_4)_2$. E. S. H.

Potentiometric investigation of hydroxide precipitation. E. HAYEK (Monatsh., 1935, 65, 233—238).—In presence of an alkali salt with the same anion basic salts of definite composition may be pptd. by NaOH from a metal salt solution. This pptn. may be followed potentiometrically. Using an Al electrode the titration (a) of $PbCl_2$ with NaOH indicates the existence of $PbCl_2$, $Pb(OH)_2$ and $3PbCl_2 \cdot Pb(OH)_2$, and (b) of $Pb(NO_3)_2$ indicates $3Pb(NO_3)_2 \cdot Pb(OH)_2$. Pb may be determined in presence of Cd, Zn, Mg, Ca, or Ba by titration of $Pb(SCN)_2$, giving an end-point at $Pb(SCN)_2 \cdot Pb(OH)_2$ with an error of approx. 5%. M. S. B.

Compounds obtained by dehydration of the double iodide of lead and potassium $PbI_2 \cdot KI \cdot 2H_2O$. P. BAFFIE (Ann. Chim., 1935, [xi], 3, 130—141).—The dehydration (I) has been followed gravimetrically and by X-rays. (I) begins at 30° and continues to 60°, when a stage of const. composition $PbI_2 \cdot KI \cdot 0.5H_2O$ is attained. (I) is renewed above 67° giving $PbI_2 \cdot KI$ (II) at 96—97°. X-Ray diagrams show that (II) is not a mixture of PbI_2 and KI. R. S.

Explosibility of molten ammonium nitrate. R. KAISER (Angew. Chem., 1935, 48, 149—150).—Experiments show that the explosion which may occur at elevated temp. is due to the gaseous products of decomp. E. S. H.

Peroxidation of nitrogen oxides in presence of ozone. E. BRINER, E. ROKAKIS, and B. SUSZ (Helv. Chim. Acta, 1935, 18, 230—234; cf. A., 1932, 1095).— O_3 exercises no catalytic action on the oxidation of NO by O_2 , and itself reacts thus: $O_3 + NO \rightarrow NO_2 + O_2$. F. L. U.

Oxidation of phosphorus with water at high temperature and pressure in the presence of alkali. Production of phosphorous acid. V. N. IPATIEV and P. V. USACHEV (J. Amer. Chem. Soc., 1935, 57, 300—302).— H_3PO_3 or H_3PO_2 is formed at < 225°, depending on the amount of NaOH present. H_3PO_4 is formed at > 250°. E. S. H.

Preparation of protoactinium. A. VON GROSSE (Ber., 1935, 68, [B], 307—309).—Criticisms of the work of Graue *et al.* (A., 1934, 1186). H. W.

Salts of hyposulphurous acid. R. SCHOLDER and G. DENK (Z. anorg. Chem., 1935, 222, 41—47).— $SrS_2O_4 \cdot 4.5H_2O$ has been prepared, by double decomp. of aq. $SrCl_2$ with $Na_2S_2O_4$, as colourless, micro-cryst., hexagonal plates readily decomposed on exposure to air

and giving off SO_2 . $BaS_2O_4 \cdot aq.$, similarly prepared, is still more unstable. $PbS_2O_4 \cdot aq.$, prepared by the action of aq. $Na_2S_2O_4$ on aq. $Pb(OAc)_2$, is also unstable, forming PbS and $PbSO_3$ when wet and $PbSO_3$ and PbS_2O_3 when dry. Hyposulphites, too unstable to be formed in the ordinary way, may be stabilised by the formation of addition compounds with C_5H_5N . The following compounds have been obtained: $CoS_2O_4 \cdot 2C_5H_5N$, $ZnS_2O_4 \cdot C_5H_5N$, $CdS_2O_4 \cdot C_5H_5N$, $MnS_2O_4 \cdot 2C_5H_5N$, $FeS_2O_4 \cdot 2C_5H_5N$. M. S. B.

Decomposition of hyposulphurous acid and its salts. R. SCHOLDEN and G. DENK (Z. anorg. Chem., 1935, 222, 48—55).—The behaviour of $Na_2S_2O_2$ in the presence of strong acids appears to indicate that the reaction $2H_2S_2O_4 = 3SO_2 + 2H_2O + S$ involves the intermediate formation of H_2SO_2 and H_2SO_3 . BaS_2O_4 (cf. preceding abstract) decomposes, after a day under the mother-liquor, into $BaSO_3$ and BaS_2O_3 . In aq. $Ba(OH)_2$, under an atm. of N_2 , it forms $BaSO_3$ and BaS . SrS_2O_4 in aq. $Sr(OH)_2$ decomposes similarly, but much more slowly. At 50°, however, the reaction is complete in 1 hr. As_2S_2 is produced by the action of "rongalite" on As_2O_3 in strongly acid solution. M. S. B.

Sulphur. II. Sulphur fluorides and oxyfluorides. M. TRAUTZ and K. EHREMAN (J. pr. Chem., 1935, [ii], 142, 79—124; cf. A., 1929, 525).—The v.-p. curve of SO_2F_2 , m.p. $-121.4 \pm 0.5^\circ$ (lit. -121°), b.p. $-49.7 \pm 0.3^\circ/748.5$ mm. (lit. $-52^\circ/1$ atm.) (improved prep.), has been determined. SO_2F_2 reacts with aq. KOH more rapidly than is stated in the lit. Its solubility in H_2O is unaffected by $KMnO_4$, and that in various org. solvents is given. Moissan's statement (A., 1901, ii, 233) concerning its thermal stability is confirmed. S_2F_2 could not be obtained free from SF_2 . Thermal decomp. of S_2F_2 begins at 90° and is fast at 200—250°. Decomp. by heat or electric spark results in vol. contraction and pptn. of S. The gaseous products are partly SF_2 and a small amount of a substance, b.p. about 30°, which probably is a polythiofluoride; SF_4 and SF_6 are not formed. An electric spark passed through a mixture of SiF_4 and S_2F_2 produced a little S and some SF_2 . Similarly a mixture of S_2F_2 and SO_2 gave SOF_2 and SO_2 , but no SO_2F_2 , whilst S_2F_2 and O_2 gave SO_2 , SO_3 , and SOF_2 , but no SO_2F_2 . When S_2F_2 and H_2 are sparked, H_2F_2 and H_2S are slowly produced. S_2F_2 is considered to have the structure $S:Sf_2$. V.-p. curves of S_2F_2 - SF_6 mixtures indicate that solid S_2F_2 has a transition point between -140° and -150° . The v.-p. curve for S_2Br_2 , m.p. -47.14° (lit. -46.0°), has been determined and the instability of S_2Br_2 above about -85° and 50 mm. pressure confirmed. The curve shows that decomp. starts below this temp. and pressure. H. G. M.

Reactions of thionyl chloride and of its thermal decomposition products with oxalates and formates. W. C. SCHUMB and C. H. HAMBLET (J. Amer. Chem. Soc., 1935, 57, 260—266).—The reactions of $SOCl_2$, S_2Cl_2 , SO_2 , and Cl_2 with PbC_2O_4 , and of $SOCl_2$ and S_2Cl_2 with $(HCO_2)_2Pb$ have been investigated quantitatively at 60°. SO_2 does not react with the Pb salts at 60°. A method of determining $SOCl_2$ in presence of its thermal decomp. products with a

recision of 0.2% is based on the above reactions. OCl_2 has m.p. -101.4° . E. S. H.

Chromium carbides. S. L. TZINBERG (Zavod. Lab., 1934, 3, 1128).—The carbide $3\text{Fe}_3\text{C} \cdot 7\text{Cr}_4\text{C}$ was isolated from Cr-Ni steel preheated at 950° for > 4000 hr. R. T.

Reaction of fluorine with water and with hydroxides. G. H. CADY (J. Amer. Chem. Soc., 1935, 57, 246—249).—The product of reaction of F_2 with cold H_2O or solid NaOH , KOH , or $\text{Ca}(\text{OH})_2$ is OF_2 . The production of O_3 is doubtful. Cold aq. solutions give powerful oxidising agents, which vary with $[\text{H}^+]$. E. S. H.

Direct oxidation of iodine, iodides, and chlorates at ultra-pressures. M. DODE and J. BASSET (Bull. Soc. chim., 1935, [v], 2, 344—354).—At pressures of O_2 of > 1000 kg. per sq. cm., the approx. quant. transformation of iodides into iodates is possible but slow. For rapid transformation 8000 atm. at 500° would be necessary. The limits of sensitivity of the different reactions for IO_3' have been determined. It has not been found possible to oxidise ClO_3' directly to ClO_4' . M. S. B.

Formation of complexes of ferric ion with carboxylic acids. W. D. TREADWELL and E. WETTSTEIN (Helv. Chim. Acta, 1935, 18, 200—210).—Aq. FeCl_3 can be titrated electrometrically with Na salts of many org. acids at p_{H} 3—5 so as to give sharp end-points, and the method can be used for the determination of tartaric, malic, malonic, citric, benzoic, cinnamic, and anisic acids. The 31 acids studied are divisible into eight groups, based on the stoichiometric ratio Fe^{+++} : acid and on the nature of the complex formed. Cationic complexes, usually containing OH , are formed with monobasic acids, and anionic with others. The complexes are sol. in H_2O , excepting those with BzOH , $\text{CHPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, $o\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, succinic, fumaric, adipic, mucic, tricarballic, and aconitic acids. F. L. U.

Basic salts. VIII. Chemistry and morphology of basic salts of bivalent metals. General. W. FEITKNECHT. **IX. Basic cobalt sulphates.** W. FEITKNECHT and G. FISCHER (Helv. Chim. Acta, 1935, 18, 28—40, 40—60; cf. A., 1934, 1068).—VIII. The subject is discussed generally from chemical, physico-chemical, genetic, and structural points of view.

IX. $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2$ crystallises with difficulty in microscopic hexagonal leaflets. The lattice consists of alternate layers of hydroxide and normal salt. The amount of H_2O , which is held in a zeolitic form, varies with the method of prep., but is usually 4 mols. The compound, which is blue, is converted by conc. aq. CoSO_4 into a violet basic salt $2\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, which may form either rhombic or monoclinic crystals. Its H_2O of crystallisation is also zeolitic. When CoSO_4 is hydrolysed by $\text{CO}(\text{NH}_2)_2$ basic salts in which the SO_4 is partly replaced by CO_3 are formed. F. L. U.

New decomposition of hyposulphite and cobalt sulphoxylate. R. SCHOLDER and G. DENK (anorg. Chem., 1935, 222, 17—40).—Aq. CoCl_2 ,

with aq. $\text{Na}_2\text{S}_2\text{O}_4$ in presence of NH_3 , $(\text{CH}_3 \cdot \text{NH}_2)_2$, or $\text{C}_2\text{H}_5\text{N}$, gives a dark red solution. On dilution with H_2O a dark brown flocculent ppt. is obtained, which, after filtering and washing under N_2 , was shown to be *Co sulphoxylate*, $\text{CoSO}_2 \cdot 2\text{H}_2\text{O}$, probably in a polymerised form. It may also be pptd. by acid or $(\text{CH}_3 \cdot \text{NH}_2)_2$. Instead of NH_3 , NaOH or, preferably, NaHCO_3 may be added to the mixture of the two salts. Under suitable conditions the decomp. of $\text{Na}_2\text{S}_2\text{O}_4$ by a Co^{II} salt into CoSO_2 and SO_2 is quant. Co can be partly replaced by Cd or Ba in the NH_3 solution or aq. suspension. With Na_2S , CoS , $\text{Na}_2\text{S}_2\text{O}_3$, and NaOH are formed. Gaseous NH_3 at -15° gives a cryst. ammine. CoSO_2 dissolves appreciably in excess of H_2SO_3 and forms an unstable additive compound, $\text{CoSO}_2 \cdot \text{SO}_2$. The reduction val. may be determined by titration with aq. $\text{Br}'\text{-BrO}_3'$. This is the only salt of the hypothetical H_2SO_2 of which the existence has been definitely established. There are indications of a corresponding, but very unstable, Ni salt. M. S. B.

Dibasic cobalt arsenate. J. BURGHELLE (Bull. Soc. chim., 1935, [v], 2, 168).—The salt $\text{Co}_2\text{H}_2(\text{AsO}_4)_2 \cdot 3 \cdot 5\text{H}_2\text{O}$ is pptd. by adding Et_2O to a 2:3 mixture of syrupy H_3AsO_4 and alcoholic $\text{Co}(\text{NO}_3)_2$. The salt readily loses H_2O . J. G. A. G.

Transition compound in the formation of complexes of tervalent cobalt. M. CHATELET (Compt. rend., 1935, 200, 461—464).—Oxidation of solutions of aq. $\text{NH}_3\text{-CoCl}_2$ in presence of NH_4Cl gave the compounds $\text{CoCl}_2(\text{NH}_3)_6$ in octahedra, and $\text{Co}_2(\text{NH}_3)_{10}\text{OCl}_4 \cdot 3\text{H}_2\text{O}$, a brown powder. Properties and composition are discussed. N. M. B.

Compounds of (A) rhodium with ammonia, (B) rhodium with thiocarbamide, (C) rhodium with acetonitrile, (D) iridium with thiocarbamide. V. V. LEBEDINSKI (Ann. Inst. Platine, 1935, 12, 67—77, 79—86, 87—92, 93—102).—(A) The instability and solubility of rhodamines are greater when the no. of basic groups is even than when odd. The prep. of $\text{Rh}(\text{NH}_3)_3\text{Cl}_3$ and $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$ is described; that of $\text{Rh}(\text{NH}_3)_2\text{Cl}_4$ was unsuccessful.

(B) [with V. S. VOLKOV]. A study of the compounds $[\text{RhR}_3\text{Cl}_3]$, $[\text{RhR}_5\text{Cl}]\text{Cl}_2$, $[\text{RhR}_5\text{Cl}]\text{C}_2\text{O}_4$, and $[\text{RhR}_6]\text{Cl}(\text{NO}_3)_2$ [$\text{R}=\text{CS}(\text{NH}_2)_2$] confirms the above rule. Attempts to prepare $[\text{RhR}_2\text{Cl}_4]$ and $[\text{RhRCl}_5]$ were unsuccessful.

(C) [with I. A. FEDOROV]. Na_3RhCl_6 , NH_4Cl , and MeCN afford $(\text{NH}_4)_2[\text{Rh}(\text{MeCN})\text{Cl}_5] \cdot \text{H}_2\text{O}$; the corresponding Rb_2 , Cs_2 , Ag_2 , and $[\text{Pt}(\text{NH}_3)]$ salts are described. Attempts at introducing further MeCN mols. were unsuccessful.

(D) [with E. S. SCHAPIRO and N. P. KASATKINA]. Na_3IrCl_6 and R afford the salts $[\text{IrR}_3\text{Cl}_3]$, $[\text{IrR}_4\text{Cl}_2]\text{Cl}$, $[\text{IrR}_5\text{Cl}]\text{X}_2$, and $[\text{IrR}_6]\text{Cl}_3$ [$\text{X}_2=\text{Cl}_2$, C_2O_4 , PtCl_4 , $(\text{ClO}_4)_2$], indicating that Ir behaves similarly to Rh with respect to introduction of basic groups. R. T.

Stromholm's triamminesulphite. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Ann. Inst. Platine, 1935, 12, 115—118).— $\text{Pt}(\text{NH}_3)_3\text{SO}_3$ (I) yields $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$ with Cl_2 , and

$\text{Pt}(\text{NH}_3)_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ with H_2O_2 . The solubility of (I) in aq. acids increases with $[\text{H}^+]$. R. T.

Platinum oxides. P. LAFFITTE and P. GRAND-ADAM (Compt. rend., 1935, 200, 456—458; cf. A., 1934, 856).—The effect of variation of pressure of O_2 in the oxidation of Pt-black to PtO and PtO_2 was investigated. PtO, obtained by the action of O_2 on Pt-black at 420—440°/8 atm., is a black powder, d 14.9—15.0, slightly sol. in HCl, the solubility increasing with the formation of PtCl_4 . PtO causes instantaneous combustion of H_2 . At 400°/1 atm. PtO_2 decomposes giving PtO and O_2 , and at 560° PtO gives Pt and O_2 . Both oxides, investigated for 4 org. reactions at various temp., are efficient hydrogenation catalysts. Pt-black, activated by heating to 150—180°/150 kg. per sq. cm., absorbs 2.3—3.4% O_2 , giving a catalyst of efficiency approaching that of PtO_2 . N. M. B.

Quantitative spectrum analysis of gas mixtures. J. HEYES (Z. physikal. Chem., 1935, 172, 95—104).—The spectrum of a condensed spark has been used for the quant. analysis of mixtures of H_2 , N_2 , O_2 , and He (cf. A., 1931, 143). With a high capacity in the secondary circuit small variations in the capacity and self-induction do not affect the relative intensities of the lines. The smallest amount of H_2 that can be detected in air by this method is ~0.75%; the H_α line obtained with ordinary air is due to H_2O . The raies ultimes of various gases and lines of equal intensity are tabulated. R. C.

Thermal conductivity method for precise determination of heavy isotope of hydrogen. H. SACHSSE and K. BRATZLER (Z. physikal. Chem., 1934, 171, 331—340; cf. A., 1934, 608).—A method permitting determination of the H^2 content of H_2 with a precision of 0.02% and requiring 0.5 c.c. of gas at 760 mm. is described. The apparatus is calibrated with mixtures of H_2 and Ne. R. C.

Adipic acid as a volumetric standard. A. H. MEYLING (J.S. African Chem. Inst., 1935, 18, 23).—Adipic acid is advocated as an acidimetric standard substance. J. S. A.

Indicator transformations of malachite-green in strongly alkaline solutions. V. N. SKVORTZOV (J. Gen. Chem. Russ., 1934, 4, 1130—1137).—Malachite-green can be used as an indicator in the titration of ZnSO_4 by KOH; the results are increasingly divergent from theoretical with increasing $[\text{ZnSO}_4]$. At low temp. and $[\text{ZnSO}_4]$ the end-point corresponds with K_2ZnO_2 formation. R. T.

Combined indicators. S. HAHNEL and B. HOLMBERG (Svensk Kem. Tidskr., 1935, 47, 4—11).—A mixture of two indicators or an indicator and a dye often gives a sharper end-point than a single indicator. The following combinations were found specially suitable. For H_2O titration: Me₂-yellow (I) methylene-blue (II) (5 : 3), p_H 3.8; Me-red + bromocresol-green (1 : 1), p_H 5.4; neutral-red (III) + (II) (5 : 2), p_H 7.1; (III) + tetrabromophenol-blue (IV) (5 : 2), 8.0. For EtOH titration: (I) + (II), 5 : 4.5 (titration of NH_2OH in 30% EtOH); (III) + (IV), 5 : 3 (titration of KOH with HCl in 70% EtOH); phenol-red + bromothymolbenzein, 3 : 2 (determin-

ation of acids and esters in spirits, 70% EtOH); cresol-red + thymolbenzein, 3 : 1 (titration of KOH with K H phthalate in 70% EtOH). R. P. B.

Preparation of diphenylbenzidine and its use as an oxidation-reduction indicator. L. A. SARVER and J. H. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 329—330).—The method of prep. described gives a 60—65% yield. The indicator is prepared by mixing one drop of a 0.1% solution in H_2SO_4 with 10 c.c. of a 1 : 1 mixture of AcOH and H_3PO_4 . E. S. H.

Water analysis. H. F. KUISEL (Helv. Chim. Acta, 1935, 18, 178—200).—Methods of analysis used in other fields of work, particularly in biochemistry, have been adapted to the examination of H_2O from the Lake of Zürich. Detailed descriptions are given for the determination of total N, NH_3 , NH_2 -acids, and NO_3^- . F. L. U.

Oxidisability in the analysis of mineral waters. V. GAZZI (Annali Chim. Appl., 1934, 24, 613—614).—In the determination of org. matter in mineral waters containing Cl' by oxidation with KMnO_4 erroneous results are obtained if the oxidation is effected in acid solution. O. J. W.

Identification of homœopathic triturations. E. STEINHAUSEN (Apoth.-Ztg., 1934, 49, 791—792; Chem. Zentr., 1934, ii, 2563).—A method of carrying out tests for certain common anions and cations on microscope slides is described. H. J. E.

Rapid determination of traces of active chlorine in water.—See B., 1935, 208.

Determination of available chlorine in hypochlorite solutions by direct titration with sodium thiosulphate.—See B., 1935, 225.

Detection of bromide and its application to the systematic analysis of mixtures of thiocyanate, iodide, bromide, and chloride. L. J. CURTMAN and H. SCHNEIDERMAN (Rec. trav. chim., 1935, 54, 158—161).—< 0.5 mg. of Br' may be detected after removing CNS' by adding 3 c.c. of conc. HNO_3 to 3 c.c. of the solution, immersing in boiling H_2O for 2 min., cooling, and shaking with 1 c.c. of CCl_4 , when yellow or brown in the CCl_4 indicates Br'. A systematic analysis (modification of Curtman's procedure) is described for CNS', I', Br', and Cl'. The low sensitivity of the Br' test in systematic analysis is due largely to the incomplete removal of Br from insol. bromides by Na_2CO_3 . R. S. B.

Analysis of very dilute ozone. E. BRINER and H. PAILLARD (Helv. Chim. Acta, 1935, 18, 234—237).—The determination of O_3 in dil. mixtures by means of KI is not vitiated by catalytic oxidation by O_3 . F. L. U.

[Detection of sulphurous acid and its salts and of tin.] F. FEIGL and H. LEITMEIER (Ber., 1935, 68, [B], 354—356).—In reply to Freytag (A., 1934, 1321) the advantages of blue litmus-silk over the irradiated 2-benzylpyridine reagent are maintained.

Volumetric determination of sulphates. G. A. AMPT (J. Proc. Austral. Chem. Inst., 1935, 2, 10—21).—A review of methods:

Determination of $\text{SO}_4^{''}$ in soluble fluorides.

A. A. BORKOVSKI and N. A. PORFIRIEV (Zavod. Lab., 1934, 3, 1089—1090).—1 g. of crude NaF is dissolved in 100 ml. of H_2O , the solution filtered, the filtrate diluted to 200 ml., 3 ml. of conc. HCl and 3 g. of H_3BO_3 are added, and $\text{SO}_4^{''}$ is pptd. and determined as BaSO_4 . Na_2SiF_6 is converted into NaF by heating at 600—650°, and $\text{SO}_4^{''}$ is determined as above. R. T.

Chemical differentiation of related sulphosalts in a polished surface by the contact method.

G. GUTZEIT and F. GALOPIN (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 53—61; cf. A., 1933, 1132).—The contact method has been applied to Fe, Co, and Ni minerals containing S. Details of the procedure in examining the specimens for Ni, Co, Fe, S, As, Sb, and Cu are given. F. L. U.

Colorimetric determination of ammonia in small quantities of substance. II.

F. ALTEN and E. HILLE (Angew. Chem., 1935, 48, 137—139).—20—50 mg. of substance are mixed with a small crystal of K_2SO_4 and 3 c.c. of conc. H_2SO_4 , and 1.5—2 c.c. of H_2O_2 are added dropwise; after heating over a small flame for 35—40 min. the brown colour disappears. The cooled liquid is diluted to 50 c.c. with H_2O , and to 2—5 c.c., 1 c.c. of thymolphthalein solution (saturated in 0.01N-NaOH) is added and the solution neutralised with 0.5N-NaOH. 20 c.c. of borate buffer of p_H 10.5 and 10 c.c. of 1% gum arabic solution are added, and after shaking the solution is diluted almost to 100 c.c. with H_2O . 2 c.c. of Nessler's reagent are added, the solution is made up to 100 c.c. and shaken, and after 0.5 hr. can be examined colorimetrically. Results agree with Kjeldahl's method. R. S. B.

Detection of nitrites with Magdala-red and detection of benzene by formation of resorufin.

H. EICHLER (Z. anal. Chem., 1935, 100, 183—184).—Magdala-red dissolved in conc. AcOH or HCO_2H (cf. A., 1934, 269) shows a fluorescence extinguished by solid or dissolved NO_2 at room temp. The formation of a blue colour may be applied to a spot test on filter-paper. C_6H_6 may be converted into PhNO_2 and thus detected as resorufin (A., 1934, 286). J. S. A.

Detection of nitrites and nitrates.—See B., 1935, 225.**Determination of calcium dihydrogen phosphate by means of carbamide.**

C. W. WHITTAKER, F. O. LUNDSTROM, and W. L. HILL (J. Assoc. Off. Agric. Chem., 1935, 18, 122—127).—The sample containing $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (I) and $\text{CaH}_4\text{P}_2\text{O}_7$ (II) is shaken w. aq. $\text{CO}(\text{NH}_2)_2$, filtered, and an aliquot part of the filtrate is treated with EtOH to ppt. (II). The P_2O_5 in EtOH [= (I) originally present] is determined. Examples of the application of the method to commercial superphosphates (III) and double (III) are given. E. C. S.

Potentiometric determination of arsenates.

C. SPACU (Z. anal. Chem., 1935, 100, 187—190).— $\text{AsO}_4^{''}$ is titrated against $\text{Hg}_2(\text{NO}_3)_2$ (in 24% aq. EtOH solution), using an amalgamated Pt indicator electrode. J. S. A.

Determination of krypton and xenon content of atmospheric air.

G. DAMKÖHLER (Z. Elektrochem., 1935, 41, 74—80).—Two different methods

were tested using (a) atm. air, and (b) O_2 from an air fractionation apparatus, of known enrichment of inert gases. Gases (a) and (b) were analysed by fractionation from charcoal and by chemical purification, and both gave the same result, 1.08 ± 0.10 p.p.m. of Kr and 0.08 ± 0.03 p.p.m. of Xe by vol. (mean), in good agreement with Moureu and Lepape (cf. A., 1926, 933). R. S. B.

Electrolytic attack of opaque minerals and its application to the technique of "prints" of polished surfaces. P. WENGER, G. GUTZEIT, and T. HILLER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 64—67; see above).—The method is described and examples of its use are given. F. L. U.

Determination of potassium in catalysts for ammonia synthesis.—See B., 1935, 225.

Spectrographic detection of caesium, rubidium, and potassium, especially in mineral waters. Spectrographic analysis in the near infra-red. V. GAZZI (Annali Chim. Appl., 1934, 24, 595—612).—The flame, arc, and spark spectra of the three elements have been examined in the near infra-red. The lines 8521 (Cs), 7947 and 7800 (Rb), 7699 and 7695 Å. (K) are very suitable for the spectrographic detection of these elements. O. J. W.

Determination of zinc. B. P. ZELENETZKI (Zavod. Lab., 1934, 3, 1081—1085).—The solution (free from Fe, Ni, and Mn) is made alkaline with aq. NH_3 , acidified with AcOH, and H_2S is passed through the boiling solution to complete pptn. of ZnS; excess of H_2S is removed, aq. AgNO_3 added, and the ppt. of Ag_2S collected and weighed. Alternatively, standard aq. I is added to the suspension of ZnS, and excess of I titrated with standard aq. $\text{Na}_2\text{S}_2\text{O}_3$. R. T.

Elements detectable by arc spectrum analysis in lead minerals. S. PIÑA DE RUBIES and J. DOETSCH (Z. anorg. Chem., 1935, 222, 107—112).—By a method previously described (A., 1934, 58) a qual., and in some cases a quant., analysis of a large no. of Pb minerals has been made. M. S. B.

Quantitative spectrum analysis of elements.

Tin-lead mixtures. H. SCHUBERT and K. CRUSE (Z. physikal. Chem., 1935, 172, 143—155).—Experiments with Sn-Pb alloys have shown that the line intensity is not \propto the Pb concn. The spectrum obtained from a given alloy under given conditions of excitation may vary considerably with the mode of prep. of the electrodes. A method of determining the properties of photographic plates is described. Sn, almost free from Pb, may be obtained by electrolyzing $\text{SnCl}_4 \cdot 2\text{EtCN}$. R. C.

Iodometric determination of thallic salts by

potentiometric and visual titration. F. ČUTA (Coll. Czech. Chem. Comm., 1935, 7, 33—43; cf. A., 1934, 1323).—Titrations of I liberated from solutions containing 0.017—0.44 g. TI per litre are 0.08% low using $\text{Na}_2\text{S}_2\text{O}_3$, and 0.24% low using Na_3AsO_3 . The results of potentiometric and visual methods are identical. R. S.

Argentometric determination of copper.

R. BIAZZO and B. TANTERI (Annali Chim. Appl., 1935, 25, 44—45).—The Cu is reduced, in solution containing

NH_3 , to Cu^{I} by $\text{NH}_2\text{OH}\cdot\text{HCl}$, excess of which is converted into acetoxime. The Cu_2O is then oxidised to CuO by $\text{NH}_3\text{-AgNO}_3$, the Ag thus pptd. being dissolved in HNO_3 and titrated by Volhard's method.

T. H. P.

Determination of small amounts of mercury. S. I. SINJAKOVA (Z. anal. Chem., 1935, 100, 190—193, and J. Gen. Chem. Russ., 1934, 4, 1081—1087).— $2\text{--}10 \times 10^{-6}$ g. of Hg is determined nephelometrically by adding $\text{KI} + \text{strychnine sulphate (I)}$ (cf. A., 1932, 923). Excess of KI interferes, causing rapid coagulation. Hg is absorbed from air by bubbling through aq.-alcoholic 1% $\text{I} + 0.01$ g. of KI . The solution is evaporated at $60\text{--}70^\circ$, 0.1 c.c. of saturated (I) added, and the vol. made up to 2 c.c. J. S. A.

Colorimetric determination of cerium and titanium by means of gallic acid. F. M. SCHEMJAKIN (Zavod. Lab., 1934, 3, 1090—1091).—2.7 c.c. of 0.001*M*-gallic acid, sufficient solution to give a final concn. of $3\text{--}7 \times 10^{-5}$ g. Ce per c.c., 2 c.c. of Et_2O or PhMe , and 5.3 c.c. of 0.1*N*- NH_3 (containing 1 g. of cryst. Na_2SO_4 per 100 c.c.) are mixed in a stoppered vessel, the aq. layer is diluted to 10 c.c., and the coloration obtained compared with that given by standard aq. Ce solution. R. T.

Colorimetric determination of aluminium by the aid of alizarin. S. A. P. MUSAKIN (Zavod. Lab., 1934, 3, 1085—1088).—5 c.c. of saturated aq. NaCl and 5 c.c. of 0.05% alizarin *S* are added to the neutral or feebly acid solution (containing 0.005—0.05 mg. of Al_2O_3), 5*N*- NH_3 is added to change of colour, and the solution is diluted to 50 c.c. Standard Al solution (0.5 mg.-% of Al_2O_3) is added to a second solution containing the same reagents as the first, to the attainment of an approx. identical coloration, when H_2O is added to 50 c.c., an identical excess of AcOH is added to both solutions, and the intensity of coloration compared. R. T.

Occurrence and determination of manganese in sea-water. T. G. THOMPSON and T. L. WILSON (J. Amer. Chem. Soc., 1935, 57, 233—236).—A modification of the method of Willard and Greathouse (A., 1918, ii, 84) is sufficiently sensitive to detect variations of 0.18×10^{-4} mg.-atom of Mn. The Mn content of sea- H_2O is 0.2×10^{-4} — 1.8×10^{-4} mg.-atom per kg. Dried muds from the sea bottom contained 0.05—0.30% of Mn. The ash of plankton contains about 0.07% of Mn, whilst H_2O rich in plankton contains less dissolved Mn. E. S. H.

Analytical chemistry of rhenium. XI. Volumetric determination of rhenium compounds. W. GEILMANN and F. W. WRIGGE (Z. anorg. Chem., 1935, 222, 56—64).—In acid solution the valency of Re oxides may be determined by oxidation with $\text{Fe}_2(\text{SO}_4)_3$, $\text{K}_2\text{Cr}_2\text{O}_7$, or $\text{Ce}(\text{SO}_4)_2$, after gentle warming. ReCl_3 requires to be boiled for a short time, but K_2ReCl_6 can be quantitatively oxidised by long boiling with $\text{Ce}(\text{SO}_4)_2$ only. KMnO_4 can be used for titrating ReCl_3 under certain definite conditions. In alkaline solution ReCl_3 and K_2ReCl_6 can be completely oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$. KMnO_4 is suitable for ReCl_3 but not for K_2ReCl_6 . Under certain conditions

$\text{Fe}_2(\text{SO}_4)_3$ may be used indirectly for the titration of alkaline solution, but it is not very satisfactory.

M. S. B.

Permanganate micro-titration of iron. J. KNOP and O. KUBELKOVA (Z. anal. Chem., 1935, 100, 161—183).—1 mg. of Fe may be accurately titrated with 0.005*N*- KMnO_4 , using Cyanin B or Erioglaucin A as indicator, in presence of a large excess of Ni or Co. Using boiled-out solutions, titration in a CO_2 atm. is unnecessary. $\text{K}_4\text{Fe}(\text{CN})_6$ is suitable for standardising 0.005*N*- KMnO_4 , but must be titrated in diffused light to prevent photodecomp. Fe^{III} may be reduced with SnCl_2 (0.8% solution in HCl), subsequently adding HgCl_2 , or, better, with electrolytic Cd in a micro-reductor (I), reduction being quant. in 30 sec. Reduction with Zn in (I) is slow and liable to variable error. J. S. A.

Determination of thorium with 8-hydroxyquinoline. F. HECHT and W. EHLMANN (Z. anal. Chem., 1935, 100, 98—103).— $\text{Th}(\text{NO}_3)_4$ solution, free from other metals pptd. by 8-hydroxyquinoline (I), is exactly neutralised, and AcOH added to give a final concn. of 2—3%. Excess of (I) is added to the boiling solution, and the AcOH then buffered by addition of NH_4OAc . The ppt., of composition $\text{Th}(\text{C}_9\text{H}_6\text{ON})_4\cdot\text{C}_9\text{H}_7\text{ON}$ (cf. A., 1934, 82), is dried at room temp. The fifth mol. of (I) is lost by heating at $160\text{--}170^\circ$, or by extracting with warm 95% EtOH . J. S. A.

Determination of thorium with picrolonic acid. F. HECHT and W. EHLMANN (Z. anal. Chem., 1935, 100, 87—98).—Excess of saturated picrolonic acid solution is added slowly to a boiling conc. solution of $\text{Th}(\text{NO}_3)_4$, free from mineral acid or NH_4 salts, but containing enough AcOH to give a final concn. of 2—3%. $\text{Th}(\text{C}_{10}\text{H}_7\text{O}_5\text{N}_4)_4\cdot\text{H}_2\text{O}$ is pptd., and is collected after cooling to 0° . The ppt. is washed with the min. amount of cold H_2O , and dried at room temp. The method is applicable to macro- and micro-determinations. J. S. A.

Compounds of vanadium with 8-hydroxyquinoline, and their analytical applications. R. MONTEQUI and M. GALLEGÓ (Anal. Fis. Quím., 1934, 32, 134—145).—Vanadate solutions, in presence of 6% AcOH , give with 8-hydroxyquinoline a bluish-black ppt. (I) or coloration, extracted by CHCl_3 to a red solution: limiting concn. 1:670,000. (I) has the composition $(\text{C}_9\text{H}_6\text{ON})_4\text{V}_2\text{O}_5$, being the anhydride of an acid $(\text{C}_9\text{H}_6\text{ON})_2\text{VO}_3\text{H}$ (not isolated), of which the Na (+7 H_2O), K (+4 H_2O), and NH_4 salts were prepared. (I) may be used for the gravimetric determination of V. J. S. A.

Specific reaction for antimony cations. G. GUTZEIT, R. WEIBEL, and R. DUCKERT (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 62—64).—A preliminary account of a reagent, of composition a present unknown, obtained during the hydrolysis of 1:2:4- $\text{C}_6\text{H}_3(\text{OAc})_3$, which gives a red coloration or ppt. with Sb^{III} . 4×10^{-6} g. of Sb can be detected in presence of a large excess of As or Sn. F. L. U.

Electro-titration of platinum and iridium. A. A. GRINBERG and B. B. PRITSIN (Ann. Inst. Platine, 1935, 12, 133—158).— Pt^{II} and Ir^{III} are determined

by electro-titration with KMnO_4 , Pt^{IV} by reduction to Pt^{II} , followed by KMnO_4 titration, Ir^{IV} by reduction with Mohr's salt (I) to Ir^{III} , and KMnO_4 titration, Ir^{IV} in presence of Pt^{IV} by titration with (I), and Ir in presence of Rh by direct KMnO_4 titration.

R. T.

Thermometers and apparatus for the determination of the points of fusion and decomposition of organic substances. R. E. STEIGER (Bull. Soc. chim., 1935, [v], 2, 284—290).—An apparatus for m.-p. measurements and sets of thermometers which avoid the necessity for exposed stem correction are described.

M. S. B.

Small vacuum metal vapour furnace. G. D. ROBINSON (Proc. Leeds Phil. Soc., 1935, 3, 12—17).—A Pyrex furnace is described. The distribution of Zn vapour near an aperture, examined with a sooted Cu target, agrees with Knudsen's cosine law.

F. L. U.

Micro-furnace and a micro-press for tablets. S. SECAREANU (Bull. Soc. chim., 1935, [v], 2, 79—80).—An externally heated two-piece bronze micro-furnace for the range 50—300° and holding ≥ 0.5 g. of substance is described. The micro-press is a glass tube of 1.5 mm. internal diameter with a well-fitting metal plunger which is pressed against a plane surface.

J. G. A. G.

Air-bath. N. M. SHAH (J. Chem. Educ., 1935, 12, 16).—An inverted truncated galvanised Fe sheet cone approx. 6.5 in. high with serrated upper and lower edges is placed in a tripod and heated by a small flame. The air-bath can be used for quant. work.

L. S. T.

Constant-temperature bath employing thermionic control. G. W. THIESSEN and L. J. FROST (J. Chem. Educ., 1935, 12, 72—73).

L. S. T.

Sodium line-reversal method of determining flame temperatures. B. LEWIS and G. VON ELBE (Engineering, 1935, 139, 168).—A criticism (cf. David, A., 1934, 1073).

C. W. G.

Sodium line-reversal method of determining flame temperatures. W. T. DAVID (Engineering, 1935, 139, 195).—A reply (cf. preceding abstract).

C. W. G.

Filling high-temperature mercury thermometers with a condensed gas. H. MOSER (Phys. Z., 1935, 36, 153—157).—The thermometer is filled with A at the b.p. of liquid air, a sufficient quantity being condensed to give the necessary pressure when the temp. is raised.

A. J. M.

Source of error in determining heats of combustion of organic substances by means of the bomb calorimeter. III. L. J. P. KEFFLER (J. Chem. phys., 1935, 32, 91—100; cf. A., 1934, 860).—The apparent val. of the H_2O equiv., q , of the calorimetric bomb was depressed by approx. the calc. amount by 0.1% of H_2 in the O_2 , but q passed through max. as the pressure of gas in the supply cylinder decreased. The differences between the results of duplicate experiments were $>$ with pure O_2 . The interpretation of these and earlier results and the errors introduced by combustible impurities in bomb calorimetry are discussed.

J. G. A. G.

Electrically-heated germinator with sterilisable plates, thermo-regulator for temperatures of 10—50°, and continuous constant water-flow. F. LORENZOLA (Annali Chim. Appl., 1935, 25, 42—43).

T. H. P.

Adiabatic cooling of magnetic substances. W. J. DE HAAS and E. C. WIERSMA (Physica, 1935, 2, 81—86; cf. A., 1934, 1062).—With initial and final fields of 24,075 and 5.5 gauss, respectively, a final temp. of 0.0159° abs. was attained.

H. J. E.

Improved differential ebullioscope. E. PLAKE (Z. physikal. Chem., 1935, 172, 105—112).—With a modified form of Swientoslawski apparatus (cf. A., 1931, 928) the b.-p. elevation of solutions as dil. as 0.006*M* can be determined with a precision of 0.0001°.

R. C.

Measurement of light absorption. II. Photo-electric spectrophotometer. Systematic errors of photo-electric spectrophotometry. R. FONTEYNE (Natuurwetensch. Tijds., 1935, 17, 10—25).—With the apparatus described, ϵ can be measured to an accuracy of 10^{-4} . Curves for camphorquinone and for $\text{K}_2\text{Cr}_2\text{O}_7$ reduced with varying quantities of glycerol are given.

D. R. D.

A method in microspectrometry and its accuracy. H. NAGAOKA and I. MACHIDA (Proc. Imp. Acad. Tokyo, 1934, 10, 629—631).—Improvements in the spectrographic detection of small amounts of elements are suggested. The accuracy is increased by reducing the amount of liquid lost by sputtering during the discharge and by increasing the amount of emitted light entering the spectrograph slit. The spectrogram is examined microphotometrically.

O. J. W.

Use of photo-electric cells for determining oxides of nitrogen and ozone. C. H. WAKKER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 145—147).—An Fe—Se—Au cell is used with an absorption tube 1 m. long for NO_2 , 2 m. for O_3 .

F. L. U.

Photo-electric apparatus adapted to investigation of light counters. K. H. REISS (Z. Physik, 1935, 93, 411—415).—The apparatus described gives monochromatic light of any desired low intensity, and is used to measure the quantum efficiency of Cd light counters.

A. B. D. C.

Discontinuities in the characteristics of photo-cells. F. M. PENNING and J. MÖUBIS (Physica, 1935, 2, 55—61).—The glass window of a photo-cell emits both photo- and secondary electrons, and therefore acts as a third electrode connected to the cathode through a high resistance. This behaviour leads to the discontinuities observed in the voltage-current characteristics.

J. W. S.

X-Ray investigation of transition processes. Application of Weissenberg X-ray goniometer to registration of transition processes. J. BÖHM and P. FELDMAN (Z. physikal. Chem., 1934, B, 27, 425—430).—The film carrier of an X-ray goniometer is moved along during exposure of the film, thus giving a continuous record of the change in the X-ray diagram during transition. Results obtained for the recrystallisation of Pt-black are

reproduced. The above device may be used in electron diffraction experiments. R. C.

Standardisation of Lovibond red glasses in combination with Lovibond 35 Yellow. K. S. GIBSON and G. W. HAUPT (Oil and Soap, 1934, 11, 246—250, 257—260; cf. A., 1928, 609; 1934, 624).—The Priest-Gibson N'' scale is satisfactory for grading Lovibond red glasses (used in conjunction with a 35 Y glass); the numerals are of approx. the same magnitude as the original Lovibond nos., and are additive within the tolerances regarded as satisfactory for the calibration of glasses intended for grading vegetable oils. The derivation of the N'' scale and units from data for the spectral transmission (T) of the glasses is fully described. The same val. of N'' is obtained whether a glass is graded by computation from T , or directly by comparison with standard glasses. E. L.

Apparatus for X-ray quantitative chemical analysis with the cathode-ray tube. W. P. JESSE (Rev. Sci. Instr., 1935, [ii], 6, 47—50).—A compact oil-immersed apparatus is described. C. W. G.

Simple apparatus for objective fluorescence measurements using a selenium cell. F. H. COHEN (Rec. trav. chim., 1935, 54, 133—138).—Fluorescence (intensity f) in solutions has been studied using a Hg-vapour lamp, a NiO filter, and a Se cell, for incident $\lambda=366\text{ m}\mu$. At p_H 8 for fluorescein (I) $f \propto \text{concn.}$ up to 10^{-5} g. per c.c., with an error of approx. 2%, and f then falls with increasing concn. f for lactoflavin (II) at a concn. 0.97×10^{-5} g. per c.c. is $1.8 \times f_{(I)}$ for the same concn. The decay in $f_{(II)}$ on continued illumination is small. R. S. B.

Light filters for the mercury arc. B. K. VALDYA (J. Univ. Bombay, 1934, 3, No. 2, 141—148).—33 filter systems for the isolation of the Hg lines are described, and approx. measurements of the energy transmitted by 8 of them are recorded. D. R. D.

"Electrodeless" metal vapour lamp for production of resonance radiation. F. FAIRBROTHER and J. L. TUCK (Trans. Faraday Soc., 1935, 31, 520—526).—Two forms of lamp are described, in each of which Na vapour at 10^{-4} — 10^{-5} mm. is excited by an "electrodeless" discharge at a frequency of 10^8 cycles. The D radiation is very intense and very narrow, and is almost completely absorbed by a few cm. of Na vapour of low d . The lamps can be operated at and above 160° , the intensity increasing with rise of temp. until the current becomes large enough to damp the exciting oscillations. F. L. U.

Laboratory apparatus for the electrolytic concentration of H^+ . G. CHAMPETIER (Bull. Soc. chim., 1935, [v], 2, 162—167).—Three types of apparatus for the successive stages of the process are described. J. G. A. G.

Continuous-reading titration apparatus. L. H. BALDINGER (J. Amer. Pharm. Assoc., 1935, 24, 6—9).—A simple apparatus is suggested for accurate continuous-reading electrometric titrations using graphite-Pt, W-Pt, and SiC-Pt electrodes with a vac. tube titration apparatus. The apparatus is tested and applied in the titration of certain Fe^{II} compounds. H. T.

High-intensity discharge tube. D. S. STEVENS (Rev. Sci. Instr., 1935, [ii], 6, 40—42).—A small constriction is placed in a d.-c. arc operating in the rare gases, O_2 , N_2 , or H_2 , 5—10 amp. at 1500—2000 volts are required. C. W. G.

Rule to demonstrate the migration of ions. A. S. FEDOROW (J. Chem. Educ., 1935, 12, 93—94).—A wooden slide-rule device is used. L. S. T.

Counter of the Wynn-Williams type. S. KIKUCHI and H. AOKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 36—41).—A diagram of the instrument is given. Oscillograph deflexions produced by γ -rays are due to the accidental coincidence of many electrons. R. S.

Greinacher hydraulic counter for quanta and ionising particles. R. D. SUMMERS (Rev. Sci. Instr., 1935, [ii], 6, 39—40; cf. Helv. Phys. Acta, 1934, 7, 360, 514).—The frequency range is extended by the use of an auxiliary ionisation gap. C. W. G.

New method for counting atmospheric ions and determining their mobilities. J. J. NOLAN and P. J. NOLAN (Proc. Roy. Irish Acad., 1935, 42, A., 15—19).—Ions are collected on an inner charged electrode (I), the observing apparatus is maintained at the same potential (20 volts), and the change in the (I) potential determined with a sensitive electrometer. This can be used as a null instrument by applying a compensating potential to the outer cylinder of the ion counter. The measured distribution of mobilities of atm. ions is independent of their concn. R. S.

Determination of the dielectric constant of conducting solutions. W. M. MAZEE (Physikal. Z., 1935, 36, 177—180).—The principle of the method is the determination of the max. resonance in a circuit including a cell containing the solution. A. J. M.

Cleaning of glass vessels. P. I. ZABELLO (Zavod. Lab., 1934, 3, 1132).—Burettes and pipettes are cleaned by $EtOH-HNO_3$ mixture. R. T.

Micro-burette. N. G. HEATLEY (Biochem. J., 1935, 29, 626—630).—The titrating fluid is contained in a bottle fitted with a delivery tube and one connecting the bottle to the burette. Liquid paraffin is displaced from the burette to the bottle, from which an equal vol. of titrating fluid is delivered. H. D.

Reading device for burettes. W. P. WHITE (J. Amer. Chem. Soc., 1935, 57, 332). E. S. H.

Apparatus for determining carbon dioxide in the air. M. L. JEAN (Bull. Soc. chim., 1935, [v], 2, 283—284).—An apparatus with an efficient absorbing pipette, which avoids the risk of trapping gas in capillary spaces, is described. M. S. B.

Apparatus for determining very small osmotic pressures in colloidal solutions. (MME.) A. DOBRY (J. Chim. phys., 1935, 32, 46—49).—The solution is in a collodion bladder (I) connected with a manometer (II) and surrounded by solvent in a glass vessel fitted with a manometer and a compensating tube which eliminates the effects of thermal expansion. In a second apparatus, which must be thermostated, the (I) with (II) is immersed in the pure solvent so that the difference between the levels of the liquid

represents the osmotic pressure (III). Evaporation losses are prevented and vols. of (III) equiv. to 1—5 mm. of H_2O are determined. J. G. A. G.

Thermal conductivity apparatus for continuous determination of the helium content of natural gas.—See B., 1935, 186.

High-speed oil diffusion pump. R. M. ZABEL (Rev. Sci. Instr., 1935, [ii], 6, 54—55).—Apiezon oil is boiled, and the vapour passes through a 4- or 7-nozzle jet. A fore vac. of 0.02 mm. is required. C. W. G.

Safety apparatus for water pump. G. MIN-GASSON and H. DELARUE (Bull. Soc. chim., 1935, [v], 2, 281—282).—Either a modification of the Bunsen valve, or a float which closes the connexion between the pump and vessel to be evacuated, may be used. In either case there is no loss of vac. M. S. B.

Condensation-fractionation flask. J. ERDOS (J. pr. Chem., 1935, [ii], 142, 145—148).—There are described (a) a simple glass apparatus for effecting condensations involving loss of H_2O and (b) a more complicated apparatus for effecting also subsequent fractionation of the product. By (b) are obtained a 95% yield of glycerylphosphoric acid in 2—2.5 hr., 85% of NH_4 cinnamate from $PhCHO$, $CH_2(CO_2H)_2$, $EtOH$, and NH_3 , and 150 g. of $Et_2C_2O_4$ and 40 g. of HCO_2Et from 150 g. of anhyd. $H_2C_2O_4$ in 3—3.5 hr. R. S. C.

Gear pump and hose as a collector of water samples for gas analysis. R. P. COWLES and C. BRAMBEL (Science, 1935, 81, 48—50).—An apparatus for the collection of H_2O samples from a depth of 25 m. or more without loss of gas is described. L. S. T.

Use of the centrifuge in determining the density of small crystals. J. D. BERNAL and D. CROWFOOT (Nature, 1935, 135, 305; cf. this vol., 21).—Priority is acknowledged. L. S. T.

Dynamic method for investigation of surfaces of powders. (Motion of loose powders in revolving bulbs.) G. SCHMIDT (Z. physikal. Chem., 1934, 171, 289—319).—A sample of the powder is contained in a bulb which is rotated about a horizontal axis by means of a string coiled about the axis and at its other end carrying a weight. The least wt., required to produce such rotation as causes the powder to form a ring around the periphery of the bulb is determined. This method has been used with CuO , ZnO , Cr_2O_3 , V_2O_5 , and mixtures of these in contact with various gases. In general, W increases with falling gas pressure, p , temp., and H_2O content of powder. At room temp. and under ~1 atm. of gas with a small viscosity, η , give a $W >$ those of larger η . Deviations from the above general behaviour, especially in respect of the variation of W with temp., indicate chemisorption (I), and occur with O_2 in contact with O_2 , with ZnO in absence of O_2 , and with CuO and V_2O_5 . (I) is always associated with high electrical conductivity. The greater is the adsorption, the less does W vary with change in p . R. C.

Cellophane and Cuprophane as membranes for analysis and electrodialysis. H. BRINTZINGER and H. OSSWALD (Kolloid-Z., 1935, 70, 198—200).—The advantages of Cuprophane are demonstrated.

Membranes 10 thick are mechanically strong and more permeable than Cellophane or parchment.

E. S. H.

New type of manometer. M. V. IONESCU (Bull. Soc. chim., 1935, [v], 2, 125—126).—A compact ensemble of manometer and pressure vessel for vac. distillations is described. J. G. A. G.

Devices for ensuring constancy in the masses of precision weights. J. J. MANLEY (Phil. Mag., 1935, [vii], 19, 243—251).—The most satisfactory method is to use a box which also contains highly absorptive charcoal. C. W. G.

Improved heated vacuum micro-desiccator. E. W. BLANK (J. Chem. Educ., 1935, 12, 43).

L. S. T.

Hydrogen sulphide apparatus. R. MONTEQUI (Anal. Fis. Quím., 1934, 32, 146—148).—A simple form is described. J. S. A.

Apparatus for pressure measurements of spreading substances. E. GORTER and W. A. SEEDER (J. Gen. Physiol., 1935, 18, 427—431).—The apparatus described depends on torsion compensation (sensitive to 0.1 dyne per cm. per 1° of scale) of the movement of a floating barrier due to changes in σ . F. O. H.

New method of counting dust nuclei in air. G. R. PARANJPE and Y. G. NAIK (J. Univ. Bombay, 1934, 3, No. 2, 58—66).—The air is expanded (ratio < 1.3) in a 10-litre flask, and the no. of drops calc. from the diameter of the diffraction ring from a monochromatic parallel beam. Errors due to nuclei escaping pptn., fusion of drops, and condensation without nuclei are shown to be absent. D. R. D.

Measurement of the moment of a couple by chronometric motor. Application to viscosity. A. GUILLET (Compt. rend., 1935, 200, 442—445).—Application of the principle of uniform angular velocity to a solid suspended in a liquid is discussed. N. M. B.

Liquid-type micro-cathetometer. F. TESSON (Compt. rend., 1935, 200, 439—441).—An apparatus, sensitive to 1μ , for measuring vertical movements of particles and thin films consists of a trough of H_2O regulated by a micro-burette and containing a horizontal oil film for which the capillary action with a point is observed. N. M. B.

Ring method for measuring surface tension. L. DU NOUY (Nature, 1935, 135, 397).—A discussion of the merits of the method. L. S. T.

Still for concentration under reduced pressure. C. J. O. R. MORRIS (Biochem. J., 1935, 29, 567—568).—A still devoid of metal parts, capable of dealing with 1.5—2 litres of aq. extract per hr. at 56° and 12 mm., is described. Difficulties due to frothing are overcome by means of a modified air-leak. W. O. K.

Sintered glass plates. V. T. IVANOV and I. A. IVANOV (Zavod. Lab., 1934, 3, 1133).—Directions for the prep. of sintered glass filter plates are given. R. T.

Lecture demonstration of the law of combining volumes. T. H. JAMES (J. Chem. Educ., 1935, 12, 87).

L. S. T.

Geochemistry.

Krypton content of air. I. BRODY and F. KOROSY (Trans. Faraday Soc., 1935, **31**, 547—556).—By comparing the relative intensities of suitable spectral lines of A and Kr in a mixture obtained chemically from the atm. with those given by mixtures of A and Kr of known composition, the proportion by vol. of Kr in air has been found to be $1.44 \pm 0.16 \times 10^{-6}$. The essential feature of the method used is the avoidance of any attempt to concentrate the Kr by physical means whereby loss might occur.

F. L. U.

Radioactivity of mountain air. H. GARRIGUE (Compt. rend., 1935, **200**, 414—415; cf. A., 1934, 386).—The Rn content of the air enclosed under the snow in the neighbourhood of the Pic-du-Midi varies with the direction of the wind. The Rn formed in the interior of the earth is shut in by the snowing up of the slopes and is liberated abundantly near the Pic when the wind is N.W.—N.E.

J. W. S.

Haber's investigations on the occurrence of gold in sea-water. J. JAENICKE (Naturwiss., 1935, **23**, 57—63).—A review of the methods used by Haber and his collaborators for the determination of Au in sea- H_2O .

A. J. M.

Mineral water of Oceslavci. S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1934, **5**, 63—71).—Analytical data are given.

R. T.

Mineral waters of Abbarghente (Romana-Sassari). A. SERRA (Annali Chim. Appl., 1934, **24**, 631—638).—Physico-chemical and analytical data are given, and compared with those of waters from Ischia, Sardara, and Célestius.

O. J. W.

Thermal water from Val Calaona (Padua). G. BRAGAGNOLO (Annali Chim. Appl., 1934, **24**, 628—630).—Physico-chemical and analytical data are given.

O. J. W.

Water from Asolo (Treviso). G. BRAGAGNOLO (Annali Chim. Appl., 1934, **24**, 626—628).—Physico-chemical and analytical data are given.

O. J. W.

Rainerian water. G. BRAGAGNOLO and B. LONGO (Annali Chim. Appl., 1935, **25**, 46—48).—This H_2O , from a spring at Battaglia, near Abano, contains H_2S and is used medicinally.

T. H. P.

Water of the Motticella Baths (Calabria). B. RICCA and P. MEDURI (Annali Chim. Appl., 1935, **25**, 18—38).—Chemical analysis and physical examination have been made. Solids, 4.8 g. (at 110°) per 100 c.c., are mainly $NaCl$, Na_2SO_4 , and $NaHCO_3$; CO_2 , H_2S , and N occur in solution. The H_2O exerts curative effects in cases of skin disease.

T. H. P.

Particulate and dissolved organic matter in inland lakes. E. A. BIRGE and C. JUDAY (Ecol. Monog., 1934, **4**, 440—474).—The protein, carbohydrate, and Et_2O extract of the centrifuge plankton and of dissolved org. matter is determined in lake waters.

CH. ABS. (p)

Transfer of silica by water vapour. F. V. SYROMYATNIKOV (Econ. Geol., 1935, **30**, 89—92).— SiO_2 and Fe_2O_3 are transferred by superheated H_2O

vapour. The reaction of serpentine formation may proceed by pneumatolysis.

L. S. T.

Geyser basins and igneous emanations. E. T. ALLEN (Econ. Geol., 1935, **30**, 1—13).—The character of the magmatic emanations in the Yellowstone Park geyser basins and their function in hot-spring development are discussed.

L. S. T.

Gwalior trap from Gwalior, India. M. P. BAJPAI (J. Geol., 1935, **43**, 61—75).—The analyses given agree with Washington's average for the Deccan trap except for the fact that the latter is somewhat poorer in alkalis. The ratios $MgO : FeO$ in the ferromagnesian minerals indicate that the pyroxene is richer in MgO than the corresponding rock, supporting the view that crystallisation enriches the Fe content of the magma. The He ratios for the rock give a min. age of 5×10^8 years.

L. S. T.

Stromboli magnetites and determination of Ti_2O_3 therein. F. SCAFILE (Annali Chim. Appl., 1935, **25**, 11—18).—The magnetite of Stromboli sand differs from those of Etna mainly in its low content of Ti and FeO. Many Etna magnetites contain Mn = about 0.5% Mn_3O_4 . In presence of FeO and Fe_2O_3 , Ti_2O_3 may be determined by titrating rapidly with $KMnO_4$ to obtain the FeO end-point, subsequent reduction of $KMnO_4$ then giving another end-point corresponding with the Ti_2O_3 ; the latter reacts only after all the FeO has been oxidised.

T. H. P.

Induced remanent magnetism of eruptive rocks. G. JOURAVSKY, P. CHERCZENKO, and G. CHOUBERT (Compt. rend., 1935, **200**, 541—543).—Ilmenite (from the Antilles), biotite (from Tchabaroul), and allanite (from Arendal) show no induced magnetism. Epidote (from Oisans) and augite (from Puy de la Rodde) show a slight and monzonite and pyroxenolite (from Monzoni, Tyrol) a larger induced magnetism. This is partly, but not entirely, due to the presence of magnetite, as the effect is not eliminated entirely by removal of the portions of the mineral attracted by a magnet or by treatment with hot 20% H_2SO_4 .

J. W. S.

Water content and dehydration of sepiolites. G. MIGEON (Compt. rend., 1935, **200**, 471—474).—Data for the variation with temp. of the H_2O content of 7 natural sepiolites indicate the composition $3SiO_2, 2MgO, 1.5H_2O$ and $4SiO_2, 3MgO, 2H_2O$.

B

Fluorescence of Japanese hyalite in ultra-violet light. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, **26**, 42—44).—Hyalite found in districts bearing radioactive minerals is fluorescent, owing to the adsorption of traces of uranyl salts.

S

Rare earths of certain minerals of Madagascar. A. KARL (Ann. Chim., 1935, [xi], **3**, 73—129).—Methods are described for the analysis of monazite, euxenite, and betafite, in which the rare earths (1) are separated quantitatively by fractional crystallisation. The composition relationships are discussed. Physical methods have been developed with which o

follow the course of the separation. Reflexion spectra of a series of (I) salts are described, together with a process for the intensification of the photographs. The bands are characteristically displaced by the anion of the salt examined. Two tubes have been constructed for the study of cathodic phosphorescence (a) of a no. of specimens in rapid succession and (b) in the visible and ultra-violet. The operation and the sensitivity of the Curie-Chèneveau magnetic balance have been improved. R. S.

Stilpnochlorane from Gobitschau, Moravia. J. HOLZNER (Centr. Min. Geol., 1934, A, 250—256).—Stilpnochlorane differs from stilpnomelane in having a higher Ca and H₂O content and in containing only Fe^{III}. On treatment with Clerici solution most of the Ca and approx. half the (Na,K)₂ is replaced by Th₂, and most of the H₂O is driven from the mol.

CH. ABS. (e)

Thorium content of pitchblendes from Great Bear Lake, N.W.T., Canada. A. MERKEL (Centr. Min. Geol., 1934, A, 312—315).—The pitchblende contained < 0.01% Th, and hence the Pb²⁰⁸ content was < 0.00046%. The total Pb was 10.9—15.8%.

CH. ABS. (e)

Dehydration of natural and of artificial lepidocrocite. A. GIRARD and G. CHAUDRON (Bull. Soc. chim., 1935, [v], 2, 119—125).—Thermomagnetic analysis shows that natural lepidocrocite (I) loses H₂O, partly in two stages, at > 300° in air, and yields cubic Fe₂O₃ which at about 500° passes rapidly to rhombohedral Fe₂O₃. The equilibrium 3Fe₂O₃ (cubic) ⇌ 2Fe₃O₄ + 0.5O₂ is set up during dehydration in vac. Artificial lepidocrocite prepared from FeO is less stable than (I), and in vac. at 525° affords a solid solution of Fe₃O₄ and Fe₂O₃. The hydrate produced by hydrolysing Na ferrite loses its H₂O at < 200°, forming a stable cubic Fe₂O₃ which changes to rhombohedral Fe₂O₃ at 700°. J. G. A. G.

Occurrences of magnesite in Russia, Manchuria, Japan, Sweden, and Norway. L. LOCH and K. A. REDLICH (Z. pr. Geol., 1935, 43, 1—10).

—The situations, nature of the deposits, and analyses are described. L. S. T.

Occurrence of schwartzite in British Columbia. H. V. WARREN and C. S. LORD (Econ. Geol., 1935, 30, 67—71).—Schwartzite occurs in one of the samples of tetrahedrite from the N. Kootenay Mine of the Windermere district. The analysis corresponds with 3(Cu,Ag)₂S.(Hg,Zn)S.(As,Sb)₂S₃.

L. S. T.

Occurrence of enargite and wulfenite in ore deposits of Northern Arkansas. E. T. MCKNIGHT (Econ. Geol., 1935, 30, 61—66).—At the Governor Eagle Mine, Marion County, Arkansas, enargite is associated with the sphalerite, a little chalcopyrite, and minor amounts of dolomite, calcite, and quartz gangue. Wulfenite occurs with cerussite as an oxidation product of galena at the Shiras Mine, Baxter County. No molybdenite was found in the galena.

L. S. T.

Tin deposits of Llallagua, Bolivia. I. F. S. TURNEAURE (Econ. Geol., 1935, 30, 14—60).—The geology of the district, the structural geology of the veins, the hydrothermal metamorphism which involved abundant deposition of low-Fe tourmaline, sericite, and quartz, the vein minerals, and their paragenesis are described.

L. S. T.

Origin of the iron ores of Spanish Morocco. P. GEIJER (Econ. Geol., 1935, 30, 92—94).—A discussion.

L. S. T.

Origin of petroleum. G. A. FESTER and J. CRUELLAS (Rev. Fac. Quim. Ind. Agric., 1934, 3; Chem. Zentr., 1934, ii, 2325).—The formation of asphalts and oils is attributed to the catalytic action of colloidal V derived from the surrounding rocks.

J. S. A.

New S. Dakota meteorite. C. C. O'HARRA (Science, 1935, 81, 72).—The meteorite, designated as the Bennett County meteorite, contains Fe 94.26, Ni 5.25, Co 0.46, S 0.04% and some graphite. Small inclusions of triolite are present.

L. S. T.

Organic Chemistry.

Electronic theory and organic chemistry. I.—See this vol., 431.

Functional groups and linkings in organic chemistry. E. PUXEDDU (Gazzetta, 1934, 64, 957—

Theoretical. The properties of org. substances are considered as those of the reactive groups, the remainder of the mol. being inactive. E. W. W.

Organic molecular compounds. P. PFEIFFER (Chem.-Ztg., 1935, 59, 205—207).—A review.

Microchemical determination of unsaturation by exposure to bromine vapour. J. BOESEKEN and D. POLS, jun. (Rec. trav. chim., 1935, 54, 162—166).—A modification of Rossmann's method (A., 1906, 31, 1000).

A few mg. of the substance are placed in a small dish (I) under a Petri dish together with a dish containing a few drops of Br. After $\frac{1}{2}$ —1 hr. excess of Br is removed by a stream of N₂ at 100°,

and (I) is re-weighed. Light is excluded with black paper. Results accord with those of Wijs' method, except for compounds containing OH, e.g., castor oil. In the latter case a little HBr is probably formed in presence of a trace of H₂O, followed by :C·OH + HBr = :CBr + H₂O, H₂O + Br₂ = HBr + HOBr. After bromination for 2.5 days ricinelaïdic acid takes up 2.4 atoms of Br per mol., in accordance with this view.

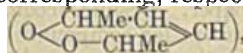
R. S. B.

Physical constants of the polymerisation products of unsaturated hydrocarbons. H. I. WATERMAN and J. J. LEENDERTSE (Rec. trav. chim., 1935, 54, 139—148).— n_D^{20} , d_4^{20} , the NH₂Ph point, and mean mol. wt. have been determined for (a) the fractions of the Δ^8 -*n*-pentene polymerides obtained at 0° with AlCl₃ as catalyst, and (b) the fractions of the isobutene polymerides obtained at > 40° with a SiO gel-Al₂O₃ catalyst, the properties being determined in each

case before and after hydrogenation. d for (a) and (b) is a linear function of temp. at 20–80°. d decreases on hydrogenation by approx. the same amount for all temp. and fractions in the case of (a), but for (b) the decrease in d is dependent on the mol. wt., and decreases with rising temp. At 20°, 40°, and 60° Dunstan's formula $\log \eta - A + Bm$ holds (A and B consts., m mol. wt.), but there is a slight deviation at 80°. After hydrogenation (a) and (b) give similar results for η , but before hydrogenation vals. of η are relatively high. The influence of T on η increases with increasing m ; the nature of the raw material has approx. no influence, and the saturation of the polymerides has a small influence, on the η - T curve. $-\log \eta - K/T + a$, where K and a are consts., for the fractions of lower mol. wt. of (a) and (b), but there is a deviation in the fractions with higher mol. wt. A plot of η_T against η_{T-20} for (a) and (b) is approx. linear. It is inferred that the fractions (a) have a cyclic character and are not quite paraffinoid, whereas fractions (b) are completely paraffinoid.

R. S. B.

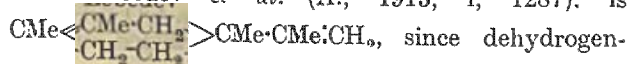
Additive reactions and polymerisation of $\beta\gamma$ -dimethylbutadiene. P. N. KOGERMAN (Sitzungsber. Naturforsch. Ges. Tartu, 1934, 41, reprint, 62 pp.).—The solid dibromide (80%), m.p. 47°, obtained from $(\text{CH}_3\text{CMe})_2$ (I) and Br-ligroin at -13° is the *trans*- $\alpha\delta$ -dibromide (II). Fractional crystallisation of the liquid products (III) (shown by a cooling curve to be a mixture of additive and substitution products) affords the *cis*- $\alpha\delta$ -dibromide, m.p. 4.0–4.1°, since, like (III), it gives $\text{CH}_2\text{Br}\cdot\text{COMe}$ on ozonolysis. Further addition of Br to (II) goes smoothly to give the Br_4 -compound, but (III) gives a mixture of additive and substitution products. With AgOAc in EtOAc at $< 25^\circ$ (II) or (III) gives mainly δ -hydroxy- $\beta\gamma$ -dimethyl- Δ^{β} -butenyl acetate, b.p. 91–92°/9 mm., and the Ac_2 derivative, b.p. 124.0–125.5°/9 mm., of $\beta\gamma$ -dimethyl- Δ^{β} -butene- $\alpha\delta$ -diol, b.p. 85.0–85.5°/8 mm., which is obtained by hydrolysis of either Ac derivative with $\text{NaOMe}\cdot\text{MeOH}$ at 40–50°. Oxidation $[\text{Pb}(\text{OAc})_4]$ of the glycol from (II) and from (III) gives CH_2O corresponding, respectively, to 9% and 44.7% of the $\alpha\beta$ -diol, but some isomerisation probably occurs during oxidation. In the autooxidation of $(\text{CHMe}\cdot\text{CH})_2$, (I), and $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ the O_2 absorbed at 20–26° is, respectively, 46.55, 24.06, and 38.8% of the wt. of diene, corresponding, respectively, to absorption of 1 mol.



1 atom $\left(\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CMe} \\ \text{CH}_2\cdot\text{CMe} \end{array} \right)$, and 1 mol.

mol.

wt. of the products is partly dependent on the solvent and concn. Under the same conditions diallyl (no conjugation) does not absorb O_2 . The thermal polymerisation of (I) at 100°, 125°, 150°, 175°, and 200° for 3–18 hr. \propto concn., and is affected by the presence of catalysts and by the nature of the glass. The ratio of dimeride (IV) to total polymeride increases with rise of temp. to a max. val. 1.9/1 at 175°. Ozonolysis of (IV) gives CH_2O , but no $(\cdot\text{CH}_2\text{Ac})_2$, hence (IV) is not *cyclooctatriene*, but, in agreement with Lebedev *et al.* (A., 1913, i, 1287). is



ation with Se at 350° affords a mixture of ψ -cumene (oxidised by KMnO_4 to trimellitic acid) and some xylenes, and (IV) adds 2 mols. HBr . The heats of combustion of (I) and (IV) are, respectively, 909 and 1817 kg.-cal. per. mol.

J. W. B.

Physical constants of dimethylacetylene. G. B. HEISIG and H. M. DAVIS (J. Amer. Chem. Soc., 1935, 57, 339–340).—Physical consts. are recorded for $(\text{CMe})_2$ (modified prep.), b.p. 27.2°, m.p. -32.8° to -32.5° .

R. S. C.

Synthesis of polychloro-compounds with aluminium chloride. I. Condensation of chloroform with tetrachloroethylene. H. J. PRINS (Rec. trav. chim., 1935, 54, 249–252).—Details for the prep. of $\text{CHCl}_2\cdot\text{CCl}_2\cdot\text{CCl}_3$ from $\text{CCl}_2\cdot\text{CCl}_2$ (I) and CHCl_3 in presence of traces of AlCl_3 (II) (cf. A., 1914, i, 648) are given, and the reversibility of the reaction is demonstrated. The ease of reaction makes it a suitable test for free (II). Long boiling of (I) with (II) gives only a little C_3Cl_6 and an oil of high, indefinite b.p. When heated with (II) in CCl_4 , $\text{CHCl}(\text{CCl}_3)_2$ affords C_3Cl_6 (III) which forms an additive compound with (II) (cf. A., 1933, 47), and no free AlCl_3 could be detected (see above) when the mol. ratio (III)/(II) is > 1 .

J. W. B.

Oxidation of iodoform [and carbon tetraiodide] solutions.—See this vol., 454.

Aliphatic nitro-compounds. III. Reactions of nitromethane halides. N. N. MELNIKOV (J. Gen. Chem. Russ., 1934, 4, 1061–1063).—The products of heating $\text{CBr}_3\cdot\text{NO}_2$ with 70% H_2SO_4 are COBr_2 and NOBr , whilst with 50% aq. KOH , N_2 , CO , NO , K_2CO_3 , KBr , KBrO_3 , KNO_2 , KNO_3 , and $\text{K}_2\text{C}_2(\text{NO}_2)_4$ have been identified; the reactions whereby these products are formed are discussed.

R. T.

α -Methoxypentan-3-ol. A. SERVIA (Anal. Fis. Quim., 1934, 32, 149–151).—The interaction (Grignard) of $\alpha\beta$ -oxido- γ -methoxypropane and MgEtBr (cf. Ribas and Tapia, A., 1933, 487) gives α -methoxypentan-3-ol (I), b.p. 151–152° (3:5-dinitrobenzoate, m.p. 55°), not $\text{OMe}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{OH}$, because (I) and $\text{K}_2\text{Cr}_2\text{O}_7$ in dil. aq. H_2SO_4 yield $\text{COPr}\cdot\text{CH}_2\cdot\text{OMe}$, b.p. 146–148°/690 mm. identified by its semicarbazone (cf. Maruyama, *ibid.*, 260).

F. R. G.

Preparation of acetylenic and di-ethylenic alcohols in the C_5 and C_6 series. R. LESPIEAU and R. LOMBARD (Bull. Soc. chim., 1935, [v], 2, 369–373).—A more detailed account of work previously summarised (A., 1934, 990). The Raman spectra of the various alcohols are described.

J. W. B.

Reaction of ethylene oxide with acetylenic Grignard reagents. G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 382–383).—By this reaction is prepared Δ^7 -noninen- α -ol (52% yield), b.p. 130–130.5°/19 mm. (urethane, m.p. 64.5°), which with PBr_3 gives α -bromo- Δ^7 -noninene, b.p. 95°/9 mm., no formed from $\text{C}_5\text{H}_{11}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr}$ and β -bromoethyl p-*enesulphonate*, b.p. 203°/5 mm.

R. S. C.

Syntheses by the aid of vinylacetylene. J. KIND and V. PLETZ (J. Gen. Chem. Russ., 1088–1090).—Dimethylvinylacetylenylcarbinol, b.p. 64°/15 mm., 75°/25 mm., is obtained from MgEt

in Et_2O , $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$, and COMe_2 ; *methyldivinylacetylenylcarbinol*, b.p. $110^\circ/8$ mm., is obtained when EtOAc is substituted for COMe , in the above reaction.

R. T.

Oxidation of ether in presence of active carbon. I, II.—See this vol., 456.

Higher β -alkyl ethers of $\alpha\gamma$ -dibromopropane [$\beta\beta'$ -dibromoisopropyl ethers]. L. SATTLER, M. ALTAMURA, and S. PRENER (J. Amer. Chem. Soc., 1935, 57, 333—334).— $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Br}$ and $\text{Hg}(\text{OAc})_2$ in the appropriate alcohol give α -bromo- β -alkoxy- γ -acetoxymercuripropenes, which with Br-KBr give the following *dibromoisopropyl alkyl ethers* in 20—32% yields: *Me*, b.p. $83.0^\circ/13$ mm., *Et*, b.p. $90.5^\circ/17$ mm., *Pr^a*, b.p. $114.2^\circ/27$ mm., *Pr^b*, b.p. $108.6^\circ/28.5$ mm., *Bu^a*, b.p. $119.0^\circ/19.5$ mm., *Bu^b*, b.p. $117.0^\circ/22$ mm., *amyl*, b.p. $137.9^\circ/23$ mm., and *isoamyl*, b.p. $137.5^\circ/27$ mm. These ethers are toxic and hypnotic.

R. S. C.

Thermal decomposition of organic compounds from the viewpoint of free radicals. XIII. Decomposition of ethyl nitrite. F. O. RICE and E. L. RODOVSKAS (J. Amer. Chem. Soc., 1935, 57, 350—352; cf. this vol., 191).—When pure $\text{NO}\cdot\text{OEt}$ (I) is decomposed at $425^\circ/\text{about } 1$ mm., the vapours produced do not affect Te mirrors. 1% of (I) in CO_2 , C_4H_{10} , or Et_2O , however, removes Te and Hg mirrors, forming TeMe_2 or HgMe_2 . Hence (I) probably terminates the reaction chain, decomp. at low pressures occurring thus: (a) $(\text{I}) \rightarrow \text{NO} + \text{OEt}^\cdot$; (b) $\text{OEt}^\cdot \rightarrow \text{CH}_3\text{O}^\cdot + \text{Me}^\cdot$; (c) $\text{Me}^\cdot + (\text{I}) \rightarrow \text{CH}_3 + \text{NO}\cdot\text{OCHMe}^\cdot$; $\text{NO}\cdot\text{OCHMe}^\cdot \rightarrow \text{NO} + \text{MeCHO}$. 1% of (I) does not, however, prevent decomp. of C_4H_{10} , as might be expected if it terminates the chain, probably because of the rapid decomp. of (I) at the required temp. The activation energy of (a) at $400\text{--}500^\circ$ is 34.3 ± 3 kg.-cal.; that of (b) and of $\text{OEt}^\cdot + (\text{I}) \rightarrow \text{EtOH} + \text{NO}\cdot\text{OCHMe}^\cdot$ are estimated at $500^\circ/0.01$ atm. to be 28—34 and 12—18 kg.-cal., respectively. HgMe_2 is determined by addition of HgBr_2 in EtOH , evaporation, steam-distillation, and collection of the volatile HgMeBr .

R. S. C.

Carbonic acid derivatives. VII. Interaction of water, ammonia, sodium hydroxide, and magnesium ethyl bromide with alkyl trichloromethyl carbonates. N. N. MELNIKOV (J. Gen. Chem. Russ., 1934, 4, 1057—1060).— $\text{CCl}_3\cdot\text{O}\cdot\text{CO}_2\text{R}$ (I) ($\text{R}=\text{Ph}$, *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}$, *Me*, *Et*, and *iso*- C_5H_{11}) reacts as follows with different reagents: $(\text{I}) + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{ROH} + \text{HCl} + \text{COCl}_2$; $(\text{I}) + 7\text{NaOH} \rightarrow 3\text{NaCl} + 2\text{Na}_2\text{CO}_3 + \text{ROH} + 3\text{H}_2\text{O}$; $(\text{I}) + 6\text{NH}_3 \rightarrow \text{CO}(\text{NH}_2)_2 + 3\text{NH}_4\text{Cl} + \text{NH}_3\cdot\text{CO}_2\text{R}$; $(\text{I}) + \text{MgEtBr} \rightarrow 2\text{C}_2\text{H}_5\cdot\text{OH} + \text{ROH} + \text{MgCl}_2 + \text{MgBr}_2$.

$\text{C}_2\text{H}_5\cdot$ is in all cases an intermediate product.

R. T.

Mechanism of hydrolysis of di-esters of orthophosphoric acid. Migration of the phosphoric acid radical during the hydrolysis of two mixed α -esters, methyl α - and β -glycerophosphate.

Interconversion of α - and β -glycerophosphates. and J. GAUME (Bull. Soc. chim., 1935, [v], 2, 354—369).—Interaction of Na_2MePO_4 with

H_2O at $60\text{--}70^\circ$ affords (in solution)

$\text{Na Me } \beta\gamma$ -oxidopropylphosphate and MeOH (no Na_2MePO_4). Similar hydrolysis of either $\text{Na Me } \alpha$ - or β - (prep. from its pure Ca salt) -glycerophosphate gives a mixture of $\text{Na}_2 \alpha$ - and β -glycerophosphate with elimination of Me only. Thus in alkaline hydrolysis migration of the PO_4 from α to β and from β to α occurs, the former predominating. In acid hydrolysis of $\text{Me } \beta$ -glycerophosphoric acid (dil. aq. solution) migration from β to α predominates (unimol. $k^{25}=0.0051\text{--}0.0058$). The mechanism of these migrations is discussed. Determination of the α - and β -glycerophosphates is effected by the methods of Fleury *et al.* (A., 1933, 696) and of Karrer *et al.* (A., 1926, 384; modified).

J. W. B.

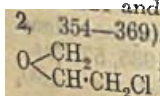
Synthesis of the isomeric glyceric acid-phosphoric acids [phosphoglyceric acids]. W. KRESSLING (Ber., 1935, 68, [B], 243—248).— $\text{Na } \beta$ -glycerylphosphate is oxidised by Br in H_2O containing $\text{Ba}(\text{OAc})_2$, N-NaOH being added so that the solution is just acid to litmus, whereby α -phosphoglyceric acid (I) (*Ba* and *Ag* salts) is obtained. Similar oxidation of $\text{Ba } \alpha$ -glycerylphosphate leads less smoothly to β -phosphoglyceric acid (II) (*Ba* and *Ag* salts), oxidised by KMnO_4 to phosphoglycolic acid (*Ba* and *Ag* salts). (I) and (II) undergo carboxylatic fission by yeast extract at the same rate to the extent of 50%, the (—)-component of (II) and the (+)-component of (I) being removed so that the residual acids have $[\alpha]_D^{20} +14.5^\circ$ and -23.5° , respectively. In dialysed yeast extract an equilibrium mixture is formed containing 80% of (II). Natural phosphoglyceric acid appears to be mainly a mixture of (+)-(I) and (—)-(II).

H. W.

γ -Trimethylene trisulphide perchlorate. II. O. HINSBERG (J. pr. Chem., 1935, [ii], 142, 135—140; cf. A., 1933, 1303).—The compound, m.p. 37° (*loc. cit.*), has the formula $\text{C}_6\text{H}_{12}\text{O}_2\text{S}_3$ and is probably $\text{AcS}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{OMe}$. The compound, m.p. 93° (*loc. cit.*), is $\text{S}(\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{SMe})_2$ (I) [oxidised ($\text{H}_2\text{O}_2\text{--Ac}_2\text{O}$) to a *sulphone*, $\text{C}_6\text{H}_{14}\text{O}_{10}\text{S}_5$, m.p. 257°], and is formed together with a mixture, m.p. about 50° , from trithian perchlorate (II), m.p. 138° . With $\text{H}_2\text{O}_2\text{--AcOH}$, (II) gives γ -trimethylene disulphoxide sulphide perchlorate (III), which explodes at about 150° and (unlike the α -compound) with aq. NH_3 forms a voluminous mass insol. in H_2O . (III) is converted by HI into the γ -iodide, $(\text{C}_3\text{H}_6\text{S}_2)_2\text{I}_2$, m.p. 112° , which with aq. $\text{Na}_2\text{S}_2\text{O}_8$ and aq. MeOH affords a γ -compound, $\text{C}_3\text{H}_6\text{S}_3\cdot\text{HI}\cdot\text{MeOH}$, m.p. 121° (decomp.) [converted into (II) by HClO_4 ; decomposes on heating to 100° to form a yellow insol. substance]. The MeOH is not removed by crystallisation from H_2O . (III) heated with MeOH affords the corresponding α -compound (IV), which explodes at about 150° and is reduced by conc. HI to β -trimethylene trisulphide (V), m.p. 247° . (IV) is converted by KOAc into α -trimethylene disulphoxide sulphide, $\text{C}_3\text{H}_6\text{O}_2\text{S}_3$, m.p. 255° (decomp.), which with HI gives (V) and with H_2O_2 gives trimethylene trisulphoxide, m.p. 270° .

H. G. M.

Tertiary pentanesulphonic acid. H. J. BACKER (Rec. trav. chim., 1935, 54, 215—218).—Interaction of CMe_2EtBr and $\text{CS}(\text{NH}_2)_2$ in hot H_2O and hydrolysis of the product affords *tert.-amyl mercaptan*, b.p.



K K

97°, oxidised by 30% H_2O_2 -AcOH at 45–50° to β -methylbutane- β -sulphonic acid + H_2O , m.p. 62–65° ($\text{Na} + 1.5\text{H}_2\text{O}$, $\text{K} + \text{H}_2\text{O}$, $\text{Ba} + 2\text{H}_2\text{O}$, $\text{Cu} + 5\text{H}_2\text{O}$, $\text{Pb} + 3\text{H}_2\text{O}$, NH_2Ph , m.p. 214–217°, *strychnine* + $2\text{H}_2\text{O}$, and *brucine* salts). J. W. B.

Derivatives of methanedisulphonic acids. G. KLAVER (Rec. trav. chim., 1935, 54, 208–215).—When heated with $\text{NH}_2\text{Bu}^\gamma$ and C_6H_6 at 160°, $\text{CH}_2(\text{SO}_3\text{Ph})_2$ (I) affords *methanedisulphon-tert.-butylamide*, m.p. 175°, NH_2Ph similarly giving the *Ph anilinosulphonmethanesulphonate*, m.p. 152°. The Na derivative of (I) with Me_2SO_4 gives the cryst. Ph ester, m.p. 52°, of ethane- $\alpha\alpha$ -disulphonic acid (II) (*diamide*, m.p. 165°; *di(tert.-butylamide)*, m.p. 152°; *dianilide*, m.p. 168; *di(ethylanilide)*, m.p. 150°), similarly converted into the Ph ester, m.p. 69–70°, of ethane- $\alpha\alpha$ -sulphonamic acid (*Ba* salt + H_2O , and *basic Ba* salt, $\text{CHMe} \begin{smallmatrix} \text{SO}_2-\text{O} \\ \text{SO}_2-\text{NH} \end{smallmatrix} \text{Ba} + 3\text{H}_2\text{O}$), which could not be resolved through its *brucine* salt. By similar methods are obtained *n-propane*- [*Ba* salt + $3\text{H}_2\text{O}$; *Ph* ester, b.p. 200°/0.005 mm.; *diamide*, m.p. 169–170°; *Ph* ester, m.p. 104° of the sulphonamic acid (*Ba* salt + H_2O); *di(tert.-butylamide)*, m.p. 133°; *dianilide*, m.p. 152°; *di(ethylanilide)*, m.p. 127–128°]; *n-butane*-, + $2\text{H}_2\text{O}$ [*Ba* salt + $2\text{H}_2\text{O}$; *Ph* ester (obtained only from $\text{CHNa}(\text{SO}_3\text{Ph})_2$ and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Pr}^a$); *di(ethylanilide)*, m.p. 124°], and *n-pentane*-, + $2\text{H}_2\text{O}$ [*Ba* salt + $2\text{H}_2\text{O}$; *Ph* ester; *di(ethylanilide)*, m.p. 84°], - $\alpha\alpha$ -disulphonic acid.

J. W. B.

$\beta\beta'$ -Disulphodiethyl ether. H. J. BACKER (Rec. trav. chim., 1935, 54, 205–207).—Oxidation of $(\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$ [obtained from $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$ (I) and $\text{CS}(\text{NH}_2)_2$] with 30% H_2O_2 -AcOH affords $\beta\beta'$ -disulphodiethyl ether (II) [*Ba* + H_2O , *Na*, *K* + $1.5\text{H}_2\text{O}$, *Tl*, *Pb*, *Cu* + $4.5\text{H}_2\text{O}$, and *NH Ph*, m.p. 232–233°, salts]. (II) is also obtained by the action of $(\text{NH}_4)_2\text{SO}_3$ on (I).

J. W. B.

Replacement series of the alkyl groups as determined by alcoholysis of esters. P. R. FEHLAND and H. ADKINS (J. Amer. Chem. Soc., 1935, 57, 193–195).—Equilibria of the reaction $\text{ROH} + \text{AcOR}' \rightleftharpoons \text{R}'\text{OH} + \text{AcOR}$ are determined in glass or steel (attained faster in the latter) at 200° for a series of esters. The data thus obtained lead to the following relative reactivities of the alcohols: Me 100, heptyl 90, dodecyl 84, γ -phenylpropyl 83, Et 81, Bu^a 80, Pr^a 79, *sec*.-octyl 68, Bu ^{γ} 66, $\text{CH}_2\text{Ph}\cdot\text{CH}_2$ 65, allyl 62, CH_2Ph 59, Pr ^{β} 55, *cyclohexyl* 55, and Bu ^{δ} 53.

R. S. C.

[Mechanism of ester condensations.] G. V. TSCHELINCEV (Ber., 1935, 68, [B], 327–329; cf. A., 1934, 868).—Scheibler's assumption (A., 1934, 991) of the formation of "unstable mol. compounds" due to subsidiary valencies is unnecessary for the explanation of the reaction between PhCHO and EtOAc in presence of Na, which proceeds thus: $\text{PhCHO} + \text{CH}_2\text{:C}(\text{ONa})\cdot\text{OEt} \rightarrow \text{OH}\cdot\text{CHPh}\cdot\text{CH:C}(\text{ONa})\cdot\text{OEt} \rightarrow \text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$. The author's hypothesis is also in harmony with the established inability of esters $\text{CHRR}'\cdot\text{CO}_2\text{Et}$ to behave as second component in ester condensations. Reply is made to Bodendorf (A., 1934, 991).

H. W.

Oxidising hydrolysis of ozonides from unsaturated acids. J. L. RIEBSOMER and R. C. TALLMAN (Proc. Indiana Acad. Sci., 1934, 43, 136–139).—Details are given for the oxidising hydrolysis of unsaturated fatty acids by H_2O_2 in AcOH (yield 62%). CH. ABS. (e)

Oxidation of organic substances as a means of investigating their constitution. [Oxidation of acetic acid by hydrogen peroxide.] G. GIACOMELLO (Gazzetta, 1934, 64, 968–984; cf. A., 1933, 1036; 1934, 653).—The action of H_2O_2 and H_2SO_4 on AcOH in H_2O at 95° yields CO_2 , O_2 , CO , H_2 , CH_4 , MeOH, $\text{CHO}\cdot\text{CO}_2\text{H}$, CH_2O , and a resin. MeOAc and NaOAc are oxidised to similar products, but HCO_2Me yields a gaseous product containing no CH_4 , and a solution containing $\text{CHO}\cdot\text{CO}_2\text{H}$. No H_2 or CH_4 was found in the gas from AcOH in absence of H_2SO_4 . The various results are considered as supporting the tautomerisms: $\text{H}\cdot\text{C}(\text{O})\cdot\text{OMe} \rightleftharpoons \text{C}(\text{OH})\cdot\text{OMe} \rightleftharpoons \text{Me}\cdot\text{C}(\text{O})\cdot\text{OH} \rightleftharpoons \text{CH}_2\cdot\text{C}(\text{OH})_2 + \text{H}_2\text{O}_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{OH})_3$. These and similar equilibria are held to be much more common than is usually supposed. Mechanisms for the above oxidations are suggested.

E. W. W.

Decomposition of acetyl peroxide. O. J. WALKER and G. L. E. WILD (J.C.S., 1935, 207–210; cf. A., 1928, 1114; 1918, i, 369).—When pure Ac_2O_2 (I) (cf. A., 1909, i, 910) is heated at various temp. between 30° and 90°, *decomp.* proceeds with evolution of a mixture of mainly CO_2 and CH_4 , but also CO , C_2H_4 , O_2 , and C_2H_6 . The yield of C_2H_6 decreases from 8.8% at 90° to 0.7% at 30°. The undecomposed peroxide contains no CH_2O , AcOH, or AcO_2H (cf. A., 1932, 929). The present work is discussed in relation to previous work on the *decomp.* of (I) and that in which (I) is assumed to be formed, and is contrary to the view that *decomp.* proceeds along the lines of the simple equation.

J. L. D.

Stability of the acetyl radical. M. BARAK and D. W. G. STYLE (Nature, 1935, 135, 307–308).—The chief products of the photo-*decomp.* of Et_2O_2 are EtOH and Ac_2 . The non-gaseous products of the photo-*decomp.* of COMe₂ and COMeEt give derivatives of Ac_2 with dinitrophenylhydrazine. Ac is more stable than is generally assumed, and plays a significant role in the photo-*decomp.* of MeCHO and COMe, at room temp.

L. S. T.

Origin of bromine liberated as bromide ion in the interaction of bromoacetic ions with bromoacetic molecules.—See this vol., 452.

Electrolysis of mixtures of propionates and nitrates. F. FICHTER and W. SIEGRIST [with H. BUSS] (Helv. Chim. Acta, 1935, 18, 18–25).—By electrolysing 4*N*-EtCO₂Na containing 2*N*-NaNO₃ with c.d. 0.1 amp. per sq. cm. at the Pt anode, 6.63 c.c. of an oil were obtained during the passage amp.-hr. The oil consisted chiefly of EtNO₃, Bu^aNO₃, ($\text{CH}_2\cdot\text{NO}_3$)₂, and NO₃·[CH₂]₄·NO₃, with much smaller quantities of EtCO₂Et. The results are discussed.

F. L. U.

Addition of carboxylic acids to vinylacetylene. J. H. WERTZ (J. Amer. Chem. Soc., 1935, 57, 204–206).—Vinylacetylene and AcOH in presence of Hg_2O_4

or BF_3 or, best, HgSO_4 -sulphoacetic acid (I) at 50° or, better, 5° gives *butadien- β -yl acetate* (II), b.p. $52\text{--}54^\circ/40$ mm., and much polymeride and resin. The corresponding *butyrate*, prep. by (I), has b.p. $59\text{--}60^\circ/11$ mm., and the *formate* and *chloroacetate*, prep. by $\text{Hg}_3(\text{PO}_4)_2$, b.p. $48\text{--}49^\circ/51$ mm. and $51\text{--}53^\circ/2$ mm., respectively. The monomeric nature of these esters is proved by the mol. wt. in C_6H_6 and the structure by conversion of (II) by hot 5% H_2SO_4 into $\text{CH}_2\text{:CH}\cdot\text{COMe}$ and thence into 1-phenyl-3-methylpyrazoline and by condensation of (II) [stabilised by $p\text{-C}_6\text{H}_4(\text{OH})_2$] with 1:4-naphthaquinone at 100° to 2-acetoxy-1:4:11:12-tetrahydroanthraquinone, cryst., oxidised by air in dil. NaOH - EtOH to impure 2-acetoxyanthraquinone, whence 2-hydroxyanthraquinone was obtained by hot KOH - EtOH . The rate of polymerisation of (II) is intermediate between that of chloroprene and of isoprene, is catalysed positively by pressure, elevated temp., or emulsification, and negatively by $p\text{-C}_6\text{H}_4(\text{OH})_2$ or pyrogallol; the product is rubber-like and slowly decomposes, liberating AcOH , as also does (II).

R. S. C.

β -Chloroacrylic acids. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 54, 167—170).—Dissolution of $\text{CH}_2\text{:C}\cdot\text{CO}_2\text{H}$ (prep. in 52% yield by the action of CO_2 on $\text{CH}_2\text{:CNa}$ described) in conc. HCl at 60° affords the less sol. *trans*- β -chloroacrylic acid, m.p. $85\text{--}86^\circ$, $k^{18}=2.22\times 10^{-4}$ (18%), and, from the mother-liquor, the more sol. *cis*- β -chloroacrylic acid, m.p. $63\text{--}64^\circ$, $k^{18}=4.77\times 10^{-4}$ (34%), converted into (I) by heating at 125° . Similar treatment of (I) effects only partial decomp.

J. W. B.

Acids of Chinese and esparto grass waxes and hydrocarbons of esparto and candelilla waxes.—See this vol., 551.

Preparation of oleyl chloride and α -mono-olein. K. TAUFEL and F. KUNKELE (Fettchem. Umschau, 1935, 42, 27—29).—Details are given for the prep. of oleyl chloride (I) from oleic acid (II) and PCl_3 and PCl_5 , and for that of α -mono-olein (III), m.p. $26\text{--}27^\circ$, b.p. $238\text{--}240^\circ/3\text{--}4$ mm., from (I) and *isopropylideneglycerol* (cf. A., 1920, i, 805). Interaction of (II) and SOCl_2 (cf. A., 1914, i, 246), and of (II) and a deficiency of PCl_5 , gave compounds, m.p. 50° and ∞ , respectively, free from Cl (and considered to be *isoleic acids*). The b.p. (6 mm.) diagram of mixtures of (I) and (II) is given. The interconversion of (III) into the form m.p. 35° is accelerated by stirring the liquid while it is cooling.

H. G. M.

Iodine values of linolenic, linoleic, and stearic acids by the Wijs and Rosenmund-Kuhnenn methods. Y. TOYAMA and T. TUTIYA (J. Soc. Ind. Japan, 1935, 38, 32—35B).—The effect on the Wijs I val. of the amount of excess (30—70%) reagent is about 3 units in the case of linolenic (I) and unimportant (> 1) in that of linoleic (II) and stearic (III) acids. The Rosenmund-Kuhnenn vals. (IV) are practically independent of the excess of reagent in the case of (I) and (II), but are 10 or 7 some 7 and 4 units, respectively, than the Wijs vals. For (III) the (IV) are always $>$ the Wijs I val. (which corresponds with the addition of 1 mol.

of halogen), and increase considerably with increasing excess of reagent.

E. L.

Dithiocyanate of linoleic acid and tetrathiocyanate of linolenic acid. Y. TOYAMA and T. TUTIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 35—36B).—Ozonolysis of *dithiocyanolinoleic acid* (I) and *tetrathiocyanolinolenic acid* (II) shows that the SCN groups are attached in the θ positions in (I) and in the θ and μ positions in (II), the double linkings most remote from the CO_2H group, as in the case of moroctic acid, being unattacked.

E. L.

Products of partial bromination of linoleic and linolenic acids. Y. TOYAMA and T. TUTIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 36—38B).—Ozonolysis of the bromides obtained by partial bromination of linoleic (I) and linolenic (II) acids shows that Br , in contradistinction from $(\text{SCN})_2$ (cf. preceding abstract), adds primarily to the unsaturated linking(s) most remote from CO_2H group. $\mu\mu$ -Dibromo- Δ^8 -octadecenoic, $\xi\theta$ -dibromo- $\Delta^{9,11}$ -octadecadienoic, and $\xi\theta\mu$ -tetrabromo- Δ^8 -octadecenoic acids have been prepared by treating (I) with one half, and (II) with one third and two thirds, respectively, of the amount of Br required theoretically for complete saturation.

E. L.

Polymerisation of the methyl esters of higher unsaturated fatty acids. XV. Structure of the polymerisation product of methyl linoleate. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 91—97).— MeOH separates the products of polymerisation of Me linoleate into a sol. portion (49%; I val. 166.0; mol. wt. 298) and an insol. *dimeride* (I) (49%; I val. 128.2; mol. wt. 541). From the products of ozonolysis of (I) are isolated $\text{CH}_2(\text{CO}_2\text{H})_2$, EtCO_2H , an acid $\text{CO}_2\text{H}\cdot\text{C}_{10}\text{H}_{18}\cdot\text{CO}_2\text{Me}$ (neutralisation val. 238.7, sap. val. 454.2, mol. wt. 472) (purified through its Mg salt), a cryst. substance, m.p. $150\text{--}158^\circ$, and an acid (neutralisation val. 412.1, sap. val. 522.8, mol. wt. 265). (I) is therefore probably $[\text{CHEt}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}-]_2$
 $\text{CO}_2\text{Me}\cdot[\text{CH}_2]_7\cdot\text{CH}-]$

J. W. B.

Ether-like compounds. XIV Acid hydrolysis of esters of tertiary alcohols. M. H. PALOMAA, E. J. SALMI, J. I. JANSSON, and T. SALO (Ber., 1935, 68, [B], 303—307; cf. A., 1934, 867).—The temp. coeffs. of acid hydrolysis of esters of *tert.*-alcohols (I) differ widely from those of *sec.*-alcohols. Reaction with (I) resembles acetal rather than ester hydrolysis. The following compounds are new: *Bur* propionate, b.p. $120\text{--}121^\circ/763$ mm.; *Bur* methoxyacetate, b.p. $62\text{--}64^\circ/22\text{--}23$ mm.; $\alpha\alpha$ -dimethylpropyl methoxyacetate, b.p. $71\text{--}73^\circ/16$ mm.; dimethylmethoxymethylcarbonyl acetate, b.p. $143\text{--}144.5^\circ/755$ mm.; α -methylpropyl formate, b.p. $94.5\text{--}95^\circ/760$ mm., and methoxyacetate, b.p. $168\text{--}168.5^\circ/756$ mm.; α -ethylpropyl formate, b.p. $116.5\text{--}117.5^\circ/768$ mm., and methoxyacetate, b.p. $184.5\text{--}185^\circ/761$ mm.; α -methylbutyl methoxyacetate, b.p. $185.5\text{--}186^\circ/755$ mm.

H. W.

Simplified apparatus for the determination of lactic acid. II. H. LIEB and M. K. ZACHERL (Z. physiol. Chem., 1935, 231, 88—91; cf. A., 1932, 1269).—Minor modifications and criticisms of Fuchs (cf. A., 1934, 56) are discussed.

J. H. B.

Mechanism of reactions of ethyl acetoacetate, the enolates, and structurally related compounds. I. C- and O-Alkylation. A. MICHAEL [with G. H. CARLSON]. II. Reaction of sodium enolates with acyl chlorides. A. MICHAEL and G. H. CARLSON (J. Amer. Chem. Soc., 1935, 57, 159—164, 165—174).—I. The formation of C- and O-derivatives of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (I) is interpreted by the author's theory of the formation of polymols. prior to reaction. The heat of combustion of $\text{CH}_2\text{EtAc}\cdot\text{CO}_2\text{Et}$ is $>$ that of $\text{OEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (II). The formation of (II) from (I) or $\text{CH}(\text{OEt})_2$ does not proceed by way of $\text{CMe}(\text{OEt})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$.

II. AcCl and BzCl with Et sodioacetoacetate (III) give directly and nearly quantitatively Et diacetate, which is thus not formed by way of an O-derivative, but by direct addition of the CO of the chloride to the $\alpha\text{-CH}$ of the ester. Excess of AcCl has no effect on the velocity of the reaction, which is interpreted on the basis of the author's polymol. theory. $\text{OAc}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}$ t (IV) is converted into $\text{CHAc}_2\cdot\text{CO}_2\text{Et}$ by (III), but not by heat, or by K_2CO_3 or the Cu enolate unless a trace of H_2O is present. (IV) reacts with $\text{ONa}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, and $\text{OBz}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (V) with (III), intramolecularly to give C-substituted products, but (V) and Na give H_2 and $\text{ONa}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{CO}_2\text{Et}$ by intramol. change. (I), BzCl , and $\text{C}_5\text{H}_5\text{N}$ give a liquid form of (V).

R. S. C.

Odour and constitution. α -Substituted γ -butyrolactones. B. ROTHSTEIN (Bull. Soc. chim., 1935, [v], 2, 80—90).—The following chlorides (I) (cf. A., 1930, 318) are described: *decyl*, b.p. $106^\circ/16$ mm., *undecyl*, b.p. $117^\circ/16$ mm., *dodecyl*, b.p. $130^\circ/15$ mm., *citronellyl*, b.p. $98^\circ/16$ mm., and *rhodinyl chloride*, b.p. $97\text{--}98^\circ/15$ mm. The appropriate (I) reacts with $\text{CH}_2(\text{CO}_2\text{Et})_2$ (Na derivative) (cf. A., 1901, i, 501) to give the following: *Et*₂ *hexyl*-, b.p. $143^\circ/15$ mm., β -ethylbutyl- (cf. A., 1932, 142), *heptyl*-, b.p. $157^\circ/18$ mm., *octyl*-, b.p. $167^\circ/16$ mm., *nonyl*-, b.p. $176^\circ/15$ mm., *decyl*-, b.p. $182^\circ/13$ mm., *undecyl*-, b.p. $192^\circ/13$ mm., *dodecyl*-, b.p. $201^\circ/13$ mm., $\gamma\gamma$ -dimethyl- Δ^8 -octadienyl-, b.p. $145^\circ/0\cdot7$ mm., *rhodinyl*-, b.p. $147^\circ/0\cdot8$ mm., and *citronellyl-malonate*, b.p. $145^\circ/0\cdot75$ mm. The Na derivatives of the above substituted malonic esters with $(\text{CH}_2)_2\text{O}$ at -15° and then at $40\text{--}50^\circ$, followed by hydrolysis with KOH and distillation under reduced pressure, give CO_2 and the following α -substituted γ -butyrolactones: *allyl*-, b.p. $110^\circ/17$ mm., *propyl*-, b.p. $107^\circ/15$ mm., *butyl*-, b.p. $124^\circ/16$ mm., *isoamyl*-, b.p. $129^\circ/15$ mm., *hexyl*-, b.p. $146^\circ/16$ mm., *sec-hexyl*-, b.p. $143^\circ/16$ mm., *heptyl*-, b.p. $156^\circ/15$ mm., *octyl*-, b.p. $123^\circ/0\cdot5$ mm., *nonyl*-, m.p. 28° , *decyl*-, m.p. 34° , *undecyl*-, m.p. 40° , *dodecyl*-, m.p. 46° , $\gamma\gamma$ -dimethyl- Δ^8 -octadienyl-, b.p. $145^\circ/0\cdot72$ mm., $\gamma\gamma$ -dimethyl- Δ^8 -octenyl-, b.p. $144^\circ/0\cdot57$ mm., $\gamma\gamma$ -dimethyl- Δ^9 -octenyl-, b.p. $150^\circ/0\cdot85$ mm., *phenyl*-, b.p. $178^\circ/13\cdot5$ mm., and *benzyl*-, b.p. $150^\circ/1\cdot15$ mm. The odour of the esters lessens with increasing mol. wt.; that of the more complex members cannot be analysed.

J. L. D.

Synthesis of ricinic (λ -ketostearic) acid. R. PERROTTE (Compt. rend., 1935, 200, 746—748; cf. A., 1934, 991).— λ -Bromoundeconitrile, b.p. $150^\circ/$

$2\cdot5$ mm., is transformed by $\text{C}_6\text{H}_{13}\cdot\text{MgBr}$ in Et_2O into α -bromoheptadecan- λ -one, m.p. $30\text{--}31^\circ$, converted by KCN in boiling EtOH into λ -keto-octadecanitrile (I), b.p. $205^\circ/1\cdot2$ mm., m.p. $38\text{--}39^\circ$. (I) is hydrolysed by $\text{KOH}\text{--EtOH}$ to γ -ketostearic (ricinic) acid, m.p. $81\text{--}81\cdot5^\circ$ (*Me* ester, m.p. $44\cdot5^\circ$). H. W.

Possibility of rupture of the carbon chain in derivatives of succinic acid. K. VON AUWERS and O. UNGEMACH (Ber., 1935, 68, [B], 349—352).—Treatment of trimethylsuccinanil with 20% $\text{KOH}\text{--MeOH}$ or of trimethylsuccinic anhydride with NH_2Ph in cold C_6H_6 gives trimethylsuccinanilic acid, m.p. $134\text{--}135^\circ$, formulated by analogy, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NHPh}$. The isomeric acid is not formed in more than traces, if at all. Similar observations are made in the prep. of trimethylsuccin-*p*-toluidic acid, m.p. 127° . Treatment of tetramethylsuccinanil, m.p. 88° , with $\text{NaOH}\text{--EtOH}$ affords tetramethylsuccinanilic acid, m.p. about 95° in a preheated bath, which cannot be obtained homogeneous from $(\text{CMe}_2\cdot\text{CO})_2\text{O}$ and NH_2Ph in C_6H_6 . Tetramethylsuccin-*p*-tolil, m.p. $91\cdot5^\circ$, is obtained from the acid and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ and tetramethylsuccin-*p*-toluidic acid from the anhydride and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ in cold C_6H_6 . $(\text{CMe}_2\cdot\text{CO}_2\text{H})_2$ is transformed by SOCl_2 into $(\text{CMe}_2\cdot\text{CO})_2\text{O}$. α -Hydroxy- $\beta\beta$ -dimethylsuccinic anhydride and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ in C_6H_6 afford α -hydroxy- $\beta\beta$ -dimethylsuccin-*p*-toluidic acid, m.p. $166\text{--}167^\circ$ (the isomeric acid does not appear to be formed), which passes when heated into α -hydroxy- $\beta\beta$ -dimethylsuccin-*p*-tolil, m.p. 134° . Fission of the C chain is not observed when any of these compounds is heated with boiling conc. alkali; the behaviour of hydroxy-trimethylsuccinic acid (A., 1934, 292) is exceptional.

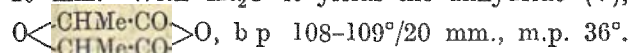
Multiple condensation of fumaric and maleic acids with ethylene glycol. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1935, 10, 17—26; cf. A., 1929, 1165).— $(\text{CH}_2\cdot\text{OH})_2$ reacts slowly with maleic acid (I) at $120\text{--}126^\circ$; above 130° (I) yields fumaric acid (II), which reacts still more slowly. ZnCl_2 catalyses both reaction and isomerisation of (I). The products, of general formula

$\text{H}[\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}]_n\text{H}$, have m.p. from 50° to 95° , according to temp. and duration of reaction; from (I), $n=3$ to 6, and from (II), 5 to 8.

E. W. W.

Dilactic [oxidodi- $\alpha\alpha'$ -propionic] acids. P. VIELES (Ann. Chim., 1935, [xi], 3, 143—224).—Successive treatments of Na in Et_2O with $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ and $\text{CHBrMe}\cdot\text{CO}_2\text{Et}$ yield a mixture of Et_2 dilactates (I), $\text{O}(\text{CHMe}\cdot\text{CO}_2\text{Et})_2$, hydrolysed with partial isomerisation by $\text{NaOH}\text{--EtOH}$ to a mixture of the corresponding acids which can be separated through their Mg salts. More advantageously, (I) is converted by conc. aq. NH_3 into dl- (II), m.p. 184° , and meso- (III), m.p. 136° , -dilactdiamide, separable by EtOH . The action of alkali on (I) or (III) furnishes solely dl-dilactic acid (IV), m.p. 112° , whereas with *N*- H_2SO_4 at 100° (II) affords (IV) and (III) gives mesodilactic acid, m.p. 72° . Treatment of (I) with NH_2Ph at 170° and of the product with EtOH affords dl-, m.p. 168° , and m.p. $124\text{--}126^\circ$, -dilactdianilide; dl-, m.p. 179° .

and meso-, m.p. 145°, *-dilactdi-p-toluidides* are obtained similarly. (IV), conveniently obtained by treatment of (I) with a large excess of NaOH, passes when distilled under atm. pressure into MeCHO, CO, CO₂, C₂H₄, and H₂O, and is largely unchanged at 20 mm. With Ac₂O it yields the anhydride (V),



With PCl₅ at room temp. it gives *dilactyl dichloride* (IV), b.p. 85°/20 mm. *Et*₂, b.p. 124·5°/21 mm., and *Me*₂, b.p. 113—114°/21 mm., *dilactate*, from (IV), the alcohol, and H₂SO₄ or, preferably, from (VI) and the alcohol, are described. The Na₂, K₂, (NH₄)₂, and Mg (+6H₂O) salts have been prepared. (II) is converted by heat into *dl*-dilactimide, m.p. 122°, which is also obtained from (III); (I) is transformed by N-H₂SO₄ into (IV). The Na, Ag, and Cu derivatives are described. (IV) appears resolvable into its optical antipodes by fractional crystallisation of the strychnine or brucine salts, but the readiest method of preparing the optically active acids consists in utilising the spontaneous resolution of (II) in all solvents studied; only in H₂O at low temp. is a hydrated *racemate* deposited. This is effected by slow evaporation at 40° of a saturated solution of (IV) containing nuclei of the active amides or by cooling a solution of (IV) saturated at 80° to 40—50° and seeding with either the *d*- or *l*-amide. *d*- and *l*-*Dilactdiamide* have m.p. 184°; [α] is quoted for various lines, temp., and concns. The crystals do not exhibit hemihedral faces. When heated at the lowest temp. necessary for evolution of NH₃ they yield (V). *d*- and *l*-*Dilactic acid* have m.p. 88°, [α]_D¹⁷ ± 126·8° in H₂O. With Ac₂O they give *anhydride*, b.p. 108—110°/20 mm., m.p. < 36°, [α]_D¹⁶ ± 18·57° in C₆H₆ (with inversion of sign). The *Et*₂ esters of same sign as acids (prep. from anhydride and EtOH, since H₂SO₄ causes racemisation) have b.p. 123—124°/20 mm., [α]_D¹⁶ ± 109·27°. The Na, [α]_D ± 84·1°, and Mg (+3H₂O), [α]_D¹⁶ ± 20·7°, salts are described. (III) is not transformed by Ac₂O into an anhydride; this property enables traces of (IV) to be removed readily from (III). The *Et*₂ ester, Na₂, K₂, (NH₄)₂, and Mg (+3H₂O) salts of (III) are described. H. W.

Tartaromanganic salts. G. LEJEUNE (Compt. rend., 1935, 200, 321—323).—When MnO₂ is added to a solution of Li or K tartrate a complex which liberates I from KI crystallises. With NH₄ tartrate two complexes are obtained in which Mn is bi- and tri-valent, separated by their solubilities in C₅H₅N.

H. D.

Reactions of methyl Δ^β-propene-ααβ-tricarboxylate. Three-carbon ring-chain prototropy involving a simple cyclopropane ring. J. W. (J.C.S., 1935, 188—194; cf. A., 1925, i, 916, 1926, 1927).—With conc. HCl Me Δ^β-propene-ααβ-tricarboxylic acid (I) [triimide, m.p. 238° (decomp.); (II) is hydrolysed (MeOH-KOH) to a Me₁ ester, m.p. 169°]. (I) with conc. HCl in AcOH at room temp. (3 days) gives Me α-bromo-*n*-propane-ααβ-tricarboxylate (III) (cf. A., 1934, 1219), which with CHNa(CO₂Me)₂ in MeOH gives Me₅ *n*-butane-ααβδδ-pentacarboxylate

(IV), m.p. 88° (cf. A., 1933, 935) [hydrolysed (HCl) to *n*-butane-αβδ-tricarboxylic acid (cf. J.C.S., 1906, 89, 1642)], and a mixture of unsaturated esters, b.p. 120—140°/1 mm., which with HBr as above gives a product (V), m.p. 45°, from which (III) and Me β-bromo-*n*-propane-ααβ-tricarboxylate (VI), m.p. 55° (β-iodo-ester, a liquid), are isolated. (III) with MeOH-KOH at 100° gives (II). (I) with HBr (10 days) also gives (V), which is not dimorphous with (III), and is not a result of the "reverse" addition of HBr to (I), because pure (I) with HBr gives only (III). (VI), a constituent of (V), is here obtained by the normal addition of HBr to the Δ-ester. (III) with boiling MeOH-AgOAc gives (II), also obtained from (III) with NaOMe in Et₂O at room temp., which suggests that cyclisation of (I) may occur through the OMe-compound rather than as a result of a ring-chain prototropic change. The Et₃ ester of (II) (A., 1884, 991), which does not reduce KMnO₄ or react with O₃, is rapidly converted by boiling MeOH-NaOMe into an ester which with O₃ affords CH₂O. This is best explained by postulating a ring-chain prototropic change catalysed by alkoxide ions. (I) with boiling MeOH containing NaOMe (1 mol.) gives Me₆ cyclohexane-1:1:2:4:4:5-hexacarboxylate (VII), m.p. 181° (after two Michael condensations), and an unsaturated residue [which contains (I)], which with HBr in AcOH at room temp. (4 days) gives a *stereoisomeride* (?), m.p. 125—126°, of (VII). (VII) is hydrolysed (boiling conc. HCl) to cyclohexane-1:2:4:5-tetracarboxylic acid, m.p. 217° (decomp.). (Me ester, m.p. 88°, which may be a mixture of stereoisomerides), dehydrogenated (Se at 310°) to pyromellitic acid. The evidence suggests that in the triple tautomeric system Δ^α-ester ⇌ Δ^β-ester ⇌ cyclopropane derivative, the equilibrium point is located mainly with the ring compound. (IV) (Na derivative) with CH₂I·CO₂Me in dry boiling MeOH gives Me₆ *n*-pentane-αβγδεε (or αβδδεε)-hexacarboxylate, b.p. about 240°/4 mm., which with boiling conc. HCl affords *n*-pentane-αβγδ (or αβδδ)-tetracarboxylic acid, m.p. 204—205° [Ba salt + 4H₂O; Me₄ ester, b.p. 180°/0·8 mm., which undergoes a Dieckmann reaction to give Me₃ cyclohexanonetricarboxylate, a gum]. Me α-bromo-*n*-propane-ααβ-tricarboxylate with AgOH in boiling MeOH gives only Me₃ *n*-propane-ααβ-tricarboxylate.

J. L. D.

Propene-ααβ-tricarboxylic acids. R. MALACHOWSKI and W. CZORNODOLA [with J. ADAMICZKA] (Ber., 1935, 68, [B], 363—371; cf. A., 1934, 757).—Et₃ propane-ααβ-tricarboxylate, b.p. 146—147°/10 mm., is converted by Br in CCl₄ into Et₃ α-bromo-propane-ααβ-tricarboxylate (I), b.p. 160—162°/7 mm. [corresponding Me₃ ester (II), b.p. 147—150°/8 mm.]. (I) or (II) with K₂CO₃ or Na₂CO₃ affords mainly the saturated ester. Boiling C₅H₅N, quinoline, or, less satisfactorily, NPhEt₃ causes removal of HBr, but the double linking becomes displaced and the product contains the saturated ester in considerable amount. Et₃ Δ^α-propene-ααβ-tricarboxylate (III), b.p. 154·0—154·5°/8 mm. (corresponding Me₃ ester, b.p. 141°/8 mm.), is obtained in 70% yield by the condensation of COMe·CO₂Et with CH₂(CO₂Et)₂ in presence of Ac₂O and anhyd. ZnCl₂. Attempts to hydrolyse (III) to the corresponding acid were fruitless. Treatment

of (III) with C_5H_5N causes isomerisation, and distillation of the equilibrium mixture thus obtained affords a const.-boiling mixture from which, by hydrolysis with $Ba(OH)_2$, Δ^2 -propene- $\alpha\beta$ -tricarboxylic acid (IV), m.p. 129°, is isolated. Ozonisation of (IV) yields CH_2O . When heated above its m.p. (IV) affords CO_2 and itaconic acid. Et_2 Δ^2 -propene- $\alpha\beta$ -tricarboxylate (V), b.p. 148.0—148.5°/8 mm., is prepared from EtI and the Ag salt of (IV). Acid hydrolysis of (III) and (V) gives no insight into their constitution since itaconic acid is produced in each case. Definite products of ozonolysis could not be isolated although the analogously constituted Et citraconate gives $COMe \cdot CO_2Et$ and Et itaconate yields $CO_2Et \cdot CO \cdot CH_2 \cdot CO_2Et$ [p-nitrophenylhydrazone, m.p. 148.5° (corr.)]. (III) and (V) are differentiated by the addition of $CHNa(CO_2Et)_2$ in absence of EtOH and presence of Et_2O , whereby (III) affords Et_5 β -methylpropane- $\alpha\beta\gamma\gamma$ -pentacarboxylate, b.p. 220—221°/8 mm., hydrolysed with difficulty by boiling conc. HCl exclusively to β -methyltricarballic acid, m.p. 164—165°, whereas (V) yields Et_5 butane- $\alpha\beta\delta\delta$ -pentacarboxylate, b.p. 223—224°/7 mm., hydrolysed to butane- $\alpha\beta\delta$ -tricarboxylic acid (VI), m.p. 121°. If condensation is effected in C_6H_6 at 80° either ester finally yields (VI) exclusively. H. W.

α -Sulphoacrylic acid. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 54, 200—205).— $CH_2=CH \cdot CO_2NH_4$ reacts with $(NH_4)_2SO_3$ in H_2O at 25° to give α -sulphoacrylic acid + $2H_2O$ (I), m.p. 87—88°, and + H_2O [$K + H_2O$ (II), KH , TI , and $NHPh_2$, m.p. 152—158° (cryst. data by TERPSTRA), salts], isolated as its Ba salt + $5H_2O$ (III). With K_2SO_3 in H_2O at 100° (II) affords the K salt, + $2H_2O$, of $\alpha\beta$ -disulphopropionic acid. With Br at 100° (III) gives Ba β -bromo- α -sulphoacrylate + H_2O [quinine salt + $2H_2O$, m.p. 211° (decomp.)]. (II) with cold $KMnO_4 \cdot Na_2CO_3$ gives a quant. yield of $K_2C_2O_4$ and K_2SO_4 . (I) with PCl_5 gives the dichloride, b.p. 111—113°/25 mm., converted by moist air into α -chlorosulphonylacrylic acid, m.p. 115°. J. W. B.

Kinetic investigation of the reaction between glutathione and methylglyoxal. J. O. GRIŠAVIČIUS and P. A. HEYFETZ (Biochem. Z., 1935, 276, 190—197).—The reaction between AcCHO and reduced glutathione proceeds in neutral aq. solution rapidly to an equilibrium which is readily displaced by addition of I, by dilution, etc. The reactions are also greatly retarded in acid solution. With varying initial concns. of reactants, 1 mol. of each is involved.

P. W. C.

Compounds of dimethylglyoxime with cobaltous chloride. D. C. SEN and P. RAY (J. Indian Chem. Soc., 1934, 11, 899—904).—The green salt obtained from $CoCl_2 \cdot 6H_2O$ and dimethylglyoxime (Feigl and Rubinstein, A., 1924, 1, 20) liberates I from acidified KI and H_2 with Zn; a saturated solution of it gives a yellow-brown cryst. chlorohydroxydimethylglyoximecobalt, OH replacing Cl. The green compound contains Co^{III} , whilst Thilo's red compound (A., 1931, 938) contains Co^{II} ; the black compound of Dubsky and Brychta (A., 1929, 543) is the green compound mixed with hydrolysis products.

F. R. S.

Ethylenic ketones obtained by dehydrating the corresponding ketols. J. COLONGE (Bull. Soc. chim., 1935, [v], 2, 57—63).— $\beta\epsilon\theta$ -Trimethyl- Δ^4 -nonen- δ -one (cf. A., 1928, 396) gives a pyrazoline, b.p. 129—131°/19 mm. The ketol derived from $COMePr^2$ when distilled with I gives $\beta\epsilon\zeta$ -trimethyl- Δ^5 -hepten- γ -one, b.p. 188—190°/750 mm. (pyrazoline, b.p. 112—114°/19 mm., converted by $PhNCO$ into a compound, m.p. 103°). Similarly prepared are $\beta\epsilon\zeta\zeta$ -pentamethyl- Δ^5 -hepten- γ -one, b.p. 91°/17 mm. (cf. A., 1931, 461) (oxime, m.p. 125°; pyrazoline, b.p. 119—120°/21 mm., converted by $PhNCO$ into a compound, m.p. 118°), reduced (Na—EtOH) to $\beta\epsilon\zeta\zeta$ -pentamethylheptan- γ -ol, b.p. 107°/20 mm., and $\gamma\delta\eta$ -trimethyl- $\gamma\eta$ -diethyl- Δ^4 -nonen- δ -one, b.p. 157—158°/28 mm. The mixed ketol obtained from fluorenone (I) and pinacolin with HCO_2H gives α -fluorenylidene- $\gamma\gamma$ -dimethylbutan- β -one, m.p. 76°. Similarly, the ketol from (I) and $COEtBu^v$ with HCO_2H gives β -fluorenylidene- δ -methylpentan- γ -one, m.p. 103°. J. L. D.

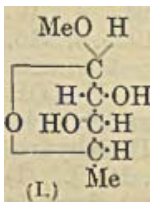
Nomenclature of the α - and β -sugars. H. S. ISBELL (J. Chem. Educ., 1935, 12, 96).—The rates of oxidation of sugars by aq. Br show that when the glycosidic OH lies in the same direction as the O forming the ring the sugar reacts with aq. Br more slowly than when the OH is directed away from the ring. The following rule is proposed. "When the O ring lies to the right, as in *d*-glucose, the more dextrorotatory member of the α - β pair shall be designated α , and the less, β ; when the O ring lies to the left, as in *l*-glucose, the more laevorotatory member shall be designated α , and the less, β ."

L. S. T.

Specificity of hydroxyl groups in sugars. T. LIESER and R. SCHWEIZER (Naturwiss., 1935, 23, 131).—Individual OH groups of sugars undergo the xanthate reaction according to experimental conditions. The view that experimental refinements can lead to a graduated substitution of OH and that particular reagents or circuitous methods are not essential for partial substitution is strengthened by the direct prep. of methylglucoside 2:6-dibenzoate, 2-methylglucosemercaptal 6-benzoate, glucosemercaptal 6-benzoate, and their derivatives. H. W.

Mechanism of carbohydrate oxidation. XVII. Preparation and structure of α -methyl-*l*-arabinomethylloside. D. R. SWAN and W. L. EVANS (J. Amer. Chem. Soc., 1935, 57, 200—202; cf. A., 1934, 173).—Ca rhamnonate and H_2O_2 - Fe^{III} give a syrup, which with HCl - $EtSH$ affords an 18% yield of *l*-arabinomethyllosediethylmercaptan, m.p. 109°, converted by $HgCl_2$ - $MeOH$ into a mixture of α - and β -methyl-*l*-arabinomethyllosides (I), $[\alpha]_D^{25}$

—129.2° in $CHCl_3$, methylated (Me_2SO_4 - $NaOH$ - CCl_4) to 2:3-dimethylmethyl-*l*-arabinomethylloside, b.p. 60—65°/6 mm.; this is hydrolysed (2% H_2SO_4) to 2:3-dimethyl-*l*-arabinomethylloside, b.p. 97—99°/6 mm., $[\alpha]_D^{25}$ -43.8° in $CHCl_3$, which with HNO_3 affords (+)-dimethoxysuccinic acid. (I) shows rapid hydrolysis of γ -glucosides, which, since it cannot have a pyranose structure, confirms the ring-structure of Haworth *et al.*



Micro-chemical analysis of monosaccharides. R. FISHER and W. PAULUS (Arch. Pharm., 1935, **273**, 83—96).—Details are given for micro-detection of monosaccharides. The following derivatives are characteristic, the m.p. given being those determined under the microscope under prescribed conditions. Mannose- (I) -phenylhydrazones*, m.p. 201°. *p*-Bromophenylhydrazones: arabinose (II), m.p. 165—166°; (I), m.p. 206—208°; galactose (III), m.p. 163—164°. Xylose- (IV) -*m*-nitrophenylhydrazones*, m.p. 164°. *o*-Nitrophenylhydrazones: (II), m.p. about 180°; (III), m.p. 174—176°; fructose (V), m.p. 162°. (II) benzoylhydrazones*, m.p. 211°. *p*-Bromobenzoylhydrazones: (II), m.p. 216—217°; rhamnose (VI), m.p. 191°; (III), m.p. 214—215°. *p*-Tolylhydrazones: (VI), m.p. 166—169°; (I), m.p. 200°. *o*-Tolylhydrazones* of (III), m.p. 182°. Phenylsazones: (II), m.p. 162°; (IV), m.p. 160°; (VI), m.p. about 184°; glucose (VII), (I), and (V), m.p. 224°; (III), m.p. about 192°. *p*-Bromophenylsazones: (VI), m.p. 216—218°; (VII) and (V), m.p. 222°. (VII) *p*-nitrophenylsazones*, m.p. 257°. Glucuronic acid can be detected as thiosemicarbazone, m.p. 223°; it interferes with all the above reactions except those marked *. Glucosides and binary mixtures of (I)—(VII) can be analysed. R. S. C.

3:6-Dimethylglucose. D. J. BELL (J.C.S., 1935, 175—176).— α - and β -Methylglucoside (1 mol.) with HBO_2 (2 mols.) in dry boiling COMe_2 give α -, $[\alpha]_D^{25} +84.4^\circ$, and β -methylglucosidediboric acid, $[\alpha]_D^{25} -60.4^\circ$, respectively (cf. A., 1932, 723) (only one of the HBO_2 complexes can be titrated with alkali), which with $\text{MeI-Ag}_2\text{O}$ in COMe_2 at 35° gives a mixture of Me 3:6- and 2:6-dimethylhexosides (I), b.p. 150°/0.4 mm., from which 3:6-dimethyl- β -methylglucoside 2:4-dibenzoate (II) is isolated after benzylation in $\text{C}_5\text{H}_5\text{N}$. The α -isomeride gives no cryst. Bz derivative. (II) is debenzoylated (cf. A., 1934, 872) to β -methyl-3:6-dimethylglucoside, a syrup, $[\alpha]_D^{25} +55.4^\circ$ in MeOH, hydrolysed to 3:6-dimethyl- α -glucose, m.p. 113—116°, $[\alpha]_D^{25} +102.5^\circ$ (initial) to $+61.52^\circ$ in H_2O . The debenzoylated residues from the crystallisation of (II) with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ afford β -methyl-2:6-dimethylglucoside 3:4-di-*n*-toluenesulphonate (cf. A., 1932, 500). J. L. D.

Preparation of crystalline *d*-mannose and of crystalline *d*-ribose. P. A. LEVENE (J. Biol. Chem., 1935, **108**, 419—420).—Details of the prep. of cryst. *d*-mannose from vegetable ivory meal (hydrolysis with 75% H_2SO_4), and *d*-ribose from pure, ash-free guanosine (hydrolysis with 0.05*N*- H_2SO_4) are given, an essential condition being the production of a colourless hydrolysate. J. W. B.

Preparation of glucosidodihydroxyacetone penta-acetate. L. C. KREIDER and W. L. EVANS (J. Amer. Chem. Soc., 1935, **57**, 229).—This compound, m.p. 103° (corr.), $[\alpha]_D^{25} -25.2^\circ$ in CHCl_3 [*p*-nitrophenylhydrazones, m.p. 187° (corr.), $[\alpha]_D^{25} -129.8^\circ$ in CHCl_3], is prepared from glucosidyl bromide penta-acetate and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OAc}$. R. S. C.

Glucosidodihydroferulic acid. N. K. RICHTMYER and R. M. HANN (J. Amer. Chem. Soc., 1935, **57**, —).—Use of Pd-black for hydrogenation in acid of tetra-acetylglucosidoferulic acid gives tetra-

acetyl- β -*d*-glucosidodihydroferulic acid, m.p. 155° (corr.), $[\alpha]_D^{25} -25^\circ$ in CHCl_3 , deacetylated by NaOMe to the acid, m.p. 179—180° (corr.), $[\alpha]_D^{25} -56.9^\circ$ in H_2O .

R. S. C.

Polysaccharides synthesised by micro-organisms. I. Molecular structure of mannocarlose produced from glucose by *Penicillium Charles II*, G. Smith. W. N. HAWORTH, H. RAISTRICK, and M. STACEY (Biochem. J., 1935, **29**, 612—621).—Mannocarlose (I) $[\alpha]_D^{25} +66^\circ$ in H_2O , is separated from the reaction products of *P. Charles II*, G. Smith, on Czapek-Dox-glucose solution. Complete hydrolysis of (I) gives only *d*-mannose (II); the mol. wt. of (I) determined by η measurements = 8—9 (I) units. That (I) consists of mannopyranose units linked at positions 1 and 6 is shown by the isolation, by fractional distillation, of 2:3:4-trimethylmethylmannopyranoside, b.p. 130—133°/0.08 mm., $[\alpha]_D^{25} +58^\circ$ in H_2O , by hydrolysis of the completely methylated (I), m.p. 95—100°, $[\alpha]_D^{25} +102^\circ$ in CHCl_3 , with conc. HCl at 15° for 4 days and subsequent glucoside formation, and also by the production of 2:3:4-trimethylmannopyrano- δ -lactone (II), b.p. 138—140°/0.04 mm., on oxidation of 2:3:4-trimethylmannopyranose, m.p. 102—103°, $[\alpha]_D^{25} +7^\circ$ in H_2O , with Br. (II) on oxidation with HNO_3 and subsequent esterification gave Me_2 meso-dimethoxysuccinate; treatment of the residue with NH_2Me gave meso-dimethoxysuccinmethylamide and *d*-arabotrimethoxyglutarmethylamide. 2:3-Dimethylmethylmannopyranoside (IV), b.p. 155—160°/0.08 mm., $[\alpha]_D^{25} +64^\circ$ in H_2O , and 2:3:4:6-tetramethylmethylmannopyranoside are also isolated from the hydrolytic products of completely methylated (I). (IV) gives 2:3-dimethylpyranose, $[\alpha]_D^{25} +16^\circ$ in H_2O . H. D.

Polysaccharides. XIX. Molecular structure of waxy maize starch. W. N. HAWORTH, E. L. HIRST, and (Mrs.) M. D. WOOLGAR (J.C.S., 1935, 177—181).—Waxy maize starch (I) (prep. described) contains a preponderance of amylose as distinct from amylopectin, is sol. in hot H_2O , gives a reddish-purple colour with I, and is hydrolysed (enzyme) at the same rate as potato starch. (I) in H_2O with EtOH gives "prepared" starch (II) which is sol. in H_2O and has $[\alpha]_D^{25} +212^\circ$ in H_2O . (II) in AcOH-Cl_2 with $\text{Ac}_2\text{O-SO}_2$ at 20—55° gives a triacetate (III), $[\alpha]_D^{25} +167^\circ$ in CHCl_3 (apparent mol. wt. 37,000), which gives no colour with I; with Ac_2O in $\text{C}_5\text{H}_5\text{N}$, (II) gives (III) (apparent mol. wt. 35,000). (III) prepared by the $\text{C}_5\text{H}_5\text{N}$ method is hydrolysed by 0.5% NaOH-EtOH at room temp. to (I). Either (III) with Me_2SO_4 in COMe_2 -30% NaOH at 55° (many treatments) gives a OMe-derivative from which a substance (IV), m.p. 153—156° (previous softening), which closely resembles the methylated amylose fraction of potato starch (cf. A., 1928, 1360; 1932, 1116) is isolated. Hydrolysis (fuming HCl at 0°) of (IV) followed by treatment of the product with boiling 3% HCl-MeOH gives tetramethylmethylglucoside (4.7%), which corresponds with a chain length of about 29 α -glucopyranose units in (I), similar to that which obtains in methylated amylose and amylopectin from potato starch, and some trimethylmethylglucoside. J. L. D.

VI. Water-soluble polysaccharide

European larch. F. C. PETERSON, M. MAUG-
AN, and L. E. WISE (Cellulosechem., 1934, 15, 109—
114).—3% of a H₂O-sol. polysaccharide is obtained
from European larch (*Larix decidua*, Mill.) by
extraction with cold H₂O, purification by the tannin-
Pb(OAc)₂ method, and removal of ash by electro-
lysis. Uronic acids, OMe, and mannose are
absent, and the product contains 11.63% of anhydro-
arabinose (furfuraldehyde, thiobarbituric acid, and
diphenylhydrazine methods) and 81.95% of anhydro-
galactose (van der Haar-Tollens method). It is thus
[(C₅H₈O₄)(C₆H₁₀O₅)₆]_n and is identical with the poly-
saccharide from West and East American larches.
The mol. wt. (by I val.) is 8000 and the Cu reduction
(Allihn) 0.06 g. Cu₂O per g. A. G.

Nitration of starch. J. GRARD (Compt. rend.,
1935, 200, 410—411).—Starch and H₂O heated to
150° (autoclave) yield a plastic mass which is pressed
into fine threads, dried, and converted by HNO₃-
H₂SO₄ into an unstable nitro-product. E. W. W.

Action of liquid bromine on cellulose. E.
BEUTEL and A. KUTZELNIGG (Monatsh., 1935, 65,
205—212).—Contrary to earlier observations, liquid
Br attacks and dissolves cellulose, giving a viscous,
reddish-brown solution (I) and HBr. Reaction takes
place suddenly, after keeping for a few min. at 100°
or several weeks at room temp. If too little liquid Br
is present a black mass, sol. in alkali with a brown
colour, is formed. By treating (I) with H₂O a brown
plastic substance, sol. in org. solvents, is obtained.
By dry distillation of this a light brown, fuming oil
distils at 58—107° and a charred residue is left.
Keratin is also completely sol. in excess of liquid
Br. M. S. B.

**Compounds of sulphur dioxide with various
amines.**—See this vol., 447.

γ -Chloro-amines and their reactions. C. MAN-
NICH and E. MARGOTTE (Ber., 1935, 68, [B], 273—
278).— α -Dimethylaminobutan- γ -ol, obtained in 85%
yield by reduction of the keto-base with Na-Hg,
is transformed by SOCl₂ in CHCl₃ into γ -chloro- α -
dimethylaminobutane (I), b.p. 38—39°/10 mm. (hydro-
chloride, m.p. 168°). γ -Chloro- α -piperidinobutane (II),
b.p. 90—91°/11 mm. (hydrochloride, m.p. 208°),
is obtained similarly in 80% yield. (I) is transformed
by boiling NPhMe₂ into α -dimethylaminobutene, b.p.
89—91° (very hygroscopic hydrochloride; methiodide,
m.p. 151°). (II) passes when boiled into α -piperidino-
butene, b.p. 59—61°/12 mm. (picrate, m.p. 91°).
(I), NH₂Ph, and Cu-bronze at 150° afford γ -anilino- α -
dimethylaminobutane, b.p. 155—157°/14 mm. [picrate,
m.p. about 157° (decomp.)]. γ -Anilino- α -piperidino-
butane (picrate, m.p. 139°) has b.p. 191—193°/11 mm.
NHMe₂, Cu-bronze, and (I) in EtOH-H₂O at 150°
give $\alpha\gamma$ -tetramethyldiaminobutane, b.p. 55—56°/12 mm.
(dimethiodide, m.p. >250°). $\alpha\gamma$ -Dipiperidinobutane,
b.p. 150—153°/11 mm., yields a picrate, m.p. about
191° (decomp.). α -Piperidino- γ -dimethylaminobutane,
b.p. 107—108°/12 mm., yields a picrate, m.p. 181°,
platinichloride, m.p. about 225° (slight decomp.),
and aurichloride, m.p. about 187° (decomp.). γ -Methyl-
amino- α -dimethylaminobutane, b.p. 55—56°/14 mm.

[picrate, m.p. about 186° (decomp.)], and α -piperidino-
 γ -methylaminobutane, b.p. 104—105°/12 mm.
[aurichloride, m.p. about 169° (decomp.)], are described.
(I), NH₃-EtOH, and Cu-bronze at 130—140° afford
 γ -amino- α -dimethylaminobutane, b.p. 55°/16 mm.
[aurichloride, m.p. about 195° (decomp.)]; picrate,
m.p. about 181° (decomp.); the Bz compound, b.p.
181°/16 mm., gives a hygroscopic hydrochloride and
hydrobromide which, like the free base, have powerful
anæsthetising action], and di-(α -dimethylamino- γ -
butyl)amine, b.p. 138°/16 mm. [aurichloride, m.p.
about 183° (decomp.)]; dihydrochloride, m.p. 198—199°,
of the Bz derivative]. γ -Amino- α -piperidinobutane,
b.p. 102—104°/14 mm. [picrate, m.p. about 141°
(decomp.)], and di-(α -piperidino- γ -butyl)amine, b.p.
215—216°/14 mm. [aurichloride, m.p. about 205°
(decomp.)]; picrate, m.p. 189°, are described. (I)
and OH·CH₂·CH₂·NH₂ at 140° yield α -dimethylamino-
 γ - β -hydroxyethylaminobutane, b.p. 130—132°/11 mm.
(hygroscopic hydrochloride, m.p. 172°). (I) and
CHNa(CO₂Et)₂ in boiling EtOH yield Et₂ γ -dimethyl-
amino- α -methyl-n-propylmalonate, b.p. 120—122°/14
mm. (yield 72%), which does not give cryst. salts.
Et₂ γ -piperidino- α -methyl-n-propylmalonate, b.p. 145—
147°/0.5 mm., is hydrolysed by aq. Ba(OH)₂ to the
corresponding acid, m.p. 156° (Ba salt). With
somewhat greater difficulty (I) is transformed into
Et γ -dimethylamino- α -methyl-n-propylacetoacetate, b.p.
130—135°/15 mm., converted by 3% KOH at room
temp. into α -dimethylamino- γ -methyl-n-hexan- ϵ -one,
b.p. 80—83°/11 mm. (semicarbazone hydrochloride,
m.p. 188°). (I) and KCN in boiling H₂O give γ -di-
methylamino- α -methylpropionitrile, b.p. 75.78°/13 mm.
(hydrochloride, m.p. 135°). NHPH·NH₂ and (I)
react very vigorously at 140° giving NH₃, NH₂Ph,
and an unstable base C₁₂H₁₄N₂, b.p. 140—142°,
probably an indole derivative. H. W.

Thermal behaviour of betaines. R. KUHN and
F. GIRAL (Ber., 1935, 68, [B], 387—395).—Betaines
with long C chains pass almost quantitatively into
the isomeric esters when heated above their m.p.,
thus resembling α -betaines (Willstätter *et al.*, A.,
1904, i, 235, 560). Salts of the corresponding un-
saturated acids or lactones are formed in traces if
at all. Since it is very improbable that conditions
maintain which favour intramol. isomerisation it
appears that very preponderatingly Me groups are
transferred from N to the O of neighbouring mols.

ξ -Aminopentadecic acid hydrochloride (I) (Kuhn
et al., A., 1934, 876) is converted by successive treat-
ment with AgNO₃-HNO₃ in EtOH and conc. NH₃
into ξ -aminopentadecic acid (II), m.p. 175—176°
(nitrate, m.p. 86°; perchlorate, m.p. 69—70°, decomp.
about 180°; platinichloride, decomp. 202° after
darkening at 195°; cuprichloride, decomp. 220° after
darkening at 200°). (II) gives a sparingly sol. sul-
phate in N-H₂SO₄ but no ppts. with saturated solu-
tions of HgCl₂, CdCl₂, or SnCl₂ in EtOH [distinction
from (III)]. (I) and EtOH-HCl afford Et ξ -amino-
pentadecate hydrochloride, m.p. 149—150°, whence
(Ag₂O in EtOH) Et ξ -aminopentadecate, m.p. 79—
81°. ξ -Trimethylpentadecabetaïne trihydrate (III)
(*loc. cit.*) loses 3Me as MeI during the determination
of NMe and readily loses 3H₂O at 100°/high vac.,

or slowly over CaCl_2 at $20^\circ/0.5$ mm.; the anhyd. material absorbs $3\text{H}_2\text{O}$ when exposed to air. (III) affords a *nitrate*, m.p. 185° , *hydrochloride*, m.p. $237-238^\circ$, *mercurichloride*, m.p. 168° , and a *compound*, $2\text{C}_{18}\text{H}_{33}\text{O}_2\text{N}\cdot\text{CdCl}_2$, m.p. $182-183^\circ$. When slowly heated/ 15 mm. (III) is transformed into *Me* ξ -*dimethylaminopentadecoate*, m.p. $28-29^\circ$ (*aurichloride*, m.p. $89-90^\circ$; *platinichloride*, m.p. $129-130^\circ$; *picrate*, m.p. $87-88^\circ$; *picrolonate*, m.p. $100-101^\circ$; *hydrochloride*, m.p. $146-147^\circ$). Dihydrocivetoneisoxime with conc. HCl at $180-190^\circ$ gives π -aminoheptadecoic acid hydrochloride (IV), m.p. $154-155^\circ$, from which π -aminoheptadecoic acid (V), m.p. 176° , is best obtained by repeated treatment with boiling, dil. EtOH . (V) yields a *perchlorate*, m.p. $76-77^\circ$, decomp. about 180° , a *platinichloride*, m.p. 205° (decomp.) after darkening at 190° , *cuprichloride*, m.p. $220-221^\circ$ (decomp.), *sulphate* $3\text{NH}_2\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, m.p. 240° , and a *compound* with CdCl_2 . *Et* π -aminoheptadecoate hydrochloride has m.p. 150° . (IV) is converted by $\text{KOH}\cdot\text{Me}_2\text{SO}_4$ in boiling H_2O into π -trimethylheptadecabetaïne (VI), m.p. $236-237^\circ$ (also $+3\text{H}_2\text{O}$), which yields an *aurichloride*, m.p. $140-141^\circ$, *platinichloride*, m.p. 220° (decomp.), and *mercurichloride*, m.p. $158-159^\circ$. When heated/ 3 mm., (VI) passes into *Me* π -dimethylaminoheptadecoate, m.p. 37.5° (*hydrochloride*, m.p. 155° ; *picrate*, m.p. $93-93.5^\circ$; *picrolonate*, m.p. $108-109^\circ$; *aurichloride*, m.p. 100° ; *platinichloride*, m.p. 134°). H. W.

Labile glutamine peptides.—See this vol., 404.

Amides and spiro-cyclic imides of methane-tetra-acetic acid. H. J. BACKER (Rec. trav. chim., 1935, 54, 194—199).—By the action of the appropriate amine on $\text{C}(\text{CH}_2\cdot\text{COCl})_4$ (this vol., 328) are obtained the *methyl*-, m.p. $209-209.5^\circ$ (*NO*-derivative, explodes at 146.5°), *tert. butyl*-, m.p. 229.5° , and *dimethylamide*, m.p. 187.5° , the *piperidine*, m.p. 168° , *anilide* (I), m.p. 271° [$(\text{NO}_2)_8$ -derivative (II), m.p. 280° (decomp.)], *p-nitroanilide*, decomp., about 300° [gives (II) with abs. HNO_3], *p-toluidide*, m.p. 260° , α -*naphthylamide*, m.p. $283-284^\circ$, *methylanilide*, m.p. 37° (*p-NO*₂-derivative, m.p. $115-125^\circ$, decomp. 137°), *diphenylamide*, m.p. $219-219.5^\circ$ [$(\text{NO}_2)_{16}$ -derivative, m.p. about 175° , decomp. 200°], of methane-tetra-acetic acid. By heating $\text{C}(\text{CH}_2\cdot\text{CO}_2\text{NH}_4)_4$ at 210° is obtained the spiro-*di-imide* $\text{C}(\text{CH}_2\cdot\text{CO})_2\text{NH}$, not melting at 340° (*Ag* derivative); similar thermal decomp. of (I) gives the spiro-*di(phenylimide)*, m.p. 330° [$(\text{NO}_2)_2$ -derivative, decomp. 150°]. J. W. B.

Formation of salts of amidoximes and benzhydroxamic acid. J. V. DUBSKÝ, M. KURAŠ, and J. TRTILEK (Coll. Czech. Chem. Comm., 1935, 7, 1—9).—Benzamidoxime (I) has m.p. 80° ; the substance, m.p. 68° , obtained along with it, is a *compound*, 2(I), PhCN . The following salts are prepared: from (I), $\text{NH}_2\cdot\text{CPh}\cdot\text{NO}\cdot\text{Cu}\cdot\text{OH}$, $+ \text{H}_2\text{O}$ and anhyd., and $(\text{NH}_2\cdot\text{CPh}\cdot\text{NO})_2\text{Ni}$, decomp. $90-125^\circ$; from amygdal-amidoxime (II), 2(II), $\text{Ni}(\text{OH})_2\cdot 2\text{H}_2\text{O}$; from oxaldi-amidoxime, $[\text{OH}\cdot\text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{NH}_2)\cdot\text{NO}]_2\text{Ni}$, $+ 2\text{H}_2\text{O}$; from aminoacetamidoxime (not isolated), $[\text{NH}_2\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{NO}]_2\text{Cu}\cdot\text{H}_2\text{SO}_4$ and another *Cu* salt, and $[\text{NH}_2\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{NO}]_2\text{Ni}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$; from

benzhydroxamic acid, $(\text{OH}\cdot\text{CPh}\cdot\text{NO})_2\text{Fe}\cdot\text{OH}\cdot\text{H}_2\text{O}$ and $(\text{OH}\cdot\text{CPh}\cdot\text{NO})_2\text{Cu}$. R. S. C.

Preparation of normal aliphatic thiocyanates. P. ALLEN, jun. (J. Amer. Chem. Soc., 1935, 57, 198—199).—The following *n*-alkyl thiocyanates are prepared in 83—95% yield from the bromide and KCNS : *amyl*, b.p. $90-91^\circ/16$ mm.; *octyl*, b.p. $141-142^\circ/19$ mm.; *nonyl* (67.3%), b.p. $156-157^\circ/19$ mm.; *decyl*, b.p. $154-155^\circ/15$ mm.; *undecyl*, b.p. $160-161^\circ/10$ mm.; *dodecyl*, b.p. $170-172^\circ/10$ mm.; *tridecyl*, b.p. $173-176^\circ/7$ mm.; *cyclohexyl* (by NH_4CNS ; 31.2%), b.p. $111-112^\circ/16$ mm. R. S. C.

Preparation of diazomethane and its homologues. D. W. ADAMSON and J. KENNER (J.C.S., 1935, 286—289).—An improved prep. of *Me* nitroso- β -methylaminoisobutyl ketone (A., 1933, 598) is described. Many nitrosoketones (I) (revised b.p. listed) are prepared similarly and give diazohydrocarbons (II) when they are distilled with Et_2O containing some Pr^sOH (Bu^sOH for the higher homologues) and 1% $\text{NaOPr}^s\text{-Pr}^s\text{OH}$. (II) are determined as their *p*-nitro- and 3:5-dinitro-benzoates. The following are described: *n*-*amyl p*-nitrobenzoate, b.p. $133^\circ/0.1$ mm.; *crotonyl*, m.p. $50-51^\circ$, and *furfuryl* 3:5-dinitrobenzoate, m.p. $84-86^\circ$. The other nitrobenzoates (listed) are identical with those prepared by Buchner *et al.* (A., 1905, ii, 274), but not with all those of Henstock (A., 1933, 372). The benzoate, nitrobenzoate, and iodide prepared from CH_3EtN_2 contains no *iso*-compounds, which indicates that decomp. of the diazonium ion is initiated or occurs simultaneously with anionic (*e.g.*, OH) attack in the α - or β -position (cf. A., 1934, 874). Equimol. amounts of $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and (I) in EtOH containing K_2CO_3 at room temp. give ethers (listed), mesityl oxide, and N_2 (cf. A., 1933, 598), which suggests that β -naphthoxy-ions more readily co-ordinate covalently with alkyl than with H , as (II) formation occurs only at $60-70^\circ$. The Pr^s ether is homogeneous (cf. A., 1898, i, 592). Vinyl diazomethane in Et_2O in daylight affords pyrazole during 36 hr. following a unimol. decomp. Propenyldiazomethane is much more stable and requires 14 days for an analogous change. J. L. D.

Organometallic compounds. R. GARZULY-JANKE (J. pr. Chem., 1935, [ii], 142, 141—144).—The results of Platz (A., 1934, 1209) are not considered to disagree with the classification of organometallic compounds (Garzuly, "Samml. chem. u. chem.-techn. Vorträge," 29, Stuttgart, 1927), where salts of TIR^I_2 (R =alkyl) are regarded as resembling those of the alkali metals. H. G. M.

Organic salts of titanium. G. CARTERET (Bull. Soc. chim., 1935, [v], 2, 159—160).—The following are described: *Na titanocitrate*, $\text{OH}\cdot\text{C}_3\text{H}_4(\text{CO}_2\cdot\text{TiO}\cdot\text{ONa})$ (easily hydrolysed in 2% solution at $\text{pH} > 7$), *alkali titanolactates* and *titanostearates* ($\text{C}_{17}\text{H}_{35}\cdot\text{CO}_2$)₂ $\text{Ti}(\text{OM})_2$ and $\text{C}_{17}\text{H}_{35}\cdot\text{CO}_2\text{TiO}\cdot\text{OM}$ (M =metal). J. L. D.

Organic compounds of gold. IV. *n*-Propyl compounds. A. BURAWOY and C. S. GIBSON (J.C.S., 1935, 219—223; cf. A., 1934, 877).—Pyridinitrichlorogold with MgPr^sBr gives di-*n*-propylmono-

bromogold (I) (cf. A., 1931, 1043), which with $(\cdot\text{CH}_2\cdot\text{NH}_2)_2$ gives ethylenediaminodi-*n*-propylgold bromide (II) (cf. A., 1932, 1316), converted by HBr into monoethylenediaminotetra-*n*-propyldibromodigold (III), a non-electrolyte, m.p. 110–111° (decomp.). (III) in CHCl_3 slowly gives (II) and (I). (III) explodes when heated, but when boiled with CHCl_3 , it gives monoethylenediaminodi-*n*-propyldibromodigold, decomp. at 140°, in which one Au atom is univalent and 2-covalent, and the other trivalent and 4-covalent. (III) with excess of HBr in CCl_4 gives (I), which with Br (2 mols.) in CCl_4 at room temp. gives mono-*n*-propyldibromogold (IV) $[\text{Pr}^+\text{AuBr}_2]_2$, m.p. 54°, which is much more stable at 18–22° than the analogous Et compound (cf. A., 1934, 877). At 80–85°, (IV) gives Pr^+Br and AuBr in 0.5 hr., and with $\text{KBr}\cdot\text{H}_2\text{O}$, it affords KAuBr_2 and (I). (IV) in $\text{CCl}_4\text{-C}_5\text{H}_5\text{N}$ gives pyridinotribromogold and pyridinodi-*n*-propylmonobromogold, m.p. 61–62° (cf. A., 1931, 78), also obtained from (II) with $\text{C}_5\text{H}_5\text{N}$ in light petroleum. The dipole moment of diethylmonobromogold is $< 1.0 \times 10^{-18}$ e.s.u., which supports the symmetrical structure (A., 1934, 877) previously assigned to this compound, whereas (IV), using a Pt condenser as Ag reacts immediately with (IV), gives a val. of $5\text{--}6 \times 10^{-18}$ e.s.u., which indicates an unsymmetrical structure. A probable structure for (IV) is suggested.

J. L. D.

Polymerisation of cyclohexene. H. I. WATERMAN, J. J. LEENDERTSE, and A. C. TER POOTEN (Rec. trav. chim., 1935, 54, 245–248).—*cyclo*Hexene (I) dissolved in C_5H_{12} in presence of AlCl_3 does not react at -78° , 0° , or 40° . At 70° polymerisation occurs giving a product the fractions of which have been studied before and after hydrogenation. Vals. of n_D^{25} for the hydrogenated product are in agreement with calc. vals. for *cyclo*hexyl compounds of the same mol. wt. Polymerisation occurs in C_5H_{12} at -78° in presence of HCl and 10% AlCl_3 , giving chlorocyclohexene (II) and a mixture of chloropolycyclohexyl compounds (III). (II), with and without the addition of (I), remains unchanged in presence of AlCl_3 in C_5H_{12} at -78° , and (I) in presence of HCl at -78° to 0° in C_5H_{12} does not react. It is inferred that (III) are formed by the addition of HCl to (I) polymerides and not from (II) as an intermediate.

R. S. B.

Polymerisation of cyclohexene in presence of phosphoric oxide. R. TRUFFAULT (Compt. rend., 1935, 200, 406–408).—*cyclo*Hexene at its b.p. polymerises in presence of P_2O_5 to *cyclo*hexyl*cyclo*hexene (80–90%). Amylene and terpenes condense similarly, and C_6H_6 with propylene to form PrPr .

E. W. W.

Normal cyclohexyl sulphite. P. CARRE and D. LIBERMANN (Bull. Soc. chim., 1935, [v], 2, 160–161).—Voss and Blanke's product (cf. A., 1931, 462) is *cyclo*hexene (I), whereas that of Kitasato and Sone (A., 1931, 819) is a mixture of (I) and *cyclo*hexanol, but contains no S, although the latter's crude product was probably mainly *cyclo*hexyl sulphite (II). (II) decomposes when heated/8 mm.

J. L. D.

Internal energy relationships among aromatic carbocyclic substances. IV. Law of distance.

O. SCHMIDT (Ber., 1935, 68, [B], 356–359; cf. this vol., 203).—It is shown mathematically that it is not possible to explain the C–C linking by exchange of electrons as in the case of H_2 and that the only possible scheme is based on Lewis' postulates. H. W.

Action of some catalytic poisons on the hydrogenation of benzene in a liquid medium at room temperature.—See this vol., 456.

Nitration of monobromotoluenes. II. Influence of cresol on the nitration. M. C. GEERLING (Rec. trav. chim., 1935, 54, 235–238).—Nitration of *o*- $\text{C}_6\text{H}_4\text{MeBr}$ (I) with HNO_3 (d 1.52) in presence of 3 : 5-dinitro-*o*-cresol (II) or 2 : 4-dinitrophenol (III) [or in presence of *o*-cresol or PhOH since these are first nitrated to (II) or (III)] occurs smoothly to give exclusively $(\text{NO}_2)_1$ -derivatives, the same proportion of 4- (20%) and 5- NO_2 - (37.4%) derivatives being obtained in each case. This is probably due to the formation of additive compounds of (I) with (II) or (III), the binary m.-p. curve proving the existence of the compound (I)–(II), f.p. 58.7°. J. W. B.

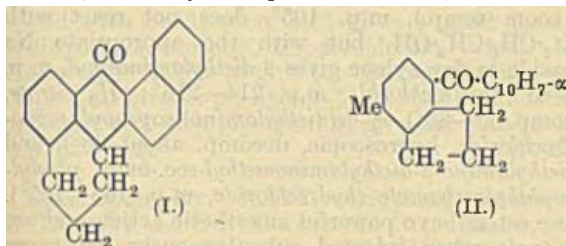
Total asymmetric synthesis by addition of bromine to an ethylenic linking. T. L. DAVIS and R. HEGGIE (J. Amer. Chem. Soc., 1935, 57, 377–379).—2 : 4 : 6-Trinitrostilbene adds Br asymmetrically in right circularly polarised light of 3600–4500 Å; the max. observed α was $+0.022^\circ$, $[\alpha] +0.04^\circ$. The product loses its optical activity when preserved.

R. S. C.

Hydrocarbons derived from phenylmethyl- and phenylethyl-acetic acids. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 108, 409–418).—The Mg compound of $\text{CHMePh}\cdot\text{CH}_2\text{Br}$ (I) (from the alcohol, obtained from the active acid), $[M]_D^{25} -3.98$, and CH_2O and hydrolysis of the product with 90% EtOH containing 2% of conc. HCl gives 1- γ -phenyl-*n*-butyl alcohol, b.p. 85–90°/0.5 mm., $[\alpha]_D^{25} -3.0^\circ$, converted by PBr_3 into the 1-bromide, b.p. 77–80°/1 mm., $[\alpha]_D^{25} -6.93^\circ$, converted (Grignard) into 1- β -phenyl-*n*-butane, $[\alpha]_D^{25} -2.3^\circ$ (A., 1933, 606). Hence (I) must have the structure assigned. Reduction (Grignard) of 1- $\text{CHEtPh}\cdot\text{CH}_2\text{Br}$ (II), $[M]_D^{25} -0.92^\circ$, gives *d*- β -phenyl-*n*-butane, b.p. 71–74°/20 mm., $[\alpha]_D^{25} +1.56^\circ$. The Mg compound of (II) with CO_2 gives 1- β -phenyl-*n*-valeric acid, b.p. 120–128°/0.4–0.5 mm., $[\alpha]_D^{25} -7.43^\circ$, and with CH_2O and hydrolysis affords 1- γ -phenyl-*n*-amyl alcohol, b.p. 86–94°/1 mm., $[\alpha]_D^{25} -1.29^\circ$, converted by PBr_3 into the 1-bromide, b.p. 78–82°/1 mm., $[\alpha]_D^{25} -7.2^\circ$, reduced (Grignard) to γ -phenyl-*n*-pentane, b.p. 38–41°/0.7 mm., α 0° . These results exclude rearrangement during the bromination of the carbinols and thus confirm the configurative relationships previously deduced (*loc. cit.*). All rotations are for the homogeneous liquids. J. W.

Synthesis of methylcholanthrene. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1935, 57, 228–229).—Pyrolysis (Elbs) of α - and β -naphthyl *ar*- α -tetrahydronaphthyl ketones gives hydrocarbons [*e.g.* (I)], m.p. 119° and 270°, respectively. *p*- $\text{C}_6\text{H}_4\text{MeBr}$ gives (Blanc) two ClCH_2 -derivatives, which by treatment with $\text{CHNa}(\text{CO}_2\text{Et})_2$ and subsequent hydrolysis and decarboxylation give an acid, the chloride of which by ring-closure affords a mixture

of two *methylbromohydrindones*, m.p. 154° and 95°, respectively, both yielding (Clemmensen) the same



methylbromohydrindene, b.p. 265—267°. The Grignard reagent therefrom with α -C₁₀H₇·COCl gives the liquid *ketone* (II), which affords (Elbs) methylcholanthrene, the structure of which is thus confirmed.

R. S. C.

Synthesis of condensed polynuclear hydrocarbons by the cyclodehydration of aromatic alcohols. III. Cyclisation of some phenylated alcohols and related olefines. R. O. ROBLIN, jun., D. DAVIDSON, and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 151—159; cf. A., 1934, 642).—Cyclisation of *sec.*-phenylalkyl alcohols is best effected by 90% H₂SO₄, first at 9—10° and then at room temp. for 2 hr. 85% acid or shorter treatment with 90% acid gives much olefines. 7- or 8-Membered rings are not formed. Usually 6-membered rings are formed in preference to or faster than 5-membered. Migration of ethylenic linking must be postulated for some cyclisations reported. The yield of cyclic product is a max. when the OH is at the δ -position relative to the Ph; if it is at the α -position, or if a styrene is the starting material, polymerisation and no cyclisation occurs. Previous and present results are summarised.

The following are prepared; α -phenyl-*n*-butyl alcohol (I), b.p. 137°/21 mm., from PhCHO and MgBuBr; α -phenylpentan- β -ol (impure) (II), b.p. 127°/15 mm. (*phenylurethane*, m.p. 80°), from CH₂Ph·MgCl and Pr·CHO; α -phenyl- γ -methylpentan- β -ol (III), b.p. 132°/15 mm. (*phenylurethane*, m.p. 103°), from CH₂Ph·CHO and MgBu^oBr; α -phenylpentan- γ -ol (IV), b.p. 130°/15 mm., from CH₂Ph·CH₂·CHO and MgEtBr; α -phenyl- γ -methylpentan- γ -ol (V), b.p. 138°/20 mm. (*phenylurethane*, m.p. 94°); Ph·[CH₂]₄·OH (VI), b.p. 137°/14 mm., from Ph·[CH₂]₃·MgBr (VII) and CH₂O or, better, CH₂Ph·CH₂·MgBr and (CH₂)₂O; ϵ -phenylpentan- β -ol (VIII), b.p. 134—135°/16 mm. (*phenylurethane*, m.p. 57°), from (VII) and MeCHO; Ph·[CH₂]₅·OH (IX), from (VII) and (CH₂)₂O or Ph·[CH₂]₄·MgBr (X) and ζ -phenylhexan- β -ol (XI), b.p. 148°/18 mm. (*phenylurethane*, m.p. 65°), from (X) and MeCHO; α -phenyl- β -methylhexan- β -ol (XII), b.p. 206° (*phenylurethane*, m.p. 64·5°), from (X) and COMe₂; η -phenylheptan- β -ol (XIII), b.p. 164°/23 mm., from Ph·[CH₂]₅·MgBr and MeCHO; α -phenyl- Δ^8 -pentan- β -ol (XIV), b.p. 206°, from CH₂Ph·CH₂·MgBr and CH₂CH·CH₂Br (XV) or (IX) and H₃PO₄; α -phenyl- Δ^6 -hexene (XVI) from (VIII) and (XV). Attempts to prepare α -phenyl- γ -methylpentan- β -ol, CH₂Ph·CH₂·CHMe·MgBr and MeCHO, and Ph·CH₂·CNAc·CO₂R and MeI, failed. By cyclisation 1-methyltetrahydronaphthalene, b.p. 218—

220° [oxidised (KMnO₄) to *o*-C₆H₄(CO₂H)₂ (XVII)], is formed from (II), (IV), (VIII), (IX), and (XIV), 1-ethyltetrahydronaphthalene, b.p. 237—238°, from (XI) and (XVI), 1-*n*-propyltetrahydronaphthalene, b.p. 253°, from (XIII), and 1-isopropyltetrahydronaphthalene, b.p. 247°, from (XII); (III) and (V) give mixtures of 1-methyl-1-ethylindane (XVIII), b.p. 218°, and 1:2-dimethyltetrahydronaphthalene (XIX), b.p. 235°, in the ratios 76·3:23·7 and 20·5:79·5, respectively. (I) gives a *polymeride*, b.p. 163—165°/2 mm. (XVIII) and (XIX) with KMnO₄ give 1-methyl-1-ethylhomophthalic acid, m.p. 115° (decomp.) (anhydride, liquid), and (XVII), respectively. The cyclic compounds were identified by dehydrogenation with S. 1-C₁₀H₇Pr obtained in this way or by Clemmensen reduction of α -C₁₀H₇·COEt, gives a picrate, m.p. 90—92°; the picrate, m.p. 140—142°, is that of the 2-Pr isomeride (cf. lit.). Physical data are given for all the compounds prepared.

R. S. C.

Preparation of tetrahydronaphthalene peroxide. W. NUSSLE, jun., G. W. PERKINS, and G. TOENNIES (Amer. J. Pharm., 1935, 107, 29—32).—Hock and Susemihl's method is modified (A., 1933, 153; B., 1933, 421). Dry air (10—12 litres per hr.) is aspirated for 45 hr. through 1 litre of tetrahydronaphthalene (I) at 75°. Unchanged (I) is removed at 1—1·5 mm. and the crystals from the residue are crystallised 3 times from light petroleum—EtOAc (70:22) giving 23 g. of peroxide, m.p. 56°.

E. H. S.

Identity of the hydrocarbon, C₁₈H₁₆, obtained by dehydrogenation of sterols and genins with 3'-methylcyclopentenophenanthrene. O. DIELS and H. F. RICKERT (Ber., 1935, 68, [B], 267—272).—Attempts to establish the identity of "sterol C₁₈H₁₆" (I) with 3'-methylcyclopentenophenanthrene (II) (Kon et al., A., 1934, 288) by conversion into the characteristic compound C₁₈H₁₃O₂N (Diels et al., A., 1928, 169) were unsuccessful but the experiments are not regarded as crucial because of the experimental difficulties of controlling the action of nitrous fumes. Fractional adsorption of (I) by Al₂O₃ from light petroleum shows the presence in it of a hydrocarbon C₁₈H₁₄, m.p. 238—239°, possibly identical with that obtained by Ruzicka et al. (A., 1933, 278) by dehydrogenation of cholatrienic acid with Se and by Kon et al. (*loc. cit.*). (I), which after purification retains the m.p. 125—126° and other properties described previously, is transformed by Br in CCl₄ in daylight into several compounds from which the substance C₁₈H₁₃Br₃, decomp. 235°, is isolated. Since this compound is also produced from (II) and the phenomena of the reaction are identical in each case, the identity of (I) and (II) is regarded as established although certain differences remain unexplained. The prep. of (II) is improved.

H. W.

[Identity of 3'-methyl-1:2-cyclopentenophenanthrene with Diels' hydrocarbon, C₁₈H₁₆.] O. DIELS and H. F. RICKERT (Ber., 1935, 68, [B], 325—326).—Mainly a reply to Hilleman (this vol., 335), whose work, in conjunction with that of Diels (preceding abstract), establishes the identity of "sterol C₁₈H₁₆" and the synthetic products of Bergmann and of Kon.

H. W.

Dicyanoamides. J. BIECHLER (Compt. rend., 1935, 200, 141—143).—Phenyl-, *p*-tolyl-, and *o*-anisylcyanamide (K or Ag derivative) in C_6H_6 containing CNBr at room temp. give phenyl- (I), m.p. 87.5°, *p*-tolyl-, m.p. 69°, and *o*-anisyl-dicyanoamide, m.p. 62°, respectively. *o*-Tolyl-, monochlorophenyl-, and α -naphthyl-cyanamide give mixtures of polymerides of the corresponding dicyanoamides. (I) when heated gives a trimeride (?). Madelung and Kern's prep. of NMe(CN)₂ (cf. A., 1922, i, 438) gives an impure product. J. L. D.

Nitro- and amino-derivatives of *tert*-butylbenzene. D. CRAIG (J. Amer. Chem. Soc., 1935, 57, 195—198).—PhBu⁺ (modified prep.; 79% yield) and H₂SO₄-HNO₃ at 20—40° give a mixture of *o*- (23 parts) and *p*- (77 parts) -NO₂-, reduced (Fe-HCl) to a mixture (I) of *o*- (II) and *p*- (III) -NH₂-compounds. *o*-NHPh-C₆H₄-CO₂Me (modified prep.) and MgMeI give the hydriodide, m.p. 180—200°, of a base, a substance, m.p. 122—124°, and *o*-*tert*-butyldiphenylamine, m.p. 71—72° (*Ac* derivative, m.p. 88—89°), also obtained in poor yield from (II) and *o*-C₆H₄Cl-CO₂H (IV). (II), β -C₁₀H₇·OH, and a drop of conc. HCl, when refluxed, give NHPh-C₁₀H₇- β . Heating (I) and its hydrochloride gives *p*-*tert*-diphenylamine (V), m.p. 66—67°, b.p. 170—173°/3 mm., also obtained in poor yield from NHPh₂ with Bu⁺Cl (AlCl₃) or Bu⁺OH (H₃PO₄), and from (IV) and (III). Long heating of (III) and its hydrochloride gives some (V), and *di*-*p*-*tert*-butyldiphenylamine, m.p. 107—108°, b.p. 190—195°/3 mm. (Bz, m.p. 192—193°, and *Ac* derivative, m.p. 160—161°), also obtained from *p*-C₆H₄Bu⁺·OH, PCl₅, and the Bz derivative of (III) by way of *p*-*tert*-butylphenyliminophenylmethyl *p*-*tert*-butylphenyl ether, m.p. 134—136°. (III), *p*-C₆H₄(OH)₂, and a trace of HCl give *di*-(*N*-*p*-*tert*-butylphenyl)-*p*-phenylenediamine, m.p. 176—177°; α - and β -C₁₀H₇-NH₂ give similarly *p*-*tert*-butylphenyl- α -, m.p. 91—92°, b.p. about 205°/2 mm., and β -naphthylamine, m.p. 76—78°, b.p. 213°/3 mm. R. S. C.

Aminoalkylamino-derivatives of carbocyclic compounds. H. WOJANN (Arch. Pharm., 1935, 273, 77—83).—NH₂Ph and aliphatic Cl-aldehydes do not give Schiff's bases; at > 100° the Cl reacts and mixtures are formed. By condensation of β -aminoaldehydes with the appropriate base and hydrogenation (Pd-BaSO₄) of the product are obtained *N*- γ -dimethylamino- $\beta\beta$ -dimethyl-*n*-propyl-aniline, b.p. 152°/17 mm. (dipicrate, m.p. 150°), -benzylamine, b.p. 150°/17 mm. (dipicrate, m.p. 138°), -phenylethylamine, b.p. 160°/17 mm. (dipicrate, m.p. 170°), and -*o*-anisidine, b.p. 173°/17 mm. (dipicrate, m.p. 138—140°; dihydrochloride, m.p. 192—193°), *N*- γ -methylamino- $\beta\beta$ -dimethyl-*n*-propyl-, b.p. 170°/17 mm. (dihydrochloride, m.p. 190°), and *N*-(β -dimethylaminomethyl-*n*-butyl)-*o*-anisidine, b.p. 180—182°/17 mm. (dipicrate, m.p. 106°), and *N*- γ -diethylamino- $\beta\beta$ -dimethyl-*n*-propyl-*p*-anisidine, b.p. 198°/17 mm. (dihydrochloride, m.p. 178°), and -*p*-aminophenol (dihydrochloride, m.p. 238—240°). R. S. C.

Preparation and properties of dialkylaminoalkyl phenyl- α -naphthylcarbamates. A. B. BOESE, jun., and R. T. MAJOR (J. Amer. Chem. Soc.,

1935, 57, 175—176).—Phenyl- α -naphthylcarbamyl chloride (from α -C₁₀H₇·NHPh and COCl₂ in CHCl₃ at room temp.), m.p. 105°, does not react with NEt₂·CH₂·CH₂·OH, but with the appropriate Na alkoxide in dry xylene gives β -diethylaminoethyl, m.p. 60—61° (hydrochloride, m.p. 214—216°; H, citrate, decomp. 50—80°), α -*di*-(diethylamino)isopropyl (monohydrochloride, hygroscopic, decomp. about 90°), and α -diethylamino- β -diethylaminomethyl-sec-butyl phenyl- α -naphthylcarbamate (hydrochloride, m.p. 165—167°). These esters have powerful anaesthetic action and are non-toxic when injected subcutaneously, but very toxic when administered intravenously. R. S. C.

Significance of some anomalous dipole moments.—See this vol., 430.

Reduction of nitro- and polynitro-compounds.

XIV. Aromatic compounds. K. BRAND and J. MAHR (J. pr. Chem., 1935, [ii], 142, 153—176; cf. A., 1932, 575).—The prep. of a no. of substituted azoxybenzenes and their intermediates is described. The following are new: 2-nitro-6-hydroxylamino-, m.p. 87°, and -6-nitroso-*p*-xylene, m.p. 134—135°; 4-nitro-6-hydroxylamino-, m.p. 126.5—127.5°, and -6-nitroso-*m*-xylene, m.p. 108°; 3:3'-dinitro-2:5:2':5'-(I), m.p. 191—192°, and -4:6:4':6'-tetramethylazoxybenzene (II), m.p. 201—202° [lit. 185—190° (decomp.)]; 5:6:7:8-tetrahydronaphthyl-2-hydroxylamine, m.p. 66—67°; 2-nitroso-5:6:7:8-tetrahydronaphthalene (impure), an oil; 2:2'-azo- (III), m.p. 127—128°, -hydrazo-, m.p. 121—122° (with cold conc. HCl gives the azo- and 2-NH₂-compounds), and -azoxy-5:6:7:8:5':6':7':8'-octahydronaphthalene, m.p. 100—101°. For formation of azoxy- from hydroxylamino- and nitroso-benzene derivatives under previously defined conditions, *k* are as follows: 2:6:2':6'-Me₄ 0.29, (I) 12.5, (II) 15—16; 1:1'-azonaphthalene, variable, 1—3.6; (III) 1.6—1.9. These and former results show that *m*-Me increases and *o*-Me decreases *k*, but that *p*-Me is almost without effect (cf. lit.). *k* for Ph·N₂O·Ph is increased 30—300 times by 0.0005—0.005*N*·KOH. R. S. C.

Action of titanous chloride on nitrophenylhydrazones; *p*-nitro- and 2:4-dinitro-phenylhydrazones. A. K. MACBETH and J. R. PRICE (J.C.S., 1935, 151—153).—Reduction of *p*-nitrophenylhydrazones with TiCl₃ results in absorption of 8 equivs. of H, scission, and formation of *p*-phenylenediamines, whilst 2:4-(NO₂)₂-compounds absorb 12H, with no scission and formation of 2:4-diaminophenylhydrazines. Phellandral gives a *p*-nitro-, m.p. 169°/170°, and 2:4-dinitro-phenylhydrazone, m.p. 202—203°, and the 2:4-dinitrophenylhydrazones of the following are described: COEt₂, m.p. 156°; *o*-C₆H₄Cl·CHO, m.p. 209°; 4-isopropylcyclohexan-1-one, m.p. 119—120°; thujone, m.p. 116—117°; protocatechualdehyde, m.p. 275° (decomp.); vanillin, m.p. 267—268°; and veratraldehyde, m.p. 264°/265°. F. R. S.

Preparation of the hydrochloride of *m*-dihydrazinobenzene through the bis-diazonium compound from *m*-phenylenediamine. H. A. J. SCHOUTISSEN (Rev. trav. chim., 1935, 54, 253—255).—Tetraazotisation of *m*-C₆H₄(NH₂)₂ at -5° to -10

in conc. HCl and reduction of the bisdazo-compound with SnCl_2 -conc. HCl gives a good yield of *m*-dihydrazinobenzene dihydrochloride, which condenses with KCN to give the disemicarbazide, with CH_3Ac_2 to give *m*-phenylene-1:1'-bis-3:5-dimethylpyrazole, and with piperonal to give the *dihydrazone*, m.p. 225—226°. J. W. B.

Heteropolarity. XXVI. Coupling processes. W. DILTHEY and C. BLANKENBURG (J. pr. Chem., 1935, [ii], 142, 177—190; cf. A., 1932, 1125).—Coupling may take place either by rearrangement of an ion, $[\text{PhN}_2]^+\text{X}^-$, in which $\text{X}=\text{CN}$, OPh, etc., or, particularly in acid, but also in alkaline solution, by addition of the diazonium ion to an activated C and subsequent rearrangement of the salt-like compound. Activation of phenols and their ethers in alkaline solution may occur by formation of



($\text{R}=\text{H}$ or alkyl); it is hindered by positive groups (Me, Cl, etc.) in the *o*- and negative groups (NO_2) in the *m*-position, but aided by the former in the *m*- or the latter in the *o*-position. Activation of C is also effected by Ph, so that ($p\text{-C}_6\text{H}_4\text{Me}$) $_2\text{C}:\text{CH}_2$ (I) and ($p\text{-OMe-C}_6\text{H}_4$) $_2\text{C}:\text{CH}_2$ (II) will couple with $p\text{-PhS-C}_6\text{H}_4\text{-CO-C}_6\text{H}_4\text{-N}_2\text{Cl-p}$ (III) (*loc. cit.*) in AcOH. The *azo*-compounds obtained by coupling (III) with the following substances in AcOH are described: NPh_3 (*perchlorate*, m.p. > 360°); resorcinol, m.p. 175°; pyrocatechol, m.p. 123—125°; phloroglucinol Me_2 ether, m.p. 135—136°; guaiacol, m.p. 149° (prep. in KOH-EtOH); $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$, m.p. 166—167° (obtained only in EtOH-NaOH); $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-OMe}$, m.p. 163—164°; $\text{CO}(\text{CH}_2\text{-CO}_2\text{Et})_2$ (slowly), m.p. 99°; (II), m.p. about 120° [*perchlorate* (IV), solid]; (I), an oil [*perchlorate* (V), *cryst.*]. The following do not couple with (III): veratrole (VI) in AcOH, anisole, $p\text{-C}_6\text{H}_4(\text{OH})_2$, $p\text{-C}_6\text{H}_4(\text{OMe})_2$, and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$. The following give oily *azo*-compounds: (VI) in NaOH or $\text{C}_5\text{H}_5\text{N}$, pyrogallol, dinaphthalene dioxide, $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$, and Et dinitrophenylacetoacetate. (IV) and (V) are formulated as $\text{R:N:N-CH}_2\text{-C}^+\text{Ar}_2(\text{ClO}_4)^-$. (III) and H_2O at 60° give *p*-hydroxy-*p*-phenylthiolbenzophenone, m.p. 159—160°. R. S. C.

Hydrogenation and hydrogenolysis of ethers.

E. M. VAN DUZEE and H. ADKINS (J. Amer. Chem. Soc., 1935, 57, 147—151).— $\text{CH}_2\text{Ph-OAlk}$ (I) and Ph-OAr (II) undergo hydrogenolysis [(II) more readily than (I)] during treatment with H_2 (150—200 atm.) in presence of Raney Ni and Et_2O , at a lower temp. (100—150°) than other ethers; PhMe AlkOH or ArOH are produced. Hydrogenation of (I) or (II) does not occur; at > 150° some of the *hydrogenolysis* products are reduced. ArOAr' (III) undergo *hydrogenolysis* at 150—200°; the *hydrogenolysis* products [but not (III)] are reduced. ArOAlk are more stable than (I)—(III); at 200° the corresponding *cyclohexyl* ether is usually produced. AlkOAlk' are stable at 200°. Raney Ni is more effective than *Kieselguhr* for fission of C-O linkings. The following are new: *Et*, b.p. 125—130°/6—7 mm., *Bu*, b.p. 125—153°/13 mm., *Ph*, b.p. 180—182°/7 mm., *m*, b.p. 223°, and *benzyl*, b.p. 186—188°/7 mm., *dodecyl*

ethers; the *Ph isoamyl*, b.p. 118°/2 mm., *benzyl Et*, b.p. 115—118°/13 mm., *Me Bu*, b.p. 144—146°, *Et Bu*, b.p. 161—162°, *Ph benzyl*, b.p. 176—181°/2 mm., and *cyclohexyl isoamyl*, b.p. 113—115°/7 mm., *ethers* of $(\text{CH}_2\text{-OH})_2$; *benzyl sec.-Bu ether*, b.p. 108—109°/29 mm.; γ -*butoxy*-, b.p. 81—85°/13 mm., and γ -*cyclohexyloxy*-, b.p. 91—93°/2 mm., *propyl alcohols*; *benzyl*, b.p. 166°/7 mm., and *Bu*, b.p. 116—118°/10 mm., γ -*phenylpropyl ethers*; *o*-, b.p. 151—153°/5 mm., *m*-, b.p. 141—143°/2 mm., and *p*-, b.p. 162—164°/5 mm., m.p. 45—46°, *tolyl anisyl ethers*; *Ph 8-phenylbutyl ether*, b.p. 144—146°/1 mm.; *cyclohexyl 8-cyclohexylbutyl*, b.p. 150—153°/5 mm., and γ -*cyclohexylpropyl*, b.p. 138—140°/5 mm., *ethers*; γ -*cyclohexylpropyl Bu ether*, b.p. 117—118°/10 mm.; *Et 7-cyclohexyloxypropyl*-, b.p. 173—175°/4 mm., and β -*cyclohexyloxyethyl*-, b.p. 162—164°/4 mm., *malonates*; *o-benzoyloxybenzanilide*, m.p. 117—118°; *s-tri-anisylbenzene*, m.p. 142—142.5°; 1:3:5-*tri-p-methoxycyclohexylcyclohexane*, b.p. 230—240°/1 mm.

H. B.

Introduction of isobutyl groups into phenols, cresols, and homologous compounds. Q. R. BARTZ, R. F. MILLER, and R. ADAMS (J. Amer. Chem. Soc., 1935, 57, 371—376).— $\text{CH}_2\text{CMe-CH}_2\text{Cl}$, b.p. 73—73.5°/746 mm., and K_2CO_3 in COMe_2 or NaOEt in dry EtOH with the appropriate phenol give the β -*methylallyl ethers* of PhOH, b.p. 70°/8 mm., *o*-, b.p. 82.5°/5 mm., *m*-, b.p. 85.5°/4 mm., and *p*-cresol, b.p. 84°/3 mm., *m*-4-, b.p. 90°/3 mm., *p*-, b.p. 88.5°/4 mm., and *o*-4-xyleneol, b.p. 98.5°/4 mm., *o*-methoxy-, b.p. 107.5°/9 mm., *p*-chloro-, b.p. 101.5°/8 mm., and *o*- β -methylallyl-phenol, b.p. 104°/5 mm., 3- β -methylallyl-*o*-, b.p. 106°/5 mm., and *p*-cresol, b.p. 118°/4 mm., 4- β -methylallyl-3-, b.p. 120°/4 mm., and 4-*isopropyl-m-cresol*, b.p. 105.6°/6 mm., and resorcinol, b.p. 128°/3 mm.; also *resorcinol di-β-methylallyl ether*, b.p. 147°/6 mm. These alone or in NPhEt_2 at about 230—245° give 50—80% yields of the following: *o*- β -methylallylphenol (I), b.p. 95°/9 mm.; 3- β -methylallyl-*o*- (II), b.p. 87°/4 mm., and *p*-cresol (III), b.p. 101°/7 mm.; 4- β -methylallyl-*m-cresol* (IV), b.p. 98°/7 mm.; 6- β -methylallyl-2:4-, b.p. 103°/6 mm., -2:5-, b.p. 100°/6 mm., and -3:4-dimethylphenol, b.p. 116°/7 mm.; 6- β -methylallylguaiacol, b.p. 115°/8 mm.; 4-chloro-2- β -methylallylphenol, b.p. 113°/8 mm.; 2- β -methylallyl-4-*isopropyl-m-cresol*, b.p. 110°/6 mm.; 2:6-di- β -methylallylphenol, b.p. 110°/2 mm.; 3:5-di- β -methylallyl-*o*-, b.p. 134°/7 mm., and *p*-cresol, b.p. 127°/7 mm.; 2:4-di- β -methylallyl-*m-cresol*, b.p. 130°/7 mm.; and 4:6-di- β -methylallylresorcinol, b.p. 145°/3 mm. By hydrogenation (PtO_2) in EtOH at 2—3 atm. are obtained 3-*isobutyl-o*-, b.p. 100°/9 mm., m.p. 41—42°, and *p-cresol* (V), b.p. 106°/9 mm., 4-*isobutyl-m-cresol*, b.p. 105°/8 mm., 6-*isobutyl-2:4*- (VI), m.p. 69—70°, -2:5-, m.p. 73—74°, and -3:4-dimethylphenol, b.p. 107°/3 mm., 2-*isobutyl-4-isopropyl-m-cresol* (VII), b.p. 111°/2 mm., 2-*isobutyl*-, m.p. 21°, b.p. 86°/6 mm., and 2:6-diisobutyl-phenol, b.p. 118°/6 mm., 3:5-diisobutyl-*o*- (VIII), b.p. 121°/2 mm., m.p. 48—49°, and *p-cresol* (IX), b.p. 121°/2 mm., and 2:4-diisobutyl-*m-cresol* (X), b.p. 120°/4 mm. Isomerisation by conc. aq. alkali gives 80% yields of 2-*isobutenylphenol* (XI), b.p. 81°/6 mm., m.p. 22°, 3-*isobutenyl-o*- (XII), b.p. 112°/18 mm.,

and *p*-cresol, b.p. 102°/8 mm., and 4-isobutenyl-m-cresol, b.p. 127°/17 mm. The following are described; acetates of (I), b.p. 98°/6 mm., (II), b.p. 116°/12 mm., (III), b.p. 115°/5 mm., and (IV), b.p. 123°/5 mm.; *p*-nitrobenzoates of (I), m.p. 42°, (III), m.p. 66—67°, (VI), m.p. 100—101°, (VII), m.p. 128.5, (VIII), m.p. 103—104°, (IX), m.p. 87—88°, (X), m.p. 130.5°, (XI), m.p. 64°, and (XII), m.p. 69.5°; aryloxyacetic acids from (III), m.p. 116—117°, (IV), m.p. 77—78°, (V), m.p. 99°, and (XII), m.p. 79—80°. Dimethyldihydrobenzofurans result by too long heating of the allyl ethers or by treating them with 2 mols. of $C_5H_5N \cdot HCl$ at 235—245° or, in some cases, by keeping the solution in moist ligroin with anhyd. $MgSO_4$. Thus are obtained 1:1-dimethyl-, b.p. 62°/7 mm., 1:1:6-, b.p. 74°/8 mm., 1:1:5-, b.p. 87°/11 mm., and 1:1:4-trimethyl-, b.p. 88°/10 mm., and 4-chloro-1:1-dimethyl-1:2-dihydrobenzofuran, b.p. 96°/5 mm. Ring closure is also effected by aq. $HgCl_2$, which leads to 1-chloromercurimethyl-1-methyl-, m.p. 81°, 1:6-, m.p. 72.5°, and 1:4-dimethyl-1:2-dihydrobenzofuran, m.p. 102.4°, and thence by KI or KBr to 1-iodo-, m.p. 73°, and 1-bromo-mercurimethyl-1:4-dimethyl-1:2-dihydrobenzofuran, m.p. 93—94°. Bu^s enhances antiseptic action of the phenols less than does Bu^a . R. S. C.

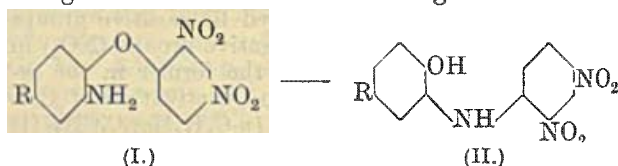
Ring fission of *o*-nitrophenols by sulphuric acid. I. O. NEUNHOEFFER and H. KÖLBEL (Ber., 1935, 68, [B], 255—263).—6-Nitro-2:4-dimethylphenol (I) is converted by H_2SO_4 at 110—120° into α -dimethylmuco- γ -lactonic acid, m.p. 156° (monoamide, m.p. 125—128°), which rapidly absorbs $1H_2$ and more slowly a further $1H_2$ with formation of a mixture of stereoisomeric dimethyladipic acids. 2:4-Dibromo-6-nitrophenol and 100% H_2SO_4 at 125° yield humic substances (characteristic of *o*-Br-derivatives), a (?) pyrrolone compound, m.p. 215°, and the two lactonic acids, $\begin{matrix} CH_3CBr \\ CO-O \end{matrix} > CH \cdot CHBr \cdot CO_2H$, colourless crystals, m.p. 175°, and

$\begin{matrix} CH-CBr \\ OH-C-O \end{matrix} > C \cdot CHBr \cdot CO_2H$, red crystals, m.p. 268—270° (partial decomp.); these are reduced by $SnCl_2$ and HCl to hydromuconic acid, catalytically hydrogenated to adipic acid. Treatment of 1-nitro- β -naphthol with 95% H_2SO_4 at $>90^\circ$ yields exclusively cinnam-*o*-hydroxamic acid (II) $OH \cdot \dot{C} \cdot (N \cdot OH) \cdot C_6H_4 \cdot CH : CH \cdot CO_2H$, m.p. 195°, which is stable towards acids and alkalis but is transformed by $MeOH$ into the *Me* ester of *o*-carboxycinnamolactone (III), m.p. 65°, and *o*-carboxymethoxycinnamic acid (IV), m.p. 152°. (III) and (IV) are hydrolysed to *o*-carboxycinnamic acid, m.p. 203° (dibromide, m.p. 215°). (II) is hydrogenated (PtO_2 in Pr^sOH) to β -*o*-carboxyphenylpropionic acid, m.p. 166°. Fission of nitrophenols does not occur with conc. HCl , with conc. HCl and $SnCl_4$ at 180°, with 20% $HClO_4$, with $POCl_3$, or with Ac_2O ; H_3PO_4 , dehydrated at 220°, behaves similarly to H_2SO_4 but reaction is slow by reason of the insolubility of the materials. The *Me* hydroxamates of β -methyl-, m.p. 114°, and α -dimethyl-, m.p. 122°, -muconic acids are obtained from *o*-nitro-*p*-cresol and (I), respectively. The mechanism of the reaction is obscure but it appears probable that an intermediate product is formed which, according

to experimental conditions, passes into either hydroxamic acid or carboxylic acid. H. W.

Benzenesulphonyl derivatives of *o*-aminophenol. C. B. POLLARD and L. H. AMUNDSEN (J. Amer. Chem. Soc., 1935, 57, 357—358).—Directions are given for the prep. of $o\text{-PhSO}_2 \cdot NH \cdot C_6H_4 \cdot OH$, $o\text{-PhSO}_2 \cdot NH \cdot C_6H_4 \cdot O \cdot SO_2Ph$, and *o*-aminophenyl benzenesulphonate, m.p. 87—87.3° (Bz derivative, m.p. 90.5—91°, also obtained from $PhSO_2Cl$ and $o\text{-NHBz} \cdot C_6H_4 \cdot OH$). R. S. C.

Rearrangement of *o*-aminodiphenyl ethers. II. K. C. ROBERTS, C. G. M. DE WORMS, and (MISS) H. B. CLARK (J.C.S., 1935, 196—20).—The rates of rearrangement (in min.) of diphenyl ethers (I) to diphenylamines (II) in $AcOH \cdot C_5H_5N$ by varying R are NH_2 (50), OMe (13), Me (7), H (5), I (15), Br (30), Cl (60). The factors governing the mechanism of the change are discussed. The following are described:



2-aminoquinol 4-benzoate, m.p. 161—164°; 2':4'-dinitro-2:4-diaminodiphenyl ether, m.p. 166—170°, converted into 2':4'-dinitro-*o*-amino-2-hydroxydiphenylamine, decomp. 237—240°; 2':4'-dinitro-5-acetdinitrophenylamido-2-hydroxydiphenylamine, decomp. above 250°, obtained directly from 1:2:4- $OH \cdot C_6H_3(NHAc)_2$ and 1:2:4- $C_6H_3Cl(NO_2)_2$ (III); 2':4'-dinitro-2-amino-4-methoxydiphenyl ether, m.p. 178°, obtained from 2-amino-4-methoxyphenol hydrochloride, m.p. 171°, converted into 2':4'-dinitro-2-hydroxy-*o*-methoxydiphenylamine, m.p. 157°; 2':4'-dinitro-2-, m.p. 123°, and -4-aminodiphenyl ether, m.p. 223° (decomp.); 4-iodo-2':4'-dinitro-2-aminodiphenyl ether, m.p. 125°, converted into 5-iodo-2':4'-dinitro-2-hydroxydiphenylamine, m.p. 145°; 4-bromo-2':4'-dinitro-2-hydroxydiphenyl ether, m.p. 140°, converted into 5-bromo-2':4'-dinitro-2-hydroxydiphenylamine, m.p. 190°; 4-chloro-2':4'-dinitro-2-aminodiphenyl ether, m.p. 152°, converted into 5-chloro-2':4'-dinitro-2-hydroxydiphenylamine, m.p. 215°; 2:4-dinitrophenyl 2':4'-dinitro-2-aminodiphenyl-4-carboxylate, m.p. 89°, hydrolysed to the acid, m.p. 115°, but not forming the diphenylamine; 2:4-dinitrophenyl 2':4'-dinitro-2-hydroxydiphenyl-5-carboxylate, m.p. 155°, hydrolysed to the acid, m.p. 185°; and 4:2':4'-trinitro-2-aminodiphenylamine, m.p. 225° (decomp.), obtained from 4-nitro-2-aminophenol and (I). F. R. S.

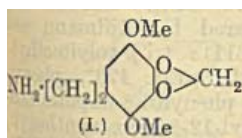
Fries reaction with α -naphthyl esters. R. W. STOUGHTON (J. Amer. Chem. Soc., 1935, 57, 202—204).— α - $C_{10}H_7$ -propionate and valerate have b.p. 134—135°/2 mm. and 172—176°/6 mm., respectively. When heated with $AlCl_3$ at 100° (2 hr.) and then at 120° (1 hr.), the appropriate α - $C_{10}H_7$ esters give 2- (I) (61%) and 4- (II) (5%) -acetyl- and 2:4-diacetyl- (III) (4%), 2- (54%) and 4- (6%), m.p. 188—189°, -propionyl- and 2:4-dipropionyl- (4%), m.p. 100—101°, 2- (55%) and 4- (3%) -butyryl and 2:4-dibutyryl- (2%), m.p. 101—102°, and 2- (40%)

m.p. 75—76°, and 4- (2%), m.p. 168—169°, -*valeryl-α-naphthol*. The diacyl compounds give o - $C_6H_4(CO_2H)_2$ on oxidation. (II), but not (I), with $AlCl_3$ under similar conditions gives a mixture of (I), (II), and (III). By Clemmensen reduction are obtained 50—63% yields of 2-ethyl-, m.p. 69—70° (lit. 68—68.5°), b.p. 128—133°/3 mm., -*propyl*-, m.p. 51—52°, b.p. 133—136°/2 mm., -*butyl*-, m.p. 71—72°, b.p. 145—149°/4 mm., and -*amyl-α-naphthol*, m.p. 55—56°, all unstable in air. R. S. C.

Isomerisation of phenolic ethers at high temperatures. II. **Isomerisation of phenyl β-naphthylmethyl ether.** O. BEHAGHEL and H. FREIENSEHNER (Ber., 1935, 68, [B], 341—343).—The $CH_2 \cdot C_{10}H_7 \cdot \beta$ resembles the CH_2Ph residue in its capacity for isomerisation (cf. A., 1934, 999). $\beta \cdot C_{10}H_7 \cdot CH_2 \cdot OPh$ passes at 250° in presence of a little Zn into $PhOH$, o - (I) and p - (II) - β -*naphthylmethylphenol*, and resin. (I), b.p. 189°/2 mm., m.p. 69°, is obtained from $NaOPh$ and $2 \cdot C_{10}H_7 \cdot CH_2Br$ in $PhMc$, whereas (II), m.p. 192°/2 mm., m.p. 96°, is prepared from $PhOH$, $2 \cdot C_{10}H_7 \cdot CH_2Br$, and Zn. H. W.

Carbylamines. XX. **Reaction between naphthols and aromatic carbylamines.** M. PASSERINI and A. NERI (Gazzetta, 1934, 64, 934—937; cf. A., 1925, i, 1298).— $\beta \cdot C_{10}H_7 \cdot OH$ and p -tolylcarbylamine react slowly in C_6H_6 to form 2-*hydroxy-1-naphthylglyoxaldi-p-methylanil*, m.p. 146—148°, which when boiled in C_6H_6 oxidises slowly to 4 : 5-*benzocoumaran-2 : 3-dionedi-p-methylanil*, m.p. 187—188°, with di- p -tolylcarbamide. E. W. W.

Pharmacodynamic properties of β-aminoethylapiole. J. V. SUPNIEWSKI (Acta Biol. Exp.



Warsaw, 1932, 7, 49—60).—Apiolealdehyde is condensed with $MeNO_2$ and the product reduced to the *oxime* and finally to β-*aminoethylapiole* (I). The *hydrochloride* of (I)

resembles mescaline in its pharmacological action.

CH. ABS. (r)

Constituents of guaiacum resin. III. **Synthesis of di-guaiaretic acid diethyl ether.** R. D. HAWORTH and I. RICHARDSON (J.C.S., 1935, 120—).—β-3-*Methoxy-4-ethoxyphenyl-α-methylcrotonic acid*, m.p. 127—128° (*Et* ester, b.p. 195—200°/15 m.p. 58—60°), from 3-methoxy-4-ethoxybenzaldehyde and $CHMeBr \cdot CO_2Et$, is reduced ($Na-Hg$) to *propionic acid*, m.p. 63—64° [*Me* ester (I), b.p. 158—160°/0.3 mm.]. 3-*Methoxy-4-ethoxyphenylacetone*, b.p. 156—158°/0.4 mm., m.p. 53—54°, 3-methoxy-4-ethoxyphenylpyruvic acid and H_2 , HCl , and (I) with $KOEt$, followed by hydrolysis, lead to β-*keto-αδ-bis-(3-methoxy-4-ethoxyphenyl)-γ-methylvaleramide*, m.p. 114—115°, converted by alkaline hydrolysis into αδ-*bis-(3-methoxy-4-ethoxyphenyl)-α-methylbutan-β-one*, b.p. 230—235°/0.3 mm., [(NO_2)₂-derivative, m.p. 133—134°]. The latter and $MgMeI$ give a carbinol, dehydrated ($KHSO_4$) to di-guaiaretic acid *Et₂ ether*, m.p. 103—104°, reduced to the *H₂-derivative*, m.p. 98—99° [134—135°, and (NO_2)₂-derivatives, m.p. 111—119°]. The inactive H_2 -derivative is also produced by reduction of *l-guaiaretic acid Et₂ ether*, m.p.

95—96°, [α]_D²⁰ -48.0° in $EtOH$, obtained by ethylation of the K salt of *l-guaiaretic acid* (II) from guaiacum resin. This confirms the structure $CH_2R \cdot CHMe \cdot CMe \cdot CHR$ [$R = 4 : 3 \cdot (OH)(OMe)C_6H_3 \cdot$] for (II). F. R. S.

Influence of alkyl- and alkylene-thiol groups on the therapeutic action of organic compounds.

III. **Some allylthiol compounds.** K. BRAND and W. BAUSCH (Arch. Pharm., 1935, 273, 65—76; cf. A., 1934, 665).—*o*-, m.p. 38—39° (lit. 54°), and *p*-Nitrophenyl allyl sulphide, m.p. 41° (lit. 38—39°) [prep. by reduction of ($NO_2 \cdot C_6H_4 \cdot S \cdot$)₂ by Na_2S and condensation of the resulting thiol with $CH_2 \cdot CH \cdot CH_2Br$], are reduced by Fe-25% HCl and a trace of Cu to *o*- (I), an oil (*hydrochloride*, m.p. 143.5—144° after sintering at 138°; *picrate*, m.p. 137.5°; Ac_2 , an oil, and carbamide derivative, m.p. 139—139.5°), and *p*-aminophenyl allyl sulphide (II), an oil [*hydrochloride*, m.p. 193° (decomp. from 140°); *sulphate*, m.p. 233—234° (decomp. from 200°); *picrate*, m.p. 144—146°; Ac , m.p. 121° (*dibromide*, m.p. 111°), and *phenylcarbamide* derivative, m.p. 93.5°]. (I) gives 8-allylthiol-2-phenylquinoline-4-carboxylic acid, m.p. 212°; (II) gives the corresponding 6-allylthiol compound, dimorphic, m.p. 168°, and 2-phenyl-1-*p*-allylthiolphenyl-4 : 5-diketopyrrolidine-4-*p*-allylthiolanil, m.p. 138—139°. The compounds have little or no pharmacological action. R. S. C.

Rearrangement of *o*-acetamido-sulphones and -sulphides. W. J. EVANS and S. SMILES (J.C.S., 1935, 181—188).—Rearrangement of *o*-aminosulphones containing a sufficiently positive C may be effected with aq. $NaOH$; the products are characterised as sulphinic acids by conversion into disulphides and subsequent degradation to derivatives of $NHPh_2$. Similarly the $NHAc$ -derivatives yield the corresponding Ac derivatives of the sulphinic acids. In the *o*-amino-sulphides, rearrangement is not effected under the same conditions as with the -sulphones, but the Ac derivatives are converted into *N*-acetylthiols. The factors controlling the rearrangements are discussed and the conclusions reached are confirmed by experimental evidence. 2-Nitro-2'-aminodiphenyl sulphide [Ac (I), m.p. 138°, $PhSO_2$, m.p. 172°, *o*-nitrobenzoyl, m.p. 150°, and *picryl* derivatives, m.p. 206—207°] with MeI and MgO gives 2-nitro-2'-methylaminodiphenyl sulphide, m.p. 110° (Ac , m.p. 124°, and *o*-nitrobenzoyl derivatives, m.p. 146°). 2-Nitro-2'-dimethylamino-5'-methylidiphenyl sulphide, m.p. 104°, is obtained from 1 : 2- $SCl \cdot C_6H_4 \cdot NO_2$ and $p \cdot C_6H_4Me \cdot NMe_2$. (I) and HNO_3 give 2 : 4'-dinitro-2'-acetamidodiphenyl sulphide, m.p. 179—180°, hydrolysed to the -*amino*-compound, m.p. 193°, deaminated to 2 : 4'-dinitrodiphenyl sulphide, m.p. 158—159°. 2 : 4'-Dinitro-2'-aminodiphenyl sulphide, m.p. 148°, forms an Ac derivative, m.p. 199°. 2-Nitro-2'-acetamidodiphenylsulphone (II), m.p. 107°, by oxidation (H_2O_2) of the sulphide, is hydrolysed to the -*amino*-compound, m.p. 132—134°; 4-chloro-2-nitro-2'-acetamido- (III), m.p. 171°, 2-nitro-2'-benzenesulphonamido- (IV), m.p. 144—145°, 2-nitro-2'-benzenesulphonylmethylamino-, m.p. 189°, and 2 : 4'-dinitro-2'-acetamido-diphenylsulphone (V), m.p. 186—187°, are similarly prepared. Oxidation (H_2O_2) of

the picryl derivative of (I) gives 2-nitro- γ -picrylamido-diphenyl sulphide, m.p. 250—251° (decomp.).

(II) with aq. NaOH forms 2-o-nitrophenylaminobenzenesulphinic acid, m.p. 124°, whilst with NaOH-EtOH followed by MeI, 2-acet-o-nitrophenylamidophenylmethylsulphone, m.p. 135—136°, is obtained. (III) and NaOH give a sulphinic acid converted into bis-2-p-chloro-o-nitrophenylaminodiphenyl disulphide, m.p. 174°, or methylated to 2-p-chloro-o-nitrophenylaminophenylmethylsulphone, m.p. 190°. (III) and NaOH-EtOH followed by MeI afford 2-acet-p-chloro-o-nitrophenylamidophenylmethylsulphone, m.p. 172°. (IV) and NaOH-EtOH-MeI yield 2-o-nitrophenylbenzenesulphonamidophenylmethylsulphone, m.p. 169°. The Na sulphinate formed by rearrangement of (IV) and HgCl₂ afford 2-o-nitrophenylbenzenesulphonamidophenyl mercurichloride, m.p. 224—225°. (V) and NaOH-EtOH and MeI give 5-nitro-2-acet-o-nitrophenylamidophenylmethylsulphone, m.p. 175—176°, whilst (V) and NaOH yield a sulphinic acid, degraded to 2:3'-dinitrodiphenylamine, m.p. 158°.

(I) and NaOH-EtOH-COMe₂ followed by MeI afford 2-acet-o-nitrophenylamidophenyl Me sulphide, m.p. 151°, hydrolysed to the 2-o-nitrophenylamino-compound, m.p. 98°. Rearrangement of 2-nitro-2'-aminodiphenyl sulphide in COMe₂ leads to 2-acet-o-nitrophenylamidophenylmercaptan, m.p. 114°, which with HI yields 2-o-nitrophenyl-1-methylbenzthiazolium iodide, m.p. 203° (decomp.), and with HClO₄ forms the perchlorate, m.p. 192°. 4-Chloro-2-nitro-2'-aminodiphenyl sulphide is rearranged to 2-acet-p-chloro-o-nitrophenylamidophenyl Me sulphide, m.p. 142°, hydrolysed to the 2-p-chloro-o-nitrophenylamino-compound, m.p. 126°. Rearrangement of 2:4-dinitro-2'-aminodiphenyl sulphide (VI) yields 2-acet-op-dinitrophenylamidophenyl Me sulphide, m.p. 155—156°; of o-nitrophenyl 2-acetamido-1-naphthyl sulphide gives 2-acet-o-nitrophenylamido-, m.p. 158°, hydrolysed to 2-o-nitrophenylamino-1-naphthyl Me sulphide, m.p. 110°; of the o-nitrobenzoyl derivative of (VI) affords 2-o-nitrobenz-o-nitrophenylamidophenyl Me sulphide, m.p. 245°; and of 2-nitro-2'-dimethylamino-5'-methylidiphenyl sulphide gives 5-nitro-2-acet-o-nitrophenylamidophenyl Me sulphide, m.p. 192—193°.

F. R. S.

cis- and trans-Chlorohydrins of cyclohexene. P. D. BARTLETT (J. Amer. Chem. Soc., 1935, 57, 224—227).—2-Chlorocyclohexanone and MgPr²Cl, MgBu²Cl, or Mg cyclohexyl chloride give 64, 72, and 27% yields, respectively, of a mixture of A- (I) (27%) (α -naphthylurethane, m.p. 165°) and B-2-chlorocyclohexanol (II) (73%), b.p. 93—94°/26 mm. (α -naphthylurethane, m.p. 94°), separable quantitatively by NaOH-aq. EtOH, which hydrolyses (I) 300 times as fast as (II). (II) and boiling NaOH give 76% of cyclohexanone. Modification of the conditions of reaction of cyclohexene and HOCl failed to produce any (II), and (I) is almost the sole product of ring-fission of cyclohexene oxide by ZnCl₂-Et₂O or conc. HCl. (I) and 0.5N-KOH-EtOH at 81° give only very slowly a little (II). (II) is assigned the trans-structure by analogies.

R. S. C.

New series of urethanes. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24,

22—23).— β -Methyl-, m.p. 132—133°, and β -amylcinnamylurethane, m.p. 77.5—78°, prepared from the corresponding alcohols, COCl₂, and NH₃, possess no hypnotic action on rats. The grouping CHPh:CR⁻, or the non-absorption of the urethane is responsible for the lack of activity. The corresponding amides are active, and therefore it seems unlikely that these urethanes are not absorbed.

H. T.

Addition of chloroform and bromoform to o-chlorobenzaldehyde. J. W. HOWARD and I. CASTLES (J. Amer. Chem. Soc., 1935, 57, 376—377).—o-C₆H₄Cl-CHO and CHCl₃ or CHBr₃ give o-chlorophenyl-trichloro-, b.p. 170—171°/6—7 mm. (acetate, b.p. 162—163°, m.p. 86°; propionate, b.p. 175°/4 mm., m.p. 38°; butyrate, b.p. 201°/15 mm.; benzoate, m.p. 81°), and -tribromo-methylcarbinol, b.p. 195—196°/8 mm. (acetate, m.p. 102—103°; propionate, m.p. 78°; butyrate, b.p. 208—210°; benzoate, m.p. 91°).

R. S. C.

β -Amino- α -diphenylpropyl alcohol. S. MACHLIS and K. C. BLANCHARD (J. Amer. Chem. Soc., 1935, 57, 176—177).—Ph₂, EtCOCl, and AlCl₃ in CS₂ give 4-propionylidiphenyl, m.p. 97° (not the 3-compound; cf. A., 1910, i, 392) (α -Br-compound, m.p. 79°), the oximino-derivative (prep. by Bu²O-NO), m.p. 176°, of which gives by hydrogenation (Pd-C) in EtOH-HCl at 35 lb. pressure β -amino- α -diphenylpropyl alcohol, unstable [hydrochloride (I), m.p. 253° (decomp.)]. (I) has pressor action one third that of ephedrine, but is sparingly sol.

R. S. C.

Halochromic salts from triarylmethylthiolacetic acids. M. GOMBERG and W. E. GORDON (J. Amer. Chem. Soc., 1935, 57, 119—124).—The following CAR₃S-CH₂-CO₂H are prepared by Biilmann and Due's method (A., 1924, i, 611): tri-p-tolylmethyl-, m.p. 185°, phenylxanthanyl-, m.p. 173°, phenylthioxanthanyl-, m.p. 180°, phenyldi- β -naphthoxanthanyl-, m.p. 202°, 12-phenyl-12- β -benzoxanthanyl-, m.p. 191° (cf. Wallis and Adams, A., 1933, 1167), tri-p-anisylmethyl-, m.p. 162°, diphenyl- α -naphthylmethyl- (I), m.p. 187°, and phenyldiphenyl- α -naphthylmethyl- (II), m.p. 118°, -thiolacetic acids. These undergo fission when treated with HClO₄, ZnCl₂, FeCl₃, or SnCl₄ (usually in AcOH and yield halochromic salts (A) of the type CAR₃Cl.ZnCl₂, which are hydrolysed to CAR₃-OH. The (A) from (I) undergo fairly rapid decomp. to 11-phenylchrysofluorene; those from (II) similarly give 11-diphenyl- (III) and (probably) 8:11-diphenyl-chrysofluorene, m.p. 190°. (III) is also obtained from l-(II) (Wallis and Adams, loc. cit.) and ZnCl₂ in AcOH. Absorption spectra of solutions of (II) (and phenyldiphenyl- α -naphthylmethyl chloride) with ZnCl₂ or HClO₄ also indicate the formation of CAR₃X (X=ClZnCl₂ or ClO₄) and not simply additive compounds. The conclusions of Wallis (A., 1931, 1050) regarding structure of such halochromic salts are based on misleading experimental evidence and do not preclude the quinonoid formulation (cf. A., 1902, i, 89).

quonocarbonium salt structure [CR₃:C₆H₄<H]⁺X⁻ (A., 1910, i, 869) explains satisfactorily the known properties. 9-Phenylfluorenylthiolacetic acid is not cleaved to any appreciable extent by ZnCl₂ or HClO₄.

halochromism is not observed. The following salts are described: *tri-p-tolylmethyl chloride zincichloride* and *ferrichloride*; *phenylxanthenyl chloride zincichloride*, *ferrichloride*, and *stannichloride*; *phenylthioxanthenyl chloride zincichloride*, *ferrichloride*, and *stannichloride*; *phenyldi-β-naphthoxanthenyl chloride zincichloride* and *stannichloride*; *12-phenyl-12-β-benzoxanthenyl chloride zincichloride*, *ferrichloride*, and *stannichloride*; *tri-p-anisylmethyl chloride ferrichloride*. *Phenylxanthenyl* and *12-phenyl-12-β-benzoxanthenyl perchlorates* have m.p. 282° and 260°, respectively.

H. B.

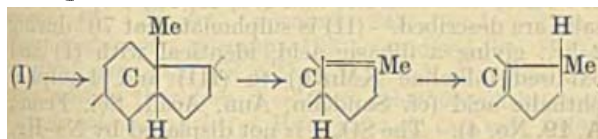
Constitution of triarylmethyl derivatives. A. HANTZSCH and A. BURAWOY (Ber., 1935, 68, [B], 329—332).—Mainly in reply to Lifschitz (A., 1934, 1000), it is maintained that there are only colourless, ester-like triarylmethyl derivatives and coloured triarylmethyl salts. The essential difference is that the acid residue is ionically united in the latter compounds. The colour of carbonium salts is due to the presence of conjugated systems in their cations.

H. W.

[Law of periodicity.] A. HANTZSCH and A. BURAWOY (Ber., 1935, 68, [B], 333; cf. A., 1934, 769).—A reply to Petrenko-Kritschenko (A., 1934, 1000).

H. W.

Migration of the quaternary methyl group during dehydrogenation of sterols and similar compounds. E. BERGMANN (Chem. and Ind., 1935, 175—176).—It is suggested that the migration of Me from C₁₃ to C₁₇ in the dehydrogenation of methoxy-estratrienol (I) is analogous to retropinacolinic rearrangement:



Similar production of 3'-methyl-1:2-cyclopentenophenanthrene from cholesterol, involving fission of the C₈ side-chain with the adjacent H as C₈H₁₈, would afford proof of the location of the Me at C₁₃.

J. W. B.

Migration of the quaternary methyl group during dehydrogenation of sterols etc. J. W. COOK (Chem. and Ind., 1935, 176).—Migration of Me is regarded as a process which accompanies the elimination of the group at C₁₇ (C₈H₁₇^β or OH) and which is independent of the dehydrogenation. The fluorescence of C₁₈H₁₆ obtained by dehydrogenation of sterols must be due to an impurity since none is exhibited by 3'-methyl-1:2-cyclopentenophenanthrene.

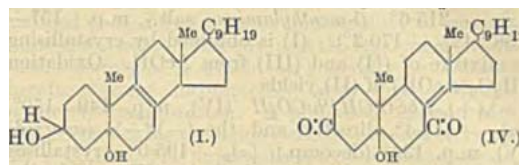
J. W. B.

Effect of varying storage conditions on deterioration of ergosterol. L. R. ELLISON and G. F. HALL (Analyst, 1935, 60, 92—95).—The effects of various manipulative treatments, and of storage in air or with or without light, on the [α]_D and m.p. of ergosterol are described (cf. A., 1931, 618). E. C. S.

Ergosterol and dehydroergosterol. M. MÜLLER (physiol. Chem., 1935, 231, 75—84).—Hydrogenation (Pd) of dehydroergosterol peroxide gives *ergostenediol II* (I), m.p. 219°, [α]_D +23.6° in CHCl₃.

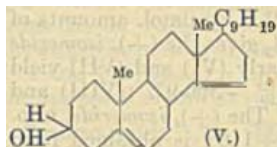
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(acetate, m.p. 196°, [α]_D +22.08° in CHCl₃), differing from the -diol I (II), obtained from ergosterol peroxide,



in the position of the double linking. Ergostatrienol (III) (A., 1930, 338) does not condense with

maleic anhydride, indicating that the double linkings are not in the same ring. Reduction of (III) or ergostadienediol with H₂-Pd gives (I). Oxidation of (I) or (II) with CrO₃-



AcOH affords 3:7-diketo-5-ergosterol (IV), C₂₈H₄₄O₃, m.p. 254° (decomp.), [α]_D +62.6° in CHCl₃, absorption max. at 254 mμ. Treatment of (I) or (II) with HCl in CHCl₃ yields *ergostadienol* (V), m.p. 171—172°, [α]_D -28.45° [acetate (VI), m.p. 174°, [α]_D -35.4° in CHCl₃]. With H₂-Pd, (VI) affords ergostanol acetate. (I) and (II) are not oxidised by Pb(OAc)₄.

J. H. B.

Determination of sterols. A. HEIDUSCHKA and H. SOMMER (Z. Unters. Lebensm., 1935, 69, 75—77).—The prep. of *phytosterol* (I) *oleate*, m.p. 83.5°, and *stearate*, m.p. 90.5°, is described. Esters of (I) and cholesterol may be determined colorimetrically using Liebermann's reaction.

E. C. S.

Synthesis of one of the dihydroanthraquinols. C. PRÉVOST (Compt. rend., 1935, 200, 408—410).—AgI(OBz)₂ (A., 1933, 711) reacts with anthracene to form the *dibenzoate* (I), m.p. 127.5—128°, of a *dihydroanthraquinol* (II), to which, with a substance, C₂₈H₁₈O₄, m.p. 250°, (I) is hydrolysed by Ba(OH)₂. When (II) is heated slowly it melts at 150—180° (decomp.); heated rapidly, it polymerises. E. W. W.

Amidine hydrochlorides. J. B. EKELEY, D. V. TIESZEN, and A. RONZIO (J. Amer. Chem. Soc., 1935, 57, 381).—*isoHex*, m.p. 113.5°, *phenoxybutyr*, m.p. 150°, *m-tolu*, m.p. 185.5°, and *p-chlorobenz-amidine hydrochloride*, m.p. 241—242°, are prepared.

R. S. C.

Reactivity of atoms and groups in organic compounds. XV. Relative reactivities of the hydrogen of the hydroxyl group in benzoic acid and certain of its derivatives. J. F. NORRIS and W. H. STRAIN (J. Amer. Chem. Soc., 1935, 57, 187—192; cf. A., 1934, 56, 406).—The relative rates of reaction of BzOH and its *o*-NO₂, *o*- and *m*-Br, *o*- and *m*-Cl, *o*- and *m*-Me, and *o*-OMe-derivatives with di-*p*-tolyl diazomethane (a non-ionic bimol. reaction) is approx. α the ionisation const. of the acid, but not to the rate of catalysed esterification.

R. S. C.

Further stereochemical studies. Optical isomerism of *d*-phenylsulphonylphenylacetic acids. W. PIECHULEK and J. SUSKO (Bull. Acad. Polonaise, 1934, A, 455—470).—PhS·CHPh·CO₂H (I) (modified prep.) is separated into the *d*- (II), m.p. 129—130°, [α]_D +216° [*cinchonidine*, m.p. 176—178° (decomp.)],

$[\alpha]_D^{25} + 38.6^\circ$, and *brucine* salt (C_6H_8), m.p. 97° , $[\alpha]_D + 55^\circ$, and the *l-isomeride* (III), m.p. $129-130^\circ$, $[\alpha]_D - 215.6^\circ$ (*l-menthylamine* salt, m.p. $157-158^\circ$, $[\alpha]_D - 170.2^\circ$). (I) is obtained by crystallising a mixture of (II) and (III) from AcOH. Oxidation (H_2O_2 -AcOH) of (II) yields $(+)_s(+)_c$ -*PhSO-CHPh-CO_2H* (IV), m.p. $149-150^\circ$, $[\alpha]_D + 419.4^\circ$, directly, and the $(-)_s(+)_c$ *isomeride* (V), m.p. 139° (decomp.), $[\alpha]_D + 195.0^\circ$, crystallises from the mother-liquor. Similarly (III) yields the $(-)_s(-)_c$ *isomeride* (VI), m.p. $148-149^\circ$ (decomp.), $[\alpha]_D - 420.4^\circ$, and the $(+)_s(-)_c$ *isomeride* (VII), m.p. 139° (decomp.), $[\alpha]_D - 191.2^\circ$. Equimol. amounts of (IV) and (V) in EtOH- $CHCl_3$ gives the $(+)_c$ *isomeride* (VIII), $[\alpha]_D^{25} + 304.4^\circ$; similarly (VI) and (VII) yield the $(-)_c$ *isomeride* (IX), $[\alpha]_D^{25} - 306.9^\circ$. (VIII) and (IX) exist in solution only. The $(+)_s$ *isomeride*, m.p. $135-137^\circ$ (decomp.), $[\alpha]_D + 116^\circ$, is obtained from (IV) and (VII) and the $(-)_s$ *isomeride*, m.p. $135-137^\circ$ (decomp.), $[\alpha]_D - 117^\circ$, from (V) and (VI). A racemate mixture, m.p. $146-147^\circ$ (decomp.), is obtained from EtOH solution of (IV) plus (VI); another racemate mixture, m.p. 135° (decomp.), is obtained from (V) and (VII). Oxidation (H_2O_2 -AcOH) of (II) or (IV) yields the corresponding *sulphonyl* compound, m.p. $180-197^\circ$ (decomp.), $[\alpha]_D^{25} + 107.6^\circ$, which racemises in $COMe_3$ to the *inactive acid*, m.p. $151-153^\circ$ (decomp.). All vals. of $[\alpha]$ are in EtOH- $CHCl_3$ (1:1 vol.). F. N. W.

Rotatory power and chemical constitution. I. Preparation and resolution of α -benzyl-*n*-hexoic acid and some derivatives. H. R. BURJORJEE, (Miss) KAMAKSHI, B. K. MENON, and D. H. PEACOCK (Proc. Indian Acad. Sci., 1934, 1, A, 407-411).— CH_2Ac-CO_2Et (Na derivative) with Bu^sBr in boiling EtOH gives a product (I), the Na derivative of which with CH_2PhCl , followed by hydrolysis, gives *dl- α -benzyl-*n*-hexoic acid* (II), b.p. $181-182^\circ/5$ mm. (*Ag* salt; resolved through its *quinine* salt, m.p. 95° , to the *d-acid*, $M[\alpha]_D^{25} + 57.6^\circ$ in C_6H_6 ; *amide*, m.p. 97° , *anilide*, m.p. 97°). Similarly are prepared *dl- α -p*, m.p. 62° (*Ag* salt; *amide*, m.p. 138° ; *anilide*, m.p. 116° ; *d-acid*, $M[\alpha]_D^{30} + 116.3^\circ$ in C_6H_6) and *-m-bromo*, b.p. $217^\circ/8$ mm. (*Ag* and *Ba* salts; *amide*, m.p. 91° ; *anilide*, m.p. 119° ; *d-acid*, $M[\alpha]_D^{30} + 57^\circ$ in C_6H_6), *dl- α -p*, m.p. 160° (*Ag* salt; *d-acid*, $M[\alpha]_D + 14.5^\circ$ in C_6H_6), and *-m-carboxybenzyl-*n*-hexoic acid*, m.p. 115° (*Ag* salt; *d-acid*, $+23.1^\circ$ in C_6H_6). The greater influence of Br than CO_2H on $M[\alpha]$ as compared with H is probably due to the electromeric effect of Br.

J. L. D.

Influence of catalysts on the reaction of sulphur with unsaturated organic compounds. I. Vulcanisation at high temperatures. O. SCHWARZKOPF (Bull. Soc. chim., 1935, [v], 2, 64-69).—Whilst Et cinnamate (I) alone does not react with S at $160-170^\circ$, approx. one atom of S is absorbed by each mol. of (I) in the presence of the vulcanisation catalysts $(CH_2)_6N_4$ and K xanthate. J. G. A. G.

Rotatory power and chemical constitution. II. Preparation and resolution of β -*p*-bromophenyl- α -benzylpropionic acid and similar compounds. H. R. BURJORJEE, B. K. MENON, and D. H. PEACOCK (Proc. Indian Acad. Sci., 1934, 1, A, 412-

417).—Et sodiobenzylmalonate with *p*- and *m*- $NO_2 \cdot C_6H_4 \cdot COCl$ in EtOH gives *Et α -benzyl- α -p-nitrobenzylmalonate*, m.p. 76° , and an oil, respectively, neither of which can be hydrolysed nor gives an amide. Et benzylacetoacetate with *p*- $C_6H_4Cl \cdot CH_2Br$, followed by hydrolysis, gives *dl- β -phenyl- α -p-chlorobenzylpropionic acid*, m.p. 86° , resolved through the *quinine* salt, m.p. 183° into the *d-acid*, m.p. 74° , $M[\alpha]_D^{25} + 27.97^\circ$ in C_6H_6 . *dl- β -Phenyl- α -m-chlorobenzyl*, m.p. 64° (*d-acid*, m.p. 73.5° , $M[\alpha]_D^{25} + 22.45^\circ$ in C_6H_6 ; *quinine* salt, m.p. 173°), *- α -p*, m.p. 92° (*d-acid*, m.p. 90° , $M[\alpha]_D^{25} + 51.35^\circ$ in C_6H_6 ; *quinine* salt, m.p. 175°), and *- α -m-bromobenzylpropionic acid*, m.p. 81° (*l-acid*, m.p. 89.5° , $M[\alpha]_D^{25} - 33.4^\circ$ in C_6H_6 ; *quinine* salt, m.p. 161°), are prepared similarly. *dl- β -Phenyl- α -p*, m.p. 212° , and *-m-carboxybenzylpropionic acid*, m.p. 159° , cannot be resolved. The following are also prepared: *β -p*, m.p. 134.5° , and *-m-bromophenylpropionic acid*, m.p. 71° , and *dl- β -p-bromophenyl- α -m-bromobenzylpropionic acid*, m.p. 110° (*amide*, m.p. 138.9° ; *anilide*, m.p. 156°), which cannot be resolved. The larger effect on $M[\alpha]$ of Br than Cl is probably due to the greater electromeric effect of Br.

J. L. D.

Twitchell's reagent. E. SCHLUTTIUS (J. pr. Chem., 1935, [ii], 142, 49-78).—The reagent prepared by condensation of $C_{10}H_8$, oleic acid, and conc. H_2SO_4 is ι - or κ -6- or 7-sulpho-1-naphthylstearic acid (I) (cf. Sandelin, G.P. 114,491), and can be partly purified through the Pb salt. Oleic acid with $C_{10}H_8$ and $1\frac{1}{2}$ mols. of Al_2Cl_6 gave ι - or κ -1-naphthylstearic acid (II) [oxidised to hemimellitic acid (III); does not form emulsions or foams, or hydrolyse fats]. The *Me* ester, *acid chloride*, and *Na*, *K*, *Al*, *Pb*, and *Cu* salts are described. (II) is sulphonated at 70° during 2 hr., giving a dibasic acid, identical with (I) and oxidised (alkaline $KMnO_4$) to (III) and 4-sulphophthalic acid (cf. Sandelin, Ann. Acad. Sci. Fenn., A, 19, No. 4). The SO_3H is not displaced by Na-Hg, and must therefore be β . Condensation of $C_{10}H_8$ in conc. H_2SO_4 with saturated and hydroxystearic (IV) acids failed to give products which hydrolysed fats. Only unsaturated acids give compounds with that property, but (IV) with 4% oleum and $C_{10}H_8$ gave a product with some hydrolysing power. H. G. M.

(-)-Phenylmethoxyacetonitrile. (Miss) I. A. SMITH (J.C.S., 1935, 194-196).— $SOCl_2$ and *r*-phenylmethoxyacetamide give a mixture of the nitrile and *BzCN*, but P_2O_5 in PhMe affords the pure nitrile. P_2O_5 and the $(+)$ -amide yield $(-)$ -phenylmethoxyacetonitrile, b.p. $120^\circ/17$ mm. $[\alpha]_D^{20} - 63.5^\circ$ in $COMe$. Racemisation with EtOH-KOH gives a final small $(+)$ -rotation, whilst with H_2O , the product is inactive. *MgPhBr* with the *r*-nitrile affords benzoin *Me* ether and with *BzCN* yields $CPh_3 \cdot OH$. F. R. S.

Hydrogenation of phenylpyruvic acid. J. JARROUSSE (Compt. rend., 1935, 200, 324-326).—Reduction of phenylpyruvic acid with Na-Hg in acid solution gives a γ -lactone (I), m.p. 225° , of α -dihydroxy- β -phenyl- γ -benzylglutaric acid (II) [*Ac* derivative (III), m.p. 168°]. Hydrolysis of (III) or the action of OH' on (I) gives (II), m.p. 140° . Maintaining (II) at $150-175^\circ$ for 2-3 min. gives an *isomeride* of (I), m.p. 136° . H. D.

Synthesis of glucocaffeic acid. F. MAUTHNER (J. pr. Chem., 1935, [ii], 142, 149—151).—Me caffeate and acetylglucosidyl bromide in aq. COMe_2 -NaOH give an oil, hydrolysed by cold 6% $\text{Ba}(\text{OH})_2$ to *glucocaffeic acid*, m.p. 159—160° after sintering.

R. S. C.

Esters of caffeic acid. B. HELFERICH and F. VORSATZ (J. pr. Chem., 1935, [ii], 142, 191—192).—Caffeic acid, the alcohol, and H_2SO_4 at 100° (2 hr.) give the *Me* (I), m.p. 162°, *Et*, m.p. 149.5°, *Pr*^a, m.p. 127°, and *Bu*^a, m.p. 110°, esters, sol. in Na_2CO_3 , but recovered therefrom by Et_2O . (I) is also formed at room temp. (several days) and the structure thus indicated is confirmed by the FeCl_3 colour characteristic of chlorogenic acid.

R. S. C.

Resolution of tertiary hydroxy-carboxylic acids. E. W. CHRISTIE, A. MCKENZIE, and A. RITCHIE (J.C.S., 1935, 153—155).—*r*-4-Methoxybenzylidene acid, obtained from KOH - EtOH and 4-methoxybenzyl, could not be resolved. *r*-Phenyl-*p*-tolylglycollic acid is resolved through the quinine salt into (+)phenyl-*p*-tolylglycollic acid, m.p. 125—127°, $[\alpha]_{\text{D}}^{25} +2.5^\circ$ in EtOH (*Et* ester, $[\alpha]_{\text{D}}^{25} +4.4^\circ$ in COMe_2), reduced to the inactive *acetic acid*. *r*-*p*-Tolylmethylglycollic acid, m.p. 102—104°, from *p*- $\text{C}_6\text{H}_4\text{Me}$ - MgBr and AcCO_2H , is resolved by quinine into the (–)acid, m.p. 140—142°, $[\alpha]_{\text{D}}^{20} -51.2^\circ$ into EtOH . *r*-Anisylmethylglycollic acid is resolved with morphine (cf. McKenzie *et al.*, A., 1932, 1037).

F. R. S.

Constitution of norcaryophyllenic acid. G. R. RAMAGE and J. L. SIMONSEN (Chem. and Ind., 1935, 151).—Dehydronorcaryophyllenic acid (I) with O_3 yields probably α -keto- β - β -dimethylglutaric acid, hygroscopic (2:4-dinitro-, decomp. 243°, and *p*-nitrophenylhydrazones, decomp. 192°), oxidised by H_2O_2 in alkali to $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. Norcaryophyllenic acid is therefore *d*-cis-3:3-dimethylcyclobutane-1:2-dicarboxylic acid (cf. Ruzicka *et al.*, this vol., 351), and (I) 3:3-dimethyl- Δ^1 -cyclobutene-1:2-dicarboxylic acid.

R. S. C.

Stereoisomeric 4-methylcyclohexane-1-carboxylic-1-acetic acids. S. GOLDSCHMIDT and G. GRAFINGER (Ber., 1935, 68, [B], 279—286).—Crit. re-examination has been made of the work of Quadrat-Khuda (A., 1931, 1055), whose 4-methylcyclohexane-1-carboxylic-1-acetic acid (I) (*A*, m.p. 137°; *B*, m.p. 129°; *C*, m.p. 174°; *D*, m.p. 146°) affords the sole instance of the existence of monocyclic compounds in more forms than can be accounted for by a plane ring structure. The constitution of *Et* 4-methylcyclohexylidenecyanoacetate (II) is confirmed since the sole product of its oxidation by KMnO_4 is 4-methylcyclohexanone, identified as the semicarbazone. The possibility of isomerisation during the addition of KCN to (II) appears excluded by the results of oxidation of the isomeric forms of (I). The possible production of mixtures of stereoisomeric acids by a different process is examined by treatment of *Ag*, 4-methylcyclohexane-1:1-diacetate with I , giving the lactone $\text{C}_{10}\text{H}_{16}\text{O}_2$, b.p. 98°/0.6 mm., and 4-methyl-1-hydroxymethylcyclohexane-1-acetic acid, which yields *C* and *A*, but affords no evidence of the existence of *B* or *D*. Re-examination

of the separation by treatment of the NH_4 salts of *A*, *B*, *C*, and *D* with EtOH as described or by a modified procedure indicates impossibility of success. *A* and *C* are isolable thereby, and the residual fractions consist mainly of *A* which can generally be obtained therefrom only incompletely and with difficulty by direct crystallisation. A preferable method consists in converting the acids into their imides (*A*, m.p. 129°; *C*, m.p. 171°) and subsequent semi-hydrolysis, whereby *A* is transformed into a sparingly sol. *semi-amide*, m.p. 191°. Indications of the existence of *B* and *D* are not obtained and they should be deleted from the lit. The mixed m.-p. diagram of *A* and *C* shows the formation of 2 additive compounds (*A*:*C*—1:1 and 4:1) the m.p. of which are approx. those of the supposed *B* and *D* varieties.

H. W.

Amino-acids. V. Modification of the reduction of benzamidoacrylic acids in the Erlennmeyer synthesis. V. DEULOFEU. VI. Preparation of 3-hydroxy-4-methoxyphenylalanine. V. DEULOFEU and O. REPETTO (Anal. Fis. Quím., 1934, 32, 152—158, 159—164; cf. A., 1933, 1159).—V. An improved method of reduction by Na-Hg of $\text{CHR}\cdot\text{C}(\text{NHBz})\cdot\text{CO}_2\text{H}$ to $\text{CH}_2\text{R}\cdot\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{H}$ ($\text{R}=\text{Ph}$, *p*- $\text{C}_6\text{H}_4\cdot\text{OMe}$, furyl, piperonyl) is described. 2:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$ and $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) when heated with NaOAc and Ac_2O give an *azlactone*, m.p. 181° (softens at 167°), which on hydrolysis with 1% NaOH yields α -benzamido-2:4-dimethoxycinnamic acid, m.p. 214—215°. Reduction with Na-Hg gives the *N*-Bz derivative, m.p. 162—164°, of α -amino- β -2:4-dimethoxyphenylpropionic acid, m.p. 241° (phenylurethane, m.p. 178°).

VI. *iso*Vanillin (II) and (I) give an *azlactone* (*Ac* derivative, m.p. 139°) which yields α -benzamido-3-hydroxy-4-methoxycinnamic acid, m.p. 194°, reduced to the *N*-Bz derivative, m.p. 180°, of α -amino- β -3-hydroxy-4-methoxyphenylpropionic acid (III), m.p. 272° (decomp.). With hydantoin and thiohydantoin, (II) gives 3-acetoxy-4-methoxybenzylidene-hydantoin (IV), m.p. 248°, and 2-thiohydantoin, m.p. 251°, respectively. Reduction of (IV) gives 3-hydroxy-4-methoxybenzylhydantoin, m.p. 194°, hydrolysed [$\text{Ba}(\text{OH})_2$ to (III)]. With diketopiperazine, (II) gives *bis*-(3-acetoxy-4-methoxybenzylidene)diketopiperazine, m.p. > 290°, which when reduced with P and HI yields 3:4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (cf. Hirai, A., 1921, i, 248).

F. R. G.

Phenylsuccinic acid series. XI. Interaction of the optically active and inactive diphenylsuccinic anhydrides with butyl alcohol and aniline. H. WREN and G. L. MILLER (J.C.S., 1935, 157—160).—Interaction of Bu°OH and *r*-diphenylsuccinic acids in various solvents in glass and SiO_2 vessels shows that the ratio of Bu°H *r*- to *meso*-diphenylsuccinate in the product depends on the nature of the vessel and of the solvent; isomerisation in glass is invariably > in SiO_2 . These two factors also operate in producing racemisation during the interaction of Bu°OH and the *d*-anhydride. In non-basic solvents the effect is almost entirely due to the glass. Reaction between NH_2Ph and the *d*-anhydride occurs so rapidly and under such mild conditions that the nature of the vessel has little influence; in sufficiently

basic solvents racemisation is very pronounced. Evidence is advanced against the view that a *r*-compound in dil. solutions necessarily behaves as a mixture of *d*- and *l*-forms. The following *diphenylsuccinates* have been prepared: *Bu^a r*-, m.p. 46—47°; *Bu^a H r*-, m.p. 129—130°; *Bu^a meso*-, m.p. 100—101°; *Bu^a H meso*-, m.p. 159.5—160.5°; *Bu^a d*-, m.p. 64—64.5°, [α]_D²⁰_{5.91} +279.5° in COMe₂; *Bu^a H d*-, m.p. 93.5—94°, [α]_D¹⁷_{6.1} +349.6° in COMe₂; *Bu^a l*-, m.p. 64—64.5°, [α]_D^{19.6}₅ -227.3° in COMe₂; and *Bu^a H l*-, m.p. 93.5—94°, [α]_D¹⁴₄ -278.8° in COMe₂. *r*-Diphenylsuccinic anhydride and PhCN give an additive product, m.p. 218—222°. Amounts of *r*- and *meso*-compounds are determined by f.p. F. R. S.

Isomeric α -cyano- β -phenyl- α -methylglutaric acids and their derivatives. S. AVERY and F. C. MCGREW (J. Amer. Chem. Soc., 1935, 57, 208—211).—The work of Carter and Lawrence (Proc. C.S., 1900, 16, 178) is amplified and in places corr. The *A*- (α -, *trans*-) and *B*- (β -, *cis*-) series of compounds described below are believed to be stereoisomeric. Et₂ α -cyano- β -phenyl- α -methylglutarate, m.p. 90° (I), with KOH-abs. EtOH gives the corresponding *A*-acid (II), m.p. 164° (*K* and *K₂* salts), which with HCl-EtOH regenerates (I) and with AcCl gives the *anhydride*, m.p. 111° [considered (*loc. cit.*) to be the imide], hydrolysed to (II) by hot H₂O; by the *brucine* salts (that of *d*-acid less sol.) it yields the *d*- and *l*-forms, m.p. 185—187°, [α]_D +7.4°, -7.5°. The corresponding *B*-acid (III), m.p. 194°, is similarly resolved, the *d*- (less sol. *brucine* salt) and *l*-forms having m.p. 164—165° (decomp.) and [α]_D +32.4°, -32.1°. All of these CN-compounds with KOH yield α -carbethoxy- β -phenyl- α -methylglutaric acid (IV), m.p. between 176° and 190° (decomp.) (no substance, m.p. 148°, was isolated), giving slowly at 125° or rapidly in H₂O at 175° β -phenyl- α -methylglutaric acid (V), m.p. 127°. (I) with H₂SO₄-AcOH yields *A*- α -carbethoxy- β -phenyl- α -methylglutarimide (VI), m.p. 149° (corr.); the corresponding *B*-ester (VII) yields similarly the *B*-imide (VIII), m.p. 128—129°, whilst the *Me* esters corresponding with (I) and (VII) give *A*-, m.p. 172—173°, and *B*- α -carbethoxy- β -phenyl- α -methylglutarimide, m.p. 167—169°, respectively. (VII) and (VIII) with K₂CO₃-EtOH afford *A*-, m.p. 163—164°, and *B*- α -carbethoxy- β -phenyl- α -methylglutaric acid (position of NH₂ unknown), m.p. 168—170°, respectively, both rapidly dehydrated by hot, conc. HCl to the corresponding imide. All the above products with HCl-AcOH at 150° give (V) and a mixture, m.p. 115—117°, of much of an *isomeride* with a little (V). (V) is obtained quantitatively from (IV) by H₂O at 140—150°. Et₂ α -cyano- β -phenyl- α - β -dimethylglutarate gives an ester-imide analogous to (VI), but none could be obtained from the β -phenyl- α -benzyl- β -methyl, or β -phenyl- α -benzyl esters. The Me₂, Pr₂, and Bu₂ esters corresponding with (I) and the α -cyano-esters of other substituted glutaric acids are less readily separated into pure isomerides.

R. S. C.

Additive reactions of unsaturated α -keto-acids.

IV. (MISSES) M. REIMER, E. TOBIN, and M. SCHAFFNER (J. Amer. Chem. Soc., 1935, 57, 211—215; cf. A., 1934, 72).—3 : 4-C₆H₃(OMe)₂·CH:CH·CO₂H (I)

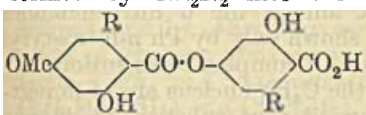
and 3 : 4-dimethoxybenzylidenepyruvic acid (II) resemble the 4- rather than the 3-OMe-acids. (II) (prep. from AcCO₂H, veratraldehyde, and KOH-MeOH), m.p. 155° (*Et*, m.p. 71—72°, and *Me*, m.p. 118°, esters), is only slightly photosensitive and with Br (1 mol.) in cold CHCl₃ gives a *dibromide*, m.p. 134—136°, which with cold H₂O or, better, hot MeOH gives β -bromo-3 : 4-dimethoxybenzylidenepyruvic acid (III), m.p. 157° (decomp.; softens at 150°) (*Me* ester, m.p. 141—142°); with 2 mols of Br in CHCl₃ (II) gives a mixture, which with Br in AcOH affords β : 6-dibromo-3 : 4-dimethoxybenzylidenepyruvic acid (*Me* ester, m.p. 171—172°), which, when heated above the m.p., 162—164° (decomp.), yields α : 6-dibromo-3 : 4-dimethoxycinnamaldehyde, m.p. 180° (decomp.) [*semicarbazone*, m.p. about 215° (decomp.)], oxidised by H₂O₂-Na₂CO₃ to the corresponding acid (IV), m.p. 233°. (I), m.p. 179—181°, gives only the *dibromide* (V), m.p. 149°. α -Bromo-3 : 4-dimethoxycinnamic acid [not obtained from (V), but readily from (III) by H₂O₂], m.p. 167—168° (*Me* ester, m.p. 83°), with cold H₂O gives α -bromo-3 : 4-dimethoxystyrene, m.p. 67° [also obtained from (V)], and α -bromo- β -hydroxy-3 : 4-dimethoxycinnamic acid, m.p. 166° (*Me* ester, m.p. 145—147°); with Br it affords α : 6-tribromo- γ -3 : 4-dimethoxyphenylpropionic acid, m.p. about 149° (resolidifies, second m.p. much >200°), which at 150° loses HBr to form (IV) (*Me* ester, m.p. 139°; oxidised by KMnO₄ to 6-bromoveratric acid), which with 25% KOH-EtOH gives an *isomeride*, m.p. 198° [*Me* ester, m.p. 92°; changes slowly to (IV) when heated], and a small amount of α : 6-dibromo-3 : 4-dimethoxystyrene, m.p. 100° R. S. C.

α -Aldehyde-carboxylic acids. II. Synthesis of 4-methoxyphthalaldehydic acid and a new synthesis of opianic acid. S. N. CHAKRAVARTI and M. SWAMINATHAN (J. Indian Chem. Soc., 1934, 11, 873—875).—Oxidation (SeO₂) of 5-methoxyhomophthalic acid gives 4-methoxyphthalonic acid, isolated as the *anilino*-derivative, m.p. 165°, which when heated yields the *anilino*-derivative, m.p. 179—180°, of 4-methoxyphthalaldehydic acid, m.p. 141°. Reduction (Na-Hg) of the acid leads to 5-methoxyphthalide, m.p. 119°. A similar series of reactions from 3 : 4-dimethoxyhomophthalic acid, m.p. 116°, gives opianic acid. F. R. S.

Lichen substances. XLVII. Constitution of physodic acid. II. Y. ASAHINA and H. NOGAMI. **XLVIII. Microphylllic acid, a new depside from *Cetraria callata* f. *microphyllina*.** A. ZAHLBRUCKNER, Y. ASAHINA, and F. FUJIKAWA. **XLIX. Synthesis of methyl sekikoate dimethyl ether.** Y. ASAHINA and M. YASUE (Ber., 1935, 68, [B], 77—80, 80—82, 132—134).—XLVII (cf. A., 1934, 891). Treatment of *Me isophysodate* Me₃ ether with conc. KOH-EtOH at 160° leads to hexoic acid and *protophysodon* Me₃ ether (I) C₂₁H₂₅O₄, b.p. 130°/0.08 mm. (I) and Br in AcOH yield a *Br₃*-derivative (II), m.p. 126—127°, regarded by analogy with the *Br*-substituted derivative of orcinol Me₂ ether (Fujikawa, this vol., 347) as 2 : 4 : 2'-tribromo-5 : 3' : 5'-trimethoxy-3-methyl-1'-n-amyldiphenyl ether. Physodic acid is therefore a depsidone derivative the skeleton of which is a Ph₂ ether derived from orcinol and

hydroxyolivetol. Oxidation of (I) with $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH causes destruction of the hydroxyolivetol nucleus with formation of 6-methoxy-2-methyl-*p*-benzoquinone, m.p. 151° , whereas similar treatment of (II) occurs at the expense of the orcinol nucleus with formation of 3-bromo-6-methoxy-2-*n*-amyl-*p*-benzoquinone, m.p. 114° . Repeated crystallisation of crude atranorin from *Parmelia physodes* leads to the isolation of chloroatranorin, m.p. $207\text{--}208^\circ$.

XLVIII. Extraction of the thalli of *C. collata* leads to the isolation of microphyllinic acid (I), m.p. 116° , which gives a violet colour with FeCl_3 but no colour with bleaching powder. (I) is transformed by CH_2N_2 into the *Me* ester, m.p. 118° ,



(I)

whilst olivetonide Me_2 ether, m.p. 94° , is also produced if excess of the reagent is used. Boiling, conc. HCO_2H

converts (I) smoothly into olivetonide and its Me_1 ether. (I) is therefore A ($\text{R}=\text{CH}_2\text{--CO--C}_5\text{H}_{11}$); it is related to α -collatolic acid in the same manner as is olivetoric to physodic acid.

XLIX. 4-Hydroxy-3:5-dimethoxyallylbenzene is hydrogenated (Pd-C in EtOH) to 4-hydroxy-3:5-dimethoxy-*n*-propylbenzene (I), b.p. $143\text{--}146^\circ/3\text{ mm.}$, (sparingly sol. *Na* salt; acetate, m.p. $87\text{--}88^\circ$; benzoate, m.p. $91\text{--}92^\circ$). (I) in anhyd. HCN is converted by HCl and AlCl_3 into 3-hydroxy-2:5-dimethoxy-6-*n*-propylbenzaldehyde (II), m.p. $94\text{--}95^\circ$. Condensation of (II) with 2:4-dimethoxy-6-*n*-propylbenzoyl chloride (from divaricic acid *Me* ether and SOCl_2) in $\text{C}_5\text{H}_5\text{N}$ affords *sekika*-aldehyde Me_2 ether, m.p. $102\text{--}103^\circ$, oxidised by KMnO_4 to *sekikaic* acid Me_2 ether (III), m.p. $141\text{--}142^\circ$, the *Me* ester, m.p. $80\text{--}81^\circ$, of which is identical with that obtained from natural sources. (III) is therefore 3-2':4'-dimethoxy-6'-*n*-propylbenzoyl-2:4-dimethoxy-6-*n*-propylbenzoic acid.

H. W.

Cannizzaro reaction applied to the aliphatic and arylaliphatic series. L. PALFRAY and S. SABETAY (Compt. rend., 1935, 200, 404-406).—Reaction of aldehydes (I) of these series with $\text{CH}_2\text{Ph}\cdot\text{OK}$ (II) (A., 1932, 867; 1934, 758) is not a simple Cannizzaro reaction, since (II) with heptaldehyde, hydroxycitronellal, or myrtanal yields BzOH , with reduction of (I). COPh_2 and (II) give BzOH and $\text{CHPh}\cdot\text{OH}$.

E. W. W.

Action of maleic anhydride on aldehydo-amine bases. G. LA PAROLA (Gazzetta, 1934, 64, 919-931).—The general reaction $\text{NR}\cdot\text{CHR}' + (\text{CH}\cdot\text{CO})_2\text{O} \xrightarrow{-\text{H}_2\text{O}} \text{NHR}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H} + \text{R}'\text{CHO}$ proceeds at $40\text{--}50^\circ$ in EtOH. Thus the product when $\text{R}=\text{H}$ and $\text{R}'=\text{Ph}$, $\text{C}_6\text{H}_4\cdot\text{OMe}$, or $\text{CHPh}\cdot\text{CH}$ is maleanilic acid; when $\text{R}=\text{C}_6\text{H}_4\cdot\text{OEt}$ and $\text{R}'=\text{Ph}$, is *p*-phenetyl-maleamic acid. When $\text{R}=\text{o}$ -, *m*-, and *p*- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{R}'=\text{Ph}$, *o*-, *m*-, and *p*-carboxyphenylmaleamic acids, m.p. 187° , 204° , and 212° , respectively, are formed; when $\text{R}=\alpha\text{-C}_{10}\text{H}_7$ and $\text{R}'=\text{Ph}$, the product is α -naphthylmaleamic acid, m.p. 142° , of which the β -isomeride is obtained when $\text{R}=\beta\text{-C}_{10}\text{H}_7$ and $\text{R}'=\text{C}_6\text{H}_4\cdot\text{OMe}$. Benzylideneaminoazobenzene yields benz-neazophenylmaleamic acid, m.p. 202° . E. W. W.

Reaction of phenylhydrazine-*p*-sulphonic acid with aldehydes. H. BILTZ [with BODENBURG and WANDERSCHECK] (Ber., 1935, 68, [B], 221-226).—The presence of SO_3H diminishes the stability of the compounds with aldehydes, which usually are hydrates, $\text{OH}\cdot\text{CHR}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$. They generally dissociate into their components in H_2O , but re-combination accompanies crystallisation. Simultaneous action of $\text{NHPh}\cdot\text{NH}_2$ and $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ affords the aldehydephenylhydrazones. Substituents which have a negative effect on C attached to CHO in the aldehyde favour the stability of the hydrate and 2 such activating groups favour the loss of H_2O and production of the true hydrazone. The following -phenylhydrazone-*p*-sulphonic acid hydrates are described: *p*-hydroxybenzaldehyde-, decomp. 245° , which does not lose H_2O at $70\text{--}80^\circ$ /diminished pressure, its *Na* salt ($+3\text{H}_2\text{O}$), and (?) the similar products from *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$; *p*-dimethylaminobenzaldehyde-, decomp. about 246° ; *p*-nitrobenzaldehyde- ($+3\text{H}_2\text{O}$) and its *Na*, *Mg*, *Pb*, and *Ba* ($+2\text{H}_2\text{O}$) salts; piperonal-, decomp. $180\text{--}190^\circ$ after softening at $160\text{--}170^\circ$ (*Na* salt). Protocatechualdehydephenylhydrazone-*p*-sulphonic acid, decomp. 260° or $248\text{--}256^\circ$ when slowly heated, its *Na* and NH_4 salts are described.

H. W.

Equilibria between amino-acids and aromatic aldehydes. I. J. M. GULLAND and I. H. MEAD (J.C.S., 1935, 210-217). The condensation of aromatic aldehydes and NH_2 -acids or esters leads (a) irreversibly, to the arylidene derivatives of arylserines and of $\alpha\beta$ -diarylhydroxyethylamines (Erlenmeyer, A., 1895, i, 281); (b) reversibly, to *N*-arylidene derivatives (Schiff's bases) (cf. Bergmann and others, A., 1925, i, 890). The Schiff's bases obtained are *Ba* 2-hydroxy-3- and -5-methoxybenzylideneglycine [condensation of the aldehyde, glycine, and $\text{Ba}(\text{OAc})_2$], and *Ba* 2:5- and 2:3-dimethoxybenzylideneglycine. Vanillin, isovanillin, veratraldehyde, and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ do not condense. Polarimetric study of the rates of reaction of *d*-phenylalanine with 2:3-, 2:5-, and 3:4-($\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CHO}$ shows that the first two aldehydes condense more rapidly and to a greater extent than the third, the products having greatly increased $[\alpha]$. Condensations are reversible, and the aldehydes and NH_2 -acids are recovered as 2:4-dinitrophenylhydrazones, α -naphthylureide or *p*-toluenesulphonyl derivative after the hydrolysis of the condensation products by acid. Structures for the condensation products are discussed.

F. R. S.

Benzeneazolignin and the phenolic nature of "dioxan-lignin." E. WEDEKIND (Naturwiss., 1934, 23, 70). "Dioxan-lignin" (I), prepared by heating lignin with dioxan-HCl at 100° , is sol. in many org. solvents and aq. NaOH (not Na_2CO_3), and still contains about 15.5% OMe. In AcOH it gives Br- and NO_2 -compounds. Its alkaline solution develops scarcely any colour with PhN_2Cl , but acid ppts. from the solution thus obtained an azo-compound (N 5.6%), electrometric titration of which leads to a formula, $\text{C}_{19}\text{H}_{20}\text{O}_6$, for (I). Diazotised *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ affords similarly a H_2O -sol. dye, which dyes animal fibres yellow.

R. S. C.

Reactions of *trans*-2-ketodecahydronaphthalene. II. E. LEHMANN and B. KRÄTSCHKE (Ber., 1935, 68, [B], 360—363; cf. this vol., 84).—The action of boiling 40% NaOH on *trans*-3-chloro-2-ketodecahydronaphthalene (improved prep.) leads to 3-hydroxy-2-ketodecahydronaphthalene, which immediately undergoes disproportionation to 2:3-dihydroxydecahydronaphthalene, m.p. 168° (oxidised by KMnO₄ in COMe₂ to *trans*-cyclohexane-1:2-diacetic acid, m.p. 107°), and non-isolable 2:3-diketodecahydronaphthalene, which suffers ring contraction with formation of 2-hydroxy-Bz-hexahydroindene-2-carboxylic acid (I) (+0.5H₂O), m.p. 134° (Me ester, m.p. 49°). (I) passes when heated into the spiro-lactide

$$\text{C}_6\text{H}_{10} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{O-CO} \\ \diagup \quad \diagdown \\ \text{CO-O} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_{10}$$
, m.p. 201°, re-converted by boiling H₂O, NaOAc, or alkali into (I). Treatment of (I) with 80% H₂SO₄ at 75—80° gives CO, Bz-hexahydroindene-2-one, b.p. 93°/12 mm. (oxime, m.p. 164°), and Δ^1 -Bz-hexahydroindene-2-carboxylic acid, m.p. 161°. The Cl₂-derivative (*loc. cit.*) is hydrolysed to (I) and hence is 2:2-dichloro-3-ketodecahydronaphthalene. H. W.

Synthesis of unsaturated compounds from β -ionone and tetrahydroionone. R. G. GOULD, jun., and A. F. THOMPSON, jun. (J. Amer. Chem. Soc., 1935, 57, 340—345).—Syntheses intended eventually to lead to reduction products of vitamin-A are recorded. β -Ionone, C₁₅H₂₂, and K *tert*-amyloxide (I) in Et₂O at -15° to 0° give a mixture, b.p. 114—117°/2 mm. (Ag salt), of γ -hydroxy- ϵ -2:6:6- Δ^1 -trimethylcyclohexenyl- γ -methyl- Δ^3 -penten- Δ^5 -inene and ϵ -keto- γ -2:6:6- Δ^1 -trimethylcyclohexenyl- Δ^5 -hexinene, which by partial hydrogenation (Pd) in MeOH or EtOH gives a mixture of the derived ethylenic compounds, which with Ac₂O or CCl₃·CO₂H gives ϵ -2:6:6- Δ^1 -trimethylcyclohexenyl- γ -methyl- Δ^5 -pentadien- α -ol, which is isolated as the oily *H* phthalate, and with PBr₃ gives α -bromo- ϵ -2:6:6- Δ^1 -trimethylcyclohexenyl- γ -methyl- Δ^5 -pentadiene, an oil. This with Et sodioacetate (II) affords after hydrolysis by 5% KOH-MeOH η -keto- α -2:6:6- Δ^1 -trimethylcyclohexenyl- Δ^5 -octadiene, b.p. 165—168°/3 mm. (semicarbazone, m.p. 160—165°), hydrogenated (PtO₂) in AcOH to η -keto- α -2:6:6-trimethylcyclohexyloctane (III) (semicarbazone, m.p. 113.5—114°). Tetrahydroionone and C₂H₂, best with (I), in Et₂O give a 75% yield of ϵ -2:6:6-trimethylcyclohexyl- γ -methyl- Δ^5 -pentinen- γ -ol, b.p. 117—118°/2 mm., hydrogenated (PtO₂) in AcOH to the corresponding OH-pentane derivative, b.p. 112—113°/2 mm. (Ac derivative, b.p. 124—125°/2 mm.), or in EtOH to ϵ -2:6:6-trimethylcyclohexyl- γ -methyl- Δ^5 -penten- γ -ol, b.p. 115—116°/2 mm. This with Ac₂O or, better (55%), CCl₃·CO₂H gives ϵ -2:6:6-trimethylcyclohexyl- γ -methyl- Δ^5 -penten- α -ol, b.p. 125—126°/2 mm. (*H* phthalate), and with PBr₃ α -bromo- ϵ -2:6:6-trimethylcyclohexyl- γ -methyl- Δ^5 -pentene, an oil, which with (II) affords η -keto- α -2:6:6-trimethylcyclohexyl- γ -methyl- Δ^5 -octene, b.p. 165—168°/3 mm. (semicarbazone, m.p. 133°), giving (III) by hydrogenation. R. S. C.

Reaction of magnesium with α -halogenoketones. C. H. FISHER (J. Amer. Chem. Soc., 1935, 57, 381).— α -Bromoacetomesitylene in Et₂O-C₆H₆

reacts with 0.6 Mg to give a OMgBr-derivative, which with acid affords C₆H₂Me₃·COMe (45%) and (C₆H₂Me₃·CO·CH₂)₂ (10%). CPh₂:CBr·COPh gives no Grignard reagents. R. S. C.

Influence of chemical nature and position of substituents on morphological relationship. C. WEYGAND and F. SCHACHER. **Determination of constitution by morphological methods. Direction of enolisation of keto-enols.** C. WEYGAND, P. KOCH, and F. SCHACHER (Ber., 1935, 68, [B], 227—234, 234—239; cf. A., 1929, 564, 815).—Of the two *m*-methylchalcones only Ph *m*-methylstyryl ketone (I) is morphologically related to the parent substance (II) whilst among the 6 nitrochalcones similar relationship is shown only by Ph *p*-nitrostyryl ketone. Assuming that in complex substitution only the groups vicinal to the C₆H₅ nucleus are of importance, it may be assumed that substitution in one C₆H₅ nucleus of (II) is governed by the same laws as in CHPh:CH·CO₂H or CHPh:CH·CHO and in the other must resemble that of COPhMe. By analogy, direct substitution in positions 3 and 4' is impossible, and these are termed "quasi-substituted," to indicate hindrance to the entry of a new atom or group. Only in these positions can a relatively simple substituent (Me, NO₂) exercise so little influence on the fine structure of (II) that morphological relationships between (II) and its derivatives are possible. Among the 4 cryst. methylchalcones, isomorphism occurs only between the 3- and 4'-derivatives. The following data appear new: *o*-tolyl styryl ketone, b.p. 218—219°/12 mm., from *o*-C₆H₄Me·CHO and COPhMe, and NaOH or NaOMe; Ph *o*-methylstyryl ketone, b.p. 209—211°/19 mm., 197°/7 mm., from PhCHO and *o*-methylacetophenone; *m*-tolyl styryl ketone, in forms m.p. 66°, 53°, 67°, and 68°, respectively; (I) forms, m.p. 51° and 61° (corresponding *dipicrate*, m.p. 107°) (Mayer's variety, m.p. 73°, could not be observed); *o*-nitrophenyl styryl ketone, m.p. 123° and 125.5°, respectively; Ph *o*-nitrostyryl ketone, m.p. 129°; *m*-nitrophenyl styryl ketone, m.p. 145°, polymerises very readily (a second form has m.p. 120°); Ph *m*-nitrostyryl ketone, m.p. 131° and 110°.

Ozonisation of CHMeBzAc in EtCl leads to products derived from CMeBz:CMc·OH and CMeAc:CPh·OH. It follows therefore that fission by O₃ permits conclusions as to the constitution in solution of keto-enols which do not suffer after-enolisation and cannot yield dienols, but throws no light on the structure of the solid. It is only certain that the diketone-form does not participate in the present equilibrium. Application of morphological methods (see above) shows that the modifications, m.p. 84° and 64° respectively, of CH₂Bz·CO·C₆H₄Me-*p* are isomorphous with forms of *p*-C₆H₄Me·CO·CH:CHPh and NO₂·C₆H₄·CH:CHPh and hence are polymorphous varieties of *p*-C₆H₄Me·CO·CH:CHPh·OH, whereas the form, m.p. 42°, is isomorphous with forms of C₆H₄Me·CH:CHBz and NO₂·C₆H₄·CH:CHBz and therefore is *p*-C₆H₄Me·C(OH):CHBz. The dibromide of (I) transformed by KOAc and K₂CO₃ in boiling EtOH into Ph α -bromo-*m*-methylstyryl ketone, b.p. 190—193°/2 mm., and thence by boiling KOH-MeOH

into *m*-methyl dibenzoylmethane (III), m.p. 53°. Solidification of (III) is provoked only by *Ph m*-methylstyryl ketone, m.p. 66° (of the possible *m*- and *m'*-methylchalcones); hence (III) is *m*-C₆H₄Me·C(OH)·CHBz. Similarly seeding of molten *o*-nitrodibenzoylmethane, m.p. 117°, with the various *o*- and *o'*-nitrochalcones establishes the constitution *o*-NO₂·C₆H₄·C(OH)·CHBz. H. W.

Steric hindrance in compounds of mesitylene and triphenylbenzene. E. P. KOHLER and L. W. BLANCHARD, jun. (J. Amer. Chem. Soc., 1935, 57, 367—371).—Steric hindrance is not evident in the reaction of β-mesityl αβ-unsaturated ketones. It is, however, shown by similar β-2:4:6-C₆H₂Ph₃ ketones and by other derivatives of C₆H₂Ph₃; formation of fluorene derivatives from the latter is very facile. *Ph* 2:4:6-trimethylstyryl ketone (I) (from C₆H₂Me₃·CHO and CPhMe), m.p. 96°, readily forms a dibromide, m.p. 140°, which with NaOMe gives *Ph* β-methoxy-2:4:6-trimethylstyryl ketone, m.p. 113°, oxidised by KMnO₄ to C₆H₂Me₃·CO₂Me and hydrolysed by acids to C₆H₂Me₃·CO·CH₂Bz. (I) and MgPhX give, by 1:4-addition, β-phenyl-β-mesitylpropionophenone, m.p. 64° (oxime, m.p. 185°), and mesityl 2:4:6-trimethylstyryl ketone (similarly prepared), m.p. 99°, with MgMeX gives similarly β-mesityl-*n*-butylomesitylene, b.p. 194°/1 mm. However, 2:4:6-trimethylstyryl ketone, m.p. 67°, reacts by both 1:4- and 1:2-addition. The following are also described: β-Mesityl-*n*-butyl Me ketone semicarbazone, m.p. 169°; mesityldimethylcarbinol, m.p. 113°; mesityldiphenylcarbinol, m.p. 88°.

1:3:5-C₆H₃Ph₃ and Br in CS₂ give 1-bromo-2:4:6-triphenylbenzene (II), m.p. 129—130°. The structure of this and other derivatives described below is proved by the reactions detailed. The Grignard reagent (III) of (II), obtained in 94% yield in C₆H₆ or xylene, but not at all in Et₂O, gives some C₆H₃Ph₃ and an 84% yield of 2:4:6-triphenylbenzoic acid (IV), m.p. 253—255° (decomp.) [Me ester, m.p. 91°, obtained by CH₂N₂, or, in poor yield, by Me₂SO₄·NaOH, but not by MeI and the Ag salt (not obtained pure)]. 2:4:6:2':4':6'-Hexaphenyldiphenyl (V), m.p. 348°, not formed from (II) and (III), is obtained in 50% yield from (III) and CuCl₂. (III) and AcCl give 2:4:6-triphenylacetophenone, m.p. 125° (benzylidene derivative, double m.p. 192 and 210°), which with MgMeI gives 1 mol. of CH₄ and a Mg-compound, from which it is regenerated by acids. 2:4:6-Triphenylbenzophenone (VI), m.p. 168—169°, is obtained similarly (60% yield) or from C₆H₃Ph₃, AcCl, and AlCl₃ (90% yield). 2:4:6:2':4':6'-Hexaphenylbenzophenone (VII), m.p. 266°, is obtained from (III) (or 1:3:5-C₆H₃Ph₃ and AlCl₃) and COCl₂ in C₆H₆, which gives also much C₆H₃Ph₃ and some (V). (V) and 0.5% Na-Hg in C₆H₆-EtOH give 2:4:6-triphenylbenzhydrol (VIII), m.p. 158°, also obtained from PhCHO and an excess of (III), but bimol. reduction could not be effected. (VIII) is indifferent to Me₂SO₄, but by MgEtBr, followed by BzCl, affords benzoate, m.p. 156°, very slowly hydrolysed by KOH-MeOH; it is oxidised to (VI) by PhCHO or (3), and with conc. acids gives 1:3:9-triphenylfluorene, m.p. 149°. (VII) with Na-Hg and C₆H₆-

MeOH yields 2:4:6:2':4':6'-hexaphenylbenzhydrol, m.p. 248—249° (decomp.), converted by HI into 1:3-diphenyl-9-(2:4:6-triphenylphenyl)fluorene, m.p. 221°. (IV) does not form a chloride; with, e.g., SOCl₂, it gives 1:3-diphenylfluorene, m.p. 183°, converted by MgPhBr into 1:3:9-triphenylfluorenol, m.p. 207°. (VI) and (VII) with Na in C₆H₆ give dark purple ketyls, decomposed by H₂O or AcOH to about equal amounts of ketone and carbinol, but not associating to bimol. compounds. R. S. C.

Reaction between organic magnesium compounds and α-bromo-ketones. II. E. P. KOHLER and M. TISHLER (J. Amer. Chem. Soc., 1935, 57, 217—224; cf. A., 1932, 616).—α-Bromo-ketones may react with Grignard reagents by metathesis (A) (to form CHR:CR·OMgBr and RBr), preliminary elimination of HBr (B), enolisation and addition at the CO (C), or, for αβ-unsaturated ketones, addition to the conjugated system. (B) may be expected only if the H in the β-position is unusually reactive. (A) must occur when (B) and (C) are prohibited by the structure of the ketone if the latter is saturated or if its ethylenic linking is sterically hindered, and it may be expected with the most reactive Grignard reagents. (C), however, generally occurs with the less reactive Mg compounds formed from acidic hydrocarbons or ketones. In other cases the course of the reaction is determined by the nature of the ketone; thus, simple halogeno-ketones with unusually reactive CO, e.g., CH₂Cl·C(OMe), react solely by addition; halogen derivatives of acidic (readily enolised) ketones react solely by (A), as also do those of β-disulphones (I). The mechanism of Howk *et al.* (A., 1933, 1049) for (A) is improbable, particularly for CPh·CBr:CPh₂ and (I). (A) probably occurs by formation of unstable addition compounds. Examples of expected and unexpected reactions are given below.

CHPh₂·CHBr·COPh (II) reacts by (A) with MgMeI, MgPhBr, and CPh₂:CPh·MgBr to form CHPh₂·CH:CPh·OMgX and the appropriate bromide. CPh:C·MgBr (III) (modified prep.) and (II) by (C) give δ-bromo-γ-hydroxy-α,α,ε-tetraphenyl-Δ^α-pentinene (IV), m.p. 135°, the structure of which is proved thus. With O₃ (IV) gives (II) and BzCO₂H; with MgMeI it gives 1 mol. of CH₄ and with NaOMe yields α,α,ε-tetraphenyl-Δ^α-pentinene γδ-oxide, m.p. 87.5—88.5°, hydrolysed by an excess of NaOMe to γ- (or δ-) hydroxy-δ- (or γ-)methoxy-α,α,ε-tetraphenyl-Δ^α-pentinene, m.p. 119°; with I (IV) affords HI and Ph γ-bromo-α-iodo-βδδ-triphenyl-Δ^α-butenyl ketone, m.p. 160°, which with 2 mols. of MgPhBr gives Ph βγδδ-tetraphenyl-Δ^α-butenyl ketone, m.p. 133°, oxidised by CrO₃-AcOH to CHPh₂·CHPh·COPh. (III) and CBr₂Bz₂ afford, by two consecutive reactions, stereoisomeric forms, m.p. 159° and 120°, respectively, of Ph α-bromo-β-hydroxy-βδ-diphenyl-Δ^γ-butenyl ketone. A solution of 3:5-C₆H₃Me₂·C(CH₂)·OMgBr (V) [obtained from MgEtBr and C₆H₃Me₂Ac; also obtained solid] with (II) at 35° gives a mixture of mesityl γ-bromo-β-hydroxy-βδδ-triphenylbutyl ketone (VI), forms, m.p. 137° and 147°, respectively, and α-mesityl-δ,ε-triphenylpenta-α,γ-dione (VII), m.p. 180—181° (Br-, m.p. 171°, and Br₂-, m.p. 121°, derivatives). With Zn dust and AcOH (VI) is dehydrated and reduced

to *mesityl* $\beta\delta\delta$ -triphenylbutyl ketone (VIII), m.p. 93°, synthesised as follows: (a) (V) and $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{COPh}$ give *mesityl* β -hydroxy- $\beta\delta\delta$ -triphenylbutyl ketone, m.p. 96°, which with $\text{Zn}\cdot\text{AcOH}$ yields a mixture of (VIII) and *mesityl* $\beta\delta\delta$ -triphenyl- Δ^{α} -butenyl ketone, m.p. 120°; (b) the Grignard reagent from $\text{CPh}_2\cdot\text{CHBr}$, m.p. 48° (best prepared from $\text{CPh}_2\cdot\text{Me}\cdot\text{OH}$ and Br), with $\text{C}_6\text{H}_5\text{Me}_2\cdot\text{CO}\cdot\text{CH}_2\text{Bz}$ gives, by condensation and dehydration, *mesityl* $\beta\delta\delta$ -triphenyl- $\Delta^{\alpha\gamma}$ -butadienyl ketone, m.p. 102°, reduced by $\text{Zn}\cdot\text{AcOH}$ to (VIII). (VII), obtained as sole product from (V) and (II) in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ at 78°, is a by-product, since it is also formed from (VI) and MgMeI ; the mechanism of migration of the Ph is not clear, but the structure is established by cleavage (40% $\text{KOH}\cdot\text{MeOH}$ at 150–160°) to $\text{C}_6\text{H}_5\text{Me}_2\text{Ac}$ and $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$. (VI) and hot $\text{K}_2\text{CO}_3\cdot\text{aq. MeOH}$ afford *mesityl* $\beta\gamma$ -oxido- $\beta\delta\delta$ -triphenylbutyl ketone (IX), m.p. 151°, which with NaOMe or 1% $\text{HCl}\cdot\text{MeOH}$ gives $\gamma\epsilon\epsilon$ -triphenyl- α -mesitylbuta- α -dione (X), m.p. 125°, and is hydrogenated (PtO_2) in EtOAc to *mesityl* γ -hydroxy- $\beta\delta\delta$ -triphenylbutyl ketone (XI), m.p. 126°. (X), obtained also by oxidation (CrO_3) of (XI), with $\text{HBr}\cdot\text{AcOH}$ gives 3-phenyl-5-mesityl-1-benzhydrylfuran (XII), m.p. 128°, formed also from (IX), along with (X), by NaOMe ; (X) is, however, stable to NaOMe and is thus not the precursor of (XII) in the last-mentioned reaction. (V) reacts with $\text{CH}_2\text{Br}\cdot\text{COPh}$ as with (II), giving at 35° a mixture of δ -bromo- γ -hydroxy- γ -phenyl-3:5-dimethylbutyrophenone, m.p. 115°, and δ -phenyl- α -mesitylbuta- $\alpha\gamma$ -dione, b.p. 161–164°/10⁻⁴ mm. (monooxime, m.p. 140°), whilst at 78° the latter is the sole product. $\text{CPh}_2\cdot\text{CBr}\cdot\text{COPh}$ with (V) similarly gives *mesityl* γ -bromo- β -hydroxy- $\beta\delta\delta$ -triphenyl- Δ^{γ} -butenyl ketone, m.p. 133°, but with MgMeI or MgPhBr gives a Mg compound, which with BzCl affords *as-dibenzoyl-diphenylethylene*, m.p. 152°, reduced to $\text{CHPh}_2\cdot\text{CHBz}_2$. $\text{CH}_2(\text{SO}_2\text{Ph})_2$ (XIII) [best, 88%, prepared from $\text{CH}_2(\text{SPh})_2$ and $\text{H}_2\text{O}_2\cdot\text{AcOH}\cdot\text{Ac}_2\text{O}$], m.p. 119–120°, is stable to Br in CHCl_3 or CCl_4 , but in EtOH , AcOH , or aq. NaOH gives the Br_2 -derivative (XIV), m.p. 158°, which with (XII) (1 mol.) affords the Br -derivative, m.p. 120°, not obtainable from (XIII) and Br . These Br -compounds react by metathesis with all Grignard reagents. (XIV) gives a $(\text{OMgBr})_n$ -derivative (not obtained pure), only one MgBr of which is, however, replaceable; thus, BzCl and CHPh_2Br lead to $\beta\beta$ -diphenylsulphonylacetophenone, m.p. 180°, and *as-diphenylsulphonyldiphenylethane*, m.p. 193°.

R. S. C.

Androsterone.—See this vol., 413.

Autoxidation processes. VIII. Steric hindrance in oxidation and racemisation of α -ketols. A. WEISSBERGER. IX. Electrolytic dissociation of α -ketols. A. WEISSBERGER and H. BACH (J.C.S., 1935, 223–225, 226–229; cf. A., 1933, 611).—VIII. A relation exists between the rates of autoxidation, oxidation with Fehling's solution, and racemisation of α -ketols $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{R}'$ in alkaline solution, and the electrolytic dissociation consts. of the RCO_2H and $\text{R}'\text{CO}_2\text{H}$. Autoxidation rates of *m*-substituted benzoins are linked without individual deviations to the dissociation consts. of the carboxylic acids but the same substituents in the *o*-position cause large devi-

ation from the relationship; the variation is due to steric hindrance. The rates of autoxidation of *mm'*-dimethoxy-, -diethoxy-, and -dichloro-, m.p. 75–76° (lit. 65–67°), *oo'*-dimethyl-, -dimethoxy-, -diethoxy-, and -dichloro-, m.p. 63–64°, and *o'*-methyl-, m.p. 74–75° (substance previously described, m.p. 108–109°, is the *p*-compound), *o*-methyl-, *o'*- and *o*-ethoxy-, and *o*-chloro-benzoin, m.p. 82.5–83.5°, are recorded. The following m.p. are corr.: *p*-methylbenzoylphenyl-, m.p. 110–111°, benzoyl-*p*-tolyl-, m.p. 118–119°, *p*-chlorobenzoylphenyl-, m.p. 89.5–90.5°, benzoyl-*p*-chlorophenyl-, m.p. 114–115°, benzoyl-*o*-ethoxyphenyl-, m.p. 82–83°, and benzoyl-*o*-tolyl-carbinol, m.p. 68.5–69.5°.

IX. The dissociation of the α -ketols has been determined by measurements of decrease in conductivity which 0.01*N*- NaOH in 90% EtOH undergoes on addition of the ketols to a concn. of 0.02*M*. The measurements show a relation to the dissociation const. of the similarly substituted carboxylic acids except in the *o*-substituted compounds. The oxidation (and racemisation) velocities, however, in all cases \propto the dissociation const. of the ketols. Theoretical conclusions are reached from these results.

F. R. S.

Positively activated hydrogen atoms. VIII. Saponification of benzil. W. DILTHEY and P. SCHEIDT (J. pr. Chem., 1935, [ii], 142, 125–134; cf. A., 1932, 514).—In the presence of CN' the conversion of benzil (I) into benzoic acid (II) with $\text{KOH}\cdot\text{EtOH}$ is completely inhibited, even at a $[\text{CN}']$ of $1:8\times 10^5$ [at $1:32\times 10^5$, traces of (II) were formed], and instead PhCHO (III) and BzOH (IV) are produced (cf. A., 1883, 805). (I) heated with $\text{CH}_3\text{R}\cdot\text{CN}$ (V) ($\text{R}=\text{Ph}$, H , Me , CO_2Et) and $\text{KOH}\cdot\text{EtOH}$ gives (IV) and $\text{CHPh}\cdot\text{CR}\cdot\text{CN}$ (VI) [with α -phenylcinnamitrile, (IV) and traces of (II) were produced]. The production of (IV) does not occur when anhyd. $\text{NaOEt}\cdot\text{EtOH}$ is used. (I) with $\text{KOH}\cdot\text{EtOH}$ and carefully purified aromatic nitriles (PhCN and $\text{C}_6\text{H}_4\text{Me}\cdot\text{CN}$) gave only (II) [$\text{C}_6\text{H}_4\text{Me}\cdot\text{CN}$ was hydrolysed to the amide; amides do not inhibit the formation of (II)]. Detectable amounts of CN' were not formed during these reactions, but CN' was detected after prolonged hydrolysis by $\text{KOH}\cdot\text{EtOH}$ of aliphatic but not of aromatic nitriles. Experiments to prepare $\text{COPh}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{CN}$ from (I), $\text{CH}_2\text{Ph}\cdot\text{CN}$, and P_2O_5 , with and without solvents, failed. The formation of (VI) is due to the interaction of (V) with (III) formed by the hydrolysis of (I) by CN' . A possible mechanism for the hydrolysis of (I) by CN' is discussed.

$\text{CH}_2\text{Ph}\cdot\text{CN}$ with 4-methoxybenzil and $\text{KOH}\cdot\text{EtOH}$ gave anisic acid and phenylcinnamitrile, but with 4:4'-dibromobenzil and diphenylbenzil only the corresponding acid and not the corresponding nitrile could be obtained. With Ac , and phenanthraquinone complex results were obtained. Camphorquinone and acenaphthenequinone (VII) were not saponified, but condensed with $\text{CH}_2\text{Ph}\cdot\text{CN}$ (1 mol.). From (VII) two isomeric nitriles were obtained. H. G. M.

Reactions with 2-methyl- α -naphthaquinone. J. MADINAVETIA (Anal. Fis. Quím., 1933, 31, 750–759).—2-Methyl- α -naphthaquinone (I) with HBr in

Ac₂O gives 3-bromo-2-methyl- α -naphthaquinone (II) (cf. A., 1922, i, 29), whereas with Ca(OCl)₂-H₂O it gives 2-methyl-1:4-diketodihydronaphthalene 2:3-oxide (III), m.p. 102°, converted by warm dil. H₂SO₄ into 3-hydroxy-2-methyl- α -naphthaquinone, m.p. 172° (Ac, m.p. 106°, Bz, Ag, and OMe, m.p. 93°, derivatives), which is reduced (Zn-Ac₂O) and acetylated to 1:3:4-triacetoxy-2-methylnaphthalene, m.p. 130°. (III) with HBr affords (II), but with MeOH affords no 3-OMe-compound. (III) with NH₂Ph in boiling EtOH-H₂O gives 3-anilino-2-methyl- α -naphthaquinone, m.p. 163° (cf. A., 1895, i, 615). (I) polymerises in sunlight by virtue of its reactive 2:3-double linking to a dimeride (IV), m.p. 235°, which is depolymerised by sublimation in vac. (IV) does not react with Ac₂O, but it affords a tetraoxime, m.p. 76°, and a monodinitrophenylhydrazone, m.p. 242°. J. L. D.

Anthraquinone series. P. C. MITTER, S. DAS-GUPTA, and S. BACHHWAT (J. Indian Chem. Soc., 1934, 11, 893—897).—1-Acetoxy-6-methylanthraquinone, m.p. 172°, is oxidised (H₂CrO₄) to 1-hydroxyanthraquinone-6-carboxylic acid, m.p. 297°, the Ac derivative, m.p. 242°, of which forms 1-acetoxyanthraquinone-6-carboxyl chloride, m.p. 182°, which with H₂ (Pd-BaSO₄) gives 1-hydroxy-6-aldehydoanthraquinone, m.p. 194°, reduced to 1-hydroxyanthraquinonyl-6-carbinol, m.p. 160—162°. Similar reactions give 1-acetoxy-3-methylanthraquinone, m.p. 156°, 1-hydroxyanthraquinone-3-carboxylic acid, m.p. 282—284° (Ac derivative, m.p. 276°), 1-acetoxyanthraquinone-3-carboxyl chloride, m.p. 162—163°, and 1-hydroxyanthraquinone-3-aldehyde, m.p. 214°, and -carbinol, m.p. 197—199°.

F. R. S.

Manufacture of 1-amino-4-hydroxy- and amino-dihydroxy-anthraquinones.—See B., 1935, 219.

Attractyligenin. IV. Halogenated derivatives. T. AJELLO (Gazzetta, 1934, 64, 938—947).—Although attractyligenin (I) does not give an additive compound with Br (cf. A., 1934, 528), it is degraded by the latter in AcOH to a compound, C₁₂H₁₇O₃Br (II), m.p. 145°, [α]_D²⁰—82.79° in EtOH. (II) yields an Ac, m.p. 174—176°, and a Bz derivative, has an acid reaction, and is reduced (Zn+AcOH) to a substance, C₁₂H₁₈O₃, m.p. 223°, which with PhNCO forms the compound C₁₂H₁₈O₃·CO·NHPh. (II) with KOH gives a substance, m.p. 219°, containing Br. (I) with HCl and HBr in AcOH yields halogenated substances of m.p. -01° and 208°, respectively. E. W. W.

Oxidation product of γ -elemic acid, and its oxime. M. MLADENOVIC (Bull. Soc. Chim. Yougoslav., 1934, 5, 57—62).— γ -Elemic acid and CrO₃ in A at 60° yield γ -elemic acid, C₃₀H₄₈O₃, m.p. -30° (oxime, m.p. 273°). R. T.

Paprika colouring matter. VIII. Constitution of capsanthin and capsorubin. L. ZECH-EISTER and L. VON CHOLNOKY (Annalen, 1935, 516, 1—45; cf. A., 1934, 657).—Results of perhydrogenation and determinations of mol. wt. of capsanthin indicate 10 C:C linkings which from the spectroscopic behaviour must be completely conjugated. Comparison with β -carotene or zeaxanthin necessitates operation of conjugated CO, since CHO and CO₂ are absent. Attempted oximation was un-

successful, but reduction of perhydrogenated (I) with Na and EtOH raises the no. of OH groups from 2 to 3. Empirical formula, function of O atoms, and no. of double linkings show the presence of a ring system in (I) which is supported by the optical activity ([α]_D²⁰—61° for the diacetate in hexane). Microhydrogenation of capsorubin (II), m.p. 201° (corr.) [diacetate, m.p. 179° (decomp.)], indicates 9 double linkings and 2CO. Spectroscopic and adsorptive behaviour require CO to be at each end of the chromophore and the structure of (II) to be otherwise analogous with that of (I). (II) is considered therefore to have a purely aliphatic, symmetrically arranged structure, whereas one end of (I) is cyclic. Considerations of carotenoid structure indicate the choice of $\cdot\text{CH}:\text{CH}:\text{CO}:\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHPr}^a\cdot\text{OH}$ or $\text{OH}\cdot\text{CHBu}^b\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}:\text{CH}:\text{CH}\cdot$ for the open terminal group in (I) or 2 groups in (II). Two OH groups cannot be present, since this would lead to a β -ionone ring at the other end of (I) which is not reconcilable with the absence of provitamin-A properties and the failure of (I) to afford geronic acid. Negative results of the titration with Pb(OAc)₄ show that 2OH cannot be attached to vicinal C atoms. Oxidation of (I) with KMnO₄ gives CO₂H·CMe₂·CH₂·CO₂H and CMe₂(CO₂H)₂, possibly derived from the ring portion of the mol. Similar oxidation of (II) gives a trace of cryst. acid and much colourless oil. Since ozonisation of (I) does not produce COMe₂ and (I) and (II) contain 4.2 and 4.4 Me groups (titrated as AcOH), respectively, the structures

$\text{OH}\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}\cdot\text{CMe}_2\end{smallmatrix}\rangle\text{C}[\text{CH}:\text{CH}:\text{CMe}:\text{CH}]_2\cdot[\text{CH}:\text{CH}:\text{CH}:\text{CMe}]_2\cdot\text{CH}:\text{CH}:\text{CO}:\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHPr}^a\cdot\text{OH}$ and $[\text{CH}:\text{CH}:\text{CMe}:\text{CH}]_2\cdot\text{CH}:\text{CO}:\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHPr}^a\cdot\text{OH}]_2$ are assigned to (I) and (II). The constitutions are compatible with spectroscopic behaviour of (I) and (II) in comparison with that of bixin dialdehyde, semi- β -carotenone, and β -carotenone. H. W.

Acids of pine oleoresin and rosin. S. PALKIN (J. Chem. Educ., 1935, 12, 35—39).—A summary of the classification, properties and reactions, and constitution of resin and rosin acids. L. S. T.

Pigments of *Lactarius deliciosus*, L. I. H. WILLSTAEDT (Ber., 1935, 68, [B], 333—340).—The fungus is extracted with EtOH and the extract is treated with Et₂O and H₂O, when the pigments pass into the Et₂O. The lyochromes remain in EtOH-H₂O and in them the presence of lactoflavin is established by the colour reaction with FeCl₃ after energetic alkaline hydrolysis and the displacement of the fluorescence colour towards blue by irradiation in neutral solution. The pigments are purified by adsorption by Al₂O₃ from light petroleum (I), development by C₆H₆-(I) (1:5), followed by elution with MeOH-(I). Reddish-violet *lactarovioline* (II) C₁₅H₁₄O, m.p. 53°, is thus isolated which is devoid of acidic properties. With HCl in (I) it affords an oxonium hydrochloride, decomp. 83—84°, resolved into its components by H₂O. (II) becomes decolorised after absorption of 1H₂ (Pd-sponge), but blue when treated with Zn dust in C₅H₅N containing a little AcOH and green when treated with 5N-HCl and warm SnCl₂.

It is rapidly decolorised by Zn and HCl. Cryst. products are not obtained by distillation with Zn dust. The chromatogram discloses the presence of 5 other pigments in minor amount. H. W.

Properties of densipimaric acid, a natural resin acid. K. SUZUKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 98—107).—"Densipimaric acid," m.p. 141—142° (J. Pharm. Soc. Japan, 1925, 49, 367, 888) [*dihydro-acid* $C_{20}H_{32}O_2$, m.p. 198—199°; HBr additive compound $C_{20}H_{32}O_2Br_2$, decomp. 174—175°; *Me*, b.p. 222—224°/10 mm., and *Et*, b.p. 228—229°/15 mm., esters; *alcohol* $C_{20}H_{32}O$, b.p. 212—214°, by reduction of the *Me* ester (Bouveault), converted by PCl_5 and treatment of the chloride with quinoline at 250° into a *hydrocarbon* $C_{20}H_{30}$, b.p. 194—196°/6 mm. (dehydrogenated by S to methylretene)], when heated at 165—170° in CO_2 undergoes a sudden change from *l*-([α]_D -70.80°) to *d*-rotation, reaching a max. val. [α]_D²⁰ +29° at 2 hr., the rotation then gradually decreasing until (18 hr.) it reaches a small, const. *l*-rotation. The m.p. similarly decreases through a min. (76—78° at 7 hr.) to approx. 90°. Similar mutarotation is observed in acid and alkaline solutions, and in $COMe_3$, EtOH, EtOAc, ligroin, C_6H_6 , and CCl_4 at 19—21°, the [α]_D-time curves showing two max. and a min. The final product in all solvents has m.p. 139—141°. No such changes are observed with abietic acid. Mutarotation is probably due to isomerisation and racemisation. J. W. B.

Chinese perilla.—See this vol., 420.

Isomerisation of α -pinene. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1934, 4, 1128—1129).— α -Pinene yields chiefly dipentene, together with small quantities of allocymene, when heated at 250° for 20 hr. with Al, $HgCl_2$, and I. R. T.

Optical rotatory dispersion of terpenes. R. PADMANABHAN and S. K. K. JATKAR (J. Amer. Chem. Soc., 1935, 57, 334—338).—The dispersions of *d*- α -pinene, *d*-limonene, *d*- Δ^3 - and Δ^4 -carene, *d*- α -thujene (I), *d*-sabinene (II), and *d*-camphene are recorded. That of (I) is complex and of (II) anomalous. Those of the other substances are simple. R. S. C.

epi-isoBorneol. I. M. LIPP and E. BUND (Ber., 1935, 68, [B], 249—255).—*epi*Camphor (I) is reduced (H_2 -Pt-sponge-AcOH) to an *epibornyl ether*, m.p. 163°, and *epi-isoborneol* (II), m.p. 194.5°, [α]_D²⁰ +13.2° in PhMe (3 : 5-dinitrobenzoate, m.p. 120°, [α]_D²⁰ +35° in PhMe; *phenylurethane*, m.p. 94—98°, [α]_D²¹ +33° in PhMe). Oxidation of (II) with $K_2Cr_2O_7$ and H_2SO_4 in AcOH affords (I). (II) is isomerised by Na in PhMe at 230° to *epiborneol* (III). The allocation of (II) to the *iso*-series is strengthened by comparison of the mol. refraction of (II) and (III), borneol and isoborneol, and the rates of hydrolysis of their acetates. *epi-isoBornyl acetate* has [α]_D¹⁵ +27.93°. H. W.

Synthetic production of camphor from pinene. B. G. S. ACHARYA and T. S. WHEELER (J. Univ. Bombay, 1934, 3, No. 2, 163—171).—The pinene (I) used is obtained by heating American turpentine with 2% of $CaCl_2$ at 100° for 2 hr. and has b.p. 158—161°. Treatment of it with dry HCl (pumice- H_2SO_4) at 9—12° give an 80% yield of the hydrochloride (II),

stabilised by washing, agitation with alkali solution, washing, and final treatment with 10% HNO_3 at 60—70°. Treatment of (II) with boiling cresol and Na tolyloxide during 6—8 hr. gives camphene (III) (yield 80—83%). (I) and (II) are unsuitable for the direct production of borneols. (III) and AcOH in presence of 50% H_2SO_4 at 70—80° for 4—6 hr. afford isobornyl acetate, b.p. 100°/14 mm., hydrolysed to isoborneols [yield 64% calc. on (III)] which are oxidised by HNO_3 (1 : 1) containing H_2SO_4 (1 : 1) at 80—85° for 9—10 hr. to camphor (IV), m.p. 172—173° (over-all yield 42%). Alternatively, (III) in AcOH is oxidised to (IV) by $K_2Cr_2O_7$ - H_2SO_4 - H_2O at 110—120° for 28—30 hr. [yield 50%; over-all yield from (I), 33%]. The following transformations could not be successfully achieved: (I) to (III); (I) to borneol; (II) to isoborneol (V); (III) to (V); (I) to (IV); (II) to (IV); esters to (IV).

H. W.

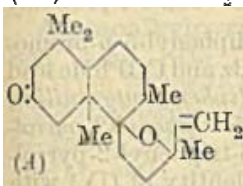
Degradation of camphor and of diketocamphane in the animal organism. F. REINARTZ, W. ZANKE, and M. KURSCHGEN (Ber., 1935, 68, [B], 310—315).—"Biological *p*-hydroxycamphor" after purification with boiling 10% aq. KOH and recrystallisation from ligroin shows the typical camphor effect at greater dilution. Vita camphor, freed from the bulk of π -aldehyde by $NaHSO_3$ and hence consisting essentially of biological 5-ketocamphor, has generally a weak but distinct physiological action. Treatment of biological *p*-diketocamphane, obtained by oxidation of the hydroxycamphor mixture with CrO_3 and subsequently by air and alkali, with p - NO_2 - C_6H_4 -COCl and C_5H_5N in PhMe gives a small amount of a (?) 4-hydroxycamphor *p*-nitrobenzoate, m.p. 120.5—122°; if $KMnO_4$ replaces O_2 for oxidation, a compound, $C_8H_{10}O_2$, m.p. 131—132.5°, possibly a further degradation product, is obtained. Metabolic products of camphor other than the previously isolated hydroxycamphors are therefore present in urine.

The identity of the acids obtained by the oxidation of *p*-diketocamphane and *cyclocamphanone* (A., 1934, 1225) is established. H. W.

New alkylammonium salt (tetramethylammonium camphorsulphonate). P. SILLANI and (SIGNA.) L. CURTI (Boll. Chim. farm., 1935, 74, 77—81).—The action and toxicity of *NMe*₄ camphorsulphonate, decomp. 280—330°, on the guinea-pig and the rabbit are investigated; it is suggested as a cardiac tonic. E. W. W.

Diterpene oxides of the resin of *Dacrydium Colensoi*. III. Ketomanoyl oxide. J. R. HOSKING and C. W. BRANDT (Ber., 1935, 68, [B], 286—290; cf. A., 1934, 897).—Treatment of ketomanoyl oxide (I) with HCl in Et_2O at 0° affords a trihydrochloride, $C_{20}H_{33}OCl_3$, m.p. 144—145°. The semicarbazone of (I) is transformed by NaOEt (Wolff-Kishner) into manoyl oxide (II), identified as manone trihydrochloride. (I) therefore differs from (II) solely by the presence of CO vicinal to CH_3 , since (I) with HCO_2Alk yields a formyl derivative. (I) or its H_2 -derivative is converted by excess of $MgMeI$ in boiling Et_2O into the carbinol (III), $C_{21}H_{36}O_2$, b.p. 151°/0.2 mm., catalytically reduced (PtO_2 -EtOAc)

to a substance, b.p. 143—145°/0.1 mm. Dehydrogenation of (III) by Se gives only small amounts of aromatic hydrocarbons. Successive treatment of (III) with $\text{HCl-Et}_2\text{O}$ at 0° and with NH_3Ph at 100° gives the hydrocarbon, $\text{C}_{21}\text{H}_{14}$, b.p. 135°/0.2 mm., dehydrogenated (Se; 240—350°) to 1:2:5:7- $\text{C}_{10}\text{H}_4\text{Me}_4$, b.p. 155—158°/12 mm. [picrate, m.p. 144—145°; styphnate, m.p. 145°; additive compound with $\text{C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 167—168°], and (?) 1:2:6:8-tetramethylphenanthrene (picrate, m.p. 177°). (I) is probably A.



H. W.

Preparation of alkoxymethylfurfuraldehydes and alkyl laevulates from carbohydrates. II. R. WEIDENHAGEN and B. KOROTKYJ (Z. Wirts. Zuckerind., 1935, 85, 131—136; cf. A., 1934, 1205).—The following alkyl laevulates (A) and α -alkoxymethylfurfuraldehydes (B) are obtained from sucrose, the alcohol, and HCl in a modified autoclave at about 160°: (A), Me (I) [semicarbazone, m.p. 150—151° (lit. 142—145°)], Pr^B , b.p. 88—90°/12 mm. [semicarbazone, m.p. 144° (lit. 141—142°)], and Bu^a , b.p. 80—90°/0.13 mm.; (B), Me (II), Pr^B , b.p. 117—120°/12 mm. (semicarbazone, m.p. 188—189°), and Bu^a , b.p. 93—125°/0.13—0.55 mm. (semicarbazone, m.p. 169—170°). (I) and (II) are obtained also from fructose.

R. S. C.

Condensation of mercaptals with 5-keto-methylpentonic acids. E. VOTOČEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1935, 7, 44—48).—5-Ketorhamnonolactone, the appropriate mercaptan, and conc. HCl give 3-ethyl-, (I), m.p. 71—72° (Ba salt , $+\text{H}_2\text{O}$), -methyl-, m.p. 140—141°, -n-propyl-, (II), m.p. 98—99°, and -n-butyl-, m.p. 68—69°, thiol-2-methylfuran-5-carboxylic acid. (I) and (II) are obtained similarly from the oil obtained by oxidation of fuconolactone with HNO_2 . The compounds are stable to hot $N\text{-HCl}$.

R. S. C.

Phototropy. Three new phototropic compounds. A. P. DE CARVALHO (Compt. rend., 1935, 200, 60—62).— $\text{CPh}_3(\text{CH}_2\text{-COPh})_2$ (I), 2:4:4:6-tetraphenyl-1:4-dihydropyridine (II), and 3:5-dibenzoyl-2:4:4:6-tetraphenyltetrahydropyran (III) are colourless in the dark but become violet on exposure to light, especially of short λ , returning to the colourless state after some hr. or days in darkness. (I) can also show tints from yellow-green to violet according to its crystal size. (II) in particular shows fatigue and after 10 reversible changes it loses its phototropic properties and its m.p. falls from 235—236° to 225°. Solutions of these compounds are insensitive to light, and solution of the coloured forms yields colourless solutions. The coloured forms lose their colour instantaneously at about 80°. ($p\text{-C}_6\text{H}_4\text{Br}$) $_2\text{C}(\text{CH}_2\text{-COPh})_2$ and 2:4:4:6-tetraphenyl- γ -pyran, closely related to (I) and (III) respectively, are not phototropic.

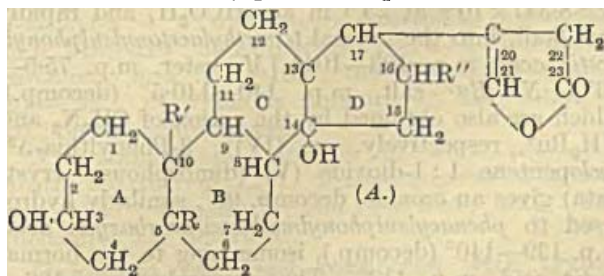
J. W. S.

Xanthane group. A. C. SINGAR and S. C. DUTT (Indian Chem. Soc., 1934, 11, 877—881).—Iazotised 3-aminoxanthone is converted into enol, xanthone-3:1'-azo-2'-naphthol, -hydroxy-3'-benzoic acid, -2'-hydroxy-3'-naphthoic

acid, -2'-naphthol-6':8'-disulphonic acid, -2'-naphthol-3':6'-disulphonic acid, -2:4'-resorcinol, and -4'-dimethylaniline. 3-Benzamidoxanthone, m.p. 212°, and 2-nitro-7-benzamidoxanthone, oxaldi-3-xanthonylamide, 3-benzylideneaminoxanthone, m.p. 153°, 3-iodoxanthone, m.p. 173°, and 2-iodo-7-nitroxanthone, m.p. 235°, are described. Azomethines are prepared from 3-aminoxanthone: o-, m.p. 256°, p-, m.p. 264°, and m-hydroxy-, m.p. 275°; 2:4-dihydroxy-, p-hydroxy-m-methoxy-, m.p. 241°; p-dimethylamino-, p-acetamido-benzylideneaminoxanthone and 3'-cinnamylideneaminoxanthone. M.p. not given are above 300°.

F. R. S.

Structure of the cardiac aglucones. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1935, 108, 497—513).—Oxidation (of the sec.-OH) of digitoxanoldiacid with CrO_3 -90% AcOH affords digitoxanondiacid, $\text{C}_{23}\text{H}_{31}\text{O}_5$, m.p. 213—215° (decomp.), reduced (Clemmensen) to digitoxandiacid, $\text{C}_{23}\text{H}_{36}\text{O}_4$, softens 210°, m.p. 218° (decomp.), the Me₂ ester, m.p. 103°, of which, with MgPhBr , gives a carbinol, oxidised ($\text{CrO}_3\text{-AcOH}$) to aetiocolanic acid (direct comparison of the acid and its Me and Et esters). This result definitely proves the presence of the sterol



ring-system in the cardiac aglucones, and revised structures for strophanthidin (A, $\text{R}=\text{OH}$, $\text{R}'=\text{CHO}$, $\text{R}''=\text{H}$), periplogenin (A, $\text{R}=\text{OH}$, $\text{R}'=\text{Me}$, $\text{R}''=\text{H}$), digitoxigenin (A, $\text{R}=\text{R}'=\text{H}$, $\text{R}''=\text{Me}$), and gitoxigenin (A, $\text{R}=\text{H}$, $\text{R}'=\text{Me}$, $\text{R}''=\text{OH}$) are given, and the evidence in their favour is summarised. Possible interpretations of other (earlier) data are discussed on the basis of these structures, especially the formation of oxide bridges with the OH at C_{14} , and the isomerisations, and spatial relationships of the various OH groups and the lactone side-chain (at C_{17}) resulting from the interconversion of the cis- and trans-configurations of rings B and C (cf. also Tschesche, this vol., 396).

J. W. B.

Plant cardiac poisons.—See this vol., 396.

Root of *Pucedanum decursivum*, Maxim.—See this vol., 420.

Structure of cyclic sulphones derived from butadienes. H. J. BACKER and J. STRATING (Rec. trav. chim., 1935, 54, 170—186).—The erroneous structures previously assigned to certain cyclic sulphones (A., 1934, 662; compounds there marked *) are corr. on the basis of their products of ozonolysis. 3:4-Dimethylthia- Δ^3 -cyclopentene 1:1-dioxide (I), m.p. 135° (loc. cit., cyclo omitted) with $\text{O}_3\text{-AcOH}$ affords 3:5-dimethyl-4-oxathia- $\Delta^{2:5}$ -cyclohexadiene 1:1-dioxide $\text{O} \begin{smallmatrix} \text{CMe:CH} \\ \text{CMe:CH} \end{smallmatrix} \text{SO}_2$, m.p. 119—120°. The Br₂ additive compound of (I) with hot $N\text{-NaOH}$ gives

4-methyl-3-methylenethia- Δ^4 -cyclopentene 1:1-dioxide, m.p. 107° (II), since ozonolysis affords 4-methylthia- Δ^4 -cyclopenten-3-one 1:1-dioxide, m.p. 163° (yellow enol form) (oxime, m.p. 146—148°). (II) with Br-AcOH gives the corresponding 3-bromo-3-bromomethyl derivative, m.p. 158—159°. The 3-bromo-4-acetoxy-derivative of (I) is converted by KOAc into 4-acetoxy-4-methyl-3-methylenethiacyclopentane 1:1-dioxide, m.p. 102—103°, since CH_2O is obtained by ozonolysis. Ozonolysis of 2:3:4:5-tetramethylthia- Δ^3 -cyclopentene 1:1-dioxide (III), m.p. 58—59°, gives di-(β -acetylthyl)sulphone, m.p. 145.5—146°. The unsaturated sulphone obtained by the action of NaOH on the Br_2 additive compound of (III) is 2:4:5-trimethyl-3-methylenethia- Δ^4 -cyclopentene 1:1-dioxide, m.p. 93—95°, converted by Br-AcOH into the corresponding 3-bromo-3-bromomethyl derivative, m.p. 125—126°. 3-*tert*-Butylthia- Δ^3 -cyclopentene 1:1-dioxide (crystallographic data by TERPSTRA) gives an ozonide, decomp. 133—134°, hydrolysed to α -trimethylacetonylsulphonylmethyl β -peroxide (IV)

$\text{COBu}^\nu \cdot \text{CH}_2 \cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix}$, decomp. 145°, which liberates I from HI, and is converted unimolecularly ($k=8.347 \times 10^{-2}$ at 25°) in aq. HCO_2H , and rapidly by alkali, into the normal trimethylacetonylsulphonylacetic acid, m.p. 103—104° [*Me* ester, m.p. 75.5—76°; NH_2Bu^ν salt, m.p. 140—140.5° (decomp.)], which are also obtained by the action of CH_3N_2 and NH_2Bu^ν , respectively, on (IV)]. 3-Phenylthia- Δ^3 -cyclopentene 1:1-dioxide (V) (dimorphous; cryst. data) gives an ozonide, decomp. 99°, similarly hydrolysed to phenacylsulphonylmethaneisocarboxylic acid, m.p. 139—140° (decomp.), isomerising to the normal acetic acid, m.p. 112°. The isomeride, m.p. 166—167° (cryst. data), formed by irradiation of (V) is not a stereoisomeride, but is the Δ^2 -isomeride, since ozonolysis affords mainly β -benzoylthanesulphonic acid, m.p. 132° (*Ba* salt), formed from the intermediate product β -benzoylthylsulphonylmethyl peroxide $\text{CH}_2\text{Bz} \cdot \text{CH}_2 \cdot \text{SO}_2 \cdot \text{CH} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix}$, decomp. 118.5—119°, which is isolated in small yield. 3:4-Diphenylthia- Δ^3 -cyclopentene 1:1-dioxide (cryst. data) affords di-(benzoylmethyl)sulphone, m.p. 124°, upon ozonolysis.

J. W. B.

Synthesis of pyrrolones from acetophenone and benzoylformanilide. T. T. BASHOUR and H. G. LINDWALL (J. Amer. Chem. Soc., 1935, 57, 178—180).— $\text{NHPh} \cdot \text{COBz}$ and $p\text{-C}_6\text{H}_4\text{BrAc}$ with NHET_2 or dil. NaOH in dry EtOH give α -hydroxy- γ -keto- α -phenyl- γ -p-bromophenylbutyranilide (I), m.p. 133—135° (phenylhydrazone, m.p. 179—180°; does not give a semicarbazone; contains 2 active H), decomposed into its components by hot 2.5% NaOH-aq. EtOH. With HCl in dry $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ (I) gives 5-hydroxy-1:3-diphenyl-5-p-bromophenyl-2-pyrrolone, m.p. 195—196° (reduces KMnO_4 , but stable to Br-CCl_4 ; contains 1 active H), which with HCl-MeOH-Et₂O or HCl-EtOH-Et₂O gives 5-methoxy- (II), m.p. 139—140° (no active H; does not add Br), or 5-ethoxy-1:3-diphenyl-5-p-bromophenyl-2-pyrrolone (III), m.p. 148—149.5°, respectively, which are also obtained directly from (I) by the same reagents. (II) with HCl-EtOH-Et₂O gives (III), and the reverse trans-

formation is effected by HCl-MeOH-Et₂O. (II) and (III) are reduced by Zn dust and AcOH to 1:3-diphenyl-5-p-bromophenyl-2-(Δ^4)-pyrrolone,

$\text{C}_6\text{H}_4\text{BrC} \begin{smallmatrix} \text{CH-CHPh} \\ \diagup \diagdown \\ \text{NPh-CO} \end{smallmatrix}$, m.p. 151.5—152.5°, probably by way of the 5-alkoxy-1:3-diphenyl-5-p-bromophenyl-2-pyrrolidone. $\text{NHPh} \cdot \text{COBz}$ and COPhMe lead similarly to α -hydroxy- γ -keto- α - γ -diphenylbutyranilide, m.p. 143—145°, 5-ethoxy-1:3:5-triphenyl-2-pyrrolone, m.p. 106—107°, and 1:3:5-triphenyl-2-pyrrolone (IV), m.p. 197—198°. The identity of (IV) with Almstrom's substance (A., 1913, i, 1240) establishes the structures of the other compounds. R. S. C.

Pyridine. XVIII. 3-Aminopyridine and its derivatives. A. BINZ and O. VON SCHICKH [with M. GEHRING] (Ber., 1935, 68, [B], 315—324).—6-Chloropyridine-3-arsinic acid (I) is reduced by Zn dust and dil. H_2SO_4 at 0° to 3':5-arsenopyridine (II) (yield 73%), oxidised by H_2O_2 to pyridine-3-arsinic acid, m.p. 154°; the electrolytic reduction of (I) to (II) at a Pb cathode is described. 6-Chloro-3-nitropyridine (III) is dehalogenated and reduced by Zn dust and boiling dil. H_2SO_4 to 3-aminopyridine (IV), m.p. 64°, in 43% yield, a similar result being obtained with 6-chloro-3-aminopyridine (V). Electrolytic reduction of (III) in 20% H_2SO_4 at a Cu cathode at 15—20° yields (V) in 53% yield; at 75° some dehalogenation occurs. Use of Pb or Sn in place of Cu or of MeOH in place of H_2O offers little advantage. (IV) is obtained in 93% yield by catalytic reduction [$\text{Pd}(\text{OH})_2\text{-CaCO}_3$] of (III) in MeOH or in 86% yield from (V). An 89% yield of (IV) is obtained by catalytic reduction of 6-bromo-3-aminopyridine, b.p. 177—178°/12 mm., m.p. 77°, prepared by treating 6-bromo-3-nitropyridine (VI), b.p. 145—147°/10 mm., m.p. 138°, with Fe powder and AcOH. Hydrogenation of (III) in EtOH containing spongy Pt yields 2:6'-dichloro-5:3'-azoxypyridine, m.p. 188°, (V), and (IV) (yields 10%, 21%, and 23.5%, respectively). In MeOH (III) is converted by H_2 (Ni) at 50° into (IV) in 62% yield. Treatment of (III) with H_2 [$\text{Pd}(\text{OH})_2\text{-CaCO}_3$] in MeOH-NaOH affords 3-amino-6-methoxypyridine, b.p. 135°/14 mm., in 90% yield. 3-Amino-6-ethoxypyridine, b.p. 123—124°/11 mm., stable to air, is obtained similarly. In Pr-OH at room temp. the main identifiable product is 2:6-dipropoxy-5:3'-azoxypyridine, m.p. 97—98°, whereas at 70° 3-amino-6-propoxypyridine, b.p. 145—147°/18 mm., is obtained in 70% yield. 3-Amino-6-butoxypyridine, b.p. 156°/16 mm., is obtained in 70% yield from (VI). 2-Chloro-3-nitropyridine in MeOH-NaOH containing $\text{Pd}(\text{OH})_2\text{-CaCO}_3$ is hydrogenated to 3-amino-2-methoxypyridine, b.p. 116—118°/19 mm. (yield 75%); under similar conditions, *o*-an $p\text{-C}_6\text{H}_4\text{Cl-NO}_2$ give essentially NH_2Ph (yield 83%), whilst 6-chloro-8-nitroquinoline affords 8-aminoquinoline, m.p. 70°, almost quantitatively, the production of OMe compounds not being observed. Dissolution of (IV) in 40% CH_2O results in γ -eneaminopyridine, m.p. 180°. Treatment of (I) with $\text{N-H}_2\text{SO}_4$ with 10% CH_2O and Zn dust leads to 3-dimethylaminopyridine (VII), b.p. 108—110°/1 mm. (hygroscopic dihydrochloride, m.p. 143°), which does not react with HNO_3 , or couple with

$-\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$. (IV) resembles NH_2Ph in a very limited degree and (VII) does not show the reactions characteristic of NPhMe_2 . H. W.

Aminoalkylpyridines. III. T. HEOU-FEO (Bull. Soc. chim., 1935, [v], 2, 103—108).—2-Methylpyridine (I) in HCl with CH_2O and $\text{NH}_4\text{Et}_2\text{HCl}$ at 85° gives 2- β -diethylaminoethylpyridine, b.p. $118^\circ/15$ mm. ($+2\text{AuCl}_3\cdot 2\text{HCl}$, m.p. 190° ; $+ \text{CdBr}_2\cdot 2\text{HBr}$, m.p. 164°), and 2- $\beta\beta'$ -di(diethylamino)isopropylpyridine, b.p. $153^\circ/16$ mm. [$+1.5\text{PtCl}_4\cdot 3\text{HCl}$, m.p. 205° (decomp.); $+1.5\text{CdCl}_2\cdot 3\text{HCl}$, m.p. 186° (decomp.); dimethiodide, m.p. 184° ; dipicrate, m.p. 164°], because the Me of (I) is more reactive than that of quinaldine. Similarly, (I) with piperidino hydrochloride and CH_2O gives 2- $\beta\beta'$ -dipiperidinoisopropylpyridine, b.p. $192^\circ/8$ mm. [$+1.5\text{PtCl}_4\cdot 3\text{HCl}$, m.p. 230° (decomp.); $+1.5\text{CdBr}_2\cdot 3\text{HBr}$, m.p. 200° ; dipicrate, m.p. 148°]. 2-Ethylpyridine in HCl with 38% CH_2O and $\text{NH}_4\text{Et}_2\text{HCl}$ at 85° gives 2- γ -diethylaminopropylpyridine, b.p. $129^\circ/18$ mm. ($+2\text{AuCl}_3\cdot 2\text{HCl}$, m.p. 183°).

J. L. D.

Preparation, alcoholysis, and hydrogenolysis of nicotinylacetylmethanes. L. F. KUICK and H. ADKINS (J. Amer. Chem. Soc., 1935, 57, 143—147).—Nicotinyl-acetyl-, b.p. 134 — $135^\circ/6$ mm., m.p. 83.5° (hydrochloride, m.p. 154°), -*n*-valeryl-, b.p. 165 — $168^\circ/8$ mm. (hydrochloride, m.p. 122°), -isovaleryl-, b.p. 134 — $135^\circ/3$ mm., m.p. 44° (hydrochloride, m.p. 128 — 129°), -trimethylacetyl-, b.p. 135 — $136^\circ/5$ mm., m.p. 44.5° (hydrochloride, m.p. 173°), -*n*-hexoyl-, b.p. 150 — $152^\circ/2$ mm., m.p. 29.5° (hydrochloride, m.p. 114°), -benzoyl-, b.p. 198 — $200^\circ/3$ mm., m.p. 121.5° (hydrochloride, m.p. 211°), and -2:4:6-trimethylbenzoyl-, b.p. 186 — $190^\circ/1$ mm., m.p. 47.8° (hydrochloride, m.p. 218 — 219°), -methanes are prepared from Et nicotinate, the appropriate COMeR , and NaOEt in xylene. Dinicotinylmethane (hydrochloride, m.p. 240 — 241°) has m.p. 198° . All the above m.p. are corr. Treatment of $\text{C}_5\text{H}_4\text{N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COR}$ (I) with EtOH at 200° results in the following % of nicotinyl cleavage: R=Me 41, Bu^a 42, Bu^b 42, *n*-amyl 43, Bu^c 50, Ph 57. The $\text{C}_5\text{H}_4\text{N}$ group, like Ph, furyl, and Bu^c, increases the relative rate of cleavage at the more distant CO. Reduction [H_2 (150—250 atm.), Raney Ni, Et_2O , or dioxan, 150—160°] of various (I) causes hydrogenolysis; the reactions (except for the hydrogenation of the $\text{C}_5\text{H}_5\text{N}$ ring) are of the same type as those previously found (this vol., 198) for other α - γ -diketones. The following appear to be new: 3-*n*-butyl- and 3-acetyl-piperidine hydrochlorides, m.p. 148° and 114° , respectively; α -3-piperidyl- ϵ -methylhexanone, b.p. 120 — $129^\circ/2$ mm., m.p. 104° ; α -3-piperidyl-88-dimethyl-pentane, b.p. 133 — $135^\circ/7$ mm. (hydrochloride, m.p. 152 — 153°), and -pentanol (?), b.p. 133 — $135^\circ/7$ mm. (hydrochloride, m.p. $175^\circ/2$ mm.); mesityl β -3-piperidylethyl ketone, b.p. 190 — $198^\circ/3$ mm. (hydrochloride, m.p. 133 — 136°).

H. B.

Syntheses the indole group. XI. Syntheses with eserine. II. T. HOSHINO and T. AKI. XII. III. Synthesis of *d*- and *l*-eserethole methiodide. T. HOSHINO and T. OBAYASHI (Annalen, 1935, 516, 76—80, 81—

94).—II (cf. A., 1934, 667). 2-Nitro-5-ethoxytoluene, m.p. 53 — 54° , from the $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Et}$, is converted into 2-nitro-5-ethoxyphenylpyruvic acid, m.p. 103 — 104° . 5-Ethoxyindole-2-carboxylic acid, m.p. 203 — 204° (decomp.), and 5-ethoxyindole, m.p. 35 — 36° , are described. 5-Ethoxyindolylacetone, m.p. 103 — 104° , obtained from Mg 5-ethoxyindolyl iodide and $\text{CH}_2\text{Cl}\cdot\text{CN}$, is reduced by Na and EtOH to 5-ethoxytryptamine, m.p. 108 — 109° . Et 5-ethoxyindole-2-carboxylate, m.p. 156 — 157° , is obtained in poor yield from the *p*-ethoxyphenylhydrazone of $\text{COMe}\cdot\text{CO}_2\text{Et}$ and ZnCl_2 in cumene. *dl*-Dinoreseremethole is resolved into its optical antipodes by treatment with *d*-bromocamphorsulphonic acid in EtOH and subsequently in H_2O , thus leading to the isolation of the H *d*-tartrate, m.p. 180 — 181° , $[\alpha]_D^{25} +190.7^\circ$ in H_2O , and the *d*-bromocamphorsulphonate, m.p. 194 — 195° , $[\alpha]_D^{25} +232.7^\circ$, of the *d*-base and the H *d*-tartrate, m.p. 180 — 181° , $[\alpha]_D^{25} -46.3^\circ$, and normal tartrate, m.p. 242 — 242.5° , of the *l*-base. Tryptamine and MeI in C_6H_6 yield exclusively dimethyltryptamine methiodide, m.p. 216 — 217° . Benzylidenetryptamine, m.p. 120.5 — 121.5° , and MeI at 100° afford 3-phenyl-4-methyl-3:4:5:6-tetrahydro-4-carboline methiodide, m.p. 218 — 219° , and 3-phenyl-3:4:5:6-tetrahydro-4-carboline, m.p. 167 — 168° , the hydrochloride, m.p. 206 — 207° , of which is obtained by the action of HCl on the Schiff's base.

XII. Mainly an extension of work previously abstracted (this vol., 227). *dl*-Dinoreserethole *d*-tartrate, m.p. 235° (decomp.), and *l*-tartrate, m.p. 235° (decomp.), are described. H. W.

Oxidation reactions connected with tryptophan. G. DEL GUERRA (Arch. Farm. speriment., 1935, 59, 86—92).—Tryptophan, eserine, strychnine, brucine, and yohimbine all give rose colours with $\text{K}_2\text{Cr}_2\text{O}_7\cdot\text{HCl}$, which oxidise the indole nucleus (I); the toad-venom bases and aspidospermine also give positive reactions. The da Silva and Mokragatz reactions for eserine are also due to (I) oxidation. The rose colour produced by $\text{K}_2\text{Cr}_2\text{O}_7\cdot\text{HCl}$ with urine is due to oxidation of (I), and of phenols to phenoquinones. R. N. C.

Preparation of alkylquinolines. I. T. HEOU-FEO (Bull. Soc. chim., 1935, [v], 2, 90—95).— NH_2Ph in excess of boiling HCl containing ZnCl_2 with MeCHO gives quinaldine in 50% yield. 4-Methyl- and 2:4-dimethyl-quinoline are prepared in improved yield by Blaise's method (cf. A., 1908, i, 566) from Me β -hydroxyethyl ketone and Me β -hydroxypropyl ketone. J. L. D.

Aminoalkylquinolines. II. T. HEOU-FEO (Bull. Soc. chim., 1935, [v], 2, 96—103).— $\text{NH}_4\text{Et}_2\text{HCl}$ with quinaldine (I) in H_2O - EtOH gives with CH_2O at 60° 2- β -diethylaminoethylquinoline, b.p. $181^\circ/12$ mm. [mono-, m.p. 124° and di-picrate, m.p. 154° ; platinichloride $+2\text{HCl}$, m.p. 185° (decomp.); zincichloride $+2\text{HCl}$, m.p. 230°]. Similarly, with piperidine hydrochloride (II), (I) gives 2- β -piperidinoethylquinoline, b.p. $181^\circ/0.2$ mm. [mono-, m.p. 170° , and di-picrate, m.p. 181° ; platinichloride $+2\text{HCl}$, m.p. about 208° (decomp.); $+ \text{CdBr}_2\cdot 2\text{HBr}$, m.p. 210°], and with NH_2Et , HCl it gives 2- β -ethylaminoethyl-

quinoline, b.p. 177—185°/12 mm. (Bz derivative, m.p. 130°). 4-Methylquinoline (III) with $\text{NH}_4\text{Et}_2\text{HCl}$ as above gives 4- β -diethylaminoethylquinoline, b.p. 182°/5 mm. (+2AuCl₃, 2HCl, m.p. 181°; +CdBr₂, 2HBr, m.p. 216°; +ZnCl₂, 2HCl, m.p. 239°; dicresol derivative, m.p. 205°), and with (II) it gives 4- β -piperidinoethylquinoline, m.p. 84° [+2AuCl₃, 2HCl, m.p. about 198° (decomp.); +CdBr₂, 2HBr, m.p. 215°; dipicrate, m.p. 198°], which is stable in air in distinction to the bases described above. (III) with $\text{NH}_4\text{Et}_2\text{HCl}$ as above gives 4- β -ethylaminoethylquinoline, b.p. 181°/2 mm. [+H₂O, m.p. 38°; Bz derivative, m.p. 115°; +AuCl₃, 2HCl, m.p. about 165° (decomp.); +CdBr₂, 2HBr, m.p. 206°]. 2:4-Dimethylquinoline with a large excess of CH_2O and $\text{NH}_4\text{Et}_2\text{HCl}$ in $\text{EtOH-H}_2\text{O}$ at 65° gives 2:4-di- β -diethylaminoethylquinoline, b.p. 189—192°/1 mm. [+3AuCl₃, 3HCl, 10H₂O, m.p. about 165° (decomp.); +1.5CdBr₂, 3HBr, m.p. 185°]. J. L. D.

Thalleioquinone reaction. (SIGNA.) L. MONTI and (SIGNA.) V. CIRELLI (Gazzetta, 1934, 64, 947—954).—This reaction of 6-hydroxyquinoline (cf. A., 1917, i, 51) is also given by 5- but not by 7-hydroxyquinoline. 8-Hydroxyquinoline gives a somewhat similar reaction, yielding a greenish-brown product (5:8-quinolinequinone?). No hydroxyquinolines with OH in the N ring give any colour reaction, nor do 5:6-methylenedioxy-compounds. 5-Chloro-, 5-amino-, and 5-nitro-6-hydroxyquinoline give the reaction, the last, however, with some difficulty. It is concluded that the reaction can be given by 6- or 5-hydroxyquinoline, or by any derivative of these having the 5 or 6 position either free or occupied by an easily detached substituent. E. W. W.

8-Aminoquinoline derivatives as basic products for production of antimalarials. III. Effect of branching of the diethylaminoalkyl chain on the antimalarial effect. O. J. MAGIDSON, N. M. DELEKTORSKAJA, and I. M. LIPOVITSCH (J. Gen. Chem. Russ., 1934, 4, 1047—1056).—8-Amino-6-methoxyquinoline (I), NaNH_2 , and iso- $\text{C}_5\text{H}_{11}\text{Cl}$ in Et_2O afford 8-isoamylamino-, b.p. 163—165° (hydrochloride, m.p. 205°), and 8-diisoamylamino-6-methoxyquinoline, b.p. 172—183° (hydrochloride, m.p. 136—138.5°). Et α -diethylaminoisovalerate and Na in EtOH yield β -diethylaminoisovaleryl alcohol, b.p. 87—93°/14 mm., converted by heating with SOCl_2 in CHCl_3 into the chloride, b.p. 85—88°/14 mm., which with (I) gives 8-(β -diethylaminoisovaleryl)amino-6-methoxyquinoline, b.p. 192° (therapeutic index, $I=4$). Diethyl- β -hydroxy- γ -methyl-n-butylamine, b.p. 181—184°, from NH_4Et_2 and $\text{CH}_2\text{Cl-CHPr}^s\text{-OH}$, or by methylating $\text{NH}_2\text{CH}_2\text{-CHPr}^s\text{-OH}$, is converted by heating with SOCl_2 in C_6H_6 into diethyl- β -chloro- γ -methyl-n-butylamine, b.p. 70—72°/12 mm., which condenses with (I) to yield 8-(β -diethylamino- α -isopropylethyl)amino-6-methoxyquinoline, b.p. 187—191°/3 mm. ($I=0$). Diethyl- γ -hydroxy- β -dimethylpropylamine, b.p. 88—89°/8 mm., obtained from NH_4Et_2 and $\text{CH}_2\text{Br-CMe}_2\text{-CH}_2\text{-OH}$ (140—150°, 30 hr.), affords the γ -Cl-derivative (II), b.p. 69—71°/11 mm. (SOCl_2 ; 100°, 5 hr.). 8-(γ -Diethylamino- β -dimethylpropyl)amino-6-methoxyquinoline, m.p. 134—136° ($I=2$),

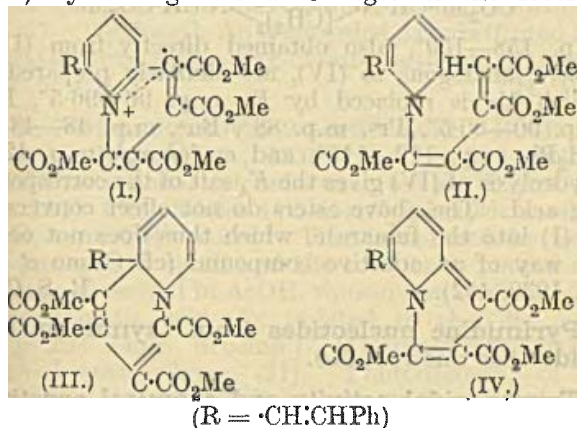
is obtained from (I) and (II) (125—130°; 2 days), and 8- β -diethylaminoisohexylamino-6-methoxyquinoline, b.p. 195—200°/1.5 mm. ($I=4$) [meconate, m.p. 153—154° (decomp.)], is prepared similarly from (I) and β -diethylaminoisohexyl chloride, b.p. 69—75° (hydrochloride, m.p. 89—91°). R. T.

Friedel-Crafts reaction with 8-hydroxyquinoline. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 124—128).—8-Hydroxyquinoline (I), EtCOCl , and AlCl_3 in PhNO_2 at 70—80° give 8-hydroxy-5-propionylquinoline [8-hydroxy-5-quinolyl Et ketone], m.p. 91° [hydrochloride, m.p. 279—280° (decomp.); H sulphate, m.p. 230—231°; picrate, m.p. 192°; platinichloride, m.p. 227—228° (decomp.); methiodide, m.p. 196—197°], the oxime, m.p. 144—145°, of which is converted by SOCl_2 into (probably) 8-hydroxyquinoline-5-carboxylethylamide, m.p. 193—194°. 5-Propionamido-8-hydroxyquinoline has m.p. 213—214°. (I), excess of $\text{o-C}_6\text{H}_4(\text{COCl})_2$ (II), and AlCl_3 in PhNO_2 at 100—110° afford 8-hydroxy-7-o-carboxybenzoylquinoline (III), m.p. 226° [hydrochloride, m.p. 244° (decomp.); platinichloride, m.p. 245° (decomp.); Me ester, m.p. 143—144° [hydrochloride, m.p. 252—252.5° (decomp.)]; hydrazide, m.p. 326° (decomp.); Ac_2 (IV), m.p. 147—150°, Bz, m.p. 195°, 5-Br-, m.p. 227—228° (decomp.) (prepared using NaOBr), and 5-I-, m.p. 224° (decomp.), derivatives], which when heated to 300° gives (I) and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ (III) and Br (2 mols.) in 0.2N-HCl at 20° afford 5:7-dibromo-8-hydroxyquinoline, m.p. 197—198°. Successive treatment of (IV) [which may be a mixed anhydride of AcOH and the Ac_1 derivative of (III)] with Br (in AcOH at 16°) and EtOH-KOH affords 7-bromo-8-hydroxyquinoline. (I) and (II) (0.5 mol.) similarly give α -8:8'-dihydroxydiquinolylphthalide (V), m.p. > 360° [hydrochloride, m.p. > 353°; platinichloride, m.p. > 315°; Ac_2 , decomp. 280—300°, Bz_2 , m.p. 325—331° (decomp.), Br_2 , m.p. > 350°, and SO_3H (+4.5H₂O), m.p. > 350°, derivatives; Na_1 and Na_2 salts], reduced (Na-Hg , H_2O) to $\text{o-carboxyphenyl-}\alpha$ -8:8'-dihydroxydiquinolylmethane, m.p. 352° (decomp.) [Me ester, m.p. 330° (decomp.); Ac_3 derivative (mixed anhydride), m.p. 288—291° (decomp.)], which when heated to 350° affords (V). In one experiment only (V) was accompanied by β -8:8'-dihydroxydiquinolylphthalide (VI), m.p. 292° [dihydrochloride (+7H₂O), m.p. 261°; platinichloride, m.p. > 320°; Ac_2 derivative, m.p. 277—279° (decomp.)], which is converted by conc. H_2SO_4 at 170—180° into a compound, $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}$, m.p. > 340°. (V) and (VI) dissolve in alkali to green and indigo-blue solutions, respectively. H. B.

Compounds of vanadium with 8-hydroxyquinoline, and their analytical applications.—See this vol., 464.

Hydroaromatic series. XXIII. Diene syntheses of hetero-rings containing nitrogen. IX. Stilbazole and acetylenedicarboxylic ester. U. DIELS and F. MOLLER (Annalen, 1935, 516, 45—61; cf. A., 1934, 782, 1367).—Stilbazole and Me_2 acetylenedicarboxylate in Et_2O at room temp. afford a labile adduct (I), m.p. 187—188°, transformed when heated above its m.p. or by boiling xylene or PhO into the “1 stable adduct” (II), m.p. 205—206°.

which passes in boiling AcOH into the "2 stable adduct" (III), m.p. 192°. (I) is not converted into (III) by boiling AcOH. Changes in the reverse



direction have not been observed. The reactions of (II) are similar to those observed in the $\text{C}_5\text{H}_5\text{N}$ series. It is smoothly oxidised by CrO_3 in AcOH to the indolizine substance (IV), m.p. 147°, is converted by Br in boiling AcOH into the tribromide, $\text{C}_{25}\text{H}_{22}\text{O}_8\text{NBr}_3$, m.p. 142—145° (decomp.) [corresponding perchlorate, $\text{C}_{25}\text{H}_{22}\text{O}_8\text{N}\cdot\text{ClO}_4$, m.p. 228° (decomp.)], transformed by Na_2CO_3 into $\text{H}_2\text{C}_2\text{O}_4$ and (IV). Hydrolysis of (II) with conc. HCl affords the chloride of a monocarboxylic acid, whilst boiling PhOH causes loss of CO_2 and MeOH with formation of a tricarboxylic ester, $\text{C}_{23}\text{H}_{21}\text{O}_6\text{N}$, m.p. 157°, possibly an indolizine derivative, also obtained by the action of boiling AcOH. Catalytic hydrogenation (PtO_2) of (II) establishes the presence of 6 double linkings. The action of CrO_3 , Br, H_2 (PtO_2), conc. HCl, and PhOH on (I) gives the same products as are obtained from (II), since all these reagents convert (I) into (II). Boiling conc. KOH removes the addendum from (I) with production of stilbazole. With CH_2N_2 (I) readily yields the compound, $\text{C}_{26}\text{H}_{25}\text{O}_8\text{N}_3$, m.p. 142—143° (decomp.), which passes at 145—150° into the substance, $\text{C}_{26}\text{H}_{25}\text{O}_8\text{N}$, 180°; (II) and (III) do not react with CH_2N_2 .

The basicity of (III) is so much > that of (II) that it dissolves readily in cold conc. HCl (this property causes difficulty in its formulation). Hydrogenation (PtO_2) of (III) causes absorption of only 5H_2 . (III) in boiling AcOH is transformed by Br into a pentabromide, $\text{C}_{25}\text{H}_{22}\text{O}_8\text{NBr}_5$, m.p. 156—157° (decomp.), converted by boiling MeOH into the dibromide (V), $\text{C}_{25}\text{H}_{22}\text{O}_8\text{NBr}_2$, m.p. 214—215° (decomp.). (V) is transformed by 35% HClO_4 into the colourless perchlorate $2[\text{C}_{25}\text{H}_{22}\text{O}_8\text{NBr}_2\text{ClO}_4]\cdot\text{HClO}_4\cdot 6\text{H}_2\text{O}$, m.p. 145—147° (decomp.), which passes in boiling MeOH (V) and a second perchlorate, m.p. 160° (decomp.). (I) is converted by boiling conc. HNO_3 into the $\text{C}_{25}\text{H}_{20}\text{O}_9\text{N}\cdot\text{HNO}_3$, m.p. 194° (decomp.), which is not hydrolysed by boiling H_2O ; the corresponding base could not be isolated. H. W.

Synthesis of β -naphthoxindole derivatives. E. KEE and H. G. LINDWALL (J. Amer. Chem. Soc., 1935, 57, 207—208).— β -Naphthisatin (I), COPhMe , in EtOH give 3-hydroxy-3-phenacyl- β -naphthoxindole, m.p. 179—180°, dissociates when

heated, which with warm HCl-AcOH yields 3-phenacylidene- β -naphthoxindole, m.p. 224—226°, converted by hot conc. HCl into 3-phenyl- β -naphthoquinoline-1-carboxylic acid, m.p. 296°, and by $\text{Na}_2\text{S}_2\text{O}_4$ into 2-phenacyl- β -naphthoxindole, m.p. 233—235°. (I) with COMe_2 and NHEt_2 gives 3-hydroxy-3-acetonyl-, m.p. 204—205° (decomp. from about 170°) (oxime, m.p. 241—242°), and with MeNO_2 3-hydroxy-3-nitromethyl- β -naphthoxindole, m.p. 246—248° (decomp.). R. S. C.

Synthesis of 5-phenyl-5-alkylbarbituric acids.

J. S. CHAMBERLAIN, J. J. CHAP, J. E. DOYLE, and L. B. SPAULDING (J. Amer. Chem. Soc., 1935, 57, 352—354).— $\text{CN}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ (I) is best (70–3%) prepared from $\text{CH}_3\text{Ph}\cdot\text{CN}$ and Et_2CO_3 by NH_2Na in dry Et_2O ; a little di-(α -cyanobenzyl) ketone, m.p. 260—262°, is also obtained, but in larger amount if H_2O is present or if heating is prolonged. (I), NH_2Na , and the appropriate alkyl iodide give Et cyanophenyl-ethyl-, b.p. 147°/11 mm., -isopropyl-, b.p. 165°/25 mm., -isoamyl-, b.p. 169°/11 mm., -n-hexyl-, b.p. 182—184°/10 mm., and -n-heptyl-acetate, b.p. 190°/9 mm., which with NaOEt and carbamide give 4-imino-5-phenyl-5-ethyl-, m.p. 264°, -5-isopropyl-, m.p. 290°, -5-isoamyl-, m.p. 251°, -5-n-hexyl-, m.p. 235—238°, and -5-n-heptyl-barbituric acid, m.p. 259°, hydrolysed by N-HCl to 5-phenyl-5-ethyl-, m.p. 172°, -5-isopropyl-, m.p. 169°, -5-isoamyl-, m.p. 181°, -5-n-hexyl-, m.p. 152—155°, and -5-n-heptyl-barbituric acid, m.p. 150°.

R. S. C.

Preparation of methylglyoxaline from carbohydrates. I. R. WEIDENHAGEN and R. HERRMANN (Z. Wirts. Zuckerind., 1935, 85, 126—130).—A 44% yield of methylglyoxaline (I) is obtained by heating glucose (100 g.), $\text{Zn}(\text{OH})_2$ (60 g.), 40% aq. CH_2O (85 c.c.), and 25% aq. NH_3 (600 c.c.) (autoclave; 5—7 atm.) at 90° for 5 hr. Fructose or invert sugar may also be used. The crude Zn salt of (I) usually contains > 0.5Zn. (I) is purified by distillation at 120—125°/0.02 mm. R. S. C.

Reaction between aminoantipyrine and phenylhydrazine. M. PASSERINI and M. RIDI (Gazzetta, 1934, 64, 931—933).—This, at 180—190°, gives rise to 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone.

E. W. W.

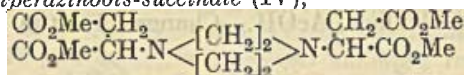
3-Carbethoxy-4-hydroxy-1-nitrotolylpyrazoles. F. D. CHATTAWAY, D. R. ASHWORTH, and M. GRIMWADE (J.C.S., 1935, 117—120).—The action of Br on substituted Et toluneazocetates (I) (obtained from diazotised nitro- and bromonitro-toluidines and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$) causes in cold AcOH replacement of Ac by Br, and the formation of Et α -bromoglyoxylate nitrotolylhydrazones (II) [which with NH in EtOH give the NH_2 -compounds (III)], and in hot AcOH bromination to bromo- (IV) and dibromo- (V) -acetoacetates. KOAc in boiling EtOH converts (IV) and (V) into 3-carbethoxy-4-hydroxy-1-nitrotolylpyrazoles (VI) and their 5-Br-derivatives (VII), also obtained by bromination of (VI), which with Cl_2 in CHCl_3 yield 5 : 5- Cl_2 -compounds (VIII). These are reduced (HI) to 5-chloropyrazoles (IX), and converted by AlkOH into alkyl diketosuccinate hydrazones (X). Chlorination of (VI) containing

Br in the tolyl nucleus yields only Cl_1 -derivatives (XI). The following are prepared (I): *Et* 2-nitro-, m.p. 142°, 3-nitro-, m.p. 104°, 6-bromo-2-nitro-, m.p. 92°, 6-bromo-3-nitro-, m.p. 126°, and 2:6-dibromo-3-nitro-, m.p. 102°, -*p*-tolueneazo-, and 5-nitro-, m.p. 128°, 4-nitro-, m.p. 131°, 6-nitro- (XII), m.p. 81°, 4-bromo-5-nitro-, m.p. 182°, 4-bromo-6-nitro- (XIII), m.p. 84°, 6-bromo-4-nitro-, m.p. 146°, -*o*-tolueneazo-acetoacetates. (II): *Et* α -bromoglyoxylate 2-nitro-, m.p. 160°, 3-nitro-, m.p. 142°, 6-bromo-2-nitro-, m.p. 99°, 6-bromo-3-nitro-, m.p. 153°, and 2:6-dibromo-3-nitro-, m.p. 99°, -*p*-tolyl-, and 5-nitro-, m.p. 150°, 6-nitro-, m.p. 132°, 4-bromo-5-nitro-, m.p. 164°, 4-bromo-6-nitro- [from (XIII) or (XII)], m.p. 127°, and 4:6-dibromo-5-nitro-, m.p. 116°, -*o*-tolylhydrazones. (III): *Et* α -aminoglyoxylate 5-nitro-, m.p. 152°, 4-bromo-5-nitro-, m.p. 174°, and 4:6-dibromo-5-nitro-, m.p. 160°, -*o*-tolylhydrazones. (IV): *Et* 2-nitro-, m.p. 139°, 3-nitro-, m.p. 113°, 6-bromo-2-nitro-, m.p. 121°, 6-bromo-3-nitro-, m.p. 137°, and 2:6-dibromo-3-nitro-, m.p. 133°, -*p*-tolueneazo-, and 5-nitro-, m.p. 136°, 6-nitro- (prep. in CHCl_3), m.p. 117°, 4-nitro-, m.p. 145°, 4-bromo-5-nitro-, m.p. 144°, 4-bromo-6-nitro-, m.p. 122°, 6-bromo-4-nitro-, m.p. 157°, and 4:6-dibromo-5-nitro-, m.p. 139°, -*o*-tolueneazo- γ -bromo-acetoacetates. (V): *Et* 2-nitro-, m.p. 141°, 3-nitro-, m.p. 143°, 6-bromo-2-nitro-, m.p. 156°, 6-bromo-3-nitro-, m.p. 157°, and 2:6-dibromo-3-nitro-, m.p. 130°, -*p*-tolueneazo-, and 5-nitro-, m.p. 170°, 6-nitro-, m.p. 88° (prep. in CHCl_3), 4-bromo-5-nitro-, m.p. 161°, 4-bromo-6-nitro-, m.p. 104°, and 4:6-dibromo-5-nitro-, m.p. 163°, -*o*-toluene- $\gamma\gamma$ -dibromo-acetoacetates. (VI): 3-Carbethoxy-4-hydroxy-1-(2'-nitro-, m.p. 119°, 3'-nitro-, m.p. 182°, 6'-bromo-2'-nitro-, m.p. 165°, and 2':6'-dibromo-3'-nitro-, m.p. 184°, -*p*-tolyl)-, and 5'-nitro-, m.p. 114°, 6'-nitro-, m.p. 99°, 4'-nitro-, m.p. 177°, 4'-bromo-6'-nitro-, m.p. 162°, 6'-bromo-4'-nitro-, m.p. 183°, and 4':6'-dibromo-5'-nitro- (XIV), m.p. 219°, -*o*-tolyl)-pyrazoles. The *Ac* derivative of (XIV) has m.p. 196°. (VII): 5-Bromo-3-carbethoxy-4-hydroxy-1-(3'-nitro-*p*-tolyl)-, m.p. 143°, and 5'-nitro-, m.p. 133°, and 6'-nitro-, m.p. 146°, -*o*-tolyl)-pyrazoles. (VIII): 5:5'-Dichloro-3-carbethoxy-1-(4'-nitro-*o*-tolyl)-4-pyrazolone, m.p. 124°, and its 2'-nitro- and 3'-nitro-*p*-tolyl, and 5'-nitro- and 6'-nitro-*o*-tolyl analogues, oils. (IX): 5-Chloro-3-carbethoxy-4-hydroxy-(4'-nitro-*o*-tolyl)-pyrazole, m.p. 181°, and its 3'-nitro-*p*-tolyl, m.p. 128°, and 5'-nitro-, m.p. 101°, and 6'-nitro-, m.p. 135°, -*o*-tolyl analogues. (X): Using MeOH , 2-*Me* 1-*Et* diketosuccinate-1-(4'-nitro-, m.p. 145°, and -1-(5'-nitro-, m.p. 139°, -*o*-tolyl)- and -1-(2'-nitro-*p*-tolyl)-, m.p. 132°, -hydrazones; using EtOH , *Et*₂ diketosuccinate-2-nitro-*p*-tolylhydrazone, m.p. 97°. (XI): 5-Chloro-3-carbethoxy-4-hydroxy-4-hydroxy-1-(6'-bromo-2'-nitro-, m.p. 168°, and -(2':6'-dibromo-3'-nitro-, m.p. 169°, *p*-tolyl)- and (6'-bromo-4'-nitro-, m.p. 202°, (4'-bromo-6'-nitro-, m.p. 164°, and (4':6'-dibromo-5'-nitro-, m.p. 165°, -*o*-tolyl)-pyrazoles.

E. W. W.

Derivatives of piperazine. III. Reactions with unsaturated esters. I. C. B. POLLARD, J. P. BAIN, and D. E. ADELSON (J. Amer. Chem. Soc., 1935, 57, 199—200; cf. A., 1934, 1112).— Me_2 maleate (I) (2 mols.) is immediately converted by anhyd. piperazine (II) (1 mol.) into a mixture of

(II) and Me_2 fumarate (III), which at 100° gives *Me*, NN'-piperazinobis-succinate (IV),



m.p. 158—159°, also obtained directly from (III). *Esters*, analogous to (IV), are similarly prepared in which *Me* is replaced by *Et*, m.p. 96—96.5°, Pr^n m.p. 90—90.5°, Pr^a , m.p. 88°, Bu^a , m.p. 48—48.5°, CH_2Ph , m.p. 112—113°, and cyclohexyl, m.p. 121°. Hydrolysis of (IV) gives the K_4 salt of the corresponding acid. The above esters do not effect conversion of (I) into the fumarate, which thus does not occur by way of an additive compound (cf. Clemo *et al.*, A., 1930, 452).

R. S. C.

Pyrimidine nucleotides from thymus-nucleic acid.—See this vol., 510.

Trypanocidal activity and chemical constitution. IV. Derivatives of benziminazole-5-arsinic acid. J. G. EVERETT (J.C.S., 1935, 155—157).—Action of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ on benziminazole-5-arsinic acid yields 1(or 3)-carboxymethyl- (I) and 1(or 3)-carbamylmethyl- (II) -benziminazole-5-arsinic acids. These are reduced ($\text{Na}_2\text{S}_2\text{O}_4$), respectively, to 5:5'-arseno-1(or 3)-carboxymethyl- (III) and -carbamylmethyl- (IV) -benziminazoles. Data on therapeutic action are given; (II) has the advantage over its analogue tryparsamide that its derivative (IV) is sol., and can be injected. E. W. W.

Schiff's bases of 2:4:6-trinitro- and 2:4-dinitro-benzaldehyde. S. SECAREANU and I. LUFAS (Bull. Soc. chim., 1935, [v], 2, 69—76; cf. A., 1934, 904, 905).—2:4:6- $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{CHO}$ (I) and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ give a compound which with boiling EtOH containing Na_2CO_3 gives 4:6-dinitro-3-hydroxy-2-*p*-ethoxyphenylindazole 1-oxide, m.p. 209° (Ag and *OEt*, m.p. 170°, derivatives). Similarly, the Schiff's base from (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (II) gives 4:6-dinitro-3-hydroxy-2-*p*-tolylindazole 1-oxide, m.p. 215° (Ag and *OEt*, m.p. 150°, derivatives). 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CHO}$ with (II) in AcOH gives 2:4-dinitro-benzylidene-*p*-toluidine, m.p. 152°, converted as above into 6-nitro-3-hydroxy-2-*p*-tolylindazole, m.p. 240° (decomp.) (*Ac* derivative, m.p. 225°), and 6-nitro-3-hydroxy-2-*p*-tolylindazole 1-oxide, m.p. 216° (Ag and *OEt*, m.p. 141°, derivatives). Similarly prepared, 4:6-dinitro-3-hydroxy-2-*p*-dimethylaminophenylindazole 1-oxide has m.p. 217° (cf. A., 1903, i, 420) (hydrochloride). The bases from (I) with $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ and $p\text{-C}_6\text{H}_4\text{MeBr}$ give no definite compounds with boiling $\text{EtOH}\text{-Na}_2\text{CO}_3$.

J. L. D.

Polymeric indoles. O. SCHMITZ-DUMONT and J. TER HORST (Ber., 1935, 68, [B], 240—243).—Diacetyldi-indole, m.p. 186—187°, from di-indole, NaOAc , and boiling Ac_2O , does not react with NaNO_2 and is hydrolysed by boiling $\text{KOH}\text{-H}_2\text{O}\text{-EtOH}$ to acetyldi-indole, m.p. 157°, contrary to Oddo it is therefore regarded as $\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NAc}$, both *Ac* being attached to N. Acetyltri-indole (I), m.p. 20°, best obtained from tri-indole (II) and Ac_2O in C_6H_6 at 0°, is converted by NaNO_2 in AcOH into dinitroso-

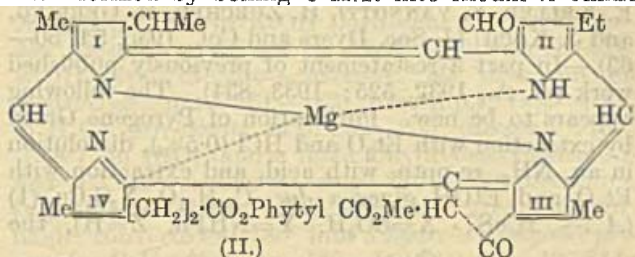
acetyltri-indole, m.p. 150—151° (decomp.). (II) is converted by prolonged boiling with NaOAc and Ac_2O into *tetra-acetyltri-indole*, m.p. 210—211°, which does not react with NaNO_2 , and is readily hydrolysed to (I). The fourth Ac is regarded as substituted in a *tert*-OH formed by ring-closure between CO and a CH or CH_2 . H. W.

6 : 7-Dimethylflavin-9-acetic acid. R. KUHN and H. RUDY (Ber., 1935, 68, [B], 300—302).—5-Nitro-4-amino-*o*-xylene is converted by $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ at 130° into 2-nitro-4 : 5-dimethylphenylaminoacetic acid, m.p. 204° (corr.). This is reduced by SnCl_2 in presence of alkali and the solution is poured into alloxan dissolved in AcOH , thus giving 6 : 7-dimethylflavin-9-acetic acid (I), isolated in the *Me* ester, m.p. 293° (corr., decomp.). (I) passes when heated into lumilactoflavin (II). Photodecomp. of (I) occurs in diffused daylight in neutral or slightly acid solution with production of (II) and 6 : 7-dimethylalloxazine. In alkaline solution (I) is tolerably stable to light and hence is not an intermediate product of the photochemical production of (II) from lactoflavin (III). (I) and its *glyceryl* ester (Ac_2 derivative) do not promote growth in rats. The tetrahydroxybutyl group therefore plays an essential part in the physiological activity of (III). H. W.

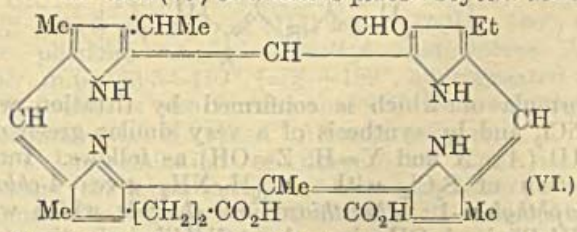
Purine derivatives from glyoxalines. P. C. MITTER and N. CHATTERJEE (J. Indian Chem. Soc., 1934, 11, 867—871).—5(or 4)-Aminomethylglyoxaline hydrochloride is brominated to a Br_3 -compound, m.p. 214°, which loses Br to give 2:4-dibromo-5-aminomethylglyoxaline, m.p. 230° (decomp.). The Br_3 -compound and KCNS form 2:4-dibromo-5-thiocarbamidomethylglyoxaline (I), m.p. 252° (decomp.), methylated to the 5-Me derivative, m.p. 220° (decomp.), which with $EtOH-C_5H_5N$ forms 8-bromo-2-methylthiol-1:6-dihydropurine, m.p. 198—200° (I), and $EtOH-C_5H_5N$ yield the thiazolinoglyoxaline derivative, m.p. 165°. F. R. S.

Chlorophyll. LIII. Chlorophyll-b. VI. Identification of the 3-position of the formyl group. H. FISCHER and S. BREITNER (Annalen, 1935, 516, 61—75; cf. A., 1934, 907).—Short reduction of rhodin-*g* Me₃ ester to rhodinoporphyrin-*g*, Me₃ ester is accompanied by considerable change in the structure of pyrrole nucleus I since oxidation leads to methylethylmaleinimide (I) but not hæmatic acid, thus affording the first instance of the isolation of (I) from chlorophyll-*b* (II). The Fe salt of rhodinoporphyrin-*g*- (III) is converted by HI in a current into rhodinoporphyrin-*g*₈ (IV) in which the *g* group of (III) is replaced by CO₂H. Total reduction of (IV) by AcOH-HI yields hæmopyrrole-carboxylic acid. (IV) is converted by anhyd. Na₂CO₃ and C₅H₅N into *phæoporphyrin-b*₇ (V), C₃₇H₃₈O₇N₄, m.p. 271° (*oxime*). Removal of the nuclear CO₂H from (V) by HBr-AcOH is accompanied by reduction of CO to CH, and leads to 3-demethyloxyphytyloerythrin ester (cf. A., 1934, 1370). CO₂H and consequently CHO from which it arose was present in position 3. (II) is therefore provisionally formulated as shown, which accounts for the non-reduction of (I) but not of hæmatic acid. Rhodin-*g*₈

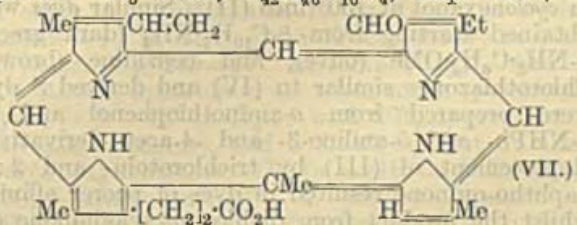
oxime, which contains CHO in position 3, is smoothly transformed by boiling C-H-N into rhodin- α , oxime



(*Me* ester $C_{35}H_{39}O_5N_5$, m.p. 211°), converted by boiling HCl into rhodin-*g*₅ (*Me*₂ ester, m.p. 189°), the constitution (VI) of which is placed beyond doubt



by its degradation by HI to rhodimorphyrin-*g*₅. The possibility of subjecting (II) and its derivatives to Perkin's reaction has been examined in the case of rhodin-*g* Me₃ ester and CH₂(CO₂Me)₂, whereby the expected Me₅ ester, C₄₂H₄₆O₁₀N₄, m.p. 205°, is

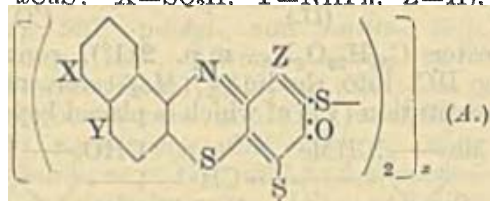


obtained; the union of the components is loose, thus probably accounting for the failure to reduce the compound to the corresponding saturated substance. The amended structure (VII) is assigned to neorhodino-
porphyrin- g_3 . H. W.

Chlorophyll. ANON. (*Nature*, 1935, 135, 275—276).—A summary of recent work. L. S. T.

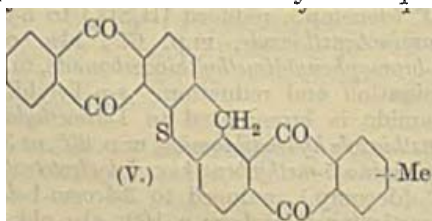
Formation and stability of polybromide derivatives of heterocyclic compounds. IV. Hydrodibromides and hydrotetrabromides of some 1-dimethylaminobenzthiazoles. M. W. BUKSHI, R. D. DESAI, and R. F. HUNTER (J. Indian Chem. Soc., 1934, 11, 863—866).—Bromination of *s*-phenyldimethylthiocarbamide gives 1-dimethylaminobenzthiazole hydrodibromide, m.p. 91—93° (decomp.), or 5-bromo-1-dimethylaminobenzthiazole hydrotetrabromide, m.p. 100° (decomp.), reduced (H_2SO_3) to 5-bromo-1-dimethylaminobenzthiazole, m.p. 67°, also obtained from *s*-*p*-bromophenyldimethylthiocarbamide, m.p. 159°, by bromination and reduction. *s*-*p*-Tolyldimethylthiocarbamide is brominated to 1-dimethylamino-5-methylbenzthiazole hydrodibromide, m.p. 90°, or 3-bromo-1-dimethylamino-5-methylbenzthiazole hydrotetrabromide, m.p. 95° (decomp.), reduced to 3-bromo-1-dimethylamino-5-methylbenzthiazole, m.p. 169°, also obtained by bromination and reduction of *s*-*o*-bromo-*p*-tolylldimethylthiocarbamide, m.p. 158°. F. R. S.

Chemistry of blue, green, and yellow sulphur dyes. H. E. FIERZ-DAVID [with E. BERNASCONI, E. KELLER, F. VANNOTTI, H. ZURCHER, R. GEERING, and J. KOCH] (J. Soc. Dyers and Col., 1935, 51, 50—63).—In part a restatement of previously published work (cf. A., 1932, 525; 1933, 834). The following appears to be new. Purification of Pyrogene Green by extraction with Et₂O and HCl (0.5%), dissolution in aq. NH₃, re-pptn. with acid, and extraction with Et₂O and EtOH gives a dye, C₃₄H₂₄O₁₀N₄S₆Cu (I) (A + xCuS: X=SO₃H. Y=NHPh. Z=H). the



formula of which is confirmed by titration with TiCl₃ and by synthesis of a very similar green dye (II) (A; X and Y=H, Z=OH) as follows. Interaction of S₂Cl₂ with α-C₁₀H₇-NH₂ gives 4-chloro-naphthylene-1:2-thiazthiazonium chloride, which with NH₂Ph in AcOH gives the 4-NHPh-derivative (red on tannin-mordanted cotton), reduced (Na₂S₂O₄) to 1-amino-4-anilino-2-naphthylthiol. Condensation of this with chloranil (III) gives a blue cotton dye (IV) (Na₂S₂O₄ or Na₂S vat), converted by Na₂S₅ in cyclohexanol at 150° into (II). Similar dyes were obtained starting from β-C₁₀H₇-NH₂ (dark green), p-NH₂-C₆H₄-OMe (olive), and benzidine (brown). Chlorothiazones similar to (IV) and derived S dyes were prepared from o-aminothiophenol and its 5-NHPh- and 5-anilino-3- and -4-aceto-derivatives. Replacement of (III) by trichlorotolu- and 2:3-naphtho-quinone resulted in dyes of poorer affinity, whilst the product from dichloro-p-xyloquinone did not give a S dye.

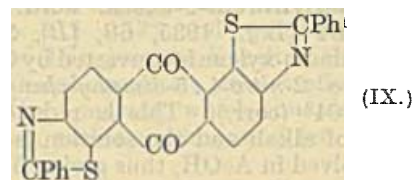
Purification of Cibanone Yellow R and Cibanone Orange R by Bernasconi's method (A., 1932, 525) gave dyes of formulae C₃₀H₁₆O₄S (V) and (C₁₅H₈O₂S)_x (VI), respectively; some 2-methylantraquinone was also isolated in each case. (V) has mol. wt. 495 (f.p. depression in perylene) and on oxidation with CrO₃-H₂SO₄ gives anthraquinone-2-carboxylic acid; attempts at milder oxidation, e.g., with H₂O₂, failed. lin.-Diphtaloyldiphenylenemethane sulphide was prepared by condensing diphenylenemethane sulphide (VII) with o-C₆H₄(CO₂)O (AlCl₃) and cyclising the intermediate acid (H₂SO₄ at 120—124°). It is very similar to (V) but weaker in its dyeing properties and affinity for cotton; (V) is probably the *trans-bisang*. compound. The relation of (V) to (VI) is probably the same as that of dehydrothio-p-toluidine



to primuline base. (VII) was prepared by condensation of diazotised o-NH₂-C₆H₄-CO₂H with PhSH,

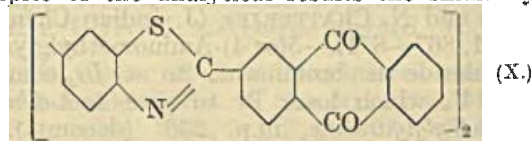
cyclisation of the o-SPh-C₆H₄-CO₂H formed (H₂SO₄), and reduction (HI-P₄) of the resulting thioxanthone.

Algol Yellow GCN (IX) is synthesised from 2:6-diaminoanthraquinone (VIII), S, and CPhCl₃ in C₁₀H₈ at the b.p. or, preferably, by conversion of the Bz₂ derivative of (VIII) into its *iminochloride* (PCl₅), which with KHS in EtOH gives the corresponding (SH)₂-compound; this is oxidised smoothly



to the dithiazole (IX) by H₂SO₄ (+MnO₂) or alkaline K₃Fe(CN)₆. The corresponding dye from 2:7-diamino-anthraquinone is not of technical interest.

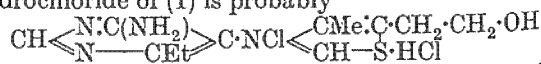
Products very similar to Indanthrene Yellow GF (X) but not identical with it (ultimate analysis) were obtained (a) by fusion of β-methylaminoanthraquinone with benzidine (XI) and S at 250°, and (b) from anthraquinone-2-aldehyde, (XI), and S in C₁₀H₈ and oxidation of the products with NaOCl. Replacement of (XI) by p-C₆H₄(NH₂)₂ gave a similar product. Fusion of 2-trichloromethylantraquinone with (XI) and S gave non-homogeneous products. In spite of the analytical results the similarity of



(X) to the products from (XI) is so close that it is assumed to be 2:2'-β-anthraquinonyl-4:4'-thiazazole.

H. A. P.

Structure of vitamin-B. R. R. WILLIAMS (J. Amer. Chem. Soc., 1935, 57, 229—230).—Vitamin-B (I) and Na₂SO₃ give 6-amino-(?)4-ethylpyrimidine-(?)5-sulphonic acid and a (?) thiazole base, C₆H₉ONS [containing a free OH, also present in (I)], which gives no CHI₃ reaction and is oxidised to the substance C₅H₅O₂NS of Windaus (A., 1934, 1415), probably 4-methylthiazole-5-carboxylic acid. The hydrochloride of (I) is probably



R. S. C.

(a) Ergot alkaloids. IV. Cleavage of ergotinine with sodium and butyl alcohol. (b) Structure of the ergot alkaloids. W. A. JACOBS and L. C. CRAIG ([a] J. Biol. Chem., 1935, 108, 595—606; [b] J. Amer. Chem. Soc., 1935, 57, 383—384; cf. A., 1934, 1116).—(a) Ergotinine (A), Na, and BuOH give NH₃ (1 mol.), α-(B), m.p. 282°, sublimes at 210—220°/0.15 mm., [α]_D²⁵ -92° in C₅H₅N [sulphate, m.p. 202° (decomp.), +H₂O (lost only at 150°/0.2 mm.)]; Ac derivative, m.p. 200°, basic, and β-dihydro-lysergol (C), C₁₅H₁₇ON·NMe, m.p. 190°, sublimes (sulphate, m.p. 305°; Ac derivative, m.p. 120°; [Keller test (K) positive with (B) and (C)], base I, ? C₁₄H₂₀N₂, m.p. 246°, sublimes at 160°/5 mm. [n NMe; no (K)], base IV, ? C₁₀H₉N, (dipicrate, [no NMe; (K) negative], base V, C₆H₁₃ON [di-p-

bromobenzoyl derivative, m.p. 149°; no NMe; (*K* negative), base VI, ? $C_9H_{13}ON$, possibly an aromatic OH-amine (*di-p-bromobenzoyl* derivative, m.p. 204°), and α -hydroxyisovaleric acid. Lysergic acid (*D*), similarly reduced, gives (*B*), (*C*), and amorphous material only. Bases II—VI originate from the part of the mol. which is not (*D*); the two parts are probably joined by isobutyrylformic acid or its precursor. Base VI is probably a phenylpropanolamine and with HNO_3 gives $p-NO_2 \cdot C_6H_4 \cdot CO_2H$.

(b) Proline Me ester (*E*) is also formed by the action of Na-BuOH or HCl-MeOH on (*A*). Base VI may be phenylalanine (*F*), base IV a substituted piperazine formed by reduction of proline anhydride, and base II a piperazine derivative from prolylphenylalanine anhydride. Base V is probably α -pyrrolidylcarbinol, formed by reduction of (*E*) or proline. It is probable that (*A*) is formed from (*D*) or ergine, joined by isobutyrylformic acid to a polypeptide from proline and (*F*).

R. S. C.

Fluorescence of quinine salts. E. CANALS, (MLLE.) S. PERROTTET, and P. PEYROT (Bull. Soc. chim., 1935, [v], 2, 21—26).—As little as 8.5×10^{-9} g. per c.c. of quinine (I) in H_2SO_4 at p_H 2 has been detected by determining the "factor of depolarisation" of the light scattered perpendicularly to the incident beam of unpolarised light. The intensity of fluorescence \propto the concn. of (I) at low concns. in H_2SO_4 at p_H 2, but is diminished by rise of p_H and by replacing H_2SO_4 with HCl.

J. G. A. G.

Veratrine alkaloids. I. Constitution of veratridine. II. Cevine. B. K. BLOUNT (J.C.S., 1935, 122—124, 124—125).—I. Veratridine (improved isolation through nitrate and sulphate; cf. J.C.S., 1878, 33, 341) is hydrolysed (KOH) to cevine and veratric acid. The "verine" of Wright and Luff (*loc. cit.*) is therefore cevine.

II. Cevine (A., 1899, i, 464) is dehydrogenated (Se at 320—330°) to *cevanthridine*, $C_{23}H_{25}N$ (a phenanthridine derivative?), m.p. 207° [hydrochloride, m.p. 245°; picrate, decomp. 230—240°; methiodide, m.p. 254—256° (decomp.)], and a hydrocarbon, m.p. 139—143°.

E. W. W.

Reduction studies in the morphine series.

v. **Dihydro- and tetrahydro- ψ -codeine methyl ethers.** L. SMALL and R. E. LUTZ. VI. **Hydrogenation of α - and β -isomorphines.** L. SMALL and

F. FARIS (J. Amer. Chem. Soc., 1935, 57, 361—363, 363—366; cf. this vol., 99).—V. ψ -Codeine Me ether (I) resembles ψ -codeine when reduced catalytically.

Hydrogenation (PtO_2) in AcOH of the hydrochloride of (I) (modified prep.; stable to Zn dust in EtOH) gives non-phenolic dihydro- ψ -codeine-

A Me ether (II) (77%), m.p. 127°, $[\alpha]_D^{25} + 35^\circ$ in EtOH [perchlorate, m.p. 243—244° (decomp.), $[\alpha]_D^{27} - 6.5^\circ$ in H_2O], and tetrahydro- ψ -codeine Me ether

F. (15%), m.p. 125—130°, $[\alpha]_D^{30} - 5^\circ$ in EtOH [hydrochloride, m.p. 251—252° (decomp.), $[\alpha]_D^{27} + 6^\circ$ in EtOH].

Use of Pd-BaSO₄ in H_2O gives more (III), principal product in 10% AcOH. The

amorphous methiodide of (I) with 25% NaOH gives non-phenolic dihydro- ϵ -methylmorphimethine-A Me

ether, m.p. 102.5°, $[\alpha]_D^{27} + 202^\circ$ in EtOH (hydrochloride, m.p. 219—220°, $[\alpha]_D^{27} + 157^\circ$ in H_2O ; per-

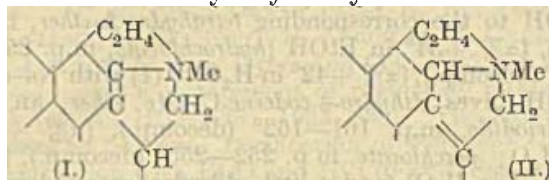
chlorate, + H_2O , double m.p. 85—87° and 155—156°, $[\alpha]_D + 136^\circ$ in H_2O), hydrogenated (PtO_2) in 7.5% AcOH to the corresponding tetrahydro-A-ether, m.p. 98.5, $[\alpha]_D + 54^\circ$ in EtOH [hydrochloride, m.p. 251—252° (decomp.), $[\alpha]_D^{27} + 42^\circ$ in H_2O]. (I) with Na-abs. EtOH gives dihydro- ψ -codeine-C Me ether, an oil [hydrochloride, m.p. 161—162° (decomp.), $[\alpha]_D^{27} + 48^\circ$ in H_2O ; perchlorate, m.p. 252—255° (decomp.), $[\alpha]_D + 38.7^\circ$ in H_2O] (and a little dihydrodeoxycodine-B and -C), the methiodide, m.p. 230—232° (decomp.), $[\alpha]_D + 43^\circ$ in H_2O , of which with TlOH gives the hydroxide, converted at 180° into dihydro- ϵ -methylmorphimethine-C Me ether, m.p. 140—140.5°, $[\alpha]_D^{25} + 138.5^\circ$ in EtOH, hydrogenated (PtO_2) in AcOH to the corresponding hexahydro-ether (IV), m.p. 138°, $[\alpha]_D^{25} + 17.4^\circ$ in EtOH. The methiodide, m.p. 250—255° (decomp.), $[\alpha]_D^{27} + 25.5^\circ$ in H_2O , of (III) leads (TlOH; 180°) to the phenolic tetrahydro- ϵ -methylmorphimethine Me ether, m.p. 156.5—157°, $[\alpha]_D^{25} + 199^\circ$, hydrogenated to (IV), which is also formed similarly from ϵ -methylmorphimethine Me ether. All m.p. are corr.

VI. Demethylation of dihydro-*iso*- and -*iso*- ψ -codeine (the latter only feasible at high temp.) gives resins. Hydrogenation (Pd-BaSO₄) of isomorphine in EtOH gives dihydro- α -isomorphine, non-phenolic, m.p. 224—226°, $[\alpha]_D^{19} - 125.8^\circ$ in MeOH (gives dihydro-*isocodine* with CH_2N_2) (hydrochloride, $[\alpha]_D^{23} - 112^\circ$ in H_2O ; hydrobromide, $[\alpha]_D - 97.9^\circ$ in H_2O ; H oxalate, $[\alpha]_D - 91.9^\circ$ in H_2O ; methiodide, $[\alpha]_D^{23} - 80.4^\circ$ in H_2O ; all cryst.). β -*iso*Morphine in EtOH or its hydrochloride (V) in H_2O gives (PtO_2) tetrahydro- β -isomorphine, m.p. 245—247° (decomp.), $[\alpha]_D^{23} - 60.4^\circ$ in 10% AcOH, unstable in air when moist (perchlorate, cryst., $[\alpha]_D^{19} - 76^\circ$ in H_2O ; with CH_2N_2 gives tetrahydroallo- ψ -codeine), and a small amount of tetrahydrodeoxymorphine. (V) in AcOH or N-HCl gives (PtO_2) equal amounts of dihydro- β -isomorphine, + H_2O , m.p. 202—203°, $[\alpha]_D^{22}$ (anhyd.) $- 104^\circ$ in MeOH (gives with CH_2N_2 dihydroallo- ψ -codeine; hydrochloride, $[\alpha]_D - 98.7^\circ$ in H_2O ; hydrobromide, $[\alpha]_D^{23} - 87^\circ$ in H_2O ; H fumarate, $[\alpha]_D^{22} - 81.3^\circ$ in H_2O ; all cryst.), and tetrahydro- β -isomorphine. R. S. C.

[Substituted] benzoates of codeine. C. F. POE and J. G. STRONG (J. Amer. Chem. Soc., 1935, 57, 380—381).—The following are prepared: codeine benzoate, m.p. about 79°, o-, m.p. 139°, m-, m.p. 99°, and p-bromo-, m.p. 166°, o-, m.p. 134°, m-, m.p. 96°, and p-chloro-, m.p. 162°, o-, m.p. 185°, m-, m.p. 173°, and p-nitro-, m.p. 159°, m-, m.p. 148°, and p-hydroxybenzoate, m.p. 140°, and salicylate, m.p. about 221°. All m.p. are "block." R. S. C.

Strychnos alkaloids. LXXXV. Experiments with derivatives of neobrucidine and neostrychnidine. Constitution of neo-forms. H. LEUCHS and H. BEYER (Ber., 1935, 68, [B], 290—296; cf. Perkin *et al.*, A., 1927, 888).—Reasons are advanced for considering the position of the double linking in neo-isomerides to be as in (I) instead of as in (II) as assumed by Robinson *et al.* (A., 1934, 788). Oxidation of dihydroxymethoxymethyldihydroneobrucidine Y (A., 1933, 1176) gives little if any of the cryst. compound $C_{19}H_{26}O_2N_2$ when oxidised with CrO_3 , whereas it is produced in 50% yield from Z; isomerisation of Y to Z under the action of acids is therefore

excluded. As ether, dihydroxymethoxymethylneodiketobrucidine is hydrolysed by 8.8*N*-HBr at 100°



to dihydroxy(hydroxymethyl)dihydroneodiketonucidine (III), $C_{18}H_{24}O_6N_2$, m.p. 309—312° (decomp.), $[\alpha]_D^{20} +156.1^\circ$ in H_2O [which does not unite with mineral acids or give an oxime, semicarbazone, Br or :CHPh derivative but yields an *Ac* compound, $C_{20}H_{26}O_5N_2$, m.p. 261—262° (decomp.), $[\alpha]_D^{20} +230^\circ$ in H_2O], and small amounts of a substance, $C_{15}H_{20}O_5N_2Br$. Hydrogenation of (III) (PtO_2-H_2O) affords dihydroxy(hydroxymethyl)dihydroneohydroxyketonucidine, m.p. 271—272°, $[\alpha]_D^{20} +112.8^\circ$ in H_2O (diacetate, m.p. 232—233°, $[\alpha]_D^{20} +136^\circ$ in H_2O , $+141.4^\circ$ in $AcOH$), hydrolysed by HBr to the anhydride, $C_{18}H_{24}O_5N_2$, m.p. 301—303°, $[\alpha]_D^{20} +119.5^\circ$ in H_2O , also obtained by similar treatment of dihydroxymethoxymethyl-dihydroneohydroxyketonucidine; it does not combine with H_2 and gives an *Ac* derivative, m.p. 245—247° (decomp.), $[\alpha]_D^{20} +136.4^\circ$ in H_2O , $+134^\circ$ in $AcOH$. Oxidation of (III) with CrO_3 in 3.6*N*- H_2SO_4 yields a compound, $C_{17}H_{26}O_6N_2$, m.p. 273—275° (decomp.), prisms, $+65.2^\circ$ in H_2O , platelets, $[\alpha]_D^{20} +63.0^\circ$ in H_2O . H. W.

Alkaloid of the seeds of *Leonurus sibiricus*.—See this vol., 422.

Dissociation constants of some aliphatic arsinic acids.—See this vol., 446.

Electrolysis of liquid ammonia solutions of sodium triphenylgermanide. L. S. FOSTER and G. S. HOOPER (J. Amer. Chem. Soc., 1935, 57, 76—78).—Electrolysis of $NaGePh_3$ in liquid NH_3 gives Ge_2Ph_6 , $GeHPh_3$, and N_2 . With a Pt anode the N_2 is approx. equiv. to the $GeHPh_3$, but is considerably less with a Hg anode. E. S. H.

Reaction of pyridine with Cleve's and Gerard's salts. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Ann. Inst. Platine, 1935, 12, 103—114).— C_5H_5N yields $Pt(C_5H_5N, Cl)_2Cl_2$ with Cleve's salt, and $[2NH_3, 2C_5H_5N, PtCl_2]Cl_2$ (I) with Gerard's salt. The prep. of three geometrical isomerides of (I) is described. R. T.

Replacement of tin, lead, arsenic, and antimony in organic compounds by mercury. K. A. KOTSCHESCHKOV and A. N. NESMEJANOV (J. Gen. Chem. Russ., 1934, 4, 1102—1113).— $HgCl_2$ or HgO reacts in neutral media with various aryl compounds of Pb, Sn, and Sb to yield $HgPhCl$, and in alkaline media with Pb, Sn, Sb, and As to yield $HgPh$. The mechanism of the reactions involved is discussed. R. T.

Optical rotation and dissociation of caseinogen. D. C. CARPENTER (J. Amer. Chem. Soc., 1935, 57, 129—131).—Caseinogen (M 96,000) (A., 1931, 855) has $[\alpha]_D^{20} -99^\circ$ in 0.9—1.5% solution in phosphate buffer (p_H 6.8); the val. increases to -105° in dil. (0.181%) solution (A). Ultracentrifugal analysis of the various solutions shows that in (A) dissociation

of the original mol. (I) into fragments of M 32,000 occurs. The dissociation is reversible since increase in the concn. from 0.1 to 1% gives a solution containing (I) only. H. B.

Binding of bromine by casein. I. S. JAIT-SCHNIKOV (J. Gen. Chem. Russ., 1934, 4, 1114—1116).—Casein absorbs 37.5% of its wt. of Br vapour. The product does not contain free Br. R. T.

Combination of ovalbumin and casein with tyrosine. Z. KERESZTES (Magyar chem. Fol., 1934, 40, 1—13; Chem. Zentr., 1934, ii, 2538).—The combination of ovalbumin (I) and casein with tyrosine (II) in solutions of different p_H proceeds in steps. No disruption of the protein mol. occurs; the reaction between (I) and (II) is reversible. H. N. R.

Thiol and disulphide groups of proteins. I. Determination. A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1935, 18, 307—323).—SH groups in proteins (I) are determined directly by treatment with cystine (II) followed by determination of the cysteine (III) formed, or indirectly by treatment with oxidising agents or CH_2I-CO_2H , removal of excess of reagent, hydrolysis of (I), and comparison of (III) in (I) and hydrolysate. The S-S groups in unhydrolysed (I) are determined by reduction to SH with $SH-CH_2-CO_2H$, (II) and (III) being determined colorimetrically by phosphotungstate. The Folin-Marenzi method for (II) in (I) (A., 1929, 1093) requires modifying [by denaturation of (I) and oxidation of SH by H_2O_2 before hydrolysis] owing to incomplete reduction of (II) by SO_3^{2-} . Data for the (II) and (III) contents of some (I) are given. F. O. H.

Hydrolysis of ovalbumin with various mineral acids and alkalis in the autoclave. V. S. SADIKOV, V. A. VADOVA, and R. G. KRISTALLINSKAJA (Biochem. Z., 1935, 276, 168—173).—The influence of the nature (HCl , H_2SO_4 , HNO_3 , H_3PO_4) and concn. of mineral acid and of its time of action on the yield of *cyclopeptides* obtained by autoclaving albumin at 180° and the distribution of N in the hydrolysis products are investigated and the results tabulated. P. W. C.

Graphical application of barometer corrections in the volumetric determination of carbon. J. I. USATENKO and N. D. AVERKIEV (Zavod. Lab., 1934, 3, 1125).—The C content is read directly from a rotating scale which automatically applies temp. and pressure corrections. R. T.

Ter Meulen's methods of organic analysis. J. GAUTHIER (Bull. Soc. chim., 1935, [v], 2, 322—324).—Simplifications (e.g., hard glass tubes instead of SiO_2) and improvements in ter Meulen's methods are suggested. Determination of S is accurate only if Pt-pumice is used as a catalyst, and with sulphonates or sulphites conc. HCl is added (H_2 stream maintained) to the boat after the initial heating to redness. Determination of O is untrustworthy when liquid or solid products pass into the absorbent, e.g., C_6H_6 from CPh_3 peroxide. Determination of N is satisfactory except when the substance chars rapidly (e.g., adrenaline) and occludes N_2 : with $(NH_4)_2$

derivatives precautions (e.g., slow initial heating) are essential for accuracy. The determination of halogens is satisfactory. J. W. B.

Assay methods for salts of organic acids. R. M. HITCHINS (J. Amer. Pharm. Assoc., 1935, 24, 11—15).—Henville's method (B., 1927, 315) may be used with any H_2O -sol. salt of the type MA where HA is moderately insol. in H_2O and appreciably sol. in a solvent immiscible with H_2O , and where the apparent dissociation const. of HA is $< 2.5 \times 10^{-3}$ and that of MOH $> 10^{-6}$. H. T.

Application of drop reactions to the identification of organic compounds. VIII. F. FEIGL, V. ANGER, and O. FREHLEN (Mikrochem., 1935, 17, 29—37; cf. A., 1934, 1240).—Dicarboxylic acids of which the CO_2H groups are separated by ≥ 2 C atoms, their anhydrides, amides, imides, and esters yield intense and characteristic yellowish-green fluorescent solutions after heating with $m\text{-}C_6H_4(OH)_2$ and conc. H_2SO_4 at 130° for 5 min., cooling, and making alkaline with aq. NaOH. Dicarboxylic acids with a $\cdot CH(OH) \cdot CO_2H$ group lose HCO_2H with H_2SO_4 , yielding β -keto-carboxylic acids, the enolic forms of which react with $m\text{-}C_6H_4(OH)_2$ as above

forming umbelliferones, which fluoresce blue in ultra-violet light. The characteristic fluorescence colours given by many compounds are tabulated. Citric acid can be detected by successive treatment with $SOCl_2$, NH_3 , and H_2SO_4 . The citrazinic acid formed shows a blue fluorescence on addition of excess NH_3 .

J. W. S.

Potentiometric titration of non-aqueous solutions applied to amino-acids.—See this vol., 450.

Determination of morphine, particularly in opium. C. MANNICH [with K. HANDKE and G. BAUMGARTEN] (Arch. Pharm., 1935, 273, 97—113).—Morphine (I) gives quantitatively the 2:4-dinitrophenyl ether, decomp. $200\text{--}260^\circ$ (hydrochloride, decomp. about 220° ; nitrate, decomp. 110°), which can be titrated by addition of much NaCl and an excess of 0.1N-HCl and back-titration. (I) can be thus determined (gravimetrically or volumetrically) alone or in drugs (after removal of most of the narcotine). An aq. $Ca(OH)_2$ extract of opium is treated with $K_2C_2O_4$ and the (I) determined in the filtrate, the results agreeing with those given by the "International" method and requiring no correction.

R. S. C.

Biochemistry.

Composition of alveolar air on Everest, 1933. R. GREENE (J. Physiol., 1934, 82, 481—485).—At 23,000 ft., at a pressure of 339 mm., alveolar CO_2 of a normal acclimatised person is 6.62% and O_2 13.3%, the R.Q. thus being 0.83. R. N. C.

Determination of gaseous pressures and their fluctuations in the organism. I. Micro-methods for alveolar air, blood, and tissues in man. II. Mechanism of intermediary gaseous metabolism. F. MEYER (Arch. exp. Path. Pharm., 1935, 177, 693—713, 714—725).—I. Apparatus for micro-gas analysis and its applications are described. The O_2 and CO_2 tensions of subcutaneous tissue in man average 37 and 41 mm. Hg, respectively.

II. The interpretation of analytical data of respiratory, alveolar, and tissue gases is discussed with reference to the diffusion of O_2 and CO_2 in the organism. F. O. H.

Blood-gas analysis apparatus with a filter-

J. PLESCH (Biochem. Z., 1935, 276, 198—).—An apparatus and its manipulation are described which permits the absorption under Hg by filter-paper of small amounts of body-fluids, the liberation by evacuation of dissolved gases and H_2O vapour, and the passage of these gases to a pipette for analysis in absence of the remaining constituents of the body-fluid. P. W. C.

Fœtal blood. IV. Oxygen and carbon dioxide dissociation curves. N. J. EASTMAN,

K. GELING, and A. M. DE LANDER (Bull. Hopkins Hosp., 1933, 53, 246—254; cf. A., 1932, 85).—At pressures of 25—60 mm. fœtal blood more effectively than that of the mother and pressures releases CO_2 more readily. The tension of (I) at the first respiration (II)

varies widely. Other factors are responsible for initiating (II). CH. ABS. (p)

Approximate determination of the carbon monoxide content of blood. H. BECKER and E. LEMPICKI (Wiadom. farm., 1934, 61, 45—47, 77—79; Chem. Zentr., 1934, ii, 2562).—Wetzel's method (A., 1890, 1200) has been developed. The sample is diluted with normal blood until the limit is reached [26.5% of carboxyhaemoglobin (I)] at which reduction with $(NH_4)_2S$ gives the absorption spectrum of haemoglobin (II). With $< 26.5\%$ of (I) a sample is first saturated with CO, and then diluted with the main sample until the spectrum of (II) is observed on reduction. H. J. E.

Reduction of the volume of the red corpuscles under the influence of fat solvents and the protective action of calciomimetic anions. B. SEKLA, P. PELNAR, and O. HORAK (Compt. rend. Soc. Biol., 1935, 118, 277—280).—The vol. of red corpuscles (I) is reduced approx. 30% by 3% Et_2O or $COMe_2$, but only by 7% $EtOH$. (I) reduction increases progressively with concn. to the haemolytic val., which is 5.5% for Et_2O , 7.5% for $COMe_2$, and 15% for $EtOH$. (I) reduction is influenced by temp., and by the time that has elapsed since the blood was drawn. The reduction does not occur in presence of $C_2O_4^{2-}$ or other calciomimetic anions. R. N. C.

Fragility and maturation of reticulocytes. C. MERMOD and W. DOCK (Arch. Int. Med., 1935, 55, 52—60).—Reticulocytes (I) are more resistant to haemolysis by certain agents, e.g., hypotonic NaCl solution, than are normal erythrocytes, but are less resistant to others, e.g., saponin, at 37° either *in vitro* or *in vivo*. The maturation of (I) in circulating blood probably does not occur appreciably. W. O. K.

Hæmoglobin. G. BRUYNOGHE (Compt. rend. Soc. Biol., 1935, 118, 824—826).—Hæmoglobin (I) does not produce sp. precipitins, either when injected alone or together with serum; benzoylated or iodinated (I) is also inactive. R. N. C.

Determination of bilirubin in serum samples containing hæmoglobin, by Van den Bergh's method. L. KATZILAMBROS (Praktika, 1933, 8, 323—324; Chem. Zentr., 1934, ii, 2257).—The original method may be used for hæmolysed sera, by working with COMe, instead of 96% EtOH.

A. G. P.

Glutathionæmia in children. R. DELÉTANG, J. DESBORDES, and S. B. BRISKAS (Compt. rend. Soc. Biol., 1935, 118, 768—770).—Reduced glutathione (I) is high in foetal blood and falls slowly after birth, becoming steady at the 6th year. Corpuscle-(I) behaves similarly. There is no difference between the sexes. R. N. C.

[Non-]existence of free choline in the blood. E. SASSO (Boll. Soc. ital. Biol. sperim., 1934, 9, 856—859).—The choline/P ratio in normal blood or serum shows that free choline is not present in measurable quantities. R. N. C.

Variations of ammonia in blood and urine after introduction of urease by different routes. L. STANOYÉVITCH and S. PETKOVITCH (Compt. rend. Soc. Biol., 1935, 118, 345—348).—Oral administration of fresh or inactivated soya-bean meal has no action on blood-NH₃ (I), but urinary NH₃ varies. Subcutaneous injection of urease (II) raises (I), the increase being larger if urea is injected simultaneously, whilst intravenous injection of (II) alone trebles (I). Inactivation of (II) destroys its effect on (I) when injected either way. R. N. C.

Variations in blood composition. S. J. FOLLEY and G. L. PESKETT (J. Physiol., 1934, 82, 486—495).—Blood concn. does not necessarily increase during stasis caused by experimental compression of the jugular vein of the cow, but increases in samples taken after release. Plasma-protein of bovine venous blood is unaffected by shaking with air. The composition of consecutive samples from the same vein under identical conditions often shows marked variations. R. N. C.

Protein content and osmotic pressure of blood-serum and lymph from various sources in the dog. M. E. FIELD, O. C. LEIGH, jun., J. W. HEIM, and C. K. DRINKER (Amer. J. Physiol., 1934, 110, 174—181).—The albumin-globulin ratio of lymph is always > that of the corresponding serum, and total protein in lymph is < in serum, the two apparently bearing a definite relation to one another. The sp. osmotic pressures of lymph and serum are similar, except for liver-lymph. R. N. C.

Ultracentrifugal investigation of serum-proteins. A. S. MCFARLANE (Biochem. J., 1935, 29, 407—429).—By means of a modification of Lamm's refractive index method of following protein (I) sedimentation in the ultracentrifuge (cf. A., 1929, 129, 1234) satisfactory sedimentation photographs were obtained with very conc. (I) solutions. Native horse serum (II) contains two mol. fractions, and the

lighter fraction, representing nearly 80% of the total (I), cannot be chemically identical with serum-albumin (III) obtained by pptn. methods in approx. the same amount as globulin (IV). Ultracentrifugal analysis reveals that the analytical (III)/(IV) ratio of 1 is approached on simple dilution of (II), and that the mol. wts. of the two fractions in native (II) are probably the same as those of (III) and (IV). Recryst. (III) [unlike repptd. (IV)] exists in a mono disperse state over a wide concn. range, but artificial mixtures of (III) and (IV) behave like an ideal solution only at very low concns., the interaction of (III) and (IV) involving a reduction in the mol. size of part of the (IV) to approx. that of (III), until, in undiluted native (II), the (III)/(IV) ratio is 4. This phenomenon is not affected by the *p_H*, or by salts present in solution. A. E. O.

Flocculation of serum in distilled water or in presence of melanin. V. CHORINE (Compt. rend. Soc. Biol., 1935, 118, 335—338).—The photometric flocculation curve obtained by adding (NH₄)₂SO₄ to serum in H₂O containing melanin lies above that for serum in H₂O alone, and macroscopic flocculation begins at a higher (NH₄)₂SO₄ concn. The mechanism of flocculation is the same in both cases. R. N. C.

(A) Formation of gels in normal human serum by addition of lactic acid. (B) Formation in syphilitic sera. W. KOPACZEWSKI (Compt. rend. Soc. Biol., 1934, 116, 869—870, 932—933).—(A) Addition of 10% lactic acid causes gel formation (I) in normal serum in 100—245 min. at 20°. In cancer [serum-globulin (II) high] (I) is more rapid. In diseases causing low (II), (I) is very slow or does not occur.

(B) In syphilis (II) is > normal, but the rate of (I) is not appreciably increased. CH. ABS. (p)

Serum gelation and animal species. W. KOPACZEWSKI (Compt. rend. Soc. Biol., 1935, 118, 339—341).—The rapidity of gelation of a sp. serum by acids depends on its globulin content and buffering power. R. N. C.

Biuret method of determining albumin and globulin in serum and urine. J. FINE (Biochem. J., 1935, 29, 799—803).—Modifications of the method are described. The violet colour developed by equal amounts of albumin and globulin is practically the same, and serum diluted to contain 0.24% of protein, which keeps for several months in presence of CHCl₃, is advocated as the standard solution for determination of both total protein and albumin. (NH₄)₂SO₄ (2*M* finally) is used for separation of globulin. The results are usually higher when Na₂SO₄ (1.5*M*) is used. P. W. C.

Crystallisation of human serum-albumin. M. E. ADAIR and G. L. TAYLOR (Nature, 1935, 135, 307).—Microscopic fine needles have been obtained. L. S. T.

Vacate oxygen and oxidation quotient of serum. I. Determination of vacate oxygen of serum. W. ROMAN (Biochem. Z., 1935, 276, 57—60).—A method for determination of "residual vacate O" vals. for serum is described depending on the oxidation of deproteinised (tungstate) serum with

$\text{KIO}_3\text{--H}_2\text{SO}_4$ and titration of the excess HIO_3 . The mean error is $\pm 5\%$. P. W. C.

Determination of lipin-phosphorus in blood. S. FIANDACA (Boll. Soc. ital. Biol. sperim., 1934, 9, 809—811).—Blood or serum is extracted twice with Bloor's $\text{EtOH--Et}_2\text{O}$ (3:1) mixture, cooled, filtered, and the filtrate evaporated to dryness. The residue is incinerated with HNO_3 and H_2SO_4 and neutralised with NaOH . The $\text{PO}_4^{''''}$ is pptd. with MgCl_2 , NH_4Cl , and NH_3 , dissolved in HNO_3 , pptd. with NH_4MoO_4 , dissolved in 0.001N- NaOH , and the excess NaOH titrated with 0.001N- HCl . The accuracy of the results is comparable with that of Bloor's method. R. N. C.

Sodium fluoride as a blood anticoagulant in blood-phosphorus determinations. J. C. J. BURKENS (Biochem. J., 1935, 29, 796—798).—The inorg. P content of serum (I) and plasma (II) to which oxalate, citrate, or hirudin has been added and of the $\text{CCl}_3\text{CO}_2\text{H}$ protein-free filtrate of blood (III), (I), or (II) increases on keeping. The increase can be prevented by addition of 10 mg. NaF per 5 ml. of (III), NaF preventing both clotting and all phosphatase action. This amount of NaF does not interfere with the later determination of P by the colorimetric method. P. W. C.

Determination of phosphorus fractions in blood-serum. R. R. ROEPKE (Ind. Eng. Chem. [Anal.], 1935, 7, 78).—Total, lipid, and total acid-sol. P are determined colorimetrically (Deniges reagent) on samples ashed with $\text{Mg}(\text{NO}_3)_2$. Green's ashing technique (cf. A., 1928, 1051) is untrustworthy. J. L. D.

Calcium in the human organism. Physiology and metabolism. H. G. OTTE (Semana Med., 1934, II, 1013—1033).—Distribution of blood-Ca is discussed and data for the umbilical cord and newly born infants are given. CH. ABS. (p)

Blood-magnesium in normal and pathological conditions. A. AGUILAR (Semana Med., 1934, II, 691—720).—The intake, distribution, and elimination of Mg are considered. CH. ABS. (p)

Determination of blood-sodium. I. TORRES and A. S. RUIZ (Anal. Fis. Quim., 1934, 32, 246—253).—The gravimetric method of Grigaut and Bouteux (A., 1931, 641) gives the best val. for serum-Na, which in normal cases is 0.305%. F. R. G.

Copper and iron in human blood. A. SACHS, V. E. LEVINE, and A. A. FABIAN (Arch. Int. Med., 1935, 55, 227—253).—The blood (I) of normal men and women contains 0.132 ± 0.0008 , 0.131 ± 0.0012 mg. Cu per 100 c.c. and 50.13 ± 0.15 , 43.42 ± 0.19 mg. per 100 c.c., respectively. The hæmoglobin content is 14.96 ± 0.045 and 12.96 ± 0.06 g. per 100 c.c., respectively. In cases of anæmia, Cu increases as Fe decreases and, in tuberculosis, high Cu vals. (0.182 and 0.195 for men and women, respectively) are found. In pregnancy, Fe is 40.44 and Cu 0.195. Cu in maternal is 2—4 times that of the foetal (I), whilst Fe is slightly lower. H. G. R.

Effect of salinity variations on the alkaline reserve of the blood of Crustacea. A. DRILHON (Compt. rend. Soc. Biol., 1935, 118, 770—771).—The

alkaline reserve rises in marine Crustacea in H_2O the salinity (I) of which is decreased slowly, and falls in fresh- H_2O Crustacea as (I) is increased. R. N. C.

Chlorine content of capillary and venous whole blood and serum in infancy. G. TÖRÖK and L. NEUFELD (Arch. Kinderheilk., 1934, 102, 217—223).—The lowest vals. are found in infants < 3 months. The relatively large variations in blood-Cl in healthy infants are more marked in the serum than in the whole blood. NUTR. ABS. (m)

Hydrogen-ion concentration of the umbilical blood of the human new-born, compared with the maternal blood. T. MIKAWA (Japan J. Obstet. Gynecol., 1934, 17, 2—9).—Blood- p_H in the umbilical vein was 7.326 and that of the artery 7.288. In asphyxial new-born both vals. were lower. Retro-placental blood had p_H 7.344 and venous blood (cubital) of the same mother immediately after parturition 7.320. CH. ABS. (p)

Hagedorn-Jensen micro-method for determining blood-sugar. G. DI MACCO (Boll. Soc. ital. Biol. sperim., 1934, 9, 1008—1009).—The technique is slightly modified. R. N. C.

Sexual differences in fasting blood-sugar. E. M. GREISHEIMER (Proc. Soc. Exp. Biol. Med., 1934, 31, 1067—1069).—Decline in blood-sugar during fasting was more marked in women (I) than in men. Ketosis developed earlier in (I). CH. ABS. (p)

Difference between the disappearance of sugar and the formation of lactic acid in blood-glycolysis. Z. DISCHE and C. RAND (Biochem. Z., 1935, 276, 132—146).—Whereas the formation of lactic acid (I) in citrated blood at 8—9 runs parallel with the disappearance of sugar, it remains considerably behind the latter with suspensions of washed red cells in physiological saline at p_H 7.2. The discrepancy is largely accounted for in terms of difference of p_H and is the greater the smaller is the concn. of red cells in the suspension. The sugar not accounted for as (I) is not lost by oxidation or by conversion into non-reducing carbohydrate, but is probably transformed into diphosphoglyceric acid. P. W. C.

Oxygen pressure and fermentation. G. LEINER (Biochem. Z., 1935, 276, 186—189).—When red cells of rabbits in $\text{NH}_4\text{Ph}\cdot\text{NH}_2$ -anæmia (large metabolism and uninjured by shaking) are saturated with O_2 at varying pressures in Ringer's solution + 0.2% glucose, fermentation is inhibited as the pressure increases until the max. val. of respiration is attained, the pressure of O_2 thereafter having no effect on fermentation. P. W. C.

Kephalins and blood coagulability. G. SPAGNOL (Rev. Sudamer. Endocrinol. Immunol. Quimioterap., 1934, 17, 619—633).—A substance resembling kephalin (I), extracted from tissues, increases coagulability. It is sol. in Et_2O and repptd. by EtOH and COMe_2 , forms a colloidal solution in H_2O , and differs from (I) only in physiological action. CH. ABS. (p)

Hæmolysis from hypotonia proceeds according to a chromatic scale. IV. A. MANAI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1017—1019). R. N. C.

Hæmolysis from physico-chemical causes and corpuscular resistance. III. Fractionation of hæmolysis from hypotonia. A. MANAI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1020—1022).—The amount of hæmolysis in a hypotonic solution (I), measured colorimetrically, \propto the time of hæmolysis and the vol. of (I), and inversely \propto the concn. of the salts etc. present in (I). R. N. C.

Oxygen consumption of rabbit red cells during lysis: oxygen consumption of plasma. R. RAMSEY and C. O. WARREN (Quart. J. Exp. Physiol., 1934, 24, 153—160).—Cells suspended for some hr. in saline lose a substance which inhibits the "bursts" (I). Plasma (II) of normal rabbits consumes small amounts of O_2 probably through autoxidation of lipins and proteins. The O_2 consumption (III) of (II) is increased to show (I) when cells are hæmolysed in it or when non-respiring hæmolysed cells are added. The (I) are heat-stable and only slightly sensitive to CN'. When cells are suspended in (II) the (III) is the sum of that of cells and (II). CH. ABS. (p)

Antibodies and carbohydrates. II. Experiments with glucose, glucosamine, amygdalin, cathartic acid, and a denitrified gum-arabic preparation. P. UHLENHUTH and E. REMY (Z. Immunitats., 1934, 82, 229—240).—Injection of amygdalin, glucosamine, cathartic acid, or glucose does not produce antibodies; $Al(OH)_3$ adsorbates or colloidion maskings are equally ineffective. Gum-arabic (I) is denitrified by pptn. from HCl solution with EtOH, washing, pptn. with $COMe_2$, drying, dissolving in cold H_2O , adding $NaNO_2$, pptn. with AcOH, washing with EtOH and $COMe_2$, pptn. with $CCl_3 \cdot CO_2H$, washing with $COMe_2$, and drying; the dry substance (II) contains 0.122% N. (II) also does not produce antibodies; hence the antigenic properties of (I) are due to a glucosidic constituent containing N.

R. N. C.

Chemistry of anti-bodies and serum-proteins. L. F. HEWITT (Biochem. J., 1934, 28, 2080—2087).—The abstract of Part I (this vol., 256) should read as follows. Cryst. albumin and globulin were readily distinguishable in respect of the Hausmann no. and cystine, tyrosine, and tryptophan content, but antitoxins and diphtheria toxin-antitoxin floccules were indistinguishable from serum-globulin fractions.

Biological effects of high pressures. Change in the antigenic specificity of serum under the influence of very high pressures. J. BASSET, M. MACHEBEUF, and J. J. PEREZ (Compt. rend., 1935, 200, 496—498).—Horse serum maintained for 30 min. at 4500 atm. produces anaphylaxis in guinea-pigs sensitised with the same serum, but not normal serum, which indicates that although the sp. antigenic property of the serum is destroyed under high pressures, it acquires a new specificity. At pressures < 4000 atm., the original specificity is maintained, and no new one appears. Since pressure does not significantly modify the arrangement of acidic and basic groups in the protein mol. (I) (cf. A., 1933, 1181), specificity probably depends on the spatial relationships in (I). J. L. D.

Serological studies of moth-proteins with special reference to their phylogenetic significance. S. MARTIN and F. B. COTNER (Ann. Entom. Soc. Amer., 1934, 27, 372—383).—An EtOH-insol. substance reacting with its homologous antiserum was isolated from moths. The substance is not hydrolysable to reducing sugars. The precipitin reaction serves to determine phylogenetic relationships between genera and sub-families of the *Phalaenidæ*. CH. ABS. (p)

Solid components of pupa oil. I. H. KANEKO and K. YAMAMOTO (Bull. Sericult. Japan, 1934, 7, No. 2, 2).—The mixed solid fatty acids consist essentially of 80% of palmitic and 20% of stearic acid; they also contain a small proportion of a higher saturated acid. P. G. M.

Composition of ringed snake fat. G. LODE (Z. Unters. Lebensm., 1935, 69, 89—90).—The *d*, m.p., *n*, sap., Reichert-Meissl. Polenske, and I vals., acidity, and % of unsaponifiable matter of the fat of *Natrix natrix* are compared with those of other reptilian fats. E. C. S.

Protoporphyrin in the yolk of birds' eggs. B. GOUZON (Compt. rend. Soc. Biol., 1934, 116, 925—926).—Protoporphyrin was detected by its fluorescence spectrum in the yolk of the egg of the fowl, duck, and gull. Its presence may be connected with subsequent hæmoglobin formation. NUTR. ABS. (b)

Nuclein metabolism. XXXV. Pyrimidine nucleotides from thymus-nucleic acid. W. KLEIN and S. J. THANNHAUSER. XXXVI. **Enzymic study of the constitution of the polynucleotide molecule.** W. KLEIN and A. ROSSI. XXXVII. **Nucleosidase.** W. KLEIN (Z. physiol. Chem., 1935, 231, 96—103, 104—114, 125—148; cf. A., 1934, 922).—XXXV. The products of enzymic fission of thymus-nucleic acid were divided into EtOH-sol. and -insol. portions. The sol. fraction, purified by way of the brucine and Ba salts, afforded ribodeoxyadenylic acid and thymosinephosphoric acid (*Ba* salt, $C_{10}H_{13}O_8N_2Ba$, sinters 225—230°, $[\alpha]_D^{21} -4.4^\circ$), yielding thymosine by enzymic fission. The more sol. brucine salts afforded *ribodeoxycytidylic acid*, m.p. 183—187° (decomp.), $[\alpha]_D^{21} +35^\circ$ (sec. *Ba* salt, $[\alpha]_D^{21} +14.4^\circ$), affording by enzymic fission cytosinedeoxy-riboside (*picrate*, sinters 191°).

XXXVI. The prep. of a diphosphoesterase (I)-free monoesterase by the method of Kurata (A., 1932, 305) was not accomplished, the ratio of the rates of fission of Ph_1 and Ph_2 phosphate being const. and independent of the origin and purity of the prep. A pure (I) was not obtained. The toxic principle of "*Habu*" (*Trimeresurus flavoviridis*) hydrolyses both Ph esters and yeast-nucleic acid. The inhibition by AsO_4^{3-} observed in the fission of the natural esters is negligible in the fission of the Ph esters. The ring structure postulated for nucleic acid by Takahashi (A., 1933, 426) is not confirmed.

XXXVII. A micro-method for control of enzymic fission of ribosides and deoxyribosides depends on the use of the Wilkstatler-Schudel determination of sugars, allowance being made for I absorption by free purines. By drying frozen organs active and

const. enzyme material is obtained. The organs richest in purine-nucleosidase (I) are spleen, lung, liver, and heart-muscle. Highly active preps. are obtained by adsorption on $\text{Al}(\text{OH})_3$ and elution with neutral AsO_4^{+++} and PO_4^{+++} solutions. Purine nucleosides are the substrates of (I); pyrimidine nucleosides, nucleotides, and nucleic acid are not hydrolysed. AsO_4^{+++} and PO_4^{+++} activate, guanine and hypoxanthine inhibit strongly, adenine less, and deoxyribose weakly. There is a special pyrimidine-nucleosidase differing from (I), which is more abundant in kidney than in spleen and red marrow. J. H. B.

Reduced glutathione in thymus gland and testicles of young and full-grown rabbits. F. MURATA (Sci.-i-Kwai Med. J., 1933, 52, 42—45).—Vals. for young rabbits were 0.201% in thymus and 0.0778% in testicles; and, in adults, 0.0898 and 0.1285, respectively. CH. ABS. (p)

Determination of oxidised and reduced glutathione content of tissue. W. QUENSEL and K. WACHOLDER (Z. physiol. Chem., 1935, 231, 65—74).—The method of Woodward and Fry (A., 1932, 1053) is the most trustworthy for micro-determination of glutathione in tissue. J. H. B.

Chemical constitution of the cornea. A. C. KRAUSE (Amer. J. Ophthalmol., 1932, 15, 422—424).—Analytical data are given. CH. ABS. (p)

Lipins of the sclera, cornea, choroid, and iris. A. C. KRAUSE (Amer. J. Physiol., 1934, 110, 182—186).—The lipins consists largely of phosphatide (I) in all the tissues except the sclera and corneal substantia propria, where fat and (I) are present in equal amounts. Cholesterol and cerebrosides increase with (I). Carotenoids are present only in min. quantities. R. N. C.

Iodine content of the human pituitary. G. F. KOPPENHÖFER (Z. ges. exp. Med., 1934, 94, 57—62; Zentr., 1934, ii, 2405).—The pituitaries of persons who have died suddenly contain approx. g. of I. In chronic patients pituitary-I is considerably lower, whilst in liver disease and pregnancy it is zero. In males it is always > in females. R. N. C.

Effect of temperature on the total iodine content of the thyroid. E. VALLESI (Arch. internat. pharmacodyn., 1934, 48, 174—179).—The I content of the thyroid of guinea-pigs (I) kept for 20—40 days at 20—22° does not differ significantly from the rat. (13.9 mg. per 100 g. of fresh gland) obtained from (I) kept 0—5°. Thus the transitory rise in found at high altitudes must be attributed to some influence other than low temp. NUTR. ABS. (m)

Chemistry of normal human thyroids. H. VON OLNITZ and R. E. REMINGTON (Endocrinol., 1933, 563—568).—The wt. and total I content of thyroids increase rapidly up to 20 years of age and then more slowly to a max. at middle age, and subsequently decline. Summer glands are relatively heavier but the % of I remains practically const. CH. ABS. (p)

Comparative distribution of organic phosphate in the skeletal and cardiac muscles of *Liulus polyphemus*. G. L. ENGEL and I. CHAO

(J. Biol. Chem., 1935, 108, 389—393).—Total P and all the P fractions, particularly the phospho-arginine-P, are higher in skeletal than in cardiac muscle, the ratios, ranging from 3 to 16, being const. for each fraction. H. G. R.

Sodium, potassium, calcium, magnesium, and phosphorus contents of skeletal and cardiac muscle, bladder, and uterus. W. WILKINS (Proc. Soc. Exp. Biol. Med., 1934, 31, 1117—1118).—In cattle, among all tissues examined, the uterus (I) contained the most Na and least K. The total P of (I) and bladder was < that of skeletal and heart-muscle. CH. ABS. (p)

Presence of iron in enamel-keratin. T. ROSEBURY (J. Dental Res., 1934, 14, 269—272).—Fe is an intrinsic component of the enamel-keratin. CH. ABS. (p)

Analysis of tooth samples composed of enamel, dentine, and cementum. C. D. CROWELL, jun., H. C. HODGE, and W. R. LINE (J. Dental Res., 1934, 14, 251—268).—Composition is not influenced by sex or by morphological type of tooth and only slightly by age. The inorg. residue [after extraction of org. matter by KOH in $(\text{CH}_2\text{OH})_2$] corresponds with $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3 \cdot \text{Ca}(\text{OH})_2$. CH. ABS. (p)

Crystal orientation in tooth enamel. J. THEWLIS (Phil. Mag., 1935, [vii], 19, 291—297).—The apatite crystals are oriented so as to have the 011 axes in common. C. W. G.

Histochemical significance of metachromasia. L. LISON (Compt. rend. Soc. Biol., 1935, 118, 821—824).—Metachromasia is exhibited by mono-esters of polysaccharides and other substances of high mol. wt. with H_2SO_4 ; the effect decreases with mol. wt. R. N. C.

Aqueous extract of the domestic cocoon. XVIII. Effects of heating and enzyme on sericin. H. KANEKO and Y. NAKAZAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 356—359).—The quantity of sericin-A (I) is diminished by drying and steaming the cocoons; in solution it decreases with the time of heating. (I) is converted into -B, which is less readily sol. By the action at p_H 8.0 at 30° of bacteria isolated from the spun silk, the quantity of (I) is unaffected, although its colloidal properties are modified; the quantity of -B is reduced. CH. ABS.

Effect of diet on the yield and composition of human milk. U. S. RUŽIČIĆ (Monatsschr. Kinderheilk., 1934, 60, 172—181).—In healthy mothers (I) in full lactation (4th—7th month) mixed diets give the greatest flow of milk. All other diets diminish secretion. Hunger almost halves the amount in (I) with large secretions and diminishes the flow much less markedly in (I) with smaller secretions. Lactose % is unchanged by all diets. Meat alone, and meat and bread or butter, raise the N content very slightly, none of the other diets having any effect. Bread and meat halve the fat content; bread alone lowers it still further, whilst meat alone has no effect. Butter alone or with meat, and fasting increase the fat by about 50%, bread and butter having a similar but less marked influence. NUTR. ABS. (m)

Resazurin reductase test [in milk]. O. WALDBAUER (Kiserlet. Kozl., 1931, 34, 128; Bied. Zentr., 1934, A, 5, 133).—Pesch's method is simpler and more rapid than the methylene-blue test. A. G. P.

Micro-determination of copper in milk. L. W. CONN, A. H. JOHNSON, H. A. TREBLER, and V. KARPENKO (Ind. Eng. Chem. [Anal.], 1935, 7, 15—23).—A comparison of different methods has been made. Colorimetric determination of Cu by Na diethyldithiocarbamate, after separation by H_2S or micro-electrolysis, is recommended for 25- to 200-c.c. samples containing >0.002 mg. Cu. Cu contents found are: raw milk 0.051—0.132, pasteurised milk 0.088—0.741, dried milk 1.37—17.15 p.p.m. E. S. H.

Micro-determination of the different fractions of phosphorus and lipins in milk. D. TORRISI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1011—1013).—Total P is determined by the Neumann-Flatter micro-method. The milk is then treated with NaOH-EtOH and extracted with Et_2O . The H_2O solution, containing P compounds, is acidified, and caseinogen separated by filtration. Inorg. P is pptd. as $MgNH_4PO_4$, dissolved in H_2SO_4 , and determined by the micro-Neumann method, whilst total acid-sol. P (I) is determined by the same method after incineration of org. matter, org. acid-sol. and acid-insol. P being calc. by difference. Total lipin is determined in the Et_2O extract by evaporation and weighing, and cholesterol extracted from the residue with $COMe_2$ and determined colorimetrically with Ac_2O and H_2SO_4 in $CHCl_3$. The $COMe_2$ residue is extracted with EtOH, and lecithin and cephalin are determined in the sol. and insol. fractions, respectively, as P by the same method as (I). R. N. C.

Biology of the cerebrospinal fluid. V. Calcium content. E. VOGT (Arch. Gynakol., 1934, 158, 60—61).—In healthy, diseased, and pregnant women the Ca content (I) of the fluid varies from 4.0 to 7.1 mg. (average about 6.0 mg.) per 100 ml. (I) varies very little despite considerable changes in blood-Ca. NUTR. ABS. (m)

Micro-determination of the fat-soluble ester glycerol contained in lymph. S. FREEMAN and T. E. FRIEDEMANN (J. Biol. Chem., 1935, 108, 471—478).—The fatty material of lymph extract (cf. A., 1928, 662) after extraction by ligroin is saponified, and the glycerol in the H_2O -sol. constituents not pptd. by $HgCl_2 + CuSO_4$ reagent is oxidised by $0.02N-KMnO_4$. A. E. O.

Hydrogen carbonate elimination through salivary glands under nervous and chemical stimulation. H. H. McCLANAHAN, jun., and W. R. AMBERSON (J. Pharm. Exp. Ther., 1935, 53, 189—197).—The CO_2 content of submaxillary saliva is increased, at the expense of the blood-plasma, by stimulation with pilocarpine and to a smaller extent with adrenaline. H. G. R.

Saliva and gastric juice. R. V. DE IPOLA (Revista Medica Córdoba, 1934, 22, 675—682).—Mixtures of saliva and dil. HCl show a diminution in free HCl and rise of p_H . The fixing action is dependent

on a const. factor for each saliva, which increases with rise of temp. R. N. C.

Relation of the secretion of mucus to acidity of the gastric juice. O. L. HELMER (Amer. J. Physiol., 1934, 110, 28—36).—Stimulation of gastric secretion in man by histamine produces an increase in acid and Cl, with a decrease of total base, N, P, and mucus-sugar, in the gastric juice. Pepsin and rennin are also increased. The increase in acid α that of Cl. Mucus is present in the gastric contents throughout in sufficient concn. to account for the main variations in acid by neutralising and diluting the secreted HCl of the parietal cells. The [HCl] in this secretion, calc. from the Na : P ratio of the gastric contents, is 161 milliequivs. per litre, which is approx. isotonic with blood. R. N. C.

Chloride concentration of gastric secretion from fundic pouches and from the intact whole stomach. C. M. WILHELMJ, L. C. HENRICH, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1934, 109, 112).—In dogs, fluid enters the stomach from the fundus, where the secretion has a high, practically const. [Cl'] from the pyloric glands (I), and from the duodenum (II). The secretion from (I) and (II) has a relatively low [Cl']. NUTR. ABS. (m)

Acid-base ratio of gastric juice, blood, and urine before, and at intervals after, stimulation of the gastric juice by histamine. L. MARTIN, E. STEIGERWALD, M. L. CARROLL, and M. MORGENSTERN (Bull. Johns Hopkins Hosp., 1934, 55, 57—80).—Changes in electrolyte concn. of gastric juice (I), blood (II), and urine (III) following administration of histamine were much greater in cases able to secrete HCl into (I) than in those unable to do so. In the former, Cl', PO_4''' , and CO_2 in (II) and (III) decreased and serum-protein increased. The (III) became alkaline and base and NH_3-N contents declined. In achlorohydrias changes were similar but smaller and (III) became more acid in most cases. CH. ABS. (p)

Effect of continued oral administration of histaminase and pancreatin on gastric secretion. F. BIGURIA and A. CANZANELLI (Amer. J. Physiol., 1934, 110, 243—245).—The acidity of the gastric juice is unaffected by continued oral administration of histaminase or pancreatin for long periods. N C

Analysis of small amounts of bile. A. G. DOUGLAS-SAUERMANN (Z. physiol. Chem., 1935, 231, 92—95). J. H. B.

Influence of bile acid on the excretion of salts in the liver-bile. III. Excretion of phosphoric acid by cholic acid with addition of amino-acids or lactic acid. Y. KAWADA (Arb. Med. Fac. Okayama, 1934, 4, 196—205; cf. A., 1934, 1383).—Increased excretion of P, ash, and dry matter following feeding of glycine or alanine is intensified by feeding cholic acid (I). Decreased excretion due to *dl*-lactic acid is also counteracted by (I). CH. ABS. (p)

Urobilin excretion of infancy and childhood. relation to blood destruction and formation. H. W. JOSEPHS (Bull. Johns Hopkins Hosp., 55, 154—168).—The ratio of urobilin excreted (I) to total hæmoglobin in the body is const. for differen

ages. Stimulation of blood formation results in an increase in (I). CH. ABS. (p)

Chemical changes in blood and intestinal juice produced by loss of intestinal juice. R. C. HERRIN (J. Biol. Chem., 1935, 108, 547—562).—The electrolyte content of succus entericus (I) is similar to that of serum; the secretion of (I) proceeds independently of the extrinsic nerves to the intestine. Continuous distention of the jejunum decreases the Cl' and fixed base (II) and increases the HCO_3' and NH_3 concns. in (I), whilst the serum-(II), -Cl', HCO_3' , and plasma-vol. decrease and the serum-Ca, -P, and -protein increase. The η of the blood increases, whilst its O_2 content decreases. H. D.

Average composition of human duodenal secretion. C. M. WILHELMJ, L. C. HENRICH, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1934, 109, 112—113).—The average alkalinity of the secretion is equiv. to 0.056N and the average Cl' content is 272 mg. per 100 ml. NUTR. ABS. (m)

Hydrogen-ion concentration of the contents of the small intestine. C. S. ROBINSON (J. Biol. Chem., 1935, 108, 403—408).—A survey of the whole length of intestine in rats and dogs indicates that each portion of the gut wall contains a definite physiological control mechanism for regulating the p_{H} of the intestinal contents in contact with it, whereby the p_{H} is caused to vary regularly from about 6.5 in the duodenum to 7.5—8 at the ileocaecal valve. A. E. O.

Relationship of the pancreas to the hydrolysis of nitrogenous substances in faeces. Relationship of disease of the pancreas to hydrolysable carbohydrates in faeces. K. SEKIKAWA (Tohoku J. Exp. Med., 1934, 24, 51—71, 72—99).—In dogs, ligation of the pancreatic ducts causes a transitory increase in the muscle-fibre content of the faeces. The carbohydrate content is slightly increased. Formation of a permanent pancreatic fistula and extirpation of the pancreas lead to the appearance of much more undigested protein and starch. NUTR. ABS. (m)

Acidity and physical characteristics of urine. C. MITCHELL (J. Amer. Inst. Homeopath., 1934, 27, 523—526).—Urinary acidity is detected by use of the Na salt of Ruby S (red coloration). CH. ABS. (p)

Renal excretion of creatinine. II. Volume of distribution. III. Utilisation constant. R. DOMINGUEZ (Proc. Soc. Exp. Biol. Med., 1934, 31, 1146—1149; cf. A., 1934, 554).—II. When a substance disappears exponentially from the body and the rate of excretion by the kidneys \propto the concn. in the plasma (I), the rate of utilisation of the unexcreted portion also \propto the concn. in (I).

III. The excretion const. loses part of its significance in renal physiology in the case of substances (xylose, creatinine) which are partly utilised and partly excreted. CH. ABS. (p)

Urine infection and detection of nitrite in K. MACHOLD (Med. Klin., 1934, 30, 1097—Chem. Zentr., 1934, ii, 2425).—The method depends on the liberation of I by NO_2' and its extraction with CHCl_3 . A. G. P.

Silver nitrate reaction with urine. T. IRO and K. TSUSHIMA (J. Chosen Med. Assoc., 1934, 24, 1027—1036).—Urines containing < 0.7% of Cl' gave positive tests with Buscaino's AgNO_3 reagent. In general samples with lower [Cl'] give the more intense tests, but no quant. relationship is apparent. CH. ABS. (p)

Nature of the reducing substances in normal dog urine. E. P. LAUG and T. P. NASH, jun. (J. Biol. Chem., 1935, 108, 479—486).—Acid pptg. agents are liable to give rise to extra fermentable sugar (I) by hydrolysis of non-nitrogenous, non-fermentable (I) in the urine. A. E. O.

Sodium nitroprusside and [determination of] acetone in urine. F. E. R. SAS (Anal. Fis. Quím., 1934, 32, 185—232).—A modification of Engfeldt's test (A., 1925, i, 1490) is described, the limiting concn. being 16 mg. per litre with 0.08 mg. of COMe_2 (I). The colours given by Na nitroprusside with other possible constituents of urine (II) are described, confusion with (I) or $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ (III) occurring only with sulphides (IV), mercaptans (V), and glutathione (VI). Methods are given for the colorimetric determination in (II) of (I) and (III) together, (IV) and (V) together, and also of (VI), the limiting concn. for (I) in presence of (IV), (V), and (VI) being 35 mg. per litre with 0.175 mg. of (I). F. R. G.

Dissolved constituents of human sweat. A. G. R. WHITEHOUSE (Proc. Roy. Soc., 1935, B, 117, 139—153).—The constituents are present in the following amounts (I): Cl > 0.15, K 0.014—0.022 (4—11% as KCl), SO_4'' 0.004, lactic acid (not derived from the blood) 0.068—0.122, and urea (probably derived from the blood) 0.023—0.046%. The Cl content is increased by severe muscular work, but the increase is < that caused by the same rise in body temp. induced by atm. conditions. The ash consists chiefly of NaCl and KCl. The ratio org. matter : ash in sweat (II) varies with duration and intensity of sweating. Fresh (II) is slightly alkaline, but rapidly acquires acidity from the skin surface. Different individuals exhibit great differences as regards (I). W. McC.

Comparative efficacy of substances employed in prevention of intraperitoneal adhesions. C. E. REA and O. H. WANGENSTEEN (Proc. Soc. Exp. Biol. Med., 1934, 31, 1060—1063).—The (decreasing) order of efficiency was: Na ricinoleate, papain, amfetin, defibrinated rabbit blood. CH. ABS. (p)

Influence of various diets on experimental amyloidosis in mice. D. Y. KU and M. A. SIMON (Arch. Path., 1934, 18, 245—251).—Production of amyloidosis (I) by injection of nutrose was greatest in mice receiving a normal diet, less with a high-protein diet, and least with a diet rich in maize starch. Low incidence of (I) in Chinese is not attributable to soya-bean diets. CH. ABS. (p)

Preparation and stability of food allergen extracts. G. A. ALLES, G. PINESS, and H. MULLER (J. Allergy, 1933, 5, 5—11).—Antigenic extracts of wheat, eggs, and milk made with KH_2PO_4 — K_2HPO_4 —glycerol were stable after 7 years (cold).

CH. ABS. (p)

Urinary proteose in allergy. J. H. BLACK (J. Allergy, 1934, 5, 373—382).—The activity and specificity of the proteose from urine of allergic patients may be due to unchanged antigen.

CH. ABS. (p)

Treatment of hay fever and asthma with viosterol. B. Z. RAPPAPORT, C. I. REED, M. L. HATHAWAY, and H. C. STRUCK (J. Allergy, 1934, 5, 541—553).—The action of viosterol in increasing the efficiency of pollen injections is not related to its ability to mobilise Ca.

CH. ABS. (p)

New-formed hæmoglobin and protein catabolism in the anæmic dog. F. S. DAFT, F. S. ROBSCHERT-ROBBINS, and G. H. WHIPPLE (J. Biol. Chem., 1935, 108, 487—496).—The total urinary N is the same for both the anæmic and the non-anæmic dog. The anæmic dog produces less new hæmoglobin when "salmon bread" (Amer. J. Physiol., 1925, 72, 395) is fed daily than when the latter is fed after a period of protein fasting.

A. E. O.

Reaction and carbon dioxide content of the venous plasma in pernicious anæmia. C. P. EMERSON, jun., and O. M. HELMER (Arch. Int. Med., 1935, 55, 254—261).—The acid-base equilibrium in anæmia is normal, although there is a slight tendency to a deficiency in alkali.

H. G. R.

Iron and copper contents and the hæmopoietic activities of stomach and liver preparations. H. JACKSON, L. KLEIN, and J. F. WILKINSON (Biochem. J., 1935, 29, 330—337).—Modifications of existing methods are used for determination of Fe and Cu in clinically tested preps. of stomach and liver used in treatment of pernicious anæmia. No obvious relationship could be detected between the Fe and Cu contents and the hæmopoietic potency of these preps.

P. W. C.

Arteriosclerotic lesions in the human aorta. D. R. MEEKER and J. W. JOBLING (Arch. Path., 1934, 18, 252—257).—With increasing severity of lesions there is an increase in total fat and total cholesterol (I), the proportion of phospholipins being unchanged. In late lesions the ratio of free to ester-(I) also increases.

CH. ABS. (p)

Uric acid content of blood. G. SCHMIDT (Z. ges. exp. Med., 1934, 94, 76—83).—The blood-uric acid of healthy subjects averages 3.53 mg. per 100 ml. (standard error ± 0.161 mg.; range 2.085—4.967). Vals. are high in disorders of renal function, gout, and arteriosclerosis, especially coronary sclerosis, normal in pyogenic diseases of the urinary tract and rheumatic arthritis, and lowest in acromegaly and liver atrophy. The method of Morris and Macleod gives vals. about 30% > those given by Thannhauser's method.

NUTR. ABS. (m)

Nature of the filterable tumour-exciting agent in avian sarcomata. J. C. G. LEDINGHAM and W. E. GYE (Lancet, 1935, 228, 376—377).—The infective "agent" from potent filtrates of avian tumours can be separated by centrifuging at 15,000 r.p.m. The infective agents in deposits of filtrates exist as elementary bodies of much smaller size than those of vaccinia. Agglutinins for the corresponding

elementary bodies are present in the serum of tumour-bearing fowls.

L. S. T.

Ammonia production by sarcoma. Sparging effect of carbohydrate. W. T. SALTER and P. B. ROBB (Amer. J. Cancer, 1934, 22, 87—95).—Sugars most readily glycolysed by sarcoma-tissue (I) (glucose, mannose) are the most effective in decreasing NH_3 production (II) by (I), but have no effect on (II) by liver-tissue. Iodoacetates inhibit glycolysis and the NH_3 -sparing effect, but CN' has no influence on either process. Elimination of non-protein-N is not affected by the presence of the sugars.

CH. ABS. (p)

Utilisation of simple derivatives of sugars by mouse sarcoma. O. O. MEYER, C. McTIERNAN, and W. T. SALTER (Amer. J. Cancer, 1934, 22, 76—86).—Normal and tumour (I) tissues utilise the same sugars and derivatives. Actively growing (I) tissues produce slightly larger amounts of acid. *d*-Mannose and *d*-glucose are glycolysed to similar extents. Pentoses and hexose derivatives containing the hexylene oxide ring are not acted on. Triose derivatives, hexoses containing the butylene oxide ring, and saccharides containing glucose are less utilised than glucose (II). Acid production from (II) persists for some time, whereas that from 3-methylglucose ceases after 2—3 hr. Glycolysis is inhibited by iodoacetates, but is not affected by CN' .

CH. ABS. (p)

Peculiarity in carbohydrate metabolism of cancer. F. H. SCHARLES, D. BAKER, and W. T. SALTER (J. Clin. Invest., 1934, 13, 687).—Saline extract of mouse sarcoma (I) incubated with glycogen produces lactic acid (II) only when hexose di- or mono-phosphate is present. It is concluded that (I) extract is unable to synthesise a precursor of (II), possibly a hexose phosphate.

NUTR. ABS. (m)

Enzymes in uterine cancer. I. Amylase. K. NAKAHORI (Japan J. Obstet., 1934, 17, 215—223).—The amylase (I) contents of normal and cancerous tissues are recorded. Optimum p_H for (I) in all tissues was 6.8—7.4.

CH. ABS. (p)

Coagulant action of tissue extracts in cancerous guinea-pigs. P. MENDELÉEVE (Compt. rend., Soc. Biol., 1935, 118, 364—369).—Coagulation of guinea-pig plasma by extracts of the thymus, pancreas, lymphatic ganglia, adrenals, and liver of cancerous guinea-pigs is quicker than that by similar extracts from normal animals. On the other hand, rate of coagulation by extracts of spleen, bone and spinal marrow, and of rabbit plasma by extract of leucocytes (I) is decreased in cancerous animals, the decrease for (I) becoming greater if it is kept 48 hr. in the dark.

R. N. C.

Histochemistry of organs of tumour-bearing rats by the micro-incineration method. W. C. HUEPER (J. Lab. Clin. Med., 1934, 19, 1286—1293).—Ash of healthy human cells consists largely of Na and K. Disintegrated tumour cells contain higher proportions of Ca. Degeneration and necrosis of kidney and heart cells following excessive administration of parathormone and viosterol is due to toxic action of intracellular accumulations of Ca.

CH. ABS. (p)

Effect of methylene-blue and other oxidation-reduction indicators in experimental tumours. M. M. BROOKS (Univ. Calif. Pub. Zool., 1934, 39, 293—302).—Of a no. of oxidation-reduction indicators injected into tumours of rats and mice only methylene-blue produced regression. CH. ABS. (p)

Colchicine and tumour growth. E. C. AMOROSO (Nature, 1935, 135, 266—267).—Colchicine effects regression of tumours in mice, and has been effective in treating a spontaneous tumour in a dog.

L. S. T.

Reproduction and cancer. J. A. CAMPBELL (Nature, 1935, 135, 396).—Evidence that under normal conditions oestrin may be responsible for providing immunity from cancer is discussed.

L. S. T.

Alleviation of pain in cancer by snake venom. J. KÖRBLER (Klin. Woch., 1934, 13, 1185—1187; Chem. Zentr., 1934, ii, 2551).—Injection of poskok (*Vipera ammodytes*) venom alleviated pain considerably in 26 cases. The toxin is apparently superior to cobra toxin for this purpose.

R. N. C.

Morphological studies on lipin antagonism: experimental cerebrosidosis. P. KIMMELSTIEL and E. LAAS (Beitr. path. Anat., 1934, 93, 417—440).—Parenteral injection into mice of cerebroside (I), cholesterol, and lecithin separately or together showed that storage occurred, that the composition of the intracellular lipid complexes was correspondingly altered, and that the absorption of lipin by the cell was dependent on the colloidal nature and not on the chemical constitution of the injected material. The antagonistic action of these lipins is not very marked. A storage of (I) in rabbits was produced which closely resembled human Gaucher's disease.

NUTR. ABS. (b)

Cystinuria in two sisters. E. M. HICKMANS and W. C. SMALLWOOD (Biochem. J., 1935, 29, 357—370).—Two cases of cystinuria (I) in sisters and results of examination for (I) in other members of the family are recorded. The urine has an abnormally high pH , does not contain tyrosine, leucine, putrescine, or cadaverine, but contains a precursor of cystine (II) from which (II) is later liberated. Excretion of large amounts of (II) may lead to damaged kidney and albuminuria. Administration of (II) or of foodstuffs with a high (II) content by mouth did not lead to increased excretion of (II). A high animal protein diet increases (I) by stimulating tissue metabolism with liberation of more endogenous (II). P. W. C.

Diabetes mellitus and the pituitary gland. A. LALL and J. A. INNES (Lancet, 1935, 228, 318—

—In a case of severe diabetes in man, marked improvement in the diabetic condition took place with development of a pituitary lesion. The condition as clinically analogous to that of an experimental animal in which both pancreas and pituitary had destroyed.

L. S. T.

Effect of spleen extracts in diabetes. F. RATHERY, I. COSMULESCO, and C. E. GRIGNON (Presse Méd., 1934, 42, 953—955).—In man the results of injecting 2 ml. of extract indicate that the spleen

produces a hormone which augments the action of insulin.

NUTR. ABS. (m)

Neuropathy in diabetes mellitus. Lipin constituents of the nerves correlated with the clinical data. W. R. JORDAN, L. O. RANDALL, and W. R. BLOOR (Arch. Int. Med., 1935, 55, 26—41).—The femoral and tibial nerves of diabetics contain less phospholipin, cholesterol, and cerebroside than do corresponding nerves from non-diabetics. The lipin abnormality appears before clinical evidence of neuropathy.

W. O. K.

Changes in intermediary protein metabolism in the liver in experimental diabetes. H. ELIAS and B. ZEMPLÉN (Z. ges. exp. Med., 1934, 94, 199—216).—The concns. of various N compounds were determined in arterial blood (I) and in (I) of portal and hepatic veins and the vena cava in depancreatized dogs. Increased protein destruction in the liver was demonstrated by (1) increase of polypeptide in the liver, although there was little difference in its concn. in afferent and efferent (I), and (2) increase in the urea and residual N in the liver and efferent (I). The absence of any increase of NH_2 -acid is due to efficient deamination and urea synthesis. The rise of NH_2 -acid in the systemic (I) is due to increased protein breakdown in other organs. Similar but less marked changes were observed after partial pancreatectomy. After insulin treatment the vals. were practically normal.

NUTR. ABS. (b)

Changes in protein-bound sugar in diabetics following simultaneous or separate administration of glucose and insulin. F. RATHERY and I. COSMULESCO (J. Physiol. Path. gen., 1934, 32, 425—431).—Whilst the free sugar of the blood-plasma of the diabetic varies markedly with ingestion of glucose and injection of insulin, the sugar combined with protein (measured after hydrolysis with mineral acid) exhibits no predictable change.

NUTR. ABS. (m)

Excretion of creatinine and glucose in diabetics. P. GOVAERTS and P. CAMBIER (Acta Med. Scand., 1934, 83, 317—327).—From measurements of glucose (I), creatinine (II), and urea (III) of the blood and urine of a fasting diabetic, before and after the ingestion of 2 g. of (II), it is concluded that with const. blood-sugar the urinary elimination of (I) runs parallel with the excretion of (II) and is independent of the intensity of diuresis and excretion of (III). This observation is in keeping with the view that whilst in the normal subject (I) and (II) pass through the glomerulus [(I) being reabsorbed and (II) excreted], in the diabetic subject the reabsorption of (I) still proceeds but is unable to cope with the increased concn. of (I) in the glomerular filtrate.

NUTR. ABS. (b)

Hypoglycæmic phase of the glucose tolerance curve. S. SOSKIN and M. D. ALLWEISS (Amer. J. Physiol., 1934, 110, 4—7).—Continuous injection of glucose solution, both in normal dogs and in diabetic dogs with blood-sugar (I) kept const. by insulin and glucose, produces a rise in (I) followed by a fall, which begins before the cessation (II) of glucose injection. After (II), (I) continues to fall for some time before returning to normal.

R. N. C.

Diabetic hyperpyrexia. H. E. HEMWICH, J. F. FAZIKAS, L. H. NAHUM, D. DU BOIS, and A. GILMAN (Amer. J. Physiol., 1934, 110, 19—27).—In diabetic hyperpyrexia (I) in dogs with polyuria as basis, rectal temp. (II), d and osmotic pressure of serum, O_2 capacity and lactic acid content of the blood are directly, and p_H and alkaline reserve inversely, \propto the blood concn. If insulin and glucose are not given, (II), d of serum, and blood-lactic acid all behave similarly, whilst blood-sugar $\propto H_2O$ ingestion. Serum-base, -Cl, and -lactic acid all increase, and $NaHCO_3$ falls, with serum concn. HSO_3^- -binding substances increase in fever, falling again when H_2O ingestion dispels it. R. N. C.

Variations in potassium content of the blood in diabetes mellitus. F. RATHERY and J. BERTOLIATTI (Compt. rend. Soc. Biol., 1934, 116, 1346—1349).—In advanced diabetes blood-K increases (up to 35%). Insulin causes a partial return to normal. CH. ABS. (p)

Blueberry in diabetes. N. K. EDGARS (Drug and Cosmetic Ind., 1934, 35, 479—480).—*Neomyrtillin* (I), $C_{24}H_{36}O_{18}$, a methoxydigalloylglucose, occurring to the extent of 2.05% in air-dried blueberry leaves, reduced the blood-sugar level of rabbits having artificial hyperglycæmia from 210 to 110 mg. per 100 c.c. in 30 min. The reactions of (I) are given and the analyses of the fruit and leaves. (I) forms insol. compounds with most alkaloids. E. H. S.

Protective action of sodium thiocyanate against dysentery toxin (Shiga) in dogs and cats. P. E. REID, M. X. ANDERSON, H. I. STUBBLEFIELD and A. C. IVY (J. Infect. Dis., 1934, 55, 112—122).—Intravenous injection of $NaSCN$ affords protection in some dogs but not in rabbits. CH. ABS. (p)

Effects of infectious ectromelia, starvation, exposure to heat, and cholesterol feeding on the cortical lipin of the adrenals in mice. R. WHITEHEAD (Brit. J. Exp. Path., 1934, 15, 279—286).—A decrease of lipin occurs in the adrenal cortex (I) of mice with infectious ectromelia and after starvation for 2 days at 13° but not at 37° . (I) of mice fed at 35 — 38° for 3 days and of mice receiving powdered cholesterol for periods up to 165 days contains normal amounts of lipin. NUTR. ABS. (m)

Creatine content of the myocardium of normal and abnormal human hearts. D. W. COWAN (Amer. Heart J., 1934, 9, 378—385).—The average creatine content (C) of the left ventricular myocardium of normal hearts was 194 mg. per 100 g. of tissue. Vals. were lower for decompensated and still lower for abnormal but not decompensated hearts. Septicæmia did not affect C. CH. ABS. (p)

Therapeutic effect of total ablation of normal thyroid on congestive heart failure and angina pectoris. IX. **Post-operative parathyroid function.** Serum-calcium and -phosphorus. D. R. GILLIGAN, D. D. BERLIN, M. C. VOLK, B. STERN, and H. L. BLUMGART (J. Clin. Invest., 1934, 13, 789—806).—Of 73 thyroidectomised patients, only 12 showed parathyroid deficiency; in 10 of these the symptoms rapidly disappeared. Post-operative

tetany was more frequent in the group with slightly subnormal serum-Ca prior to operation. The symptoms are attributed to injury to, rather than to removal of, parathyroid glands. The serum-Ca is not so markedly reduced nor the serum-P so much raised as in chronic hypoparathyroidism of either idiopathic or post-operative origin.

NUTR. ABS. (b)
Blood-lactic acid in patients with hepatic diseases. Basal value. Induced variations. F. KAYSER and N. MASIUS (Compt. rend. Soc. Biol., 1935, 118, 207—210).—Ingestion of Na lactate by normal subjects (I) causes a rise of blood-lactic acid (II) to a max. 40 min. after ingestion, followed by a fall to approx. zero in 2 hr. In cirrhotics (III), (II) rises steadily for 2 hr. after ingestion, and a similar curve is obtained in catarrhal icterus. Intravenous injection in both (I) and (III) produces a rapid rise of (II) to a max. in 10 min., which is higher in (III) than in (I), followed by a steady fall at approx. the same rate in each case. (II) is $>$ normal only in serious cases of hepatic disease. R. N. C.

Blood-chloride after administration of sodium chloride in subjects with healthy or diseased liver. P. VEGH (Orvosi Hetilap, 1934, 78, 874—876).—In liver diseases the rise in blood-Cl following injection into the duodenum of 15 g. of NaCl in 200 ml. of H_2O is less marked than in cases with healthy liver. NUTR. ABS. (m)

Use of galactose in the differential diagnosis of jaundice. K. A. OWEN (J. Lab. Clin. Med., 1934, 19, 1311—1319).—The level of urinary galactose following ingestion of 40-g. doses serves to indicate the nature of biliary affections. CH. ABS. (p)

Phosphatase in obstructive jaundice. A. R. ARMSTRONG, E. J. KING, and R. I. HARRIS (Canad. Med. Assoc. J., 1934, 31, 14—20).—Obstruction of the bile duct results in large increases of serum-phosphatase, vals. for dogs being much $>$ in man. Hæmolytic jaundice causes only slight changes. CH. ABS. (p)

Porphyrins appearing in chloroma and myeloid leucæmia. J. THOMAS and E. J. BIGWOOD (Compt. rend. Soc. Biol., 1935, 118, 381—383).—An Et_2O -AcOH aq. extract of a chloromatous tumour contained a porphyrin fraction showing all the properties of protoporphyrin, which was also isolated and identified from an extract of the green aortic and mesenteric ganglia in a case of myeloid leucæmia. R. N. C.

Field and laboratory tests for detection of mastitis. J. M. ROSELL (Sci. Agric., 1934, 169—175).—Chemical and bacteriological tests are examined. A. G. P.

Therapeutic value of bismuth-violet. G. I. KITCHEN and F. E. KITCHEN (North Amer. Veterinarian, 1934, 15, 12—16).—Bi-violet is lethal to Gram-positive organisms and is effective in treatment of metritis and mastitis in cows. CH. ABS. (p)

Chlorides in meningitis. L. O. FINKELSTEIN and F. S. MERSON (Rev. franç. Pédiat., 1934, 10, 204—217).—A study of the Cl' content of blood, cerebrospinal fluid, tissue-lymph, urine, and gastric

ence indicates a demineralisation during meningitis. The diet must counteract this tendency.

NUTR. ABS. (b)

Actual reaction of cerebrospinal fluid in meningeal affections. CERUTI and MAESTRI (Boll. oc. ital. Biol. sperim., 1934, 9, 896—899).—Cerebrospinal fluid in the different types of meningitis and in uramic coma shows a fall of p_H , which oscillates between well-defined limits. R. N. C.

Blood-manganese in some nerve diseases. L. URECHIA, G. PAMFIL, and RETZEANU (Paris éd., 1934, 24, 330—331).—Serum-Mn varies from 0.01—0.03 mg. per 100 ml. of serum, and shows no relation in amount to the nature of the disease. There is less Mn in red cells than in serum.

NUTR. ABS. (m)

Diets low in calories containing varying amounts of protein. Their effect on loss in weight and on the metabolic rate in obese patients. R. W. KEETON and D. D. BONE (Arch. t. Med., 1935, 55, 262—270).—Sp. dynamic action of protein is lowered in the obese. H. G. R.

Blood-fat tolerance tests in malnutrition and obesity. H. BLOTNER (Arch. Int. Med., 1935, 55, 21—130).—In fasting thin persons the plasma-cholesterol following administration of 500 c.c. of 10% cream shows the normal small rise, but after a period of insulin therapy much higher and prolonged post-absorptive cholesterolaemia (I) is produced. Obese persons and patients suffering from diabetes insipidus showed marked hypercholesterolaemia following administration of cream but (I) was prevented by administration of pituitary extract. W. O. K.

Blood-fat and blood-fat reaction in obesity. V. RAAB (Z. ges. exp. Med., 1934, 94, 284—292).—Obese do not differ from normal subjects as regards fasting blood-fat or the blood-fat curve after ingestion of oil, but lipotrin (I) does not inhibit the lipaemia in the obese. This may be due to an org. lesion or to a constitutional reduction (II) of the sensitivity of the fat centre to (I). The failure of (I) to produce hepatic absorption of fat leads to excess deposition of unsplit fat in the peripheral tissues. The failure of (I) to reduce obesity in many cases may be due to (II), and perhaps to its lack of action on tissue-fat.

NUTR. ABS. (m)

Comparative volumetric and gravimetric determinations of blood-fat. M. T. SCHNORBUSCH (Z. ges. exp. Med., 1934, 94, 63—75).—Determination of serum-fat (I) of healthy subjects by the lipocrit method (II) gives results about 12% < those given by the gravimetric method with larger amounts of serum. In patients (III) with diabetes or psoriasis the results of (II) are 23% lower, probably on account of the nature of (I). In (III) with disturbance of lipin metabolism (hepatosplenomegaly and xanthomatosis) the results of (II) are higher by about 10%. Small amounts of serum (0.15 ml.) require for (II) enable the hourly changes in serum-fat after ingestion of fat to be followed; an increase is always observed after administration of 100 g. of olive oil and 5 g. of cholesterol.

NUTR. ABS. (m)

Calcium and phosphorus metabolism in osteomalacia. II. Response to vitamin-D of patients with osteomalacia. S. H. LIU, R. R. HANNON, H. I. CHU, K. C. CHEN, S. K. CHOU, and S. H. WANG (Chinese Med. J., 1935, 49, 1—21).—Osteomalacia occurs in two types characterised by low serum-Ca (I) and low serum-inorg. P (II), decalcification (III) being most pronounced in the latter. Vitamin-D (IV) therapy is effective in both cases, improvement being most marked where (III) is extensive. Under the action of (IV), (I) returns to normal more rapidly than (II). H. G. R.

Blood-amylase in experimental pancreatitis. A. C. GLASEN, P. N. JOHNSTONE, and T. G. ORR (Surgery, Gynecol., Obstet., 1934, 59, 756—761).—Injury to the pancreas is followed by a temporary increase in blood-amylase which \propto the severity of the injury. CH. ABS. (p)

Colloid-osmotic pressure of blood in normal and pathological conditions. X. Changes in osmotic pressure of blood and pleuritic exudates. XI. Effect of removal of fluid on protein concentration and colloid-osmotic pressure in cases of pleurisy. XII. Changes during muscular exercise. K. NISHIYAMA (Tohoku J. Exp. Med., 1934, 22, 505—525, 526—540, 541—555).—X. Simultaneous variations in colloid-osmotic pressure (I) and protein concn. (II) are recorded.

XI. Removal of fluid and replacement with NaCl solution are followed in 5—7 days by return of (II) to the original val.

XII. Exercise causes parallel increases in (I) and (II), the pressure per unit of protein remaining unchanged. With heavy exercise all three factors increase. Haemoglobin changes are relatively small.

CH. ABS. (p)

State of cholesterol and the nature of the cholesterol-protein complex in pathological body-fluids. M. BRUGER (J. Biol. Chem., 1935, 108, 463—470).—Since cholesterol (I) and, to a smaller extent, (I) esters in body-fluids are selectively adsorbed by kieselguhr, the combination between (I) and protein, if such exists, must be a feeble one.

A. E. O.

Serum-cholesterol during pregnancy. G. TEILUM (Hospitalstidende, 1934, 77, 140—153).—Blood-cholesterol (I) increases during pregnancy from the 3rd or 4th month to a max. at term, when it is >50% > normal. Rapid return to normal follows delivery. In albuminuria (with and without eclampsia) the cycle of changes is as in normal pregnancy, but in spontaneous abortion (I) does not increase.

NUTR. ABS. (m)

Lipin composition of white blood-cells in women during pregnancy, lactation, and the puerperium. E. M. BOYD (Surgery, Gynecol., Obstet., 1934, 59, 744—751).—Age and parity did not affect the lipin levels of leucocytes. Before parturition vals. varied widely, although cholesterol and neutral fat levels were < those in non-pregnant women.

CH. ABS. (p)

Creatine metabolism and ovarian function. H. THEISS (Arch. Gynakol., 1934, 158, 164—172).—Since ingestion of creatine (I) by healthy pubescent

females leads to creatinuria during the menstrual and intermenstrual periods (I) utilisation is probably independent of ovarian function. In pregnancy utilisation of (I) is frequently reduced.

NUTR. ABS. (m)

Glutathione and gestation. S. L. SALA (Rev. sudamer. Endocrinol., 1934, 17, 634—650).—Glutathione (I) decreases during gestation and increases slowly at the end of the puerperium. Blood of the umbilical cord has more reduced (I) than maternal blood. Vals. are still higher in the foetus, oxidised (I) remaining normal.

CH. ABS. (p)

Blood-proteins in pregnancy. G. PICINELLI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1060—1062).—Blood-fibrinogen in pregnancy is increased, especially during parturition and in albuminurics. Total globulins are generally increased, but total protein is generally < normal; thus the albumin-globulin ratio is decreased. Euglobulin is usually increased.

R. N. C.

Calcium in pregnancy. E. A. MARSHALL and E. GOODSIT (J. Amer. Inst. Homeopath., 1934, 27, 604—608).—The literature is reviewed. To prevent guanidino (I) poisoning in rabbits, massive doses of Ca salts must be given prior to (I).

CH. ABS. (p)

Carbohydrate metabolism. II. Carbohydrate metabolism in various obstetrical and gynaecological conditions, including diabetes with pregnancy. E. W. WINTER (Arch. Gynakol., 1934, 157, 509—520).—Certain disturbances of glucose tolerance occur in carcinoma, endometritis, and pregnancy, especially during labour; deviations from normal are more striking in hyperemesis and diabetes. Normal results are obtained before, during, and after menstruation, in menstrual disorders, eclampsia, and other conditions.

NUTR. ABS. (m)

Effects of restricting or suppressing renal function. V. SCAFFIDI. VI. Water content of skin and blood. P. GILIBERTI. VII. Changes in mineral constituents of blood (sodium, potassium, chlorine, phosphorus, magnesium, calcium). E. MORACCI. VIII. Blood-urea and -ammonia. P. GILIBERTI (Riv. Patol. sperim., 1934, 13, 109—114, 115—133, 135—139).—VI. After bilateral nephrectomy in dogs and rabbits the H₂O content of the skin and blood is unchanged. The oedema of nephritis is therefore independent of renal function, and its development is probably linked with the underlying cause of the renal lesion.

VII. There is a rise in blood-K, -P, and -Mg, a fall in Cl, and variations in either direction in -Na and -Ca. Normal [H⁺] and total ion concn. are always maintained.

VIII. The blood-urea rises, but the -NH₃ remains unchanged.

NUTR. ABS. (m)

Significance of the phenolsulphonephthalein test of renal function. E. M. MACKAY and D. A. RYTAND (Arch. Int. Med., 1935, 55, 131—140).—If the Addis ratio is taken as measuring the amount of functioning renal tissue, the excretion of phenolsulphonephthalein in 2 hr. is a measure of renal function.

O. K.

Chloride and urea excretion as a measure of the functional activity of healthy and diseased kidneys. F. H. SMIRK (Clin. Sci., 1933, 1, 131—158).—The composition of urine in cases of advanced chronic nephritis is examined.

CH. ABS. (p)

Glycogen of the organs in Bright's disease after repeated injections of hypertonic sugar solutions. E. MARTIN and F. SOICLOUNOFF (Compt. rend. Soc. Biol., 1935, 118, 751).—Glycogen is increased in all organs.

R. N. C.

Attempts to produce uric acid calculi in albino rats. S. RANGANATHAN (Indian J. Med. Res., 1934, 22, 71—75).—The urinary excretion (I) of uric acid (II), allantoin, and total N in young rats of both sexes is not appreciably affected by ingestion of (II) or Na₂ urate (up to 200 mg. daily) or of spleen (5—10 g. of fresh material daily). (I) is increased by parenteral administration of (II) in isotonic solution, although the increase is not \propto the amount of (II) injected. Experimental production of (II) calculi in rats is not possible.

NUTR. ABS. (m)

Acid metabolism in rheumatic children. W. W. PAYNE (Arch. Dis. Childhood, 1934, 9, 259—266).—Urinary excretion of acid in rheumatic is > in normal or asthmatic children. The excess is partly due to org. acids. The acid : base ratio is unchanged.

CH. ABS. (p)

Blood-iodine in rickets. D. TOEPFER (Z. Kinderheilk., 1934, 56, 405—407).—Nitschke's view that blood-I (I) is low in rickets is not confirmed. The distribution of fasting (I) vals. is normal before and after treatment.

NUTR. ABS. (m)

Blood-iodine of rachitic infants. H. FASOLD (Z. Kinderheilk., 1934, 56, 408—409).—Blood-I determined by Pfeiffer's method in rachitic infants, before treatment of any kind, was within the normal range. Nitschke's idea that the thyroid is involved is therefore not supported.

NUTR. ABS. (b)

Incurable rickets. II. Role of the "local factor" and of viosterol in the pathogenesis of rickets due to beryllium. A. E. SOBEL, A. R. GOLDFARB, and B. KRAMER (J. Biol. Chem., 1935, 108, 395—401).—The calcifying power of the bones of rats with Be rickets (I) is low. Administration of calciferol does not prevent (I) in rats receiving Be but there is a rise in serum-Ca \times P.

H. G. R.

Comparative sensitiveness of schizophrenic and normal subjects to glycerol extract of adrenal cortex. H. FREEMAN and R. G. HOSKINS (Endocrinol., 1934, 18, 576—582).—In schizophrenics there is a marked increase in the % of pressor reactions produced by cortex extract, whilst the mean systolic and diastolic pressures show significant rises compared with those of normal subjects.

R. N. C.

Biochemistry of blood in scurvy. N. C. MATCHEV (Questions of Nutrition, U.S.S.R., No. 4, 74—78).—The alkali reserve of the blood in scurvy (I) is apparently undisturbed but the blood sugar and -cholesterol (II) are reduced, dependent on the degree of anaemia which accompanies (I). During recovery the (II) level increases parallel with that of the erythrocytes.

NUTR. ABS. (m)

Biochemistry of silicosis. F. J. NIEUWENHUYZEN (Acta Brev. Neerl. Physiol., 1933, 3, 108—109; Chem. Zentr., 1934, ii, 2566).—SiC and Fe₂O₃ do not induce silicosis. SiO₂ is somewhat sol., and the resulting colloidal silicic acid ppts. protoplasmic protein.
H. J. E.

Metabolism of blood-phosphorus during some infectious diseases of childhood (diphtheria, tuberculous meningitis, and measles). E. ESNE, P. ZIZINE, and S. B. BRISKAS (Compt. rend. Acad. Biol., 1934, 116, 1309—1311).—Decreased inorg. P of blood occurs during the diseases. Total and inorg. P vary irregularly.
CH. ABS. (p)

Blood-glutathione in tuberculosis. R. N. DOMIS and F. BOGEN (Amer. Rev. Tuberc., 1934, 30, 45—509).—The increased total and reduced glutathione contents, and the lowered difference between these values, in tuberculosis indicate that the latter involves an actual condition of suboxidation.
CH. ABS. (p)

Vigantol in tuberculosis therapy. R. HUSSA (Wien. med. Woch., 1934, 84, 973; Chem. Zentr., 1934, ii, 2547).—The favourable action of vigantol is shown in the rapid increase in the blood-Ca and -P.
A. G. P.

Iodine tolerance test for thyroid insufficiency. W. ELMER (Endocrinol., 1934, 18, 487—496).—The I excreted following injection of KI serves as a test of thyroid activity.
CH. ABS. (p)

Determination of metabolism by the interometer. H. WOLLSCHITT, W. BOTHE, H. RUSKA, and E. G. SCHENCK (Arch. exp. Path. Pharm., 1935, 7, 635—654).—The application of the Zeiss interometer to gas analysis for metabolic determinations is described and appropriate tables are given.
F. O. H.

Chemical nature of the amphibian organiser. Use of the kephalin fraction of mammalian brain as an inducing agent. L. G. BARTH (Biol. Bull., 1934, 67, 244—249).—The organiser may be identical with kephalin or an impurity in it.
CH. ABS. (p)

Catalase in embryonic development. I. Fertilisation and activity of catalase in the eggs of *Salmo irideus*, *Esox lucius*, and *Barbus*. U. SAMMARTINO (Arch. Farm. sperim., 1935, 59, 49—85).—The catalase activity (I) of the mature eggs of *Salmo irideus* (II), *Esox lucius* (III), and *Barbus plebeius* (IV) is high in the egg recently released from the oviduct, but is lowered by depositing the eggs in tap-H₂O, the fall being > 50% for (IV). (I) of eggs thus treated falls slightly in the first 4—6 h afterwards rising slowly. Fertilisation (V) does not affect this behaviour, but the (I) ratio between fertilised and non-fertilised eggs varies with the species. In (II) it is > 100% immediately after (V), afterwards tending to fall to 100%; in (III) it is < 100% after (V), afterwards tending towards, but not reaching, 100%; whilst in (IV) it falls slowly from > 100% to < 100%.
R. N. C.

Behaviour of peroxidases during embryonic development. A. SPIRITO (Boll. Soc. ital. Biol., 1934, 901—903).—Peroxidase (I) is dis-

tributed uniformly in the eggs of cyclostomes, but is found only at the animal pole in those of fish. In the developing embryos, (I) disappears after the appearance of the circulation. Traces of (I) are found at the animal pole in amphibian eggs. In the later stages of development (I) reappears in the yolk-sacs of fish-embryos, and on the abdominal side of the amphibian. In the frog this stage occurs before the appearance of haemoglobin, which is therefore not responsible for the (I) activity.
R. N. C.

Distance action of enzymic oxidation of quinol on the development of the eggs of the sea-urchin. J. MAGROU (Compt. rend. Soc. Biol., 1935, 118, 763—765).—Eggs of *Paracentrotus lividus* exposed in quartz vessels to oxidation of quinol by peroxidase show abnormal development.
R. N. C.

Changes in the concentration of reducing substances during the metamorphosis of *Galleria mellonella* (Bee-moth). F. CRESCITELLI and I. R. TAYLOR (J. Biol. Chem., 1935, 108, 349—353).—The concn. of reducing substances increases during the prepupal and pupal stages. There is a decrease at the commencement of the pupal life and just prior to emergence.
H. G. R.

Hibernation. I. Reduced glutathione contents of the various tissues of *Rana nigromaculata* throughout all seasons. II. Metabolism in the muscle of *R. nigromaculata*. T. YAZAWA (Sei-i-Kwai Med. J., 1934, 53, 134—156).—I. Reduced glutathione (I) contents of nearly all organs were in summer > in winter. Only the ovary and skin had more (I) during hibernation (II). Organs of male frogs contained more (I) than those of females, except kidneys and skin.

II. Frog muscle had higher fat (III), acid, and glycogen (IV) contents during (II), max. vals. occurring at the beginning of (II). In the breeding season metabolism increased rapidly, and (III) and (IV) decreased. Cholesterol and undetermined unsaponifiable matter showed no seasonal variation. Creatine and creatinine increased gradually during the active season.
CH. ABS. (p)

Mechanism of respiration. A. SZENT-GYORGYI (Nature, 1935, 135, 305).—In the main process of respiration in the breast muscle of the pigeon, no substances other than succinic (I), fumaric (II), and malic acids (III), are oxidised directly by the Warburg-Keilin "Atmungsferment-Cytochrom" system. (I) and (III) are activated by the corresponding sp. dehydrogenase. (I) and (III) are reversibly oxidised to (II) and hydroxyfumaric acids, respectively. Foodstuffs are oxidised by dismutating them with oxidation products of (I), and these products become reduced again and thus act as catalytic H carriers. The oxidation system is an enzyme complex acting specifically on (I) and its oxidation products.
L. S. T.

Respiration of *Ascaris suilla*. F. KRUGER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 101—104).—The R.Q. of the parasites was measured. It fell from 4.0 gradually to 1.1—0.7. The fall is faster for small worms than for large; it is probably due to starvation. The abnormal R.Q. found is due

to a balance between anaerobic processes leading to fatty acid production and ordinary oxidative processes. Hence R.Q. studies are fallacious. The end-product is probably hexoic acid, not valeric acid as previously stated.

H. T.

Oxygen consumption of rabbit bone-marrow in relation to its morphology. C. O. WARREN, jun. (Amer. J. Physiol., 1934, 110, 61—73).—O₂ consumption (I) of normal marrow is variable, due to differences in histological composition. The principal variable affecting (I) is the myeloid-erythroid ratio, which increases with (I). The mature normoblast has a similar (I) to the myeloid; in the immature erythroid it is relatively high. Fat content (II) of the marrow is not an index of metabolic activity except in extreme cases where high (II) and low (I) are associated and *vice versa*.

R. N. C.

Gaseous interchanges through the visceral pleura of the cat. M. KREMER, A. T. WILSON, and S. WRIGHT (J. Physiol., 1934, 82, 414—422).—CO₂ passes from the blood through the visceral pleura about 1500 times as slowly as into the normally ventilated alveoli; a pressure gradient of 40—50 mm. between the blood and the outside air is necessary to eliminate all the CO₂. O₂ passes inwards even more slowly, a pressure gradient of several hundred mm. only slightly influencing the % O₂ saturation of the blood.

R. N. C.

Physiological basis of the sensation of cold. I. Influence of the initial skin temperature on the excitability of the cold end-organs. J. M. O'CONNOR. II. Analogy between human cold sensations and shivering in the rabbit. J. M. O'CONNOR, M. MORIARTY, and O. FITZGERALD. III. Influence of the body temperature on the resting oxygen consumption. A metabolic analogy to cold sensations. J. M. O'CONNOR (Proc. Roy. Irish Acad., 1935, 42, B, 327—344, 345—350, 351—357).—III. As temp. falls the rise at 33° in O₂ consumption of the rabbit (I) with no shivering resembles a phase of the excitability of human and (I) skin at 29°. The activity of the skin of (I) corresponds with the basal metabolism.

H. G. R.

Changes in chemical composition of horse's blood after a race. S. I. BANAITIS and V. V. OPPEL (J. Physiol., U.S.S.R., 1934, 17, 112—123).—Sugar, lactic acid, and inorg. P (I) reached max. 10 min. after the race. After 90 min. (I) fell to < the initial val.

CH. ABS. (p)

Alkalinisation of the muscle during contraction. R. MARGARIA and C. PULCHER (Boll. Soc. ital. Biol. sperim., 1934, 9, 879—880).—The sartorius of a frog that has previously been injected with a vital-stain indicator, mounted in air containing sufficient CO₂ to give an acid reaction, shows colour changes towards the alkaline side when stimulated to contract.

R. N. C.

Apparent change of p_H on stretching a muscle. R. MARGARIA (J. Physiol., 1934, 82, 496—497).—The sartorius of a frog injected before excision with an indicator and mounted in air containing sufficient CO₂ to give an acid reaction shows on stretching a reversible colour change in the alkaline

direction to about the same extent as when stimulated to contract. This may be due to an alteration in the acid or alkaline dissociation consts. of protein chains.

R. N. C.

Effect of inspiration of oxygen and of air rich in carbon dioxide, or poor in oxygen, on energy exchange and intermediate carbohydrate metabolism. II. Effect of physical work on gas metabolism. III. Effect of fatigue during muscular exercise. K. KODERA (Tôhoku J. Exp. Med., 1934, 23, 298—320, 321—335).—II. Intermittent stimulation of the ischiadic nerve of rabbits results, in normal air, in a temporary increase in blood-lactic acid (I). The O₂ consumption (II) falls abruptly on cessation, and, after a secondary rise, returns to normal. The CO₂ output (III) varies correspondingly. Inspiration of CO₂-rich air (IV) increases the respiratory vol. (V) during work (VI) and rest (VII). In periods of (VI), (II), O₂ deficit (VIII), O₂ requirement (IX) and (III) all increase. The R.Q. increases considerably even after cessation. Inspiration of O₂-poor air (X) during (VI) causes increased (I) and (II) while (VIII) and (IX) become > when (IV) is inspired. (V) decreases during (VII) and is > normal during (VI). The (III), initially high, increases slightly during (VI). The R.Q. declines during (VI) and in subsequent (VII) period attains subnormal vals.

III. During fatigue (XI), (I) increases. Inspiration of pure O₂ has little effect on the development of (XI). Inspiration of (IV) shortens the period (XII) over which muscles continue to contract and (I) remains practically const. Inspiration of (X) shortens (XII) and increases (I) at the height of (XI).

CH. ABS. (p)

Effect of breathing oxygen or carbon dioxide-rich or oxygen-poor air on energy and intermediary carbohydrate metabolism. V. Effect on lactic acid synthesis of nephrectomised animals. K. KODERA (Tôhoku J. Exp. Med., 1934, 24, 21—36).—In nephrectomised rabbits after lactate administration under various respiratory conditions (inhalation of O₂, CO₂-rich air, or O₂-poor air), the removal of the blood-lactic acid is retarded and the return to normal of the blood-CO₂ and the O₂ consumption delayed. The kidney furthers lactic acid removal directly by excretion and indirectly by its regulatory action on the acid-base equilibrium, acidosis or alkalosis hindering lactic acid resynthesis.

NUTR. ABS. (b)

Carbohydrate and respiratory metabolism in muscle during alkalosis due to hyperventilation. K. KODERA and H. SUGIMOTO (Tôhoku J. Exp. Med., 1934, 24, 37—50).—Hyperventilation alkalosis increases the production of lactic acid from glucose in the intact dog gastrocnemius. The O₂ consumption and the CO₂ formation are increased. Thus a condition arises which tends to bring back to normal the disturbed acid-base equilibrium.

NUTR. ABS. (b)

Carbohydrate and respiratory metabolism muscle of animals of low glycogen content. Fasting animals. II. Phloridzinised fastn. dogs. III. Pancreatctomised animals. SUGIMOTO (Tôhoku J. Exp. Med., 1934, 24, 118—13,

137—148, 149—166).—I. In dogs fasted 5—14 days (H_2O -fasted) the resultant acidosis (I) causes the resting lactic acid (II) val. of the gastrocnemius muscle to be < normal. After lactate administration the removal of (II), owing to liver disturbance, is considerably retarded. The sugar and O_2 consumption behave in accordance with these results.

II. In fasting phloridzinised dogs the resting (II) of the muscle is still lower, as the acidosis is greater, and the (II) resynthesis is greatly disturbed, due to the action of phloridzin (III) on the liver.

III. In pancreatectomised dogs the resting blood-(II) is abnormally high, due to insulin deprivation (IV). The resting muscle-(II) is very low, and (II) resynthesis is even more disturbed than after (III), (I) and (IV) producing a cumulative effect.

NUTR. ABS. (m)

Glycogen content of the heart. G. EVANS (J. Physiol., 1934, 82, 468—479).—Cardiac glycogen (I) in fed rats is < in fasting rats; there is no decrease in (I) between the 24th and 48th hr. of fasting. (I) is not increased by feeding with glucose; simultaneous injection of insulin increases (I) except when hypoglycaemia occurs, when it is lowered. Adrenaline, exercise, and p_H changes in the blood of the intact fasting animal do not materially change (I). (I) falls rapidly in anoxaemia, but quickly recovers on relief.

R. N. C.

Phosphorus compounds in the perfused heart of the dog. H. POLLACK, E. FLOCK, H. E. ESSEX, and J. L. BOLLMAN (Amer. J. Physiol., 1934, 110, 9—101).—The creatine phosphate (I) of perfused hearts remains normal even under adverse conditions when inorg. PO_4''' and P_2O_7''' and creatine fall. (I) increases to 2—3 times the normal val. in some cases, especially if glucose is added to the perfusing liquid. Addition of insulin or PO_4''' apparently has no additional effect. Addition of glucose lowers the hexose monophosphate of the heart.

R. N. C.

Changes in the phosphorus compounds in the perfused hind limb of the dog. H. POLLACK, E. FLOCK, P. MASON, H. E. ESSEX, and J. L. BOLLMAN (Amer. J. Physiol., 1934, 110, 102—104).—Perfusion of the hind limb produces an increase in creatine phosphate (I), regardless of the glycogen content. Addition of PO_4''' does not affect the inorg. PO_4''' of the muscle. Addition of glucose or insulin does not

Cyanosis in the limb causes decreases in (I) and nucleotide pyrophosphate, and a rise in exose monophosphate.

R. N. C.

Compounds of phosphorus in the heart and striated muscles of the dog: methods of determination and normal values. H. POLLACK, E.

J. L. BOLLMAN (Amer. J. Physiol., 1934, 110, 105—110).

— $CCl_3 \cdot CO_2H$ extracts of cardiac (I) and (II) tissue are separated by $Ba(OH)_2$ pptn. into sol. fractions containing creatine phosphate (II), a hexose phosphate, and insol. fractions containing inorg. and org. PO_4''' , as Ba salts. (III) of the (II) val. The org. P pptd. by $Ba(OH)_2$ is largely adenylyl pyrophosphate, the remainder probably being other nucleotides. The insol. fractions in (I) and (II) both give positive reactions for uracil and cytosine. Total P is about

the same in (I) and (II), but in (II) a larger proportion is acid-sol.

R. N. C.

Serum-phosphate changes induced by injection of glucose into dogs under various conditions. H. POLLACK, R. F. MILLET, H. E. ESSEX, F. C. MANN, and J. L. BOLLMAN (Amer. J. Physiol., 1934, 110, 117—122).—Continuous injection of glucose causes a fall in serum- PO_4''' , which returns to normal after a definite period in spite of the continued injection of glucose. Hepatectomy and adrenalectomy do not produce any appreciable alteration. In depancreatized dogs the fall does not occur unless insulin is also injected. In the Markowitz-Essex visceral organism there is no fall of serum- PO_4''' . Perfusion of a dog's hind limb in a heart-lung prep. results in a rapid fall of sugar and PO_4''' in the perfusing blood. The PO_4''' is presumably deposited in the muscle.

R. N. C.

Metabolism of natural l-phosphoglyceric acid by animal tissues. H. K. BARRENSCHEEN and H. BENESCHOVSKY (Biochem. Z., 1935, 276, 147—167).—The formation of $AcCO_2H$ (I) from l-phosphoglyceric acid (II) does not occur with intact blood but does occur with haemolysates prepared by freezing of whole blood or red cells, the difference in behaviour being due to the non-permeability of red cells by (II). Natural (II) is converted into (I) by muscle pulp and extract more quickly than is the racemic prep. Liver pulp does but kidney pulp does not effect formation of (I). The optimum p_H for the conversion with blood or muscle is 6.68 and the amount of (I) formed usually exceeds the amount of PO_4''' liberated. Addition of (II) does not lead to the formation of lactic acid. $CH_2Br \cdot CO_2H$ and CN' inhibit neither the dephosphorylation of (II) nor the formation of (I), but F' inhibits both completely. In haemolysates and muscle extracts inactivated by ageing, dephosphorylation does but formation of (I) does not occur. The power of these extracts to give (I) is, however, restored by addition of adenosinetriphosphoric and muscle-adenylic acids. Kidney pulp in presence of these acids can also form considerable amounts of (I). The presence of Mg^{++} is also necessary for the reaction. Adenosine, adrenaline, and $p\text{-}C_6H_4(NH_2)_2$ also act as activators of (I) formation.

P. W. C.

Phosphorylation of various sugars by extracts of intestinal mucous membrane. L. LASZT (Biochem. Z., 1935, 276, 44—48).—Glycerol extracts of rats' intestinal mucous membrane bring about with galactose, glucose, and fructose in PO_4''' buffer a decrease of inorg. PO_4''' which is in all cases inhibitable by 1/5000 $CH_2I \cdot CO_2Na$ (I). With mannose and xylose, decrease of PO_4''' does not occur. The activity of the extracts is lost after heating at 52—65°. Only those sugars which show selective absorption inhibitable by (I) show this PO_4''' decrease.

P. W. C.

Absorption of hexose di- and mono-phosphate compared with other hexoses. F. MATHIEU (Biochem. Z., 1935, 276, 49—54).—Hexose di- and mono-phosphate are absorbed from the intestine of rats as quickly as fructose but less quickly than glucose at the same concn.

P. W. C.

Rôle of diffusion and membrane activity in the absorption of various sugars from the intestine. F. VERZAR (Biochem. Z., 1935, 276, 17—27).—The same amounts of glucose (I) and galactose (II) are absorbed by rat's intestine in the same time at any concn., but with mannose, sorbose, and xylose the more conc. is the solution the more sugar is absorbed. Fructose occupies a mean position. Absorption of (I) and (II) is the result of an active cellular process; that of the other sugars is purely a diffusional process. P. W. C.

Absorption from the intestine of isotonic solutions of glucose and sorbose in comparison with sodium sulphate. F. VERZAR and L. LASZT (Biochem. Z., 1935, 276, 28—39).—In the living rabbit, glucose (I) is absorbed 5 times as quickly as Na_2SO_4 (II) from solutions containing (I) and (II) in amounts isotonic with blood, neither substance having any influence over the velocity of absorption of the other. After 1 hr. survival, the intestine behaves like a non-living membrane, (II) then diffusing more rapidly than (I). Absorption of (I) is, but of (II) is not, inhibited by $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ (III). Sorbose is absorbed much more slowly than (I) and the rate of absorption is not decreased by (III). The slow absorption of (II) corresponds with the rate of its physical diffusion. P. W. C.

Absorption of glucose and xylose at different p_{H} . L. LASZT (Biochem. Z., 1935, 276, 40—43).— $\text{PO}_4^{'''}$ buffer accelerates glucose absorption only at p_{H} 7. Borate and acetate buffers similarly accelerate only at 7. Absorption of xylose is not affected by p_{H} . P. W. C.

Absorption of glucose from the human gastrointestinal tract. M. WISNIOFSKY (J. Lab. Clin. Med., 1934, 19, 1286—1293).—If the blood-sugar curve (I) is an expression of the insulin (II) produced by the pancreas, and if the (II) produced by any one diabetic is const. in amount, (I) should indicate the rate (III) of glucose absorption from the gut. (III) seems to be independent of the amount present in the gut and of the concn. of the solution. In 2 hr. an adult absorbs 50—75 g. of glucose.

NUTR. ABS. (m)

Blood-sugar curves and the digestive canal. O. KESTNER, H. E. NEVER, and H. SEHESTEDT (Pflüger's Archiv, 1934, 234, 544—549).—Administration of glucose to dogs through a Vella or Thiry or duodenal fistula or intraperitoneally did not produce such marked hyper- or hypo-glycaemic phases as when given *per os*. Administration of meat without carbohydrate produced a definite rise in blood-sugar (I) followed by a hypoglycaemic phase. Ingestion of 300 ml. of 0.9% NaCl by 3 human subjects caused a slight rise and fall of (I). The normal (I) curve probably depends on the activity of all the digestive organs. P. W. C.

NUTR. ABS. (b)

Adaptation of intestinal absorption to the composition of ingested food. H. G. K. WESTENBRINK (Arch. neerl. Physiol., 1934, 19, 563—583).—The rate (I) of absorption of glucose (II) from rat's intestine is significantly increased by prior feeding for ≤ 5 days on a diet containing (II), fructose (III),

or galactose (IV), whilst (I) of (III) or (IV) is increased only by prior feeding with (III) or (IV), respectively. Hence the data of Cori *et al.* (A., 1926, 429) are dependent on the diet used. The increased (I) is possibly due to increased elaboration of the appropriate enzymes (*e.g.*, esterases). F. O. H.

Selective absorption of sugar. S. DONHOFFER (Arch. exp. Path. Pharm., 1935, 177, 689—692).—The partial inhibition of the absorption (I) of glucose (II) in rats by phloridzin is confirmed (*cf.* A., 1933, 630, 1076). (I) of arabinose is $<$ that of (II) and is not inhibited by phloridzin. Similar phenomena occur with the ligatured rabbit's intestine, the inhibition of (II), however, being complete. The phloridzin-inhibited part of (I) is independent of the concn. of sugar. The data do not support the theory that the same physical process applies to the intestinal (I) of all sugars. F. O. H.

Effect of repeated ingestion of sugar and starch on blood-sugar. Muscular lactacidogen and glycogen in cases of complete and partial inanition. N. N. JAKOVLEV (Compt. rend. Soc. Biol., 1935, 118, 784—786).—In both types of case there is a large increase in muscular lactacidogen and glycogen. Glycosuria is irregular. R. N. C.

Hydrolysis, oxidation, and energy exchanges in a dog. I. Formation and removal of lactic acid in the organs during starvation and during oxidation of galactose, glucose, and maltose. II. Lactic acid arising from or deposited in organs during the metabolism of fructose, in respect to control experiments with inositol, acetaldehyde, and sodium lactate. M. WIERZUCHOWSKI and F. SEKURACHI (Biochem. Z., 1935, 276, 91—111, 112—131).—I. Lactic acid (I) circulation in starvation and during oxidative metabolism of galactose, glucose, and maltose in resting dogs in amytal narcosis is investigated. Hexolysis *in vivo* is much smaller than under anaerobic conditions, is least in muscle, greater in the organs of the head, and greatest in the portal vein organs. Replacing fat with glucose leads to increased production of (I) by these organs, (I) being then absorbed by the liver. The prevailing direction of H_2O between vessels and tissues does not direct the stream of (I).

II. A second, type of (I) circulation is brought about by prolonged intravenous injection of fructose, injection of other substances, *e.g.*, inositol, MeCHO, Na lactate, serving as controls. Under these conditions, the liver is the chief organ flooding the organism with (I). Neither the R.Q. nor the (I) balance in the organs is influenced by administration of inositol. The considerable elimination of (I) muscle on administration of MeCHO only affects the blood-(I) to a moderate extent. P. W. C.

Ketosis. V. Comparative glycogenic and ketolytic action of glucose and some carbohydrate intermediates. I. SHAPIRO (J. Bio Chem., 1935, 108, 373—387).—Glycogenic substances exert a ketolytic effect. Both EtOH (I) and $(\text{CH}_2\cdot\text{OH})_2$ (II) show a ketolytic action together with an increased urinary N. During metabolism (I) is probably converted into (II) rather than into MeCH. H. G. R.

Digestion of carbohydrates in mulberry leaves by silk-worms. II. **Digestion in different stages of growth.** K. KATO (J. Agric. Chem. Soc. Japan, 1934, 10, 691—695).—Max. vals. for digestibility coeff. and amounts of total carbohydrate, reducing sugar, and sucrose digested were obtained with partly mature leaves. Accumulation of fat and glycogen by the silk-worms was also more rapid.

CH. ABS. (p)

Effect of fat and protein on fasting hypoglycaemia in infants. H. SCHONFELD (Jahrb. Kinderheilk., 1934, 143, 153—158).—In infants the fall of blood-sugar (I) produced in 16 hr. by hunger is almost completely prevented by ingestion of protein (II); fat has only a very slight effect. Ketonuria generally \propto the degree of hypoglycaemia, but may be present with (II) feeding and absent with fat feeding, although (I) is lower in the latter case.

NUTR. ABS. (m)

Formation of carbohydrate from fat in the liver of the rat. C. L. GEMMILL and E. G. HOLMES (Biochem. J., 1935, 29, 338—349).—The R.Q. of liver slices of a rat fed on a normal and on a butter diet is 0.79 and 0.58, respectively, the carbohydrate content of the slices in the latter case showing a definite increase after shaking for 3 hr. in NaHCO_3 -Ringer medium at 37°. The glycogen content of the liver of rats fed on butter falls almost to zero on the first day of this diet and then gradually increases to a max. of 1% on the 4th—5th day. The CO_2 content of the urine of these rats reaches a max. on the 3rd—4th day. Conversion of fat into carbohydrate occurs therefore in the livers of rats fed on butter.

P. W. C.

Changes in the lipin content of blood passing through the lung. A. FRANCAVIGLIA (Riv. Patol. sperim., 1934, 13, 45—50).—After passage of the blood through the lung (dog) small changes, in either direction, were usually observed in the various lipin fractions, but there was no indication that the lung plays a special part in fat regulation.

NUTR. ABS. (b)

Rôle of the liver, spleen, and reticulo-endothelial system in fat and lipin metabolism. I. **Total fatty acids and cholesterol of blood following liver injury.** II. **Total fatty acids and cholesterol of blood following splenectomy and blockade of the reticulo-endothelial system.** Y. SHIRATO (Tôhoku J. Exp. Med., 1934, 23, 578—587, 588—598).—I. The total fasting serum-fatty acid and -cholesterol of rabbits are increased on poisoning with P and phloridzin, and fat and lipins injected intravenously remain in the blood-stream longer than normally. The liver is affected since liver-fat metabolism is greatly disturbed, serum-bilirubin is increased, and the rate of excretion of Congo-red (I) is decreased.

II. Splenectomy (II) in rabbits causes an increase blood-fatty acids (III) and -cholesterol (IV) and intravenously injected fat remains in circulation longer than normally whilst (I) excretion is retarded. Blockade of the reticulo-endothelial with India ink does not change the total (III) and (IV) whilst (III) vals., increased by fat injection,

return to normal in 3 hr. (as in normal rabbits) and the excretion of (I) is not affected thereby. Fat metabolism is probably therefore affected by (II) secondarily through disturbances of liver function.

NUTR. ABS. (m)

Cholesterol content of the adrenals of fatigued animals. S. E. DE JONGH and W. ROSENTHAL (Acta Brev. Neerl. Physiol., 1933, 3, 86—88; Chem. Zentr., 1934, ii, 2542).—Cholesterol in the adrenals of fatigued rats is < in normal animals. Blood-cholesterol is unchanged by fatigue.

R. N. C.

Influence of phosphatide-rich rations on the animal organism. **Resorption of phosphatides.** A. TRAUTMANN (Z. Tierzucht., 1934, 24, 27—41; Bied. Zentr., 1934, A, 5, 5—6).—The effect of feeding soya-bean lecithin (I) to dogs, rabbits, and pigs varied with dosage and the age of the animals. In very young animals (I) improved growth (1—2 g. daily) but heavier doses restricted live-wt. increases and hair growth. Older animals assimilated relatively large amounts (150 g. daily for pigs). Phosphatides were stored in the body only to a small extent, the major proportion being transformed into neutral fats.

A. G. P.

Nutritive value of the fatty acids of lard and some of their esters. S. LEPKOVSKY, R. A. OUER, and H. M. EVANS (J. Biol. Chem., 1935, 108, 431—438).—“Synthetic” lard prepared by the esterification of the fatty acids (I) of lard with glycerol is fully as satisfactory for the normal growth of rats as untreated lard, whether fed as 25 or 60% of the diet. The free (I), as sources of energy, are equal to the glyceride at 25% but inferior at the 60% level. Good growth occurs when the Me or Et esters of (I) are fed as 25% of the diet, but growth is very poor with the Me and moderately good with the Et esters at the 60% level. The esters of $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ are comparable with, but those of $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{OH}$ (toxic) and of $\text{OH}\cdot[\text{CH}_2]_4\cdot\text{OH}$ are much inferior to the glycerides as growth-promoters.

A. E. O.

Paradoxical hypolipæmia in the dog after ingestion of butter. C. ACHARD, M. BARIETY, and A. CODOUNIS (Compt. rend. Soc. Biol., 1935, 118, 779).—Blood-fatty acid falls below normal 6—9 hr. after ingestion, returning to normal after 25 hr. Cholesterol is unaffected.

R. N. C.

Protein and the dietary production of fatty livers. H. J. CHANNON and H. WILKINSON (Biochem. J., 1935, 29, 350—356).—Groups of rats were fed on complete diets containing 40% of fat with varying amounts of protein (5—50%) for 3 weeks and their livers and carcasses analysed for fat content. The diets were free from choline (I) except for the fact that each rat received 1.5 mg. of (I) per day as yeast extract. The amount of protein in the diet controls the amount of fat appearing in the liver irrespective of any effect of (I), the degree of infiltration increasing with decreasing protein content. Similarly in the “cholesterol” fatty liver, the relative amounts of glyceride and cholesteryl ester depend in the case of these (I)-free diets on the protein content of the diet. The possibility of protein controlling liver-fat by giving rise to (I), betaine, or

substances of similar physiological action is discussed. No relationship exists between the amount of fat infiltration in the liver and the amount of depôt-fat.

P. W. C.

Choline and liver-fat. D. L. MACLEAN and C. H. BEST (Brit. J. Exp. Path., 1934, 15, 193—199).—Choline prevents fat deposition in livers of diabetic dogs or of those receiving a high-fat diet.

CH. ABS. (p)

Inhibition by phloridzin of fat absorption. F. VERZAR and L. LASZT (Biochem. Z., 1935, 276, 1—10).—When olive oil is introduced into the stomach of a 150—200-g. rat, 1 g. is absorbed in 6 hr. and 3 g. in 24 hr., whereas when olive oil or lard is fed with the rest of the diet or when it is injected directly into the intestine, all the fat fed is absorbed in 24 hr. Urethane narcosis inhibits emptying of the stomach, but has practically no influence on absorption of fat. Phloridzin inhibits fat absorption both when the oil is given *per os* and when it is injected, the inhibition lasting 8 hr.

P. W. C.

Inhibition of fat absorption after extirpation of the adrenals. F. VERZAR and L. LASZT (Biochem. Z., 1935, 276, 11—16).—Fat absorption in rats, the adrenals of which have been removed 3 days previously, is very greatly retarded, olive oil not being absorbed at all in 6—10 hr. and the animals dying in 12—24 hr. Inhibition is also seen when the oil is injected directly into the intestine. The toxicity of olive oil with adrenalectomised animals is due to the great sensitivity of these animals to org. acids. Thus citric, formic, and ascorbic acids are all much more toxic to these animals.

P. W. C.

Influence of protein intake on the urea clearance in normal man. W. GOLDRING, L. RAZINSKY, M. GREENBLATT, and S. COHEN (J. Clin. Invest., 1934, 13, 743—748).—On a diet containing only 9 g. of protein the urea clearance of normal subjects was significantly < when the diet contained 100 g. An increase of protein to 280 g. had little or no effect.

NUTR. ABS. (b)

Allantoin during high-purine diet in man. V. GAUDIO (Riv. Patol. sperim., 1934, 12, 465—474).—As there is only a slight rise in allantoin in the urine, but a marked rise in uric acid, after a high-purine diet, the existence of an emergency uricolytic function is unlikely. There is also a rise in urea and usually a fall in the Cl' val.

NUTR. ABS. (b)

Nuclein metabolism. IV. Oxidative deamination of nucleic acid with organic catalysts. K. MAKINO (Z. physiol. Chem., 1935, 231, 149—152).—NH₃ is eliminated from nucleic acid by oxidative deamination in presence of various catalysts, *e.g.*, benzoquinone, C and methylene-blue, and hydroxy-benzenes (adrenaline, pyrogallol, etc.).

J. H. B.

Relation between acidosis and intermediary metabolism. I. Y. KIN (J. Chosen Med. Assoc., 1934, 24, 945—956).—Artificial lowering of the alkali reserve is accompanied by an increase in non-protein-N (I) and sugar (II) and a decrease in Cl' in blood. In starvation acidosis (I) and Cl' increase and (II) decreases. Acidosis of rabbits having renal blood supplies cut off can be remedied by NaHCO₃ (III)

or NaCl, but not by glucose (IV). (III) causes an increase in (II) and Cl', but not in (I). Injection of (IV) causes a decrease in (I) and Cl'. The survival period of such an animal can be prolonged by (III) only.

CH. ABS. (p)

Effect of sodium chloride on acid-base equilibrium. P. NUZZI and M. NAPOLI (Boll. Soc. ital. Biol. sperim., 1934, 9, 987—990).—Variation of the NaCl in the food of the dog does not affect the alkaline reserve of the blood, or the NH₃ and *p*_H of the urine.

R. N. C.

Acid-base equilibrium in the blood following administration of sodium chloride. H. GLATZEL and F. SCHMITT (Z. ges. exp. Med., 1934, 94, 370—377).—Changes in blood composition were determined following ingestion of NaCl and H₂O when the previous diet had been (1) NaCl-rich and H₂O-poor, (2) NaCl-poor and H₂O-rich, (3) acid (NH₄Cl), or (4) alkaline (NaHCO₃). The fasting val. of the blood-CO₂ was lower on diet (2) than on (1). After the ingestion of aq. NaCl the fall in blood-CO₂ was greater when the previous diet was NaCl-rich [diet (1)] than when NaCl-poor [diet (2)]: the fall was even more marked with diets (3) and (4). The effect of NaCl on acid-base equilibrium depends on the relative amounts of NaCl and H₂O ingested, on the nature of the previous diet, and probably also on the temp. of the aq. NaCl, if given intravenously, and on some unknown factors.

NUTR. ABS. (b)

[Total circulating] calcium and the moulting of brachyural Crustaceæ. A. DRILHON (Compt. rend., 1935, 200, 858—859).—The total Ca (I) of the circulating fluid (II) in *Maia squinado* is determined at various stages of development. (I) and (II) remain const., but during moulting both increase, (I) about threefold. (I) gradually returns to normal as calcification of the shell proceeds.

J. L. D.

Calcium absorption in white mice. A. R. BLISS and D. B. MORRISON (J. Tenn. Acad. Sci., 1934, 9, 233—242).—The efficiency of absorption of Ca salts was in the decreasing order, lactophosphogluconate, lactate, gluconate, chloride, inositol-gluconate, diphosphate, glycerophosphate.

CH. ABS. (p)

Liberation of calcium by stimulation of heart nerves. A. LANCZOS (Arch. exp. Path. Pharm., 1935, 177, 752—754).—Stimulation of the vagosympathetic nerve in perfused (0.6% aq. NaCl) frog's heart preps. liberates Ca which, on re-perfusion, enhances the heart-beat during the post-stimulatory period (cf. A., 1907, ii, 110).

F. O. H.

Influence of the mineral composition of the ration on the calcium, phosphorus, and total carbon dioxide contents of the blood-serum. J. MAREK, O. WELLMANN, and L. URBANEK (Z. Zucht., 1933, 27, B, 267—286; Bied. Zentr., 1934, A, 5, 5).—Data are given for pigs and horses.

A. G. P.

Potassium changes during incubation of the hen's egg. A. LEULIER and F. PAULANT (Compt. rend. Soc. Biol., 1935, 118, 254—256).—The mean K content of the embryo increases steadily with wt. up to hatching.

R. N. C.

Ratio of phosphorus to nitrogen in bone during the growth of the rat. A. ROCHE and I. GARCIA (Compt. rend. Soc. Biol., 1934, 116, 1029—1932).—Curves correlating the P and N contents of dried bones with body-wt. (I) indicate that ossification takes place in two stages. Development of the org. matrix predominates in the period from birth until (I) is about 110 g., and deposition of mineral salts in the period of (I) from 110 to 150 g. The P:N ratio, as a function of (I), first falls and then rises slowly in the first period; it rises rapidly in the second and is const. in adult rats. NUTR. ABS. (m)

Nitrate content of animal tissues and the fate of ingested nitrate. M. WHELAN (Biochem. J., 1935, 29, 782—787).—When NO_3^- is administered to dogs, only 50% of the NO_3^- -N is recovered in the urine. The NO_3^- -N content of the tissues increases by 6—10 times, but the abs. amount accounted for in this way is small. It is suggested that the NO_3^- disappearing is destroyed in the tissues. P. W. C.

Water exchange. VI. Water and ash in the bodies of animals subjected to diets poor and rich in water. M. SAVIANO (Boll. Soc. ital. Biol. sperim., 1934, 9, 990—993).—The H_2O and ash of the bodies of rats is raised by limiting the H_2O supply (I), and reduced by increasing it, whilst the H_2O /ash ratio increases inversely with (I), as do also the dry residue and ash of the urine. R. N. C.

Effect of homotypic conditioning of water on the growth of fishes: chemical factors involved. W. C. ALLEE, E. S. BOWEN, J. C. WELTY, and R. OESTING (J. Exp. Zool., 1934, 68, 183—213).—Fish grew more rapidly in H_2O after homotypic conditioning (presence of same species for 22 hr. previously). In this period the electrolyte content of well- or artificial pond- H_2O was unchanged, but was increased in lake- or distilled H_2O . Biological conditioning (by fish or mussels) results in the accumulation of NH_3 , NO_2^- , NO_3^- , org. N, and other compounds. Death of fish in distilled H_2O is due to loss of electrolytes. The growth-promoting substance in conditioned H_2O survives 121° for 15 min. and may be conc. and rediluted without loss of efficiency. It is org. in nature. CH. ABS. (p)

Relationship between Widmark's " β " and " r " factors in rabbits and the action of alcohol on body oxidations and a comparison of the blood-alcohol and -sugar curves. H. H. MEYER (Biochem. Z., 1935, 276, 174—182).—The " β " vals. (the decrease of concn. of EtOH in the blood in the post-absorptive state) are not const. for the same type of animal (rabbit) but vary with usage, body-wt., external temp., and vary inversely with the " r " val. (ratio of mean concn. of EtOH in the body to that in the blood). The " r " val. is usually >1 in rabbits. Comparison of the blood-EtOH and -sugar curves shows that small amounts of EtOH lead to increased oxidation and to inhibition of the utilisation of sugar. P. W. C.

Dependence of narcotic action in muscle on the concentration of calcium and the significance for irritability of motor nerve-fath. H. SCHEIN and O. RIESSER (Arch. exp. Path. Pharm., 1935, 177, 463—474).—The fatigue (I)

of the nerve supply to stimulated muscle (frog's sartorius) is of quicker onset the lower is the $[\text{Ca}^{++}]$ of the medium. (I) in presence of low $[\text{Ca}^{++}]$ ($<0.030\%$) is removed by increasing $[\text{Ca}^{++}]$. The same phenomenon occurs with narcosis by EtOH, urethane, chloral hydrate, or novocaine, the max. $[\text{Ca}^{++}]$ being also 0.030%. Increase of $[\text{K}^+]$ has the same effect as the equiv. decrease in $[\text{Ca}^{++}]$ and *vice versa*; Ca cannot be replaced, however, by Sr. The role of Ca in the irritability of motor nerve-endings is discussed. F. O. H.

Effects of some narcotics on the sedimentation of red blood-cells. M. HINO (Tôhoku J. Exp. Med., 1934, 22, 556—558).—Anæsthesia for 60 min. with Et_2O , solæsthin, CHCl_3 (I), avertin (II), N_2O , or EtCl causes delayed sedimentation (III) followed by a period of accelerated (III), reaching a max. in 3 hr. except in the case of (I) and (II) in which max. was attained in 9 hr. CH. ABS. (p)

Methyl chloride poisoning. C. A. BRICH (Lancet, 1935, 228, 259—260). L. S. T.

Comparison of cyclopropane and ethylene with reference to body saturation and desaturation. M. H. SEEVERS, S. F. DE FAZIO, and S. M. EVANS (J. Pharm. Exp. Ther., 1935, 53, 90—104).—The gas depôt method is used to determine the comparative rates of absorption and elimination of cyclopropane (I) and C_2H_4 (II) from the splanchnic (III) and skin (IV) regions of the rabbit and the dog. (III) reaches saturation twice as rapidly as (IV), and both saturate and desaturate with (I) in half the time required by (II). Rabbit tissues reach saturation with gases about 50% more rapidly than those of the dog. The CO_2 tension in tissues during (I) is higher than that during (II) anæsthesia. A. L.

Distribution of barbiturates in the brain. E. KEESER and I. KEESER (J. Pharm. Exp. Ther., 1935, 53, 136).—A reply to Koppányi (this vol., 118). After small doses of barbital there is a difference in the distribution in various portions of the brain. A. L.

Relationship between pharmacological action and chemical structure of barbituric acid derivatives. E. E. SWANSON (Proc. Soc. Exp. Biol. Med., 1934, 31, 961—963).—Among a no. of 5:5-substituted barbituric acids, an increase in the no. of C atoms in the alkyl group (I) (*n* or *sec.*) is associated with a decrease in min. anæsthetic and min. lethal doses, until (I) has >5 C, when the vals. again increase. The duration of action decreased as the (I) lengthened. CH. ABS. (p)

Action of some derivatives of aminomethylbenzdioxan and aminomethylcoumaran on the nictating membrane of the cat. Z. M. BACQ and D. BOVET (Compt. rend. Soc. Biol., 1935, 118, 359—361).—The compounds tested fall into five definite types as regards their action on sympathetic excitation and adrenaline secretion. R. N. C.

[Pharmacological] action of tetrazoles. B. VON ISSEKUTZ, M. LEINZINGER, and E. NOVAK (Arch. exp. Path. Pharm., 1935, 177, 398—414).—"Cardiazol" (I) and 9 other tetrazole derivatives were investigated. The action of (I) on the central nervous

system is increased 10- to 20- and 2- to 3-fold by insertion of *o*- and *p*-Me, respectively, into the $(\text{CH}_2)_5$ ring. The effect of decrease in size of the $(\text{CH}_2)_n$ ring is offset by alkylation. F. O. H.

Action of cardiac stimulants on the chloroform-impaired circulation. B. VON ISSEKUTZ (Arch. exp. Path. Pharm., 1935, 177, 415—434).—The impaired cardiac function due to CHCl_3 narcosis in cats is improved by administration of tri- and tetra-methylenetetrazole, strophanthin, adrenaline, or "sympatol," to a smaller extent by that of theophylline or ephedrine, and not at all by that of "cardiazol," coramine, hexetone, or caffeine. F. O. H.

Tetramethylammonium camphorsulphonate.—See this vol., 496.

Surface activity and spasmodic action. W. BIEHLER (Arch. exp. Path. Pharm., 1935, 178, 101—103).—"Octin" ($\text{NHMe}\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CH}\cdot\text{CMe}_2$) is equal or even superior to "perparin" (an isoquinoline derivative) in its inhibition of peristalsis and tonus of normal and spastically contracting guinea-pig's intestine (cf. A., 1934, 1030). F. O. H.

Comparison of toxicity and general effects of natural and synthetic camphor on guinea-pigs. R. HAZARD and R. LARDÉ (J. Pharm. Chim., 1935, [viii], 21, 97—101).—The min. lethal dose of *r*-camphor (I) is much < that of natural (I). In addition to greater toxicity, synthetic (I) produces more violent and convulsive physiological effects on guinea-pigs. H. T.

Pharmacodynamic properties of β -amino-ethylapiole.—See this vol., 485.

Nitrogen metabolism. III. Toxic action of salicylic acid, benzonaphthol, and phenol, and protective action of base-forming substances. P. SPOTO and G. SARZANA (Arch. internat. Physiol., 1934, 39, 24—33).—Na citrate prevents the loss of wt. and negative N balance following administration of NH_4 salicylate (I), benzonaphthol (II), or PhOH . The protective action is less marked with PhOH than with (I) or (II). NUTR. ABS. (m)

α -Dinitrophenol and its influence on metabolism. W. E. ROBERTSON (J. Lab. Clin. Med., 1934, 19, 1280—1285).—Administration of 2 : 4-dinitrophenol in cases of obesity causes a rapid increase in the rate and degree of oxidation whether given during fasting or with a glucose meal. Oxidation occurs at the expense of fats. CH. ABS. (p)

Mechanism of the stimulant action of dinitro-derivatives on cellular respiration. H. HANDOVSKY and C. SCHEPENS (Compt. rend. Soc. Biol., 1935, 118, 369—371).—Respiration of muscle activated by muscle-extract (I) from the same species is further stimulated by dinitrophenols (II), which also activate respiration in presence of a non-sp. (I). Action of (II) is destroyed by cooling (I) to -180° , but not by heating to 100° , and is hence due to one or more thermostable constituents of (I), which, although unimportant in normal respiration, require for their action more sp. conditions than the normal respiratory enzymes and co-enzymes. R. N. C.

Metabolic activity of compounds related to dinitrophenol. M. L. TAINTER, F. W. BERGSTROM, and W. C. CUTTING (J. Pharm. Exp. Ther., 1935, 53, 58—66).—Using body-temp. as an index, the effect of fifty compounds related to 2 : 4-dinitrophenol (I) on the metabolism of rats, pigeons, and dogs is studied. When either other groups are substituted for the OH or NO_2 in (I), or the position of these is changed, the effect is greatly reduced. In some cases only, active compounds are obtained by adding extra groups to the (I) mol. or by introducing NO_2 in other cyclic compounds. Picramic acid, dinitrohydroxydiphenyl, and 2 : 6-dinitrophenol were slightly active, whereas 2 : 4-dinitro- α -naphthol was inactive in rats, but 25% more toxic in pigeons than (I) for the same activity. Dinitro-*o*-cresol was active in rats and pigeons but more toxic, and 2 : 4-dinitro-*o*-cyclohexylphenol and the similar cyclopentyl compound were not more active in pigeons but slightly less toxic than (I). A. L.

Impairment of the heart by dinitro-compounds. H. STAUB and K. MEZEY (Arch. exp. Path. Pharm., 1935, 178, 52—56).—2 : 4-Dinitro-*o*-cresol and, to a smaller extent, 2 : 4-dinitrophenol in conens. of $1 : 10^5$ — 10^6 markedly decrease the contraction of isolated frog's heart or heart-muscle and diminish the output of heart-lung preps. (cat). The data confirm the danger of their application in man. F. O. H.

Influence of ovariectomy and bile acid on alimentary glycosuria. H. YUUKI (Arb. Med. Fak. Okayama, 1934, 4, 211—218).—Ovariectomy causes increased glycosuria (I) after intravenous injection of glucose. Subcutaneous injection of cholic acid decreases (I) in normal and ovariectomised rabbits. CH. ABS. (p).

Relation of sex to susceptibility to toxicity of bile salts. S. HONGO (Sei-i-Kwai Med. J., 1934, 53, 50—54).—The higher susceptibility of male frog muscle is not related to its phospholipin content. CH. ABS. (p)

Spectrographic changes in the blood of hens after injection of a lecithin-perhydryte complex. D. ABRAGAM, J. MAGAT, and M. MAGAT (Compt. rend. Soc. Biol., 1934, 116, 1326—1329).—Lecithin and "perhydryte" ($\text{urea}\cdot\text{H}_2\text{O}_2$) form a stable complex which when injected intravenously does not liberate O_2 but causes a reversible transformation of blood-pigment into a dark substance. Absorption curves for darkened and normal bloods are given. CH. ABS. (p)

Correlation of the spermicidal efficiencies of aromatic aldehydes with their chemical reactivities, and electrometric alkaline titrations of gelatin in presence of aromatic aldehydes. J. M. GULLAND and T. H. MEAD (Biochem. J., 1935, 29, 397—406; cf. A., 1932, 648).—A series of mono- and di-methoxybenzaldehydes arranged in order of spermicidal efficiencies closely resembles the series of the same aldehydes arranged in order of their capacities for condensation with the gelatin anion, as measured by the deflexion of the titration curve towards a more acid reaction at p_H 8—10. A similar deflexion also occurs between the isoelectric point and p_H 6—7. A. E. O.

Toxicological detection of ergot. H. KLUGE (Z. Unters. Lebensm., 1934, 68, 645—650).—After ingestion or injection of extract of ergot (I), or addition of the extract to minced organs, (I) can be identified in the organs by isolation of scleroerythrin, (I) alkaloids, and the red pigment which is not pptd. by $\text{Pb}(\text{OAc})_2$, but not by the cock's comb reaction.

E. C. S.

Chemistry and toxicity of mussel poison. H. MULLER (J. Pharm. Exp. Ther., 1935, 53, 67—89).—The concn. of mussel-poison (I) preps. is described, 1.7×10^{-6} g. of the most active prep. containing 35% of ash being toxic for mice on intraperitoneal injection. (I) is basic, but gives no colour reactions for alkaloids, and is not pptd. by the usual reagents.

A. L.

Action of lupanine and of infusion of *Lupinus albus* seeds on blood-sugar, and on diabetic glycosuria and hyperglycæmia. A. CLEMENTI and D. TORRISI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1004—1008).—Subcutaneous injection in sublethal doses of lupanine (I) in the rabbit produces a hypoglycæmia lasting 3—5 hr. Oral administration of extract or infusion of *Lupinus* seeds (II) has no effect on rabbits, but produces a heavy fall of blood-sugar in the fowl. Both (I) and (II) in sublethal doses reduce slightly glycosuria and hyperglycæmia in diabetics.

R. N. C.

Croton resin. I. Toxicity studies using goldfish. II. Toxic and vesicant action of certain of its derivatives. J. R. SPIES. III. Combined acids. N. L. DRAKE and J. R. SPIES (J. Amer. Chem. Soc., 1935, 57, 180—182, 182—184, 184—187).—I. When a MeOH extract of unshelled croton beans (seeds of *C. tiglium*) is fractionally extracted with ligroin (b.p. 55—70°), the active material is preferentially removed; successive fractions give darker and harder resins. The product (I) is more toxic to goldfish than is rotenone.

II. Hydrogenation (Pd or Ni) of (I) reduces the I val. from 53 to 38, but does not affect the toxic or vesicant action. The latter is connected with free OH. since acetylation (which indicates 3.4% OH) partly and methylation by $\text{Ag}_2\text{O}-\text{MeI}$ [11.7% OMe; 1.2% in (I)] completely removes it. (I) forms no H_2O -sol. salt with dil. KOH and gives no colour with FeCl_3 -EtOH; however, it probably contains phenolic as indicated by the large decrease in sap. val. caused by methylation.

III. Hydrolysis of (I) gives about 32% of ligroin-acids, including tiglic, heptolic, octolic, lauric, myristic, palmitic, oleic, and linoleic acids, but no stearic or higher saturated acids, and no acids with 3 or more ethylenic linkings.

R. S. C.

Assay of *Strophanthus*. Mortality curve for *Xenopus*. J. W. C. GUNN and N. SAPEIKA (Quart. J. Pharm., 1934, 7, 656—660).—A mortality curve \bar{X} *lavis* to strophanthin is described. The average fatal dose for frogs which have recovered from the first injection returns to the normal val. in 3 weeks.

A. E. O.

Po.ency of digitoxin. J. C. GAGE (Quart. J. Pharm., 1935, 7, 654—655).—Biological assays using frogs or guinea-pigs give similar results.

A. E. O.

Influence of digitoxin and strophanthin on oxidation processes of *in-vitro* systems and of surviving heart-muscle. K. SALOMON and O. RIESSER (Arch. exp. Path. Pharm., 1935, 177, 450—462).—Digitoxin (I) has not a characteristic m.p. (I), m.p. 262° (corr.), $[\alpha]_D^{25} +17.7^\circ$ in CHCl_3 , does not influence the oxidation of systems containing linseed oil or hæmin. Neither (I) nor strophanthin (II) influences the action of purified catalase preps. or the respiration of nucleated or non-nucleated erythrocytes, isolated frog's heart, or heart-muscle pulp (frog, mouse, rabbit). Hence the action of (I) and (II) is not related to cell-oxidation.

F. O. H.

Combination of *Digitalis* glucosides with blood-proteins. L. LENDLE and F. PUSCH (Arch. exp. Path. Pharm., 1935, 177, 550—563).—Ultrafiltration experiments indicate that ovalbumin (I) (2%) does not combine with 0.002% aq. digitoxin (II) whilst, following addition of 25% of serum, only 25% of (II) occurs in the ultrafiltrate from 0.004% (II). No such combination occurs with strophanthin (III). Purified (II) and (III) show no cataphoretic migration either alone or in presence of (I). Hence the combination of (II) and (III) in the organism is not explained by characteristic surface potentials.

F. O. H.

Adsorption of *Digitalis* glucosides and strophanthin on various substances in presence and absence of proteins. F. PUSCH (Arch. exp. Path. Pharm., 1935, 177, 564—573).—Strophanthin (I) (in 0.9% aq. NaCl), but not digitoxin (II) or digitoxigenin (III) (in 2—4% aq. EtOH), is adsorbed by $\text{Al}(\text{OH})_3$. (II) and (III), but not (I), are adsorbed by $\text{Fe}(\text{OH})_3$ and kaolin. A relation between concn. and adsorption of (II) or (III) is not apparent. With $\text{Al}(\text{OH})_3$, but not $\text{Fe}(\text{OH})_3$ or kaolin, addition of serum influences the adsorption, that of (II) being increased and that of (I) diminished. Comparison is made with adsorption of dyes (methylene-blue, eosin, and Congo-red). The data obtained afford no explanation for the action of (I), (II), and (III) in the organism.

F. O. H.

Baljet's colour reaction for *Digitalis* substances. L. LENDLE and W. SCHMELZER (Arch. exp. Path. Pharm., 1935, 177, 622—627).—The alkaline picric acid reaction (I) (A., 1919, ii, 438; 1922, ii, 882) is given both by aglucones of the glucosides (II) and the sugar components (B., 1926, 339). Scillaren A (A., 1933, 811) does not give (I), indicating that the unsaturated lactone group of (II) is responsible; this is confirmed by the negative (I) of hydrolysed strophanthidin. The scope of application of (I), which is also given by 0.1% aq. glucose, is indicated.

F. O. H.

Physico-chemical properties of *Digitalis* glucosides. Capillary activity and influence on the permeability of Traube's membrane. W. SCHMELZER (Arch. exp. Path. Pharm., 1935, 177, 614—621).—The capillary activity (measured by diminution of σ) of digitoxin (I), digitoxigenin, strophanthin (II), and allied substances is slight. With $\text{Cu}_2\text{Fe}(\text{CN})_6$ membranes, the permeability to H_2O is decreased by relatively high concns. [0.005% of (I) and 0.033% of (II)] and increased by lower concns.,

(I) being somewhat more effective than (II). No correlation between these properties and the action of the glucosides in the organism appears to exist.

F. O. H.

Elimination of uric acid from rat's liver by the action of phenylcinchoninic acid (cinchophen) and ethyl *p*-tolylcinchoninate (tolysin). O. FURTH and E. EDEL (J. Pharm. Exp. Ther., 1935, 53, 105—112).—The normal uric acid content of the liver of albino rats fed on bacon and bread is 6.5 ± 1 mg. per 100 g. and whilst this is diminished by phenylcinchoninic drugs, the elimination is never complete. Cinchophen (I) and tolysin (II) both exert their max. effect in doses of 0.01 g. per kg. daily, but whereas 0.2 g. of (I) per kg. daily causes in 8 days 18—22% loss in body-wt., the same effect is obtained only after administration of 0.6 g. of (II).

A. L.

Action of curare and of tetanus toxin on the muscle-potassium of the guinea-pig. A. LEULIER and G. VANHEMS (Compt. rend. Soc. Biol., 1935, 118, 256—257).—Curare causes reduction of K to variable extents in muscles, the greatest loss occurring in the striated fibres of the myocardia. Tetanus toxin produces similar results, but the max. fall is in striated voluntary muscles, whilst the cardiac region of the stomach shows an increase.

R. N. C.

Sensitising action of cocaine to adrenaline in relation to the different constitutional elements of its formula. E. PHILIPPOT (Compt. rend. Soc. Biol., 1935, 118, 802—805).—The sensitising action of cocaine is associated with its *l*-rotation, N^{III} atom, and the esterification of the CO₂H and OH groups of ecgonine by alkyl and an aromatic acyl, respectively.

R. N. C.

Curariform activities of strychnine metho-salts and curarine chloride. S. L. COWAN and H. R. ING (J. Physiol., 1934, 82, 432—437).—Strychnine methiodide (I) is slightly more active as a curarising agent on the isolated sartorius prep. than curarine chloride (II). In the decerebrate frog (I) is less active than (II) as a paralysing agent, as it is excreted more rapidly in the urine. In a frog paralysed with strychnine methochloride (III) to prevent urine secretion, (III) accumulates in the liver, and to a smaller extent in the kidneys.

R. N. C.

Effect of some papaverine derivatives on the excised intestine. S. SAKURABA (Tôhoku J. Exp. Med., 1934, 22, 556—558).—Derivatives containing NMe increased, and those having no NMe decreased, the tonus of isolated rabbit intestine.

CH. ABS. (p)

Mechanism of morphine hyperglycæmia. I. Influence of opium alkaloids on respiratory movements in rabbits. H. GYOKU (Folia Pharmacol. Japon., 1934, 18, 224—246).—Opium alkaloids having a phenanthrene nucleus depress respiratory movement and produce a greater hyperglycæmia in rabbits than those having an isoquinoline nucleus.

CH. ABS. (p)

Respiratory effects of morphine, codeine, and related substances. III. Effect of morphine, dihydromorphine, dihydromorphinone (dilaudid), and dihydrocodeinone (dicodid) on the

respiratory activity of the rabbit. C. I. WRIGHT and F. A. BARBOUR (J. Pharm. Exp. Ther., 1935, 53, 34—45).—The min. doses of morphine, dihydromorphine, dilaudid, and dicodid required to reduce respiratory activity in the rabbit are 0.32, 0.22—0.27, 0.027—0.035, and 0.21—0.30 mg. per kg., respectively. The effects on the rectal temp., heart rate, and sensitivity to CO₂ stimulation of the above are also described.

A. L.

Effect of morphine on the oxygen consumption of brain-tissue in the rat. E. G. GROSS and I. H. PIERCE (J. Pharm. Exp. Ther., 1935, 53, 156—168).—Brain (I) from non-tolerant animals (III) killed after subcutaneous injection of morphine (II), in contrast to (I) from tolerant (III) and to normal (I), shows an increased O₂ consumption due to added glucose. Subcutaneous injection of (II) into non-tolerant (III) produces no change in the metabolic rate of kidney and testes.

H. G. R.

Comparison of the actions of morphine and dihydromorphinone (dilaudid) hydrochloride on the intact small intestine of the dog. C. M. GRUBER and J. T. BRUNDAGE (J. Pharm. Exp. Ther., 1935, 53, 120—136).—The min. effective intravenous dose of dilaudid hydrochloride (I) on the jejunal Thiry-Vella loop of the dog is about 2×10^{-4} , that of morphine sulphate (II) 2×10^{-3} mg. per kg. For the ileum 3×10^{-4} of (I) and 3×10^{-3} mg. per kg. of (II) are required. Both drugs decrease the amplitude of the rhythmic contractions (III) during the period of increased tonus, and increase the height of (III) during the return of the gut to normal tonus.

A. L.

Action of morphine on the permeability of the nervous tissue in theophyllinised animals to sodium ferrocyanide. G. B. GIORDANO (Boll. Soc. ital. Biol. sperim., 1934, 9, 932—934).—The passage of Na₄Fe(CN)₆ into the brain of theophyllinised guinea-pigs is accelerated temporarily by morphine.

Effect of caffeine on basal metabolism. N. A. WOMACK and W. H. COLE (Proc. Soc. Exp. Biol. Med., 1934, 31, 1248—1250).—Daily feeding of 70 mg. of caffeine citrate progressively increased the rate of O₂ consumption. Lugol's solution or thyroidectomy tended to inhibit this effect.

CH. ABS. (p)

Pharmacological studies of aromatic guanidine derivatives. I. General action and influence on blood-coagulation. A. KURODA (Folia Pharmacol. Japon., 1934, 18, 106—120).—Effects are recorded of 3:4-dihydroxybenzyl-, phenoxyethyl-, *p*-hydroxyphenyl-, *p*-methoxybenzyl-, and α -phenylethyl-guanidine.

CH. ABS. (p)

Pharmacological action of the active principles of extracts of the crystalline lens. BIETTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 980—983).—Aq., 1% aq. AcOH, and EtOH extracts of the cryst. lens contain a depressor, which has also oxytotic action and inhibits intestinal movement, and hence is not histamine, choline, or acetylcholine.

R. N. C.

Histamine-like substance liberated by antidromic excitation of sensitive nerves. G. UNG

M. R. ZERLING, and A. POCOULE (Compt. rend. Soc. Biol., 1935, 118, 778—779).—The action of the substance liberated is not inhibited by atropine, and hence it is not acetylcholine. Total acidity of the gastric juice produced by stimulation of the peripheral end of the crural nerve is similar to that of juice produced by histamine. R. N. C.

Nicotine-like action of choline, acetylcholine, and "cholazyl" on sympathetic ganglia. F. T. BRUCKE (Arch. exp. Path. Pharm., 1935, 177, 532—542).—Choline, acetylcholine (I), and "cholazyl" (a chloroacetylcholine chloride-urea prep.) stimulate the superior cervical ganglion (II) in cats. (I) shows nicotine-like properties, the first phase of stimulation being followed by a second phase of paralysis. The chemical transference of stimuli at (II) is discussed. F. O. H.

Fatigue of isolated muscle in relation to the possible effect of acetylcholine liberated during excitation of the nerve. V. KRUTA (Compt. rend. Soc. Biol., 1935, 118, 757—760).—Muscles treated with eserine contract to a smaller degree than untreated muscles, which does not suggest that acetylcholine is liberated during nerve excitation. R. N. C.

Chemistry and pharmacology of fermented foodstuffs. W. KEIL and B. KRITTER (Biochem. Z., 1935, 276, 61—65).—Fermentation of cucumber (I) follows the same stages as that of cabbage (II), lactic acid bacteria being the active agents and acetylcholine (III) being formed. (III) is also formed using extract of (I) with a culture of these bacteria. During fermentation of (I), loss of protein does not occur. The deproteinised extract of (II) does, but that of (I) does not, contain arginine and choline. (III), histamine, and putrescine present in the fermented (I) and (II) arise during fermentation. P. W. C.

Physiological action of substances used in treatment of flour. J. VON DARANYI and S. VON VITÉZ (Z. Unters. Lebensm., 1934, 68, 597—612).—Of the substances used in the treatment of flour it is the oxidising agents which affect the health and development of rats, mice, and dogs. Of these, NaBO_3 and Bz_2O_2 are most harmful; $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is less so. E. C. S.

Chemotherapy of dyes. Reticulo-endothelial system. A. RISI (Arch. exp. Path. Pharm., 1935, 178, 36—51).—Small doses of acidic dyes (trypan-red and -blue), in association with various substances [CH_2Ph cinnamate, $\text{Mn}(\text{OH})_2$, allyl sulphite, HCO_2Na , HCO_2Et , CHPh_3] or as an electro-negative complex with phenol-red, have a stimulating action (indicated histologically) on the reticulo-endothelial system. The application of these complexes to the treatment of tuberculosis in guinea-pigs (resulting in no noteworthy improvement) is described. F. O. H.

Chemotherapy of helminthics. M. OESTERLIN and KRAINICK (Zentr. Bakt. Par., 1934, I, 132, 228).—*Fasciola hepatica* was particularly sensitive to phenoxazine dye cresyl-blue 2RN *in vitro*, *in vivo*. *Strongyloides stercoralis* and *Microfilis diurna* were similarly sensitive to acridine dyes (I) (flavizide, rheonin), *Opisthorchis felineus* to phenols

(hexylresorcinol), *Schistosoma nansoni* to (I), but very resistant *in vivo*. A. G. P.

Anthelmintic studies of alkylhydroxybenzenes. I. Alkylpolyhydroxybenzenes. P. D. LAMSON, H. W. BROWN, and C. B. WARD. II. *o*- and *p*-n-Alkylphenols. P. D. LAMSON, H. W. BROWN, R. W. STOUGHTON, P. D. HARWOOD, R. BALTZLY, and A. D. BASS. III. 6-*n*-Alkyl-*m*-cresols. P. D. LAMSON and H. W. BROWN. IV. Isomerism in polyalkylphenols. V. Phenols with other than *n*-alkyl side-chains. P. D. LAMSON, H. W. BROWN, R. W. STOUGHTON, P. D. HARWOOD, R. BALTZLY, and A. D. BASS (J. Pharm. Exp. Ther., 1935, 53, 198—217, 218—226, 227—233, 234—238, 239—249).—I. Hexylresorcinol (I) is the most active anthelmintic of the 4-*n*-alkylresorcinols (II) and is non-toxic. It is more effective for *Ascaris* than for hookworm. It causes slight local irritation but this is not parallel with the anthelmintic activity (III). (III) of (II) is exhibited between amyl- and dodecylresorcinol. The m.p. of active substances is generally < 80° and the solubility range between 1 : 1000 and 1 : 35,000.

II. (III) of *o*- and *p*-*n*-alkylphenols increases to *n*-amylphenol and then falls, the activity of the *p*- being slightly > that of the *o*-isomeride. The toxicity (IV) and irritant action (V) decrease with the length of the side-chain. *o*-*n*-Heptylphenol has about 50% of the activity of (I) and has no effect on the mucous membrane of the mouth.

III. (III) of 6-*n*-alkyl-*m*-cresols increases to butyl-*m*-cresol and then falls, (IV) and (V) decreasing with the length of the chain. 6-*n*-Hexyl-*m*-cresol, given in large doses, has no effect on the tissues and has lower (III) than (I).

IV. Substitution in the Ph nucleus of several alkyl radicals of the same total no. of C atoms as a single *n*-chain does not increase (III).

V. None of the synthetic alkylphenols other than those having *n*-alkyl side-chains shows any decided (III). H. G. R.

Behaviour of carbohydrate reserve at high altitudes. E. SAPEGNO (Boll. Soc. ital. Biol. sperim., 1934, 9, 886—888).—Liver- and muscle-glycogen (I) in mice kept at 2910 m. above sea-level fall during the first few days, afterwards rising steadily. If the animals are then brought back to low levels (I) returns to normal after a short lag. R. N. C.

Blood-sugar, reducing power, and glutathione content at high altitudes. A. ROSSI and E. SAPEGNO (Boll. Soc. ital. Biol. sperim., 1934, 9, 888—890).—The blood-sugar of normal human subjects is increased at 2910 m. above sea-level, and other reducing substances are also increased to variable extents. The increases in total and reduced glutathione are not uniform. R. N. C.

Effect of the piqure diabétique on the blood-sugar and the mean blood-pressure of dogs with the adrenal glands or medullæ removed. T. KAIWA and M. WADA (Tohoku J. Exp. Med., 1934, 23, 536—555).—Puncturing the fourth ventricle of the dog in the region of the *ala cinerea* (without injury to the cerebellum) caused

hyperglycæmia (I) with varying changes in the blood-pressure (II). When the adrenal glands, or their medullæ, were previously removed the pique (I) was reduced whilst the (II) changes were unaffected. Previous section of the vagi did not affect the (I). The adrenalectomised dogs received a diet rich in carbohydrate. NUTR. ABS. (b)

Intrinsic regulation of the circulation in the hypothalamus of the cat. C. F. SCHMIDT (Amer. J. Physiol., 1934, 110, 137—152).—The circulation is regulated by a humoral rather than a nervous mechanism. Hypothalamic vessels are dilated by excess CO_2 and lack of O_2 , and constricted by increased ventilation. Changes of p_{H} produced by fixed acid or alkali have no direct effect. Adrenaline causes weak but prolonged constriction, and histamine and choline derivatives are dilators, whilst pituitrin and Ca have no direct action. R. N. C.

Phenomena following iodoacetic acid poisoning. III. Oxygen consumption and respiratory quotient in pigeons poisoned by iodoacetic acid after injection of dinitrophenol. U. LOMBROSO and G. SARZANA (Boll. Soc. ital. Biol. sperim., 1934, 9, 803—804).— O_2 consumption is raised by $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH}$, whilst the R.Q. is raised if glucose is administered, but the increase is < that of normal pigeons injected with the same amount of glucose. R. N. C.

Effect of injection of iodoacetic acid and sodium cyanide on the mammalian heart. L. H. NAHUM and H. E. HOFF (Amer. J. Physiol., 1934, 110, 56—60). R. N. C.

Chronic carbon monoxide poisoning. K. SUFFLE (Deut. med. Woch., 1934, 60, 1263—1267; Chem. Zentr., 1934, ii, 2551).—In dogs breathing air containing small quantities of CO daily for some hr., considerable alterations and compensating effects are produced \propto the CO content, which are considered to be the result of partial O_2 deprivation. The nature of acute CO poisoning depends on O_2 withdrawal. In the animal's body repeated separation of part of the hæmoglobin (I) occurs, followed by formation of CO-(I), and is compensated by increased (I) and erythrocyte production. The animal is sensitive to prolonged exposure to 0.02% CO; concns. of 0.01% or less have no harmful effect. R. N. C.

Methylene-blue in illuminating-gas poisoning. L. MACK and E. A. SMITH (Proc. Soc. Exp. Biol. Med., 1934, 31, 1031—1032).—The lethal interval in rats exposed to an atm. containing 1.89% of illuminating gas was not increased by injection of methylene-blue, but was much decreased by administration of desiccated thyroid gland or 2:4-dinitrophenol. CH. ABS. (p)

Remedies for cyanide poisoning in sheep and cattle. A. B. CLAWSON, H. BUNYEA, and F. J. COUCH (J. Washington Acad. Sci., 1934, 24, 369—385).—Intravenous injection of methylene-blue, $\text{Na}_2\text{S}_2\text{O}_5$ (I), NaNO_2 (II), or a mixture of (I) and (II) afforded protection. A. G. P.

Effect of excito-metabolic substances on the alkaline reserve and p_{H} of the blood. C. ZUMMO and G. SCOZZARI (Boll. Soc. ital. Biol. sperim., 1934,

9, 808—809).—NaOAc and Na citrate administered orally to dogs produce an increase in the alkaline reserve (I) of the blood, and p_{H} is raised 0.03—0.05. The increase of (I) is less with NH_4OAc and NH_4 citrate, whilst p_{H} is affected very slightly in most cases. R. N. C.

Mechanism of the action of hypertonic solutions of sodium chloride. C. COLOMBI (Boll. Soc. ital. Biol. sperim., 1934, 9, 976—978).—The spleen is relaxed by 5% NaCl but contracted by 20% and more conc. solutions. NaCl has a double action in inhibiting sympathetic response and directly exciting plain muscle. R. N. C.

Action of different salts introduced intravenously on intestinal peristalsis. A. COSTANTINI and G. BALLARIN (Boll. Soc. ital. Biol. sperim., 1934, 9, 1029—1032).—Peristalsis is generally stimulated by Na^+ and glucose at high concns., and by dil. K^+ and Mg^{++} , but is arrested by conc. K^+ and Mg^{++} solutions. R. N. C.

Ciliary motion in relation to electrolytic equilibrium. M. BENAZZI (Boll. Soc. ital. Biol. sperim., 1934, 9, 880—881).—In the ionic equilibrium controlling the ciliary motion of *Mytilus*, K may be replaced by Rb, Cs, or NH_4 , Na by Li, and Ca by Sr or Ba. R. N. C.

Stimulation of peripheral nerve-elements subserving pain-sensibility by intra-arterial injections of neutral solutions. R. M. MOORE (Amer. J. Physiol., 1934, 110, 191—197).—The nerve-elements are stimulated by Li^+ , Na^+ , Cs^+ , Mg^{++} , Ca^{++} , and Sr^{++} in hypertonic solution, and by hypotonic solutions and isotonic K^+ , Rb^+ , and Ba^{++} solutions in the absence of Mg^{++} , Ca^{++} , and Sr^{++} , suggesting that stimulation is associated with the permeability of the nerve-membrane to the different ions. R. N. C.

Permeability of capillaries in man, studied by the concentration curve of glucose injected into the humoral artery and recovered from the vena mediana. G. C. DOGLIOTTI and V. TAGLIONI (Boll. Soc. ital. Biol. sperim., 1934, 9, 859—861).—The curve rises almost immediately to a sharp. max. and then falls again in normal subjects, but in certain pathological conditions it remains high for some time owing to the decreased capillary permeability.

Effect of p_{H} on the lumen of the capillaries. F. SCHUPFER (Boll. Soc. ital. Biol. sperim., 1934, 9, 861—864).—Fall of p_{H} in the capillaries produces vaso-dilatation, and conversely, rise of p_{H} produces vaso-constriction, these changes probably leading to the vaso-motor reactions of the peripheral ring observed on change of p_{H} . R. N. C.

Effect of calcium and potassium ions on the variations of the lumen of the capillaries. F. SCHUPFER (Boll. Soc. ital. Biol. sperim., 1934, 9, 864—866).—Introduction of KCl into the circulation causes a vaso-dilatation of the capillaries, whilst CaCl_2 produces a vaso-constriction. K^+ and Ca are antagonistic in their effects on tissue- p_{H} and e sensitivity of the capillaries to p_{H} changes. R. N. C.

Action of heavy water on reviving animals. L. PLANTEFOL and G. CHAMPETIER (Compt. rend., 1935, 200, 587—589).—Movement of *Macrobistius macronyx*, Duj., after imbibition of 18 and 57% H₂O occurred as early as after imbibition of H₂O. Movement was delayed when 98% H₂O was used. The survival period in drop cultures was curtailed by 57 and 98% H₂O. Revival of desiccated *Rotifer vulgaris*, Schr., was slightly retarded in some cases by H₂O. A. G. P.

Action of sulphur on gaseous metabolism in man. D. CAMPANACCI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1064—1066).—O₂ consumption is lowered by administration of small quantities of S, the effect being similar to that of insulin. R. N. C.

Effect of fluorine on blood and respiration. D. A. GREENWOOD, E. A. HEWITT, and V. E. NELSON (Proc. Soc. Exp. Biol. Med., 1934, 31, 1037—1040).—Puppies receiving orally 0 to 4.52 mg. of F as NaF per kg. of body-wt. showed slight increases in haemoglobin and coagulation time, no change in plasma-Ca, and a slight fall, increasing with the dosage, in the acid-sol. inorg. P of the plasma. NUTR. ABS. (b)

Action of sodium fluoride on serum-calcium and -inorganic phosphorus in rabbits. S. B. BOGDANOVIC (Arch. exp. Path. Pharm., 1935, 178, 104—108).—Intravenous injection for 3 weeks of small amounts of NaF generally increases the serum-Ca and -inorg. P, probably due to the action on the liver and parathyroid gland. F. O. H.

Behaviour of digestive enzymes in experimental intoxication by sodium fluoride. A. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1934, 9, 916—918).—Intragastric injection of NaF in guinea-pigs causes a decrease in the activity of pancreatic invertase (I), amylase (II) and lipase (III), whilst intraperitoneal injection increases (I), decreases (II), and does not affect (III). R. N. C.

Mottled enamel of deciduous teeth. M. C. SMITH and H. V. SMITH (Science, 1935, 81, 77).—The use of H₂O containing high concns. of F (12—16 p.p.m.) during the period of formation of temporary teeth in human beings appears to produce mottled enamel of a severe type. L. S. T.

Micro-determination of lead in biological materials. Titrimetric-extraction method. E. S. WILKINS, jun., C. E. WILLOUGHBY, E. O. KRAEMER, and F. L. SMITH (Ind. Eng. Chem. [Anal.], 1935, 7, 33—36).—Pb is separated from other metals by extraction with diphenylthiocarbazone (I) dissolved in CHCl₃, and subsequently determined by titration with (I). The method is sensitive to 0.001 mg. Pb. E. S. H.

Dependence of urinary porphyrin excretion in lead-poisoned rabbits on the acid-base economy. I. SCHREUS and H. POUILLAIN (Arch. exp. Path. Pharmacol., 1935, 177, 543—549).—Rabbit's urine contains coproporphyrin (I), the content with a diet of being > that with one of green vegetables (II). Oral administration of PbCO₃ increases the excretion of (I) with a diet of (II) but not (III). ^aæces contain proto-, smaller amounts of deuto-

(IV), and, in traces, copro-porphyrin. Administration of Pb increases only (IV). F. O. H.

Reversibility of acidosis in acute uranium nitrate nephritis. L. BRULL (Compt. rend. Soc. Biol., 1935, 118, 811—812).—The alkaline reserve of the blood in acute UO₂(NO₃)₂ nephritis in dogs is not raised by anastomosis of normal liver, muscle, or kidneys with the circulation. R. N. C.

Poisoning by uranium nitrate. I. Modifications of the liver. S. MARRAS (Boll. Soc. ital. Biol. sperim., 1934, 9, 820—823). R. N. C.

Localisation of polonium in the organism as a function of the nature of the injected solution. A. LACASSAGNE and M. SERVIGNE (J. Pharm. Chim., 1935, [viii], 21, 145—151).—A known quantity of Po was injected into rabbits in aq. solution (I) and in neutral olive oil (II). Like Bi and Ra-E, more Po is retained in the lungs with (I) and the animals show a greater resistance when (II) is injected. The Po excreted in the urine reaches a max. for (I) and then falls, whilst excretion is uniform in the case of (II). The localisation of the Po does not seem to depend on the form in which it is combined when injected but on the nature of the solvent used. H. T.

Relation between chemical structure and biological activity of diphenylmethylarsine dihydroxide and its derivatives. V. M. KARASIK and M. M. LICHATSCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 314—316).—Diphenylmethylarsine dihydroxide, diphenyldimethylarsine hydroxide (I) and the nitrate of (I) are less toxic when injected subcutaneously than the corresponding compounds containing one Ph group less. F. N. W.

Passage of arsenic through the human placenta following arsphenamine therapy. N. J. EASTMAN and A. L. DRPPEL (Bull. Johns Hopkins Hosp., 1933, 53, 288—296).—As occurs in the meconium of newborn infants after maternal treatment with arsphenamine. Simple diffusion cannot explain transmission of As. CH. ABS. (p)

Arsenoxide in relation to the toxicity and therapeutic activity of arsphenamine and neoarsphenamine. J. F. SCHAMBERG, J. A. KOLMER, and H. BROWN (Amer. J. Syphilis, 1934, 18, 37—55).—The naphthaquinone test for arsenoxide (I) gives positive results with arsphenamine (II) and neoarsphenamine (III) after exposure to air but not in freshly prepared solutions. The test is less delicate for (I) in tissues after administration of (II). The toxicity of alkaline solutions of (II) is approx. doubled when 34% has been oxidised to (I). Other factors than (I) are concerned in the toxicity of (III). CH. ABS. (p)

Influence of drugs used in antisyphilitic therapy on the reticulo-endothelial system. K. B. MUIR and S. W. BECKER (Arch. Path., 1934, 18, 370—377).—Comparison is made of the effects of neoarsphenamine, thioarsene, colloidal Bi, mercurosal, tryparsamide, Na Au thiosulphate, sulpharsphenamine, Bi arsphenaminesulphonate, K Bi tartrate, HgCl₂, and Na cacodylate. The reticulo-endothelial system participates in disposing of drugs injected intra-

venously, but the proportion of thiol compounds present is insufficient to explain its rôle in oxidation-reduction processes. CH. ABS. (p)

Toxicity of arseno-protein compounds. P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1934, 9, 919—922).—The toxicity of As-ovalbumin complexes is $>$ that of an equiv. amount of Na_2HAsO_4 . R. N. C.

Fixation of elementary arsenic by ovalbumin in presence of radium emanation. P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1934, 9, 922—925).—The amount of As fixed by ovalbumin in H_2O saturated with Rn is $>$ the amount fixed in pure H_2O . The amount of Co fixed is increased by Rn. R. N. C.

Influence of therapeutic radium and X-ray treatment on blood-cholesterol and liver. K. FUGE (Strahlenther., 1934, 50, 157—166; Chem. Zentr., 1934, ii, 2242).—The level of cholesterol (I) in blood, and the proportion between total (I) and (I) esters, was unaffected by irradiation. A. G. P.

Nature of enzymes. J. ALEXANDER (Science, 1935, 81, 44—45).—A reply to criticism (cf. this vol., 121). L. S. T.

Inactivation of catalases from certain marine plants by oxygen. G. W. MARKS (Biochem. J., 1935, 29, 509—512).—Phosphate buffer extracts of marine plant catalases (I) are inactivated by mol. O_2 as the pseudo-unimol. rate of inactivation is greater when (I) is kept under air than under N_2 . The inactivation occurs over the p_{H} range 4.5—10.0. The rate of inactivation increases with rise in temp. in accordance with the Arrhenius equation. E. A. H. R.

Peroxidase in algæ. H. TAMIYA (Planta, 1934, 23, 284—288).—Distribution of peroxidase (I) in various species of algæ is recorded. (I) extracted from *Plocamium coccineum* has an active p_{H} range 1.2—5.8 with optimum at 3.0—4.0, is heat-resistant, and, unlike other peroxidases, does not react with guaiacol or pyrogallol but has a positive action on benzidine and *o*-tolidine. There is no reaction with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, $\alpha\text{-C}_{10}\text{H}_7\text{-OH}$, quinol, or *p*-cresol. The activity of the enzyme is not inhibited by Et urethane but is weakened by KCN, Na_2S , and NH_4OH (0.02M). A. G. P.

Influence of adenylic acid on certain enzymic, especially oxidative, processes in muscle extract. C. G. HOLMBERG (Skand. Arch. Physiol., 1934, 68, 1—88; Chem. Zentr., 1934, ii, 2549).—In the presence of cozymase (I) the system muscle-hexose diphosphate decolorises methylene-blue. (I) acts as co-enzyme for all forms of carbohydrate fission involving 3-C chains. A. G. P.

Dehydrogenases and hydrogen donors in the brains of narcotised and hypnotised animals. Animal immobilisation. H. WAELSCH (Klin. Woch., 1934, 13, 1177—1180; Chem. Zentr., 1934, ii, 2551).—Brain-pulp of narcotised animals decolorises methylene-blue more rapidly than that of normal animals. Previous poisoning of the animal with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ does not delay the decolorisation, so that increased lactic acid production is not responsible

for the acceleration. A similar acceleration occurs in the brains of animals immobilised by hypnosis. R. N. C.

Mechanism of oxidative processes. XLI. Dehydrogenation of alcohol by yeast. H. WIELAND and F. WILLE (Annalen, 1935, 515, 260—272; cf. A., 1933, 865).—The impoverishment of yeast by agitating its suspension in H_2O with O_2 proceeds rapidly initially and declines to a const. rate. The main process appears to consist in the oxidative removal of simple and readily hydrolysed carbohydrates (I) followed by an action controlled by the slow saccharification of glycogen. The content of (I) decreases by about 50% whereas that of lipins (II) increases about 100%. Non-hydrolysable compounds decrease about 8%. Increase due to (II) is about 10% of the decrease due to loss of (I). Of 14 mols. of EtOH 11 are completely oxidised, 2 transformed into fat, and 1 into carbohydrate; re-synthesis in the sense of Meyerhof (A., 1925, i, 993) therefore does not take place. Yeast can form much less cell material from AcOH than from EtOH; lactic acid is an unfruitful material. Since the oxidation of EtOH proceeds through AcOH it is remarkable that about twice as much $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ is produced from the former as from the latter whereas citric acid is not formed. Fumaric acid is intermediately produced. The decolorisation of methylene-blue (III) in presence of EtOH is accompanied by production of the corresponding amount of AcOH: $\text{EtOH} + 2(\text{III}) \rightarrow \text{AcOH} + 2 \text{leuco-(III)}$. H. W.

Tyrosinase of tea-leaves, and its probable rôle in tea manufacture. A. I. POTAPOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 323—325).—Tyrosinase has been found in green tea-leaves, and is connected with their change of colour during drying. Tyrosine was found in finished tea. F. N. W.

Effect of added fat and protein on the hydrolysis of rice starch. M. M. KIBE (Poona Agric. Coll. Mag. 1934, 26, 55—61).—Hydrolysis of pure rice starch (I) by diastase, pancreatin, and conc. HCl was adversely affected by the addition of 1—5% of rice fat (II) (from polish by Et_2O). Rice containing no (II) but only (I) and protein was hydrolysed more rapidly than the pure (I). CH. ABS. (p)

Characterisation of different amylases. K. V. GIRI (J. Indian Inst. Sci., 1934, 17, A, 127—129).—A method of characterising α - (I) and β -amylase (II) depends on the extent to which starch is hydrolysed by (I) and (II). Agar impregnated with starch gives a violet diffusion zone with (II) and a colourless one with (I) on addition of 0.005N-I. A mixture of amylases gives two diffusion zones, a central colourless one and a violet one surrounding it. E. A. H. R.

Banana amylase. B. N. SASTRI and G. R. ROW (Proc. Indian Acad. Sci., 1934, 1, B, 318—323).—Extracts (prep. described) of banana skin (I) have a definite saccharifying action on solutions of starch, whereas the pulp (II) has nearly none. Extracts of whole banana are more active than those of (I), due probably to activators in (II). Amylolytic activity is inhibited by tannin [present in unripe (II)], which explains the failure of previous investigators to get results (cf. B., 1928, 796). J. L. D.

Hydrolysis of glycogen by glycerol extract of muscle. A. CARRUTHERS and W. Y. LEE (J. Biol. Chem., 1935, 108, 525—533).—A glycerol extract of rabbit muscle (A., 1930, 249) was dialysed and incubated with glycogen (I) at 37°. Protein and unchanged (I) were removed, and fractions were separated by pptn. with EtOH (A) and EtOH-Et₂O (B), and the residue was conc. (C). The $[\alpha]_D$ and reducing power before and after hydrolysis, and the mol. wt. of the Ac products of the fractions were determined. A and B were predominantly disaccharide whilst C contained more monosaccharide. H. D.

Hydrolysis of glycogen by muscle and liver extracts. A. CARRUTHERS (J. Biol. Chem., 1935, 108, 535—545).—Oyster and rabbit-liver glycogen (I) are hydrolysed by dialysed (II) and undialysed glycerol extracts (III) of rabbit muscle at 37° and the course of hydrolysis is followed by (I) and sugar determinations. The hydrolysis products (IV) with (II) have reducing powers > those with (III). (II) hydrolyses maltose, the reaction being inhibited by glycerol. The (IV) of (I), maltose, and glucose all inhibit the amylase activity of (II). Complete conversion of (I) into glucose is possible only when small amounts of (I) are present in the reaction mixture. H. D.

Amylosynthase. XXI—XXIII. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 379—381, 382—387, 388—392).—XXI. After pptn. of yeast extract by FeSO₄, Fe₂(SO₄)₃, and Al₂(SO₄)₃, amylosynthase (I) was reactivated by (NH₄)₂SO₄ from the FeSO₄ filtrate and the Al₂(SO₄)₃ ppt. (I) was damaged by addition of Cr alum. K alum and Fe alum ppt. (I) incompletely. The ppts. have the action of (I). The enzyme action could not be reactivated by (NH₄)₂SO₄. On dissolving pancreatin in H₂O, pptg. with (NH₄)₂SO₄, and repptg. with EtOH, the ppt. lost its amylase action but retained its accelerating effect on barley amylase.

XXII. The nature and concn. of substrate (glucose polyanhydrides), p_H , and temp. affect the reaction velocity of (I).

XXIII. The ppt. obtained from yeast extract with 10% EtOH has an accelerating action on (I); that obtained with 95% EtOH has only the action of a complement of amylase. Although glutathione and cysteine accelerate amylase action they retard the action of (I). H₂S is toxic; a very small quantity of H₂O₂ is favourable, but > 0.03% retards the action. (I) treated with conc. H₂O₂ is easily reactivated by dilution. CH. ABS.

Water relations of enzymes. I. Influence of viscosity on invertase action. Z. I. KERTESZ (J. Amer. Chem. Soc., 1935, 57, 345—347).—The rate (r) of hydrolysis of sucrose by invertase is unaffected by high viscosity caused by addition of citrus pectin, contrary to the theory of Colin *et al.* (A., 1929, 722), whose data are open to objection. The effect of temp. on r is not correlated with η . R. S. C.

Cholesterol and cholic acid in lung autolysis. GATTI Soc. ital. Biol. sperim., 1934, 9, 940—941. —Cholesterol (I) shows an initial rise, and afterwards oscillates over a range of vals. > normal.

Cholic acid shows an initial fall, and generally behaves inversely to (I). R. N. C.

Autolysis of algæ. B. ALEEV (Biochem. Z., 1935, 276, 55—56).—Pure cultures of *Pediastrum boryanum* (I) and *Kirchneriella lunaris* (II) are allowed to autolyse at 37° in physiological saline under PhMe, and the increase of residual and NH₂-N is determined. Proteinase activity is greater with (II) and the optimum p_H for proteinase of (I) is 6.

P. W. C.
Dilatometric determination of the relative digestibility of proteins. H. B. SREERANGACHAR and M. SREENIVASAYA (Biochem. J., 1935, 29, 291—294).—The course of the digestion by trypsin of the globulins of *Phaseolus mungo* and *Dolichos lablab* are followed by the dilatometric (I) and the Van Slyke methods. In both cases the (I) depression \propto the increase in NH₂-N. A. L.

Protein structure and synthetic substrates for proteases. K. SHIBATA (Acta Phytochim. Japan, 1934, 8, 173—178).—Neutral diketopiperazines (I) are not attacked by trypsin (II) or pepsin (III), but those having a $\cdot\text{CO}_2\text{H}$ are hydrolysed by (II), and those with free $\cdot\text{NH}_2$ by (III). Glycylamino- and diamino-propionic anhydrides were hydrolysed by (III). The existence of (I) groups in the protein mol. is indicated. CH. ABS. (p)

Application of quantum mechanics to certain cases of homogeneous catalysis. II. Enzyme action. A. E. STEARN (J. Gen. Physiol., 1935, 18, 301—306).—From a consideration of the effect of foreign rigid dipoles (cf. this vol., 43) on the energy of an activated configuration (I) of the atoms involved in the reaction $\text{:C:N:} + \text{H}_2\text{O} \rightleftharpoons \text{:C:OH} + \text{:NH}$ (e.g., hydrolysis of a peptide linking), the dipole effects and lowering of activation energy are obtained for acidic and alkaline reactions, a dipole distance of 0.3 μ being assumed. Under such arbitrary conditions, the lowering of the potential energy of (I) would result in an increased reaction velocity of 6- to 4700-fold at room temp. The data indicate that groups found in ordinary proteins may be capable of active catalysis if suitably placed with respect to the reacting substrate. F. O. H.

Reabsorption of pancreatic enzymes after ligation of the ducts. E. MILLA (Boll. Soc. ital. Biol. sperim., 1934, 9, 835—847).—Serum- and urinary amylase rise to a max. 24—36 hr. after ligation, returning steadily to normal after 10—15 days. Injection of secretin produces a similar rise. Serum-maltase and insulin secretion are unaffected. The increase is the result of the reabsorption of the pancreatic juice and its passage into the serum. R. N. C.

Digestive enzymes in cattle. M. SALVIETTI (Riv. Biol., 1932, 14, 64—77; Bied. Zentr., 1934, A, 5, 3).—Pepsin and chymase occur only in the abomasum (I), the former decreasing in concn. from the entrance of the omasum (II) toward the pylorus. Lipases occur in all stomach divisions in amounts which decrease from (II) towards (I), proportions in the rumen (III) and reticulum (IV) being small. The amylase concn. is highest in (II), declining in the

order, (III), (I), and (IV) (nil). Invertase is similarly distributed. A. G. P.

Purification, specificity, and inhibition of liver-esterase. Z. BAKER and C. G. KING (J. Amer. Chem. Soc., 1935, 57, 358—361).—A simple method of concentrating this enzyme is described. The product has the properties of an albumin; the Et butyrase is distinct from other esterases. Inhibition by a no. of substances changes from a competitive to a non-competitive type with increasing concn. R. S. C.

Factors influencing the activity of fungus-lipase. D. KIRSH (J. Biol. Chem., 1935, 108, 421—430).—The H₂O-sol. lipase of *Penicillium oxalicum* (I) and of *Aspergillus flavus* is most active at p_H 5.0, but is very unstable in aq. solution at this p_H . (I)-lipase is highly non-sp., is activated by CaCl₂ (but inhibited by chicken- and ox-bile), and does not follow the Schutz law. A. E. O.

Mammalian lipins. IX. Enzymic fission of liver-polydiaminophosphatide. A. ROSSI (Z. physiol. Chem., 1935, 231, 115—124).—The rates of hydrolysis of polydiaminophosphatide by various phosphatase preps. differ widely from the rates shown on glycerophosphate or lecithin substrates. The best prep. was a NaCl extract of dried powdered spleen. The activity was doubled in presence of 0.026 mol. of Mg salts (I) per litre. Bile acid salts (II) also increase the activity, which is further enhanced by the combination of (I) and (II). PO₄''' or AsO₄''' inhibit completely. J. H. B.

Phosphatase of pig's kidney. H. KOSTER and T. BERSIN (Z. physiol. Chem., 1935, 231, 153—156).—Glutathione has no effect on the phosphatase; thio-lactic and dithiodilactic acids inhibit only slightly. Various oxidising agents are almost without action. J. H. B.

Phosphatase in blood and urine. E. WALDSCHMIDT-LEITZ and W. NONNENBRUCH (Naturwiss., 1935, 23, 164).—In urine only the acid phosphatase (I) (p_H optimum 5—6) is found. (I) also predominates in blood. (I) is associated with the red corpuscles as only slight phosphatase activity is found in serum. The (I) found in organs may be due to the erythrocytes present; the alkali phosphatase would then be the one peculiar to the organ. (I) in the urine is probably derived by dissolution of the erythrocytes. E. A. H. R.

Phosphatases. Influence of some electrolytes on the phosphatases of animal tissue. Phosphatases of the liver, kidney, serum, and bones of the rabbit. S. BELFANTI, A. CONTARDI, and A. ERCOLI (Biochem. J., 1935, 29, 517—527).— p_u -activity curves of rabbit-liver and -kidney phosphatase indicate the existence of an "acid" phosphatase (I) (max. activity at p_H 4.5) and an "alkaline" phosphatase (II) (max. activity at p_H 9.5). NaF (III) and Na₂C₂O₄ (IV) inactivate (I) but not (II). In bone and serum extracts the activity due to (I) is very small and (II) is partly inhibited by (IV) but not by (III). E. A. H. R.

Phosphatase. H. VON EULER (Svensk Kem. Tidskr., 1935, 47, 16—25).—A review. E. A. H. R.

Unicellular chemistry. Part played by external influences in determining chemical character and biological behaviour of unicellular organisms. J. V. EYRE (J.C.S., 1935, 201—207).—A lecture. F. O. H.

Velocity of alcoholic fermentation. L. S. ORNSTEIN and J. W. MEYER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 12—24).—The kinetics of the alcoholic fermentation process are discussed with the help of data for the rate of evolution of CO₂. Four characteristic consts. are involved. The same principles can be applied to all cases where an organism forms a substance which limits its activity. M. S. B.

Enzymic decomposition of sugar to carbon dioxide, alcohol, and lactic acid, with intermediate formation of triose (or triosephosphoric acid). A. N. LEBEDEV (Bull. Acad. Sci. U.R.S.S., 1934, 1291—1297).—Earlier work is summarised. New work on the fermentation of sucrose by distillery yeast shows the formation of triose, AcCO₂H, CO₂, glycerol, EtOH, and MeCHO. T. H. P.

Influence of alkali cations on the fermentation capacity of yeast. A. LASNITZKI and E. SZORENYI (Biochem. J., 1935, 29, 580—587).—The rate of anaerobic fermentation of glucose by living yeast (measured by CO₂ production) is markedly increased by RbCl or KCl (0.01M), less markedly by NaCl or CsCl, whilst the effect of LiCl is slight. These effects, especially with CsCl, are quantitatively somewhat variable. MgSO₄ or MgCl₂ (0.02M) exerted no significant effect. W. O. K.

Combined action of monochromatic light and photodynamic substances on the fermenting power of *Saccharomyces cerevisiae*. G. GUERRINI (Boll. Soc. ital. Biol. sperim., 1934, 8, 816—820).—The stimulant and inhibitory actions of photosensitive dyes (I) on the fermenting power of *S. cerevisiae* are augmented by monochromatic light, the augmentation increasing with λ . The actions of (I) are independent of the positions of their absorption bands. R. N. C.

Irradiation of *Saccharomyces* with monochromatic ultra-violet light. IV. Relation of energy to observed inhibitory effects. R. H. OSTER and W. A. ARNOLD (J. Gen. Physiol., 1935, 18, 351—355; cf. A., 1934, 1262).—Variations in the inhibition (I) of cell division of yeast irradiated with monochromatic ultra-violet light indicate, when analysed by Curie's method (A., 1929, 357), that the degree of (I) or killing is related to the no. of "quantum hits." F. O. H.

Detection of volutin in living yeast cells by neutral-red. R. HEUCKE and W. HENNEBERG (Zentr. Bakt. Par., 1934, II, 90, 425—427).—A staining technique is described. A. G. P.

(A) Growth factor from wheat germ: extraction by lead acetate: action on a fungus. (B) Crystallised vitamin-B as a growth hormone for micro-organisms (*Phycomyces*). W. H. SCHOPFER (Arch. Mikrobiol., 1934, 5, 502—510, 511—549).—(A) A growth-promoting substance stimulating the

development of *Phycomyces* (I) is isolated from wheat germ and from rice polishings.

(b) Normal development of (I) is impossible in purely synthetic media. Addition of vitamin- B_1 induces rapid growth, which increases with the supply of N. The action of $-B_1$ is optimum at p_H 7.0–7.2, is unaffected by heating at 135°, but is much reduced by autoclaving with alkali. Neither $-B_1$ nor $-B_2$ affects alcoholic fermentation by *Saccharomyces cerevisiae*. A. G. P.

Metabolism of *Fusarium lycopersici* and *F. lini*. G. LUZ (Phytopath. Z., 1934, 7, 585–638).—In culture media with NH_4NO_3 as N source, growth of the organisms is marked by four phases of reaction change, viz., an initial change of p_H 3.9–3.5 characterised by the production of org. acids, followed by a phase of increasing alkalinity (to p_H 7.5) coinciding with preferential intake of NO_3-N , a third phase of slight acidification (p_H 7.5–7.2) in which intake of NH_4-N predominates, and a final stage in which, with exhaustion of sugars, the org. acids are slowly utilised and p_H rises to 8.5. The growth curve shows a point of inflexion corresponding with a decrease in ash contents of the mycelium and the completion of sugar utilisation. Subsequently EtOH is the principal source of C. The change of C source corresponds with the change of N source. Metabolic products of the organisms include volatile and non-volatile org. acids, EtOH as an intermediate product from sugars, but no aldehyde. These changes are discussed in relation to wilt disease of flax (see this vol., 554). A. G. P.

Culture methods for fungi. J. L. HARLEY (New Phytol., 1934, 33, 372–385).—The absorption and release of substances by fungi may involve very considerable changes in the composition of the medium. A p_H gradient is set up from the centre of the culture extending outwards. Increased alkalinity due to absorption of NO_3^- from media results in pptn. of K, Mg, and PO_4^{3-} and formation of additional HCO_3^- . Intake of sugar by *Neocosmospora* is inhibited by high acidity developing in NH_4 salt media. The influence of these changes on results of biochemical and physiological investigations of fungi considered. A. G. P.

Influence of calcium on the growth of micro-organisms. U. STOEß (Diss., Göttingen, 1932; Bied. Zentr., 1934, A, 5, 136).—An abs. need of Ca by some micro-organisms cannot always be demonstrated. Fungi which react favourably to Ca are those which are sensitive to injury by small dosages of Mg. The corrective action of Ca on Mg injury is explained by colloidal phenomena. Sr can, at least partly, replace Ca in this respect. A. G. P.

Metallic mixtures as co-catalysts of growth of moulds. N. NIELSEN and V. HARTELIUS (Biochem. Z., 1935, 276, 183–185).—A mixture of the chlorides of Ba, Be, Hg, Cr, Ca, Zn, Cd, Cu, Mn, Co, and Li is a more powerful co-catalyst of growth on *A. niger* than an HCl extract of filter-paper (cf. A., 1932, 661; 1933, 189, 638, 1205). The mixture contains most of these metals. The metals are for the most part individually inactive. P. W. C.

Physiological action of elements on the growth of *Aspergillus niger*. (Stimulation and toxicity.) K. PIRSCHLE (Planta, 1934, 23, 177–224).—The effects of Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Ba^{++} , Sr^{++} , Ca^{++} , Be^{++} , Mg^{++} , Cu^{++} , Cd^{++} , Hg^{++} , Ag^+ , Au^{+++} , Cl^- , Br^- , I^- , F^- , ClO_3^- , BrO_3^- , IO_3^- , and IO_4^- in various concns. on the growth and spore production of the organism are determined. A. G. P.

Importance of potassium in the metabolism of *Aspergillus niger*. A. RIPPEL (Arch. Mikrobiol., 1934, 5, 561–577).—In K-deficient media, *A. niger* stores NH_3 in the mycelium, produces $H_2C_2O_4$ (I) in the substrate, and exhibits a lowered sugar economy coeff. The influence of K on carbohydrate metabolism is discussed. Cultures of strains freely producing (I) contain > those producing small amounts of (I). A. G. P.

Chemistry of mould tissue. VII. Lipins of *Penicillium aurantiobrunneum*. E. H. KROEGER, F. M. STRONG, and W. H. PETERSON (J. Amer. Chem. Soc., 1935, 57, 354–356; cf. this vol., 255).—The mould contains ergosterol and lipins, from which by hydrolysis are obtained palmitic, stearic, oleic, and linolenic acids. R. S. C.

Production of fat by *Penicillium javanicum*, var. *Beijma*. L. B. LOCKWOOD, G. E. WARD, O. E. MAY, H. T. HERRICK, and H. T. O'NEILL (Zentr. Bakt. Par., 1934, II, 90, 411–425).—In cultures of *P. javanicum*, the wt. of mycelium increased steadily for 60 days, but max. yields of fat (I) and max. titratable acidity in the media occurred at approx. 20 days. The optimum sugar concn. for mycelial growth was 20%, but highest (I) yields were obtained with 30% sugars. The effects of various nutrient materials and of toxic ions on the organism are recorded. Fermentative actions on a no. of sugars, org. acids, and alcohols are examined. A. G. P.

Metabolism of protozoa. I. Nitrogenous metabolism and respiration of *Bodo caudatus*. N. R. LAWRIE (Biochem. J., 1935, 29, 588–598).—In cultures of *B. caudatus* (I) feeding at 25° on living resting bacteria, the rate of NH_3 formation during the first 8 hr. approx. \propto the no. of (I) present. From about the 8th to the 26th hr. the NH_3 formation increases less rapidly or even becomes approx. const., although the nos. continue to increase rapidly. Up to the 16th–18th hr. the O_2 uptake increases \propto the no. of (I) in the culture but it then begins to fall although the no. continues to increase. W. O. K.

Chemotherapy of protozoa. E. FOURNEAU (Chem. Weekblad, 1935, 32, 90–100).—A lecture. F. O. H.

Numerical distribution of micro-organisms in the atmosphere. A. S. HORNE (Proc. Roy. Soc., 1935, B, 117, 154–174).—Results obtained by the plate method (chiefly in orchards) treated by Fisher's statistical procedure indicate that bacteria and fungi are distributed at random in the atm. W. McC.

Photometric studies on the multiplication of bacteria. M. FAGUET (Compt. rend., 1935, 200, 498–500; cf. A., 1932, 545, 779).—The proportion

of the incident light passing through a simple optical system which is scattered by cultures of bacteria is measured by means of a photo-electric cell and gives a measure of the ρ of the bacterial population. Each strain has a different rate of multiplication, which is not significantly affected by the intensity of the light.

J. L. D.

Growth of bacteria in organic acid media.

W. F. BRUCE (J. Amer. Chem. Soc., 1935, 57, 382).—Certain bacteria can use as sole source of C the Na salts of AcOH, $\text{Pr}^n\text{CO}_2\text{H}$, $\text{Pr}^i\text{CO}_2\text{H}$, lactic, glyceric, and α -hydroxyacrylic acid, alanine, and, very feebly, glyceric, glycollic, and β -hydroxy-*n*-butyric acids, but not HCO_2H , $\text{CH}_3\text{C}(\text{CO}_2\text{H})_2$, EtCO_2H , α -hydroxyisobutyric or α -amino-*n*-butyric acid. Regularities concerning chain-length are pointed out.

R. S. C.

Methionine as an impurity in natural leucine preparations. J. H. MUELLER (Science, 1935, 81, 50—51).—S determinations indicate the presence of considerable amounts of methionine in commercial leucine preps. This affects the data obtained on the growth of diphtheria bacilli.

L. S. T.

Toxaemia and carbohydrate metabolism.

A. B. CORKILL and S. OCHOA (J. Physiol., 1934, 82, 399—406).—Injection of young rabbits with diphtheria toxin does not appear to affect the normal breakdown of muscle-glycogen to lactic acid, but the liver is unable to resynthesise glycogen from lactate.

R. N. C.

Diphtheritic pseudoglobulin and toxin-antitoxin flocculate. L. VELLUZ (Compt. rend. Soc. Biol., 1935, 118, 745—747).—The flocculate is chemically similar to pseudoglobulin.

R. N. C.

Recovery of diphtheria antitoxin coagulated by the toxin by means of the sodium salts of aminonaphthalenetrisulphonic acid. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 118, 220—223).—Addition of $\text{NH}_2\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{Na})_3$ and citric acid to bring the p_H to 4—5, or of $\text{NH}_2\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})(\text{SO}_3\text{Na})_2$, alone, to dil. antidiphtheria serum ppts. the globulins (I) together with the antitoxin (II), without destroying its neutralising power. The same salts, added to the toxin-(II) coagulate, ppt. (I) and (II), leaving the toxin in solution more or less changed, together with the albumins, part of (I), sol. N compounds and their salts. Similar results are obtained with the "ana-toxin"-(II) coagulate. (II) thus recovered retains most of its activity, but its stability and its avidity for the antigen are decreased. The toxin when separated from the complex is extremely labile.

R. N. C.

Staphylococcus toxoid. D. S. MURRAY (Lancet, 1935, 228, 303—306).—The amount of circulating staphylococcal antitoxin in normal cases is not greatly different from that in cases where chronic superficial lesions occur. It can readily be increased by the injection of staphylococcus toxoid.

L. S. T.

Coccidioides immitis, Stiles. IV, V. Cultural, biochemical, pathogenic, and micromorphological characteristics *in vivo* and *in vitro* of typical and degraded strains. R. CIFERRI and P. REDAELLI (Boll. Soc. ital. Biol. sperim., 1934, 9, 961—962, 963—964).

R. N. C.

Behaviour towards acids of coliform bacteria occurring on green plants. G. RUSCHMANN and W. MEYER (Arch. Mikrobiol., 1934, 5, 477—501).—The effects of changes of p_H on the activity of these organisms (I) are examined with special reference to their survival during the ensilage of green fodder. In general mineral acids are less inhibitory than org. acids [except lactic acid (II)], HCl and H_3PO_4 are tolerated to p_H 4.5—5.0, HNO_3 , H_2SO_4 , (II), and tartaric acid to 5.0—5.5, $\text{H}_2\text{C}_2\text{O}_4$, HCO_2H , and AcOH to 5.5—6.5, and PrCO_2H to 6.0—6.5. The limit of viability of (I) in (II) or AcOH is higher if the acids are of microbiological origin, e.g., by fermentation of sugar or EtOH.

A. G. P.

Oxidation-reduction potentials and ferricyanide-reducing activities. (A) In peptone cultures and suspensions of *Escherichia coli*. C. E. CLIFTON, J. P. CLEARY, and P. J. BEARD. (B) In glucose-peptone cultures and suspensions of *E. coli*. C. E. CLIFTON and J. P. CLEARY (J. Bact., 1934, 28, 541—560, 561—569).—(A) The oxidation-reduction potential (I) in peptone (II) cultures of *E. coli* declines during the period of rapid growth and a max. reduction potential occurs in or near the max. stationary growth period. (I) is probably the resultant of the metabolic activities of the cells.

(B) The initial fall in (I) is more marked in glucose (III)-(II) cultures. Maltose, (III), and lactose are readily oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ in suspensions of resting *E. coli*. The ability of the organisms to use these sugars decreases with the E_h of the oxidant.

A. G. P.

Nodule bacteria of *Astragalus sinicus*, Genge. III. Fermentation of carbohydrates with special reference to the carbon and nitrogen source. A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1934, 6, 341—369).—The ability of the organisms to ferment carbohydrates varied in the order, arabinose (I), xylose (II), glucose (III), galactose (IV), mannose (V) > fructose (VI), sucrose, mannitol > lactose, maltose > raffinose and dextrin. The suitability of these C sources for growth, however, was in the order, (III), (V), (VII), (II), (VI) > (I), (IV), the remainder producing no satisfactory growth. A N source is not necessary for growth but is required for fermentation, NH_4^+ , NO_3^- , and peptone being effective in this respect.

A. G. P.

Cholesterol and reduced glutathione contents in the blood of rabbits immunised with typhoid bacilli. F. MURATA (Sei-i-Kwai Med. J., 1933, 52, 46—57).—Data for normal, splenectomised, and immunised rabbits are given.

CH. ABS. (p)

Fission by bacteria of inorganic complex salts and the use of these salts in differential media. F. SANDER (Zentr. Bakt. Par., 1934, I, 132, 465—470).—Decomposition of various complex ferrocyanides in the presence of carbohydrates is followed by colour changes in the media and serves to characterise various strains of typhoid bacteria.

A. G. P.

Sodium nitroprusside as a means of differentiating the paratyphoid group of organisms. R. HÖFFLING (Zentr. Bakt. Par., 1934, I, 133, 113—121).—Addition of nitroprusside to carbohydrate

media permits differentiation between the principal types of the paratyphoid group in fermentation reactions.

A. G. P.

Metabolism of the strict anaerobes. II. Reduction of proline by *Cl. sporogenes*. L. H. STICKLAND (Biochem. J., 1935, 29, 288—290).—Washed suspensions of *Cl. sporogenes* reduce *l*-proline at the expense of the oxidation of alanine to δ -amino-*n*-valeric acid.

A. L.

Anaerobic decomposition of plant materials. I. Rice straw (*Oryza sativa*). C. N. ACHARYA (Biochem. J., 1935, 29, 528—541).—The anaerobic fermentation of rice straw yields AcOH (I), butyric acid (II), CH₄, and CO₂. The ratio CO₂/CH₄ is approx. 1, indicating that these gases are formed by the decomp. of (I) and (II), and that CH₄ is not formed by the reduction of CO₂ with H.

E. A. H. R.

Products of bacterial oxidation of thiosulphate in inorganic media. R. L. STARKEY (J. Gen. Physiol., 1935, 18, 325—349).—Bacteria oxidising S₂O₃²⁻, grown in media containing inorg. salts (I) and Na₂S₂O₃ at *p*_H 7.8, yield primarily Na₂S₄O₆ and NaOH (increasing the *p*_H); secondary reactions give S₃O₆²⁻, S₃O₆³⁻, SO₄²⁻, and S (decreasing the *p*_H of the medium). *Thiobacillus novellus* oxidises Na₂S₂O₃ to Na₂SO₄ and H₂SO₄, the *p*_H diminishing steadily with growth and oxidation; the ratio SO₄-S: assimilated C=56:1. With *Th. thioparus*, S is also formed (SO₄:S=3:2), whilst S₂O₃-S oxidised: C assimilated=125:1; org. compounds are synthesised from (I).

F. O. H.

Dissociation of *Mycobacterium tuberculosis*. II. K. E. BIRKHAUG (Ann. Inst. Pasteur, 1935, 54, 195—244).—Varieties of avian, bovine, and human tubercle bacilli differ in their assimilation of carbohydrates, resistance to the bacteriostatic action of dyes and disinfectants, cataphoretic migration, *p*_H of agglutination, acid-resistance, and virulence.

F. O. H.

Differences between mammalian tubercle bacilli, paratubercle bacilli, and *Streptothrix*, revealed by the comparative toxicities of sulphuric and acetic acids. A. SAENZ, M. SADETTIN, and L. COSTIL (Compt. rend. Soc. Biol., 1935, 118, 215—217).—Human tubercle bacilli are destroyed by 5% AcOH, but not by 20% H₂SO₄. Paratubercle bacilli are destroyed by 10% H₂SO₄ or AcOH, whilst 5% AcOH permits very slight growth. *Streptothrix* and *Nocardia epingieri* are destroyed by 5% AcOH or H₂SO₄.

R. N. C.

Microbial agglutination and lysis of bacteriophage. V. SERTIC (Compt. rend. Soc. Biol., 1935, 118, 780—781).—Agglutination occurs only with the lysin-secreting bacteriophages.

R. N. C.

Chemotherapy. XI. Trypanocidal titre of rabbit serum after intravenous injection of various compounds of arsenic. F. MURGATROYD, H. SELL, and W. YORKE (Ann. Trop. Med., 1934, 28, 227—242).—Arsenobenzene (I) and As^{III} compounds (II) confer an immediate and very high trypanocidal titre which \propto the dosage. The subsequent decline is much more rapid for (II) than for (I). As^V compounds produce a small action, increas-

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ing steadily, but final vals. are much < those for (I) and (II).

A. G. P.

Relative efficiencies of germicidal [dental] cements. T. J. HILL (J. Amer. Dental Assoc., 1934, 21, 1565—1571).

CH. ABS. (p)

Influence of certain quinoline derivatives on growth [of bacteria]. FROM and MONCHOT (Compt. rend., 1935, 200, 485—487).—8-Hydroxyquinoline (I) in concns. < 0.0005*N* (optimum concn. is 0.00005*N*) in soil causes *Azotobacter* colonies to proliferate. Concns. > 0.0005*N* retard development. Concns. of (I) which benefit the bacterial colonies do not increase the fertility of the soil because (I) is toxic.

J. L. D.

Sterilising power of neutral 8-hydroxyquinoline sulphate (sunoxol) on cultures of pathogenic bacteria. A. MOREL, A. ROCHAIX, F. DENARD, L. PERROT, and C. DESSAIGNES (Compt. rend. Soc. Biol., 1935, 118, 257—260).—The min. toxic concns. are given for a no. of bacilli.

R. N. C.

Long wave-length limit of photolethal action in the ultra-violet. A. C. GIESE and P. A. LEIGHTON (Science, 1935, 81, 53—54).—*Paramecium multimicronucleata* are vesiculated by a dosage of 33,000 ergs per mm.² at 3025 Å. A dosage of 16,500 ergs per mm.² kills the *Paramecia* 24 hr. after irradiation. At 3130 Å., however, no injury results from irradiation with dosages much > those which are fatal at 3025 Å.

L. S. T.

Influence of ultra-violet rays on the physiological activities of *Azotobacter*. I. Lethal action on *A. chroococcum*. A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1934, 6, 383—392).—Exposure of the bacteria to radiation from a Hg lamp, in vessels of varying transmission rates, was injurious except in the case of brief exposures in quartz and hard glass flasks. A stimulative effect resulted in these instances.

A. G. P.

Action of soft X-rays on bacteria. B. S. LEVIN and I. LOMINSKI (Compt. rend., 1935, 200, 863—865).—Exposure of many strains of bacteria, previously cultured for 18 hr.—8 days, to soft X-rays during 1 sec. to 10 min. prevents their further development. Acid-resisting and sporulating bacilli are least affected, whereas Gram-negative bacilli are very sensitive. A lethal or sub-lethal dose causes morphological and cytological variations; the latter are followed by a latent period (up to 5 days) during which no development occurs.

J. L. D.

Action of liver extract on blood-calcium and -phosphorus. J. A. COLLAZO and A. S. RUIZ (Anal. Fis. Quim., 1934, 32, 173—185).—Intramuscular injection of liver extract (I) has a "tetanogenic" effect on the serum (II) of dogs, lowering the total Ca by 3.17 mg. per 100 c.c. (normal 10.6 mg.), lowering the Ca by 0.039 mg. per 100 c.c. (normal 2.156 mg.), raising the P by 0.45 mg. per 100 c.c. (normal 3.07 mg.) of (II), and raising the total CO₂ by 14 vols. per 100 c.c. (normal 58 vols.) of plasma. The blood-*p*_H is lowered from 7.42 to 7.34. Intravenous injection of (I) has a similar effect on rabbits.

F. R. G.

Detoxicating hormone of the liver (yakriton). XLIX. Effect of yakriton on a negative Arakawa reaction. L. Effect in counteracting cardiac dilation. LI. Effect on the chloride content of blood. A. TAKAMATSU (Tôhoku J. Exp. Med., 1934, 23, 372—380).—XLIX. Milk from a woman inadequately supplied with vitamin-B gave a negative Arakawa reaction and contained a toxic substance resembling AcCHO. The latter disappeared after injection of yakriton (I) alone or supplemented with dietary vitamin-B.

LI. Injection of (I) maintained blood-Cl const. in rabbits despite intraperitoneal injection of 10% aq. NaCl. CH. ABS. (p)

Function of nephrohormone in regulating blood- and urinary chloride. K. ISHIDA (J. Chosen Med. Assoc., 1934, 24, 525—548).—Renal venous blood contains a substance (I) capable of lowering the blood-Cl in rabbits and accelerating urinary excretion of Cl. The (I) does not occur if tubules are damaged by ligation or by injection of $K_2Cr_2O_7$, but is present if only glomeruli are damaged by cantharidin. CH. ABS. (p)

Relation of nephrohormone to blood-calcium. H. MIYAZAKI and Y. SATO (J. Chosen Med. Assoc., 1934, 24, 1015—1026).—The renal nephrohormone decreases serum-Ca in normal and increases that of hypocalcaemic animals. CH. ABS. (p)

Response of the canine and human pancreas to secretin. W. L. VOEGTLIN, H. GREENGARD, and A. C. IVY (Amer. J. Physiol., 1934, 110, 198—224).—Secretin is extracted from pigs' duodena with 0.4% HCl, pptd. with NaCl, extracted with EtOH, freed from proteins by isoelectric pptn. at p_H 5.4, and pptd. with $CCl_3 \cdot CO_2H$. The dry ppt. is dissolved in HCl and impurities are pptd. with $COMe_2$ and NH_2Ph , which are then removed by evaporation and the secretin is extracted with MeOH and pptd. with Et_2O . The product contains C, H, N, and Cl (ionisable), but no S. Intravenous injection in the dog and in man produces no consistent increase in the concn. of the enzymes of the pancreatic juice, but the enzyme production per min. is almost always increased during the first 15 min. following injection. The d of the juice generally shows a slight increase. In man, repetition of the test on the same individual does not produce strictly const. results. R. N. C.

Glucose content of blood from the femoral artery and vein during hypoglycaemia provoked either by secretin or by incretin. J. LA BARRE and J. LEDRUT (Compt. rend. Soc. Biol., 1935, 118, 797—799).—In dogs injected with secretin or incretin arterial blood-sugar (I) is > venous (I) throughout the hypoglycaemia; both have the same val. in controls. R. N. C.

Effect of callicrein on diuretin hyperglycaemia. H. HERLING (Z. ges. exp. Med., 1934, 94, 99—100; Chem. Zentr., 1934, ii, 2409).—Callicrein does not necessarily lower the hyperglycaemia produced by diuretin, but it checks the increase of blood-sugar under certain conditions. R. N. C.

Effect of insulin on blood-lactic acid. I. FRIESZ and E. MOHOS (Orvosi Hetilap, 1934, 78,

907—908).—Injection of 20 units of insulin into non-diabetic subjects was followed by a rise in blood-lactic acid, the average vals. being 8.2 mg. per 100 ml. before and 13.3 mg. 2 hr. after the injection.

NUTR. ABS. (b)

Effect of insulin on the immediate deposition of absorbed carbohydrate and fat in the organism. H. SCHUR, A. LOW, and A. KRÖMA (Wien. Arch. inn. Med., 1934, 25, 203—210).—Insulin favours the deposition of fat from fat or sugar, hinders the deposition of carbohydrate (I) from (I), accelerates the lowering of (I) in the liver following fat ingestion, and favours the deposition of (I) following fat in the omentum. NUTR. ABS. (m)

Effect of insulin on the excretion of allantoin by the normal dog. P. S. LARSON and I. L. CHAIKOFF (J. Biol. Chem., 1935, 108, 457—462).—Excretion of allantoin is greatly increased without alteration of urine vol. A. E. O.

Blood-sugar in "heat-stroke" under the influence of insulin. D. DI MACCO (Boll. Soc. ital. Biol. sperim., 1934, 9, 1009—1010).—The hypoglycaemia produced by insulin in guinea-pigs with hyperthermia is > that of control animals without insulin. R. N. C.

Muscle chemistry and insulin. S. GRZYCKI (Klin. Woch., 1934, 13, 1089—1090; Chem. Zentr., 1934, ii, 2409).—Occasional muscular weakness with haemoglobinuria in horses after prolonged exertion is improved by injection of insulin. During the attacks blood-lactic acid, sugar, and particularly creatine and PO_4''' are increased. R. N. C.

Action of insulin and adrenaline in young adrenalectomised rabbits. O. COPE and A. B. CORKILL (J. Physiol., 1934, 82, 407—413).—Young adrenalectomised rabbits injected with insulin (I) fail to show any deposition of liver-glycogen as compared with normal animals. This effect is the result of hypoglycaemic convulsions rather than of (I). Glycogen deposition occurs when adrenaline (II) and (I) are administered together, or (II) alone, in absence of cortical deficiency. R. N. C.

Destructive action of erythrocytes on insulin. F. ROSENTHAL, I. FRIEDHEIM, and R. NAGEL (Klin. Woch., 1934, 13, 1121—1124).—Insulin is inactivated by haemolysed erythrocytes (I) but not by plasma or stroma. (I) lose this power on heating for 1 hr. at 70°. NUTR. ABS. (m)

Biological standardisation of adrenal cortex hormone. C. BOMSKOV and K. BAHNSEN (Arch. exp. Path. Pharm., 1935, 178, 1—14).—Adrenal cortex preps. are standardised by their action on the survival period of young adrenalectomised mice (7—11 g. in wt.), a "corticodynamic mouse-unit" being defined as the min. dose necessary to maintain the survival of 80% of such mice for 8 days after daily injections. The average error is ± 25 , 20, and 15% when 5, 10, and 35 mice, respectively, are used. Fresh ox adrenal glands (1 kg.) yield 40.5 mg. of a prep. (method of Swingle and Pfiffner; B., 1933, -0a) which on purification by repeated extraction from aq.

solution by Et_2O and *vice versa* at various $[\text{H}^+]$ affords a prep. of which 2×10^{-5} g. is a mouse-unit.

F. O. H.

Standardisation of extracts of the adrenal cortex. R. MENDEZ (Quart. J. Pharm., 1934, 7, 641—644).—The mortality in adrenalectomised rats varies so largely that it is impossible to use the survival period after injecting cortical extract (I) as a basis for standardisation. Injection of an active (I) maintains the life of orchidectomised and adrenalectomised rats, the mortality among which is normally 100%.

A. E. O.

Relation of the adrenal cortical hormone to vitamin- B_1 , -C, and - B_2 . W. M. FIROR and A. GROLLMAN (Amer. J. Physiol., 1934, 109, 35).—Removal of the ascorbic acid (I) present in adrenal cortical preps. did not influence their life-prolonging effects on adrenalectomised animals, and such effects were not produced by (I) alone. The adrenal cortical hormone had no activity in experimental avitaminosis- B_1 or - B_2 of rats.

NUTR. ABS. (b)

Adrenal cortex hormone (cortin) and sex apparatus. J. FREUD and F. OESTREICHER (Acta Brev. Neerl. Physiol., 1933, 3, 82—83; Chem. Zentr., 1934, ii, 2407).—Injection of cortin (I) together with the anterior pituitary sex hormone (II) produces a more marked growth of the preputial glands (III) than (II) alone. The (III): seminal-vesicle wt. ratio is altered in favour of (III) by (I) or (II), and to a higher degree by the two combined.

R. N. C.

Behaviour of adrenalectomised rats with and without cortin in a running-wheel. R. KOOY (Acta Brev. Neerl. Physiol., 1933, 3, 114—115; Chem. Zentr., 1934, ii, 2408).—The performance of adrenalectomised rats in the running-wheel is increased considerably within 24 hr. by injection of cortex extract; the increase \propto the amount injected.

R. N. C.

Adrenalinuria (Viale reaction) in physiological conditions. F. DOMENICI (Boll. Soc. ital. Biol. sperim., 1934, 9, 908—910).—In normal subjects adrenaline is present in fresh urine in small concns., but disappears on keeping 72 hr.

R. N. C.

Comparative action of adrenaline and p - t -sympatol. B. BEHRENS and H. TAEGER (Arch. exp. Path. Pharm., 1935, 178, 64—85).—An investigation of the pharmacology of adrenaline and 'sympatol' (β -hydroxy- β - p -hydroxyphenylethyl-methylamine) indicates that the dissimilarity is not so marked as claimed by Kuschinsky (A., 1931, 120), the difference being qual. and not quant.

F. O. H.

Action of adrenaline on serum-potassium. J. L. D'SILVA (J. Physiol., 1934, 82, 393—398).—Injection of adrenaline in cats causes a rapid increase in serum-K (I) followed by a more prolonged fall to a val. $<$ normal. The effect is unaltered by anaesthesia on or decerebration. Posterior pituitary extract, BaCl_2 , and hæmorrhage produce similar effects. The effect of adrenaline is abolished by ergotoxine, but not by atropine. Sympathetic stimulation raises (I) if the adrenals are not already exhausted. Ephedrine produces a marked but delayed increase, and acute asphyxia and Et_2O are also effective. Intra-

venous injection of KCl or K gluconate increases (I), which, however, rapidly returns to normal. The fall of (I) below normal is nearly abolished after pancreatectomy.

R. N. C.

Action of adrenaline on serum-potassium. H. SCHWARZ (Arch. exp. Path. Pharm., 1935, 177, 628—634).—Injection of adrenaline (0.09—0.24 mg. per kg. of body-wt.) into rabbits increases the serum-K, the effect being inhibited by curare or ergotamine.

F. O. H.

Significance of the augmented adrenaline liberation by piqure for the fluctuation of blood-sugar and of mean blood-pressure, simultaneously occurring. M. WADA and T. KAIWA (Tôhoku J. Exp. Med., 1934, 23, 556—577).—Piqure hyperglycæmia is attributed to a combination of two processes, (a) an output of adrenaline (I) from the adrenals, and (b) a sugar output, independent of (I), caused by nerve impulses travelling in the splanchnics, probably to the liver.

NUTR. ABS. (m)

Assay of parathyroid hormone by magnesium sulphate. A. SIMON (Arch. exp. Path. Pharm., 1935, 178, 57—63).—A method based on the diminution of toxicity of subcutaneously injected MgSO_4 in mice following administration of parathyroid hormone is described (cf. A., 1927, 380).

F. O. H.

Effect of parathormone on basal metabolism of normal dogs. I. E. STECK, D. S. MILLER, and C. I. REED (Amer. J. Physiol., 1934, 110, 1—3).—The metabolic rate is not increased by large doses of parathormone as it is by viosterol.

R. N. C.

Effects of hypercalcæmia produced by parathyroid hormone and irradiated ergosterol on the activity of the cerebral cortex by means of conditioned reflexes. L. ANDREYEV and L. A. PUGSLEY (Quart. J. Exp. Physiol., 1934, 24, 189—206).—The hypercalcæmia caused exaggeration of the inhibitory process. The effect is dispelled by caffeine.

CH. ABS. (p)

Effect of irradiated ergosterol and parathormone on blood-phosphorus. J. F. SYKES, N. B. TAYLOR, and C. B. WELD (Amer. J. Physiol., 1934, 109, 104—105).—The rise in the total and inorg. P in the blood and serum of dogs is greater after administration of irradiated ergosterol than after dosage with parathormone (I). In the former case it accompanies, and in the latter follows, the rise in serum-Ca. The primary effect of (I) is not on P metabolism.

NUTR. ABS. (m)

Thyro-parathyroidectomy and diffusible calcium of serum. C. ROERSCH (Compt. rend. Soc. Biol., 1935, 118, 809—811).—Thyro-parathyroidectomy in dogs produces a lowering of total and ultrafilterable blood-Ca, but the diffusible: colloidal Ca ratio is increased.

R. N. C.

Action of thyroid extract on the respiration of tissues of invertebrates. R. ASHBEL (Nature, 1935, 135, 343).—Thyroid extract largely increases the O_2 consumption (I) of organs of various invertebrate animals. Comparative figures are given for the eggs of *Bombyx mori*, Crustaceæ, Mollusca, and the ovaries of Echinoderma and Tunicata. Synthetic thyroxine has no effect on (I).

L. S. T.

Efficacy of various thyroid preparations. I. ABELIN (Arch. exp. Path. Pharm., 1935, 177, 359—366).—Administration to rats of various thyroid preps. (dried gland, iodothyroglobulin and its fractions, etc.) containing the same amount of thyroxine (I) produces metabolic disturbances differing in type and degree. The variation is probably due to non-(I) substances containing I which, although themselves inactive, influence the action of (I). F. O. H.

Action of thyroid activation on the iodine economy of thyroid tissue. H. PAAL (Arch. exp. Path. Pharm., 1935, 177, 367—378).—Activation of rabbit's thyroid tissue *in vitro* (A., 1934, 222) by anterior pituitary prep. (I) increases the EtOH-sol. (II) at the expense of the EtOH-insol. fraction (III). With repeated subcutaneous injection of (I), the I content of the thyroid gland (IV) decreases, whilst (II) increases until it approximates to (III). Freezing of active (IV) diminishes the ability to liberate inorg. I, whilst frozen resting (IV) is no longer activated by (I). Thyroxine also induces *in-vitro* liberation of inorg. I from resting (IV) and from (IV) activated *in vivo* by (I). The correlation between liberation of inorg. I and activation of (IV) is discussed. F. O. H.

Action of thyroxine on the metabolism of cold-blooded vertebrates. E. DREXLER and B. VON ISSEKUTZ, jun. (Arch. exp. Path. Pharm., 1935, 177, 435—441).—The production of sugar by the liver of frogs before and after adrenaline administration is not influenced by treatment with thyroxine (I). Neither (I) nor thyrotropic hormone increases the metabolic rate of frogs, turtles, or fish.

F. O. H.

Site of thyroxine action. B. VON ISSEKUTZ and B. VON ISSEKUTZ, jun. (Arch. exp. Path. Pharm., 1935, 177, 442—449).—With narcotised [urethane or luminal (I)] cats, administration of thyroxine (II) increases the respiration, temp., and basal metabolism within a few hr. With deep (I) narcosis, decapitation, or cervical section of the spinal cord, (II) is without action, whilst section at the first or second dorsal vertebra does not produce inhibition. Hence the site of (II) action is the temp.-regulating centre in the mid-brain.

F. O. H.

Effect of thyroxine on the tissue metabolism of excised frog heart. J. E. DAVIS, E. DA COSTA, and A. B. HASTINGS (Amer. J. Physiol., 1934, 110, 187—190).—Perfusion of the intact heart for prolonged periods with citrated Ringer's solution containing thyroxine (I) causes a rise in metabolism, whereas without (I) it falls. The effect is not shown by sliced heart.

R. N. C.

Action of thyroxine on pancreatic amylase, lipase, and trypsin. G. SCOZ (Boll. Soc. ital. Biol. sperim., 1934, 9, 971—973).—Amylase is reduced by 80%, lipase by 40—50%, and tryptic activity approx. 30% by thyroxine. There is apparently no relation between variations of enzyme activity and of wt.

R. N. C.

Action of thyroxine on the dog's plasma-phosphatase power. G. SCOZ and P. L. MARANGONI (Boll. Soc. ital. Biol. sperim., 1934, 9, 973—

976).—Plasma-phosphatase is raised to 2—3 times the normal val. by injection of thyroxine. It returns to normal in approx. 8 days.

R. N. C.

Action of thyroxine on the rat's bone-phosphatase. G. SCOZ and P. L. MARANGONI (Boll. Soc. ital. Biol. sperim., 1934, 9, 969—971).—The phosphatase is increased approx. 33% in rats treated with thyroxine, the increase being of the same order in presence or absence of Mg.

R. N. C.

Action of thyroxine on the weight of the internal organs in the rat. G. SCOZ (Boll. Soc. ital. Biol. sperim., 1934, 9, 837—839).—The wet and dry wts. of the organs are increased by thyroxine. H₂O is increased in the spleen and muscles, but diminished in the liver and kidneys.

R. N. C.

Percentage of nitrogen in tissues in the rat treated with thyroxine. P. L. MICHELI (Boll. Soc. ital. Biol. sperim., 1934, 9, 978—980).—The % of N in the liver, kidney, spleen, and muscles is generally increased by thyroxine.

R. N. C.

Effect of hormones on reduced glutathione in tissues and blood. J. VILAR, A. MUNILLA, and J. SILVEIRA (Compt. rend. Soc. Biol., 1934, 116, 1206—1208).—Injection of thyroxine in rabbits raised the reduced glutathione (I) content of the myocardium (II), thyroid (III), and blood (IV), and lowered that of the lung (V) tissue. Parathormone increased the (I) in all tissues. Adrenaline caused increases in (II), voluntary muscles, and (IV). Insulin increased (I) in muscles and slightly lowered the amounts in (III), (V), kidneys, and (IV).

CH. ABS. (p)

Influence of various hormones on intestinal absorption. I. Sodium chloride solution. II. Glucose solution. S. ISAWA (J. Chosen Med. Assoc., 1934, 24, 603—618, 1037—1047).—I. Absorption of 0.9% NaCl solution is temporarily reduced by injection of thyroxine (I), accelerated and subsequently much retarded by insulin (II), accelerated by adrenaline (III), and unaffected by pituglandol (IV). The blood-Cl level and rate of absorption of Cl are unrelated.

II. Absorption of 5% glucose solution is accelerated by (I), temporarily retarded by (IV), and by (II) (which accelerates in cases of hypoglycemia and (III)).

CH. ABS. (p)

Effects of various endocrine products and vegetative nerve poisons on the liver function. H. KUROKAWA (Sei-i-Kwai Med. J., 1934, 53, 1—45).—Liver function in rabbits, as determined by the urinary urobilinogen and urobilin and the serum-bilirubin, was affected most by insulin, followed, in order, by adrenaline, pituitrin, thyroxine, pilocarpine, eserine, hypophorin, ergotoxine, and atropine.

CH. ABS. (p)

Changes in the chlorine ions of blood-serum under the influence of the thyroid and pituitary. V. BERGAUER, J. BOUCEK, and V. PODROUSEK (Compt. rend. Soc. Biol., 1935, 118, 281—284).—Addition of aq. thyroid extract (I) to fresh serum diluted with 0.9% NaCl in a HgCl electrode produces a fall of potential that increases with the amount of (I) added, indicating a desorption of NaCl from

the protein micelles into the solution. When (I) concn. reaches 1—2%, desorption ceases through establishment of equilibrium. Pituitary extract produces an analogous rise of potential through adsorption, whilst prolactin gives variable results.

R. N. C.

Thyrotropic hormone and basal metabolism. F. ZAJIC (Compt. rend. Soc. Biol., 1935, 118, 273—276).—Injection of normal dogs, and dogs the basal metabolism (I) of which had been previously increased by feeding with thyroid (II), with thyrotropic hormone (III) produces a considerable rise in (I), which falls below normal after cessation of the injections. Resumption of injections in the dogs with artificially raised (I) accelerates the fall. Injection of thyroidectomised dogs with (III) does not affect (I), even when (I) has been kept normal by (II) feeding. Hence the effect of (III) on (I) is indirect through (II).

R. N. C.

Effect of thyrotropic hormone on serum-cholesterol. L. I. PUGSLEY (Biochem. J., 1935, 29, 513—516).—Injection of thyrotropic hormone extract (I) into rats and dogs leads to a decrease in the serum-cholesterol (II) level followed by a subsequent recovery. The curve obtained has a reciprocal relationship to the basal metabolic rate curve of rats receiving injections of (I). A thyroparathyroidectomised-hypophysectomised dog showed no significant decrease in (II) after injection of (I).

E. A. H. R.

Effect of the ovary on the secretion of the thyrotropic hormone. A. LOESER (Klin. Woch., 1934, 13, 766—767; Chem. Zentr., 1934, ii, 2240).—Ovariectomy in young guinea-pigs raises the thyrotropic hormone content of the pituitary. The thyroid undergoes histological alteration.

R. N. C.

Origin of the hypoglycæmia provoked by the thyrotropic hormone of the anterior pituitary. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1935, 118, 794—797).—The thyrotropic hormone (I) does not produce hypoglycæmia in thyroidectomised dogs. The increased insulin secretion (II) produced by (I) in normal dogs is not inhibited by vagotomy. Hence (I) stimulates (II) through the thyroid.

R. N. C.

Inhibition of thyroid action by the metabolic hormone of anterior pituitary gland. I. LIVERGLYCOGEN. H. MAGISTRIS (Arch. exp. Path. Pharm., 1935, 178, 15—26).—Anterior pituitary preps. ("orophysin") contain a H₂O-sol. anti-thyroid principle (I) which produces a return to normal of the diminished liver-glycogen due to thyroid administration (cf. A., 1933, 1086). (I) occurs in the blood, being liberated by the action of thyroid preps. or thyroxine. The nature and relation to other hormones of (I) are discussed.

F. O. H.

Effect of the anterior pituitary growth hormone on protein metabolism. N. K. SCHAEFFER

LEE (J. Biol. Chem., 1935, 108, 355—371).—During the treatment of rats with anterior pituitary growth hormone, free NH₂-acids (I), peptide (I), urea (II), and non-protein-N decreased in the whole carcass (III), liver (IV), and muscle: the amounts were > could be accounted for by retention of H₂O.

In hypophysectomised rats, there was a decrease in body-protein \propto the time after hypophysectomy; in (III), free (I) and (II) plus NH₃ increased, and in (IV), free (I) decreased, and (II) plus NH₃ increased.

H. G. R.

[Fat] metabolism hormone of the pituitary. M. ORRÙ (Boll. Soc. ital. Biol. sperim., 1934, 9, 1055—1057).—Rabbits injected with dried pituitary show an intense hyperketonæmia (I); the increase with prolactin is much smaller. The increase on injection of pregnancy urine is variable. Rats show (I) when injected with pregnancy serum, or repeatedly with pregnancy blood.

R. N. C.

Action of pituitary extracts on the ketone content of blood. G. LEINER (Z. ges. exp. Med., 1934, 94, 84—93; Chem. Zentr., 1934, ii, 2406).—The hypolipæmic "lipoitricin" (I) lowers blood-ketones (II) in the dog. The hyperketonæmic "orophysin" (III) does not affect blood-fat (IV) or (II) in the dog. (III) sometimes increases (II) in rabbits, but does not affect (IV). (I) and (II) are thus two non-identical active substances the hormonal character of which has not been established.

R. N. C.

Repair of the reproductive system of hypophysectomised female rats by combinations of a pituitary extract (synergist) with pregnancy-prolactin. H. M. EVANS, R. I. PENCHARZ, and M. E. SIMPSON (Endocrinol., 1934, 18, 601—606).—The effect of prolactin and the pituitary synergist on the ovaries of hypophysectomised female rats is as great as on normal rats.

R. N. C.

Maintenance and repair of the reproductive system of hypophysectomised male rats by pituitary synergist, pregnancy-prolactin, and combinations thereof. H. M. EVANS, R. I. PENCHARZ, and M. E. SIMPSON (Endocrinol., 1934, 18, 607—618).—The testes of male hypophysectomised rats injected with prolactin (I), pituitary synergist (II), or the two combined (III) for 10—20 days after operation continue to grow, those of animals receiving (III) or (II) reaching the normal wt. range. Injections 40 days after hypophysectomy produce a repair of the seminiferous tubules, though (II) does not affect the interstitial tissues or the seminal vesicles; (I) produces a repair of these and an increase in Leydig tissue.

R. N. C.

Action of pituitary extracts in castrates. (Difference between gonadotropic urine extracts.) J. FREUD (Acta Brev. Neerl. Physiol., 1933, 3, 84—86; Chem. Zentr., 1934, ii, 2541).—Injection of anterior pituitary extract simultaneously with male or female hormone in young and growing castrated human subjects essentially strengthens the effect of the male hormone on the preputial glands and of menformone on the seminal vesicles.

R. N. C.

Difference between the effects of gonadotropic (early pregnancy) urine and anterior pituitary extracts. J. FREUD (Acta Brev. Neerl. Physiol., 1933, 3, 101—102; Chem. Zentr., 1934, ii, 2543).

R. N. C.

Oestrogenic gonadotropic substance of the anterior pituitary of the guinea-pig. A. LIPSCHUTZ and E. VINALS (Compt. rend. Soc. Biol., 1935,

118, 229—230).—The anterior pituitary of the guinea-pig has no oestrogenic action on young ovariectomised female rats. The oestrogenic action on normal rats is not diminished by preliminary extraction with Et_2O , and is hence due to an Et_2O -insol. gonadotropic hormone similar to the follicular and luteinising hormones. R. N. C.

Pituitary changes in severe atrophy and fibrosis of the testicles. W. BERBLINGER (Endocrinol., 1934, 14, 73—85; Chem. Zentr., 1934, ii, 2541).—The anterior pituitary, in primary atrophy of the testicles, shows the same changes as in castration. Since the interstitial cells of the atrophied testicles increase in no., they cannot be the chief source of the male hormone. R. N. C.

Nature of the gonadotropic hormone found in the urine of a case of teratoma testis. R. J. MAIN and S. L. LEONARD (Endocrinol., 1934, 18, 629—632).—The urine contains folliculin, but no luteinising hormone. It resembles pregnancy urine in not producing indefinite enlargement of the ovaries. R. N. C.

Fate of prolactin injected into the rabbit. A. LIPSCHUTZ, A. FUENTE-ALBA, and T. VIVALDI (Compt. rend. Soc. Biol., 1935, 118, 226—229).—The curve of disappearance of prolactin from the blood is logarithmic. R. N. C.

Prolactin and yeast metabolism. M. REISS, L. SCHWARZ and M. GÖTHE (Endocrinol., 1934, 14, 257—260; Chem. Zentr., 1934, ii, 2542).—Highly purified prolactin preps. increase respiration and fermentation of yeast. The effect is probably due to a metabolically active substance (Euler's "Z factor") associated with prolactin. R. N. C.

Sex hormone and mucosa separation in the genital apparatus. S. E. DE JONGH (Acta Brev. Neerl. Physiol., 1933, 3, 112—113; Chem. Zentr., 1934, ii, 2404).—Menformone (I) produces considerable alterations in the epithelium of the seminal vesicles of young castrated male mice, which become thickened, the extra layers separating after cessation of the action of (I). R. N. C.

Does follicle-juice contain, besides menformone, a substance influencing metabolism? E. DINGEMANSE and S. E. DE JONGH (Acta Brev. Neerl. Physiol., 1933, 3, 79—81; Chem. Zentr., 1934, ii, 2405).—The effect of menformone-free follicle-juice extract on the development and growth of tadpoles is not different from that of serum. R. N. C.

Lactation inhibition. S. E. DE JONGH (Acta Brev. Neerl. Physiol., 1933, 3, 88—90; Chem. Zentr., 1934, ii, 2405).—Menformone (I), injected into suckling rats, inhibits lactation. Injection of gonadotropic extract (II) produces the same effect, even if the mother has been castrated after littering. Hence the action of (II) is not due to stimulation of (I) secretion. R. N. C.

Site of the action of menformone on the lacteal gland. S. E. DE JONGH (Acta Brev. Neerl. Physiol., 1933, 3, 99—100; Chem. Zentr., 1934, ii, 2405).—Menformone in a lacteal transplant produces variable outgrowth of the ducts, and formation of a secretion is always observed. R. N. C.

Protein nature of prolactin and follicle-stimulating hormones. R. W. BATES, O. RIDDLE, and E. L. LAHR (Proc. Soc. Exp. Biol. Med., 1934, 31, 1223—1224).—Both substances are destroyed by trypsin at 37° and 8.0. CH. ABS. (p)

Effect of injections of pregnancy urine on the magnesium, calcium, and phosphorus of the blood. F. GUERCIO (Boll. Soc. ital. Biol. sperim., 1934, 9, 1057—1060).—Blood-Mg is increased 50% of the initial val. in 10—12 days. The effect is not altered by preliminary administration of Mg, which is excreted in the urine. Ca is unaffected, whilst P shows a small increase, due possibly to P in the pregnancy urine, and to its acidity, which disturbs PO_4''' equilibrium. R. N. C.

Hormones in the urine following oophorectomy during pregnancy. H. ALLAN and E. C. DODDS (Biochem. J., 1935, 29, 285—287).—No change in the anterior-pituitary hormone content of the urine is caused by bilateral oophorectomy. The oestrone content of the urine is decreased. A. L.

Experimental uterus growth by ovarian hormone. M. BORST (Endocrinol., 1934, 14, 85—87; Chem. Zentr., 1934, ii, 2541).—Castrated rabbits repeatedly injected with ovarian hormone show a conspicuous uterine growth. R. N. C.

Effect of the corpus luteum on basal exchange. O. RIML and E. ENGELHART (Klin. Woch., 1934, 13, 735—736; Chem. Zentr., 1934, ii, 2240).—The O_2 consumption of adult female rabbits, served with a sterile buck to produce apparent pregnancy, falls to a min. (24% of the normal val.) in 9—12 days, and rises again to normal in 15—22 days. This effect is due to association of the corpus luteum and the thyroid, and the resultant effect on the carbohydrate metabolism of the liver. R. N. C.

Biological properties of equilin. K. DAVID and S. E. DE JONGH (Biochem. J., 1935, 29, 371—377).—Equilin (A., 1932, 433) is fully as active as oestrone, and is not an undesirable contaminant when present in commercial oestrogenic preps. A. E. O.

Isolation of androstanone from the neutral products of the oxidation of cholestane. E. FERNHOLZ and P. N. CHAKRAVORTY (Ber., 1935, 68, [B], 353—354).—The neutral products of the oxidation of cholestane (I) are treated with COMe_2 to remove unchanged (I). The residue after treatment with $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ affords androstanone, m.p. 121° [semicarbazone, m.p. 275 (decomp.)], which is physiologically active. H. W.

Function of the pineal body. W. SAPHIR (Endocrinol., 1934, 18, 625—628).—Implantation of human pineal gland into white mice does not inhibit the sex cycle, nor show gonadotropic effect in infantile mice. It does, however, produce castrus in castrated female mice, each pineal gland containing mouse-units of oestrogenic hormone. R. N. C.

Oxytocic hormone of the posterior lobe of the pituitary gland. V. Recognition as an oxidation-reduction system. VI. Action of oxidising and reducing agents. J. M. GULLAND and S. S. RANDALL (Biochem. J., 1935, 29, 378—39, 1

391—396).—The oxytocic activity of the hormone (I) (see A., 1932, 655) falls to $\frac{1}{2}$ the normal val. when (I) is reduced by H_2S , and also [but this time with partial destruction or adsorption of (I)] when reduced by H_2 , catalytically or electrolytically. (I) reduced by H_2S is completely reactivated by oxidised methylene-blue, and partly and temporarily reactivated by air, or by removal of H_2S anaerobically. (I) contains a redox system having $E_0' + 0.025$ volt at p_H 6, the activity being 100% when this is oxidised and 50% when reduced. At potentials between -0.1 and -0.25 volt, in presence of suitable indicators, the activity again increases from 50 to 100%, possibly due to the presence of a second reducible group.

VI. Na_2SO_3 , $NaCN$, and Cl_2 inactivated (I) completely and irreversibly. Aq. I also inactivates, but SO_2 , HCN , and H_2O_2 all bring about a temporary decrease in activity (II), followed by reactivation and finally by a second decrease in (II).

A. E. O.

Effect of oxytocin and vasopressin on the action of insulin. M. R. GURD (Quart. J. Pharm., 1934, 7, 661—671).—The anti-insulin effect of vasopressin (I) is approx. twice that of oxytocin (II). The effect of (I) in diminishing the hyperglycaemic action of adrenaline is also $>$ that of (II).

A. E. O.

Effect of posterior pituitary extract and thyroxine on the water, sodium, and chlorine contents of the tissues. F. G. DIETEL and H. DIRSCH (Klin. Woch., 1934, 13, 1174—1177; Chem. Zentr., 1934, ii, 2407).—Guinea-pigs injected daily for 10 days with 6 Voegtlin units of pituitrin show a storage of $NaCl$ in the muscles and liver, but not in the skin; Na storage is not always accompanied by H_2O storage. Simultaneous administration of thyroxine wholly or partly inhibits this separation.

R. N. C.

Metabolism apparatus (pituitrin, histamine). I. E. UYLDERT (Acta Brev. Neerl. Physiol., 1933, 3, 103—104; Chem. Zentr., 1934, ii, 2415).— CO_2 production in rats was decreased by injection of pituitrin (I) (0.5—3.0 units), pitressin, pitocin (2—2.5 units), or histamine (II). Simultaneous injection of (I) and (II) effects no change.

A. G. P.

Relation between pituitary and products of internal secretions as reflected in reduced glutathione contents of blood. H. KAWAI (Sei-i-Kwai Med. J., 1934, 53, 104—133).—Hypophysectomised dogs (I) had lowered reduced glutathione (II) contents in blood. Subcutaneous injection of pituitrin or oophormin into normal or (I) increased (II), especially in (I). Insulin produced the opposite effect. Antuitrin, pituglandol, and thyroxine decreased (II) in normal and increased this in (I). Effects of adrenaline are less accentuated.

CH. ABS. (p)

Hormones of the pituitary of the infantile rat. O. SWEZY (Endocrinol., 1934, 18, 619—624).—Implants into adult hypophysectomised male rats of pituitaries from male rats 1—13 days old have effect on the testes, but those from day-old rats implanted into normal rats 21 days old produce effects equal to those from adult pituitaries. Hence

the pituitary of the infantile rat contains no maturity hormone, but a factor that can stimulate the adult pituitary to increased hormone production.

R. N. C.

Effect of intensive X-ray irradiation of the pituitary on blood-magnesium and magnesium exchange. L. CANNAVO and R. BENINATO (Boll. Soc. ital. Biol. sperim., 1934, 9, 804—808).—Destruction of the rabbit's pituitary by X-rays produces a fall of blood-Mg, which remains low until death. Blood- PO_4''' is also decreased, but Ca is unaffected. Mg excretion in urine and faeces is also considerably reduced, PO_4''' less so, whilst Ca excretion scarcely varies.

R. N. C.

Vitamin synthesis. O. BAUER (Pharm. Zentr., 1935, 76, 129—136).—A review.

Vitamin-A content of carrot varieties. N. N. IVANOV and M. A. SMIRNOVA (Bull. Appl. Bot. Leningrad, 1934, Suppl. 67, 53—64).—Red carrots were richest as a source of vitamin-A, yellow were less rich, and white almost valueless.

NUTR. ABS. (b)

New crystalline derivatives of vitamin-A. K. KAWAKAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 77—81).—The Ac derivative of the biosterol (I) from the liver oil of *Theragra chalcogramma* with maleic anhydride in C_6H_6 at 80° (CO_2 atm.) affords *acetylsukesioic acid anhydride*, $C_{30}H_{36}O_8$, m.p. 261 — 262° , and that from *Stereolepis ishinagi* gives the isomeric *acetylisingiic acid anhydride*, m.p. 221 — 222° . The Bz derivative of (I) (from cod-liver oil) gives *benzoylsukesioic acid anhydride*, m.p. 263 — 264° , and fractional distillation of the hydrogenation product of (I) affords *hydrovitamin-A*, $C_{20}H_{38}O$, b.p. 190 — $192^\circ/7$ mm. (isolated as its H phthalate).

J. W. B.

Crystalline derivative of vitamin-A. S. HAMANO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 26, 87—90).—The liver oil of *Stereolepis ishinagi* with maleic anhydride (I) in C_6H_6 at 90 — 100° (CO_2 atm.) affords *palmitylvitamin-A dimaleic anhydride adduct* (II), $C_{44}H_{64}O_8$, m.p. 220° , hydrolysed by dil. alkali to palmitic acid and the lactone acid, $C_{28}H_{36}O_8$, also obtained by hydrolysis of the similar adduct, m.p. 262° (cf. preceding abstract), of acetylvitamin-A, prepared from the active prep. of (III) previously obtained (this vol., 260). (II) is synthesised by addition of (I) to the palmitate of vitamin-A (III) [prepared from (III) and palmityl chloride in C_6H_6 — C_6H_5N]. (III) is therefore present as its palmitate in ishinagi-liver oil.

J. W. B.

Influence of administration of yeast on hyper-vitaminosis-A in young rats. A. KANTER (Klin. Woch., 1934, 13, 1157; Chem. Zentr., 1934, ii, 2544).—Pressed yeast contains a heat-resistant factor which inhibits the decline in wt., but has no effect on other symptoms, of hypervitaminotic rats.

A. G. P.

Vitamin-A deficiency in turkeys. W. R. HINSHAW and W. E. LLOYD (Hilgardia, 1934, 8, No. 9, 281—304).—General effects of vitamin-A-deficient diets on young turkeys and chicks are compared. The -A requirement of the former is approx. double that of the latter.

A. G. P.

(A) Extraction of vitamin-B. (B) Simplified method for preparing lactoflavin and its growth effect. (C) Possible role of thiol group in vitamin-B₂ deficiency. S. ITTER, E. R. ORENT, and E. V. MCCOLLUM (J. Biol. Chem., 1935, 108, 571—577, 579—583, 585—594).—(A) Vitamin-B (I), extracted from yeast with 4N-HCl in MeOH, was just as active as yeast in its growth response (II) in (I)-deficient rats. The residue from the extraction was inactive. The extract contained a high % of total solids, but only traces of Na, Ca, and Mg. The solubility of (I) in the MeOH-HCl was not due to the presence of H₂O, nor was a saturated solution of MeCl in MeOH able to extract (I) from yeast.

(b) Lactoflavin (III) was prepared by extraction of dry whey powder with boiling EtOH; lactose was removed by chilling and vitamin-B₂ (IV) adsorbed with fuller's earth (V). After elution with C₅H₅N-MeOH-H₂O colloidal (V) was pptd. with MeOH and other impurities with COMe₂. (III) was pptd. from the conc. residue by EtOH. Picric acid did not produce a ppt. on addition to a solution of (III) prepared in this way. A daily dose of 0.1 mg. of (III) produced a (II) in (IV)-deficient rats.

(c) The -SH content of blood and liver of (IV)-deficient rats was < that of controls; addition of autoclaved yeast, cystine (VI), and glutathione (VII) to the diet restored only the liver vals. to normal; adrenalectomy was without influence on the blood-(VII) of dogs and anterior pituitary extract failed to increase the liver-(VII) of rats. (IV)-deficient rats showed a (II) with doses of (VI), (VII), and (III), whilst their alopecia was cured only by (VI) and (VII). H. D.

Effect of deficiency of vitamin-B complex on the oxido-reduction system in the eye-lens. S. N. RAY, P. GYORGY, and L. J. HARRIS (Biochem. J., 1935, 29, 735—740).—The indophenol-reducing capacity (I) of a single rat lens is determined by a back titration method described (error $\pm 10\%$). In rats kept on diets deficient in various constituents of the vitamin-B complex (I) is greatly diminished: in extreme cases (I) disappears and ascorbic acid is oxidised by extract of the lens. The diminished (I) appears to be due to a factor (II) not identical with vitamin-B₁, -B₂, -A, or -"H." (II) occurs in large amount in raw egg-white, which has marked prophylactic and curative properties. W. McC.

Vitamin-B-sparing action of fat. H. G. K. WESTENBRINK (Acta Brev. Neerl. Physiol., 1933, 3, 95; Chem. Zentr., 1934, ii, 2411).—Symptoms of polyneuritis appeared later in pigeons receiving a high-fat diet than in those with a fat-free ration. A. G. P.

Sparing action of fat on vitamin-B. VIII. Loss of vitamin-B from the rat's tissues. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1935, 108, 439—455).—In growing rats, fat appears to exert a measurable sparing action on the vitamin-B (I) content of the tissues [especially on the (I) content of the muscles of rats reared without (I)] by decreasing the amount of (I) dissipated in metabolism. The greatest initial withdrawal of (I) takes place in the liver. (I) avitaminosis has no great effect on total

blood-fat, or on the fat in the heart, but a correlation exists between heart- and blood-fat contents. With a (I)-free diet poor in fat, the I val. of the heart-fat and the total sterol of the blood-fat are both high. A. E. O.

Relationship between the B-vitamins and the protein, fat, and carbohydrate content of the diet. I. VOGT-MØLLER (Diss., Levin & Munksgaard, Copenhagen, 1934, 165 pp.).—In mice receiving standard diet [modified to yield food rich in carbohydrate (I), protein (II), or fat], dried yeast as a source of the vitamin-B complex, and a modified tikitiki extract, freed from -B₂, as a source of -B₁ and -B₄, -B₁ + -B₄ bears a quant. relation to the (I) content of the diet, and -B₂ bears a similar relationship to the fat content and probably also to (II). With a high fat diet relatively less -B₁ is required than when mice are fed on a balanced ration or on a high-(I) diet. Blood-sugar vals. show no significant change in avitaminosis-B. Feeding of thyroid gland (III) to mice on vitamin-B₁-deficient diets shortens the time of survival. The effect \propto the amount of (III) given. NUTR. ABS. (m)

Crystalline vitamin-B₁. H. W. KINNERSLEY, J. R. O'BRIEN, and R. A. PETERS (Biochem. J., 1935, 29, 701—715).—The identity of hydrochlorides (possibly C₁₂H₁₆ON₄S₂·2HCl) of the vitamin from different sources has been demonstrated. Biological activity (average 437 international units per g.) is best measured by the catatorulin test on avitaminous brain and is not destroyed by CH₂O. The nitrate, decomp. 164—165°, and sulphates 2X(SO₄)₂ (X = base), m.p. 203° (corr.), prepared at 3, and 2X(SO₄)₄, m.p. 276—278° (corr.) prepared at p_H 1 are described. W. McC.

Improved yields of vitamin-B₁. H. W. KINNERSLEY, J. R. O'BRIEN, and R. A. PETERS (Biochem. J., 1935, 29, 716—717; cf. A., 1933, 541).—By means of improvements [use of special yeast (I), adsorption on charcoal at p_H 6.5, clarification of filtrate from initial boiling of (I) with double quantity of Pb(OAc)₂ after centrifuging, addition of light petroleum to hot alcoholic mother-liquors after concentrating, rapid pptn. of Au compound which is kept cool] in methods of isolation increased yields [up to 73.2 mg. per kg. of (I)] of the cryst. hydrochloride of the vitamin are obtained. W. McC.

Ultra-violet absorption of crystalline vitamin-B₁. E. R. HOLIDAY (Biochem. J., 1935, 29, 718—721; cf. A., 1933, 645).—Purest cryst. vitamin-B₁ (samples from Kinnersley *et al.*, Windaus, Van Veen) in 75% EtOH + 0.005N-HCl exhibits selective absorption (I) with max. at 245—247 m μ . Kind of solvent and [H⁺] greatly affect (I). W. McC.

Test for vitamin-B₁. W. H. SCHOPFER (Z. Vitaminforsch., 1935, 4, 67—75).—*Phycomyces blakesleeanus* does not grow on artificial media but addition of 0.00005 $\times 10^{-6}$ g. of vitamin-B₁ per c.c. permits its development. P. W. C.

Water-soluble B-vitamins. IV. Components of vitamin-B₂. H. CHICK, A. M. COFFING, and C. E. EDGAR (Biochem. J., 1935, 29, 722—734).—Vitamin-B₂ (I), the heat-stable constituent of the

vitamin-*B* complex which must be added to diets containing all other dietary essentials [including -*B*₁ (II)] in order to maintain growth and health in the rat and to prevent dermatitis, is an association of a flavin with a supplementary substance (III) (factor *Y* or vitamin-*B*₆). (III) occurs in yeast extract, liver, and egg-yolk (but to a small extent only in egg-white), is stable to heat and alkali, dialyses through Cellophane, is not adsorbed by fuller's earth at *p*_H 1.0 or pptd. by Pb(OAc)₂ at *p*_H 8.0 or 4.0, and is present in small amount in (II) prepared by Peters' method. Puro hepato- (IV) or lacto-flavin (V) added to a basal diet containing adequate (II) but free from (I) restores growth in rats to a small extent, but in order to attain normal growth (III) must also be given. (IV) or (V) has no curative effect (sometimes a stimulating effect) on the florid dermatitis of rats deprived of (I) and only occasionally cures the more general type of skin disease. (III) alone neither restores growth nor appreciably affects the disease (VI) but (IV) or (V) accompanied by (III) cures (VI) and restores normal growth. (IV) and (V), but probably not (III), are destroyed by exposure to visible light. W. McC.

Vitamin-*B*₂ complex. I. Differentiation of lactoflavin and the "rat antipellagra" factor. II. Distribution of lactoflavin and of the "pellagra-preventing factor" (vitamin-*B*₆) in natural products of animal origin. III. Inactivation of lactoflavin and vitamin-*B*₆ by visible light. P. GYRGY (Biochem. J., 1935, 29, 741—759, 760—766, 767—775).—I. "Rat pellagra" (I) is produced on a vitamin-*B*-free basal diet with added purified -*B*₁ (II) and this result is not affected by addition also of lactoflavin (III). For prevention of (I) a "supplementary substance" or -*B*₆ (IV) is necessary. A suitable source of (IV) free from (III) is obtained in Peters' "charcoal eluate" from yeast. The combined administration of (III), (IV), and (II) leads to marked increase of growth in rats. The term vitamin-*B*₂ is retained for the (III)+(IV) complex.

II. Determination of the (IV) and (III) activities of various foodstuffs show wide abs. and relative variations. Muscle of herring, salmon, and haddock is a rich source of (IV), but is almost devoid of (III), whilst egg-white has a high (III) content but no antipellagra activity. The (III) and (IV) contents of striated muscle of ox, calf, and chicken, of ox-heart muscle, of chicken gizzard, liver, and milk are also given.

III. Both (III) and (IV) are destroyed by visible light, the inactivation of (IV) occurring in solutions free from (III). The possibility is discussed that (IV) like (III) may be a natural dyestuff. P. W. C.

State of vitamin-*B*₂ in cow's milk. R. KUHN and H. KALTSCHMITT (Ber., 1935, 68, [B], 386—387).

In an electric field, the milky suspension of freshly-skimmed cow's milk wanders towards the anode whereas the pigment remains stationary; after dialysis at 0° and concn. of the dialysate in vac., wandering of the pigment is not observed. The pigment of milk is therefore not identical with the active group of the yellow enzyme and lactoflavin in milk is present in the non-esterified form. H. W.

Synthetic vitamin-*B*₂-phosphoric acid. R. KUHN and H. RUDY (Ber., 1935, 68, [B], 383—386).—Lactoflavin (I) is transformed by POCl₃ in C₅H₅N into lactoflavin *H*₂ phosphate, isolated as the Na salt (II). (I) and (II) are identical in colour as solids and in colour and fluorescence in solution. Contrary to (I) but similarly to the active group of the yellow enzyme (III), (II) passes rapidly to the anode in an electric field.

[With T. WAGNER-JAUREGG and E. F. MOLLER.] Under given conditions and in contrast with (I), (II) shortens the time required for decolorisation of methylene-blue but the effect is slight in comparison with that of (III). H. W.

Identity of vitamin-*B*₂ and flavin and the nomenclature of vitamins. B. C. P. JANSEN (Nature, 1935, 135, 267; cf. this vol., 262).—The view that lactoflavin and vitamin-*B*₂ are identical is supported. L. S. T.

Renoflavin and vitamin-*B*₂. B. C. GUHA and H. G. BISWAS (Current Sci., 1935, 3, 300).—Purified renoflavin is normally deficient in vitamin-*B*₂ activity, but the latter is enhanced by supplements of the filtrates from adsorption of the flavin on fuller's earth, which were devoid of vitamin-*B*₁ and -*B*₄ and had been previously heated for 1 hr. at *p*_H 9 under pressure. P. G. M.

Nomenclature of vitamin-*B*₂. B. C. GUHA (Nature, 1935, 135, 395—396).—In "vitamin-*B*₂" four factors, the flavin, the heat-stable, the anti-dermatitis, and the anti-cataract factor, appear to be involved. The term "vitamin-*B*₂" should provisionally be reserved for the entire complex, which supplements the usual vitamin-*B*₂-deficient diet for the promotion of good growth in rats. The other factors should be indicated by their special characteristics. L. S. T.

Flavin and the pellagra-preventing factor as separate constituents of a complex vitamin-*B*₂. L. J. HARRIS (Biochem. J., 1935, 29, 776—781).—Flavin (I) (lactoflavin of Kuhn) has no antipellagra action. For adequate growth (i.e., for wt.-promoting action and cure and prevention of symptoms approx. equal to that of the total complex in the form of marmite) vitamin-*B*₁ (II) must be supplemented with both (I) and the "antipellagra substances" (III) of Peters' eluate. Administration only of (II)+(III) led to subnormal body-wts. and of (II)+(I) to the development of severe pellagra which was prevented or cured by addition also of (III). The International standard of (II) appears to be contaminated with (III). P. W. C.

Egg-white as sole source of protein and vitamin-*B*₂ for young rats. F. J. GORTER (Biochem. J., 1935, 29, 322—329).—Dermatitis in young rats, brought about by feeding egg-white (I) as the sole source of protein and vitamin-*B*₂, can be prevented by replacement of part of (I) by purified caseinogen. The curative factor is insol. in dil. or conc. acid, EtOH, or Et₂O and is also present in liver, yeast, and egg-yolk. It differs in solubilities from the *B*-vitamins. P. W. C.

Ascorbic acid content of the crystalline lens of guinea-pigs on a scorbutogenic diet. G. BIETTI and A. CARTENI (Boll. Soc. ital. Biol. sperim., 1934, 9, 983—985).—The ascorbic acid of the crystalline lens falls to a mere trace after 30 days of a scorbutogenic diet, that of the adrenals being slightly larger. R. N. C.

Variations of ascorbic acid in the aqueous humour following administration of vitamin-C. G. BIETTI and A. CARTENI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1066—1070).—Rabbits given orange-juice orally, or ascorbic acid (I) intravenously, show an increase of (I) in the aq. humour similar to that in serum (II). In the dog no increase is shown except a slight transitory increase in (II) immediately after injection, and (I) is eliminated rapidly in the urine; hence the animal has no storage capacity for (I). R. N. C.

Vitamin-C in the skin. A. GIROUD, C. P. LEBLOND, and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1935, 118, 321—322).—The mucosa of the skin contains an appreciable quantity of ascorbic acid, the content of other parts being negligible. R. N. C.

Vitamin-C content of human milk. W. NEUWEILER (Z. Vitaminforsch., 1935, 4, 39—54).—Breast milk contains 4—7 mg. of ascorbic acid (I) per 100 c.c. Colostrum contains the same amount as early or late milk. The amount is determined by the food supply. In cows the (I) content of the milk is decreased during pregnancy. The dichlorophenol-indophenol titration method gave results in good agreement with the biological assay. P. W. C.

Vitamin-C in dried fruit, berries, and vegetables. A. N. SHIVRINA and N. P. ONOKHOVA (Bull. Appl. Bot. Leningrad, 1934, Suppl. 67, 89—102).—The vitamin survives drying in black currants, dog-rose fruits, and apples, but in potatoes only 10—16% is preserved. NUTR. ABS. (m)

Vitamin-C preparation from fruits of the dog-rose. N. N. IVANOV, V. I. MARGA, and N. P. ONOKHOVA (Bull. Appl. Bot. Leningrad, 1934, Suppl. 67, 155—160).—From 48 kg. of dog-rose fruits, 42 g. of concentrate was obtained, which cured guinea-pigs of scurvy in a dose of 0.004 g. and retained its activity on storage. NUTR. ABS. (b)

Mexican tomatoes as an antiscorbutic remedy. E. N. ZORIN (Questions of Nutrition, U.S.S.R., 1934, 3, No. 3, 125—129).—The tomatoes contain < 100 antiscorbutic "guinea-pig" units per kg. NUTR. ABS. (m)

Needles of forest trees as a source of the antiscorbutic vitamin. P. A. YAKIMOV, T. N. KUZNEZOVA-ZARUDNAYA, and A. A. RYABININ (Bull. Appl. Bot. Leningrad, 1934, Suppl. 67, 143—153).—The min. daily prophylactic dose for guinea-pigs of fresh spruce or pine needles is 1.0 g. NUTR. ABS. (m)

Antiscorbutic action of juice of raw sorrel and of rhubarb. T. L. IZUMRUDOVA (Questions of Nutrition, U.S.S.R., 1934, 3, No. 4, 91—94, 94—98).—Fresh sorrel and rhubarb juice proved a fairly good source of vitamin-C as tested by prophylactic

experiments on guinea-pigs, the antiscorbutic activity being about 140 "units" per kg. NUTR. ABS. (b)

Vitamin-C consumption and storage in the animal. H. VON EULER and M. MALMBERG (Svensk Kem. Tidskr., 1935, 47, 25—29).—An increase in the daily dose of ascorbic acid (I) leads to an increase in the amount of (I) in the urine of the rat and (much smaller) the guinea-pig (II). The (I) content of the adrenal gland (III) of the hypervitaminised (II) is approx. 1.6 mg. per g. of organ as against the normal val. of 0.8 mg. The amount of (I) stored in the (III) of the rat does not appear to be affected by increasing the quantity of (I) administered. Hypervitaminosis of the (II) does not affect the (I) content of the lens of the eye. E. A. H. R.

Urinary excretion of vitamin-C. P. ROEMER, N. BEZSSONOFF, R. SACREZ, and E. STOERR (Compt. rend. Soc. Biol., 1934, 116, 1414—1416).—Infants of 3—8 months excrete the vitamin (I) in their urine whether it is present in the diet or not. Possibly synthesis occurs. In children over 11 months, adults, and guinea-pigs, in contrast with rats and birds, (I) is only excreted in the urine if present in the diet. NUTR. ABS. (m)

Influence of animal tissues on the oxidation of ascorbic acid. C. A. MAWSON (Biochem. J., 1935, 29, 569—579).—The aerobic oxidation of aq. solutions of ascorbic acid (I) in presence of phosphate buffer at 7.4 is inhibited by the presence of small quantities of animal tissues or tissue extracts. Similar inhibition is produced by glutathione (II), cysteine (III), cystine (IV), or H_2S . The inhibiting mechanism present in the tissues becomes less effective in presence of Cu or Fe, whilst a somewhat similar but less marked effect is produced on the (II) inhibition by Cu. Dialysed tissue extracts retain their anti-oxidative properties in full, whilst after pptn. with $\text{Hg}(\text{OAc})_2$ or $\text{CCl}_3\cdot\text{CO}_2\text{H}$ their activity is only partly lost. The (II), (III), and (IV) contents of the tissues probably account for only part of their activity. (I) is relatively stable in glass-distilled H_2O , but Cu and to a smaller extent Fe and especially mixtures of the two catalyse aerobic oxidation of (I). The known concns. of Fe and Cu in tissues and blood-serum would, in the absence of an anti-oxidant, effect rapid oxidation of (I). Lemon juice contains no anti-oxidant, the stability of (I) being entirely due to the low

Influence of vitamins on the catalase content of blood. II. H. J. JUSATZ (Klin. Woch., 1934, 13, 727—728; Chem. Zentr., 1934, ii, 2544, cf. A., 1933, 645).—Administration of ascorbic acid to rabbits increases the catalase activity of the blood. Carotene and vitamin-A have no effect. K

Ascorbic acid and blood-catalase. G. TOROK and L. NEUFELD (Klin. Woch., 1934, 13, 1205—1207).—In premature, wasted, or healthy infants, administration of daily doses of 10—30 mg. of the acid (I) for 2 weeks has no effect on the blood-catalase (II). Dogs and guinea-pigs on a diet devoid of vitamins show, usually between the 7th and 10th day, a definite fall in (II) level and a marked rise after daily doses of 10 mg. of (I); intravenous in-

jection of 50 mg. causes an immediate rise. (I) has a direct effect on the (II)-producing mechanism.

NUTR. ABS. (m)

Experimental scurvy in connexion with the character of the chief diet. M. F. GLASUNOV and K. L. POVOLOTZKAYA (Bull. Appl. Bot. Leningrad, 1934, Suppl. 67, 217—224).—Addition of autoclaved hay to Bezssonoff's diet rendered it much more satisfactory for use in prophylactic tests with guinea-pigs.

NUTR. ABS. (b)

Vitamin-C and chemically related compounds: configuration and antiscorbutic action. O. DALMER (Deut. med. Woch., 1934, 60, 1200—1202; Chem. Zentr., 1934, ii, 2546).—Only a part of the titrimetrically-determined vitamin-C in some samples of orange juice is biologically active. Ascorbic acid (I), solid or in suitable solution, retains its activity in the absence of air. Only COME₂-(I) is fully active.

A. G. P.

Chemical method of determining vitamin-C. B. AHMAD (Biochem. J., 1935, 29, 275—281).—For the determination of ascorbic acid (I) in solutions and in natural material by titration with 2:6-dichlorophenol-indophenol, the (I) concn. should be > 2 mg. per 100 ml., the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ (II) concn. $> 5\%$, and the solution titrated against the indicator with a time limit of 1—2 min. (I) in fruits and vegetables should be extracted with 20—25% aq. (II).

A. L.

Determination of ascorbic acid. J. P. SPRUYT and W. F. DONATH (Meded. Volksgezond. Ned.-Ind., 1934, 23, 117—128).—Ascorbic acid (I) oxidises very quickly in aq. solution to dehydroascorbic acid (II). The rate of oxidation is greatly restricted by 0.25% $\text{CCl}_3\cdot\text{CO}_2\text{H}$, but to a much smaller extent by higher concns. up to 20%. Reduction of (II) by H_2S is quant. in all concns. of $\text{CCl}_3\cdot\text{CO}_2\text{H}$ up to 20%. Aq. (I) can be stored without oxidation, apparently indefinitely, under H_2S . Titration of (I) with 2:6-dichlorophenol-indophenol is, within wide limits, independent of p_{H} (up to 7.4) and of concn. The (I) content of oranges, determined by this method, is 0.56—0.71 mg. per ml. of juice. NUTR. ABS. (m)

Determination of ascorbic acid. Vitamin-C content of various plant and animal tissues. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1935, 108, 563—570).—Vitamin-C (I) is determined in tissue extracts, prepared by the method of Emmerie (A., 1934, 1043), by addition of $\text{K}_3\text{Fe}(\text{CN})_6$ and heating at 40° for 3 min. On cooling, ferric gum ghatti (Folin, A., 1929, 1096) is added and the colour compared with that produced in a standard solution (I). (I) added to urine is not destroyed by pptn. with $\text{Hg}(\text{OAc})_2$. The (I) contents of a variety of plant and animal tissues are determined. H. D.

Determination of vitamin-C in blood. M. VAN ECKELEN, A. EMMERIE, and L. K. WOLFF (Acta prev. Neerl. Physiol., 1933, 3, 104—105; Chem. Zentr., 1934, ii, 2415).—Fresh blood (20 c.c.) is mixed 10 c.c. of 20% $\text{CCl}_3\cdot\text{CO}_2\text{H}$ (I) and centrifuged, and a portion of the centrifugate is titrated with 2:6-dichlorophenol-indophenol. To another portion KOH is added until the mixture contains 0.25% of (I).

The liquid is saturated with H_2S for 6 hr., freed from the gas by a current of N_2 , and titrated. The ascorbic acid content of blood so determined is 0.5 mg. per 100 c.c. before and 2.05 mg. after reduction.

A. G. P.

Determination of vitamin-C in blood-serum. E. GABBE (Klin. Woch., 1934, 13, 1389—1392).—The vitamin-C (I) in serum determined by dichlorophenol-indophenol in patients with various diseases was 0.14—1.21 mg. per 100 c.c. The lowest vals. occurred in the most serious cases, whilst the highest vals. were found in the lighter and convalescent cases. There was no evidence that lack of (I) promoted the onset of infection, for cases of acute infection (appendicitis, cholecystitis, etc.) showed high rather than low vals. In most cases the vals. could be correlated with the (I) content of the diet; with particularly low vals. a disorder of the endogenous metabolism of (I) may be involved.

NUTR. ABS. (b)

Ergosterol increases the prolific capacity of animals, and normal sexual functions intensify their resisting power against the toxicity of ergosterol. E. AGDUHR (Z. Vitaminforsch., 1935, 4, 54—66).—With mice, the males are much more susceptible than the females to an overdose of irradiated ergosterol (I). Administration of (I) causes heat, considerably increases the prolific capacity of the animals, and influences the post-natal development of several endocrine glands. Mice allowed normal sexual intercourse show considerable increase in resistance to the toxicity of (I).

P. W. C.

Is it possible to confer antirachitic activity on phosphorus sub-oxidation derivatives by introduction of a benzene ring? M. L. BARBAN (Compt. rend. Soc. Biol., 1935, 118, 771—773).—Na dimethylaminophosphinite and hydroxybenzylphosphinite and guaiacol phosphite are without antirachitic effect.

R. N. C.

Action of activated ergosterol in the chicken. III. Evidence for the existence of only one provitamin-D in crude ergosterol. C. E. BILLS, O. N. MASSENGALE, F. G. McDONALD, and A. M. WIRICK (J. Biol. Chem., 1935, 108, 323—330).—Ergosterol (I) from different sources does not vary in its effect on the blood and bones of chicken after irradiation. Vitamin-D (II) of irradiated (I) has a greater effect on Ca and P of serum than on the calcification of the bones, whilst the reverse is true for (II) from cod-liver oil.

H. G. R.

Influence of vitamin-D on the p_{H} of faeces. A. QUERIDO (Acta Brev. Neerl. Physiol., 1933, 3, 96; Chem. Zentr., 1934, ii, 2547).—Vitamin-D feeding decreased the p_{H} of rat faeces.

A. G. P.

Supplementary action of vitamin-B and -D and their joint influence on blood chemistry. H. J. JUSATZ and F. WENZEL (Klin. Woch., 1934, 13, 1082—1083).—The onset of hypervitaminosis-D in rabbits could be delayed by giving at the same time large doses of vitamin-B, which delayed and lessened the severity of the hyperphosphatemia produced by the excess of vitamin-D.

NUTR. ABS. (b)

Preparation and properties of vitamin-E concentrates. H. M. EVANS, E. A. MURPHY, R. C. ARCHIBALD, and R. E. CORNISH (J. Biol. Chem., 1935, 108, 515—523).—The vitamin-E (I) activity of the unsaponifiable fraction of wheat-germ oil (II) decreases with the age of the germ. (II) retains its activity for > 3 years stored in glass in vac. The Marcus process (A., 1929, 103) does not give complete extraction and destroys a part of the (I). The loss of (I) caused by saponification with EtOH-KOH is avoided by distilling the EtOH from NaOH, or by using anhyd. MeOH. Saponification at room temp. causes a loss of (I). Et₂O is the best solvent for extraction of the unsaponifiable residue; the extracts of (II) by AcOH, HCO₂H, and (CH₂-OH)₂ are not (I)-active whilst the residues are. H. D.

Appearance of paresis in adult rats suffering from chronic avitaminosis-E. A. RINGSTED (Biochem. J., 1935, 29, 788—795).—Characteristic neuropathic disturbances developing in adult albino rats fed on various vitamin-E-free food mixtures for a long time (4—7 months) are described. P. W. C.

Hormonal nature of the [growth]-inhibiting action of leaves of *Bryophyllum crenatum*. A. UHROVA (Planta, 1934, 22, 411—427; Chem. Zentr., 1934, ii, 2403).—Application of cut leaf stem to one side of the shoot stump inhibits development of axial buds on that side. The active material diffuses into agar and occurs in the expressed juice and Et₂O extract of tissues. A. G. P.

Integration of plant behaviour. V. Growth substance and traumatic curvature of the root. F. KEEBLE and M. G. NELSON (Proc. Roy. Soc., 1935, B, 117, 92—119).—Root tips of *Zea mays* contain growth substance (I) which inhibits growth of root. The supposed wound substance previously mentioned (New Phytol., 1930, 29, 289) as occurring at the surface of stumps (II) after amputation of tips is an exudation of preformed (I). (II) do not differ from intact roots as regards sensitivity to the action of gravity, but no geotropic curvature takes place in (II) until they have acquired sufficient (I). The distribution (III) of (I) and the effect on (III) of wounding suffice to explain the traumatic behaviour of the root without invoking sp. wound stimulus. Secretion (IV) of (I) is most active in the extreme tip of the root and the concn. rapidly decreases with distance from the tip [no (IV) beyond 2 mm. from tip]. Curvature (VII) of wounded roots is due to gradient (V) of concn. of (I) on opposite sides. There is no quant. relation between growth (VI) and (VII), (VI) being determined by concn. of (I) and (VII) by (V). W. McC.

Phototropic sensitivity in relation to wavelength. E. S. JOHNSTON (Smithsonian Misc. Coll., 1934, 92, No. 11, 1—17).—The phototropic sensitivity curve of the coleoptile of *Avena sativa* deduced by use of the plant photometer rises sharply from 410 to a max. at 440 mμ. It then shows a min. at 457.5, rising again to a max. at 470—480 mμ. There is a rapid fall to 500, and then a gradual fall to the threshold at 546 mμ. A. L.

Intimate problem of radicular assimilation. A. ORIOL I ANGUERA and M. VIDAL DE CÀRCER (Arxius, 1935, 122—141).—The isolation of inorg. and org. colloids of the soil is described. In most of the colloids the electric charge can be reversed, and an isoelectric point exists. The application of this fact to the mechanism of assimilation by the roots of plants is discussed. The idea of base exchange is extended to PO₄''' and other essential anions. R. N. C.

Assimilative activity and growth of *Ficaria verna*. F. MUDRACK (Planta, 1934, 23, 71—104).—Effects of light and temp. on rates of assimilation and respiration and dry-matter increases are examined. A. G. P.

Importance of leaf-colour in the breeding of white and Swedish clovers. K. BOEKHOLT (Zuchter, 1933, 7, 157—159; Bied. Zentr., 1934, A, 5, 66—67).—Darker leaves of clovers have higher chlorophyll and protein contents, which serve as characteristics in the selection of plants for breeding. A. G. P.

Relation between the presence of anthocyanin colours and the assimilative capacity of some cultivated plants. IV. K. HIROSI (J. Dept. Agric. Kyushu, 1933, 3, No. 9; Bied. Zentr., 1934, A, 5, 56).—The occurrence of anthocyanin pigments or the chromogens in plants is associated with increased assimilative power. A. G. P.

Chemical changes during the formation and germination of the rice grain. D. L. SAHAS-RABUDDHE and M. M. KIBE (J. Univ. Bombay, 1934, 3, No. 2, 121—134).—Determinations are recorded of the % H₂O, proteins, Et₂O extract, crude fibre, and sol. carbohydrates (dextrin, glucose, sucrose, starch) in the stem and inflorescence of the rice plant from the time of flowering to that of complete maturity of the grain. Similar study of the seed from the time of sowing until it is completely depleted of its food constituents shows (1) that the seed begins to absorb H₂O rapidly and retains a high H₂O content throughout the whole period, (2) very little dry matter remains at the end of the period, (3) crude fibre and ash are utilised to only a small extent, (4) proteins are utilised to the extent of 90%, (5) the Et₂O extract increases for some time due to formation of fatty acids, (6) the sol. carbohydrates are first converted into glucose and finally utilised by the growing parts of the new plant. The presence of an amylohydrolytic enzyme in the H₂O extract of germinating rice seed is established. The extract contains some starch which is transformed into glucose, and added starch is similarly converted. W.

Carbon dioxide: carbohydrate ratio in the aerobic and anaerobic respiration of rice. R. H. DASTUR and R. M. DESAI (Ann. Bot., 1935, 53—69).—In rice germinating in air, periods of high total sugar content are associated with high output of CO₂. When germination occurs in N₂ no hexoses occur in any stage; sucrose is present only in small amounts but EtOH is formed. In aerobic and anaerobic respiration CO₂ is produced in amount > equiv. to the carbohydrate lost. The excess

probably derived from the oxidation of org. acids formed during protein synthesis. A. G. P.

Interconvertibility of glucose and fructose in plant tissue. M. NURMIA (Nature, 1935, 135, 345; cf. A., 1934, 1420).—Glucose and fructose are readily converted into each other in the plant tissues, especially the stems, of grasses and legumes.

L. S. T.

Variation in the methoxyl and cellulose values of the fibre of the fruit of *Cocos nucifera* during its growth. S. R. K. MENON (Biochem. J., 1935, 29, 282—284).—OMe and cellulose vals. reach a max. and min. respectively in the fibre of nuts ten months old.

A. L.

Translocation in seedling tomato plants. I. W. SELMAN (Ann. Rept. Exp. Res. Sta. Cheshunt, 1933, 93—97).—The rates of translocation (I) and of assimilation are proportional in summer but not in winter. (I) increases with light intensity with a min. at 1000 ft. c.p. The H_2O content of the tissues is a secondary factor. (I) is also influenced by the enzyme content and the relative amounts of phloem in leaves and stems.

CH. ABS. (p)

Water content and assimilation of seedling tomato plants. R. MELVILLE (Ann. Rept. Exp. Res. Sta. Cheshunt, 1933, 87—92).—The H_2O content (I) of plants increases gradually from summer to winter. Assimilation rates increase with rising (I) to an optimum val. and subsequently fall rapidly as (I) continues to increase.

CH. ABS. (p)

Influence of light and temperature on the assimilation rate of seedling tomato plants, variety E.S.1. B. D. BOLAS (Ann. Rept. Exp. Res. Sta. Cheshunt, 1933, 84—87).—Light intensity (I) had little effect on assimilation rates (II) at < 15.5°. Above this temp. (I) and the temp. of max. (II) increased simultaneously in the ranges 100—1000 ft. c.p. and 17—32°.

CH. ABS. (p)

Water and [sugar] cane ripening. C. E. HARTT (Hawaiian Planters Rec., 1934, 38, 193—206).—Synthesis of sucrose in leaf blades is favoured by watering the plants. Some photosynthesis occurs at the wilting point. Differences in sugar and polysaccharide contents in sheaths and stems of watered (I) and unwatered plants are attributable to greater utilisation or better translocation (II) in (I) plants. In (II) sucrose moves against the diffusion gradient.

CH. ABS. (p)

Influence of temperature on respiration and carbon dioxide assimilation of certain green

F. VAN DER PAAUW (Planta, 1934, 22, 396—Chem. Zentr., 1934, ii, 2237).—Changes of emp. produce parallel effects on respiration (I) and CO_2 assimilation (II) in *Stichococcus bacillaris*. In 22° h + variations in (I) and (II) are similar below higher temp. (I) increases more rapidly than (II). At lower ranges of temp. the (I) of *amydomonas* responds more strongly than (II) to changes of temp.

A. G. P.

light on the nutrient intake of

M. GRAČANIN (Bull. Soc. Bot. Czechoslov.,

1932, No. 11; Bied. Zentr., 1934, A, 5, 61).—The intake of PO_4''' is not affected by light. A. G. P.

Removal of oxygen from water by cut branches. W. A. CANNON and E. A. PURER (Science, 1935, 81, 100).—Cut flowers and the cut ends of leafy branches of several shrubs and trees remove O_2 from distilled H_2O . Contrary to the case with rooted plants, temp. has little effect on the rate of removal of O_2 , which may, however, be decreased by exposure to light.

L. S. T.

Carbohydrate supply as a primary factor in legume symbiosis. F. E. ALLISON (Soil Sci., 1935, 39, 123—143).—Current literature indicates that the development and distribution of nodules in the root system are directly dependent on the carbohydrate supply in the roots. In plants generously supplied with NO_3' nodulation is restricted as a result of the lowered C reserve in the roots.

A. G. P.

Constancy of the ratio of carbon to nitrogen in natural systems undergoing oxidation, and the problem of protein synthesis. N. R. DHAR (J. Indian Chem. Soc., 1934, 11, 883—891).—Analysis of different soils shows a const. ratio C to N of 10:1, and a similar ratio is observed in the starvation metabolism of different animals. The carbonaceous matter in the soil protects the soil-protein from oxidation.

F. R. S.

Determination of carbon dioxide assimilation. Comparison of apparatus of Warburg with that of van der Paauw. F. VAN DER PAAUW (Planta, 1934, 22, 393—395; Chem. Zentr., 1934, ii, 2237).—Warburg's method is suited for general work with algae and gives more rapid results. The author's apparatus is superior for special work since a film of single-cell thickness is examined on a natural culture medium.

A. G. P.

Pollen and pollen extracts. XI. Chemical nature of pollen allergens. L. UNGER, M. B. MOORE, H. W. CROMWELL, and C. H. SEEGER. XII. Enzyme digestion of pollen allergens. M. B. MOORE and L. UNGER (J. Allergy, 1934, 5, 115—123, 338—340).—XI. The allergen (I) in ragweed and grass pollens has a protein-like character. The polysaccharide fraction has no part in the sp. activity.

XII. Ordinary proteolytic enzymes slowly digest (I).

CH. ABS. (p)

Preservation of pollen extracts by drying and preparation of concentrated pollen solutions. B. Z. RAPPAPORT (J. Allergy, 1933, 5, 13—18).—Dried ragweed pollen may be stored for 18 months without loss of activity and solutions of any concn. may be made from the product.

CH. ABS. (p)

Ultrafiltration of ragweed pollen extracts. W. C. SPAIN and J. M. NEWELL (J. Allergy, 1934, 5, 455—465).—The allergic substance can be removed from solution by ultrafiltration (No. 12,000 Cellophane). Non-protein-N is similarly removed from ragweed pollen extracts without appreciable reduction of their activity. The N precipitable by phosphotungstic acid does not correspond exactly with allergic activity but affords the most practical means of standardisation.

CH. ABS. (p)

Apparent lignin and skeleton substance of the leaves of plants. R. S. HILPERT and R. WAGNER (Ber., 1935, 68, [B], 371—380).—Investigation of green and faded leaves of beech, plane, and hazel shows that the customary methods of investigating wood and cellulose are not applicable. Extraction with EtOH- C_6H_6 removes so much material, either lignins (I) or producers of lignins (II), under the action of acids, that the pre-treatment becomes an integral part of the analysis. The actual wax content, determined by use of EtOH-free solvents, is 2—6%. Fading of the leaves is accompanied by considerable change in a portion of the carbohydrate resulting in increased solubility in org. media and decreased solubility in H_2O . Treatment with acids shows increase in (I) but, as in the case of sugars, the % of (I) found frequently varies greatly according as HCl or H_2SO_4 is used. Elementary analysis of leaf-(I) gives results comparable with those of (I) in general, but the leaf-(I) [or (II)] differ from those of straw or wood in their partial solubility in H_2O . From these solutions they are pptd. by acids; they have only 1.5% OMe. The vals. obtained by determining (I) in the whole leaf are considerably different from the sum of the vals. observed in the residue and aq. extract of the leaf and vary also according as HCl or H_2SO_4 is used. Even when the acid is greatly cooled, formation of (I) is observed, the leaves appearing to contain material which is much more sensitive to acid than is fructose. Treatment of wheat, straw, papyrus stalks, or lucerne with Na_2CO_3 at 160° removes the bulk of the (II) to a const. amount which is probably associated with the fibres, leaving an almost white residue. Similar treatment of foliage leaves affords brown and scarcely fibrous products and the relative decreases in (I) and total substance differ little from one another. Even with a large excess of NaOH it is not possible to remove (II) from leaves in the same measure as from straw and wood and the residues are dark brown masses differing in composition from cellulose. Alternate treatments with Cl_2 and Na_2SO_3 give a white residue in 60% yield from wood after 4 repetitions, but in the case of leaves 10 repetitions does not reduce the % of (II) below 19%, although nearly 80% of the total material is dissolved. The skeleton matter of foliage leaves therefore differs entirely from known cellulose carriers and it is doubtful whether any cellulose is present. (II) appear chemically united with other carbohydrates, with which they pass into solution. As in wood, OMe appears closely associated with the (II), the content of which can be approx. calc. from % OMe. H. W.

Beech-wood lignin, a reaction product of carbohydrates in the determination of lignin. R. S. HILPERT and H. HELLWAGE (Ber., 1935, 68, [B], 380—383).—Treatment of red beech-wood with saturated HCl at -10° leaves after 2 hr. only 12% of residue intermediate in composition between wood and lignin; after 24 hr. the amount of ppt. increases. The stage of the reaction is so characteristic that the presence of a component in wood, liberated by acids, is postulated. By use of HCl (d 1.19) reaction can be so decelerated that only

30—40% passes into solution; the residue has the composition of the original wood and when treated with 43% HCl at 15—20° passes into lignin. Dilution of the acid solutions with H_2O causes pptn. (about 50% of the wood) of a methylated cellulose anhydride (I), $2C_6H_{10}O_5 \cdot H_2O$, with 1 OMe per 2 anhydride residues which with conc. HCl at 15—20° gives lignin of normal elementary composition but with 21% OMe. The filtrate from (I) contains only carbohydrates and materials sol. in H_2O , but no lignin in the accepted sense. The total lignin of beech is therefore not a component of the wood but a product of the reaction, derived by the action of acids on carbohydrates. H. W.

Cellulose of marine algæ. T. DILLON and T. O'TUAMA (Sci. Proc. Roy. Dublin Soc., 1935, 21, 147—152).—Cellulose was prepared from dried *Laminaria digitata* by steeping in 1% HCl followed by aq. NH_3 , and repeated boiling with 5% NaOH, in the form of a cream-coloured powder. The only product of complete hydrolysis is glucose.

P. G. M.

Preparation and properties of alginic acid; extraction of marine algæ with various solvents. V. BARRY and T. DILLON (Sci. Proc. Roy. Dublin Soc., 1935, 21, 165—166).—Boiling H_2O extracts 41% of the dried fronds of *Laminaria digitata*. A finely divided material separates out from this extract and this, after extraction with methylated EtOH, gives a non-viscous solution in alkali, from which gelatinous alginic acid is pptd. on acidification.

P. G. M.

Chemical constituents of Irish lichens. *Lecanora gangleoides*. I. J. HARDIMAN, J. KEANE, and T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1935, 21, 141—145).—An Et₂O extract of the dried lichen yields a product from which light petroleum removes a red oil, leaving a residue from which are obtained a product (I), m.p. 196.5°, and *gangleoidin* (II), $C_{18}H_{14}O_7Cl_2$, m.p. 214—215°. (I) is probably atranorin mixed with chloroatranorin. (II), a depside, yields a *monoacetate*, m.p. 245—246°, and a *compound* $C_{16}H_{12}O_5Cl_2(OMe)_3$, m.p. 198.5°, on treatment with MeOH-KOH. Further quantities of (I) are obtained by extraction of the lichen residue with $COMe_2$ and $CHCl_3$. (II) contains 2 OMe and gives no colour with EtOH- $FeCl_3$.

P. G. M.

Fermentable sugars of wheat flour. L. GENEVOIS and M. PAVLOV (Compt. rend., 1935, 200, 690—692).—Determination of the reducing sugars before and after hydrolysis, and of the readily fermentable sugars, in H_2O -macerations of flour indicate that those which are rich in factor Z contain sugars readily fermentable in 3—5 hr., in addition to the slowly fermented sugars (maltose) (0.0025 and 0.001 g., respectively, from 0.1 g. of flour after extraction for 1.5 hr.). J. W. B.

Composition of maple sap. J. BRODIL (Vestn. Czechoslov. Akad. Zemed., 1934, 10, 258—261; Chem. Zentr., 1934, ii, 2237).—Fresh sap from *Acer platanoides* and *A. pseudoplatanus* contains much diastase and catalase with smaller proportions of zymase, invertase, emulsin, and proteases. Oxidase,

peroxidase, tyrosinase, and lipase were absent. Analytical data include 0.08 g. of malic acid per litre.

A. G. P.

Alkaloid of *Eurycles amboinensis*. L. B. OLIVEROS and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1934, 4, 41—42).—A substance $C_{16}H_{17}O_4N$, m.p. 250°, was isolated and shown to be licorine (hydrochloride hydrate, m.p. 206.5°; picrate, m.p. 196°).

CH. ABS. (r)

Sugar grass (*Sorghum saccharatum*). V. CUCULESCU (Z. Unters. Lebensm., 1934, 68, 651—652).—The % of H_2O , N, fat, starch, H_2O -sol. substances, and sugars in the seeds, stem, and syrup of sugar grass are given.

E. C. S.

Isolation of the poisonous principle of *Dimorpha cuneata*, Less. J. S. C. MARAIS and C. RIMINGTON (Onderstepoort J. Vet. Sci., 1934, 3, 111—117).—The poisonous constituent is linamarin (I). An enzyme linamarase was also isolated, which hydrolysed (I) but did not affect amygdalin, salicin, or α -methylglucoside. An aq. extract of yeast after purification by pptn. with EtOH liberated HCN from (I). *D. cuneata* yields approx. 280 mg. of HCN per plant. The min. lethal dose for rabbits was 14—20 g. of plant (at seeding stage), i.e., 14 mg. of HCN per kg. body-wt.

CH. ABS. (p)

***Leonurus cardiaca*.** W. PEYER and H. VOLLMER (Pharm. Zentr., 1935, 76, 97—102).—The botanical characteristics, physiological action, chemical behaviour, and constituents of the plant are described. Alkaloids and tannins are present. The physiological action (on mice) is due to the tannins (5—9%).

E. H. S.

Chemistry and pharmacology of extracts obtained from different parts of the seed of *Strophanthus kombe*. B. SANNA (Boll. Soc. ital. Biol. sperim., 1934, 9, 830—831).—The husk extracts reduce Fehling's solution, are least toxic, and contain mostly amorphous material. The other extracts are non-reducing and more toxic, the endosperm extracts being largely cryst. H_2SO_4 gives characteristic colours with all the extracts.

R. N. C.

Presence of 2-acetylpyrrole in stabilised official valerian. E. CIONGA (Compt. rend., 1935, 200, 780—782).—The residues obtained from fresh valerian rhizome stabilised by EtOH are freed from EtOH and treated with Et_2O . After removal of the solvent an acid residue remains which is neutralised with 25% Na_2CO_3 and treated with Et_2O . The brown mass obtained after removal of Et_2O is hydrolysed by 10% KOH-EtOH. The EtOH is evaporated and the residue treated with H_2O and Et_2O . 2-Acetylpyrrole, m.p. 90°, is isolated from the Et_2O extract. It is probably identical with the alkaloid of Chevalier (A., 1907, ii, 193).

H. W.

Seed oil of *Aegle marmelos*, Corr. R. CHILD (J. Amer. Chem. Soc., 1935, 57, 356—357).—The oil (5—35% of the seed) had d_{40}^{20} 0.918, n_D^{20} 1.4647, sap. val. 193.6, 196.8, I val. 108.0, 107.1, saturated acids 23.9%, unsaponifiable 1.58%. The acids consist of approx. 15.6% palmitic, 8.3% stearic, 28.7% oleic, 33.8% linoleic, and 7.6% linolenic acid.

R. S. C.

Acids of Chinese and esparto grass waxes and the hydrocarbons of esparto and candelilla waxes. F. J. E. COLLINS (J.S.C.I., 1935, 54, 33—35r).—The free and combined acids in Chinese (I) and esparto waxes (II) were investigated by fractional distillation of the corresponding Et esters, followed by mol. distillation. From (I) Et esters were obtained which melted between the limits 54° and 74° (22% between 62.5° and 70°); from (II) the esters melted between 58° and 72° (92% between 63° and 72°). X-Ray measurements indicate that the bulk of the acids present in (I) contain 24—30, and in (II) 26—34, C atoms. (II) contains 65—70% of the hydrocarbon $C_{31}H_{64}$, similar to that present in (I). The hydrocarbon from both sources was isolated, and the X-ray spacing, transition points, and m.p. were compared with those of an authentic synthetic specimen.

Origin and distribution of colour in the anther and pollen of petunia. M. C. FERGUSON and B. HUNT (Bot. Gaz., 1934, 96, 342—352).—In young anthers all cells except those of connective tissue contain chlorophyll. Formation of yellow pigment (I) in older anthers and pollen begins with the disappearance of chloroplasts. The mature anther and pollen always contain (I), although this is frequently obscured by anthocyanin (II). The presence of two flavones in (I) is demonstrated. A magenta pigment (III) [non-(II)] appears first in the cell sap of the sterile tissue on the inner side of the microsporangia. True (II) pigment is formed immediately prior to the dehiscence of the anther, its origin being related to (III). Both red and blue (II) pigments are present. In uniformly coloured anthers (II) occurs in all cells except the connective. Pigments of pollen and anthers are probably of common origin.

A. G. P.

Pigments of *Lactarius deliciosus*, L.—See this vol., 495.

Determination of the common carotenoids; analyses of β -carotene and leaf-xanthophyll in thirteen plant tissues. E. S. MILLER (J. Amer. Chem. Soc., 1935, 57, 347—349).—The MeOH-ligroin method, applied to synthetic mixtures of β -carotene (I) and leaf-xanthophyll (II), reveals only about 90% of the (I). A more rapid and accurate method of analysing such mixtures (using $COMe_2$ and Et_2O) is described. The (I) and (II) content of 13 grasses and sugar canes are determined.

R. S. C.

Optical properties of autumn coloured leaves. H. SPOHN (Planta, 1934, 23, 240—248).—Changes in autumn leaf-pigments are examined spectrophotometrically.

A. G. P.

Sugar, ash, nitrogen, and phosphorus of forage and of sugar beetroots, and of their hybrids. H. COLIN and E. BOUÏY (Compt. rend., 1935, 200, 853—855).—The ash, P, and N content of forage beet (I) is relatively (with respect to sugar) much > in sugar beet (II). About 1/6 of the P in (II) is sol. in dil. AcOH and < 1/2 in (I), although (I) is richer in mineral phosphates than (II).

J. L. D.

Total nitrogen, phosphorus, and calcium contents of common weeds and native grasses in

Oklahoma. H. J. HARPER, H. A. DANIEL, and H. F. MURPHY (Proc. Oklahoma Acad. Sci., 1934, 14, 36—44).—Analytical data for 50 species in various growth stages are recorded. In general weeds contained more N, P, and Ca than grasses. CH. ABS. (p)

Distribution of total nitrogen in the orange tree. S. H. CAMERON and D. APPLEMAN (Proc. Amer. Soc. Hort. Sci., 1933, 30, 341—348).—Roots contain a higher % of N than the aerial parts, but the abs. quantity is relatively small ($\approx 21\%$ of the total N). CH. ABS. (p)

Photochemical aspect of nitrate assimilation in plants. W. E. TOTTINGHAM and E. J. LEASE (Science, 1934, 80, 615—616).—A discussion. L. S. T.

Penetration of anions in *Valonia*, and its relation to cell growth. H. ULLRICH (Planta, 1934, 23, 146—176).—The mechanism of intake of NO_3^- , Br^- , and salicylate ions is examined. The cell membrane is not an important factor controlling intake since its permeability is much $>$ that of the plasma. The passage of anions into the cell from external liquids is represented as a system of anionic exchange in the aq. phase, wherein CO_3^{2-} and HCO_3^- are significant factors and the size and mobility of the various ions exert a controlling influence. A. G. P.

Possible differentiation between pedigreed wheats based on variation in chemical composition of the expressed sap and ash components of the plant at different vegetative phases. F. REICHERT and E. PAULSEN (Rev. fac. agrón. vet., 1931, 7, 329—344).—Characteristic differences in sugar content, sugar : N ratios in sap, and in N, K, P, Ca, and SiO_2 contents of ash are examined. CH. ABS. (p)

Effect of liming on the reaction of plant juices. B. MALAČ (Věstn. csl. Akad. Zeměd., 1934, 10, 426—430).—The $[\text{H}^+]$ of the sap of plants is little affected by liming the soil. The $[\text{H}^+]$ and titratable acidity of the sap of the Trifoliaceae are $>$ those of the Gramineae grown under similar conditions. NUTR. ABS. (m)

Action of heavy water on the germination of a pollen. L. PLANTEFOL and G. CHAMPETIER (Compt. rend., 1935, 200, 423—425).— H_2O containing much H_2^{18}O (I) is not only non-toxic to germination (II) of pollen of *Narcissus papyraceus*, but in 57% H_2^{18}O (II) is greater, and bursting of grains much more rare, than in normal H_2O (III), suggesting that hydrolysis by (I) is slower than by (III). In presence of sugar, (II) proceeds even in 98% (I). E. W. W.

Effect of deuterium oxide on respiration of germinating seeds. G. J. MELOT (Proc. Soc. Exp. Biol. Med., 1934, 32, 79—83).—Wheat seeds in 14.8, 38, and 94% H_2^{18}O germinate without showing any macroscopical difference from controls in H_2O under the same conditions. No significant differences are observed in the R.Q. of the seeds in H_2O and H_2^{18}O during the first and second days of germination. R. N. C.

Accumulation of electrolytes [in plants]. VII. Organic electrolytes. II. A. G. JACQUES (J. Gen. Physiol., 1935, 18, 283—300; cf. this vol., 266).—The inorg. cations (I) of leaf-juices (*Rheum*,

Rumex, *Oxalis*) and of ashed plant tissues are $>$ the inorg. anions. The data indicate that the phenomenon is due to passage of (I) into the protoplasm as MOH and accumulation as org. salts (e.g., oxalates) or non-polar compounds (II). K and Na occur as sol. ionisable compounds, whilst Mg and Ca are present probably as insol. org. salts or as components of (II). F. O. H.

Influence of boric acid on plants, especially on germinating pollen grains. T. SCHMUCKER (Planta, 1934, 23, 264—283).—In a no. of species examined, 0.001—0.01% aq. H_3BO_3 favoured the germination of pollen grains, either by accelerating the growth of pollen tubes or by increasing the % germination. In the absence of B growth is restricted or ceases. Sensitivity of fungi to H_3BO_3 varied considerably. B influences the production of cell membranes. A. G. P.

Biochemistry of flowers. Mineral nutrition of the corolla. R. COMBETS (Compt. rend., 1935, 200, 578—580).—The mineral content of the corolla of *Lilium croceum* increases up to the time of full bloom and, contrary to Ivanov's view, declines until the flower fades. A. G. P.

Determination of soluble ash in plant material. J. G. LOUW (Onderstepoort J. Vet. Sci., 1934, 3, 191—195).—The material is dried at 103° for 3 hr., ignited at 450° for 2 hr., and the total ash (I) weighed. (I) is evaporated at 100° with 3 ml. of conc. HCl and dried at 100° for 1 hr. It is then heated for a few min. with 20 ml. of H_2O and 2 ml. of conc. HCl, cooled, and filtered. The filtrate and washings (vol. 100 ml.) are used for the determination of Ca, Mg, K, and Na. The insol. residue (II) is dried for 15 min. at $300\text{--}350^\circ$. The difference between the wt. of (II) and that of (I) is the wt. of sol. ash. NUTR. ABS. (m)

Absorption of germanium by plants. W. GEILMANN and K. BRUNGER (Biochem. Z., 1935, 275, 387—395; cf. A., 1931, 455).—The roots and other parts of plants (I) (e.g., oats, mustard, buckwheat, barley) take up Ge from soils which contain sol. Ge compounds, the amount (II) absorbed usually varying little with (I) species. (II) is large in the case of oats. Low concns. of Ge stimulate growth, but high concns. are toxic. *Aspergillus niger* absorbs (and is not poisoned by) relatively large amounts of Ge from a medium containing GeO_2 . W. McC.

Molybdenum content in leaves. H. TER MEULEN and H. J. RAVENSWAAY (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 7—10).—Mo content in leaves remains const. or increases and Mo does not migrate to branches in autumn. A relationship seems to exist between leaf colour and Mo content. Brown leaves contain nearly twice as much Mo as the green variety. H. T.

Distribution of copper in the rice plant cultivated on soils containing copper. M. SHIKATA, I. TACHI, and N. YASUZAKI (J. Agric. Chem. Soc. Japan, 1934, 10, 368—373).—Cu contents (% of dry matter) were: roots 0.064, stems 0.006—0.010, leaves 0.007—0.011, ears 0.009, rice hulls 0.004, unpolished rice 0.002—0.007, polished rice 0.001.

The normal rice plant contains a small quantity of Cu. The root contains much Fe. CH. ABS.

Importance of copper for the development of plants in comparison with boron and manganese: copper-deficiency phenomena. E. BRANDENBURG (Angew. Bot., 1934, 16, 505—509).—Cu-deficiency disease in oats is examined.

A. G. P.

Action of vanadium on cultivated plants. K. SCHARRE and W. SCHROPP (Z. Pflanz. Düng., 1935, 37, 196—202).—The growth of wheat in sand cultures was increased by small amounts and retarded by larger additions of NaVO_3 . Barley, rye, oats, and (notably) peas were injured by all dosages examined. The effect on roots was relatively > that on tops.

A. G. P.

Effect of chromium and chromate ions on cultivated plants. K. SCHARRE and W. SCHROPP (Z. Pflanz. Düng., 1935, 37, 137—149).—Small additions of $\text{Cr}_2(\text{SO}_4)_3$ (I) to culture media improved the growth of oats and rye; wheat and maize responded to a smaller extent, but barley and peas were highly sensitive to injury. Large applications of (I) caused injury in all cases. In some instances small concns. of CrO_4^{--} proved beneficial, but in general the min. injurious concn. was much < that of (I). Replacement of Fe^{+++} in nutrient media by increasing proportions of Cr^{+++} produced generally unfavourable effects on the growth of aerial portions of plants but tended to increase the proportional wt. of roots when the proportion of Cr : Fe was < 7 : 1.

A. G. P.

Iron content of pastures. ANON. (New Zealand Dept. Sci. Ind. Res., 8th Ann. Rep., 1933—1934, 18—19).—Since the Fe content of healthy and unhealthy [bush sickness (I)] pastures is low in every case (0.006%) no support is given to the theory that the sole cause of (I) is low Fe content of the pastures (II). The Fe and Mn contents of 10 species of legumes and grasses from different (II) are given. NUTR. ABS. (m)

Iodine in cabbage. J. F. McCLENDON and C. E. HOLDRIDGE (Biochem. J., 1935, 29, 272—274).—A combustion tube for destruction of org. matter in dried cabbages, without loss of I, is described.

A. E. O.

Mineral iodine in seaweeds. A. TROFIMOV (Planta, 1934, 23, 56—70).—The distribution of I' in several species of algæ varied considerably. After heating fresh samples in H_2O 32—100% of the total I is in the form of I'. Grinding of the phylloid lamellæ of *Laminaria digitata* (I) resulted in the disappearance of I' and the deposition of a viscous gum-like substance from the cell walls. Ensilage of the algæ causes a rapid decrease in mobile I and a slow decline in total I content. Factors influencing the elimination of free I by (I) are examined.

A. G. P.

Calcite formed under the influence of plants. J. WALLNER (Planta, 1934, 23, 51—55).—The form of CaCO_3 derived from land and marine plants is discussed.

A. G. P.

Phosphates in [plant] solution cultures. A. L. SOMMER (Ann. Rept. Alabama Agric. Exp. Sta., 1932,

14).—The min. $[\text{PO}_4^{---}]$ for growth differs with different plants and in most field crops was inversely related to the root surface exposed to the solution. The no. of root hairs (I) was a dominant factor. Wheat and buckwheat with very numerous (I) were maintained by 0.1 p.p.m. of PO_4^{---} . Cotton did not maintain growth when P was removed from the nutrient although previously exposed to an excess for 64 days.

CH. ABS. (p)

Phosphorus in alternate-bearing sugar prunes. C. COMPTON (Proc. Amer. Soc. Hort. Sci., 1933, 30, 151—153).—The P content of wood, bark, and spurs, but not of leaves, reflected the alternate-bearing condition.

CH. ABS. (p)

Factors affecting the absorption of magnesium by the potato plant. R. L. CAROLUS (Proc. Amer. Soc. Hort. Sci., 1933, 30, 480—484).—Mg deficiency is characterised by very low Mg, rather low Ca, and high N contents in lower leaves.

CH. ABS. (p)

Effect of potassium deficiency on the composition of the tomato plant. T. G. PHILLIPS, T. O. SMITH, and R. B. DEARBORN (New Hamps. Agric. Exp. Sta. Tech. Bull., 1934, No. 59, 16 pp.).—Deficient plants (I) had less ash and K and more Ca, Mg, and P (% of dry wt.) than those receiving a complete nutrient. On a fresh wt. basis, (I) were high in total solids, reducing sugars, and insol. N. Leaves contained much sucrose and stems had relatively low proportions of dextrin and starch. In the early stages of K deficiency there was no evidence of disturbed N metabolism.

A. G. P.

Sulphur metabolism of plants. K. MOTHES and W. SPECHT (Planta, 1934, 22, 800—803).—The significance of SO_4^{--} reduction in yeast and green leaf tissues is considered in relation to cystine formation and the redox system $\cdot\text{SH} \rightleftharpoons \cdot\text{S}\cdot\text{S}\cdot$ in plants.

A. G. P.

Sulphur metabolism of maize and tobacco. E. HEISERICH (Z. Pflanz. Düng., 1935, 37, 55—72).—The S metabolism of maize (I) and tobacco (II) is largely influenced by the nature of the N source. The total S in plants receiving NO_3^- is much > that of those supplied with NH_4^+ , although the latter have the higher proportion of protein-S (III). Lower leaves of (II) in NO_3^- media have approx. 20 times the SO_4^{--} content of NH_4^+ -fed plants. The glutathione-S (IV) is unaffected by N nutrition. Assimilation of S is dependent on reduction processes in the leaves. In S-deficient plants SO_4^{--} and (IV) are present only in minute amounts. N deficiency in (II) and S deficiency in (I) and (II) result in a large proportion of (III) becoming H_2O -sol. Feeding SO_4^{--} to such plants causes a return to normal S distribution. Carbohydrates increase in S-deficient plants but to a smaller extent than in N deficiency. In dormant maize seed > 50% of the (III) is H_2O -sol., but this proportion declines rapidly with the commencement of germination.

A. G. P.

Effect of ultra-violet rays on growth and on calcium and phosphorus contents of plants. H. M. BENEDICT (Bot. Gaz., 1934, 96, 330—341).—Rays of 290—310 m μ increased the dry matter production of all plants examined (except maize)

and also the % of Ca. Rays $< 290 \text{ m}\mu$ caused a decrease in dry wt. without affecting the % of Ca. No definite influence on $\text{PO}_4^{'''}$ intake was apparent.

A. G. P.

Aberrations in the chemical composition of peas from plants affected with root-rot. Z. I. KERTESZ, J. G. HORSFALL, and A. H. ROUSE (J. Agric. Res., 1934, 49, 799—814).—Peas from affected plants have lower H_2O contents, N, and ash and larger proportions of total carbohydrates. Of the latter, sugars are $<$ and starch is $>$ in normal plants.

A. G. P.

Cause of wilt in flax. H. GROSSMANN (Phytopath. Z., 1934, 7, 545—583).—Culture solutions of *Fusarium lini* and other species induce wilt in flax. The toxic substance is non-volatile and thermolabile.

A. G. P.

Influence of temperature on nitrogen content and rust-resistance of young cereal plants. G. GASSNER and W. FRANKE (Phytopath. Z., 1934, 7, 315—326).—Protein content and sensitiveness to rust in wheat increased with falling growth temp. The sol. N in grain showed smaller and less definite changes.

A. G. P.

"Little-leaf" or "rosette" of fruit trees. W. H. CHANDLER, D. R. HOAGLAND, and P. L. HIBBARD (Proc. Amer. Soc. Hort. Sci., 1933, 30, 70—86).—Affected shoot-leaves and stems have subnormal Zn contents.

CH. ABS. (p)

Metabolic physiology of leaf-roll in potatoes. J. HARTSCH (Planta, 1934, 22, 692—719).—Protein metabolism in healthy (I) and diseased (II) plants was not fundamentally different. Increased conversion of starch into dextrin in (II) is due to the greater activity of dextrinogen-amylase. Amylase activity in (II) occurs with p_{H} 3.5—4.5 and in (I) with 6.5—7.0.

A. G. P.

Physiology of mosaic disease of tomato. W. H. READ (Ann. Rept. Exp. Res. Sta. Cheshunt, 1933, 64—67).—In healthy plants (H) the concn. of reducing sugars (I) in the laminae remained const. and non-reducing sugars (II) increased during daylight to a max. at 3 p.m. In diseased plants (D), (I) increased to a max. at 3 p.m. and subsequently decreased rapidly, whereas (II) increased from noon to a max. at 6 p.m. Mean vals. of (II) in H were $>$ those in D. Differences in (I) were small. Starch contents were higher in laminae of D. In petioles of H (I) was $>$ (II), the former showing max. at 6 p.m. and min. at 2 a.m., and (II) remaining approx. const. In D, (I) and (II) were practically equal between 8 a.m. and 7 p.m., with max. at noon and 6 p.m. Subsequently (II) fell to a very low val.

CH. ABS. (p)

Potato tests of the relationship between the potential of the tubers and the incidence of virus. E. KOHLER and A. HEY (Zentr. Bakt. Par., 1935, II, 91, 255—267).—Active virus in potato results in a change of potential towards the negative side.

A. G. P.

Deamination in virus-infected plants. A. V. V. IYENGAR (Nature, 1935, 135, 345).—The increased production of NH_3 observed in spiked sandal is due to greater oxidative deamination in the diseased tissues. OH-acids, especially malic, are increased in the early stages, and in the more diseased tissues succinic acid is formed. An active deaminase appears to be present in infected plants.

L. S. T.

Mill for fine grinding of difficult (especially plant) materials. R. FEULGEN and M. BEHRENS (Z. physiol. Chem., 1935, 231, 85—87).—The coarsely ground material suspended in C_6H_6 is drawn between a rotor and stator of fine emery.

J. H. B.

Preparation of semipermeable sac-membranes. J. DUCKWORTH (Biochem. J., 1935, 29, 656—659).—A method for preparing collodion membranes of uniform permeability, and an apparatus for carrying out ultrafiltration with them, are described.

W. O. K.

Determination of the acid-base balance in food materials. J. DAVIDSON and J. A. LECLERC (J. Biol. Chem., 1935, 108, 337—347).—The acid-base balance is determined by titration to p_{H} 7.4 of the ash, with corrections for S and Cl lost during the ashing. The results are $<$ those obtained by the usual computation method.

H. G. R.

Determination of chlorine in small amounts of tissue. W. NIEMIERKO (Acta Biol. Exp. [Warsaw], 1932, 7, 101—106).—Tissue is decomposed by HNO_3 containing AgNO_3 . The AgCl formed is dissolved in aq. NH_3 and treated with $(\text{NH}_4)_2\text{S}$. The Ag_2S ppt. is dissolved in HNO_3 and Ag determined by Volhard's method.

CH. ABS. (p)

Determination of selenium in animal matter and clinical test in urine. H. C. DUDLEY and H. G. BYERS (Ind. Eng. Chem. [Anal.], 1935, 7, 3—4).—Earlier procedure (B., 1934, 798) is modified.

E. S. H.

Physiological arsenic and the use of the Kjeldahl flask in its detection. G. LOCKEMANN (Z. anal. Chem., 1935, 100, 20—29).—The As content of glass Kjeldahl flasks vitiates the analysis. SiO_2 flasks are recommended.

R. S.

Comparative investigation of the methods of Mendel and Goldscheider and of Friedemann and Kendall for determination of lactic acid. G. INGVARSSON (Biochem. Z., 1935, 276, 297—308).—Using aq. solutions of lactic acid (I) and treating with $\text{HPO}_3\text{--CuSO}_4\text{--CaO}$ (II) the Mendel-Goldscheider method (III) gave higher results than the Fürth-Charnass method as modified by Friedemann and Kendall (IV). When (I) is added to blood and (II) used for removal of protein and carbohydrate, a recovery of 87 and 98% of the added (I) is obtained by methods (III) and (IV), respectively. With both methods after administration of adrenaline there is always an increase of (I); after glucose in 16 cases an increase, and in one case a decrease, of (I) was obtained.

P. W. C.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

MAY, 1935.

General, Physical, and Inorganic Chemistry.

Excitation of Balmer series of hydrogen to high order of terms by electrodeless discharge. H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, **26**, 156—163; cf. this vol., 135).—From the purity of the Balmer lines observed by photographing the axial part of a discharge tube it is concluded that in this region the H is present in the at. state or as protons. The effects produced by the introduction of canal rays, ionising agents, and halogen compounds are discussed. W. R. A.

Stark effect in the molecular spectrum of hydrogen. H. SNELL (Phil. Trans., 1935, **A**, 234, 115—144).—Full data and analyses are tabulated for the range $\lambda\lambda$ 4860—6620. About 350 lines showed measurable displacements in a field of 90,000 volts per cm. Some new lines, and classified undisplaced lines, are given. The patterns agree, in general, with the restrictions of theory. N. M. B.

Fulcher bands of HH^2 and H_2^2 . G. H. DIEKE and R. W. BLUE (Physical Rev., 1935, [ii], **47**, 261—272).—The production and photography under high dispersion of the mol. spectra of H_2 , HH^2 , and H_2^2 in the ultra-violet-infra-red range, giving many new H_2 lines, are described. Preliminary data for the Fulcher bands are tabulated, and the band consts. for the three mols. are given. The heat of dissociation of the normal mol. is 4.43—4.52 volts. N. M. B.

$\text{B}^2\Sigma \rightarrow \text{A}^1\Pi$ and $\text{C}^2\Sigma \rightarrow \text{A}^1\Pi$ bands of carbon monoxide. R. SCHMID and L. GERO (Z. Physik, 1935, **93**, 656—668).

Pre-dissociation in the upper level of the second positive group of nitrogen ($\text{C}^3\Pi$). D. COSTER, E. W. VAN DIJK, and A. J. LAMERIS (Physica, 1935, **2**, 267—272; cf. A., 1933, 991).—Using a SiO_2 discharge tube of very high intensity, no pre-dissociation was detected in the $0 \rightarrow 0$ band up to $J=90$. For $v=4, 3$, and 2 , pre-dissociation sets in at $J=29, 44$, and 56 , respectively. J. W. S.

Analysis of the atomic spectrum of oxygen. B. EDLEN (Z. Physik, 1935, **93**, 726—730).—15 lines due to impurities have been eliminated (cf. A., 1933, 991) and the analysis is completed. A. B. D. C.

Reversal of neon lines. H. NAGAOKA and T. MISHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, **26**, 136—155).—The reversal of the 6507, 6402, 6266, 6143 6096, and 5852 Å. Ne lines has been studied under different conditions of excitation, temp., pressure, and form of tube. W. R. A.

Radiation of resonance lines in the sodium discharge and the production of an absolute light unit. H. SCHMELLENMEIER (Z. Physik, 1935, **93**, 705—725).—A Na discharge tube has been constructed to give low variation of intensity with pressure and current; the intensity can be maintained to $\pm 2\%$. Discharge phenomena in the positive column are discussed theoretically. A. B. D. C.

Intensity distribution in pressure-broadened spectral lines. R. MINKOWSKI (Z. Physik, 1935, **93**, 731—740).—Distribution within the D-line broadened by A accords with Kuhn's theory (A., 1934, 1281). A. B. D. C.

Presence of argon in stellar atmospheres. M. NICOLET (Bull. Acad. roy. Belg., 1935, [v], **21**, 186—194).—A comparison of $\lambda\lambda$ and intensities of stellar lines and the experimental spectrum of A shows that, owing chiefly to the large no. of coincidences of lines of O_2 and N_2 , only the λ 4348 line can be definitely attributed to A. N. M. B.

Hyperfine structure of the resonance lines of potassium. D. A. JACKSON and H. KUHN (Proc. Roy. Soc., 1935, **A**, 148, 335—352).—The hyperfine structures of the resonance lines of K and Na were examined by means of the absorption of an at. beam. Each line consists of 2 close components, the separations of which are given. In the case of K, the hyperfine structure is due to the K^{39} , of which the nuclear magnetic moment is calc. to be between 0.43/1838 and 0.47/1838 Bohr magneton. The nuclear magnetic moment of Na is 2.05/1838 Bohr magneton. L. L. B.

Band spectrum of cadmium. T. S. SUBBARAYA (Proc. Indian Acad. Sci., 1935, **1**, **A**, 484—488).—Available experimental data are analysed and a comparison is made with the structure of the corresponding Hg bands. N. M. B.

Band spectra of elements of the fifth group. G. NAKAMURA and T. SHIDEI (Japan. J. Physics, 1935, **10**, 11—25).—The absorption band spectra of Bi and Sb vapours and of their mixtures have been studied. The latter show a new group of bands at 2530—2400 Å., attributed to SbBi . All groups are analysed and the mol. consts. of Sb_2 , Bi_2 , and SbBi calc. J. W. S.

Spectral photo-effect of compact caesium layers. W. KLUGE (Z. Physik, 1935, **93**, 636—643).—These layers show selective max. at 500, 360, 285, and 240 m μ . A. B. D. C.

Displacement and broadening by mercury and xenon of the higher series terms of caesium, and their broadening by potassium and argon. C. FUCHTBAUER and F. GÖSSLER (Z. Physik, 1935, 93, 648—655). A. B. D. C.

Intensity ratio of hyperfine structure components of the caesium line 4555 Å. D. A. JACKSON (Z. Physik, 1935, 93, 809—812). H. BARTH (*ibid.*, 813).—Polemical (cf. A., 1934, 1280). A. B. D. C.

Arc spectrum of neodymium, at normal pressure, between 3100 and 2400 Å. S. PINA DE RUBIES (Anal. Fis. Quím., 1934, 32, 43—48).—184 lines are recorded. H. F. G.

Arc spectrum of samarium and gadolinium. Normal electron configurations of the rare earths. W. ALBERTSON (Physical Rev., 1935, [ii], 47, 370—376).—Data and classifications are tabulated for 453 lines, 175 levels of Sm I, and 71 lines, 35 levels of Gd I. Electron configurations and transitions are discussed. N. M. B.

Short ultra-violet in the solar spectrum. S. RODIONOV, E. PAVLOVA, N. REJNOV, N. STUPNIKOV, and A. JUZEFOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 26—28).—Radiation has been measured to 2700 Å. at 4000 m., and a diurnal variation noted. A. B. D. C.

Observations of night sky luminescence by the extinction method. N. DOBROVIN, I. FRANK, and P. TSCHERENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 110—117).—Observations made at a point 3200 m. above sea level at Mount Elbrus (Caucasus) in Aug., 1934, are discussed. W. R. A.

Intensity variation of the auroral green line in the night sky. A. A. LEBEDEV and I. A. CHVOSTIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 118—124).—During a night the intensity first rises sharply and then declines slowly, the max. intensity being 2.8 times > initial intensity and agreeing with Dobrovin *et al.* (see above). The emission of the green line is due to dissociation of O₂ into O and the energy of the emission is the same as the energy of dissociation of mol. O₂. W. R. A.

Electromagnetic fields due to variable electric charges and the intensities of spectrum lines according to quantum theory. C. E. EASTHOPE (Proc. Roy. Soc., 1935, A, 148, 453—470).—Mathematical. Comparison of the intensity of radiation as given by Hertz' formula with that given by Schott's method (A., 1933, 206) proves that, in the case of a fixed H atom with a general axiosymmetrical Schrödinger distribution, the usual method of calculating the intensities of spectral lines gives the correct results, provided the frequency of the radiation is such that $(2\pi\nu/\gamma)^2$ can be neglected. This condition holds for optical line spectra. For higher frequency radiation (e.g., X-ray), where $(2\pi\nu/\gamma)^2$ is not negligible, the classical formula gives too great a val. for the intensity of radiation. L. L. B.

Spectral and impact phenomena in the Faraday dark space. K. G. EMELEUS and O. S. DUFFENBACK (Physical Rev., 1935, [ii], 47, 460—466).—Mechanisms based on observations of the spectra

of the negative glow and Faraday dark space in pure He, and in He containing a trace of N₂, are discussed. N. M. B.

Line strengths in intermediate coupling. G. H. SHORTLEY (Physical Rev., 1935, [ii], 47, 295—300).—Mathematical. N. M. B.

Radiation damping and the width of X-ray lines. J. A. PRINS (Physica, 1935, 2, 231—238).—The classical formula for the half-width of spectral lines broadened by radiation damping, modified by the quantum theory, is used to calculate the yields of fluorescence from line widths observed in the long-λ X-ray region. J. W. S.

K-Series X-ray emission lines of iron in several compounds. II. S. TANAKA and G. OKUNO (Japan. J. Physics, 1935, 10, 1—4; cf. A., 1934, 1052).—The Kα₁, Kα₂, Kβ₁, and Kβ' lines of Fe were investigated for FeCO₃, FeSO₄, Fe₂(SO₄)₃, FeC₂O₄, and (NH₄)₂Fe(SO₄)₂. As with Fe₂O₃, separation of Kβ' from Kβ₁ was obtained. Except with FeCO₃ the Kβ₁ line was displaced relative to that of pure Fe. J. W. S.

Efficiency coefficient, *u*, of the characteristic K-radiation and the ratio of ionisation of air to energy of X-rays. E. ARENDS (Ann. Physik, 1935, [v], 22, 281—310).—Previous work on the determination of *u* is reviewed. An apparatus for measuring *u* for monochromatic X-rays, making use of ionisation of air, is described. *u* was obtained for Fe, Ni, Cu, Zn, Se, Mo, Ag, and Sn. A. J. M.

Electric polarisation of hydrogen adsorbed on metal surfaces and its effect on the recombination of hydrogen atoms. R. SUHRMANN and H. CSESCH (Z. physikal. Chem., 1935, B, 28, 215—235).—The spectral photo-electric sensitivity curves of Ag, Al, Ti, and Pt surfaces before and after treatment with at. H have been determined, and the emergence potentials, *ψ*, calc. The change in *ψ* caused by the at. H plotted against *ψ* for the various metals gives a straight line, and the activity in catalysing the recombination of H atoms ∝ the *ψ* of the clean surface. It is concluded that the H atoms are polarised in the electric field of the metal surface. R. C.

Ionisation of inert gases by positive alkali ions. R. N. VARNEY (Physical Rev., 1935, [ii], 47, 483—487).—Ionisation potentials were determined by a new method which employs the neutralisation of an electron space-charge by the newly-formed positive ions to show the ionisation. No ionisation was given by Li⁺ ions, none by Na⁺ ions except in Ne, or in Ne by any ions but Na⁺. Self-consistent corr. ionisation potentials are obtained. N. M. B.

Photo-electric properties of the (100) and (111) faces of a single copper crystal. N. UNDERWOOD (Physical Rev., 1935, [ii], 47, 502—505).—Two specimens were heated simultaneously by electronic bombardment at various red-heat temp. for 1500 hr. Outgassing above the evaporation temp. is liable to destroy the original face by a form of etching due to evaporation. The max. difference in the work function for the two faces, found after 500 hr., corresponds with threshold λλ 2540 and 2200 Å. for the (111) and (100) faces, respectively. N. M. B.

Tungsten-thorium problem. II. Anomalous activation. E. CHALFIN (Physikal. Z. Sovietunion, 1934, 5, 838—847; cf. *ibid.*, 1932, 2, 59).—Anomalies in the activation of thoriated W are caused by fluctuations in the distribution of Th atoms on the W surface. CH. ABS. (e)

Transformation of light images into electron images. W. SCHAFFERNICHT (Z. Physik, 1935, 93, 762—768).—The light image is projected on to a photo-electric cathode and the electron streams are subsequently focussed by a magnetic lens.

A. B. D. C.

Relations between mean values in electron mechanics. R. ZATCOFF (J. Phys. Radium, 1935, [vii], 6, 53—54).—Mathematical. N. M. B.

Mean kinetic energy and mean energy spent in excitation by electrons drifting through dense gases. F. E. NULL (Physical Rev., 1935, [ii], 47, 301—305).—Mathematical. N. M. B.

Polarisation of electrons when scattered by crystals. V. WEISSKOPF (Z. Physik, 1935, 93, 561—581).—Partial polarisation can take place on reflexion at a potential barrier, and crystals can reflect unpolarised beams partly polarised.

A. B. D. C.

Velocity of migration of electrons in alkali halide crystals. A. SMAKULA (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1934, [ii], 1, 55—65; Chem. Zentr., 1934, ii, 2801).—The mobility in an electric field of electrons produced thermally in crystals of NaCl, NaBr, and NaI, and the corresponding K and Rb salts, has been measured. H. J. E.

Energy of transfer of electrons from metals to dielectrics. N. KALABUCHOV (Z. Physik, 1935, 93, 702—703).—Energy of transfer of electrons from K and Pt to NaCl is 2.28 volts as found for Ag (this vol., 5).

A. B. D. C.

Emission of electrons by swift-moving mercury ions. L. H. LINFORD (Physical Rev., 1935, [ii], 47, 279—282).—Targets of Ni, Cu, Mo, Al, W, Ag, Sn, Mg, and Cd bombarded by swift Hg ions emit 7—20 electrons per incident ion. The emission is an increasing function of the ionic energy in the range 0.7—2.35 mv. Targets of Mo and W heated in vac. show temporarily a decreased emission. Freshly-formed alkali metal films show steadily increasing emission for some time after formation. For Li, the effect is very rapid, and the emission reaches 50 electrons per incident ion. N. M. B.

Excitation of molecular vibration by impact of slow electrons. H. S. W. MASSEY (Trans. Faraday Soc., 1935, 31, 556—563).—Mathematical.

F. L. U.

Elastic scattering of electrons in (I) argon and krypton, (II) molecular hydrogen. G. M. WEBB (Physical Rev., 1935, [ii], 47, 379—383, 384—388).—I. Coeffs. were determined experimentally for the angular range 5—150° and incident electron energies 25—950 volts. Calc. and experimental scattering curves are given and discussed.

II. Angular distribution data and curves were obtained for the angular range 5—150° and incident electron energies 30—912 volts, and are compared

with theory. The theoretical mol. curve agrees better than the at. curve with the 100-volt experimental curve. An attempt is made to detect the diffraction pattern in the experimental H₂ curve. N. M. B.

Emission of electrons under the influence of chemical action. V. Theory of the chemical electron emission and its application to certain reactions involving halides. A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1935, A, 148, 533—564; cf. A., 1934, 468, 937).—A study is made of the energy distribution and of the abs. val. of the total emission current of the electrons emitted from the liquid alloy K₂Na, when it is acted on by chemically active gases (e.g., the halogens) at pressures of the order of 10⁻⁵ mm. The electron emission is regarded as an immediate result of a bombardment, by free metallic electrons, of the unstable (excited) chemical linkings formed on the metal surface during collisions of the gas mols. with the metal. The physical problems involved relate to (1) collisions of the second kind between free electrons and the electronically excited chemical linkings, and (2) the escape of electrons from the metal surface. Problem (1) is treated by introducing a mathematical expression for the electron de-excitation function which represents the chance of a successful collision. Application of the theory to the experiments leads to a determination of the vals. of the consts. included in the electron de-excitation function, and also of the val. of the total potential barrier of the alkali metal. The duration of the excited states is estimated. L. L. B.

Internal conversion of γ -rays with the production of electrons and positrons. J. C. JAEGER and H. R. HULME (Proc. Roy. Soc., 1935, A, 148, 708—728).—Theoretical. The internal conversion coeff. for an element of at. no. 84 has been calc. in both dipole and quadrupole cases. Expressions are obtained for the no. of pairs created by the absorption of the γ -rays emitted by the nucleus. For energies of about 5 mc² it is of the order of 10⁻⁴—10⁻³ pair per γ -ray quantum. The no. of positrons emitted per unit energy range increases steadily with the energy of the positrons. There is thus a marked difference in the average energies of the electrons and positrons emitted, the asymmetry arising when the influence of the nucleus is included. For very light elements there is symmetrical distribution of the energy between positron and electron. The results are in satisfactory agreement with those obtained experimentally by Alichanov and Kosodaev (A., 1934, 1150).

L. L. B.

Application of the Wilson chamber to the study of spark discharge. U. NAKAYA and F. YAMASAKI (Proc. Roy. Soc., 1935, A, 148, 446—453).—The formation and distribution of ions produced at the initial stages of spark formation have been studied by means of the Wilson chamber. Photographs of ion clouds produced under various conditions are reproduced. The negative cloud is diffuse and spindle-shaped, whilst the positive cloud consists of a bundle of streamers. L. L. B.

Triatomic ions in mixtures of the hydrogen isotopes. O. LUHR (J. Chem. Physics, 1935, 3,

146—149).—A mass-spectrograph analysis of aged ions in mixtures of H_2 and 84 to < 1% H_2^+ showed that after drifting through 5 cm. of gas at about 0.5 mm. pressure the ions were > 95% triat., consisting of H_3^+ , H_2H^+ , HH_2^+ , and H_3^+ . Relative proportions, as deduced from heights of triat. ion peaks, are tabulated. N. M. B.

Probability of collision for slow H^+ , $(H^+H^+)^+$, $(H^+H_2^+)^+$, $(H_2^+H^+)^+$, $(H_2^+H_2^+)^+$, and He^+ ions in argon. E. B. JORDAN (Physical Rev., 1935, [ii], 47, 467—472).—Vals. and probability curves for various energy ranges are given and discussed. N. M. B.

Periodic system of the elements. Z. WOJNICZ-SIANOŹEŃSKI (Rocz. Chem., 1934, 14, 1446—1466).—The history of the development of the periodic law is described, and its significance is discussed. R. T.

Application of international, rational, and practical at. wts. A. BASIŃSKI (Rocz. Chem., 1934, 14, 1467—1473).—The application of Schoorl's "rational" at. wts. (A., 1919, ii, 72) or of Bruhn's "practical" at. wts. (Z. angew. Chem., 1929, 42, 645) in practice is not advocated. Where a high degree of accuracy is required, the buoyancy correction should be calc. for each compound individually. R. T.

Two relations between atomic number and at. wt. of chemical elements. F. J. LEVINSON-LESSING (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 46—54).—Relations previously described (A., 1923, ii, 146) are discussed with more accurate data. A. B. D. C.

At. wts. of several radiogenic leads. G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1935, 57, 467—471).—The at. wts. of 7 specimens of radiogenic Pb from different sources have been determined. The at. wt. of U-Pb does not appear to vary systematically with the age of the mineral source. E. S. H.

Indium isotope 113. M. WEHRLI (Helv. phys. Acta, 1934, 7, 611—619; Chem. Zentr., 1934, ii, 2953—2954; cf. A., 1934, 1286).—Absorption measurements with InI give an $In^{115} : In^{113}$ abundance ratio of 11 : 1. H. J. E.

Displacement of isotope series by β -radiation, and the isotopy of the rare earth elements. A. S. LIPEROVSKI (J. Gen. Chem. Russ., 1934, 4, 1157—1167).—Theoretical. R. T.

Radioactivity of material derived from old roofs. A. BOUTARIC (Ann. Guebbard-Severine, 1934, 10, 400—403).—The radioactivity acquired by material exposed to the open air is produced chiefly by contact with rain. J. G. A. G.

Heat loss of polonium; calorimetric determination of radioactive constants. A. SANIELEVICI (J. Phys. Radium, 1935, [vii], 6, 73—77).—Vals. obtained by the adiabatic micro-calorimeter are: loss of heat per hr. 27.24 g.-cal. per curie of Po; life period 138.7 days; no. of ion pairs produced in air by a Po α -ray 1.53×10^5 . N. M. B.

Radioactivity of He^3 . I. V. KURTSCHATOV, K. D. SINELNIKOV, G. SCHTSHEPKIN, and A. VIBE (Physikal. Z. Sovietunion, 1934, 5, 922—926).—Decomp. of He^3

into H^3 and a positron is possible energetically, but was not detected. CH. ABS. (e)

Radioactivity of potassium and rubidium. O. KLEMPERER (Proc. Roy. Soc., 1935, A, 148, 638—648).—The data for the β -emission of K or Rb conflict with Fermi's theory or with Sargent's equations (A., 1933, 443). Experiment shows that none of the processes (β -coincidences, α - β decay, β - β decay) suggested by Gamow to explain this contradiction (A., 1934, 715) exists. It is suggested that K^{40} and Rb^{86} exist and are responsible for the radioactivity of K and Rb. The existence of a nuclear spin of 4 or 5 for K^{40} is probable, and would explain the contradiction between lifetime and β -ray velocity. L. L. B.

Period of radium. E. GLEDITSCH and E. FOYN (Amer. J. Sci., 1935, [v], 29, 253—259).—From experiments on uranite from North Carolina and Norwegian broeggerite the const. λ of Ra has been found to be 4.12×10^{-4} and 4.13×10^{-4} year $^{-1}$, respectively. The mean of these and earlier determinations gives half-life of 1686 years. R. S. B.

Ionisation curves for CF_4 and SF_6 due to Po α -radiation. B. GRINBERG and A. M. DA SILVA (J. Phys. Radium, 1935, [vii], 6, 69—70).—The retardations, relative to air, as determined from the ionisation curves, are 2.63 and 3.87 for CF_4 and SF_6 , respectively. N. M. B.

β -Particle from actinium. D. E. HULL, W. F. LIBBY, and W. M. LATIMER (J. Amer. Chem. Soc., 1935, 57, 593).—The upper energy limit is about 220,000 e.v. E. S. H.

β -Spectra of some radioactive elements. A. I. ALICHANOV, A. I. ALIOHANIAN, and B. S. DŽELEPOV (Nature, 1935, 135, 393).—The β -spectra of the radioactive elements obtained by bombarding Cl_2 , Br, and I with neutrons from a Be+Rn source have been investigated. The spectral limits are the same for Cl^{36} , Br^{80} , Br^{82} , and I^{128} , and with Br^{80} and I^{128} the shape of the spectral curve is the same and analogous to that of Ra-E. The emission of hard γ -rays is probable. L. S. T.

Induced radioactivity and particle emission. F. H. NEWMAN and H. J. WALKER (Phil. Mag., 1934, [vii], 19, 661—693).—The induced radioactivity of many elements is discussed, methods of producing certain missing isotopes being suggested and their modes of disintegration predicted. H. J. E.

Radioactivity excited by neutrons. P. PREISWERK (Compt. rend., 1935, 200, 827—829).—Neutrons from a Rn+B source are less numerous and less rapid than those from a Rn+Be source. Relative intensities of radioactivity excited by neutrons from the two sources are 1:10 for elements showing the protonic effect, and extend to 1:1 for others. Data on relative absorption of neutrons by screens of various thicknesses with and without a paraffin shield are given. N. M. B.

Experiments on artificial transmutation using the cloud-track method. P. I. DEE (Proc. Roy. Soc., 1935, A, 148, 623—637).—When H^2 is bombarded by artificially accelerated dipions, the products of transformation are emitted in the opposite

pairs of ranges 15.3 and 1.7 cm., respectively, in accordance with $\rightarrow {}_1\text{H}^1 + {}_1\text{H}^3$. The observed val. for the max. neutron energy of 1.8×10^6 e.v. is in good agreement with the calc. val. A study of the short-range products emitted during the bombardment of Li with protons yields evidence in favour of ${}_3\text{Li}^6 + {}_1\text{H}^1 \rightarrow {}_2\text{He}^4 + {}_2\text{He}^3$. L. L. B.

Disintegration of Li^6 by protons. I. V. KURTSCHATOV and K. D. SINELNIKOV (Physikal. Z. Soviet-union, 1934, 5, 919—921).—The α -particle ranges of 1.15 and 0.65 cm. observed on bombarding Li^6 with protons are attributed to nuclei of He^3 and He^4 . The γ -ray emission is ascribed to addition of an electron to He^3 giving H^3 . CH. ABS. (c)

Disintegration of lithium atoms by slow protons. K. P. JAKOVLEV (Z. Physik, 1935, 93, 644—647).—Disintegration begins at 27 kv.

A. B. D. C.
Chemical identification of the radio elements produced from carbon and boron by deuteron bombardment. D. M. YOST, L. N. RIDENOUR, and K. SHINOHARA (J. Chem. Physics, 1935, 3, 133—136).—A series of chemical eliminations indicate that B yields C^{11} and C yields N^{13} , the latter having a half-life of 10.5 min. compared with 14 min. for that found by Curie and Joliot on bombarding B with α -particles. N. M. B.

Period of radionitrogen. C. D. ELLIS and W. J. HENDERSON (Nature, 1935, 135, 429; cf. A., 1934, 579).—A redetermination under improved conditions gives 11.0 ± 0.1 and not 14 min. for the period of radio-N formed by bombardment of B with α -particles. This val. agrees with that for ${}_7\text{N}^{13}$ formed from C, and the two substances appear to be identical. L. S. T.

Transmutations of nitrogen by deuterons. E. O. LAWRENCE, E. McMILLAN, and M. C. HENDERSON (Physical Rev., 1935, [ii], 47, 273—277).— N_2 bombarded by deuterons emits three α -particles and two proton groups. For deuterons of max. energy 1.4 mv. traversing an air target the α -particle group ranges are 6.9, 7.8, and 12.7 cm. The reaction is $\text{N}^{14} + \text{H}^2 \rightarrow \text{C}^{12} + \text{He}^4$, and the N^{14} mass is 14.0069. Excited levels in C^{12} at 3.8 and 4.7 mv. are indicated. The proton groups from a thin air target bombarded by 1.25-mv. deuterons have ranges 24 and 85 cm.; the reaction is $\text{N}^{14} + \text{H}^2 \rightarrow \text{N}^{15} + \text{H}$, and the N^{15} mass is 15.0041. There is an excitation level in N^{15} at 4.7 mv. For 1.2-mv. deuterons the effective nuclear collision cross-sections for the α -particle and proton reactions are approx. 10^{-27} and 3×10^{-29} cm.², respectively. N. M. B.

Artificial radioactivity produced by the deuteron bombardment of nitrogen. E. McMILLAN and M. S. LIVINGSTON (Physical Rev., 1935, [ii], 47, 452—457).— N_2 bombarded with H^2 gives a radioactive substance which emits positive electrons of max. energy 1.2 mv., has half-life 126 ± 5 sec., and by chemical analysis is an isotope of O. The probable reactions are: $\text{N}^{14} + \text{H}^2 \rightarrow \text{O}^{15} + n$; $\text{O}^{15} \rightarrow \text{N}^{15} + e^+$. The nuclear cross-section for the activation of N at 2 mv. H^2 energy is 6×10^{-27} cm.², and for C three times this val. The active product could be deposited on a metal surface by recoil. N. M. B.

Transmutations of aluminium by deuterons. E. McMILLAN and E. O. LAWRENCE (Physical Rev., 1935, [ii], 47, 343—348).—Al bombarded by 2.2-mv. deuterons emits protons, neutrons, and α -particles, with probable formation of Al^{28} , Si^{28} , and Mg^{25} . Al^{28} has half-life 156 ± 5 sec., emitting negative electrons and intense γ -rays. The protons are the most abundant and have a complex spectrum; the α -particles indicate a reaction energy of 6.6 mv. for the formation of Mg^{25} . N. M. B.

Artificial radioactivity of bismuth. L. SOSNOWSKI (Compt. rend., 1935, 200, 1027—1029).—Bi bombarded with neutrons from Be irradiated with Ra γ -rays yields a radioactive isotope emitting β -rays and with a half-life-period of about 1 hr., not identical with Ra-E. J. W. S.

[Artificial radioactivity.] M. DE BROGLIE (Compt. rend., 1935, 200, 1029—1030; cf. preceding abstract).—Radioactive isotopes have now been obtained of the same at. wt., but of different properties. Notation of atoms by at. no. and at. wt. is now insufficient. J. W. S.

Radioactivity of some rarer elements produced by neutron bombardment. S. SUGDEN (Nature, 1935, 135, 469).—The following half-life periods (± 0.1 hr.) and relative intensities ($\text{Ag}=1$) were observed when the oxides of some rarer elements were bombarded by neutrons from a Be+Rn source, specimen and source both being surrounded by paraffin wax: Eu 9.2 hr., 19; Tb 3.9 hr., 0.5; Er 2.9 hr., 3; Yb (? Lu) 2.5 hr., 0.6; and Ge approx. 2 hr., 0.1. With Eu, γ -rays little absorbed by 4 mm. of Pb were also detected. Gd_2O_3 freed from Eu and Tb gave no detectable activity, whilst Sc_2O_3 gave no activity after 15 hr. irradiation with 100 millicuries. The Er used may have contained other rare earths and hence an observed weaker activity with a period of approx. 30 hr. cannot be definitely ascribed to it. L. S. T.

Chemical properties of elements 93 and 94. A. V. GROSSE (J. Amer. Chem. Soc., 1935, 57, 440—441).—The properties are forecast according to (a) the periodic system and (b) the Bohr theory. E. S. H.

Identity of Fermi's reactions of element 93 with element 91. A. V. GROSSE and M. S. AGRUSS (J. Amer. Chem. Soc., 1935, 57, 438—439).—Chemical evidence is adduced (cf. A., 1934, 826). E. S. H.

Production of radiation of energy comparable with that of soft cosmic rays. F. JOLIOT and L. KOWARSKI (Compt. rend., 1935, 200, 824—827).—Wilson cloud-track photographs were obtained of long-range electrons arising from the irradiation of a Ag target with neutrons from Po+Be. Trajectories deflected by a magnetic field at right angles correspond with kinetic energies of $20\text{--}30 \times 10^6$ e.v. Mechanisms of production are discussed. N. M. B.

Comparison measurements of cosmic and γ -rays with ionisation chambers and counter tubes. R. HILGERT (Z. Physik, 1935, 93, 589—610).—Comparison measurements give the influence of secondary rays in the two instruments. A. B. D. C.

Absorption of cosmic radiation. P. AUGER (Compt. rend., 1935, 200, 739—742).—Measurements under a screen of 8 m. of earth, equiv. to 20 m. of H_2O , indicate two groups of corpuscular radiations in the atm. A hard group has an absorption coeff. in Pb of 0.7×10^{-3} sq. cm. per g. (cf. Regener, A., 1933, 552) and a soft one, 35×10^{-3} sq. cm. per g. The origin of the second group is discussed.

M. S. B.

Characteristics of the two corpuscular components of cosmic radiation. P. AUGER, A. ROSENBERG, and F. BERTEIN (Compt. rend., 1935, 200, 1022—1024; cf. A., 1934, 1285; this vol., 278, 426).—Cosmic radiation in a cellar 850 cm. below ground level is almost pure "*D*"-radiation. Under such conditions 10 cm. of Pb absorbs the remainder of the "*M*"-radiation and part of the secondary electrons (*S*-group) of energy $< 10^8$ e.v. which accompany penetrating radiation. The absorption of *D*-radiation (protons ?) is similar in Pb and in Cu, but *M*-radiation (electrons ?) is preferentially absorbed by elements of greater at. wt. J. W. S.

Cosmic rays. R. A. MILLIKAN (Science, 1935, 81, 211—215).—A crit. summary of present knowledge. L. S. T.

Absorption of cosmic rays. H. J. WALKE (Nature, 1935, 135, 472).—The Klein-Nishina formula cannot be applied to the cosmic-ray problem.

L. S. T.

Variation with altitude of the production of bursts of cosmic-ray ionisation. C. G. MONTGOMERY and D. D. MONTGOMERY. **North-south asymmetry of cosmic radiation.** G. LEMAITRE, M. S. VALLARTA, and L. BOUCKAERT. **Frequency and magnitude of cosmic-ray bursts as a function of elevation.** R. D. BENNETT, G. S. BROWN, and H. A. RAHMEL (Physical Rev., 1935, [ii], 47, 429—434, 434—436, 437—443).

N. M. B.

Nuclear structure of beryllium and the mass of the neutron. H. J. WALKE (Phil. Mag., 1935, [vii], 19, 549—557; cf. A., 1934, 471).—A discussion of the nuclear structure of Be in relation to disintegration experiments. The nucleus of Be^8 consists of 2 α -particles and that of Be^9 of 2 α -particles and a loosely-bound neutron. The mass of the neutron is 1.01118.

H. J. E.

Auger effect. E. H. S. BURHOP (Proc. Roy. Soc., 1935, A, 148, 272—284).—All the experimental features of the Auger effect are accounted for by the quantum mechanical theory. The theory predicts the form for the variation of the effect with at. no. and for the relative magnitude of the effect in the different shells and sub-shells of an atom. L. L. B.

General form of wave equation. R. ZAICOFF (J. Phys. Radium, 1935, [vii], 6, 52).—Mathematical.

N. M. B.

Second approximation in Born's method. J. WINTER (J. Phys. Radium, 1935, [vii], 6, 71—72).—Mathematical. A discussion of validity. N. M. B.

Physical magnitudes in Dirac's theory. L. GOLDSTEIN (J. Phys. Radium, 1935, [vii], 6, 78—88).—Mathematical.

N. M. B.

Dirac's theory of permutations. M. MARKOV and G. RUMER (Acta Physicochim. U.R.S.S., 1934, 1, 56—63).—Mathematical.

M. S. B.

Nucleus formation in metastable phases. H. FLOOD (Tidsskr. Kjemi, 1935, 15, 25—27).—A crit. discussion of current theories.

R. P. B.

Electronic energy bands in metallic lithium. J. MILLMAN (Physical Rev., 1935, [ii], 47, 286—290).—Mathematical. The method of Wigner and Seitz, as extended by Slater (cf. A., 1934, 828), is applied to Li. The conduction electrons in Li are much more tightly bound than those of Na.

N. M. B.

Empirical stability limits of atomic nuclei. G. RACAH (Z. Physik, 1935, 93, 704).—Polemical, against Gamow (A., 1934, 939).

A. B. D. C.

Polarisability of the hydrogen molecule. H. STEENSHOLT (Z. Physik, 1935, 93, 620—623).—Theoretical.

A. B. D. C.

Incoherent scattering and the concept of discrete electrons. A. H. COMPTON (Physical Rev., 1935, [ii], 47, 367—370).—A comparison of classical and wave-mechanical theories of scattering indicates that the most accurate classical analogue of Schrodinger's $\psi\psi^*$ is the probability of occurrence of discrete electrons, and that a particular electron is associated with each particular function

N. M. B.

Anomalous scattering and structure of light nuclei. G. BECK and L. H. HORSLEY (Nature, 1935, 135, 430—431).—Theoretical.

L. S. T.

Ratio of the magnetic moment of the proton to the magnetic moment of the deuteron. L. FARKAS and A. FARKAS (Nature, 1935, 135, 372).—The ratios of the magnetic moment of the proton to that of the deuteron, redetermined by the method previously used (A., 1934, 608), are 3.85, 4.03, and 4.07 at 83°, 193°, and 293° abs., respectively.

L. S. T.

Experimental evidence regarding the field of the deuteron. E. POLLARD and H. MARGENAU (Nature, 1935, 135, 393).—The range at which anomalous scattering begins for α -particle impacts with protons and with deuterons has been determined.

L. S. T.

Quantum mechanical effects in reactions involving hydrogen. R. P. BELL (Proc. Roy. Soc., 1935, A, 148, 241—250).—Expressions are obtained for the permeability of a parabolic potential barrier to a stream of particles with Maxwellian energy distribution, and their application to barriers of various dimensions is illustrated. If the barrier has dimensions of the order of magnitude met with in chemical reactions, and the particle is an H atom or proton, the system will deviate from classical behaviour at easily attainable temp. The effect of mass of the particle is investigated with special reference to the isotopes of H, where it may lead to large differences in the kinetic behaviour of H^+ and H^- .

L. L. B.

Theoretical constitution of metallic lithium. F. SEITZ (Physical Rev., 1935, [ii], 47, 400—412; cf. A., 1934, 1283).—Mathematical.

N. M. B.

Action of the Nernst lamp. P. LEROUX (J. Phys. Radium, 1935, [vii], 6, 65—68).—Data obtained

with a prism (rock-salt) spectrograph are tabulated for the emission of two Nernst filaments as a function of λ for the range 0.5–10 μ . Filament temp. were measured with a disappearing filament. The emission curves show irregularities depending on the working conditions of the lamp. N. M. B.

Permeability of the atmosphere and of glasses to ultra-violet radiation. J. DOETSCH (Anal. Fis. Quim., 1934, 32, 65–71).—The limit of transmission in the region 2890–3200 Å. by the atm. of Madrid (October, 700 m. above sea-level) lies at about 3020 Å. The compositions and transmission limits of a no. of types of glass are recorded. The shortest λ limit is observed when Mn is present, and the longest when the Mn is replaced by Co. H. F. G.

Precision absorption measurements with prism mirror spectrometers and thermo-elements. C. LEISS (Z. Physik, 1935, 93, 814–815).—Polemical, against Gude (this vol., 427). A. B. D. C.

Precision absorption measurements with prism mirror spectrometers and thermo-elements. R. SCHURMANN (Z. Physik, 1935, 93, 815).—Gude's publication (this vol., 427) is disclaimed. A. B. C. D.

Simple and general relationship between molecular spectra and the electrons and electronic shells of the constituent atoms. H. DESLANDRES (Compt. rend., 1935, 200, 603–607; cf. A., 1934, 828, 1054; this vol., 281).—Conditions of electronic excitation of gaseous HCl, cryst. Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, and liquid C_6H_6 are deduced from their Raman spectra. J. W. S.

Significance of molecular absorption spectra. P. K. SEN-GUPTA (Z. Physik, 1935, 93, 816).—Corrections (A., 1934, 715). A. B. D. C.

Absorption spectrum of ozone at a low temperature. (MLLE.) L. LEFEBVRE (Compt. rend., 1935, 200, 653–654; cf. A., 1934, 1054).—Between 4400 and 6500 Å. the absorption spectrum of O_3 at -80° is identical with that at room temp. It is suggested that Chappuis (A., 1882, 1017), who obtained an increase in the no. and intensity of the bands, used higher gas pressures at the lower temp. J. W. S.

Effect of the temperature of the stratosphere on the spectrum of ozone. D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1935, 200, 1063–1065).—The atm. O_3 bands at 3100–3400 Å., corr. for absorption by other gases, show sharper max. and min. than those obtained at 15° , indicating the very low temp. of most of the atm. O_3 . This may provide a method of determining temp. of the upper layers of the atm. J. W. S.

[Effect of temperature of the stratosphere on the spectrum of ozone.] C. FABRY (Compt. rend., 1935, 200, 1165–1066; cf. preceding abstract).—The advantages of using stellar rather than solar radiation in observation of atm. absorption are pointed out. J. W. S.

Band spectra of the hydrides of lithium. I. Li^2H^2 . F. H. CRAWFORD and T. JORGENSEN, jun. (Physical Rev., 1935, [ii], 47, 358–366).—Measurements, assignments to 35 two-branch bands, and

data for 80% of the lines of the $^1\Sigma \rightarrow ^1\Sigma$ spectrum in the range 3200–4300 Å. are tabulated. Consts. and band origins are found, and corresponding vibrational const. for Li^7H are computed from the simple isotope theory. N. M. B.

The $^1\Pi \rightarrow ^1\Delta$ system of NH molecules. G. NAKAMURA and T. SHIDEI (Japan J. Physics, 1935, 10, 5–10).—Three band systems of simple structure observed at $\lambda\lambda$ 3035, 3240, and 3610 Å. in the spectrum of a discharge in NH_3 vapour are identified as the (1, 0), (0, 0), and (0, 1) bands of the $^1\Pi \rightarrow ^1\Delta$ transition system. The const. of the $^1\Delta$ and $^1\Pi$ systems and the vibrational frequencies of the $^3\Sigma$ and $^3\Pi$ states are deduced. J. W. S.

Band spectrum of nickel hydride: Bands at 5713, 6246, and 6424 Å. A. G. GAYDON and R. W. B. PEARSE (Proc. Roy. Soc., 1935, A, 148, 312–335).—Bands with wide-spaced structure have been observed at 5713, 6246, and 6424 Å. in the spectrum obtained by introducing the vapour of $\text{Ni}(\text{CO})_4$ into the air hole of a Meker burner. The assignment of the bands to NiH has been confirmed by their production in other sources containing Ni and H_2 . The bands consist of *P*, *Q*, and *R* branches with missing lines, consistent with a transition of the type $^2\Delta_{21} \rightarrow ^2\Delta_{21}$. The three bands have the same lower levels. The rotational term differences have been obtained, and vals. of rotational const. calc. A catalogue of the $\lambda\lambda$ of the lines measured in the spectrum of the $\text{Ni}(\text{CO})_4$ flame, together with estimates of their intensities, their wave-nos., and the classifications of those attributed to NiH is given. The general agreement between the calc. and observed intensities supports the assignment of the bands to a $^2\Delta_{21} \rightarrow ^2\Delta_{21}$ transition. L. L. B.

Photochemical studies. XXI. Absorption spectrum of germane. H. E. MAHNCKE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1935, 57, 456–458).— GeH_4 shows no banded absorption at $> \lambda$ 1550 Å. Continuous absorption extends from about 1700 Å. to shorter $\lambda\lambda$. E. S. H.

Absorption spectrum of NaH^2 . E. OLSSON (Z. Physik, 1935, 93, 816).—Corrections (cf. this vol., 279). A. B. D. C.

$^4\Pi$ state of CO. L. GERO (Z. Physik, 1935, 93, 669–675). A. B. D. C.

β -Bands of boron monoxide. J. FUNKE and C. F. E. SIMONS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 142–148).—The β -bands of BO are tabulated. They are simple, only one *P*- and one *R*-branch being found for the $\Sigma \rightarrow \Sigma$ transitions. The doublet splitting is negligible. The wave-nos. of the zero lines are given. A. J. M.

Rotational analysis of the ultra-violet bands of phosphorus monoxide. A. K. S. GUPTA (Proc. Physical Soc., 1935, 47, 247–257).—Complete data and rotational analyses of the (0, 0), (0, 1), and (1, 0) ultra-violet bands of PO, each consisting of 8 branches, are given. From the potential energy curves for the upper and lower states of the system the Condon parabola for the intensities of the bands

is obtained. Mol. consts. are given, and products of dissociation in the different states are discussed.

N. M. B.

Absorption spectrum of lead oxide. E. N. SHAWHAN and F. MORGAN (Physical Rev., 1935, [ii], 47, 377—378).—A new system has been found. Previously unclassified bands and new bands are assigned.

N. M. B.

New diatomic band spectra. H. G. HOWELL and G. D. ROCHESTER (Proc. Durham Phil. Soc., 1934, 9, 126—134).—The absorption spectra of PbO, PbS, SnS, PbSe, SnSe, PbTe, and SnTe vapours have been investigated and compared. The emission band spectra of the oxides of Fe, Ni, Co, Cu, W, Te, Pt, Mo, Ce, and Th, excited in an arc between electrodes of the metal or of C, are illustrated. AgO and ThO showed no mol. spectra. No nitride bands were observed with Mg and Al arcs in N₂. The emission spectra of Pb halides, BiF₃, BiBr₃, FeF₃, SnBr₃, SnI₃, SbCl₃, SbBr₃, SbI₃, PCl₃, PF₃, TiF₃, TiCl₃, TiBr₃, and MnCl₂ vapours have been obtained by high-frequency discharge with external electrodes.

J. W. S.

Spectrum of boron fluoride. R. B. DULL (Physical Rev., 1935, [ii], 47, 458—460).—Measurements of band heads $\lambda\lambda$ 5993.8—5664.0, degrading to the violet, and 5470.8—4443.5, degrading to the red, are given. In the ultra-violet three new bands, $\lambda\lambda$ 3552.2—3545.4, 3399.40—3392.85, and 3256.61—3250.94, were found; the structure appears similar to that of the third positive bands of CO.

N. M. B.

Band systems of cadmium fluoride. R. K. ASUNDI, R. SAMUEL, and M. ZAKI-UD-DIN (Proc. Physical Soc., 1935, 47, 235—246; cf. A., 1934, 828).—Data and analyses are given for an orange and a yellow-green band system in the ranges 6000—6300 and 5300—5530 Å., of approx. origins 16,558 and 18,871 cm.⁻¹, respectively, and having a common lower state. Vibrational coeffs., and heats and products of dissociation and the electronic structures of the three states of CdF are discussed.

N. M. B.

Band systems of MgCl, CaCl, and SrCl. A. E. PARKER (Physical Rev., 1935, [ii], 47, 349—358).—A detailed vibrational analysis is given of the two, three, and two systems due to MgCl, CaCl, and SrCl, respectively. The isotope effect due to Cl³⁵ and Cl³⁷ is observed in all transitions. The rotational structure is partly resolved.

N. M. B.

Interpretation of the absorption spectrum of silver halides. A. K. DATTA (Trans. Bose Res. Inst., 1932—1933, 8, 248—256).—The normal form of Ag halides in the vapour state is claimed to be ionic and not at. (cf. Franck and Kuhn, A., 1927, 1007).

R. S.

Effect of light on stannous chloride vapour. K. BUTKOV (Physikal. Z. Sovietunion, 1934, 5, 906—910).—At 315° continuous absorption begins at 2000 Å. With rising temp. it extends to longer $\lambda\lambda$. Absorption max. were found at 4130, 3204, and 2430 Å. At the first two max. polymerised mols. of Sn₂Cl₄ are dissociated, whilst at 2430 Å. dissociation into SnCl and Cl occurs.

CH. ABS. (e)

Absorption spectra of lead halide vapour. S. C. DEB (Trans. Bose Res. Inst., 1932—1933, 8, 257—266).—Absorption is continuous. The mechanism and the products of dissociation are discussed.

R. S.

Band spectrum of aluminium bromide. H. G. HOWELL (Proc. Roy. Soc., 1935, A, 148, 696—707).—A band system extending from 2750 to 3000 Å. has been obtained by means of a high-frequency discharge in AlBr₃ vapour. The resemblance of the spectrum to that of AlCl₃, the vibrational analysis, and measurements of the isotope effect show that it is due to the AlBr mol. The bands are degraded to the red and have Q and R heads, the latter being double owing to the presence of equal nos. of AlBr⁷⁹ and AlBr⁸¹ mols.

L. L. B.

Photo-dissociation of some polyatomic molecules. Y. HUKUMOTO (J. Chem. Physics, 1935, 3, 164—168).—The continuous absorption spectrum without a neighbouring band spectrum and a convergence limit was investigated in the ultra-violet for 78 org. substances. Absorption limits and calc. dissociation energies are tabulated. Structure, Raman effects, and infra-red spectra, as related to linking energies, are discussed.

N. M. B.

Isotope effect in acetylene. W. F. COLBY (Physical Rev., 1935, [ii], 47, 388—390).—Normal frequencies for C₂H₂, C₂HH², and C₂H₃ are calc. vibrational frequencies for C₂HH² and C₂H₃ are in good agreement with observed vals.

N. M. B.

Structure of the ultra-violet absorption bands of acetylene. A. IONESCO (Compt. rend., 1935, 200, 817—819; cf. Lewis, A., 1934, 129).—Data and analysis of the 44,309 cm.⁻¹ band are tabulated. Mol. states and consts. are considered on the basis of Hund's theory of diat. mols.

N. M. B.

Absorption spectra of acetylene and ethane in the far ultra-violet. W. C. PRICE (Physical Rev., 1935, [ii], 47, 444—452).—Data for C₂H₂ in the range 1520—1050 Å., and an analysis made by obtaining the spectrum of C₂H₂ prepared from 50% H₂O are given. The limit of the two Rydberg series corresponds with an ionisation potential of 11.35 volts. Strong predissociation around 1520 Å. yields a val. of approx. 187 g.-cal. per mol. for the strength of the C:C linking. A similar set of bands appears for C₂H₄ in the range 1750—1200 Å.; the limit of the one strong Rydberg series corresponds with an ionisation potential of 10.41 volts. No analysis could be made of the very diffuse spectrum of C₂H₆.

N. M. B.

Absorption spectrum of acetone vapour in the far ultra-violet. A. B. F. DUNCAN (J. Chem. Physics, 1935, 3, 131—132; cf. this vol., 10).—Data are tabulated for the range 1800—850 Å.; absorption is continuous for 1300—850 Å. A description and qual. interpretation are given. One Rydberg series was found, converging to an ionisation potential of 10.20 volts.

N. M. B.

Structure, ionisation, and ultra-violet spectra of methyl iodide and other molecules. R. S. MULLIKEN (Physical Rev., 1935, [ii], 47, 413—415; cf. A., 1934, 1288).—Conclusions as to electronic structures in normal and low excited states, and

interpretation of observed ionisation potentials and ultra-violet absorption spectra are summarised.

N. M. B.

Study of substitution and decomposition reactions by means of photo-electric cells. I. Absorption of light of wave-lengths 3650 and 4360 Å. by vapours of various halogen derivatives of ethane. S. HAMAI (Bull. Chem. Soc. Japan, 1935, 10, 43—50).—No absorption occurs with $s\text{-C}_2\text{H}_4\text{Cl}_2$, $s\text{-C}_2\text{H}_4\text{Br}_2$, $\text{C}_2\text{H}_3\text{Cl}_3$, $s\text{-C}_2\text{H}_2\text{Cl}_4$, C_2HCl_5 , C_2Cl_6 , and HCl . Cl_2 absorbs and the apparatus is therefore suitable for the study of Cl substitution in C_2H_6 , and for the decomp. of $\text{C}_2\text{H}_4\text{I}_2$ to C_2H_4 and I .

R. S. B.

Ultra-violet absorption spectra of fumaric, maleic, mesaconic, and citraconic nitriles. E. RUPPOL (Bull. Acad. roy. Belg., 1935, [v], 21, 236—246).—Data and absorption curves for the nitriles and the corresponding amides and Me esters, in H_2O and MeOH as solvents, are given.

N. M. B.

Ultra-violet absorption spectrum of methylamine. V. HENRI and V. LASAREV (Compt. rend., 1935, 200, 829—830).—A preliminary analysis is reported of 45 bands photographed in the region 2529—1986 Å., for pressures 0.1—432 mm., and temp. 15—290°.

N. M. B.

Ultra-violet absorption spectrum of pyridine. V. HENRI and P. ANGENOT (Compt. rend., 1935, 200, 1032—1034).—226 absorption bands of $\text{C}_5\text{H}_5\text{N}$ vapour have been measured between 3099.8 and 2513.4 Å., and 170 of them classified. The characteristic frequencies of separation of the bands are 542, 600, 1029, and 1488 cm^{-1} . The first is attributed to the activated state of the mol. and the others, which are also observed in the infra-red and Raman spectra, to the normal state of the mol.

J. W. S.

Absorption spectrum of α -substituted furan derivatives. S. ABE (J. Chem. Soc. Japan, 1934, 55, 901—904).— $\text{CH}_2\text{-CH}_2\text{-CO}_2\text{H}$ derivatives of furan showed agreement in absorption with the alkyl derivatives.

CH. ABS. (e)

Variation of the absorption spectrum of tyrosine, tyramine, adrenaline, thyroxine, and diiodotyrosine with the p_{H} of the medium. G. FLORENCE, J. ENSELME, and M. POZZI (Bull. Soc. Chim. biol., 1935, 17, 283—289).—Whereas with tyrosine (I) alkalinisation increases absorption and displaces the max. away from the ultra-violet, with tyramine variation of p_{H} has no effect on the absorption. The spectrum of adrenaline is the same both p_{H} 1.75 and 3.10 and is closely related to that of (I) in acid solution. Both thyroxine and diiodotyrosine give spectra closely related to that of (I) in acid solution; the former is affected by change of p_{H} but the latter is not.

P. W. C.

Spectral behaviour of methæmoglobin. R. M. LAYER (Naturwiss., 1935, 23, 180).—The visible spectrum of methæmoglobin, unlike that of oxyhæmoglobin, depends on p_{H} . Between p_{H} 8.33 and 8.679, the spectrum consists of five bands. Only the band at 501 m μ can be evaluated spectrophotometrically, and is independent of p_{H} over a considerable range.

A. J. M.

Absorption of selected organic dyes in the region of the visible spectrum and the conditions of their constancy. H. ALBERTS (Z. wiss. Phot., 1935, 33, 234—248, 249—265).—Absorption curves have been measured for 13 dyes, in aq. and/or EtOH solution. Most of the results conform with Beer's law, although some exceptions are noted. The changes in the spectra after the solutions have been "aged" by several weeks' exposure to light have also been examined. The results are fully detailed.

J. L.

Spectroscopic method for detecting some forms of chelation. G. E. HILBERT, O. R. WULF, S. B. HENDRICKS, and U. LIDDEL (Nature, 1935, 135, 147—148).—The absence of normal infra-red (1.4—1.6 μ) absorption in mols. showing OH by ordinary chemical tests forms the basis of a method for indicating chelation through H. Salicylaldehyde, *o*-nitro- and 2:6-dinitro-phenol, Me salicylate, *o*- $\text{C}_6\text{H}_4\text{Ac-OH}$, salicyl- α -phenyl- α -methylhydrazone, and $\gamma\text{-NEt}_2\text{[CH}_2\text{]}_3\text{-OH}$ give no absorption characteristic of mols. containing OH. Benzoin and 8-hydroxyquinoline, which form chelated salts, give characteristic OH absorption, as do Et lactate and tartrate.

L. S. T.

Absorption spectra of some organo-metallic compounds. R. K. ASUNDI, C. M. B. RAO, and R. SAMUEL (Proc. Indian Acad. Sci., 1935, 1, A, 542—554).—Data in the Schumann and ultra-violet regions are given for HgMe_2 , HgEt_2 , HgEtCl , HgPh_2 , HgPhCl , and PbPh_4 . The interpretation of the absorption curves, excitations, and linkings is discussed.

N. M. B.

Spectrography of cholesterol and its derivatives.—See this vol., 616.

Near infra-red absorption spectra of liquefied, gaseous, or dissolved ammonia. G. COSTEANU, R. FREYMAN, and A. NAHERNIAO (Compt. rend., 1935, 200, 819—822).—Displacements of the 1.04 μ band are tabulated in the range 0.8—1.2 μ for NH_3 liquid at -45° to -70° , gaseous at room temp., and at various concns. in H_2O , MeOH , and EtOH . Passing from liquid NH_3 to 50% aq. solution there is a systematic displacement towards shorter λ . The displacement of bands on dilution or in passing to the gaseous state is explained by the breaking down of polymerides.

N. M. B.

Absorption spectra of organic and inorganic derivatives of ammonia in the near infra-red. P. JOB, (MME.) M. FREYMAN, and R. FREYMAN (Compt. rend., 1935, 200, 1043—1044; cf. A., 1933, 1228).—Aq. solutions of NH_3 , NH_2Ph , NH_2Et , N_2H_4 , NHPh-NH_2 , $(\text{CH}_2\text{-NH}_2)_2$, and $\text{CO(NH}_2)_2$ show an absorption band at about 1.04 μ , but this is not found with aq. NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, NH_4OAc , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NH_4OH , HCl , or $\text{C}_6\text{H}_4(\text{NH}_2)_2\text{HCl}$, whilst $[\text{Co(NH}_3)_5\text{(H}_2\text{O)Cl}]_3$, $3[\text{Co(NH}_3)_5\text{Cl}]\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4$, $[\text{Co(NH}_3)_5\text{(H}_2\text{O)}]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$, $[\text{Co}\{(\text{CH}_2\text{-NH}_2)_2\text{Cl}_2\}]$, $[\text{Co}\{(\text{CH}_2\text{-NH}_2)_2\text{(H}_2\text{O)}_2\text{Cl}_2\}]$, $[\text{Cu(NH}_3)_4\text{Cl}_2]$, and $[\text{Cu(NH}_3)_4]\text{SO}_4$ show only a slight inflexion in the absorption curve in this region. It is concluded that this band does not exist when N atom is tetra-co-ordinated. The strong band with aq. NH_3 indicates that this solution is mainly $\text{NH}_3 \cdot n\text{H}_2\text{O}$, and not NH_4OH .

J. W. S.

Intramolecular isomerism and infra-red absorption spectra. J. ERRERA and P. MOLLET (Compt. rend., 1935, 200, 814—817; cf. A., 1934, 1288).—Absorption curves at 60° and 120° are given for PhOH and salicylaldehyde: for the former the OH band shows displacement with rise of temp., the CH band being unchanged; for the latter the OH band is not found. Results suggest a co-ordination covalency between the H atom in the OH group and the O atom in the CHO group. Support is afforded by curves for *p*- and *m*-OH·C₆H₄·CHO, where such is not possible, and which show the OH band. *o*-C₆H₄Cl·OH shows the OH band. N. M. B.

Distribution of intensity in the rotational Raman spectra of gases. S. BHAGAVANTAM and A. V. RAO (Proc. Indian Acad. Sci., 1935, 1, A, 419—424).—In view of the differences in intensity distribution for gases and liquids, data and curves are given for CO₂ and N₂O when gradually compressed at temp. < crit. temp. Agreement with theoretical curves is found at low pressures and considerable divergence at high pressures. N. M. B.

Raman spectrum of gaseous carbon disulphide. S. IMANISHI (Nature, 1935, 135, 396).—Details are recorded. L. S. T.

Raman effect and temperature. I. Ammonium chloride, bromide, iodide. A. C. MENZIES and H. R. MILLS (Proc. Roy. Soc., 1935, A, 148, 407—422).—The change with temp. of the Raman spectra of NH₄Cl, NH₄Br, and NH₄I has been studied. The appearance of a lattice frequency in the chloride (but not in NH₄Br or NH₄I) when the temp. is < -30° suggests that there is an asymmetry in the chloride which is absent in the others. It is concluded that the NH₄ tetrahedra are similarly situated in the cold chloride lattice, and arranged antisymmetrically in the Br and I lattices below their respective transition temp. It is assumed that a rotation sets in at the transition temp. L. L. B.

Raman spectra of amorphous substances. M. F. VUKS and E. F. GROSS (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 214—217).—Vals. are recorded for the Raman spectra of B₂O₃, Na₂B₄O₇, HPO₃, and H₄P₂O₇. B₂O₃ gave sharp lines (810, 1120, and 1257 cm.⁻¹), the other substances giving broad bands in place of normal Raman lines (breadth 50—100 cm.⁻¹). H. J. E.

Reactivity and constitution of nitric and sulphuric acids. I. General. E. BRINER. II. Reactivity of nitric acid in aqueous and acetic acid media. E. BRINER and P. BOLLE. III. Raman spectra, viscosities, and melting points of mixtures of nitric and acetic acids. E. BRINER, B. SUSZ, and P. FAYARGER. IV. Raman spectra of mixtures of nitric acid and nitrogen pentoxide. B. SUSZ and E. BRINER (Helv. Chim. Acta, 1935, 18, 363—367, 368—375, 375—378, 378—381).—II. Rates of nitration of PhOH (0.025*N*) and of oxidation of NO by HNO₃ of various concns. are much higher in AcOH than in aq. solution. Both effects are attributed to undissociated HNO₃.

III. Densities and viscosities at 24.9°, and f.p. of HNO₃-AcOH mixtures are given. The formation

of an equimol. compound indicated by these results is supported by the Raman spectra.

IV. In HNO₃-N₂O₅ mixtures the intensity of the Raman lines 1046 and 1396 cm.⁻¹, the latter of which has been previously observed in H₂SO₄-HNO₃ mixtures, increases with the N₂O₅ content. The frequency 1396 cm.⁻¹ is not observed with 100% HNO₃.

F. L. U.

Raman spectra of double linkings conjugated in a nucleus. G. B. BONINO (Gazzetta, 1935, 65, 5—13).—The conclusions of Truchet and Chapron (A., 1934, 830) are criticised. The strong line at 1460 cm.⁻¹ can not be attributed to C:C. O. J. W.

Splitting of spectral lines by scattering in liquids. S. M. MITRA and S. MEHTA (Ann. Physik, 1935, [v], 22, 311—312).—Hg 4358 Å. was scattered in CS₂ and C₆H₆, respectively. The splitting was determined in directions making angles of 45°, 90°, and 135° with the incident light by a Fabry-Perot interferometer and glass spectrograph. Definite splitting was found, in each case > that given by the formula of Gross (A., 1930, 1345, 1498; 1932, 676). Higher components were not observed. A. J. M.

Raman effect in nitromethane. L. MEDARD (J. Chim. phys., 1935, 32, 136—141; cf. A., 1934, 716).—Raman frequencies for nitromethane, CH(NO₂)₃, CCl₃·NO₂, and C(NO₂)₄ are recorded and discussed. F. L. U.

Raman effect in some terpenes. G. V. NEVGI and S. K. K. JATKAR (J. Indian Inst. Sci., 1934, 17, A, 189—196).—In *d*- and *l*-pinene (I), -sabinene (II), and -Δ³-carene (III), *d*-Δ⁴-carene, and *d*-α-thujene, the frequencies due to aliphatic CH are 2875, 2915, 2975 cm.⁻¹, and with (III) 2830. The frequency due to HC< is 3025, excluding (II) which give 3035 due to CH₂:C. All give a frequency 1650 due to C:C, and 1450 due to ·CH₂·. The frequencies 145 and 845 are characteristic of (I), 370 and 868 of (II), and 719 of (III). Δ⁴- is distinguishable from Δ³-carene by the presence of additional frequencies 758, 958, and 1067 in the former. R. S. B.

Raman effect in certain derivatives of cyclohexane. G. V. NEVGI and S. K. K. JATKAR (J. Indian Inst. Sci., 1934, 17, A, 175—187).—In cyclohexane, methyl- and 1:3-dimethyl-cyclohexane, cyclohexene (I), cyclohexyl acetate and propionate (II), cyclohexanol, *o*-, *m*-, and *p*-methylcyclohexanol, cyclohexanone (III), and *o*-, *m*-, and *p*-methylcyclohexanone (IV), the frequencies 2850 and 2950 cm.⁻¹ are due to aliphatic CH, 1450 to the transverse vibration of CH in CH₂, 800 to the ring, and 200—1300 to C chains. In (I) the frequency 3033 is assigned to HC<, 1655 to C:C, and 1100—1400 to the transverse vibration of α- and β-CH with respect to C:C. In (II) frequency 1735 is due to ester CO, in (III) and (IV) 1705 is due to ketonic CO. R. S. B.

Phenomenon of "wings" and the vibrational Raman effect in benzene and naphthalene crystals. E. GROSS and M. VUKS (Nature, 1935, 135, 431).—Experiments on the Raman effect of single crystals of C₆H₆ and C₁₀H₈ confirm the previous results obtained with Ph₂O (this vol., 281). Distinct vibrational Raman lines replace the wings observed

in the liquids. The central part of the "wings" appears to be characteristic of the liquid state.

L. S. T.

Examination of molecularly scattered light with a Fabry-Perot etalon. II. Liquids: toluene and carbon tetrachloride. B. V. R. RAO (Proc. Indian Acad. Sci., 1935, 1, A, 473—483; cf. this vol., 146).—Interference patterns, free from continuous background, of Hg $\lambda\lambda$ 4047, 4358 allow the Doppler components to be distinguished from the hyperfine structure satellites. The Doppler shifts of $\lambda\lambda$ 4078 and 4358 are given. For PhMe the observation of Doppler shifts has been extended to Hg λ 5461. Appearance of the continuous background with PhMe and not with CCl_4 shows that this is a characteristic feature of mol. anisotropy of the liquid.

N. M. B.

Raman effect and free rotation. B. TRUMPY (Z. Physik, 1935, 93, 624—628).—Depolarisation measurements for $s\text{-C}_2\text{H}_4\text{Cl}_2$, $s\text{-C}_2\text{H}_4\text{Br}_2$, and $s\text{-C}_2\text{H}_2\text{Cl}_4$ show that these mols. exist primarily in the *trans*-form.

A. B. D. C.

Fine structure of Rayleigh radiation. L. S. ORNSTEIN and P. H. VAN CITTERT (Physica, 1935, 2, 221—229; cf. A., 1934, 1155).—Mathematical. The theory that light is scattered at discrete points of the crystal lattice, the positions of which are prescribed by stationary vibrations, explains the existence of a Rayleigh component of unchanged frequency as well as two components of modified frequency.

J. W. S.

Kerr constants and the Raman effect. E. H. L. MEYER (Physikal. Z., 1935, 36, 212—214).—The additivity of the Kerr const. is discussed. The polarisation ellipsoid corresponding with a mol. is influenced by the medium in which the mol. is placed. A similar effect in the Raman spectrum could not be found.

A. J. M.

Theory of molecular dispersion of light in unsymmetrical heated crystals. M. LEONTOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 97—110).—Mathematical.

W. R. A.

Principal optical polarisabilities of the naphthalene molecule. M. RAMANADHAM (Proc. Indian Acad. Sci., 1935, 1, A, 425—430).—The principal optical polarisabilities, calc. from the observed depolarisation factor of the vapour and from the Cotton-Mouton const. and n in the molten state, taking account of the anisotropic polarisation field, are 25.85, 22.25, and 9.00 ($\times 10^{-21}$). The optic moments, calc. from n by a new method based on the theory of the anisotropic polarisation field, are in fair agreement with the above vals.

N. M. B.

Migration velocity of electron colour centres in crystals. Y. FRENKEL (Physikal. Z. Sovietunion, 1934, 5, 909—918).—The mechanism of migration of the coloured region due to an electron cloud in the crystal is discussed. Partial crystallisation of the metal atoms to form a colloidal solution may occur.

CH. ABS. (e)

Anisotropic liquids. P. GAUBERT (Compt. rend., 1935, 200, 679—680; cf. A., 1934, 18, 478).—When aq. solutions of methylene-blue and neutral-red are

evaporated rapidly on a microscope slide they pass through a liquid crystal phase, with strong polychroism.

J. W. S.

Fluorescence of quinine salts.—See this vol., 505.

Influence of temperature on absorption and polarisation of fluorescence in fluorescein. P. CHERUY (J. Chim. phys., 1935, 32, 155—160).—The total energy absorbed between 4600 and 5400 Å. by an alkaline glycerol solution of K fluorescein increases with rise of temp. and its spectral distribution becomes more uniform. The max. polarisation of the fluorescence at great dilution and when there is no mol. rotation ($\eta \rightarrow \infty$) is independent of temp. True depolarisation and depolarisation by secondary fluorescence decrease with rise of temp.

F. L. U.

Phosphorescence. I. Hyperbolic law of decay of phosphorescence. V. L. LEVSHIN and V. V. ANTONOV-ROMANOVSKI. II. Quenching of phosphorescence by infra-red rays and its application to photography in the infra-red region of the spectrum. V. L. LEVSHIN, V. V. ANTONOV-ROMANOVSKI, and L. A. TUMERMANN (Physikal. Z. Sovietunion, 1934, 5, 796—810; cf. B., 1934, 429).—I. Examination of Zn phosphors showed that over long time intervals the Becquerel equation for decay (D) becomes $I = At^{-\alpha}$ (I is emitted light intensity, A a const., numerically the val. of I when $t=1$, and α a const. characteristic of the rate of D). Self-excitation decreases D , the effect being greater in the thicker layers.

II. Interrelationships between the total energy of the quenching light, the total phosphorescent light emitted, and the quenching effect are examined. Applications to infra-red photography are considered.

CH. ABS. (p)

Preparation of phosphorescent substances. VIII. Boric acid. II. N. F. SHIROV, T. E. GETMAN, and E. J. MATENKO (J. Appl. Chem. Russ., 1934, 7, 1382—1397).—Tiede's rule is not followed in the case of B_2O_3 activated by condensed ring systems; i.e., the λ of the phosphorescence does not increase with the no. of rings.

R. T.

Zinc sulphide and zinc cadmium sulphide luminophores and their importance for the problem of television. A. SCHLEEDER (Oesterr. Chem.-Ztg., 1935, 38, 55).—ZnS, alone or mixed with CdS, is capable of photo-luminescence without activation by foreign metals. Its activity depends on the co-existence of Zn blende and wurtzite lattices, and is a max. when these are in equal proportions. The sensitivity to all types of excitation and the short duration of the resonance, especially with ZnS-CdS mixtures, are important in the use of these luminophores for X-ray or other fluorescent screens especially in television.

J. W. S.

Luminescence excited in minerals by X-rays. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 258—275).—The intensity of luminescence (i) excited in fluor spar (I), calcite (II), and apatite by X-rays (a) increases asymptotically with time of excitation, and no solarisation is observed as with Hg-

vapour lamp excitation of (I) and (II) (b). i_a is $> i_b$ and the luminescence is more persistent. R. S. B.

Decomposition voltage of Grignard reagents in ethereal solution. W. V. EVANS, F. H. LEE, and C. H. LEE (J. Amer. Chem. Soc., 1935, 57, 489—490).—The decomp. voltages of the following Mg bromides in *M* solution in Et₂O at 22° are recorded: Ph 2.17, Me 1.94, Pr^a 1.42, Bu^a 1.32, Et 1.28, Bu^β 1.24, Pr^β 1.07, Bu^γ 0.97, allyl 0.86 volt. If the discharge potential of the Mg is const., these figures give the relative discharge potentials of the org. anions; they are lowered by replacement of H in Me by alkyl.

R. S. C.

Effect of heat, ultra-violet light, and X-rays on crystal rectification. S. R. KHASTGIR (Phil. Mag., 1934, [vii], 19, 557—564).—Fe pyrites, galena, magnetite, pyrolusite, Si, zincite, and carborundum showed a decrease in rectification on heating or on exposure to X-rays. Ultra-violet light had little effect.

H. J. E.

Transference of electrons from sodium in rock-salt. V. M. JUSHAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 428—433).—The current, *I*, flowing when a NaCl crystal was coloured by the direct transference of electrons from Na embedded in the crystal was determined. At 710°, $I = 4.8 \times 10^{-6} E$ amp. per sq. cm., where *E* is the applied potential in volts per cm.

A. J. M.

Crystal photo-effect in naturally coloured rock-salt crystals. L. V. GROSCHEV (Compt. rend., Acad. Sci. U.R.S.S., 1935, 1, 217—220).—Data are recorded and discussed.

H. J. E.

Electron properties of tellurium and Wilson's mechanism of semi-conductivity. C. H. CARTWRIGHT and M. HABERFELD-SCHWARZ (Proc. Roy. Soc., 1935, A, 148, 648—664; cf. A., 1934, 19).—Since the electrons are bound so tightly in Te that there is only 1 free electron per 10⁶ atoms, certain mechanisms may be postulated which might also occur in ordinary metals, where they would, however, be masked by the greater electron density. The lack of agreement among various investigators concerning electron properties of Te is probably due to the presence of impurities, rather than to the existence of allotropic modifications. A study has been made of the effect of small quantities of metallic impurities on the electrical conductivity and thermoelectric power of pure Te. The conductivity increases with the addition of foreign metals, but the increase is not \propto that of the added metal. The conductivity of the purest Te could be accounted for by the presence of $< 0.01\%$ of Sb or Bi. Probably the resistance of ideally pure Te would be much $>$ has been observed. The tendency for cracks to occur in Te explains a difficulty in obtaining reproducible results, and also some of the anomalous effects due to heat-treatment. The results confirm Wilson's theory of semi-conductivity.

L. L. B.

Electrical and optical properties of semi-conductors. X. Electrical determinations with zinc oxide. O. FRITSCH. XI. Photo-electric conduction in natural lead chromate. G. KAPP (Ann. Physik, 1935, [v], 22, 375—401, 257—280).—X. The conductivity of single crystals, plates, and

vaporised layers of ZnO was determined from room temp. to the b.p. of liquid air. The Hall effect (I) for ZnO was negative. (I) was redetermined for Cu₂O, and, contrary to current views, found to be positive. The mobility of ions in ZnO is only slightly dependent on temp. This is probably due to the superposition of two opposing Hall effects.

XI. For periods of illumination (II) of the order of 1 sec., PbCrO₄ shows an increase in conductivity due to secondary effects, which is not \propto potential or intensity of light. For shorter (II) primary currents alone occur. Saturation does not occur even at 2000 volts per cm., and an electrode separation of 4 mm. The efficiency is therefore very small, being about 0.001 quantum equiv. The spectral curve of the efficiency is drawn and discussed. The mean life period of electrons concerned in photo-electric conduction is dependent on intensity of light and on potential.

Electrophoresis in the positive column of a gas discharge. M. J. DRUYVESTYEN (Physica, 1935, 2, 255—266).—Calculations are made of the difference in gas pressure between the cathode and anode regions of the positive column of a discharge tube containing inert gas, in the stationary state. The results are in accord with the measurements of Rüttenauer (Z. Physik, 1922, 10, 269). The distribution of metallic vapour (Mg) mixed with the gas is also calc.

J. W. S.

Conductivity produced in neon and helium by irradiation with their own resonance radiations and the effect of foreign gases on this conductivity. R. W. SMITH and O. S. DUFFENDACK (Physical Rev., 1935, [ii], 47, 473—478).—Investigations over the pressure range 0.25—14 mm. are discussed. Traces of A and Kr increase the conductivity of Ne or He due to the action of metastable atoms of the main gas in ionising the A or Kr. Ne greatly decreases the conductivity of He, whilst He has no measurable effect in Ne.

N. M. B.

Influence of gas ions on the electro-thermal homogeneous effect. C. BENEDICKS and C. W. BORGMANN (Ark. Mat. Astron. Fys., 1934, B, 24, 5 pp.; Chem. Zentr., 1934, ii, 3096—3097).—Data are recorded for Pt at 200—550° and 1—0.01 mm. Hg. They differ from those with constantan, Cu, and liquid Hg. The effect of entry of gas into the metal is discussed.

H. J. E.

Theory of permanent currents in metallic conductors. F. ODORE (Nuovo Cim., 1934, 11, 361—371; Chem. Zentr., 1934, ii, 2661).—Theoretical.

H. J. E.

Effect of pressure on the electrical conductivities of the alkalis. N. H. FRANK (Physical Rev., 1935, [ii], 47, 282—285).—Observed effects for Li and Na are explained by taking into account the change of binding with pressure of the conduction electrons.

N. M. B.

Magneto-resistance of liquid sodium-potassium alloy. J. E. ARMSTRONG (Physical Rev., 1935, [ii], 47, 391—392).—Using very fine containing tubes to minimise errors due to liquid motion the liquid alloy Na-K was investigated for change of resistance in a magnetic field. The effect due to a longitudinal field

is $>$ that due to a transverse field. For fields > 200 gauss magneto-resistance \propto field. N. M. B.

Modifications of silver mercury iodide. A. A. KETELAAR (Wis- en natuurk. Tijds., 1934, 7, 31—35; Chem. Zentr., 1934, ii, 2944—2945); cf. A., 1934, 947, 1056).—In agreement with X-ray measurements, a discontinuity occurs at 50° in the sp. electrical conductivity of Ag_2HgI_4 . H. J. E.

Magneto-resistance change of nickel studied with alternating current. M. M. S. GUPTA, H. MOHANTY, and S. SHARAN (Current Sci., 1935, 3, 351).—Effects with a.c. and d.c. are compared. Hysteresis is not found with a.c. N. M. B.

Electrical resistances at the contact of two semi-conducting materials. G. DECHENE (Compt. rend., 1935, 200, 648—651; cf. A., 1934, 474).—The resistances of the combinations $\text{Hg-HgO-Na}_2\text{CO}_3\text{-Hg}$, $\text{Hg-HgO-CuSO}_4\text{-Hg}$, and $\text{Hg-Na}_2\text{CO}_3\text{-Cu}_2\text{O-Hg}$ have been studied. If one of the semi-conductors is not highly compressed, the contact resistance (r) is of the same order as the ohmic resistance of a few mm. or cm. of the poorer conductor, but if highly compressed it is very low. With low-resistance materials the r diminishes with increasing potential. After prolonged passage of current the resistance is asymmetrical, and shows a decrease on reversal. Both the resistance of the conductors and their r decrease with rise of temp. A p.d. exists between the two solids before passage of a current, the latter producing a polarisation potential changing with time. J. W. S.

Crystal structure and electrical properties. V. Conductivity surfaces of bismuth crystals. II. O. STIERSTADT (Z. Physik, 1935, 93, 676—691; cf. A., 1934, 253). A. B. D. C.

Rate of formation and electrical conductivity of β -silver sulphide. Formation of surface films on metals. H. REINHOLD and H. MOHRING (Z. physikal. Chem., 1935, B, 28, 178—188).—The rate of formation of $\beta\text{-Ag}_2\text{S}$ on a Ag wire in S at $130\text{--}170^\circ$ is given by $k=17e^{-10,500/T}$, where T is abs. temp. The sp. conductivity, κ , of $\beta\text{-Ag}_2\text{S}$ containing excess of S varies with the proportion of the latter. For Ag_2S in contact with molten S at $130\text{--}170^\circ$ $\kappa=8 \times 10^8 e^{-10,700/T}$, whilst for Ag_2S free from excess of S $\kappa=6 \times 10^6 e^{-6,800/T}$ at $20\text{--}180^\circ$. The sp. conductivity to be substituted in Wagner's equation for k (A., 1933, 564) is that of $\beta\text{-Ag}_2\text{S}$ saturated with S. Diffusion data show that $\beta\text{-Ag}_2\text{S}$ free from excess of S is a mixed conductor with $> 99\%$ electronic conduction. R. C.

Nature of the electrical conductivity of borate glasses of low alkali content. R. MULLER and B. MARKIN (Acta Physicochim. U.R.S.S., 1934, 1, 160—167).—The distribution of potential along rods of vitreous Na borates containing 2.6 and 25% of Na_2O , respectively, has been determined. The results are not incompatible with the view that electrical conductance through glasses of low alkali content is ionic and not electronic. M. S. B.

Electrical resistance and volume changes [with pressures] up to 20,000 kg. per sq. cm. P. W. BRIDGMAN (Proc. Nat. Acad. Sci., 1935, 21, 109—113).—With increase of pressure from atm. to

20,000 kg. per sq. cm., R of black P decreases to 0.69% of its initial val., whilst the temp. coeff. increases from -0.0077 to $+0.0025$, being zero at 12,000 kg. per sq. cm. Similar results for two different orientations of cryst. To indicate that at high pressures both Te and black P more closely resemble metals. Cu_2S behaves differently, the effect of pressure being small. Data of pressure-vol.-temp. relations of Li, Na, and K are given and discussed. F. O. H.

Dielectric saturation and hindrance of free rotation in liquids. P. DEBYE (Physikal. Z., 1935, 36, 193—194).—The Debye theory (this vol., 430) gives a satisfactory quant. explanation of the discrepancy between the observed fall in dielectric const. of associated liquids in a strong field, and the much greater val. given by the simple theory for free dipoles. A. J. M.

Dielectric constants of gases and vapours. I. M. KUBO (Sci. Papers Inst. Phys. Chem. Tokyo, 1935, 26, 242—257).—For CO_2 and air ϵ agreed with published vals. From ϵ in the vapour state the at. polarisation (in c.c.) and electric moment (μ , in 10^{-18} e.s.u.) have been determined: CH_4 0.4, 0; C_2H_6 0.1, 0; C_3H_8 0.4, 0; C_5H_{12} 0.3, 0; C_6H_{14} 0.6, 0; C_7H_{16} 0.5, 0; MeOH 1.4, 1.69; EtOH 1.8, 1.67; Pr^nOH 4.3, 1.58; Bu^nOH 1.5, 1.63. Despite free rotation the mol. polarisation of the alcohols is strictly linear with temp.; μ for the primary alcohols is $>$ for the sec. μ for the alcohols is $<$ vals. determined by others in solution in C_6H_6 and Et_2O , in disagreement with the theory of Muller (A., 1933, 1103). R. S. B.

Variation of dielectric constant of ionic crystals with temperature. M. BLACKMAN (Trans. Faraday Soc., 1935, 31, 545—546; cf. A., 1933, 661).—The temp. coeff. of the dielectric const. is calc. from Born's lattice theory. F. L. U.

Chemical applications of recent dielectric constant theory. J. W. WILLIAMS (J. Franklin Inst., 1935, 219, 211—235; cf. this vol., 283).—The variation of the dielectric const., ϵ , of a substance with frequency is considered, and the method of obtaining mol. wt. and effective radius is outlined. Limitations of the theory are discussed. Cases of the anomalous dispersion of ϵ are considered with reference to mol. orientation, and other explanations. Work on the problem of energy losses in dielectrics is reviewed. A. J. M.

(A) **Effect of solvent in dipole moment measurements: polarisation and moment of nitrobenzene.** M. A. G. RAU and B. N. NARAYANASWAMY. (B) **Theory of the solvent effect in dipole moment measurements.** M. A. G. RAU (Proc. Indian Acad. Sci., 1935, 1, A, 489—497, 498—509; cf. A., 1934, 1292).—(A) Vals. of polarisations and moments of PhNO_2 in hexane, heptane, cyclohexane, CCl_4 , C_6H_6 , and dioxan are given for the range $10\text{--}40^\circ$. The moment of the N-O linking calc. from the observed moment of PhNO_2 is 1.61, compared with the expected val. 7.23.

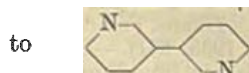
(B) On the basis of Raman and Krishnan's theory of anisotropic field consts. a rigorous expression is derived for the polarisation of a solute at infinite

dilution in a non-polar solvent, after eliminating the influence of the solvent, and this is applied to the data for I in PhNO_2 . N. M. B.

Polarity of chemical compounds. VIII. K. HIGASHI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 146—162; cf. A., 1934, 1291).—The dependence of electric moment (μ) of HCN , PhCl , PhNO_2 , and COMe_2 on the solvent is explained by assuming the mol. to be an ellipsoid of revolution with a (radius of axis of symmetry) $> c$ (axis perpendicular to a). With MeOH , EtOH , PrOH , BuOH , NH_2Ph , CHCl_3 , and Et_2O , $a < c$ ($\mu_{\text{vapour}} < \mu_{\text{solution}}$). General methods for determining for substances which cannot be vaporised are discussed. R. S. B.

Dipole moment of acetonitrile. J. R. PARTINGTON and E. G. COWLEY (Nature, 1935, 135, 474).—The vals. obtained are $\mu = 3.44 \pm 0.02D$ in C_6H_6 at 20° , P_{200} 262 ± 1.5 c.c., and P_E 11.1 c.c. L. S. T.

Electric moments of pyridine derivatives. C. A. GOETHALS (Rec. trav. chim., 1935, 54, 299—306).—The following electric moments (μ), in Debye units, have been determined: $\text{C}_5\text{H}_5\text{N}$ 2.23, 2- and 3-bromo- 2.98 and 1.93, 2:6- and 3:5-dibromo- 3.43 and 0.98, 2:4:6-trimethyl- 2.05, 2:6-dimethyl- 1.65, 2- (I), 3-, and 4-amino-pyridine 2.17, 3.19, and 3.79, 2:2'- (II) < 0.68 and 4:4'-dipyridyl (III) < 0.55 . Results agree approx. with vals. calc. by vector analysis, and indicate that the charge on the N is —. Except with 2-derivatives there is no important interaction. μ for (I) is dependent on temp. The low val. for (III) indicates a stretched mol.; the angle between the $\text{C}_5\text{H}_5\text{N}$ groups is approx. 168° . The small μ for (II) indicates a structure near



R. S. B.

Calculation of the refractive index of guanidinium iodide. W. THEILACKER (Z. Krist., 1935, 90, 77—81).—The index is calc. following the methods of W. L. Bragg, and the result is used to check accurately the C—N distance found from X-rays.

B. W. R.

Optical rotatory dispersion in the carbohydrate group. V. Tetramethyl- γ -gluconolactone. R. W. HERBERT, E. L. HIRST, H. SAMUELS, and C. E. WOOD (J.C.S., 1935, 295—299; cf. this vol., 66).—Data are given for various $\lambda\lambda$ and with H_2O , EtOH , CHCl_3 , C_6H_6 , and dioxan as solvents. Vals. for the epimeric tetramethyl- γ -mannonolactone are compared. The relative effects of the second and fourth C of the lactones with respect to the induced dissymmetry of the C=O group are discussed.

N. M. B.

Rotatory power of α -phenylethylamine and of its halogen salts. M. Y. K. HENG (Ann. Physique, 1935, [xi], 3, 270—320).—Racemic $\text{NH}_2\text{-CHPhMe}$ (I) has been prepared and resolved into its active components. The rotatory power α of the halogen salts of (I) in H_2O and EtOH , using $\text{Hg } \lambda$ 5461, increases with concn., indicating that the active cations are deformed in the field of the anions. Since the absorption bands in the ultra-violet remain const. it is probable that the deformation is local and is limited to the NH_2 . A neutral salt has the same effect as

increase of concn. Salts of multivalent anions have a deforming effect $>$ salts of univalent ions and the val. of α is correspondingly increased. Salts of long-chain org. acids, beginning with $\text{Pr}\cdot\text{CO}_2\text{Na}$, produce an effect too large to be attributed to this cause alone. If the added salts form double salts with the hydrochloride of (I), as do $\text{Na}_2\text{C}_2\text{O}_4$ and Na malate, there is little change in α , and similarly for salts of $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ and $\text{CCl}_3\cdot\text{CO}_2\text{H}$, with which double decomp. takes place. M. S. B.

Magnetic rotatory power of ammoniacal nitrogen. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1935, 200, 823—824).—From measurements on gaseous NH_3 the at. and mol. rotations of N were 6.8×10^{-5} and 2×10^{-5} , respectively. Data for substituted amines are tabulated; contributions due to N, NH, and NH_2 are equal and approx. const.; slight divergences from the additivity law are attributed to impurities. N. M. B.

Electric birefringence of isotropic p -azoxyanisole. (MRS.) J. Z. K. EISENMANN (Compt. rend., 1935, 200, 822—823).—A positive birefringence is found for the substance in an electric field of 150—16,000 volts per cm. The direction of max. polarisation is perpendicular to the axis of the mol.; the dipole moment is discussed. N. M. B.

Thermal variation of magnetic birefringence and molecular electric moments. A. GOLDT (Compt. rend., 1935, 200, 654—656).—The ratio C_2/C_1 [where C_2 and C_1 are the vals. of the "const." C in $C = \beta nT / (n^2 - 1)(n^2 + 2)$ at T_2° and T_1° abs., respectively; $T_2 - T_1 = 50^\circ$] decreases with increasing dipole moment of the mol. The effect is attributed to thermal variation of mol. association and to electrical forces modifying the magnetic orientation of the mols. J. W. S.

Studies with vibrating mechanical models. I. Benzene, toluene, and phenyl halides. D. E. TEETS and D. H. ANDREWS. II. The series $\text{C}_6\text{H}_5\text{Cl}$ — C_6Cl_6 . T. W. MURRAY, V. DEITZ, and D. H. ANDREWS (J. Chem. Physics, 1935, 3, 175—180, 180—188; cf. A., 1930, 1349).—I. Mechanical models were constructed for C_6H_6 , PhMe , PhCl , PhBr , and PhI . Mechanical frequencies of the simpler types of motion are correlated with spectral lines and the frequency shifts in passing down the series. Observed types of motion are in fair agreement with those deduced on group theory.

II. Models based on Pauling's resonance formula for C_6H_6 were constructed for C_6H_6 , PhCl , o -, m -, and p - $\text{C}_6\text{H}_4\text{Cl}_2$, 1:2:3-, 1:2:4-, and 1:3:5- $\text{C}_6\text{H}_3\text{Cl}_3$, and C_6Cl_6 . Comparison of the mechanical and Raman spectra allows the identification of several lines connected with the motions of the Cl atoms and of the line at 992 cm^{-1} associated with the symmetrical expansion of the C_6H_6 ring. The types of motion show an evolution from C_6H_6 to C_6Cl_6 . N. M. B.

Rotation of molecules in crystals. H. H. NIELSEN (J. Chem. Physics, 1935, 3, 189—196).—Mathematical. The treatment is generalised to include polyat. configurations. Two models, of which the homo- and hetero-polar diat. mols. are special cases, are considered. N. M. B.

Molecular rotation in liquids. P. DEBYE (Bull. Acad. roy. Belg., 1935, [v], 21, 166—174).—Mathematical. N. M. B.

Natural classification of chemical compounds. IV. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1934, 4, 1034—1041; cf. A., 1933, 1232).—Theoretical. R. T.

Trihydrol controversy. T. C. BARNES (Science, 1935, 81, 200—201).—A criticism (cf. this vol., 437). L. S. T.

Constitution of water in solutions. I. R. RAO and C. S. RAO (Current Sci., 1935, 3, 350—351).—Changes in the structure of the Raman band of H_2O containing dissolved strong and weak electrolytes and non-electrolytes are summarised, and are attributed to variations in the constitution of H_2O due to changes in the equilibrium between single, double, and triple mols. The temp. variation of the band structure with the same concn. of a solute is similarly explained. N. M. B.

Constitution of sulphur monochloride, and derivatives of $(S\cdot OH)_2$.—See this vol., 614.

Stereochemical conception of the complex structure of the acids of phosphorus. R. REINICK (Ann. Guehard-Severine, 1934, 10, 418—429; cf. A., 1934, 476).—The localised valency forces from P are directed towards the apices of a tetrahedron, and since P is tervalent, one of these apices is non-functional. The other four angles of the circumscribing cube are occupied by other elements; e.g., H_3PO_4 is regarded as derived from PH_3 , thus, $(PO_4)H_3$. These conceptions lead to structures for the hydrides, oxides, and oxy-acids of P, and analogous considerations are applied to compounds of Si, S, Cl, and B. J. G. A. G.

Magnetic measurement of ionic deformations in crystals. G. W. BRINDLEY and F. E. HOARE (Nature, 1935, 135, 473—474).—In the alkali halides, the only important exceptions to the additivity principle for the diamagnetic susceptibilities (I) of ions in crystals are the chlorides, bromides, and iodides of Li and Cs. The interat. forces which thrust apart the negative ions in the Li halides and result in a change of structure in the Cs halides produce deformations of the ions which lower their (I). This conclusion also holds for the NH_4 halides. L. S. T.

Variation of the carbon-halogen link distances in different types of organic structure. H. DE LASZLO (Nature, 1935, 135, 474).—The C—halogen distance, determined by the electron diffraction method, varies in aliphatic, ethylenic, aromatic, and acetylenic compounds. The vals. for C—Cl, C—Br, and C—I recorded for such compounds decrease for a given halogen in the order aliphatic > ethylenic > aromatic > acetylenic. L. S. T.

Constants for halogens and their gaseous diatomic compounds. C. H. D. CLARK (Trans. Faraday Soc., 1935, 31, 585—596).—Theoretical. At. radii, internuclear distances, dielectric consts., and dipole moments are calc. F. L. U.

Exchange interaction between two nuclei. P. PAVINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 93—96).—Theoretical. The energy of exchange be-

tween two H nuclei and between two Li nuclei is discussed. W. R. A.

Resonance energy in diphenyl and its derivatives. L. BRULL (Gazzetta, 1935, 65, 28—37).—Resonance energies are calc. from heats of formation using Pauling's procedure. The structure of Ph_2 is discussed. O. J. W.

Acidities of ketones and the mechanism of prototropic change. H. B. WATSON, W. S. NATHAN, and L. L. LAURIE (J. Chem. Physics, 1935, 3, 170—174).—Observed acidity in brominated acetones is attributed to co-ordination of C in C=O and OH ion, preceded by electromeric change to the semipolar form, and acid- and base-catalysed prototropy to a similar change caused by interaction with the catalyst, followed by transformation of the semipolar form to ketone or to enolic ion. The measured velocity thus depends on the rate of reaction of ketone and catalyst, and the proportion of semipolar form changed to enol. These views and the conception of quantum mechanical resonance explain a no. of observations on prototropic changes of C=O compounds. N. M. B.

Thermodynamic properties of sulphur compounds. I. Hydrogen sulphide, diatomic sulphur, and the dissociation of hydrogen sulphide. P. C. CROSS (J. Chem. Physics, 1935, 3, 168—169; cf. this vol., 280).—Mathematical. Results are calc. from structure as obtained by infra-red band analysis. The energy of dissociation of H_2S into normal atoms is 173.8 kg.-cal. per mol. N. M. B.

Energy levels of a symmetrical double minima problem with applications to the NH_3 and NH_3^+ molecules. M. F. MANNING (J. Chem. Physics, 1935, 3, 136—138).—Energy levels are calc. for the double-min. energy curve. Calc. and observed vals. agree for NH_3 and NH_3^+ . The height of the NH_3 pyramid is 0.37 Å., and of the potential hill 2076 cm.⁻¹; the dissociation energy is approx. 5 volts. N. M. B.

Application of a modified Morse formula to simple hydride diatomic molecules (di-atoms). C. H. D. CLARK (Phil. Mag., 1935, [viii], 19, 476—485).—The term "di-atom" is proposed for "diat. mol." in spectroscopic nomenclature. Results are tabulated for the application of a modified Morse formula to KH type di-atoms and to neutral and ionised di-atoms of the LH period. It is suggested that (internuclear distance)³ enters into Morse's relation on account of polarisation phenomena. N. M. B.

Periodicity of Morse's function. C. H. D. CLARK (Physical Rev., 1935, [ii], 47, 238—240; cf. preceding abstract).—Morse's function is shown to possess a periodic character, and can be modified by the introduction of group nos. and period consts. based on a suggested classification of diat. mols. Results are satisfactory for simple non-hydride diat. mols., and for hydrides of the KH period. N. M. B.

Potential functions of polyatomic molecules. G. B. B. M. SUTHERLAND and D. M. DENNISON (Proc. Roy. Soc., 1935, A, 148, 250—271).—A new representation of the force field in a polyat. mol. is investigated. The potential energies of mols. containing the groups CH_2 or Me are expressed as the sums of the potential

energies of groups of atoms within the mol. plus simple interaction energies between the groups. It is assumed that the potential function is independent of the mol. in which the group lies, and that the potential describing the interaction between the groups depends only on the distance between the two neighbouring atoms of the groups. Relations are deduced concerning the "parallel" frequencies of the mols. C_2H_4 , CH_2O , C_2H_6 , MeF , $MeCl$, $MeBr$, MeI , and CH_4 , and comparison of the results with the experimentally determined frequencies indicates that the above assumptions are valid for the treatment of such vibrations. The potential consts. characterising the CH_2 and Me groups vary only by a few % from mol. to mol., in agreement with the fact that mols. containing these groups exhibit characteristic infra-red and Raman frequencies. L. L. B.

Inner potential of zinc blende. S. MIYAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 216—224).—From electron diffraction experiments the val. 12.18 volts is obtained. R. S. B.

Rotational energy of polyatomic molecules. J. H. VAN VLECK (Physical Rev., 1935, [ii], 47, 487—494).—Mathematical. N. M. B.

Determination of the heat of dissociation from a study of the long wave-length limit of the continuous absorption by gaseous molecules. S. DATTA and B. CHAKROBORTI (Current Sci., 1935, 3, 349—350).—The effect of pressure on the true long- λ limit is discussed. Heats of dissociation for HBr and HCl from thermal and optical measurements are in agreement when the latter are made at atm. pressure, confirming that the H halides are dipolar mols. with at. linkings. N. M. B.

Theory of refractive index of crystals for cathode rays and breadth of reflexion line. S. KIKUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 225—241).—The potential function for Zn blende is calc., and it is inferred that only 4—5 layers of the crystal are effective in the second-order, and 10—15 in the fifth-order, reflexion spectrum. The mean free path for inelastic collision is 270 Å. R. S. B.

Increment in the parachor of hydrocarbon molecules with abnormal intramolecular strains. V. S. GUTIERIA (J. Gen. Chem. Russ., 1934, 4, 1147—1152).—The increment in the parachor of hydrocarbons of the series C_2H_2 —cyclobutane is expressed by $0.091m\alpha - 1.083$ (cf. Mumford and Phillips, A., 1929, 1219), where m is the no. of abnormally directed valencies, and α the angle between neighbouring C atoms. The significance of Mumford's and of Sugden's formulæ is discussed. R. T.

Photometry of X-ray reflexion. II. Comparison of the photographic and ionisation methods. J. A. BARASOAIN and R. SALVIA (Anal. Fis. Quím., 1934, 32, 53—64).—Under suitable conditions, the two methods give the same results. Modifications of the Bragg ionisation spectrometer are described. Practically no difference is observed when convergent or divergent beams are employed. It is better to rotate the crystal rather than the ionisation chamber. In the photographic method the darkening

cc the incident energy for vals. of S up to 0.9. Repeated exposure for the fainter lines is recommended, to obtain approx. const. darkening. H. F. G.

Determination of numbers of small particles from Debye-Scherrer photographs. H. S. SCHIDANOV (Z. Krist., 1935, 90, 82—91).—Theory is given of a method of deducing, from no. of separate specks occurring in a Debye-Scherrer ring, the no. of particles in the powder specimen. The method is used to follow the recrystallisation of Cu through a heat-treatment. B. W. R.

X-Ray Laue diagrams of piezo-electric oscillating crystals. F. KLAUER (Physikal. Z., 1935, 36, 208—211).—Increase in the intensity of the Laue pattern was observed when quartz was oscillating. No effect was obtained with tourmaline, where the electrical and optical axes coincide. A. J. M.

Orientation of lead chloride and bromide by muscovite mica. L. ROYER (Compt. rend., 1935, 200, 567—569; cf. A., 1934, 249, 376, 834).—Crystallisation of $PbCl_2$ or $PbBr_2$ in presence of freshly cleaved muscovite mica leads to the (010) plane of the $PbCl_2$ crystals being formed coincident with the (001) plane of the mica, and the (001) planes of the $PbCl_2$ taking the same direction as the (010), (310), or (310) planes of mica. J. W. S.

Calomel from physical and chemical standpoints. C. H. LAWALL and J. W. E. HARRISSON (J. Amer. Pharm. Assoc., 1935, 24, 97—102).—The macroscopic and microscopic appearance of Hg_2Cl_2 varies with the method of prep., the particulate and cryst. condition being least marked with pptd. Hg_2Cl_2 . The bearing of the data on pharmacopœial uses is indicated. F. O. H.

X-Ray investigation of the transformation from face-centred to body-centred cubic lattice [in iron]. Z. NISHIYAMA (Sci. Rep. Tôhoku, 1934, 23, 637—664).—The γ - α change in Fe occurs by shear along the (111) plane of γ - Fe . According to the proposed mechanism there are 12 possible shears resulting in 12 different orientations, and a transformed single γ crystal may become a large no. of α crystals. The γ - α change occurs by shear along γ (111) plane in the direction of γ (211), expansion and contraction also occurring until γ (111) \rightarrow α (011) and γ (011) \rightarrow α (100). W. P. R.

Lattice parameter alteration of α -iron on charging with hydrogen. F. WEVER and B. PFARR (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1933, 15, 147—148; Chem. Zentr., 1934, ii, 2737).— H atoms enter the vacant spaces in the α - Fe lattice, and cause an increase in the lattice parameter of 0.12% per at.-% of H . J. S. A.

Structure of ammonium bromide at low temperatures. J. WIEGLE and H. SAINI (Arch. Sci. phys. nat., 1934, 51, 225—229).—Below -39° the cubic crystal contracts about 3% along two axes and changes about 2.5% by movement of Br' along the third. C. W. G.

Structure of caesium cobalt chloride (Cs_3CoCl_5). H. M. POWELL and A. F. WELLS (J.C.S., 1935, 359—362).—X-Ray examination of the tetragonal crystals

gives space-group D_{2h}^{18} , 4 mols. per unit cell, a 9.18, c 14.47 Å. Positions of the atoms were determined from intensity comparisons. CoCl_4 groups are in approx. regular tetrahedral configuration, with an additional simple Cl ion, giving the formula $\text{Cs}_3^{1+}[\text{CoCl}_4]^{2-}\text{Cl}^{1-}$. An analogous unstable Rb compound has a 8.7, c 14.0 Å. N. M. B.

Crystal structure of the alums. H. LIPSON and C. A. BEEVERS (Proc. Roy. Soc., 1935, A, 148, 664—680).—The complete structure of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is given by a 12.13 Å., space-group $Pa\bar{3}$, 4 Al on (0, 0, 0), etc., 4 K on ($\frac{1}{2}$, $\frac{1}{2}$, etc., 8 S on (0.31, 0.31, 0.31), etc., 8 O on (0.24, 0.24, 0.24), etc., 24 O on (0.30, 0.27, 0.43), etc., 24 H_2O on (0.02, 0.02, 0.16), etc., 24 H_2O on (0.04, 0.13, 0.30), etc. Of the two sets of H_2O , one forms octahedral groups around the Al atoms, each H_2O having a plane distribution of its three linkings; the other set links together the SO_4 tetrahedron, the $\text{Al}_6\text{H}_2\text{O}$ octahedra, and the K atom, and the arrangement of the linkings is approx. tetrahedral. L. L. B.

Crystal lattice of samarium sulphate octahydrate. W. H. ZACHARIASEN (J. Chem. Physics, 1935, 3, 197—198).—The monoclinic unit cell has a 20.30 ± 0.06 , b 6.76 ± 0.03 , c 13.53 ± 0.05 Å., β $118^\circ 16'$, 4 mols. per cell, space-group $A2/c$ (C_{2h}^2). The 8 Sm atoms lie in general positions: $\pm(xyz) \pm(\frac{1}{2}-x, y, \frac{1}{2}-z) \pm(x+\frac{1}{2}, \frac{1}{2}-y, z) \pm(x, y+\frac{1}{2}, z+\frac{1}{2})$. The Sm parameters were x 0.106 ± 0.003 , y 0.025 ± 0.006 , z -0.231 ± 0.003 . The closest distance Sm—Sm is 5.08 Å. Interat. distances in the isomorphous Gd salt are 0.2% <, in the Er salt 1.1% <, and in the Nd salt 0.7% >, in the Sm salt. N. M. B.

X-Ray study of anhydrous sodium metaphosphates. A. BOULLÉ (Compt. rend., 1935, 200, 658—660).—Maddrell's salt (metaphosphate A'), formed on dehydration of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ above 250° , is an insol. $(\text{NaPO}_3)_3$; heating to 400 — 550° yields the insol. metaphosphate B , of undetermined polymerisation. On heating either A' or B to 550 — 640° , the sol. metaphosphate A is formed. Fusion of any of the above yields the solid vitreous $(\text{NaPO}_3)_6$ (metaphosphate C), which on prolonged heating in the solid state at any temp. yields A . A and A' have identical X-ray spectra, distinct from that of B . C is amorphous. J. W. S.

Crystal structure of witherite. M. Y. COLBY and L. J. B. LACOSTE (Z. Krist., 1935, 90, 1—7).—The cell contains 4 mols. of BaCO_3 ; a_0 5.28, b_0 8.83, c_0 6.39 Å., space-group V_h^{18} . At. parameters are determined, giving a structure similar to that of aragonite and cerussite. B. W. R.

Crystal structure of berzeliite. W. BUBECK and F. MACHATSCHKI (Z. Krist., 1935, 90, 44—50).—The O atoms in $(\text{Ca}, \text{Na})_3(\text{Mg}, \text{Mn})_2[\text{AsO}_4]_3$ are located as carefully as possible from intensity measurements; the As—O spacing is compared with the Si—O distance in silicates. B. W. R.

Structure of phosgenite. E. ONORATO (Periodico Min., 1934, 5, 37—61; Chem. Zentr., 1934, ii, 2667).—From X-ray measurements the crystals are of the simple Γ type of the Bravais system ($a:c$ 1:0.543;

2 mols. $\text{PbCl}_2 \cdot \text{PbCO}_3$ in unit cell; space-group probably D_{2h}^{18}). H. J. E.

Space lattices of berthollides. A. GLAZUNOV (Coll. Czech. Chem. Comm., 1935, 7, 77—83).—A study of the space lattices of intermetallic compounds confirms the existence of "berthollides" (I), or compounds of variable composition, as contrasted with "daltonides" (II) which obey the law of fixed proportions. In (I) the atoms are distributed statistically and in (II) they are arranged regularly according to a definite law. M. S. B.

Structure of halloysite and metahalloysite. M. MEHMEL (Z. Krist., 1935, 35—43).—Halloysite has space-group C_3^2 , a_0 5.20, b_0 8.92, c_0 10.25 Å., $\beta \sim 100^\circ$; metahalloysite has a_0 5.15, b_0 8.9, c_0 7.57 Å., $\beta \sim 100^\circ$. At. parameters are approx. located and the structures and refractive indices compared with those of kaolinite. B. W. R.

Crystals with optical anomalies. R. HOCART (Bull. Soc. franç. Min., 1934, 57, 5—125; Chem. Zentr., 1934, ii, 3103—3104).—Optical and X-ray data for boleite, pseudoboleite, boracite, pharmakosiderite, senarmontite, and apophyllite are recorded and discussed. H. J. E.

Crystal structure of guanidinium halides. II. Structure of guanidinium iodide, $\text{C}(\text{NH}_2)_3\text{I}$. W. THEILACKER (Z. Krist., 1935, 90, 51—76).—The dihexagonal pyramidal cell contains 4 mols., space-group C_{6h} , a_0 7.19, c_0 12.30 Å. The at. parameters are determined; the I atoms form a layer lattice of graphite type, and the C is coplanar with the three associated N atoms. B. W. R.

Crystal structure of calcium barium propionate. L. P. BIEFELD and P. M. HARRIS (J. Amer. Chem. Soc., 1935, 57, 396—399).— $2(\text{EtCO}_2)_2\text{Ca} \cdot (\text{EtCO}_2)_2\text{Ba}$ has d^{27} 1.44, and crystallises in the cubic system with a_0 18.3 ± 0.1 Å. The unit cell contains 8 mols. of double salt. X-Ray data indicate a co-ordination structure of Ba^{++} and Ca^{++} with O of the propionate groups. E. S. H.

Crystal structure of dicalcium barium propionate. I. NITTA and T. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 164—177).—X-Ray examination of $2(\text{EtCO}_2)_2\text{Ca} \cdot (\text{EtCO}_2)_2\text{Ba}$ by Laue, oscillation, rotation, and powder photographs gives a cubic unit with a_0 18.20 Å., space-group $O_h^1 Fd\bar{3}m$. The cell contains 8 mols.; $d_{\text{calc.}}$ 1.444. Each Ba atom is surrounded by 12 O and each Ca by 6 O. The CO_2H has the symmetry C_{2v} mm and its behaviour towards Ba and Ca atoms is different. The Me groups rotate. Pauling's rule of compensation of electrostatic linkings is obeyed. W. R. A.

Crystal structure of naphthazarin. J. PALAÇIOS and R. SALVIA (Anal. Fís. Quím., 1934, 32, 49—52).—The monoclinic crystals of 1:4-dihydroxynaphthoquinone have a_0 3.85, b_0 8.02, c_0 14.5 Å., β $97^\circ 6'$; 2 mols. in unit cell; space-group C_{2h}^2 . The results confirm the view that the H atoms of the OH oscillate with their valency electrons within the field of action of the quinonoid O atoms. H. F. G.

Hydrocarbons of esparto and candelilla waxes.—See this vol., 551.

Liquid "structure" of methyl alcohol. W. H. ZACHARIASEN (J. Chem. Physics., 1935, 3, 158—161; cf. Warren, A., 1934, 244).—Conclusions concerning liquid mol. configuration are reached from radial distribution of atoms around any one atom, as obtained from analyses of X-ray diffraction patterns, in the case of MeOH and nonyl alcohol. MeOH gives strong indication of (dipole) H binding between O atoms of neighbouring mols., with short "life" of a given intermol. linkings. The Bragg equation cannot be applied to the diffraction peaks. N. M. B.

Scattering of X-rays from fluids containing polyatomic molecules. W. H. ZACHARIASEN (Physical Rev., 1935, [ii], 47, 277—278).—Mathematical. The radial distribution function can be obtained directly from the observed scattering curve if the mol. structure is known. N. M. B.

Diffraction of electrons by colloidal gold. L. BRU (Anal. Fis. Quím., 1934, 32, 20—29).—The Scherrer formula for particle size determination by means of X-rays reduces to $\Delta = 0.94\lambda(B-b)$ when an electron stream is employed, b being a const. dependent on the divergence of the beam and on the degree of absorption. Measurements with colloidal Au prepared by reduction with P and deposited on a collodion film gave concordant results, the mean val. of Δ being 149 Å. H. F. G.

Electron diffraction investigation of the molecular structures of (1) chlorine monoxide, oxygen fluoride, dimethyl ether, and 1:4-dioxan, and of (2) methyl chloride, methylene chloride, and chloroform, with some applications of the results. L. E. SUTTON and L. O. BROCKWAY (J. Amer. Chem. Soc., 1935, 57, 473—483).—The mol. structures of Cl₂O, OF₂, Me₂O, and 1:4-dioxan, as determined by electron diffraction, show that the O valency angle is increased above its val. in H₂O when comparatively heavy groups are linked to O. When these groups are Cl or Me the increase is > 5°. The observed C—O linking distance agrees with the covalent radius sum, but the Cl—O distance is 0.06 Å. greater. In the chlorinated methanes the C—Cl distance is const. and equal to the covalent radius sum. The tetrahedral angle in CCl₄ is increased by 2° or 3° in CHCl₃ and CH₂Cl₂. The influence of the mutual effect of dipoles in different linkings of the same mol. on the interpretation of dipole moment data is discussed. E. S. H.

Hall effect in sodium, potassium, and caesium. F. J. STUDER and W. D. WILLIAMS (Physical Rev., 1935, [ii], 47, 291—295).—The Hall const. of carefully purified Na, K, and Cs, distilled in vac. into thin flat Pyrex moulds with sealed in electrical leads, was: Na —0.0021, K —0.0042, Cs —0.0078. The Hall effect in each case was independent of c.d. in the specimen, and of the magnetic field intensity. N. M. B.

Thermo-electromotive force and electric conductivity of antimony and cadmium. B. N. VOLFSON and V. N. ROSHDESTVENSKI (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 447—453).—The compositions Sb₃Cd₅, Sb₅Cd₄, and Sb₅Cd₃ are proposed. CH. ABS.

Seignette salt in the neighbourhood of spontaneous orientation. I. V. KURTSCHATOV (J. Exp. Theor. Phys., U.S.S.R., 1933, 3, 537—544).—The dependence of the polarisation of Na K tartrate on the field strength and the thickness of the crystal has been investigated in the region of spontaneous orientation. CH. ABS.

Change in thermal energy which accompanies a change in magnetisation of nickel. (Miss) A. TOWNSEND (Physical Rev., 1935, [ii], 47, 306—310).—A new method of measuring directly the thermal energy change occurring when the magnetisation of a ferromagnetic substance is altered is applied to a hard-drawn Ni rod. The thermal energy decreases on demagnetisation and increases on magnetisation. N. M. B.

Effect of slight impurities on the elastic constants, particularly the compressibility, of zinc. P. W. BRIDGMAN (Physical Rev., 1935, [ii], 47, 393—397).—Hanson's results (cf. A., 1934, 480), tested by compressibility measurements, are explained by errors due to small internal strains. Revised compressibility data are given. N. M. B.

Elastic constants of the zinc crystal. E. P. T. TYNDALL (Physical Rev., 1935, [ii], 47, 398—399; cf. preceding abstract).—An alternative interpretation of Hanson's results is proposed. Consts. for the Zn crystal, based on the measurements of Hanson and of Bridgman, are given. N. M. B.

Plasticity of crystals. P. DUWEZ (Physical Rev., 1935, [ii], 47, 494—501).—On the basis of a "secondary structure" in crystals a theory is given establishing a relation between stress and strain in a crystal when deformed plastically. The forms and areas of the hysteresis cycles are deduced. Experimental verifications for Cu are given. N. M. B.

Formation of twin crystals of zinc. N. N. DAVIDSON, A. F. KOLESNIKOV, and K. V. FEDOROV (J. Exp. Theor. Phys., U.S.S.R., 1933, 3, 350—360).—Curves show the dependence of the formation of twins on the tension at various temp. The resistance to the formation of twins is expressed as a (cleavage) force along the plane and in the direction of twinning. CH. ABS.

Theory of the allotropic transition process in dipole compounds. J. FRENKEL, O. TODES, and S. ISMAILOV (Acta Physicochim. U.R.S.S., 1934, 1, 97—112).—Theoretical. A quant. consideration of the changes in vibrational and rotational energy during the transition from a dipole to a non-polar mol. with special reference to the behaviour of cryst. HCl. M. S. B.

Vitreous state. W. H. ZACHARIASEN (J. Chem. Physics, 1935, 3, 162—163).—Polemical against Hagg (cf. this vol., 285). N. M. B.

Cathode sputtering. R. SEELIGER and K. SOMMERMEYER (Z. Physik, 1935, 93, 692—695).—Knudsen's cosine law applies. A. B. D. C.

Supersonic velocity in gases. C. ISHII (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 201—207).— $V_p - V_0[1 + (0.00023 \pm 0.00001)p]$, where V_p = velocity of sound in air at 730 kc. frequency with

partial v.p. of $\text{H}_2\text{O} = p$. The influence of H_2O decreases and V_0 increases as the frequency increases.

R. S. B.

Influence of ultra-sound on some physico-chemical properties. L. HAUSS (Bull. Soc. chim. Belg., 1935, 44, 81—95).—Preliminary. Apparatus for the production of ultra-sonic waves is described.

R. S.

Magnetic effects in superconductors. F. G. A. TARR and J. O. WILHELM (Canad. J. Res., 1935, 12, 265—271).—Magnetic effects in metals cooled from above the transition temp., when in an applied magnetic field, have been studied. Contrary to the results of Meissner *et al.* (A., 1934, 19), the effective permeability does not generally become zero, but there are wide variations in the amount of flux reduction depending on the shape and composition of the superconductor and the direction of the applied field. This agrees with Mendelsohn *et al.* (*ibid.*, 492).

M. S. B.

Magnetic behaviour of ferromagnetic substances when the magnetising field is cut off. G. KIESSLING (Ann. Physik, 1935, [v], 22, 402—420).—The variation of the current induced in a ferromagnetic substance with time was determined.

A. J. M.

Ferromagnetism of platinum-chromium alloys. E. FRIEDERICH and A. KUSSMANN (Physikal. Z., 1935, 36, 185—192).—The ferromagnetism of Pt-Cr alloys is not confined to any definite stoichiometrical proportion of Pt and Cr, but is found in one phase of varying composition, as shown by the steady increase of the Curie point. X-Ray and micrographic tests show that the ferromagnetic region lies in the transition zone between a mixed crystal and superstructure phase. The concn. range for ferromagnetism is 7—20% Cr. The Curie point extends to 0° abs. on the Pt side, and disappears at > 900° on the Cr side.

A. J. M.

Magnetic properties of amorphous manganese. L. F. BATES and D. V. R. PANTULU (Proc. Physical Soc., 1935, 47, 197—204).—The prep. in vac. of pure amorphous Mn is described. The Mn is paramagnetic, and obeys the Curie-Weiss law, $\chi = 2.174 \times 10^{-2}/(T + 1540)$, at 90—600° abs.; χ at 20°, 11.80×10^{-6} .

N. M. B.

Paramagnetism of the cobalt ion in very dilute solutions. R. MERCIER (Ann. Physique, 1935, [xi], 3, 201—269).—Magnetic susceptibilities of dil. solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in MeOH have been measured at different temp. The at. moment is independent of concn. but diminishes with falling temp. Near the 'p. of MeOH the electron spin only remains active. This may be due to a Stark effect of the atoms of the solvent on Co^{++} . The general theory is discussed.

M. S. B.

Magneto-chemical investigations. I. Complex rhodium compounds. J. A. CHRISTIANSEN and R. W. ASMUSSEN (Kong. dansk. Viden. Selsk., mat.-fys. Medd., 1934, 12, No. 10, 21 pp.; Chem. entr., 1934, ii, 2666).—Vals. of χ are recorded for various compounds of the types $[\text{RhX}(\text{NH}_3)_5]\text{X}'_2$, ' , being halogens or monobasic acid radicals),

$[\text{RhCl}_2(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}$, and $[\text{Rh}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{NO}_3$, for $\text{PtCl}_6 \cdot \text{H}_2\text{O}$, and for two hexammines.

H. J. E.

Diamagnetic susceptibilities of palladium salts. R. B. JANES (J. Amer. Chem. Soc., 1935, 57, 471—473).—All the compounds examined were diamagnetic. An explanation is advanced.

E. S. H.

Magnetic susceptibility and structure of hæmin. L. CAMBI and L. SZEGO (R. Ist. lomb. Sci. Lett., Rend., 1934, [ii], 67, 275—278; Chem. Zentr., 1934, ii, 2681; cf. A., 1934, 1337).—Vals. are recorded at 84°, 192°, and 294° abs. Hæmin (I) obeys the Curie law (magneton no., 28.75), behaving as a Fe^{III} salt. A solution of (I) in anhyd. $\text{C}_5\text{H}_5\text{N}$ was paramagnetic after 19 days, although insol. products separated.

H. J. E.

Rotational heat of the molecule H^1H^2 . K. CLUSIUS and E. BARTHOLOMÉ (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1934, [ii], 1, 1—14; Chem. Zentr., 1934, ii, 2943).—Vals. are calc. for the rotational heats of H_2 , HH^2 , and H^2_2 . The calc. vals. for HH^2 and H^2_2 have max. at 53° and 92° abs., respectively. Measurements are recorded (34.7—67.8° abs.) confirming the calc. vals.

H. J. E.

Variation with temperature of the specific heats of perfect gases. G. RIBAUD (J. Phys. Radium, 1935, [vii], 6, 55—64).—The theorem of equipartition of energy is corr., for diat. gases, for the expansion of the mol. by centrifugal force, for anharmonic vibrations as indicated spectroscopically in place of harmonic vibrations assumed by the Einstein formula, and for electronic structure modifications induced by high temp. The total sp. heat increases at 5000° abs. are: O, 0.6, H_2 0.67, OH 0.7, N_2 0.21, CO 0.21. In the case of monat. mols. the sp. heat 4.96, const. at low temp., tends to rise with modification of electronic structure, the increase for O being 0.22 at 5000° abs.

N. M. B.

Theory of the specific heat of crystals. I. Lattice theory and continuum theory. II. Vibrational spectrum of cubical lattices and its application to the specific heat of crystals. M. BLACKMAN (Proc. Roy. Soc., 1935, A, 148, 365—383, 384—406).—I. The one-dimensional lattice is compared with the one-dimensional Debye continuum, and the general conclusions drawn are confirmed by the calc. sp. heat and a numerical comparison. The points of difference in the three-dimensional case are similarly dealt with, and the connexion of the 0_D val. ($0_D = h\nu_D/K$, where ν_D is the max. frequency) with that derived from optical data is discussed. A rough theory of the sp. heat of crystals of the NaCl type is given for the special case where the masses of the ions are very different.

II. An investigation of the features of the vibrational spectrum of a cubical crystal has been made by a geometrical method; the two-dimensional case is treated in detail, the three-dimensional case in outline. The chief result is the discovery of several max. of the density of the vibrations. The significance of the results is discussed, especially in relation to the Debye theory of sp. heat. The theoretical justification of the Nernst-Lindemann theory, which represents the spectrum by two peaks, is established.

L. L. B.

Specific heat and electronic activation in crystals. J. E. AHLBERG and S. FREED (J. Amer. Chem. Soc., 1935, 57, 431—437).—The determination of that part of the sp. heat associated with electronic transitions in crystals of rare earth compounds is discussed. The heat capacities of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ at 17—295° abs. are recorded and compared with those of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Good agreement is obtained between the observed and calc. electronic sp. heats.

E. S. H.

Heat capacity of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ from 16° to 300° abs. J. E. AHLBERG and C. W. CLARK (J. Amer. Chem. Soc., 1935, 57, 437—438).—Data are recorded.

E. S. H.

Atomic heat of nickel at liquid helium temperatures. W. H. KEESOM and C. W. CLARK (Physica, 1935, 2, 230).—The at. heat (C) at 1—4° abs. \propto the abs. temp. (T) in accord with Sommerfeld's formula for free electrons, but the vals. are much $>$ those calc. from this formula. The contribution to C due to variation of magnetisation with temp., which $\propto T^{3/2}$, is $\ll C$.

J. W. S.

Specific heats at low temperatures. F. SIMON and R. C. SWAIN (Z. physikal. Chem., 1935, B, 28, 189—198).—Measurements of the sp. heat, C , of Li at 15—300° abs. have revealed an anomalous variation of C with temp. which, like the thermal expansion (A., 1930, 986), points to a thermally excited quantum transition. Measurements have been made with Fe at 30—220°, calcite at 15—80°, and corundum at 30—280° abs. For activated C at 15—80° abs. C is for compact graphite. For A adsorbed on C, C corresponds at 60—80° abs. with a two-dimensional gas; below 60° it begins to fall and approaches zero at 12°.

R. C.

Heat content and lattice state of active magnesium oxide. R. FRICKE and J. LUKE (Z. Elektrochem., 1935, 41, 174—183).—The energy content of MgO , prepared by dehydration of $\text{Mg}(\text{OH})_2$, is the greater the lower is the temp. of dehydration, and the shorter the time of heating. The results are discussed in relation to the lattice structure determined by parallel X-ray examination.

E. S. H.

Heat capacities at low temperatures of the oxides of strontium and barium. C. T. ANDERSON (J. Amer. Chem. Soc., 1935, 57, 429—431).—Data are recorded for the range 55—300° abs. The corresponding entropies are 13.0 and 16.8 g.-cal. per degree, respectively.

E. S. H.

Specific heat of liquids. II. N. A. DE KOLOSOVSKI and V. V. UDovenko (J. Gen. Chem. Russ., 1934, 4, 1027—1033).—The formula $C = a + bT$, where C is the mol. sp. heat, T the temp., and a and b are consts., is shown to hold for a no. of org. liquids.

R. T.

Thermal properties of halides. IX. M.p. and b.p. and polarisation effects of manganide halides. W. FISCHER and R. GEWEHR (Z. anorg. Chem., 1935, 222, 303—311).—The m.p. of some "manganide" halides (cf. Biltz *et al.*, A., 1933, 996), viz., CrCl_2 , CrBr_2 , FeI_2 , NiCl_2 , NiBr_2 , NiI_2 , and CrCl_3 , have been determined. The variations of m.p. and b.p. of the dihalides of the series of metals from Ca

to Zn indicate that the polarisation properties of ions in which the 3d level is not completely filled differ from those of Zn^{++} with 18 outside electrons. The m.p. and b.p. are $>$ instead of being $<$ those of Zn salts. Polarisation effects are more strongly marked in the cryst. state than in the liquid or gaseous state. There is, in general, a min. of m.p. for Mn^{II} salts; the 3d level of Mn^{++} is half-filled.

M. S. B.

Properties of thallium triethyl. E. G. ROCHOW and L. M. DENNIS (J. Amer. Chem. Soc., 1935, 57, 486—487).— TlEt_3 , prepared by reaction of LiEt with TiClEt_2 , has m.p. -63.0° , b.p. 192.1° (decomp.), $d_{20}^{25} 1.957$. The v.p. has been measured and some chemical properties investigated.

E. S. H.

Chemical constant of S_2 . I. GODNEV and A. CHUDJAKOV (J. Gen. Chem. Russ., 1934, 4, 1238—1242).—The chemical const. of S_2 , calc. from v.-p. data for S_2 over FeS , is given by $j = 2.38 \pm 0.4$. The heat of formation of FeS from $\alpha\text{-Fe}$ and rhombic S at 18° is 21.5 kg.-cal.

R. T.

Thermal conductivity of carbon dioxide near its critical point. W. SELLSCHOPP (Forsch. Ingenieurw., A, 1934, 5, 162—172; Chem. Zentr., 1934, ii, 2810).—Vals. are recorded for 10—40° and 45—90 atm. Near the crit. point the thermal conductivity depends mainly on the density.

H. J. E.

Vapour pressure and m.p. of dimethyl- and trimethyl-amine. E. WIBERG and W. SUTTERLIN (Z. Elektrochem., 1935, 41, 151—153).— NHMe_3 has m.p. -93.0° , $\log p_{\text{mm}} = -1802.5/T + 1.75 \log T - 7.6045 \times 10^{-3}T + 7.1619$. NMe_3 has m.p. -117.3° , $\log p_{\text{mm}} = -1357.8/T + 1.75 \log T - 3.9161 \times 10^{-3}T + 4.6091$.

E. S. H.

System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$. III. Optical properties, X-ray patterns, and m.p. of the anhydrous sodium borates. S. S. COLE, N. W. TAYLOR, and S. R. SCHOLES. **IV. Vapour pressures of boric oxides, sodium metaborate, and sodium diborate between 1150° and 1400°.** S. S. COLE and N. W. TAYLOR (J. Amer. Ceram. Soc., 1935, 18, 79—81, 82—85).—III. Anhyd. cryst. borates with $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratios of 1:2, 1:3, and 1:4 were prepared and their physical properties are recorded.

IV. The v.p. of B_2O_3 (I), $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ (II) and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ (III) were measured by the dynamic method (dry N_2 at atm. pressure) at 50° intervals for the range 1150—1400°, assuming that the v.d. was normal. The calc. b.p. and molar entropy of vaporisation for (I), (II), and (III) are 1860°, 1434°, and 1575°, and 65,600, 96,910, and 72,410 g.-cal. per 1°, respectively. (I) and (II) volatilised unchanged but (III) dissociated at all temp., yielding a vapour Na_2O 51.6, B_2O_3 48.4%. V.-p. vals. are calc. on the dissociation of (III).

J. A. S.

Critical state and the theory of continuity. I. TRAUBE (Kolloid-Z., 1935, 70, 302—305).—Theoretical.

E. S. H.

Equation of state for helium in the intermediate region of temperature. W. JACYNA, S. DEREWJANKIN, A. OBNORSKY, and T. PARFENTIEV (Bull. Acad. Polonaise, 1934, A, 379—386).—The equation $vp = RT - ap\{10T_0 - t(1 - 11e^{bt/T})\}$ where

$a = -1.085 \times 10^{-6}$, $b = -6.85 \times 10^{-4}$, $T_0 = 273.22^\circ$ abs., and $R = 211.82$ (units: m., kg.) reproduces the observed vals. of νp for the range -150° to 500° with a max. deviation of ± 0.0003 and a mean deviation of $\pm 3 \times 10^{-5}$. J. G. A. G.

Application of De Donder's thermodynamic synthesis to the Nernst and Ettingshausen transverse effects. (MLLE.) Y. DUPONT (Bull. Acad. roy. Belg., 1935, [v], 21, 175—185).—Mathematical. N. M. B.

Liquids. T. S. WHEELER (Current Sci., 1935, 3, 347—348; cf. A., 1934, 1159).—Expressions previously deduced are modified to give density, surface tension, and internal latent heat near the m.p. Vals. are calc. for He, H₂, Ne, A, and N₂. N. M. B.

Activity coefficients of gases. R. H. NEWTON (Ind. Eng. Chem., 1935, 27, 302—306).—The fugacity, f , of a gas, is a function which if substituted for P , the pressure, enables the simple form of thermodynamic relations to be preserved for real as distinct from ideal gases. f/P , the "activity coeff.", can be calc. graphically for any gas of which the crit. consts. are known from the law of corresponding states. Where P - V - T data are available over a wide range f/P can be calc. directly without any assumptions. A series of curves showing the relation between f/P and the reduced pressure P_R for various vals. of T_R (reduced temp.) are given. For 24 gases it is shown to be a function only of P_R and T_R , some adjustments being required for H₂, He, and Ne. C. I.

Viscosity, vapour pressure, and latent heat. J. N. FRIEND (Trans. Faraday Soc., 1935, 31, 542—545).—Relations between viscosity (η), latent heat of evaporation, and b.p. are deduced from the empirical observation that $\eta n^{\frac{1}{2}}$ ($n = v.p.$) rises linearly with temp. F. L. U.

Kinematic viscosity, and a case of anomalous viscosity. E. ERDHEIM and L. STEINER (Rocz. Chem., 1934, 14, 1526—1533).—Whilst differences in surface tension may theoretically vitiate results obtained using Steiner's viscosimeter, yet in the case of oils the influence of this factor is negligible. The η of oil cooled from 100° to 20° may be 25% of that of the same oil heated from room temp. to 20° ; this difference is ascribed to super-cooling or -heating of the higher-m.p. fractions of the oil. R. T.

Variation of viscosity of paramagnetic gases in a magnetic field. M. TRAUTZ and E. FROSCHEL (Ann. Physik, 1935, [v], 22, 223—246).—Previously published work suggests that determinations of viscosity (I) by the flow method indicate that a magnetic field has no effect on (I) of paramagnetic gases. All other methods show that there is an effect. The transpiration method was used with O₂ and NO. There is no qual. difference between the effect of a magnetic and an electric field. Gases (II) and liquid crystals (III) show saturation phenomena. For O₂ this occurs between 6 and 10 k.-gauss, according to pressure. For (III) a fall of temp. increases the effect of the field. For (II) the reverse is the case, although the permeability of O₂ increases with falling temp. The effect is independent of the direction of the field. The mechanism may be that the mean

free path is decreased, following an increase in the effective cross-section, or the collision force is decreased. The effect is approx. \propto abs. temp.

A. J. M.
Changes of state of viscous systems. X. Turbulence viscosity. H. UMSTÄTTER (Kolloid.-Z., 1935, 70, 285—288; cf. this vol., 438).—Theoretical. E. S. H.

Viscose-elasticity. E. MADELUNG and S. FLÜGGE (Ann. Physik, 1935, [v], 22, 209—222).—The properties of substances intermediate between purely elastic and purely liquid substances e.g., jellies, may be described by a complex elasticity modulus, with respect to periodic motion. The question becomes one of the elastic dispersion theory. The theory is tested with glycerol and aq. solutions of gelatin. A. J. M.

Theory of viscous liquids. C. W. OSEEN (Ark. Mat. Astr. Fys., 1934, A, 24, No. 20, 23 pp.; Chem. Zentr., 1934, ii, 2966).—Theoretical. H. J. E.

Viscosity, thermal conductivity, and diffusion in gas mixtures. XXXI. Definition and corrections of the diffusion constants of gases. XXXII. Vaporisation process for the determination of diffusion constants. XXXIII. Correction of diffusion constants previously obtained by the vaporisation process. XXXIV. New determinations of diffusion constants, and final summary on the diffusion constants of gases. M. TRAUTZ and W. MÜLLER (Ann. Physik, 1935, [v], 22, 313—328, 329—332, 333—352, 353—374).—XXXI. Definitions of diffusion const. (D) are compared. If Maxwell's diffusion equation is accepted, Fick's definition is of val. for stationary diffusion processes only when the concn. decreases linearly.

XXXII. The calculation of D in the vaporisation process, the sole process yet used for the investigation of stationary diffusion processes, is discussed, and the principal errors are estimated.

XXXIII. Vals. previously obtained by the vaporisation process are corr.

XXXIV. Vals. of D for CCl₄-O₂ and CMe₂-H₂ mixtures have been obtained. It is possible with certain substances, e.g., substituted hydrocarbons, to calculate D from the mol. wt. A summary of results by various observers is given. A. J. M.

Densities of aqueous boric acid solutions and the apparent molecular volume of H₃BO₃ in them. A. VON ENDREDEY (Z. anorg. Chem., 1935, 222, 285—288).—From the d vals. at different temp. expansion coeffs. and mol. vols. have been calc. Between 0.1M and saturated solution, H₃BO₃ behaves as an almost ideal non-electrolyte. M. S. B.

Equilibria in liquid mixtures and solutions. III. B.p. and composition of the vapour phase of the systems benzyl chloride-toluene and ethylene chlorohydrin-water. V. A. KIREEV, S. I. KAPLAN, and V. N. ZLOBIN (J. Appl. Chem. Russ., 1934, 7, 1333—1338).—The b.p./760 mm. of CH₂PhCl-PhMe, of CH₂Cl-CH₂-OH (I)-H₂O, and of CHMeCl-CH₂-OH (II)-H₂O mixtures, and the composition of the vapour phase, have been determined. The azeotropic mixture of (I) and H₂O boils at 97.8° ,

and contains 43.5% of (I), whilst that of (II) and H_2O boils at $96^\circ/743$ mm., and contains 49.1% of (II). R. T.

V.p. of binary solutions of ethyl alcohol and cyclohexane at 25° . E. R. WASHBURN and B. H. HANDORF (J. Amer. Chem. Soc., 1935, 57, 441—443).—V.p. data are recorded. Deviations from ideal behaviour are discussed and explained on the basis of the difference in polarity and internal pressure of the two components. E. S. H.

Influence of temperature on the solid solubility of (A) aluminium in magnesium, (B) the compound $MgZn_2$ in aluminium. P. J. SALDAU and M. I. ZAMOTORIN (Ann. Inst. Anal. Phys. Chim., 1935, 7, 21—30, 31—38).—(A) The solid solubility, S , of Al in Mg is 6.08% from 20° to 300° , 10.9% at 400° , and 12.6% at 436° (eutectic).

(B) S of $MgZn_2$ in Al rises from 1.58% at 15° to 3.57% at 300° , 13.99% at 400° , 24.70% at 460° , and 30% at 475° (eutectic). R. T.

Solid solubility of copper in magnesium. N. I. STEPANOV and I. I. KORNILOV (Ann. Inst. Anal. Phys. Chim., 1935, 7, 89—98).—Conductivity, temp. coeff. of conductivity, and hardness data indicate that the solubility of Cu in Mg rises from 0.2% at 300° to 0.3% at 400° , and to 0.55% at 480° . R. T.

Limits of the α -phase in the system copper-cadmium. S. A. POGODIN, V. I. MICHEEVA, and G. A. KAGAN (Ann. Inst. Anal. Phys. Chim., 1935, 7, 39—47).—The solid solubility of Cd in Cu rises from 1.0% at room temp. to 1.2% at 250° , 1.6% at 400° , 2.1% at 475° , 2.5% at 525° , and 2.8% at 550° . The limits of the α -phase have been determined. R. T.

Phase diagram of alloys of silver with aluminium, for the range 0—10% of aluminium. N. V. AGEEV and D. N. SCHOJCHET (Ann. Inst. Anal. Phys. Chim., 1935, 7, 59—73).—The limits and the structure of the α - and γ -phases are derived from microstructure, X-ray analysis, and hardness data. The β -phase decomposes at 400° to yield a mixture of α - and γ -phases. R. T.

Diagram of state of the system silver-indium. F. WEIBKE and H. EGGERS (Z. anorg. Chem., 1935, 222, 145—160).—Temp.-composition data and the diagram of state are given. Five solid phases (besides Ag and In) have been recognised thermally, microscopically, and by X-rays. The only eutectic is between In and the ϕ -phase (probably $AgIn_3$) at 140° . Properties of the alloys are described. F. L. U.

The system nickel-manganese. S. VALENTINER and G. BECKER (Z. Physik, 1935, 93, 795—803).—X-Ray, magnetic, and electrical measurements show the formation of the strongly paramagnetic alloy Ni_3Mn ; electrical conductivity and X-ray photographs show the presence of $NiMn$. A. B. D. C.

Palladium-manganese alloys. A. T. GRIGORIEV (Ann. Inst. Anal. Phys. Chim., 1935, 7, 75—87).—Pd-Mn alloys consist of a series of solid solutions, from which PdMn separates on cooling below 1150° . The transition points observed at 730 — 797° and 1040 — 1089° are ascribed to conversion of β - into α - and of γ - into β -Mn, respectively. R. T.

Physico-chemical investigation of (A) the γ -phase of thallium-bismuth alloys, (B) alloys of thallium, bismuth, and lead, (C) alloys of bismuth, thallium, and cadmium. N. S. KURNAKOV and A. V. AGEEVA (Ann. Inst. Anal. Phys. Chim., 1935, 7, 49—58, 99—121, 123—133).—(A) [With N. V. AGEEV.] The γ -phase (I) contains 55—65 at.-% of Bi, and is not a definite compound; its space lattice corresponds with that of Bi. (I) exhibits superconductivity at 6.4° .

(B) Thermal, conductivity, and microstructure data suggest the presence of (I) in the ternary alloy, in the form of a solid solution containing up to 20 at.-% of Pb.

(C) The presence of (I) is established as above in the ternary alloy; Cd is insol. in (I). R. T.

Magnetism and the atomic state of metallic solid solutions. E. VOGT (Z. Metallk., 1935, 27, 40—43).—From a review of recent work on the magnetic susceptibility of solid solution alloys of Cu, Ag, and Au with Mn, Cr, and metals of group VIII of the periodic system it is inferred that the ionisation and quantum state of any kind of atom in an alloy is not const., but depends to a considerable extent on the nature of the other metal. A. R. P.

Thermal changes occurring during transformations in a solid solution. C. SYKES (Proc. Roy. Soc., 1935, A, 148, 422—446).—A modified cooling curve method is described which is more trustworthy than the standard methods when applied to transformations consisting of at. rearrangement in a homogeneous solid solution. A sp. heat-temp. curve is needed to determine the heat involved in such transformations, and a new experimental method for obtaining such curves is described. Transformations occurring in β -brass and Fe-Al alloys have been studied by means of these two methods. L. L. B.

Electrical conductivity of ternary solid solutions. K. YAMAGUCHI and K. NAKAMURA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 73—75).—The connexion between electrical conductivity and composition has been determined for the pairs: Cu_5Zn_8 — $NiZn_3$; ϵ of $CuZn$ — ϵ of $AgZn$; Cu_5Zn_8 — $Cu_{31}Sn_8$ (δ); $CuZn$ — $NiZn$; Cu_5Zn_8 — γ of $AgZn$. An approx. linear relation between wt. composition and sp. resistance is found except in $CuZn$ — $NiZn$. W. R. A.

Determination of the solubility of silver chloride by an electrometric titration method. A. S. BROWN and D. A. MACINNES (J. Amer. Chem. Soc., 1935, 57, 459—465).—Electrometric titration technique, which reduces to a min. the uncertainty due to liquid junction potentials, is described. The data obtained are discussed theoretically. Determinations of the solubility of $AgCl$ yield the val. 1.314×10^{-5} . E. S. H.

Solubility of copper sulphide in alkali polysulphide solutions. R. HÖLTJE and J. BECKERT (Z. anorg. Chem., 1935, 222, 240—244).— CuS is practically insol. in Na_2S , but its solubility in $Na_2S_{1.5}$ is too great to be neglected in analytical determinations. It is more sol. in K_2S_x than in Na_2S_x , and in each case the solubility increases rapidly with increase

in S content of the polysulphide, and also with increasing concn. of polysulphide and rise of temp.

M. S. B.

Amphoteric behaviour of metal hydroxides.

IX. Solubility of barium hydroxide in sodium hydroxide solutions. R. SCHOLDER and R. PATSCH (Z. anorg. Chem., 1935, 222, 135—144; cf. this vol., 35).—The solubility of BaO in aq. NaOH at 20° reaches a min. at about 6*N*, and thereafter increases to a max. at 12*N*. This behaviour is attributed to a weakly amphoteric character. The solid phases in equilibrium with a saturated solution in 12—13*N*. and 14—17*N*-NaOH, respectively, are the hydrates BaO,5H₂O and BaO,2.5H₂O. The hydrate BaO,4H₂O, reported by Schreinemakers, was not observed.

F. L. U.

Precipitation from supersaturated solutions of strontium sulphate. A. N. CAMPBELL and E. J. R. COOK (J. Amer. Chem. Soc., 1935, 57, 387—390).—The equiv. conductivity of SrCl₂ at infinite dilution and 30° has been determined and the ionic conductivity of Sr⁺⁺ calc. Solutions of SrSO₄ (>50% supersaturated), produced by mixing aq. K₂SO₄ and SrCl₂, crystallise spontaneously, but the conductivity does not fall to normal. The solutions remain permanently supersaturated (30—40%) in presence of large particles of SrSO₄.

E. S. H.

Solubilities of the double magnesium nitrates of the cerium group. J. N. FRIEND and (in part) W. N. WHEAT (J.C.S., 1935, 356—359).—The solubility curves of 3Mg(NO₃)₂·2Pr(NO₃)₃·24H₂O and of 3Mg(NO₃)₂·2Ce(NO₃)₃·24H₂O are very similar and lie between those of the more sol. 3Mg(NO₃)₂·2Nd(NO₃)₃·24H₂O and the less sol. 3Mg(NO₃)₂·2La(NO₃)₃·24H₂O. Addition of the Ce salt may assist separation of the pure Pr salt during fractional crystallisation of rare-earth salts.

J. W. S.

Radioactive indicators. I. Determination of the solubility of lead salicylaldoxime with thorium-B as radioactive indicator. M. ISHIBASHI and H. KISHI (J. Chem. Soc. Japan, 1934, 55, 1070—1073).—Using Th-B as indicator the measured solubility of salicylaldoxime in H₂O at 25° is 1.37 × 10⁻³ g. per litre.

CH. ABS. (e)

Physico-chemical properties of lactose. VI. Solubility of lactose in salt solutions; isolation of a compound of lactose and calcium chloride. B. L. HERRINGTON (J. Dairy Sci., 1934, 17, 805—814; cf. this vol., 200).—The solubility of lactose (I) in solutions of CaCl₂ or Ca(NO₃)₂ is > in H₂O and increases with the salt concn. This phenomenon is related to anomalous rotation vals. observed. A compound of α-lactose (1 mol.) with CaCl₂·6H₂O has been isolated. Conc. solutions of hydrated (I) in aq. CaCl₂ are supersaturated with respect to the above compound. The stability of supersaturated solutions of (I) in ice cream and milk powders is considered.

A. G. P.

Solubility of morphine in various solvents. H. BAGGESGAARD-RASMUSSEN and F. REIMERS (Arch. Pharm., 1935, 273, 129—139).—The solubility of morphine (I) in H₂O, in aq. buffers (II), and in mixtures of H₂O and MeOH, H₂O and EtOH, CHCl₃ and Pr^oOH,

and CHCl₃ and EtOH, has been determined. From the solubility in (II) the solubility products and dissociation consts. of (I) regarded as an acid and a base, and the isoelectric point have been calc. The vals. agree with those of Kolthoff (A., 1926, 125). The solubility in solvents containing CHCl₃ depends on the purity of the CHCl₃. Ordinary CHCl₃ and Et₂O are ill-defined solvents and give varying results.

H. G. M.

Distribution of (A) isovaleric acid, (B) propionic acid, (C) butyric and isobutyric acid between two contiguous liquid phases. N. A. DE KOLOSOVSKI, F. S. KULIKOV, and A. BEKTUROV (J. Gen. Chem. Russ., 1934, 4, 1153—1156, 1224—1230, 1231—1237).—(A) Data are given for the systems Bu^oCO₂H-H₂O-xylene (I), CHCl₃, PhNO₂, and *iso*-C₅H₁₁·OH (II), at 25°.

(B) Data are given for the systems EtCO₂H-H₂O-(I), *cis-trans*-decahydronaphthalene, CHCl₃, CCl₄, EtBr, PhNO₂, (II), and Et₂O, at 25°.

(C) Data are recorded for the systems Pr^oCO₂H-H₂O-CCl₄, PhNO₂, and *n*-C₅H₁₁·OH (III), and also for Pr^oCO₂H-H₂O-CCl₄, PhNO₂, (II), and (III).

R. T.

Distribution of saturated organic acids between two liquid phases. N. A. DE KOLOSOVSKI, F. S. KULIKOV, and A. BEKTUROV (Bull. Soc. chim., 1935, [v] 2, 460—479; cf. A., 1934, 955; this vol., 159).—Distribution coeffs. (C₁/C₂) are given for HCO₂H in H₂O-PhNO₂, *o*-nitrotoluene (I); AcOH in H₂O-PhNO₂, -(I); EtCO₂H in H₂O-(I), -Bu^oOH; PrCO₂H in H₂O-(I), -Bu^oOH; Bu^oCO₂H in H₂O-CCl₄, -EtBr, -(I), -Bu^oOH (see also preceding abstract); BzOH in H₂O-Bu^oOH; CH₃Ph·CO₂H in H₂O-PhMe, -PhNO₂, *iso*-C₅H₁₁·OH (II); α-lactic acid in H₂O-(II); CH₂(CO₂H)₂ in H₂O-Bu^oOH, -C₅H₁₁·OH, -(II); (CH₂·CO₂H)₂ in H₂O-(II); CH₂(CO₂Me)₂ in H₂O-C₅H₁₁·OH, -Et₂O; tartaric acid in H₂O-(II); citric acid in H₂O-(II). C₁/C₂ decreases from ∞ at zero total concn.

In some cases C₁/C₂ becomes < 1, and finally increases with C₁+C₂. If the solvents become completely miscible at high C₁+C₂, C₁/C₂ tends to 1, otherwise tends to a limiting val. which is the same for a given acid in H₂O and a series of solvents. A method for the exact determination of the C₁+C₂ which gives a min. val. of C₁/C₂ is described.

R. S.

Distribution of small amounts of substances between liquid and solid crystalline phases. II. Distribution of barium nitrate between saturated aqueous solution and strontium nitrate crystals. A. POLESITSKI (Z. physikal. Chem., 1935, 172, 300—303; cf. A., 1934, 358).—The simple distribution law is valid at 35° and 100°. The distribution ratio increases in favour of the solid phase with rise in temp., but the change is not commensurable with the influence of temp. on the relative solubilities of the components.

R. C.

Iron and nitrogen. A. SIEVERTS and G. ZAPP (Z. physikal. Chem., 1935, 172, 314—315).—The solubility of N₂ under 1 atm. in Fe at 1200—1540° has been measured.

R. C.

Sorption of sulphur dioxide by active charcoal. V. Mechanism of the sorption. K. ARII (Bull.

Inst. Phys. Chem. Res. Japan, 1935, **14**, 99—114; cf. this vol., 159).—Adsorption and absorption are involved, in agreement with McBain (A., 1910, ii, 21). Experiments are described which afford clear evidence of diffusion of SO_2 within the particles of C.

W. R. A.

Sorption of vapours by active silica. L. M. PIDGEON (Canad. J. Res., 1935, **12**, 41—56).—Sorption isotherms of active SiO_2 , prepared by the action of acids on serpentine, for H_2O , C_6H_6 , and EtOH have been determined. The results show that the active SiO_2 is inferior to SiO_2 gel, but superior to commercial Al_2O_3 .

E. S. H.

Kinetics of sorption processes of hydrogen on iron. N. M. MOROZOV (Trans. Faraday Soc., 1935, **31**, 659—668).—By measuring separately the rapid and slow sorption of H_2 on Fe in the range -190° to 400° it is shown that the total sorption process is composed of van der Waals adsorption, activated adsorption (I), and activated dissolution or diffusion (II). The activation energy of (I) is 20 and of (II) 8 kg.-cal. per mol. At 300 — 400° (I) is instantaneous and completely reversible.

F. L. U.

Theory of adsorption. S. MIYAMOTO (Kolloid-Z., 1935, **70**, 275—277).—The theory is based on the assumptions that (a) mols. can escape from the adsorbed layer only when their vibration energies perpendicular to the surface are $>$ a limiting val., and (b) mols. can condense on the surface only when they strike it with a velocity the vertical component of which is $>$ a limiting val.

E. S. H.

Theory of electrical double layers in adsorbed films. R. W. GURNEY (Physical Rev., 1935, [ii], 47, 479—482).—The nature of an adsorbed layer, and the factors governing the sign and magnitude of the electrical double layer, are discussed in terms of quantum mechanics.

N. M. B.

Steric factor in the equation of activated adsorption. O. I. LEIPUNSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 30—33).—A steric factor comes into play in diffusion from the surface into the lattice.

A. B. D. C.

Physico-chemical analysis of protein molecules adsorbed at the interface solid-liquid. G. LINDAU and R. RHODUS (Z. physikal. Chem., 1935, **172**, 321—347).—Langmuir's isotherm is valid for the adsorption of gelatin and ovalbumin (I) from aq. solution on quartz, and the amount adsorbed at saturation corresponds with a unimol. layer. Up to this point adsorption is irreversible; whether there is further adsorption at higher concns. is uncertain, but if so it is reversible. The ζ -potential of quartz powder with adsorbed (I) in buffer solutions of p_H 4.8, as deduced from electrophoretic measurements, falls linearly with increasing adsorption and reaches zero at saturation. From ζ -potential determinations at p_H 3.3 it appears that the space demand of an adsorbed (I) mol. at this p_H is three or four times that at p_H 4.8, and from a surface saturated at p_H 4.8 about half the (I) can be washed away by a buffer of p_H 3. Measurements of speed of wetting indicate that when the quartz is about half saturated with (I) its surface changes quickly from hydrophilic to hydrophobic. At this

point the surface of the adsorbent is apparently just covered with a coherent layer of adsorbate in which are patches of bare surface. The charge, size, and general behaviour of adsorbed (I) are the same as for dissolved (I); owing to its size, the mol. projects so far from the adsorbent surface that the outer part is out of range of the adsorbent forces. A theory of the connexion between vol. and p_H for proteins is discussed.

R. C.

Diffusion of mercury on tin. T. ALTY and A. R. CLARK (Trans. Faraday Soc., 1935, **31**, 648—659).—Surface diffusion of Hg on Sn is much more rapid than vol. diffusion, and conforms to an ordinary diffusion equation. It is faster in H_2O and slower in light petroleum than in air. The energy of activation of the mobile atoms on pure Sn is calc. from the temp. coeff. of diffusion to be 1920 g.-cal. per g.-atom. The diffusion of Hg on an amalgam containing 8 at.-% of Hg has a negative temp. coeff.

F. L. U.

Mechanism of flotation with water-insoluble reagents. Role of non-polar phase in the adsorption of the reagent on the particles of the suspension. Z. V. VOLKOVA, N. N. SERB-SERBINA, and A. V. SAPOROSHEZ (Kolloid-Z., 1935, **70**, 323—328).—In the 4-phase system H_2O -non-polar liquid (containing a H_2O -insol. flotation reagent)-mineral powder-air it is shown that the optimal flotation conditions are attained by correct adjustment of the amount of the non-polar liquid and the amount of the flotation reagent.

E. S. H.

Permeability of Cellophane films to dry or moist air. J. J. TRILLAT and M. MATRICON (J. Chim. phys., 1935, **32**, 101—115).—Ordinary Cellophane is almost impermeable to dry air. A membrane 0.02 mm. thick lets through air saturated with H_2O at the rate of 3.15×10^{-10} g. per sec. (measured dry) per sq. cm. at 20° and 1 atm. pressure difference. The wt. of H_2O vapour passing under the same conditions is 7.3×10^{-6} g.

F. L. U.

Electrical factors influencing the rate of filtration of aqueous electrolyte solutions through Cellophane membranes. H. L. WHITE, B. MONAGHAN, and F. URBAN (J. Gen. Physiol., 1935, **18**, 515—521).—The filtration rate (I) of ThCl_4 solutions through Cellophane membranes rises above (I) for H_2O with increasing $[\text{ThCl}_4]$, passes through a max. at the isoelectric point, and then falls below (I) for H_2O , passing through a min. There is an inverse relation between (I) and the ζ -potential.

F. A. A.

Comparison of electrophoretic velocities of Cellophane and collodion suspensions with electro-osmotic velocities through membranes of the same materials. B. MONAGHAN, H. L. WHITE, and F. URBAN (J. Gen. Physiol., 1935, **18**, 523—530).—Electrophoretic ζ -potentials of small particles of Cellophane (I) and collodion (II), and electro-osmotic velocities through membranes of (I) and (II), have been measured in ThCl_4 solutions. The $[\text{ThCl}_4]$ at the isoelectric point is greater for electro-osmosis than for electrophoresis; this may be due to the pore size being too small to allow complete formation of the electrical double layer.

Theoretical considerations on the methods of micro-cataphoresis. G. E. VAN GILS (Chem. Weekblad, 1935, 32, 173—176).—The mathematics of the motions of particles in pure liquids due to cataphoresis and electroendosmosis, in various types of cell are discussed. S. C.

Physico-chemical connexion between, and the occurrence of, osmotic pressure and vapour pressure lowering. K. FREDENHAGEN (Physikal. Z., 1935, 36, 194—208).—Theories of osmotic pressure (I) and its connexion with lowering of v.p. are reviewed. It is suggested that (I) must have its origin in an interaction between solvent and solute whereby some of the solvent mols. are rendered inactive with regard to v.p. Such an appropriation of solvent mols. takes place in stoichiometric proportions, and where this does not occur, deviations from the usual laws of (I) are found. This gives a satisfactory basis for a kinetic and thermodynamic theory of (I).

A. J. M.

Behaviour of compounds of high mol. wt. in solution. I. Vapour pressure lowering and osmotic pressure. K. H. MEYER and R. LÜHDEMANN (Helv. Chim. Acta, 1935, 18, 307—332).—The abnormally high osmotic pressures (P) shown by conc. solutions of high mol. wt. are not adequately accounted for by van der Waals forces between solute and solvent, since they are also observed when the heat of dilution is zero or negative. It is postulated that a mol. large enough to be flexible possesses an intramol. Brownian movement, and the kinetic energy associated with it is $> 1.5RT/N$, so that the P of the solution is $>$ that corresponding with the no. of mols. calc. from the chemical formula. The theory has been examined by calculating P of solutions of oleyl oleate (I) and of dioleoyl thapsate (II) in cyclohexane, n -hexane, CHCl_3 , and CCl_4 from measurements of the lowering of v.p. For Raoult's law to be applicable to these solutions the effect of intermol. forces must be eliminated. This is done by correcting the mol. fraction (N_1) of the solvent by the factor $e^{-Lc/RT}$, in which L is the relative heat content of the solvent and c is an empirical const. L was determined from the temp. coeff. of the relative lowering of v.p. The calc. mol. wt. of (I) varies from 466 for $N_1=0.996$ to 245 for $N_1=0.125$, and of (II) from 695 for $N_1=0.993$ to 240 for $N_1=0.125$, the respective formula wts. being 532 and 787. Thus at high concns. the apparent mol. wt. tends to a limit corresponding with a chain length of 17 CH_2 groups, and does not depend on the formula wt. of the compound. F. L. U.

Regularities in the volume changes of solutions on neutralisation. I. I. SASLAVSKI and V. I. SACHAROV (J. Gen. Chem. Russ., 1934, 4, 1199—1203).—Vol. changes are associated with disappearance or formation of hydrated ions, or with change in the valency of existing ions; thus, in the titration of strong acids by strong bases, the total no. of ions diminishes, resulting in increase in vol. In titration of H_3PO_4 , formation of KH_2PO_4 leads to increase in vol., of K_2HPO_4 to restitution of the original vol., and of K_3PO_4 to diminution in vol., owing to formation of tervalent PO_4^{3-} ; analogous results are obtained with carbonates. R. T.

Tonometry of saline solutions. J. PERREU (Compt. rend., 1935, 200, 1030—1032).—The v.p. of aq. solutions of Na_2SO_4 and Na_2CO_3 have been determined by the differential tensimeter method. The results confirm previous relations (cf. A., 1934, 249). J. W. S.

F.p. of anti-coagulant salt solutions. D. I. HITCHCOCK and R. B. DOUGAN (J. Gen. Physiol., 1935, 18, 485—490).—F.p. data are given for NaF, Na oxalate, and Na citrate which may be used to prepare solutions isotonic with biological fluids of known f.p. F. A. A.

Structure and composition of metal ions in aqueous solution. Aquo-complexes and hydration of metal ions. H. BRINTZINGER and C. RATANARAT (Z. anorg. Chem., 1935, 222, 113—125; cf. this vol., 181).—The ionic wt. of 18 metal ions has been determined by measuring their diffusion coeff. against that of $\text{S}_2\text{O}_3^{2-}$. Independent transport experiments enable the total hydration thus found to be differentiated into chemically bound (aquo-complexes) and electrostatically bound H_2O . The results obtained vary from 0 to 4 for K^+ to 18 to 41 for Fe^{3+} . The total hydration is a linear function of the ionic potential. F. L. U.

Concentration of hydrions in aqueous solutions of cobaltammines and their absorption spectra. T. UÉMURA and H. SUEDA (Bull. Chem. Soc. Japan, 1935, 10, 50—73).—Absorption and p_H (using a Sb electrode to prevent reduction by H) measurements have been made on dil. solutions of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ (I), $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_4\text{OH}]\text{Cl}_2$ (II), $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ (III), $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ (IV), $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]\text{Cl}$ (V), $[\text{Co}_2(\text{NH}_3)_8(\text{OH})_2]\text{Cl}_4$ (VI), $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2(\text{SO}_4)_3]$ (VII), $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{SO}_4$ (VIII), and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]\text{SO}_4$ (IX) for 2500—4500 Å. Except where decomp. occurs, variation in the extinction coeffs. with p_H is small. For $p_H > 7$ (I) \rightarrow (II) and (V) \rightarrow (VI). (VII) \rightarrow (IX) for $p_H > 6.5$ —8, whereas (III) does not give (V), and (IV) and (VIII) do not exchange Cl for OH in alkaline solution. R. S. B.

Viscosity and plasticity of disperse systems. II. Plastic properties of dough by the rotating-cylinder method. M. P. VOLAROVITSCH and K. I. SAMARINA (Kolloid-Z., 1935, 70, 280—285).—Plasticity consts. (I) have been determined by the rotating-cylinder method. Relations between (I), sorption of H_2O , and ability to bind H_2O have been established. E. S. H.

Plastometric investigations on substances of high consistency. III. Determination and evaluation of velocity distribution curves. G. UNGAR (Kolloid-Z., 1935, 70, 277—280; cf. A., 1934, 1194).—Apparatus and technique for determining the velocity distribution in plastic substances are described. E. S. H.

Chromatic emulsions. I. Preparation of stable chromatic emulsions of cod-liver oil. II. Theory of their stability from the viewpoint of viscosity and surface tension. C. S. NARWANI (Kolloid-Z., 1935, 70, 297—302).—Stable, chromatic

emulsions of (a) cod-liver oil (I) and amyl acetate (II) (10:1) with 1.1% gelatin-glycerol, and (b) (I) and (II) (100:1) with 0.5% gelatin-glycerol containing 18% of sucrose have been prepared. The influence of gelatin and glycerol on the interfacial tension between (I) and (II) and on the stability of the emulsion has been investigated. The influence of the viscosity of the disperse phase on stability is discussed. E. S. H.

(A) Nature of hygroscopicity of liquid dielectrics. (B) Influence of the form of distribution of water on electrical stability of liquid dielectrics. A. M. LAZAREV (J. Tech. Phys. U.S.S.R., 1934, 5, 973—987, 988—995).—(A) The tendency of H_2O to dissolve or emulsify in the presence of surface-active matter in transformer oils, tetralin, and hexane is examined. The stabilisation of emulsions is in accordance with the Langmuir-Harkins-Gibbs mechanism. For a given oil- H_2O composition, with low concn. of naphthenic acid (I) H_2O is emulsified, but with higher concn. of (I) it is in mol. solution.

(B) Effects of dissolved and emulsified H_2O are compared. CH. ABS. (p)

Sols of emeraldine. I. Chemical nature, preparation, and properties. V. PTSCHELIN (Kolloid-Z., 1935, 70, 306—311).—A positively-charged, green sol containing emeraldine is formed by oxidation of $NH_2Ph.HCl$ by $K_2Cr_2O_7$ in presence of gelatin. Dialysis, electrodialysis, or addition of $NaOH$ produces a blue sol, which is due to the emeraldine base and can be converted into the green sol by addition of acid. The green-blue change is accompanied by decrease of dispersity and leads ultimately to coagulation.

E. S. H.

Diffusion coefficients of dye solutions and their interpretation. C. ROBINSON (Proc. Roy. Soc., 1935, A, 148, 681—695).—The diffusion coeffs. (D) of pure dyes, measured by a modification of the Nistler microdiffusion apparatus (A., 1929, 962), are in all cases very high, in accordance with the theoretical predictions of Hartley and Robinson (A., 1932, 18). The particle size cannot be derived from the val. of D for the pure dye, but it has been found that in the presence of excess of electrolytes the particle diffuses according to the Stokes-Einstein equation. The fall in D with increasing quantity of electrolyte is at first rapid, but, in the case of dyes not easily flocculated by electrolytes, it reaches a const. val. at higher concns., and from this the particle size may be calc. Measurements indicate that Bordeaux-extra is very nearly in true solution, but that the particles of "meta-" benzopurpurin contain > 10 anions, in agreement with osmotic pressure data. The diffusion results cannot be correlated with the mobility measurements of Robinson and Moilliet (A., 1934, 362). L. L. B.

Influence of acidity of agar on the Liesegang rings of lead chromate and lead iodide. H. M. MAPARA (J. Indian Chem. Soc., 1935, 12, 48—50; cf. A., 1934, 598).—The optimum p_H range for the formation of the rings, and the variation of the thickness and spacing with p_H , have been determined.

R. S.

Influence of light on periodic precipitations in gelatinous media. Precipitation of silver

chromates, phosphate, and arsenate. E. DUCHEMIN (Compt. rend., 1935, 200, 927—928).—The stratified ppt. obtained when $AgNO_3$ solution is dropped on a gelatin gel containing $K_2Cr_2O_7$ is modified by previous exposure of the gel to light, the rings becoming finer and closer. Gels containing $PO_4^{'''}$ or $AsO_4^{'''}$ yield discontinuous ppts. with $AgNO_3$ in darkness, but after the gel has been exposed to light. $AgNO_3$ gives a continuous ppt. J. W. S.

Effect of colloids on crystallisation and formation of calculi. A. DE KUTHY (J. Chim. phys., 1935, 32, 126—135).—Crystallisation of PbI_2 from supersaturated (N/75) aq. solutions is just prevented by the following substances at the % concn. indicated: Na deoxycholate 0.010, Na taurocholate 0.012, Na glycocholate 0.012, dextrin 0.025, agar 0.040, gelatin 0.080, ovalbumin 0.5. The effect of smaller concns. is to suppress growth in successive directions until finally it is suppressed in all. The non-pptn. of cholesterol from bile and of uric acid from urine is attributed to similar protective action. F. L. U.

Influence of uni- and tri-dimensional micelle growth on some properties of certain colloids. R. HOUWINK (Chem. Weekblad, 1935, 32, 158—164).—Theoretical. Differences in physical properties of various high-mol. compounds and of their solutions are correlated with the occurrence of unidimensional long chains (e.g., in polystyrene) or of tridimensional cross-linking (e.g., in Bakelite resins). Raw rubber is regarded as a straight-chain polymeride, and the possibility of the occurrence of cross-linking by means of S bridges during vulcanisation is discussed.

D. R. D.

Action of iron, aluminium, and chromium salts on gelatin. S. J. SOKOLOV and R. A. DULITZKAJA (Kolloid-Z., 1935, 70, 314—320).—Measurements of conductivity, p_H , η , and electrophoresis show that (a) the amount of salt bound increases with its concn., reaching a max. at 100 milliequiv. of salt per 100 g. of gelatin; (b) with increasing salt concn. η and electrophoretic velocity pass through a max. and then fall; (c) H^+ is bound in addition to the metal ions; (d) in gelatin sols containing $Al^{'''}$ or $Fe^{'''}$ the p_H increases slightly with time, whereas in those containing $Cr^{'''}$ the p_H falls rapidly. The mechanism of these changes is discussed. E. S. H.

Colloid chemical-topochemical relations in photographic images. W. KUHN and G. ERDÖS (Kolloid-Z., 1935, 70, 261—267).—A discussion of the known phenomena in terms of photodissolution and photo-coagulation (cf. following abstract).

H

Optically produced anisotropy of thixotropic gels. W. KUHN and G. ERDÖS (Kolloid-Z., 1935, 70, 241—261).—Dichroism is induced in thin films (0.01 mm.) of 5% thixotropic cotton-yellow solutions by irradiation with linearly polarised light. The effect remains after the light source is removed. Observations with the polarising microscope show that the effect depends on a definite, diffuse fibrillar structure of the particles. The particles arrange themselves parallel to the electric vector of the incident light; a saturation val. is obtained with a radiation intensity of 4500 ergs per sq. cm. per sec. after about 30 min. The

influence of λ has been studied. The dichroic effect has the same sign in the visible and ultra-violet regions, and the sign can be reversed by alternately irradiating with horizontally and vertically polarised light. Mechanical orientation of the particles by the electric field of light is excluded. The effect is ascribed to photodissolution of mols. in the surface of favourably oriented particles through absorption of light. E. S. H.

Elimination of cations from swollen gelatin. Effect of cholesterol and lecithin on swelling. W. VON MORACZEWSKI and T. SADOWSKI (Biochem. Z., 1935, 276, 388—397; cf. A., 1933, 568; Bigwood, A., 1930, 1250).—The distribution (I) of ions between gelatin (II) and an aq. medium (III) depends on $[H^+]$, the differences between the ion content of (II) and that of (III) being greater with cations (Ca^{++} , K^+ , Na^+) than with anions (Cl^-). Interchange of ions between (II) and (III) occurs if the ion content of (III) or its p_H is changed. The degree (IV) of swelling of (II) is not affected by addition of cholesterol (V) or lecithin (VI) to (III), but (IV) is altered by dissolving or suspending (V) (increase) or (VI) (decrease) in (II). Addition of (V) has no effect on (I) or on the distribution of Cl between (II) and (III). The Cl content of (II) is not increased by passing CO_2 through (III). The whole of the H_2O bound to (II) during swelling cannot be removed by lowering the temp.; the residual amount of H_2O always exceeds that which is absorbed at the lower temp. W. McC.

Contractions accompanying the swelling of gelatin. L. FRIEDMAN and (Miss) B. BROWN (J. Amer. Chem. Soc., 1935, 57, 508—510).—The contraction in total vol. when 85% dry gelatin swells in H_2O at 10° is a min. at the isoelectric point and p_H 2.2 and a max. at p_H 3.5 and 8. The contraction is attributed to (a) hydration, (b) increase in the electric field around the micelles as the p_H departs from the isoelectric point, and (c) decrease in vol. of the H_2O in the small gelatin pores caused by high internal pressures. R. S. C.

Viscosity of very dilute solutions of cellulose nitrate in ether-alcohol. J. GREVY (Compt. rend., 1935, 299, 742—744).—For a solution containing 0.3 g. of cellulose nitrate (I) per litre the sp. viscosity changes only very slightly when the proportion of EtOH is increased from 18 to 90%. Deviations from constancy become very large as the concn. of (I) increases and reach a max. for 5 g. per litre. The sp. viscosity of the solutions falls on keeping. The rate of fall is greatest with 60% EtOH. For higher concn. of (I) the max. rate of fall occurs at lower $[EtOH]$. M. S. B.

Viscosity of gluten dispersed in alkali, acid, and neutral solvents. R. C. ROSE and W. H. COOK (Canad. J. Res., 1935, 12, 63—81).—The viscosity of gluten (I) dispersed in aq. $CO(NH_2)_2$ or Na salicylate is $>$ in aq. NaOH or AcOH, and shows a greater increase with increasing concn. In aq. $CO(NH_2)_2$, η is independent of $[H^+]$ between 6.1 and 9.2; the system is stable within this region. In NaOH, $CO(NH_2)_2$, and Na salicylate solutions η decreases at first, whilst in dispersions of (I) in aq. AcOH η decreases continuously. The character of the ppt. obtained by salting out indicates that the neutral solutions alter the (I) $<$ acid or alkali. (I) obtained

from flours of different protein quality has the same η when dispersed in alkali or acid, but in the neutral solutions have markedly different η , which can be partly correlated with the quality of the (I).

E. S. H.

Chemical reactions during the formation of starch paste. V. V. LEPESCHKIN (Kolloid-Z., 1935, 70, 312—313).—The formation of starch paste involves (a) hydration of polysaccharides and (b) swelling of the products (amylopectin and amylose) in H_2O . Paste formation does not occur at a definite temp., but it is possible to determine the time required for the formation of paste at a given temp. E. S. H.

Bikerman hypothesis concerning swelling pressure. E. M. BRUINS (Rec. trav. chim., 1935, 54, 317—321; cf. A., 1931, 38).—Theoretical. The force function implied by Bikerman's theory has been calc. Although the theory is not strictly true, good agreement is obtained for graphitic acid ($< 90\%$), and calc. and observed vals. of max. extension of the network agree. R. S. B.

Upward propagation of imbibition. C. E. GUYE (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 162—165).—An expression for the ascent of a liquid in a vertical absorbent strip is derived. F. L. U.

Propagation of imbibition. II. C. E. GUYE (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 183—184).—A theoretical comparison of imbibition with diffusion. C. W. G.

Thermodynamics of imbibition and amalgamation. H. SAINI (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 189—195).—Theoretical. C. W. G.

Birefringence of dried colloidal drops. A. T. BERNARD (Compt. rend. Soc. Biol., 1935, 118, 609—611). A. L.

Chemical constitution and the dissociation constants of monocarboxylic acids. III. J. F. J. DIPPY, F. R. WILLIAMS, and (in part) R. H. LEWIS. IV. J. F. J. DIPPY, H. B. WATSON, and F. R. WILLIAMS (J.C.S., 1935, 343—346, 346—350; cf. A., 1934, 364; this vol., 165).—III. Conductivity measurements lead to the following $K \times 10^5$ vals. for substituted benzoic acids: *p*-fluoro-, 7.22, *o*-, 11.4, *m*- 14.8, and *p*-chloro- 10.55, *o*- 14.0, and *p*-bromo- 10.7. The acids are in reverse order relative to the halogenoacetic acids. The results for the chlorobenzoic acids are in partial agreement with those of Saxton and Meier (A., 1934, 1173). K_e for *p*- $NH_2 \cdot C_6H_4 \cdot CO_2H$ decreases with diminishing concn. to a min., followed by a gradual increase.

IV. Data recorded previously are discussed in relation to side-chain activity. The behaviour of nitro- and alkoxy-substituted acids is attributed to the inductive effect of the substituent and to quantum-mechanical resonance (A., 1933, 1151). The effect of the halogen attached to the C_6H_5 nucleus is interpreted by supposing the halogen to give rise to a reversal of field (A., 1933, 499). J. W. S.

Determination of dissociation constant of tri-*n*-butylamine. P. DAMSGAARD-SØRENSEN and A. UNMACK (Z. physikal. Chem., 1935, 172, 389—397).—Conductivity measurements lead to 6.7×10^{-4} at 18° ,

a val. regarded as more probable than that of Hall and Sprinkle (A., 1932, 1089).

R. C.

Activity in mixtures of strong electrolytes. L. BRULL (Gazzetta, 1935, 65, 14—19; cf. A., 1934, 1307).—From e.m.f. measurements of cells of the type $\text{Zn}|\text{Hg}|\text{ZnCl}_2(c_1)|\text{MCl}_2(c_2)|\text{Hg}_2\text{Cl}_2|\text{Hg}$ the activity coeffs. of ZnCl_2 in presence of alkaline-earth chlorides (MCl_2) have been calc.

O. J. W.

Thermodynamic study of systems of the type $\text{PbCl}_2\text{--RCl--H}_2\text{O}$ at 25°. III. (MISS) D. M. BRASHER and H. N. PARTON. IV. H. N. PARTON (Trans. Faraday Soc., 1935, 31, 681—686, 686—689; cf. A., 1933, 906).—III. The activity of PbCl_2 in presence of NaCl in aq. solution, up to saturation with both salts, has been calc. from e.m.f. measurements. The results are shown in a diagram and tables.

IV. Similar experiments with LiCl are described. In alkali halide solutions, at the same ionic strength, the activity of PbCl_2 is greatest in presence of LiCl and least in presence of KCl .

F. L. U.

HO_2 radical in solution. J. WEISS (Trans. Faraday Soc., 1935, 31, 668—681; cf. this vol., 174).— $\text{N}_2\text{H}_4\text{SO}_4$, in which Pd saturated with H_2 was immersed, contained H_2O_2 and O_3 in the mol. ratio 9:1 after passage of O_2 at 5—7°. This result is attributed to the formation and subsequent decomp. of HO_2 thus: $\text{H} + \text{O}_2 = \text{HO}_2$; $2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2 + 49 \text{ kg.-cal.}$; $\text{HO}_2 + \text{H} = \text{H}_2\text{O}_2 + 94 \text{ kg.-cal.}$; $2\text{HO}_2 = \text{O}_3 + \text{H}_2\text{O} + 35 \text{ kg.-cal.}$ Similar results were obtained by decomp. Na_2O_2 or KO_2 with aq. H_2SO_4 . Whilst the absorption spectrum of acid solutions of O_3 resembles that of the gas, in pure H_2O and alkaline solutions absorption in the ultra-violet decreases, and in 40% KOH at -40° is replaced by absorption in the blue, considered to be due to O_2' ion arising from the dissociation of HO_2 . A quant. explanation of the decomp. of O_3 in H_2O and of the reaction between O_3 and H_2O_2 is given. The O_3 in these reactions is decomposed in a chain mechanism: $\text{O}_3 + \text{OH} = \text{O}_2 + \text{HO}_2 + 34 \text{ kg.-cal.}$; $\text{O}_3 + \text{HO}_2 = 2\text{O}_2 + \text{OH} + 33 \text{ kg.-cal.}$

F. L. U.

Colour of nickel salts in hydrobromic acid solution. Application of the law of mass action in concentrated solution. P. JOB (Compt. rend., 1935, 200, 831—832; cf. A., 1934, 364).—The change from green to greenish-yellow has been studied by measuring the absorption over the range 500—700 various $[\text{HBr}]$.

Evidence for the formation of NiBr_2 and NiBr_4^{--} has been obtained.

N. M. B.

Hydrolysis of betaine hydrochloride in aqueous solution and determination of the acidic dissociation constants of the betainium ion. O. WEIDER (Ber., 1935, 68, [B], 263—267).—Between 0° and 25° and for concn. $> 1 \text{ mol. } ^+\text{NMe}_3\cdot\text{CH}_2\cdot\text{CO}_2^-$ $K = 1.45 \times 10^{-2}$.

H. W.

Complex cobalt ions in the dissolved state. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 222, 312—316).—By a dialysis method previously described (A., 1928, 121) it is shown that the following ions exist in solution: $[\text{Co}(\text{NH}_3)_6]^{+++}$, $[(\text{NH}_3)_5\text{Co}\cdot\text{O}\cdot\text{O}\cdot\text{Co}(\text{NH}_3)_5]^{++++}$, $[\text{Co}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_3(\text{H}_2\text{O})_{12}]$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$,

$[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{++}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++}$, $[\text{Co}(\text{NH}_3)_4\text{SO}_4]^{+}$, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^{+}$, $[\text{Co}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})]^{++}$, $[\text{Co}(\text{NO}_2)_6]^{+++}$, $[\text{Co}(\text{SO}_3)_2(\text{CN})_4]^{2++++}$.

M. S. B.

Ions of some oxygen acids in the dissolved state. H. BRINTZINGER and C. RATANARAT (Z. anorg. Chem., 1935, 222, 317—320).—By dialysis (cf. preceding abstract) the following ions are shown to exist in solution: $[\text{As}(\text{OH})_6]^{+++}$, $[\text{Te}(\text{OH})_6]^{+++}$, $[\text{Se}(\text{OH})_6]^{+++}$, $[\text{SO}_4\cdot 2\text{H}_2\text{O}]^{++}$, $[\text{SeO}_4\cdot 2\text{H}_2\text{O}]^{++}$, MoO_4^{++} , WO_4^{++} , $[\text{C}_2\text{O}_4\cdot 4\text{H}_2\text{O}]^{++}$, $[\text{PO}_4\cdot 24\text{H}_2\text{O}]^{++}$, $[\text{AsO}_4\cdot 24\text{H}_2\text{O}]^{++}$. The ionic wt. found for WO_4^{++} is too small. The following metal ions, which form colloidal hydroxides, are combined with a large amount of H_2O : $[\text{Th}(\text{H}_2\text{O})_{12}]^{+++}$, $[\text{Al}(\text{H}_2\text{O})_{18}]^{+++}$, $[\text{Fe}(\text{H}_2\text{O})_{18}]^{+++}$, $[\text{Cr}(\text{H}_2\text{O})_{15}]^{+++}$, $[\text{Be}(\text{H}_2\text{O})_{12}]^{++}$.

M. S. B.

Physico-chemical behaviour of solutions of alcohols and phenols in liquid hydrogen fluoride. W. KLATT (Z. anorg. Chem., 1935, 222, 225—239).—Determinations of b.p. and conductivity of solutions in HF of aliphatic and aromatic OH -compounds indicate that easily decomposed additive compounds are formed in solution. The degree of ionisation into A, H^+ ($\text{A} = \text{OH}$ compound) and F^- depends not only on the no. of OH groups in the solute, but also on their position. Anthracene forms similar additive compounds. Negative substituents, such as halogen or NO_2 , have a marked depressing effect on the solubility, and the compounds formed have only a small degree of dissociation.

M. S. B.

Solutions of organic acids in hydrogen fluoride. W. KLATT (Z. anorg. Chem., 1935, 222, 289—302).—B.p. and conductivity measurements have been made for a no. of org. acids and acid anhydrides in HF . The results show that the acids are rather more capable of reacting chemically with HF to form fluorides than the alcohols (cf. preceding abstract). AcSH in HF rapidly evolves H_2S , whilst EtSH gives none. For the most part, however, an additive cation is formed and the original compounds are easily recoverable. Unsuccessful attempts have been made to isolate the acid fluorides from the solutions.

M. S. B.

Hydrated alumina. C. F. PRUTTON, S. H. MARON, and E. D. UNGER (J. Amer. Chem. Soc., 1935, 57, 407—413).—A v.-p. study of the system $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$ at 25° indicates the existence of $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3\cdot 2.5\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3\cdot 2\text{H}_2\text{O}$, and possibly $\text{Al}_2\text{O}_3\cdot 1.5\text{H}_2\text{O}$.

E. S. H.

Fusion curves of solid solutions with formation of a chemical compound. A. MŁODZIEJOWSKI (Physica, 1935, 2, 159—168).—Theoretical. J. W. S.

Systems metal nitrate-acetamide. P. T. DANILTSCHENKO and V. G. EDIGER (Ann. Inst. Anal. Phys. Chem., 1935, 7, 255—263).—The m.p. diagrams for the systems $\text{NH}_2\text{Ac--NH}_4\text{NO}_3$, AgNO_3 , and $\text{Pb}(\text{NO}_3)_2$ have been determined; the compounds $\text{AgNO}_3\cdot\text{NH}_2\text{Ac}$, m.p. 71° (decomp.), and $\text{Pb}(\text{NO}_3)_2\cdot 3\text{NH}_2\text{Ac}$, decomp. 70.2° , are indicated.

R. T.

M.-p. diagrams for binary systems of brom-ural and veronal with salol and phenacetin. K. HRYNAKOWSKI and M. SZMYTÓWNA (Arch. Pharm., 1935, 273, 163—169).—The components in each

system are miscible in all proportions in the fused state, and form a eutectic mixture the composition of which agrees with that required by the formula of Kordes (A., 1932, 228) when the eutectic mixture contains only a small proportion of one of the components.

H. G. M.

Ternary system ammonia-hydrogen chloride-water. N. S. KURNAKOV and D. N. SCHOJCHET (Ann. Inst. Anal. Phys. Chim., 1935, 7, 245—254).—The 0°, 25°, 50°, and 75° isotherms, the ice field, and the cryohydrate line have been determined.

R. T.

System CaCO_3 - CaSO_4 - H_2O at 159° to 252°, and the effect of additions of sodium salts. L. M. CLARK and E. HUNTER (J.C.S., 1935, 383—391).— $[\text{CO}_3]:[\text{SO}_4]$ ratios have been determined for solutions in equilibrium with the solid phases CaCO_3 (calcite) and CaSO_4 (anhydrite) at 159—250°. The ratios increase less rapidly with rise of temp. than is indicated by previous calc. vals., and above 230° are < the latter. The ratio is greatly reduced in presence of Na_2SO_4 and less so in presence of NaCl . Addition of NaOH leads to appreciable $[\text{Na}_2\text{SO}_4]$ at equilibrium, and the greatly reduced $[\text{CO}_3]:[\text{SO}_4]$ ratio is mainly due to Na_2SO_4 , but in part to NaOH . Applications to boiler scaling phenomena are discussed.

J. W. S.

Equilibrium $\text{Sn}+2\text{H}_2\text{O}$ SnO_2+2H_2 . G. MEYER and F. E. C. SCHEFFER (Rev. trav. chim., 1935, 54, 294—298).—The relation between $K = p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ and T is given by $\log K = 2301/T - 2.693$; the heat of reaction is 21.0 kg.-cal., in agreement with the calc. val. 21.7 kg.-cal.

R. S. B.

Equilibria of aqueous systems containing bromine and potassium in connexion with the industrial exploitation of Solikamsk sylvinites for bromine. V. I. NIKOLAEV (Ann. Inst. Anal. Phys. Chim., 1935, 7, 135—158).—The systems $\text{KCl-KBr-H}_2\text{O}$, $\text{KBr-MgBr}_2\text{-H}_2\text{O}$, $\text{MgCl}_2\text{-MgBr}_2\text{-H}_2\text{O}$, and $2\text{KBr}+\text{MgCl}_2$ $2\text{KCl}+\text{MgBr}_2$ have been investigated at 25°. The Br content of the quaternary system approaches a min. at the eutonic point.

R. T.

Metastable hydrates of magnesium sulphate in the system magnesium chloride-magnesium sulphate-water. N. S. KURNAKOV and V. G. KUZNETZOV (Ann. Inst. Anal. Phys. Chim., 1935, 7, 181—209).—The composition of the solid phase at 25—35° varies from $\text{MgSO}_4 \cdot 7$ to $4\text{H}_2\text{O}$ as the $[\text{MgCl}_2]$ is increased; the MgSO_4 content of saturated solutions can be reduced to 2.5% by adding $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to the solution at 50°. Trustworthy data for the composition of the solid phase are obtained by determining the v.p. of the various systems in contact with the solid phase, and by examining the crystals in polarised light; Ostwald's method may yield misleading results. The solid phases at the eutonic point are $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, and not, as reported by Blasdale (A., 1920, ii, 237), $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. The crystal parameters of the various hydrates of MgSO_4 have been determined.

R. T.

Singular elements of chemical diagrams. S. KURNAKOV and M. I. RAVITSCH (Ann. Inst. Anal. Phys. Chim., 1935, 7, 211—223).—Theoretical.

R. T.

Singular fold of the ternary system sodium chloride-platinic chloride-water. N. S. KURNAKOV and M. I. RAVITSCH (Ann. Inst. Anal. Phys. Chim., 1935, 7, 225—233).—Equilibrium relations have been investigated.

R. T.

Singular elements of the ternary system lithium oxide-nitric anhydride-water. Influence of hydration. M. I. RAVITSCH (Ann. Inst. Anal. Phys. Chim., 1935, 7, 235—244).—The 0°, 15°, 25°, 28.5°, 65°, and 130° isotherms and the cryohydrate line have been determined.

R. T.

Equilibria in the system $\text{NaF-Na}_2\text{BeF}_4\text{-H}_2\text{O}$. A. V. NOVOSELOVA (J. Gen. Chem. Russ., 1934, 4, 1206—1210).—Solubility data at 0—94° are recorded.

R. T.

Potassium lead sulphate, lead sulphate, potassium sulphate, and iodide ions at 25°. M. RANDALL and D. L. SHAW (J. Amer. Chem. Soc., 1935, 57, 427—429).—Equilibrium data are recorded.

E. S. H.

System cadmium acetate-acetic acid-water at 25°. W. C. CAGLE and W. C. VOSBURGH (J. Amer. Chem. Soc., 1935, 57, 414—415).— $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ can exist in stable equilibrium with saturated solutions in which the ratio $\text{AcOH}:\text{H}_2\text{O} < 1.57$. When the ratio is between 1.57 and 22.6 the solid phase is $3\text{Cd}(\text{OAc})_2 \cdot 4\text{AcOH} \cdot 4\text{H}_2\text{O}$.

E. S. H.

Amphoteric acetates in acetic acid as solvent. A. W. DAVIDSON and E. GRISWOLD (J. Amer. Chem. Soc., 1935, 57, 423—427).—The solubilities of $\text{Cu}(\text{OAc})_2$ in AcOH containing KOAc , and of $\text{Zn}(\text{OAc})_2$ in NH_4OAc solutions have been determined at different temp. and concns. The compounds $\text{KOAc} \cdot 2\text{Cu}(\text{OAc})_2 \cdot 2\text{AcOH}$ and $\text{Zn}(\text{OAc})_2 \cdot 2\text{NH}_4\text{OAc} \cdot 6\text{AcOH}$ have been isolated. Analogies with systems containing H_2O are discussed.

E. S. H.

Section $\text{CaO-SiO}_2\text{-MnO-SiO}_2$ of the ternary system $\text{SiO}_2\text{-CaO-MnO}$. E. VOOS (Z. anorg. Chem., 1935, 222, 201—224).—A vac. resistance furnace with new type of temp. regulator is described, by means of which MnSiO_3 has been synthesised in a pure state, m.p. 1205+2°. $\beta\text{-CaSiO}_3$ and MnSiO_3 form a continuous series of solid solutions stable below 1374°. Thermal analysis has been supplemented by microscopical and X-ray examination, and refractive indices have been measured.

F. L. U.

Thermodynamics of solutions. Chemical constants of dissolved substances. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1934, 4, 1180—1192).—Theoretical.

R. T.

Thermodynamics of solid solutions. II. Deviations from Raoult's law. H. SELTZ (J. Amer. Chem. Soc., 1935, 57, 391—395; cf. A., 1934, 365).—Theoretical. The forms of phase diagrams for binary systems showing complete solid miscibility are considered in relation to the types of deviations from Raoult's law in the liquid and solid solutions.

E. S. H.

Thermodynamic data for metallic sulphates. III. Calcium sulphate. O. KAMIKE (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 163—170).—The e.m.f. of the cell $\text{CaHg}|\text{CaSO}_4 \cdot 2\text{H}_2\text{O} (s), \text{saturated}$

solution, $\text{Hg}_2\text{SO}_4(s)|\text{Hg}$ is 2.6537 volts at 18° , whence the standard free energy and heat change for the formation of CaSO_4 from $\text{S} + 2\text{O}_2 + \text{Ca}$ have been calc. to be $-311,472$ and $-338,450$ g.-cal., respectively, at 25° . The entropy change for the hydration of CaSO_4 is 25.66 at 25° . R. S. B.

Thermodynamic study of the fundamental corrosion reactions of iron with hydrogen under pressure. K. MURATA (J. Soc. Chem. Ind. Japan, 1935, 38, 52—58B).—Previous results on the corrosion of Fe in an Fe half cell in an atm. of H_2 (A., 1932, 813, 999) are discussed in the light of thermodynamic equilibria between Fe'' , Fe''' , H^+ , OH^+ , and H_2 . It is shown that in all cases, whether Fe'' , Fe''' , or a mixture is present, there is a crit. partial pressure below which equilibrium is never reached but corrosion continues with pptn. of the appropriate oxide. Free energy data for a no. of the reactions are summarised. C. I.

Free energy of solids at high temperature. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1934, 4, 1197—1198).—Mathematical. R. T.

Determination of integral heats of dissolution. II. N. A. DE KOLOSOVSKI and E. V. GRISCHKUN (J. Gen. Chem. Russ., 1934, 4, 1289—1293).—The expression $S = S_0 - 4.573[\log(p/p_0) + T.d \log(p/p_0)/dT]$ is derived, where S is the entropy of a solvent in saturated solution, S_0 that of the pure solvent, and p and p_0 are the corresponding v.p. at temp. T . R. T.

Calorimetric measurements with heavy water. E. BARTHOLOME and K. CLUSIUS (Z. physikal. Chem., 1935, B, 28, 167—177).—The mean mol. heat of liquid H_2O at 0 — 18° is 18.1_8 and that of solid H_2O between -20° and 0° is 8.1_8 g.-cal. The heat of sublimation at the triple point, 3.82° , is 12,631, and the heat of fusion 1522 g.-cal. The difference between these vals. and those for H_2O is due to the differing intermol. zero point energies of H_2O and H_2O . At 0° the v.p. of solid H_2O is 3.65 and at 3.82° 5.06 mm. R. C.

Heat effect in monocalcium silicate formation from gypsum and silicic acid. O. F. HONUS (Zement, 1934, 23, 415—419; Chem. Zentr., 1934, ii, 3161—3162).—The Nernst theorem has been applied to the reaction $\text{CaSO}_4 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{SO}_2 + 0.5\text{O}_2$. The heat of formation of CaSiO_3 at room temp. is 21.7 ± 0.6 kg.-cal. H. J. E.

Heats of combustion of some diphenyl derivatives. L. BRULL (Gazzetta, 1935, 65, 19—28).—Heats of combustion of Ph_2 and 21 derivatives have been measured and compared with those of C_6H_6 derivatives. O. J. W.

Conductivities of aqueous solutions of glycine, *dl*-valine, and *l*-asparagine. J. W. MEHL and C. L. A. SCHMIDT (J. Gen. Physiol., 1935, 18, 467—479).—Only approx. agreement is found between the calc. and experimental data for these and other NH_2 -acids previously reported (A., 1933, 230). F. A. A.

Electrical conductivity of solutions of lithium, sodium, and rubidium iodides in molten iodine. V. A. PLOTNIKOV, J. A. FIALKOV, and V. P. TSCHALIJ

(Z. physikal. Chem., 1935, 172, 304—313).—The sp. conductivity, κ , at 130 — 140° rises with the concn., c , at first, but ultimately becomes const. At 130° with increasing c the mol. conductivity falls continuously for NaI, passes through a max. for RbI, and rises to a const. val. for LiI. For LiI and RbI the temp. coeff. of κ is negative at low c and positive at higher c . The conductivity is ascribed to ionisation of polymerised polyiodides. For molten I $\kappa = 0.9 \times 10^{-5}$ at 140° . R. C.

Solution of the conductance equation. R. M. FUOSS (J. Amer. Chem. Soc., 1935, 57, 488—489).—Mathematical. E. S. H.

Decomposition potentials and conductivities of magnesium oxide and of the alkaline-earth oxides in fused fluorides. M. DE K. THOMPSON and A. L. KAYE (Trans. Electrochem. Soc., 1935, 67, 243—264).—Decomp. potentials (E) for saturated solutions, and conductivities (κ) for a range of oxide concn. have been determined at 900 — 1100° for MgO in fused $\text{MgF}_2 + \text{BaF}_2 + \text{NaF}$, CaO in fused $\text{CaF}_2 + \text{NaF}$, SrO in fused $\text{SrF}_2 + \text{NaF}$, and BaO in fused $\text{BaF}_2 + \text{NaF}$. The p.d. was measured with Pt and graphite, the difference giving the depolarisation due to C, 1.14 ± 0.01 volt, in agreement with the calc. val. E for MgO and CaO agree with the calc. vals., the oxides on decomp. giving metal, but with BaO and SrO no metal is formed, and E probably refers to the formation of a suboxide. After prolonged electrolysis BaO and SrO evolve F_2 . E decreases linearly with rise in temp. The addition of CaO and SrO to the mixed fluorides increases κ to a max.; with BaO and MgO κ decreases with increasing concn. of oxide. With MgO and CaO κ increases linearly with rise of temp., but with SrO and BaO κ is linear only for $< 9\%$ oxide. A new thermoregulator, const. to 1° at 1000° , and a new technique for κ , are described. R. S. B.

Salt error and normal electrode potential of the quinhydrone electrode at 25° . F. HOVORKA and W. C. DEARING (J. Amer. Chem. Soc., 1935, 57, 446—453).—The salt error has been determined with an accuracy of ± 0.00003 volt for 14 solutes at concns. of 0.05 — $2N$. The salt error is linearly related to the concn. of solute, and is additive for many mixtures. The normal electrode potential is 0.69938 ± 0.00003 volt. The standard quinhydrone electrode has a potential of 0.69915 ± 0.00003 volt with respect to the H_2 electrode. E. S. H.

Solubility product of silver sulphide and standard electrode potential of sulphur. G. KIMURA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 94—98).—Reproducible e.m.f. are given by the cell $\text{Ag}|\text{Ag}_2\text{S}, \text{H}_2\text{S} (p \text{ atm.}), \text{HCl}(0.1M)|\text{HCl}(0.1M)|\text{H}_2 (p \text{ atm.})$. The solubility product of Ag_2S is 6.0×10^{-52} and the standard electrode potential of rhombic S is 0.51 volt; these agree with the corresponding vals. 9.5×10^{-52} and 0.50 volt obtained by Noyes and Freed (A., 1920, ii, 288) using a different method. W. R. A.

Significance of diffusion in concentration cells. H. LARSSON (Svensk Kem. Tidskr., 1935, 47, 51

52).—The extent of diffusion across the liquid junction in a concn. cell is calc. from Fick's law.

E. A. H. R.

of saturated calcium carbonate solutions.

I. SAJANIEMI (Suomen Kem., 1935, 8, B, 8).—The determined by the glass electrode is 8.01.

E. S. H.

Indicators. XXV. Alcohol error of indicators. A. THIEL and D. GREIG (Z. physikal. Chem., 1935, 172, 245—276; cf. this vol., 38).—The equilibria in aq.-EtOH indicator solutions have been studied optically. The behaviour of phenolphthalein (I) is fundamentally the same in aq. EtOH as in aq. solution. If the ionic strength, μ , is kept const., the classical mass law is valid. The equilibrium consts., however, are affected by the EtOH; this favours the colourless, lactoid form, which explains why the colour is not as intense as in aq. solution. The classical indicator consts. of various indicators in aq.-EtOH solutions for const. μ and the ionic product of H_2O , K_w , for such solutions have been determined. K_w is little affected by even high [EtOH]. For the indicators studied, other than (I), addition of EtOH deepens the colour. The results indicate that strong electrolytes are completely dissociated in aq.-EtOH solutions.

R. C.

Reduction potentials of naphthoquinones.

L. F. FIESER and (Mrs.) M. Fieser (J. Amer. Chem. Soc., 1935, 57, 491—494).—The following reduction potentials, E_0 , at 25° in 37—70% EtOH are recorded: (a) α -naphthoquinones: 2-Me-, 0.4080; 2:3-, 0.3399; 2:6-, 0.4051, and 2:7-Me₂-, 0.4069; 2-OH-6-Me-, 0.3357; 3-OH-2:6-Me₂-, 0.2775; 2-Ph-, 0.4515; 2-OAc-, 0.4750; 2-Bz-, 0.5031; 2-CHPh-, 0.4328; 2-NH₂-, 0.2742; 2-NHMe-, 0.2318; 2-NMe₂-, 0.2889; 2-NHAc-, 0.4165; 2-NHPh-, 0.2858; (b) β -naphthoquinones: 4-, 0.5315, and 6-Me-, 0.5315; 3:7-Me₂-, 0.5350; CH(CO₂Et)-, 0.5976; 4-NH₂-, 0.3249; 4-NHMe-, 0.2933; 4-NHEt-, 0.2966; 4-NHBu-, 0.2952; 4-CH₂Ph-NH-, 0.2997; 3-, 0.5545, and 4-NHAc-, 0.5461. Substitution in the benzenoid nucleus has less effect than that in the quinonoid. E_0 lowered or raised by substituents which facilitate or retard, respectively, substitution in a C₆H₅ derivative. The following is a provisional order of efficiency: NHR, NH₂, OH, OR, Me, CH₂Ar, CH.CHR, Ph, NHAc, OAc. In general, however, the results are too erratic to allow the position of substituents to be determined by E_0 . The prep. of the following is improved: α -amino- β -naphthol hydrochloride, α - and β -naphthoquinone, α -amino- β -naphthol-4-sulphonic acid, 1:2-naphthoquinone-4-sulphonic acid, 1:4-naphthoquinone-2-sulphonic acid, and 2-hydroxy-1:4-naphthoquinone. The following are prepared from 4-ethoxy-1:2-naphthoquinone and NH₂R in EtOH at 45°: 4-methyl-, (also obtained by NHMe₂), decomp. 247—249°, -ethyl-, decomp. 248—250°, -n-butyl-, decomp. 228—230°, and 4-benzyl-amino-1:2-naphthoquinone, decomp. 205—208°.

R. S. C.

Oxidation-reduction potentials. IV. Changes of these potentials in the hydrolysis of fats and oils. V. Changes in the hydrolysis of carbohydrates. Y. NAKAMURA (J. Chem. Soc. Japan,

1934, 55, 887—889, 880—883).—Hydrolysis of fats and oils by alkalis, acids, and enzymes lowers the oxidation-reduction potentials as the reaction proceeds.

V. Reduction is indicated in the hydrolysis of carbohydrates, but evidence of a secondary oxidising reaction has been obtained.

CH. ABS. (e)

Constitution of the double layer and the appearance of the potential curve in the electrolytic neutralisation of metallic ions. N. THON (Compt. rend., 1935, 200, 907—909; cf. A., 1934, 32, 718).—Regarding an electrode as an ohmic resistance with a capacity in parallel, an expression is deduced which, it is claimed, agrees with the actual form of electrode potential-current curves.

J. W. S.

Electrolysis of extremely dilute solutions. Normal potentials of bismuth and polonium. M. HAISINSKY (J. Chim. phys., 1935, 32, 116—125; cf. this vol., 169).—Minute quantities (down to $3 \times 10^{-12}N$) of Bi can be detected, and its concn. approx. determined, by measuring the radioactivity of the cathodic deposit obtained at suitable potentials (given) from solutions to which Th-C has been added as an indicator. A similar method can be applied to Pb, using Th-B as indicator.

F. L. U.

Passage of the current at potentials below the decomposition potential of electrolytes. I. ZLOTOWSKI (Compt. rend., 1935, 200, 733—735).—A polarographic study of current-potential curves for electrolyte solutions, below the decomp. potential, indicates that the "residual current" is not different from the ordinary electrolytic current; the ions travel to the electrodes but cannot be discharged below a certain e.m.f. and the current ceases.

M. S. B.

Cathode film in electrolysis of solutions containing chromate. E. MULLER and W. STEIN (Z. physikal. Chem., 1935, 172, 348—352).—On cathodic polarisation of Au and Pt in, or on dipping base metals into, a solution containing Cr₂O₇²⁻ the metal becomes covered with an invisible film, the presence of which is shown by the observation that Ag deposited on it from a CN⁻ solution can be rubbed off. This film renders Ag and less noble metals resistant to chemical attack.

R. C.

Anodic passivation. W. J. SHUTT (Trans. Faraday Soc., 1935, 31, 636—637).—Reply to a criticism by Armstrong and Butler (this vol., 39).

F. L. U.

Mechanism of the photo-potential of sheets of oxidised copper. J. ROULLEAU (Compt. rend., 1935, 200, 920—922).—Sheets oxidised completely to Cu₂O show no photo-potential (I) in aq. electrolytes unless a thin metallic film is produced on the surface. (I) is of the same order in aq. solutions and in org. liquids rendered conductive with KI. Max. sensitivity occurs at about 4700 Å. Sheets of Cu with surfaces oxidised to Cu₂O and then coated with a thin layer of metal show max. (I) at 3900 and 4700 Å. These max. are attributed to max. of the photo-chemical and electronic effects, respectively. Cu coated with CuO shows no photo-electric effect.

J. W. S.

Physico-chemical study of electrodes photo-sensitised with dyestuffs. (MLLE.) C. STORA (Compt. rend., 1935, 200, 1034—1037; cf. A., 1932, 898; this vol., 429).—In the absence of light the electrode potential of Pt covered with collodion coloured with Nile-blue or methylene-blue, in solution of const. $[H^+]$, follows an S curve with varying concn. of reducing agent ($Na_2S_2O_4$ or $TiCl_3$). The inflexion point coincides closely with the normal potential of the indicator. On illumination the corresponding photo-potential is negative in absence of reducing agent, but reverses in presence of the latter, remains almost const. in the region of the inflexion point, and proceeds to a max. at higher reducing agent concn. The max. corresponds with a definite small proportion of oxidised dye (1 in 10^6 — 10^7). Oxidation occurs under the action of light, possibly owing to absorption by the oxidised form, followed by photolysis of the H_2O and subsequent oxidation of the reduced form. J. W. S.

Activated complex in chemical reactions. H. EYRING (J. Chem. Physics, 1935, 3, 107—115).—Mathematical. The calculation of abs. reaction rates is formulated. F. L. U.

Kinetics of exothermic reactions. I. Law of initial acceleration. II. Role of intermediate compounds in chain reactions. N. SEMENOV (Acta Physicochim. U.R.S.S., 1934, 1, 113—130, 131—138).—I. It is shown that the law of initial acceleration, $w = A \cdot e^{kt}$, where w is its velocity, A is a function of the no. of chains initiated per sec. by the heat motion, $\phi = Cp^n e^{-E/RT}$, and t is the time, is quantitatively applicable to a large no. of oxidations, such as of H_2 , H_2S , CH_4 , C_2H_6 , C_5H_{12} , C_6H_6 , and C_2H_4 , and to the decomp. of Cl_2O , $EtSH$, $PrSH$, glyceryl nitrate, $C_6H_5Me(NO_3)_3$, Pb styphnate, Hg fulminate, and BaN_6 . It is also in qual. agreement with a no. of other reactions.

II. The theory of chain reactions, including branching chains, and its evolution from other theories of intermediate compounds in autoxidation, are illustrated by reference to the oxidation of P vapour, CS_2 , H_2 , CH_4 , and H_2SO_3 . Many exothermic decomp. characterised by an induction period, and also many cases of heterogeneous catalysis, are probably to be explained similarly. M. S. B.

Application of the Rayleigh interferometer to the measurement of reaction velocity. D. B. LUTEN, jun. (J. Physical Chem., 1935, 39, 199—211).—The quant. relations between change of d and change of refractive index n have been determined. Change of n can be used equally with change of d for following the course of a reaction. The method of application of the Rayleigh interferometer to measurements of velocity of reaction is described. The method of deducing the velocity coeff. is discussed. M. S. B.

Determination of flame velocity of combustible gas mixtures.—See B., 1935, 258.

Mechanism of explosions and combustion. II. W. JOST (Z. Elektrochem., 1935, 41, 232—252; cf. this vol., 451).—A further review.

Anomalous pressures and vibrations in gas explosions. Determination of the dissociation energy $2H_2O \rightarrow 2OH + H_2$. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1935, 3, 63—71; cf. A., 1934, 1310).—From data given by explosions of H_2 , O_2 , and He, and with the aid of accurate thermodynamic functions of the gases concerned, the energy of dissociation of H_2O into OH and H_2 is calc. to be $126 + 2$ kg.-cal. per 2 mols. of H_2O . Theoretical explosion pressures have been calc. and compared with observations on different mixtures containing H_2 and O_2 . Explanations of discrepancies are offered. Vibrations which occur on exploding certain slow-burning mixtures are attributed to variation of the heat capacity with time within the duration of an explosion. F. L. U.

Kinetics of the reaction between hydrogen and sulphur. II. 1. Formation and characteristics of the unimolecular layer of hydrogen sulphide on the glass surface. 2. Independence of the reaction of the presence of oxygen, moisture, and sulphur dioxide. E. E. AYNLEY and P. L. ROBINSON (J.C.S., 1935, 351—356).—The characteristics of the homogeneous reaction (I) already reported (this vol., 307) are maintained with 20—686 mm. of H_2 (measured at 15°), and the velocity at 301 — 343° is not affected by SO_2 , 7 vol.-% of O_2 , or 2 vol.-% of H_2O (cf. J.C.S., 1923, 123, 696). By using approx. 1 mm. of H_2 , it was found that (I) is accompanied by a heterogeneous reaction at the glass surface. All of the H_2S formed at the surface is retained as a unimol. layer which prevents further participation of the surface in the reaction.

J. G. A. G.

Kinetics of recombination of bromine atoms. E. RABINOWITCH and H. L. LEHMANN (Trans. Faraday Soc., 1935, 31, 689—705).—The dissociation of Br_2 mols. has been studied by measuring the decrease of the mol. absorption coeff. of the illuminated vapour, from which the equilibrium $Br_2 \rightleftharpoons Br + Br$ is calc. The effect of admixed He, A, N_2 , CO_2 , and CCl_4 vapour was examined, and the homogeneous and wall reactions were differentiated. The velocity of the former \propto (pressure) $^{\frac{1}{2}}$. The abs. val. of the recombination const. of the reaction $Br + Br + He \rightarrow Br_2 + He$ is 2.7×10^{15} (concns. in g.-mol. per c.c.). F. L. U.

Ortho-para transformation in solid hydrogen. E. CREMER (Z. physikal. Chem., 1935, B, 28, 199—214; cf. A., 1933, 786).—The bimol. velocity coeff., k , begins to fall rapidly when about two thirds of the o - H_2 has changed. No such fall occurs in the transformation in the liquid phase, or in solid H_2 two thirds converted before freezing. If a mixture in which k has commenced to fall is melted and refrozen, k regains its normal val. The fall in k may be due to diffusion in solid H_2 being too slow to maintain a statistical distribution of o - and p -mols., but the proportion of o - H_2 when change has ceased, $19 \pm 5\%$, is too large for this to be a complete explanation. The catalysis of the change by solid air present as impurity is due to O_2 . The coeff. of self-diffusion of liquid H_2 at 20° abs. is ~ 3 sq. cm. per day. R. C.

Thermal reaction between formaldehyde and chlorine. K. B. KRAUSKOPF and G. K. ROLLEFSON

(J. Amer. Chem. Soc., 1935, **57**, 590).—The observed behaviour is in accordance with the reaction sequence $\text{CH}_2\text{O} + \text{Cl}_2 \longrightarrow \text{COHCl} + \text{HCl} \longrightarrow \text{CO} + 2\text{HCl}$.

E. S. H.

Kinetics of the thermal decomposition of gaseous methyl iodide. E. W. R. STEACIE and R. D. McDONALD (J. Amer. Chem. Soc., 1935, **57**, 488).—Evidence is adduced in support of the inferences of Ogg (cf. A., 1934, 493).

E. S. H.

Recombination of hydrogen ions. W. STEINER (Trans. Faraday Soc., 1935, **31**, 623—636).—Results given in an earlier paper (A., 1931, 1239) are corr. for diffusion. In addition to the three-body collision reaction there is a wall reaction which may contribute 30% of the total at low pressures, but is relatively unimportant at higher. An upper limit for the recombination const. when the third colliding particle is a mol. is calc.

F. L. U.

Reversible aquotisation reactions in the cobalt-amine group. K. SANDVED (Tidsskr. Kjemi, 1935, **15**, 21—22).—Velocity and equilibrium measurements were carried out for the reactions $[\text{CoCl}(\text{NH}_3)_5]^{++} + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{++} + \text{Cl}^-$ and $[\text{Co}(\text{NO}_3)(\text{NH}_3)_5]^{++} + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{++} + \text{NO}_3^-$ at varying acid concns. Mechanisms are suggested.

R. P. B.

Reactions between oxalic acid, iodine, and the iodate and iodide ions. II. Dark kinetics of iodine-oxalic acid reaction. E. ABEL and K. HILFERDING (Z. physikal. Chem., 1935, **172**, 353—368).—The experimental data on which the theory of the reaction is based (A., 1931, 690) are given. The velocity coeffs. agree fairly well with those found by Griffith and McKeown (A., 1932, 1210). The reaction by way of HOI consists of two concurrent processes, the velocities of which are determined by $\text{H}_2\text{C}_2\text{O}_4 + \text{HOI} = 2\text{CO}_2 + \text{HI} + \text{H}_2\text{O}$ and $\text{HC}_2\text{O}_4' + \text{HOI} = 2\text{CO}_2 + \text{I}^- + \text{H}_2\text{O}$, respectively.

R. C.

Oxidation of quinol solutions. I. Solutions of quinol in pure water and in presence of alkali or alkaline-earth hydroxides. A. SAINT-MAXEN (J. Chim. phys., 1935, **32**, 161—172).—The rate of oxidation by air of 0.2*M*-aq. quinol (I) solutions decreases with time owing to the accumulation of acidic oxidation products. The temp. coeff. for 10° between 18° and 50° is about 3. In presence of NaOH , KOH , LiOH , $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, or $\text{Ba}(\text{OH})_2$ the initial rate $\propto R$ = equivs. of base/mols. of (I) when $R > 0.2$, then increases to a max. between $R = 0.6$ and 1.0, and afterwards decreases slightly. It is independent of [(I)] and of the nature of the base, and with alkaline-earth bases is not affected by substituting 20% aq. glycerol for H_2O .

F. L. U.

Hydrolysis of diketopiperazine and of glycylglycine by hydrochloric acid. I. S. JAITSCHIKOV and A. S. SPIRIDONOVA (J. Gen. Chem. Russ., 1934, **4**, 1286—1288).—Diketopiperazine is hydrolysed to glycylglycine (I) by *N*-HCl after 25 days at 15°, or after 1 hr. at 95°. (I) is very slowly hydrolysed to glycine at 15° (13.2% after 25 days), and more rapidly at 95° (100% after 30 hr.); more protracted hydrolysis leads to diminution in total acidity, corresponding with complete recombination after 98 hr.

R. T.

Rate of hydrolysis of sucrose and the acidity and viscosity of the medium. S. TRAUTMANN and L. AMBARD (Compt. rend. Soc. Biol., 1935, **118**, 1083—1085).—The presence of glycerol (I) increases the rate of hydrolysis of 2% sucrose in 0.1*N*-HCl to an extent in agreement with that calc. from the restriction of solvent space due to the (I).

F. O. H.

Kinetics of adsorption. I. Velocity of adsorption of nitrous and nitric oxides by glass. M. CRESPI (Anal. Fis. Quim., 1934, **32**, 30—42).—The mean rates of adsorption of NO and N_2O on glass at 16°/95 and 190 mm. are recorded. The process is not one of condensation and evaporation as expressed by the Langmuir and Freundlich equations, but accords with $dy/dt = k(a-y)(y_e-y)/y$, where y is the quantity adsorbed at time t and y_e the equilibrium val. of y , which is derived theoretically.

H. F. G.

Chemical inertia. M. LEMARCHANDS and M. JACOB (Bull. Soc. chim., 1935, [v], **2**, 479—487; cf. A., 1933, 1018).—The temp. 0° at which O_2 reacts with mirrors of degassed Li, Na, K, Mg, Ca, Zn, Cd, Al, Ti, Sn, and Pb has been determined, and the b.p., T_{mo} , of the oxides formed calc. from the relation $0' = k'T_m \cdot T_{mo}$, where $\times 10^{-4}$ and T_m is the b.p. of the metal. The results are in good agreement with experimental vals. of T .

R. S.

Velocity of oxidation of tin. E. COHEN and H. L. BREDEE (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 130—132).—By means of a gas dilatometer it is proved that Sn oxidises at a measurable rate in dry air at 18°. The oxidation plays an important part in the polymorphic transition of tin.

A. J. M.

Dissolution of magnesium in aqueous salt solutions. IV. L. WHITBY (Trans. Faraday Soc., 1935, **31**, 638—648; cf. A., 1934, 36).—Increasing the thickness of air-formed films affords no protection against attack by solutions containing Cl^- or SO_4^{--} . The rate of dissolution (I) of Mg in aq. NaCl , and the solubility of $\text{Mg}(\text{OH})_2$, show max. at 2*N*, and (I) again increases at higher concns. In aq. Na_2SO_4 the behaviour depends largely on the sample of metal used. (I) and (II) have also been determined for LiCl and KCl .

F. L. U.

Determination of the velocity of dissolution of soaps. E. SAUER and W. BURCK (Angew. Chem., 1935, **48**, 171—174).—The velocity of dissolution, v , of Na palmitate, stearate, and oleate has been determined by titration of the amount dissolved from the end of a standard cylinder by H_2O at const. temp. and const. rate of flow. v increases slightly with the H_2O content of the soap.

R. S.

Influence of dehydration products on the course of dehydration. S. ŠKRAMOVSKY (Coll. Czech. Chem. Comm., 1935, **7**, 69—76).—The dehydration of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $6\text{H}_2\text{O}$ has been studied at different temp. with varying additions of dehydration products, using an automatic registration method previously described (A., 1932, 1227). The presence of lower hydrates shortens the induction period of decomp. or causes an accelerated decomp. to $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$ (I) which, after a halt and further period of induction, undergoes additional decomp. at a

smaller velocity. In the absence of added dehydration products there is continuous dehydration to a lower hydrate with $1.5\text{H}_2\text{O}$, without the definite intermediate formation of (I). M. S. B.

Mechanism of the primary reaction between carbon dioxide or oxygen and graphite. Kinetics of combustion of coal. H. MARTIN and L. MEYER (Z. Elektrochem., 1935, 41, 136—146).—The reaction between C (graphite) and CO_2 up to 2600° abs. is of zero order, and the reaction yield is only about 10 times as great as the velocity of vaporisation of C. The heat of activation is about 90 kg.-cal. It appears that the surface of C is poisoned by bound O atoms, and that reduction of CO_2 occurs only when an O with the neighbouring C evaporates from the surface as CO, exposing a reactive C. Further experiments on the reaction between C and O_2 confirm the results previously obtained (A., 1932, 816). E. S. H.

Mechanism of the primary reaction between carbon dioxide or oxygen and graphite. Kinetics of combustion of coal. A. EUCKEN (Z. Elektrochem., 1935, 41, 146—147).—Polemical (cf. preceding abstract). E. S. H.

Kinetics of salt-hydrate dissociations: $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{MnC}_2\text{O}_4 + 2\text{H}_2\text{O}$. B. TOPLEY and M. L. SMITH (J.C.S., 1935, 321—325).—The dissociation of masses of minute crystals has been studied at 25 — 70° after nucleation at 90° . The activation energy, E , of the dissociation in vac. is 24.3 kg.-cal. With increase of H_2O vapour from 0 to 12.8 mm. in the atm. surrounding the dissociating solid, the velocity coeff., k , falls strongly to a min., increases strongly to a max. of approx. the same magnitude as k in vac., and then falls more slowly. The phenomena are interpreted in terms of the energy barrier which H_2O mols. have to surmount when changing between the combined and the adsorbed states at the interface. The positive catalysis is attributed to a lowering of E for dissociation and an increase of E for recombination, in the reaction zone, by the electrostatic attraction of suitably oriented H_2O dipoles. J. G. A. G.

Physical and chemical relations in fluid-phase heterogeneous reaction. P. S. ROLLER (J. Physical Chem., 1935, 39, 221—237).—Nernst's theory of a stationary film in heterogeneous reactions is not supported by experimental evidence. Assuming that the measured rate of fluid-phase heterogeneous reaction is the resultant of chemical reaction at the interface and physical transport to or from the interface taking place simultaneously, and with no arbitrary assumptions as to mechanism, equations are deduced which are in good agreement with the experimental data for five typical reactions. M. S. B.

Catalytic effect of hydrogen in the carbon monoxide flame. W. E. GARNER and F. H. POLLARD (Chem. and Ind., 1935, 341—342).—A reply to Bradford (*ibid.*, 295). The effect of pressure variations on K_p can be explained in terms of the removal of H atoms by the walls. C. W. G.

Heterogeneous-homogeneous catalysis of the reaction between hydrogen and oxygen. M. V.

POLJAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 454—457).—The explosion of a mixture of H_2 and O_2 was compared with the catalytic reaction. With 2 parts of H_2 to 1 part of O_2 about 10% H_2O_2 was found in the products of the explosion, when cooled to -180° . The yield of H_2O_2 (I) is much smaller in the catalytic process. (I) decreases with total pressure of the gases, and varies with the partial pressures of H_2 and O_2 . (I) also depends on the diameter and shape of the reaction vessel, both the catalytic and explosive reactions being affected to the same degree. For higher partial pressures of O_2 , measurable quantities of O_3 were produced in both reactions, the amount of H_2O_2 being less. (I) in the catalytic process is increased with rise in temp. Below 250° , no H_2O_2 is formed. On the basis of these results it is argued that the H_2O_2 is formed by a homogeneous reaction which is, however, initiated at the surface of the catalyst. It is proposed to call this phenomenon heterogeneous-homogeneous catalysis. The formation of H_2O_2 is in favour of the presence of OH in the chain mechanism. A. J. M.

Deactivation of chemically activated oxalic acid. II. K. WEBER (Z. physikal. Chem., 1935, 172, 459—469; cf. A., 1934, 849).—The reduction of HgCl_2 with HCO_2H in aq. solution is not retarded by phenols or vat dyes, which disproves Krauss' contention that the reduction by activated $\text{H}_2\text{C}_2\text{O}_4$ is really effected by HCO_2H (A., 1933, 792). Utilising the theory of Dimroth (*ibid.*, 1123), a relation between the retarding action of a foreign substance and the normal oxidation-reduction potential, E , of the latter has been derived. This is essentially similar to Baur's relation (A., 1932, 578) and is confirmed experimentally. In general, the retarding action of a foreign substance appears to depend, however, not merely on E ; the rate at which equilibrium is established in the oxidation-reduction system seems also to play a part. Retardation by mixtures of foreign substances is covered. R. C.

Oxidation of carbon disulphide by Kjeldahl's method. J. MILBAUER (Z. Elektrochem., 1935, 41, 149—151).—The reaction in presence of different catalysts yields SO_2 , CO_2 , CO, and in some cases COS. The relative effectiveness of the catalysts (as measured by SO_2 production) is in the order $\text{Pd} > \text{Se} > \text{Pt} > \text{CuSO}_4 > \text{Te} > \text{HgSO}_4 > \text{Sb}_2\text{O}_3 > \text{MoO}_3 > \text{As}_2\text{O}_3 > \text{Ti}_2\text{SO}_4 > \text{Bi}_2\text{O}_3 > \text{WO}_3 > \text{Ag}_2\text{SO}_4$. E. S. H.

Application of quantum mechanics to certain cases of homogeneous catalysis. II. Enzyme action.—See this vol., 533.

Enzymic fission of salicin by emulsin in heavy water. E. W. R. STEACIE (Z. physikal. Chem., 1935, B, 28, 236—238).—Reaction in H_2O is 25% more rapid than in ordinary H_2O . R. C.

Acceleration of slaking of lime by aqueous electrolytes.—See B., 1935, 268.

Catalytic exchange of deuterium and methane. K. MORIKAWA, W. S. BENEDICT, and H. S. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 592—593).—Examination of infra-red absorption spectra of the

products shows that H^2 is substituted for H^1 in CH_4 at Ni catalyst surfaces in the temp. range 184–305°.

E. S. H.

Mechanism of ethylene hydrogenation on platinum. B. BRUNS and K. ABLESOVA (*Acta Physicochim. U.R.S.S.*, 1934, 1, 90–96).—The velocity coeff. of hydrogenation of C_2H_4 on platinumised C has been determined for temp. –50° to 100° and for [Pt] on C of 0.01–0.1%. The results give a satisfactory bimol. coeff. for each different temp. and [Pt], with a max. at 25° for all [Pt]. Hydrogenation on pure Pt-black (I) has also been studied. The adsorption of H_2 is much > that of C_2H_4 . If C_2H_4 is brought into contact with (I) charged with H_2 no reaction takes place, but a H_2 – C_2H_4 mixture in contact with (I) saturated with H_2 reacts. The adsorption of C_2H_4 is greatly reduced by the presence of adsorbed H_2 . Possible mechanisms for the hydrogenation are discussed.

M. S. B.

Alteration of catalytic activity of metals at transformation points. K. FISCHBECK and F. SALZER (*Z. Elektrochem.*, 1935, 41, 158–169).—Changes in catalytic activity, corresponding with transformations of the catalyst, have been demonstrated for the decomp. of NH_3 in presence of Fe, and the reaction $CO_2 + 4H_2 = CH_4 + 2H_2O$ with a Co–Ni catalyst. No discontinuity in the catalytic activity of Ni or Ni–Cu alloys at the temp. of loss of magnetisability was observed.

E. S. H.

Energetics of catalysis. IV. Influence of deactivation by heat-treatment on the value of the activation energy. E. B. MAXTED and C. H. MOON (*J.C.S.*, 1935, 393–396; cf. A., 1933, 680).—Although the rate of decomp. of H_2O_2 by Pt-black was progressively diminished to 2.6% of its initial val. by successive sintering treatments of the Pt at <400°, the activation energy, E , 8700 g.-cal., calc. from the 10–30° temp. coeff. remained const. E for the range 0–15° is 10,800. Similar phenomena were observed in the hydrogenation of crotonic acid catalysed by Pt-black, E being 7500. J. G. A. G.

Kinetics of catalytic hydrogenation of hydrocarbons. A. A. ALTSCHUDSHAN, A. A. VEDENSKI, V. R. SHARKOVA, and A. V. FROST (*J. Gen. Chem. Russ.*, 1934, 4, 1168–1179).—The velocity, v , of hydrogenation of C_6H_6 in presence of α -Pd is > that of PhMe; at <200° v is independent of the $[H_2]$ and $[C_6H_6]$ or [PhMe], whilst at >240° $v \propto [C_6H_6]$. At 240°, and in presence of H_2 (<8 atm.) α -Pd is transformed into β -Pd, in presence of which v is at 240° $\propto [C_6H_6]$ and $1/[H_2]$. *cyclo*Hexane has no effect on v in systems not near equilibrium. The temp. coeff. is approx. 2 at <225°, <2 from 240° to 268°, and <1 at >268°.

R. T.

Catalytic decomposition of alkyl chlorides.—See this vol., 604.

Vanadium and chromium catalysts for the manufacture of sulphuric acid.—See B., 1935, 268.

Iron catalysts for ammonia synthesis.—See B., 1935, 268.

Catalytic pyrolysis of methane and coal gas.—See B., 1935, 258.

Catalysis in hydrocarbon chemistry, I–III.—See B., 1935, 292.

Laboratory arrangement for electrolytic fractionation of hydrogen isotopes. III. H. ERLÉNMEYER and H. GARTNER (*Helv. Chim. Acta*, 1935, 18, 419–426; cf. A., 1934, 1325).—The further treatment of H_2O mixtures containing 3–4% of $H_2^{18}O$ is described. The $H_2^{18}O$ content, when >10%, is conveniently determined interferometrically.

F. L. U.

Electrolysis of alkali fluophosphates. J. M. GARCIA MARQUINA (*Anal. Fis. Quim.*, 1933, 31, 840–851).—Electrolysis of conc. solutions of R_3FPO_3 ($R = K, Na, \text{ or } NH_4$) yields two peracids, viz., H_2FPO_4 and $(HFPO_3)_2$; in the first the group O–OH' is attached to the P, whilst in the second the two P are linked in a chain by two O. The free acids have not been isolated. The yield, with 25% K_2FPO_3 solution, is only about 1.9% at the optimum c.d., and variations of η_{rel} have but little influence. With 25% K_2FPO_3 solution containing 30 g. per 100 c.c. of KF, and an anodic c.d. of 3 amp. per sq. cm., yields >45% are obtained at 16°; prolongation of the electrolysis reduces the yield, the quantity of monoperacid (I) diminishing first. The yield is greatly dependent on the cation, falling in the order K^+, NH_4^+, Na^+ , and in the approx. ratio 40 : 12 : 1. The peracids decompose in alkaline solution, whilst in acid solution the diperacid decomposes, in part to form (I). Electrolysis of $NH_4F_2PO_3$ produces almost exclusively a diperacid, in approx. the same yield as with $(NH_4)_2FPO_3$, which in acid solution is converted into (I).

H. F. G.

Electrometallurgy of aluminium.—See B., 1935, 362.

Preparation of thin layers of uranium oxide U_3O_8 by electrolysis. M. FRANCIS and CHENG DA-CHANG (*Compt. rend.*, 1935, 200, 1024–1027; cf. A., 1934, 387).—Electrolysis at 60° of a solution containing 0.01 g. of U_3O_8 [as $UO_2(NO_3)_2$], 2.25 c.c. of *N*-AcOH, 2 c.c. of *N*- NH_3 , and 15 c.c. of EtOH with a Pt cathode yields deposits up to 0.2 mg. per sq. cm. which are adherent after washing with EtOH and drying. These deposits can be used as radioactive standards.

J. W. S.

Calculation of the capacity of the lead accumulator.—See B., 1935, 315.

Electrolytic dehalogenation of organic compounds. I, II.—See this vol., 604.

Effect of direct current on the nitration and oxidation of toluene. R. C. KIRK and W. E. BRADT (*Trans. Electrochem. Soc.*, 1935, 67, 285–297).—Conc. HNO_3 (I) + conc. H_2SO_4 (II) + PhMe (III) were placed in the anodic compartment of a cell with a porous diaphragm and a Pt anode, and the effect of d.c. on oxidation and nitration studied mainly at 50°, with stirring. A nitration yield of 46% was increased to 48.3% by d.c. The increase in nitration yield with d.c. decreases as the concn. of (II) increases. C.d. has little influence provided current \times time is kept const. With mixtures giving >50% nitration d.c. has no influence on the nitration, but increases oxidation. Yields increase with stirring up to 600–800 r.p.m., and remain const. for higher speeds.

Mn⁺⁺, Bi⁺⁺⁺, Ce⁺⁺⁺, Hg⁺⁺, Cr⁺⁺, V⁺⁺⁺⁺, and I increase nitration, Mn⁺⁺ being the most effective. WO₃ decreases nitration, and all increase oxidation. Results are discussed in terms of a layer of very conc. (I) at the anode surface. R. S. B.

Active hydrogen. A. C. GRUBB and A. B. VAN CLEAVE (J. Chem. Physics, 1935, 3, 139—145).—Dry H₂ can be activated in an electric discharge if the pressure and voltage are carefully regulated. Active H reduces metallic sulphides having heats of formation $\geq 22,000$ g.-cal., and is decomposed by 3 cm. of well-packed glass wool. Less active H is formed if the tube is coated with stearic acid or H₃PO₄. A method of determination is given. The decay reaction follows the expression for a unimol. reaction; the decay rate is independent of wall surface; the half-val. period at room temp. and 40 mm. pressure is approx. 0.2 sec.; energy of formation is approx. 18,000 g.-cal. The energy of activation for the decay of the active constituent is approx. 17,800 g.-cal. The active form is considered to differ markedly from H or H₂. N. M. B.

Influence of the electric discharge on the region of spontaneous ignition in the mixture 2H₂-O₂. G. GORCHAKOV and F. LAVROV (Acta Physicochim. U.R.S.S., 1934, 1, 139—144).—By the use of an electric spark it is shown that the phenomenon of the second limit of inflammation is not connected with the condition of the walls of the vessel, since the limit is displaced with the change of the sparking energy and the spark occurs at a considerable distance from the walls. The mechanism of the process is still obscure, but may involve a deactivation of the active branches of a chain by triple collision. The third limit decreases with increase in sparking energy. Below 450° and a little above 500° only one limit occurs. M. S. B.

Photochemical decomposition of nitrous oxide and energy of dissociation of nitrogen. L. HENRY (Compt. rend., 1935, 200, 656—658; cf. A., 1932, 1187).—The absorption spectrum of N₂O at 0.25—4 atm. and 20—675°, using absorption thicknesses of 35—100 cm., is continuous. The absorption limit is independent of pressure and of the thickness of the absorbing layer, but moves towards longer with rise of temp., passing from 2246 Å. at 20° to 2604 Å. at 675°. The probable mechanism of the decomp. is N₂O (¹Σ) + 132,000 g.-cal. = NO (²Π) + N* (²D). The calc. heat of dissociation of N₂ is 158,000 g.-cal., in agreement with previous vals. J. W. S.

Bleach-out images by diffuse after-exposure. LUPPO-CRAMER (Z. wiss. Phot., 1935, 33, 266—272).—The solarisation produced is ascribed to the destruction of the nuclei which are in the interior of the Ag halide crystals, and are not removable by, e.g., CrO₃. The effects are studied in plates bathed in dye+KBr solution, and also in AgI emulsions. J. L.

Chlorine-sensitised photochemical oxidation of gaseous chloroform. A. T. CHAPMAN (J. Amer. Chem. Soc., 1935, 57, 416—419).—The reaction yields COCl₂ and HCl without accompanying thermal or chlorination reactions. The rate for small light absorptions \propto light intensity and [Cl₂], and is inde-

pendent of [CHCl₃] and [O₂]. The temp. coeff. is 1.44; the quantum yield is approx. 100 mols. of CHCl₃ oxidised per einstein of radiation absorbed.

E. S. H.

Peroxidation of chloroform. A. T. CHAPMAN (J. Amer. Chem. Soc., 1935, 57, 419—422).—Thermal oxidation of CHCl₃ by air yields an intermediate peroxide, which gives COCl₂ and HCl as final products. The photo-reaction differs only in an accelerated rate and a smaller yield of peroxide. The mechanism is discussed. E. S. H.

Photo-oxidation of liquid carbon tetrachloride. E. H. LYONS, jun., and R. G. DICKINSON (J. Amer. Chem. Soc., 1935, 57, 443—446).—In absence of O₂ and H₂O, CCl₄ is not decomposed by irradiation with light of λ 2537 Å. In presence of O₂ oxidation occurs, probably 2CCl₄+O₂ \rightarrow 2COCl₂+2Cl₂. Using a CH₃Cl-CO₂H actinometer, the quantum yield observed is 1 mol. of CCl₄ oxidised per quantum absorbed. E. S. H.

Effect of an electric field on a photochemical reaction. M. SUZUKI and M. VOLMER (Naturwiss., 1935, 23, 197).—That the photochemical polymerisation of anthracene (I) is a secondary effect of the inner photo-effect in (I) is shown by the fact that if an electric field of 2000—14,000 volts per cm. is applied to (I) the formation of dianthracene is completely prevented. A. J. M.

Preparation of deuterium-free water. Deuterium content of ordinary water, and the at. wt. of hydrogen. Electrolytic separation of the oxygen isotopes. H. L. JOHNSTON (J. Amer. Chem. Soc., 1935, 57, 484—486).—H₂O containing < 1 H² atom in 10⁶ H¹ atoms has been prepared by fractional electrolysis. The influence of H² on the *d* of ordinary H₂O is 19.1 \pm 1 p.p.m., corresponding with an abundance ratio of 5750 \pm 250 for H¹:H². The electrolytic separation factor for O¹⁶ relative to O¹⁸ is 1.008 \pm 0.003. From the H¹:H² ratio the at. wt. of normal H is calc. as 1.00795 on the O¹⁶ scale and 1.00770 or 1.00775 on the chemical scale. E. S. H.

Biological effects of heavy water.—See this vol., 657.

Metallic compound of lithium and ammonia. H. JAFFE (Z. Physik, 1935, 93, 741—761).—A saturated solution of Li in NH₃ (approx. 4 mol. of NH₃ to 1 of Li) solidifies at -180° to a Cu-coloured compound with metallic reflexion; the sp. resistance of the solution is 0.5 of that of Hg at room temp., and that of the solid at -190° 0.25 of the former. The saturated solution has *d* 0.48 at room temp. The Hall effect shows that at -190° there is one free electron per Li atom, and that a transition point occurs near -200°. A. B. D. C.

Sodium amalgam with iron impurity. V. LUKASCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 439—443).—Whilst Na-Hg in presence of Fe decomposes H₂O very rapidly, when Fe is introduced with Na into the amalgam the latter only takes up traces of Fe, and decomposes H₂O slowly. The energetic reaction must be due to metallic impurities adhering to the surface of the amalgam. A. J. M.

Application of differential thermal analysis to anhydrous sodium metaphosphates. A. BOULLE (Compt. rend., 1935, 200, 832—834; cf. this vol., 571).—Heating curves C_1 for room temp.—m.p. (640°) and cooling curves C_2 from just below the m.p. were obtained. For NaH_2PO_4 (A form), C_2 shows dehydration at 550—640°; for the dehydration product (A' form) at < 300° of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, C_1 shows irreversible transitions to an insol. B form at 430°, and to a sol. A form at 550—590°. The B form, obtained by heating $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ to 400—500°, passes irreversibly to the sol. A form at 525—590°. A vitreous C form crystallises sharply at 300—310°.

N. M. B.

Disodium orthoarsenate and its hydrates. A. CHRETIEN and P. GENET (Compt. rend., 1935, 200, 834—836).—Transition points in the temp.-concn. curves of the system $\text{H}_2\text{O}-\text{Na}_2\text{HAsO}_4$, investigated in the range < 0—120°, indicate the formation of the anhyd. salt and hydrated forms containing 0.5, 5, 7, and 12 H_2O . The normal b.p. of the saturated solution is 116°.

N. M. B.

Ortho-salts of oxy-acids. E. ZINTL, M. MORAWIETZ, and G. WOLTERSDORF (Naturwiss., 1935, 23, 197).—Some ortho-salts have been prepared by the action of Na_2O on the salts of oxy-acids, or on weakly acidic metallic oxides. Such salts are Na_3NO_4 , Na_3NO_3 , Na_6ZnO_4 , and Na_4CuO_3 . They are usually decomposed by H_2O or CO_2 . The co-ordination no. (I) of the anionic central atom (II) of these salts increases in general with increasing size of (II), e.g., the series Na_2CO_3 , Na_4SiO_4 , Na_4SnO_4 , Na_6PbO_6 . In the first short period (I) decreases at first, and then increases (e.g., Na_6BeO_4 , Na_3BO_3 , Na_2CO_3 , Na_3NO_4). An explanation is given.

A. J. M.

Decomposition of sodium carbonate solutions. H. LIANDER (Iva, 1934, 4, 84—89).—Data of Straub and Larson (A., 1933, 129) on the decomp. of aq. Na_2CO_3 in high-pressure steam boilers are compared graphically with those of List (Wasser, 1932, 6, 168—202), the latter being in error. CH. ABS. (e)

Complex cupric perchlorates and bromates formed with some primary amines. J. AMIEL (Compt. rend., 1935, 200, 672—674).—By the action of the respective amines on partly dehydrated $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, the following compounds have been prepared: $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_3$; $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_2\text{Me}$; $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_2\text{Et}$; $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{NH}_2 \cdot \text{CH}_2\text{Ph}$; $\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{en} \cdot \text{H}_2\text{O}$; $\text{Cu}(\text{ClO}_4)_2 \cdot 3\text{en} \cdot \text{H}_2\text{O}$; $\text{Cu}(\text{BrO}_3)_2 \cdot 4\text{NH}_3$; $\text{Cu}(\text{BrO}_3)_2 \cdot 4\text{NH}_2\text{Me}$; $\text{Cu}(\text{BrO}_3)_2 \cdot 4\text{NH}_2\text{Et}$; $\text{Cu}(\text{BrO}_3)_2 \cdot 4\text{NH}_2\text{Pr}^a$; $\text{Cu}(\text{BrO}_3)_2 \cdot 4\text{NH}_2 \cdot \text{CH}_2\text{Ph}$; $\text{Cu}(\text{BrO}_3)_2 \cdot 2\text{en} \cdot \text{H}_2\text{O}$; $\text{Cu}(\text{BrO}_3)_2 \cdot 3\text{en} \cdot \text{H}_2\text{O}$. [$\text{en} = (\text{NH}_2 \cdot \text{CH}_2)_2$]. All are blue to violet in colour and are insol. in Et_2O , C_6H_6 , and alcohols, and practically so in CMe_2 . They are decomposed with liberation of amine on warming with NaOH or KOH . Cl_2 and HCl convert the perchlorates into cupritetrachlorides, and HBr converts the bromates into cupritetrabromides (this vol., 312). All these compounds explode on heating, and data are given of the induction periods at various temp.

J. W. S.

Separation of metals from their solutions by the action of organic reducing agents under

pressure. V. I. LAINER and A. D. MAJANTZ (J. Appl. Chem. Russ., 1934, 7, 1423—1453).—Cu and Hg are obtained in practically quant. yield when the acid solutions of their salts are heated at 240° for 4 hr. with sawdust, cotton- and sunflower-seed hulls, or with other org. waste products. The method is not applicable to metals readily sol. in acid solutions, or to those yielding insol. basic salts on hydrolysis of their aq. salts.

R. T.

Ability of thiolacetic acid and its derivatives, particularly thiolacet- β -naphthylamide, to form complex metallic derivatives. R. BERG and W. ROEBLING (Ber., 1935, 68, [B], 403—407).—In mineral acid solution the complex compounds of Cu, Ag, and Au with $\text{SH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ are stable, whereas those of other metals are unstable. The colour changes in formation of the Cu compound are very characteristic. With $\text{SH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ stable compounds of Cu, Au, Ag, Hg, Sn, As, Sb, Pt, and Pd result. The compounds derived from these metals and thiolacet- β -naphthylamide (I), m.p. 111—112°, are less sol. in mineral acid and more stable towards heat. (I) can therefore be used as an analytical reagent, its sensitivity being such that Ag⁺ can be detected in the filtrates from pptd. AgCl. In AcOH, neutral, or alkaline solution other metals (e.g., Cd, Pb, Ni, Co, Mn, and Tl) are pptd., whereas in NH_3 -tartrate solution Tl alone is pptd. The determination of metals is effected by weighing the complex dried at 105°, by ignition, volumetrically (titration with I or by the filtration method), colorimetrically, or nephelometrically. (I) is readily removed from the filtrates by oxidation with I, occlusion or adsorption not being observed.

H. W.

Recovery of silver and iodine from silver iodide. J. R. SPIES (Ind. Eng. Chem. [Anal.], 1935, 7, 118—119).—AgI is converted into AgCl by treatment with aqua regia. The ICl formed simultaneously is hydrolysed to I and HIO_3 , which is reduced to I by $\text{Na}_2\text{S}_2\text{O}_4$. Ag is obtained from AgCl by dissolving in aq. NH_3 and reducing with $\text{Na}_2\text{S}_2\text{O}_4$.

E. S. H.

Hydrates of magnesium sulphate and some double salts of magnesium. E. DUCHEMIN (Bull. Soc. chim., 1935, [v], 2, 526—532; cf. A., 1934, 1158).—The influence of change of temp. on $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (I) and $\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (II) has been studied. (I) loses $5\text{H}_2\text{O}$ at 100° and $6\text{H}_2\text{O}$ at 130—135°. Progressive heating of (II) produces $\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, and their constituents, finally giving MgSO_4 above 260°. The heats of hydration and heats of dissolution of MgSO_4 , $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$ (III), and their hydrates are given. Determinations of magnetic susceptibility show, in agreement with the thermal measurements, that the first H_2O fixed by MgSO_4 is different. The addition of $6\text{H}_2\text{O}$ to (III) weakens the mol. binding, which is very feeble in (II).

R. S.

Gypsum problem from the colloid chemical viewpoint. D. BALAREV and A. KOLUSCHEVA (Kolloid-Z., 1935, 70, 288—297).—Repetition of classical work confirms that dehydration of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ by heating or at lower temp. over P_2O_5 yields CaSO_4 , which on hydration yields $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

and finally $\text{CaSO}_4 \cdot \text{H}_2\text{O}$. The spontaneous decomp. of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ has not been observed, but it is probably metastable. E. S. H.

Reduction of zinc oxide with natural gas. C. CÂNDEA and I. KUHN (Bul. Soc. Chim. Romania, 1934, 16, 121—130).—Reduction with natural gas containing 98.7% CH_4 begins at 750° and is complete at 900° . The degree of reduction (r) at 900° with a continuous stream of CH_4 passes through two max. as the streaming velocity (v) increases from 0 to 28 litres per hr. With low v CH_4 dissociates and the main reaction is $\text{ZnO} + \text{C}$ (from CH_4) = $\text{Zn} + \text{CO}$. With higher v the dissociation is less and the main reaction is $\text{ZnO} + \text{CH}_4 = \text{Zn} + \text{CO} + 2\text{H}_2$. As v increases past the second max. r remains const., since the first reaction is eliminated. The gaseous products are CO and H_2 , 1:5, the % CO_2 and H_2O being very small; no reoxidation of Zn by H_2O occurs. R. S. B.

Action of metalloids on basic oxides. M. LEMARCHANDS and (MLLE.) D. SAUNIER (Compt. rend., 1935, 200, 1041—1043; cf. A., 1934, 613).—Grinding of the reactants together, followed by heating in the absence of air and H_2O , leads to direct combination between I and HgO , CdO , CuO , or SrO . The vermilion compound HgOI_2 formed with HgO is insol. in cold H_2O , but treatment with cold Et_2O , EtOH , or COMe_2 , or hot H_2O or heating at 110 — 115° leads to decomp. into HgI_2 and $\text{Hg}(\text{IO}_3)_2$. J. W. S.

Iodomercuric acid. F. GALLAIS (Compt. rend., 1935, 200, 836—839).—Investigation of the Faraday effect for aq. and EtOH solutions of HgCl_2 and HI in various proportions indicates the formation of the unstable compound H_2HgI_4 . N. M. B.

Preparation of a new hydroxyfluoboric acid. F. J. SOWA, J. W. KROEGER, and J. A. NIEWLAND (J. Amer. Chem. Soc., 1935, 57, 454—456).—The prep. of $\text{HBF}_2(\text{OH})_2$, b.p. $159.1^\circ/745$ mm., n_D^{20} 1.3414, d_4^{25} 1.6569, surface tension at 25° 58.294 dynes per cm., is described. The chemical properties have been investigated. E. S. H.

Chemical and physical structure of the protective layer on aluminium. F. PAVELKA (Oesterr. Chem.-Ztg., 1935, 38, 39—41).—By comparison with the behaviour of a porous diaphragm with a metallised surface it is shown that the electrolytically formed protective layer (I) on Al is a porous layer of dehydrated Al_2O_3 . It is to this porosity that the capacity, internal resistance, residual current, and light phenomena of (I) are due. A chemically formed layer of $\text{Al}(\text{OH})_3$ has similar properties, but is distinguished by a much greater power of adsorption for dyes. The dehydration of the (I) is attributed to an arcing in the pores which is the probable origin of the luminosity at high potentials. There is an optimum p_H for the formation of (I). M. S. B.

Rare earths.—See this vol., 606.

Primary reaction of metal oxides with solid carbon. W. BAUKLOH and R. DURRER (Z. anorg. Chem., 1935, 222, 189—200, and Iron and Steel Inst., Carnegie Schol. Mem., 1934, 23, 1—12; cf. B., 1931,

802).—Both CO_2 and CO may be formed as primary products in the reduction of metal oxides by solid C, the proportion of the former increasing with the reducibility of the oxide. Oxides of Pb , Cu , Mn , Co , and Ni give nearly 100% of CO_2 , ZnO and SnO_2 about 40%, and SiO_2 20%. The results support the view that combustion of solid C in air leads primarily to CO . F. L. U.

[Primary processes in the oxidation of graphite.] V. SIHVONEN (Suomen Kem., 1935, 8, B, 13—16; cf. A., 1934, 978, 1082; this vol., 50).—The author's theory is restated. J. W. S.

Double salts formed by lead chloride and bromide. A. COLANT (Bull. Soc. chim., 1935, [v], 2, 545—548).—The prep. of salts $\text{PbCl}_2 \cdot \text{PbBr}_2$, $\text{PbCl}_2 \cdot \text{PbC}_2\text{O}_4$, $\text{PbCl}_2 \cdot \text{CH}_2(\text{CO}_2)_2 \cdot \text{Pb} \cdot \text{H}_2\text{O}$, and $\text{PbCl}_2 \cdot (\text{CH}_2 \cdot \text{CO}_2)_2 \cdot \text{Pb}$ is described. The compounds are dissociated by H_2O . R. S.

Basic lead chromate and its transition. H. WAGNER and H. SCHIRMER (Z. anorg. Chem., 1935, 222, 245—248).—In the formation of basic Pb chromate, by the addition of KOH to a Pb salt and K_2CrO_4 , the product changes with increasing $[\text{KOH}]$ from an orange-red (chrome-orange) through a pure red (chrome-red) homogeneous product to an orange-red heterogeneous mixture. The first two are the same cryst. tetragonal basic chromate, $\text{PbO} \cdot \text{PbCrO}_4$ (I), the difference in colour being due to a difference in size of crystal. The third appears to be a mixture of red (I) with yellow PbO . If (I) is kept in the mother-liquor in contact with air a light yellow double salt, $\text{K}_2\text{CO}_3 \cdot \text{PbCrO}_4$, is formed and, by the action of $\text{Ca}(\text{OH})_2$, may be changed into (I) again. M. S. B.

Action of ammonia on the tetrameride of phosphorus dichloronitride. A. M. DE FICQUELMONT (Compt. rend., 1935, 200, 1045—1047; cf. A., 1934, 615).—Passage of dry NH_3 through an Et_2O solution of $(\text{PNCl}_2)_4$ (I) yields a ppt. of NH_4Cl and a solution containing an unidentified compound (II), the compound $\text{P}_4\text{N}_4\text{Cl}_6(\text{NH}_2)_2$ (III), and the compound $\text{P}_4\text{N}_4\text{Cl}_4(\text{NH}_2)_4$ (IV). (II) is removed by solution in light petroleum and (III) and (IV) separated by fractionation from C_6H_6 solution. (III) forms white clinorhombic prisms, m.p. 217 — 218° , which distil in a vac. at 150 — 200° or in air at 250° with partial decomp. (IV), m.p. 161 — 162° , quadratic, is sparingly sol. in ordinary solvents; it is stable below 80° , but decomposes about 150° yields the insol. and infusible compound $\text{P}_4\text{N}_4\text{Cl}_2(\text{NH}_2)_2(\text{NH})_2$. Prolonged action of NH_3 on (I) in Et_2O yields the white compound $\text{P}_4\text{N}_4(\text{NH}_2)_8$ which decomposes when heated yielding PN_2H . NH_3 also reacts with pure $(\text{PNCl}_2)_4$ at 150 — 200° , yielding successively (II), (III), and (IV), and finally PN_2H . On further heating at 750° P_3N_5 is produced (80% yield). J. W. S.

Oxidation of nitrogen. V. A. KARSHAVIN (J. Gen. Chem. Russ., 1934, 4, 1193—1196).—Piankov's view that NO is oxidised directly to N_2O_3 when present in low concns. (A., 1934, 161) is not supported by his figures, which point to $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. R. T.

Oxidation of nitric oxide at low pressures. M. TEMKIN and V. PUZHOV (*Acta Physicochim. U.S.S.R.*, 1934, 1, 177).—At liquid-air temp. and 10^{-2} mm. pressure the half time of reaction of $\text{NO} + \text{O}_2$ on the glass or paraffin walls was approx. 1 min. No reaction was observed at -112° and -78° .

CH. ABS. (c)

Direct synthesis of nitrates at ultra-pressures. J. BASSET and M. DODE (*Compt. rend.*, 1935, 200, 744—746).—Using mixtures of N_2 and O_2 containing 33% of O_2 , and a pressure of 3600 kg., it is possible to transform CaO , BaO , or mixtures of BaO and KOH into nitrates at comparatively low temp. At 500° the reaction is very slow, but a good yield can be obtained in 2 hr. at 800 — 900° . M. S. B.

Blue flame in the system nitrogen pentoxide-ozone. T. M. LOWRY and J. T. LEMON (*Nature*, 1935, 135, 433).—When dry N_2O_5 is vaporised in a stream of ozonised O_3 , and then passed through a glass tube heated by a small flame, the colourless gas becomes brown, owing to the formation of NO_2 , a short distance before the flame is reached. A narrow dark greyish-blue zone hovers at the boundary and is preceded by a zone of clear blue. In a long tube, the blue flame strikes back under certain conditions. The formation and disappearance of the blue zone may be due to the production and decomp. of a higher N oxide, possibly NO_3 . L. S. T.

Reduction of mixed oxides. K. GRASSMANN and E. J. KOHLMAYER (*Z. anorg. Chem.*, 1935, 222, 257—278).— V_2O_5 , Nb_2O_5 , Ta_2O_5 , and CeO_2 are more readily reduced when mixed with NiO than alone. Reduction takes place above 1380° in a current of H_2 . Some of the oxide always remains, and, above a certain limiting proportion of oxide to NiO , no further increase in reduced metal can be obtained. The limit is reached at the mol. proportions $3\text{Ni} : 3\text{V}$, 2Nb , or Ta . Addition of a third easily reducible metal oxide, such as WO_3 or MoO_3 , improves the yield. ≈ 1 —3% reduction of ZrO_2 or SiO_2 is observed, even in ternary mixtures. The degree of intermixing of the oxides and the extension of time of heating beyond 1 hr. have no influence. The addition of C_6H_6 to the H_2 improves the yield, but, beyond a certain concn., causes a separation of carbide. The replacement of Ni by Cu , which has a smaller solvent power for H_2 than Ni , reduces the yield, as also does the replacement of NiO by Ni . The metals of which the oxides appear to be most easily reducible in presence of NiO are also those which most readily form mixed crystals with Ni . Solvent power for H_2 runs parallel with reducibility of the oxides; Zr is an exception. M. S. B.

[Preparation of protoactinium.] O. HAHN (*Ber.*, 1935, 68, [B], 478—479).—Comments on the publication of von Grosse (this vol., 460). H. W.

Fractionation of oxygen isotopes in an exchange reaction. L. A. WEBSTER, M. H. WAHL, and H. C. UREY (*J. Chem. Physics*, 1935, 3, 129).—The equilibrium const. at 0° of the reaction $2\text{H}_2\text{O}^{18} + \text{CO}_2^{16} = \text{H}_2\text{O}^{16} + \text{CO}_2^{18}$ is calc. to be 1.097, leading to a fractionation factor 1.047. This val. is confirmed by experiments in which CO_2 was passed through spirals

of H_2O , then mixed with H_2 and reduced on a Ni catalyst, the d of the resulting H_2O being measured.

F. L. U.

Sulphur monoxide. V. Reaction and mol. wt. of sulphur monoxide. P. W. SCHENK and H. PLATZ (*Z. anorg. Chem.*, 1935, 222, 177—188; cf. this vol., 51).—The pressure change observed when SO (prepared by the action of a high-potential arc on a mixture of S vapour and SO_2 at reduced pressure) is decomposed into S and SO_2 indicates that 64% of SO mols. are associated to $(\text{SO})_2$. With H_2O at 0° , SO gives S'' , SO_3'' , and S; with aq. KOH , S'' , SO_3'' , and smaller quantities of $\text{S}_2\text{O}_3''$; and with NaOEt-EtOH , SO_3'' , and S'' in the proportion required by $3\text{SO} + \text{H}_2\text{O} = 2\text{SO}_2 + \text{H}_2\text{S}$. These reactions afford ground for rejecting the theory that SO is an intermediate product in the formation of polythionic acids from aq. SO_2 and H_2S or from $\text{Na}_2\text{S}_2\text{O}_3$ and mineral acids. F. L. U.

Reduction of selenium dioxide by carbon monoxide. E. BARNES (*J. Indian Chem. Soc.*, 1935, 12, 22).—A slow reduction occurs above 250° . Ultra-violet light is without effect at room temp.

R. S.

Telluric acids. P. PASCAL and M. PATRY (*Compt. rend.*, 1935, 200, 708—711).—By heating orthotelluric acid (I) in a sealed tube at different temp. for different lengths of time indications of the presence of allotelluric acid (II) are already observed at 100° . A product containing 90% of (II) may be prepared by heating at 150° for 12 min., thus avoiding the formation of colloidal condensed products. In aq. solution (II) is gradually retransformed into (I). The change, which has been observed cryoscopically, is accelerated by increase of p_H . The conductometric neutralisation curve has a min. at $\text{Na} : \text{Te} = 0.1$ after correcting for (I) and could be used for the determination of (II) in a mixture. Differences between the results of cryoscopic and conductometric observations suggest that (II) is not a single individual. It apparently contains a strongly acid condensed constituent. It easily loses H_2O in a vac. or at 80° , and H_2TeO_4 is formed at 120° . (II) can be extracted from a mixture of (I) and metatelluric acid by HNO_3 . M. S. B.

Polonium. I. Compounds of bivalent polonium. V. G. CHLOPIN and A. G. SAMARTSEVA (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 4, 433—439).—The isomorphism of Po^{II} and Te^{II} salts is made use of. The prep. of Na_2Te containing Po is described. The distribution coeff. of Po between the crystals of Na_2Te and the mother-liquor is const., indicating that a compound Na_2Po , aq. exists, and is isomorphous with Na_2Te . The compound $\text{Po}(\text{CH}_2\text{Ph})_2$ is isomorphous with $\text{Te}(\text{CH}_2\text{Ph})_2$. PoMe_2 has been synthesised. A. J. M.

Rhenium oxythiocyanate. J. G. F. DRUCE (*Rec. trav. chim.*, 1935, 54, 334—335).— $\text{ReO}(\text{CNS})_4$ (I) has been prepared by mixing a HCl solution of KReO_4 and KCNS with an acid solution of SnCl_2 . The deep red solution is extracted with Et_2O , from which dark red crystals are obtained. (I) softens on heating and emits a garlic odour, is sol. in H_2O , EtOH , COMe_2 , Et_2O , C_6H_6 , and $\text{C}_5\text{H}_{11}\text{OH}$, but

not in glacial AcOH. Partial hydrolysis occurs in H_2O , giving a brown deposit. Zn and HCl give with (I) ReO_2 ; Na_2O_2 converts (I) into NaCNS and NaReO_4 . On mixing aq. (I) with $\text{C}_5\text{H}_5\text{N}$, HCl and KCNS a dark red oily substance, $(\text{C}_5\text{H}_5\text{N}, \text{HCNS})_2, \text{ReO}(\text{CNS})_4$, dried over $\text{Mg}(\text{ClO}_4)_2$, separates. With quinoline red $(\text{C}_5\text{H}_5\text{N}, \text{HCNS})_2, \text{ReO}(\text{CNS})_4$ is similarly prepared.

R. S. B.

Complex salts of bivalent cobalt. J. MEYER and K. HOENNE (Z. anorg. Chem., 1935, 222, 161—166).—The following salts are described:

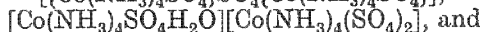
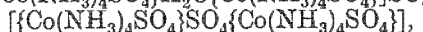
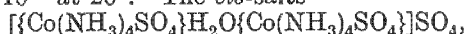
$\text{Li}_4\text{CoBr}_6, 12\text{H}_2\text{O}$; $\text{en}_2\text{H}_4\text{CoCl}_6$; $\text{en}_2\text{H}_4\text{CoBr}_6$; $\text{en}_2\text{H}_4\text{CoI}_6$. All are blue and very sol. in H_2O .

F. L. U.

Hydrazinates of metallic thiosulphates. P. RAY and A. K. MAZUMDAR (J. Indian Chem. Soc., 1935, 12, 50—52).—Co, Ni, Zn, and Cd thiosulphates give hexaco-ordinated hydrazinates: $[\text{Co}(\text{N}_2\text{H}_4)_3]\text{S}_2\text{O}_3$, light yellow; $[\text{Ni}(\text{N}_2\text{H}_4)_3]\text{S}_2\text{O}_3, 0.5\text{H}_2\text{O}$, pink; $[\text{Zn}(\text{N}_2\text{H}_4)_3]\text{S}_2\text{O}_3$; $[\text{Cd}(\text{N}_2\text{H}_4)_3]\text{S}_2\text{O}_3$. NiS_2O_3 also gives a light blue tetraco-ordinated compound $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{S}_2\text{O}_3, 1.5\text{H}_2\text{O}$.

R. S.

Tetrammine complexes of trivalent cobalt. (MLLE.) M. G. TER HORST (Rec. trav. chim., 1935, 54, 257—274).—*cis*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3, 2.2\text{H}_2\text{O}$ (I) and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2(\text{SO}_4)_3, \text{H}_2\text{O}$ (II) have been prepared and their solubility and conductivity in H_2O determined. The hydrolysis const. for (II) is 10^{-3} — 10^{-2} at 20° . The *cis*-salts



$[\text{Co}(\text{NH}_3)_4\text{SO}_4\text{H}_2\text{O}]_2\text{SO}_4$ have been identified, but the *trans*-salts could not be obtained pure. In solution (II) is slowly converted into *cis*. *cis*- and *trans*- (impure) $[\text{Co}(\text{NH}_3)_4\text{OH}(\text{H}_2\text{O})\text{SO}_4$ and their polymerides have been prepared. In disagreement with Jorgensen the speed of transformation of *trans* \rightarrow *cis*-aquo-chloro-cobalt tetrammines is of the same order as for the sulphates (I) and (II). Jorgensen's method of identifying *cis*- and *trans*-isomerides is inexact, since nitrito-compounds are formed as intermediates, and these become *cis* and *trans* in acid and alkaline media, respectively, the nature of the final product depending on the medium. R. S. B.

Reduction of ammonium ruthenate: alkali tetra-halogen ruthenium compounds. (FRL.) M. BUIVIDAITE (Z. anorg. Chem., 1935, 222, 279—284).—The compound $\text{NH}_4\text{RuCl}_4, 2\text{H}_2\text{O}$ has been prepared by the reduction of NH_4 ruthenate with SnCl_2 . The salt is stable and loses H_2O at 220 — 230° only, and NH_3 above 230° . Three only of the atoms of Cl can be removed by AgNO_3 . By pptn. with RbCl or CsCl the compounds $\text{RbRuCl}_4, 4\text{H}_2\text{O}$ and $\text{CsRuCl}_4, 5\text{H}_2\text{O}$, respectively, have been obtained. The latter, when dried at 100° , loses 1 mol. of H_2O . The salts are very stable aquo-salts. M. S. B.

Magneto-optic method of chemical analysis. H. G. MACPHERSON (Physical Rev., 1935, [ii], 47, 310—315).—Sharp min., characteristic of the substance investigated, as reported by Allison (cf. *ibid.*, 1932, [ii], 40, 1052) are not confirmed. N. M. B.

Equivalence point in acid-base titrations, and effect of electrolytes. S. KILPI (Z. physikal. Chem.,

1935, 172, 277—299).—Equations for the stoichiometrical equivalence point, P , have been derived, taking as P the point at which the sum of the concns. of free acid and base is a min. It is deduced that in potentiometric titration the end-point, E , is independent of the electrolyte concn., c , if one reactant is strong and the dissociation const. of the other $>10^{-8}$. The H^+ activity at P , however, depends on c , particularly if only one reactant is weak. In the potentiometric titration of AcOH with NaOH or NH_3 , and of HCl with NH_3 , E is independent of c . R. C.

Salt error of indicators in acid-base titration.

S. KILPI and A. LAAKSONEN (Suomen Kem., 1935, 8, B, 9—10).—No change in end-point could be detected with varying electrolyte concn. in HCl-aq. NH_3 titrations, using Me-red as indicator. The amount of NaOH required for titration of AcOH with phenolphthalein as indicator increases with $[\text{NaOAc}]$ at low concn., but diminishes at higher $[\text{NaOAc}]$. NaCl does not affect the end-point appreciably. The NH_3 consumed in titration of AcOH with bromothymol-blue as indicator is too low at low $[\text{NH}_4\text{OAc}]$, but is correct in presence of appreciable $[\text{NaCl}]$ or $[\text{NH}_4\text{OAc}]$.

J. W. S.

Determination of p_H with indicator papers by Holl's method. H. A. FREYE (Chem.-Ztg., 1935, 59, 278).—Indicator papers cover the range p_H 1—14. The colours produced are matched against standards.

E. S. H.

Use of colour indicators for the measurement of the p_H of strongly coloured and viscous substances. F. TODT (Chem. Fabr., 1935, 8, 90—91).—Suitable indicators and a colour scale are described for determining the p_H of coloured or viscous solutions by the drop method within the range p_H 1.2—9.6.

A. R. P.

Reaction between hydrogen peroxide and cerous hydroxide. A. LAWSON and E. W. BALSON (J.C.S., 1935, 362—365).— H_2O_2 is rapidly absorbed by a suspension of $\text{Ce}(\text{OH})_3$ at p_H 5.8—9.0, but determinations by earlier methods gave low results with small quantities of H_2O_2 . The total oxidising power of the H_2O_2 remains in the solution, but is distributed as Ce^{IV} and H_2O_2 , the former increasing and the latter correspondingly decreasing with time, probably as follows: (1) $\text{Ce}(\text{OH})_3 + \text{H}_2\text{O}_2 = \text{Ce}(\text{OH})_2\text{O} \cdot \text{OH} + \text{H}_2\text{O}$ (complete in 3 min. at 25°), (2) $3\text{Ce}(\text{OH})_2\text{O} \cdot \text{OH} + \text{H}_2\text{O} = 2\text{Ce}(\text{OH})_3\text{O} \cdot \text{OH} + \text{Ce}(\text{OH})_3$ (15 min.), (3) $\text{Ce}(\text{OH})_3\text{O} \cdot \text{OH} + 2\text{Ce}(\text{OH})_3 + \text{H}_2\text{O} = 3\text{Ce}(\text{OH})_4$ (slow). The mixture is acidified with H_2SO_4 , and from the O_2 liberated, $2\text{Ce}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 = \text{Ce}_2(\text{SO}_4)_3 + \text{O}_2 + \text{H}_2\text{SO}_4$, and the excess of H_2O_2 (determined by excess of KMnO_4 and back titrating iodometrically) or Ce^{IV} (determined iodometrically) remaining in solution, the proportions of H_2O_2 and Ce^{IV} in the suspension are deduced. $2-8 \times 10^{-5}$ g.-mol. of H_2O_2 in 25 c.c., with 25 c.c. of 0.03N- $\text{Ce}_2(\text{SO}_4)_3$ at p_H 5.8—9.0, is determined with an error $< \pm 3\%$ provided > 6 hr. elapse before acidification.

J. G. A. G.

Rapid test for chlorate ion. Qualitative and approximately quantitative test especially suitable for work with plant extracts. H. R. OFFORD (Ind. Eng. Chem. [Anal.], 1935, 7, 93—95).—The test is based on the yellow coloration produced when

a test paper impregnated with NH_4CNS is oxidised by ClO_3^- . 0.01 mg. per c.c. of NaClO_3 can be detected. A similar coloration is produced by halogens, BrO_3^- , IO_3^- , hypohalites, $\text{S}_2\text{O}_8^{2-}$, peroxides, and Cu^{++} .

E. S. H.

Use of artificial radioactive elements as indicators in chemical investigations. A. V. GROSSE and M. S. AGRUSS (J. Amer. Chem. Soc., 1935, 57, 591—592).—The exchange of Br atoms between free Br and NaBr dissolved in H_2O has been demonstrated by using radio-Br.

E. S. H.

Volumetric determination of iodine in mercury compounds. Evaluation of reagents containing $[\text{HgI}_2]'$. D. KOSZEGI and N. TOMORI (Z. anal. Chem., 1935, 100, 257—259).—The sample is boiled with $\text{KOH} + 40\%$ aq. CH_2O . The solution is diluted to 100 c.c., and filtered from reduced Hg. An aliquot portion is neutralised (phenolphthalein), and its I' content determined with AgNO_3 or (in presence of Cl or Br) iodometrically.

J. S. A.

Colorimetric determination of small quantities of iodide in presence of other halides. A. C. BOSE and K. N. BAGCHI (Analyst, 1935, 60, 80—82).—I is liberated by HNO_3 , extracted with CCl_4 , and determined colorimetrically. Results of determinations in presence of F' , Cl' , and Br' are given.

E. C. S.

Determination of iodides in presence of bromides and chlorides by potentiometric titration. S. K. TSCHIRKOV and A. I. SCHPIKELMAN (J. Appl. Chem. Russ., 1934, 7, 1511—1518).—The solution is electro-titrated with $\text{Cl}_2\text{-H}_2\text{O}$, when the first rise in potential corresponds with completed titration of I' , and the second with that of Br' ; owing, however, to side reactions, the titration of Br' in presence of I' is not trustworthy.

R. T.

Colorimetric determination of traces of fluorine. L. SZEGOE and B. CASSONI (Chimica e l'Ind., 1935, 17, 81—82).—Geremia's statement that it is possible to obtain a linear relationship between the amount of F in a solution and the diminution in colour of peroxidised Ti solution by maintaining the ratio $\text{TiO}_2:\text{F}$ at the val. 8:1 (Atti Accad. Sci. Padova, 1934) is erroneous (cf. A., 1908, ii, 426; 1934, 380). The reaction depends on the formation of TiO_2F_2 , not Ti_2F_6 .

T. H. P.

Determination of fluorine in sulphuric acid and oleum.—See B., 1935, 354.

[Detection of] fluorine in drinking water.—See B., 1935, 384.

Detection of minimal quantities of oxygen by extinction of phosphorescence. H. KAUTSKY and A. HIRSCH (Z. anorg. Chem., 1935, 222, 126—134; cf. A., 1932, 213).—The phosphorescence of certain substances (trypanflavin, euchrysin 3R, and uranin are suitable) adsorbed in SiO_2 gel is quenched by O_2 at very small partial pressures, e.g., 0.0005 mm. Detailed operating conditions are given. F. L. U.

Fluorescence of gaseous acetone as a test for traces of oxygen. G. H. DAMON (Ind. Eng. Chem. [Anal.], 1935, 7, 133—134).—The fluorescence test is sensitive to approx. 1 micromol. of O_2 ; it is adaptable

to the determination of traces of O_2 in other gases, but is not recommended for quantities of O_2 large enough to be accurately determined by the Hempel method.

E. S. H.

Determination of sulphur dioxide in air.—See B., 1935, 335.

Potentiometric determination of sulphite. G. SPACU and C. DRAGULESCU (Z. anal. Chem., 1935, 100, 259—263).—0.1N- AgNO_3 is titrated potentiometrically in an inert atm. in 60—70% aq. EtOH with the SO_3^{2-} solution; Ag_2SO_3 is screened from light.

J. S. A.

Mechanism of precipitation processes. XVI. BaSO_4 containing KMnO_4 . Z. KARAOGLANOV (Z. anorg. Chem., 1935, 222, 249—256).—Pptn. of BaSO_4 in presence of KMnO_4 under different conditions gives results which appear to show that KMnO_4 forms a crystal lattice with the BaSO_4 , but that a portion is probably distributed at random through the BaSO_4 lattice. This explains the protective action of BaSO_4 for KMnO_4 against the action of reducing agents, solvents, and heat. The quantity of KMnO_4 taken up increases if the crystallisation of BaSO_4 is slow. KMnO_4 is not only pptd. together with BaSO_4 , but is also adsorbed if BaSO_4 is kept in a solution of KMnO_4 . The presence of KCl , KNO_3 , and HNO_3 reduces the amount of KMnO_4 taken up, probably owing to the formation of secondary pptn. products containing these compounds, thus reducing the amount of free BaSO_4 .

M. S. B.

Calcium hypochlorite as a volumetric oxidising agent. Stability and standardisation of the solution. Determination of ammonia. I. M. KOLTHOFF and V. A. STENGER (Ind. Eng. Chem. [Anal.], 1935, 7, 79—81).—Solutions of " H.T.H. " $\text{Ca}(\text{OCl})_2$ are stable in the dark and may be standardised against As_2O_3 , using Bordeaux as indicator. The determination of NH_3 (0.5—20 mg.) by $\text{Ca}(\text{OCl})_2$ is described. The solution may be converted into $\text{Ca}(\text{OBr})_2$ by adding excess of NaBr.

E. S. H.

Determination of albuminoid ammonia in drinking water.—See B., 1935, 384.

Accurate determination of nitrates. R. MEURICE and P. MARTENS (Ann. Chim. Anal., 1935, [iii], 17, 92—93).—Reduction with Devarda's alloy is the most accurate method.

J. S. A.

Determination of nitrite, especially in preserving salts.—See B., 1935, 304.

Determination of nitrogen and phosphorus in Kjeldahl's decomposition using selenium. K. TAUFEL, H. THALER, and K. STARKE (Angew. Chem., 1935, 48, 191—192).—Kjeldahl's reaction proceeds much faster when Se is used as catalyst than with K_2SO_4 or CuSO_4 , and % N or P is not influenced. N and P may be determined on the same decomp. product. 1.5—4 g. of substance is heated with 20 c.c. of conc. H_2SO_4 and 0.1 g. of Se until colourless or almost so. The product is diluted to 250 c.c., two portions of 100 c.c. of this solution are neutralised by KOH using phenolphthalein, and P is determined in the usual way; two portions of 20 c.c. are used for determining N.

R. S. B.

Mechanism of catalysis by sulphur analogues (Se and Te) in determination of nitrogen by oxidation with sulphuric acid. V. V. ILLARIONOV and N. A. SOLOVJEVA (*Z. anal. Chem.*, 1935, **100**, 328—343).—The catalytic effect of Se \propto the amount of Se present and is due to the oxidising action of H_2SeO_3 formed by reaction of Se with H_2SO_4 . H_2SeO_3 has twice the catalytic activity of Se. Loss of N on prolonged heating is due to the decomp. $3(\text{NH}_4)_2\text{SeO}_3 = 9\text{H}_2\text{O} + 2\text{NH}_3 + 3\text{Se} + 2\text{N}_2$, and \propto the amount of Se and the temp. of heating (*i.e.*, is increased by addition of K_2SO_4). Te and H_2TeO_3 also catalyse the oxidation, but less actively than Se. No loss of N occurs with Te. J. S. A.

Determination of phosphorus in drinking water.—See B., 1935, 384.

Step-photometric determination of phosphorus by the method of Fiske and Subbarow. F. ROTH-SCHILD (*Helv. Chim. Acta*, 1935, **18**, 245—247).—The step-photometer gives results of about the same accuracy as is obtained in the colorimetric method. A curve showing the extinction coeff. is given for solutions containing > 0.05 mg. of P. F. L. U.

Sources of error in determining phosphoric acid by the citrate method.—See B., 1935, 304.

Marsh-Liebig method for detecting arsenic. G. LOCKEMANN (*Angew. Chem.*, 1935, **48**, 199—203).—Modified apparatus and technique are described for determining 10^{-5} to 10^{-7} g. As. For the preliminary destruction of org. matter the customary hard-glass Kjeldahl flasks may yield small amounts of As. SiO_2 flasks are recommended. When present in a large vol. of liquid, As is pptd. by means of Fe alum-aq. NH_3 . A. G. P.

[Rapid] test for absence of arsenic. T. VON FELLEBERG (*Mitt. Lebensm. Hyg.*, 1935, **25**, 318—322).—0.1 g. of sample is oxidised with 1.5 c.c. of H_2SO_4 and HNO_3 and/or H_2O_2 and is then distilled with 2.5 c.c. of HNO_3 , 0.25 g. of cryst. FeSO_4 , and 0.02 g. of KBr; aq. H_2S is added to the distillate. The liquid is filtered until clear and the colour remaining on the paper is matched against those on papers which have been used to filter 0.03—0.3% solutions of K_2CrO_4 . The min. amount matchable is 10^{-5} g. of As. Results are given for acids, metals, and old and modern artificial pigments containing 0—3.25 mg. per g., and for ceramic wares (*cf.* A., 1930, 799, 1198). J. G.

Micro-determination of silicon and phosphorus in aluminium.—See B., 1935, 273.

Determination of silicon, titanium, vanadium, and chromium in cast iron.—See B., 1935, 358, 359.

Separation and detection of cyanide. L. J. CURTMAN and S. M. EDMONDS (*Ind. Eng. Chem. [Anal.]*, 1935, **7**, 121—122).—HCN is displaced by an air stream and detected by the Prussian-blue test. The method is sensitive to 0.2 mg. CN' and is applicable in presence of $\text{Fe}(\text{CN})_6'''$, $\text{Fe}(\text{CN})_6'''$, CNS', CO_3'' , SO_3'' , $\text{S}_2\text{O}_3''$, or S. E. S. H.

Determination of atmospheric carbon dioxide.—See B., 1935, 288, 335.

Simultaneous determination of carbon and sulphur in ferrous alloys.—See B., 1935, 272.

Silver xanthates. R. F. MAKENS (*J. Amer. Chem. Soc.*, 1935, **57**, 405—406).—Xanthates are determined in aq. solutions by adding excess of 0.1N- AgNO_3 and titrating back with KCNS. The ppt. formed in presence of excess of Ag' contains $\text{AgS}\cdot\text{CO}_2\text{Et}$ and Ag_2S . E. S. H.

Determination of alkalis by Lawrence Smith's method. W. VAN TONGEREN (*Chem. Weekblad*, 1935, **32**, 224—225).—Improvements in technique are described. D. R. D.

Detection of potassium with "Gardinol W." B. REICHERT (*Arch. Pharm.*, 1935, **273**, 232—233).—2.5 c.c. of 0.1N-KBr must be added to 0.3 g. of NaCl in 10 c.c. of H_2O before a ppt. is obtained with "Gardinol W." This test is thus $< 1/5$ as sensitive as that with cobaltinitrite. R. S. C.

Argentometric determination of sodium sulphide and sodium hydrosulphide in mixtures. N. A. TANANAEV and J. N. KREMER (*Z. anal. Chem.*, 1935, **100**, 271—273).—To the solution of $\text{Na}_2\text{S} + \text{NaSH}$, excess of AgNO_3 is added. Ag_2S is pptd. and HNO_3 equiv. to the NaSH is liberated. NaCl is added to ppt. the excess of Ag, and free HNO_3 titrated with NaOH. The excess of Ag is titrated back on a second sample. J. S. A.

Analysis of technical sodium fluoride.—See B., 1935, 268.

Little-known reactions in qualitative inorganic analysis. L. SZNAJDER (*Przemysl Chem.*, 1935, **19**, 13—18).—A no. of tests for Ag', Pb'', Bi''', Cu'', As''', Sb''', Sn'', Zn'', Mn'', Cr'', Fe'', Ni'', Co'', Al'', Ca'', Mg'', Na'', SO_4'' , SO_3'' , BO_3''' , I', CN', and CNS' are described. R. T.

Gravimetric determination of calcium as oxalate. H. SIBELIUS (*Suomen Kem.*, 1935, **8**, A, 25—27).—The Goy-Brunek method of determination of Ca as CaC_2O_4 (A., 1933, 1024) is trustworthy. J. W. S.

Spectrum-analytical determination of magnesium, manganese, silicon, and iron in duralumin.—See B., 1935, 361.

Colour reactions in the micro-chemical determination of minerals. J. A. WATSON (*Min. Mag.*, 1935, **24**, 21—34).—Characteristic colour reactions for 37 elements are described and tabulated. The method is based on that of Feigl ("Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1931). L. J. S.

Electro-analytical determination of zinc in presence of iron. R. WIENER [with F. KAISER] (*Z. Elektrochem.*, 1935, **41**, 153—158).—Experiments with acid, simple alkaline, and complex cyanide baths, using cathodes of Cu on Pt, Ag on Pt, or Hg on brass, show that quant. results are not obtained. The Zn deposit is contaminated with Fe, especially in acid solutions with Hg electrodes, and least in complex cyanide solutions. Previous claims for quant. separation are traced to the fortuitous compensation of different errors. For the electro-

determination of Zn the previous removal of Fe is recommended. E. S. H.

Quinaldinic acid as analytical reagent. II. Determination of zinc in presence of iron, aluminium, uranium, beryllium, and titanium. P. RAY and A. K. MAJUNDAR (*Z. anal. Chem.*, 1935, 100, 324—327, cf., A., 1934, 270).—Zn, but not Fe^{III} , Al, U, Be, or Ti, is pptd. from slightly alkaline solutions in presence of Na K tartrate (I) by quinaldinic acid (II). Fe^{II} is oxidised to Fe^{III} , 2—3% of (I) is added, and then NH_4Cl . The solution is neutralised with NH_3 , using Me-red + methylene-blue as indicator; excess of NH_3 must be avoided. Zn quinaldinate is then pptd. by (II), and dried at 125° . Low results are obtained in presence of Cr. J. S. A.

Volumetric determination of zinc in magnesium and its alloys.—See B., 1935, 272.

Determination of lead in solutions of basic lead acetate. M. DOMINIKIEWICZ and M. KIJEWSKA (*Spraw. Prac. dzia. Chem.*, 1933, No. 2, 7 pp.; *Chem. Zentr.*, 1934, ii, 2716).—The Pb solution is titrated with aq. $\text{K}_2\text{Cr}_2\text{O}_7$ (7.365 g. per litre, with addition of sufficient aq. NH_3 to give a yellow colour), using benzidine as external indicator (0.5 g. in 25 c.c. of EtOH and 5 c.c. of AcOH). Liq. plumbi acetici is titrated as above after addition of dil. AcOH and dilution. H. J. E.

Potentiometric determination of copper with sodium sulphide. C. PRASAD and J. B. JHA (*J. Indian Chem. Soc.*, 1935, 12, 1—3).—The determination is best carried out in buffered solutions of p_{H} 3—5. R. S.

Determination of small amounts of copper in rocks. A. W. GROVES (*Min. Mag.*, 1935, 24, 35—41).—The colorimetric method with Na diethyldithiocarbamate (A., 1930, 53) is applied to silicate igneous rocks. The rock is decomposed with $\text{HF} + \text{H}_2\text{SO}_4$ and special precautions are taken to remove Fe before applying the test. The method has a range of 0.001—0.25% CuO with samples of 2 g. L. J. S.

Determination of copper in steel.—See B., 1935, 360.

Application of the benzidine complexes to quantitative analysis. J. BARCELO (*Anal. Fis. Quim.*, 1934, 32, 91—104).—Details are given of the determination of Hg^+ , Cu^+ , Cd^+ , and Zn^+ by pptn. of the respective complexes formed with benzidine (I); the method cannot be used for Pd, as one complex is sol. and the other cannot be filtered, or for Ag, Au, Pb, Pt, or metals yielding easily hydrolysed salts (Sn, Bi, etc.). Cu and Hg may be separated by pptg. the latter as the complex chloride, removing the excess of (I) as sulphate, and pptg. the Cu with NaOH at the b.p.; the max. error is about 0.5%. H. F. G.

Microchemical detection of mercury in food-stuff and toxicological analysis.—See B., 1935, 284.

Sensitive reagent for aluminium. Separation of aluminium and beryllium. T. GASPAR Y ARNAL (*Ann. Chim. Analyt.*, 1935, [iii], 17, 89—91).—A 2% solution of $\text{Ca}_3\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$ (I) in approx. 40% aq. EtOH gives a ppt. with 0.02 mg. of Al per c.c.

Al may be so determined nephelometrically, or by adding excess of (I) and titrating back with KMnO_4 . Be does not give a ppt. with (I) in dil. solution. J. S. A.

Spectrophotometric determination of manganese in steel.—See B., 1935, 272.

Separation of manganese on the mercury cathode. V. M. ZVENIGORODSKAJA (*Z. anal. Chem.*, 1935, 100, 267—271).—Mn is deposited on the Hg cathode to the extent of 10—30% of the total Mn in solution. The amount deposited is increased by the presence of reducing agents, but is independent of the time of electrolysis. Mn can therefore not be separated either from the metals quantitatively deposited on Hg, or from the baser metals. J. S. A.

Assay of reduced iron.—See B., 1935, 359.

Electrometric analysis of ferrous sulphate solutions. N. A. SCHISCHAKOV (*Analyst*, 1935, 60, 83—86; cf. A., 1932, 575).— Fe^{III} in a mixture of Fe^{II} and Fe^{III} can be determined to within 0.1—0.2% by ascertaining the oxidation-reduction potential by means of a rotating Pt electrode. E. C. S.

Determination of ferrocyanide by means of dichromate; internal indicator method. II. F. BURRIEL and F. SIERRA (*Anal. Fis. Quim.*, 1934, 32, 87—90).—Determination of $\text{Fe}(\text{CN})_6^{\text{IV}}$ with $\text{K}_2\text{Cr}_2\text{O}_7$ yields results which vary irregularly with the of the solution. Accurate results are obtained by using a $\text{K}_2\text{Cr}_2\text{O}_7$ solution containing the optimum quantity of HCl, as determined by preliminary experiments under the conditions obtaining; thus for 30 c.c. of approx. 0.1N- $\text{K}_4\text{Fe}(\text{CN})_6$, 0.02N- $\text{K}_2\text{Cr}_2\text{O}_7$ containing 150 c.c. of 2N-HCl per litre should be used. This method is not satisfactory for the indirect determination of Zn, i.e., by pptn. with $\text{K}_4\text{Fe}(\text{CN})_6$ and titration of the excess; it is necessary to use more conc. $\text{K}_4\text{Fe}(\text{CN})_6$ (30 g. per litre) and $\text{K}_2\text{Cr}_2\text{O}_7$ (2.95 g. per litre) solutions, when the determinations are influenced but little by p_{H} , and to perform a blank with a known quantity of Zn. H. F. G.

Employment of potassium ferrocyanide in standardisation of dilute potassium permanganate. E. J. DE BEER and A. M. HJORT (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 120—121).—0.01N- KMnO_4 can be conveniently standardised by titration with 0.01N- $\text{K}_4\text{Fe}(\text{CN})_6$ in presence of H_2SO_4 and 0.1% aq. eriolgaucine as indicator. E. S. H.

Electroanalysis and macro-electroanalysis of nickel with iron electrodes. J. GUZMAN and G. GARCIA (*Anal. Fis. Quim.*, 1934, 32, 72—86).—Determinations of Ni (0.1—0.2 g.) in ammoniacal sulphate solutions containing phosphate, borate, formate, acetate, oxalate, and tartrate, using Fe electrodes, yield results which agree to within 0.3%, except in the case of the last-named. Poor deposits are obtained with the solutions containing phosphate. The presence of nitrate merely increases the time required for deposition by about 25%. Satisfactory results are also obtained by macro-deposition. Simplification of the determination by using two Pb accumulators as the source of current and omitting resistances etc. yields results about 0.4% low. H. F. G.

Colorimetric determination of molybdenum in steels in presence of other elements.—See B., 1935, 360.

n-Propylarsinic acid for [determination of] zirconium. G. C. CHANDLEE (J. Amer. Chem. Soc., 1935, 57, 591).—The directions for separation of Zr and Sn (this vol., 319) are inadequate. E. S. H.

Flame temperatures. W. T. DAVID (Nature, 1935, 135, 470—471; cf. this vol., 138).—Additional evidence supporting the view that flame temp. determined by the Na line reversal method are > the true flame temp. is recorded. L. S. T.

Calculation of the temperatures of flames. G. RIBAUD and A. R. ZAER (Compt. rend., 1935, 200, 665—667; cf. A., 1930, 418).—A graphical method for calculating the temp. of flames from the heats of reaction and of dissociation of the reactants is described. The calc. temp. of the $2\text{H}_2 + \text{O}_2$ flame, both reactants being initially at 0° , is 2960° . J. W. S.

Lowest temperature yet reached. W. J. DE HAAS (Naturwiss., 1935, 23, 180).—Using the method of adiabatic demagnetisation with K Cr alum, a temp. of 0.0044° abs. has been reached. A. J. M.

Thermoregulator working without a relay. M. CENTNERSZWER and J. SZPER (Bull. Soc. chim., 1935, [v], 2, 495—496).—The regulator (I) is of the usual PhMe pattern with a U-tube at the top containing Hg connected to the Hg in (I) by oil. (I) is in series with the heating element and the 8-volt current is cut off when the temp. rises by a Pt contact on the inside limb of the U. R. S.

Toluene regulators. H. SMITH (Rev. Sci. Instr., 1935, [ii], 6, 82).—The PhMe is contained in a copper vessel, and the Hg in glass, the two being sealed together. The use of a metal container gives a quicker response. C. W. G.

Measurement of the heat liberated by the absorption of γ -radiation. W. SWIENTOSLAWSKI and I. ZLOTOWSKI (Compt. rend., 1935, 200, 660—662).—In the calorimetric apparatus described the radioactive material is surrounded by a Pb shield, suspended by four thermally-insulating fibres and enclosed in an evacuated vessel. The rise of temp. of the Pb is measured with thermocouples. The heating effects due to α - and β -radiation are eliminated by circulating H_2O through a double-walled vessel inserted between the Pb and the sample. J. W. S.

Apparatus for measuring the m.p. of an organic substance. K. SUZUKI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 177—178).—The capillary tube containing the substance is heated in a brass air-bath provided with windows. R. S. B.

Monochromatic green filter. B. LYOT (Compt. rend., 1935, 299, 738—739).—Nd glass or a saturated solution of the nitrate may be used in the construction of green filters. By combining with a Schott's VG3 glass of suitable thickness it is possible to obtain a filter which transmits a spectral band of a width $\approx 82 \text{ \AA}$. and has a max. transparency of 10% for $\lambda 5590 \text{ \AA}$. M. S. B.

Glow discharge tube of high light intensity for spectroscopic investigation of traces of substances. H. SCHULER and H. GOLLNOW (Z. Physik, 1935, 93, 611—619).—The discharge tube is described and applied to hyperfine structure measurements of rare elements. A. B. D. C.

Precision optical pyrometers. M. MILFORD, R. J. BRACEY, F. A. CUNNOLD, and A. C. EGERTON (J. Sci. Instr., 1935, 12, 80—84).—Full optical details are given. Alternative magnifications of 20 and 5 correspond with working distances of 24 and 48 cm. Green and red monochromatic filters are included, compensated to equal optical thickness. Temp. $> 5000^\circ$ abs. can be measured by the use of one or more neutral absorption screens. At the Au point temp. can be measured to 1 in 3000. C. W. G.

Precision lattice constants from X-ray powder photographs. M. U. COHEN (Rev. Sci. Instr., 1935, [ii], 6, 68—74).—A general method for the calculation of lattice consts. from powder photographs is given. Systematic errors can be calc. by the method of least squares. C. W. G.

Photo-electric thermoregulator. W. L. WALSH and N. A. MILAS (Ind. Eng. Chem. [Anal.], 1935, 7, 122—123).—The apparatus gives a temp. control of about $\pm 0.25^\circ$ over the range 100—500°. E. S. H.

Polariscope of high light intensity. E. M. BRUMBERG (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 35—36).—Equal transparent and opaque coarse lines on the surface of a plate of Iceland spar cut parallel to the cleavage plane appear completely transparent to unpolarised light with the plate thickness adjusted, by tilting, to give the extraordinary ray filling the opaque lines of the ordinary ray; the lines appear with transmitted polarised light, giving a powerful analyser. A. B. D. C.

Liquid-liquid junction. D. N. GHOSH (J. Indian Chem. Soc., 1935, 12, 15—22).—A liquid-liquid junction free from diffusion effects is achieved by the contact of two droplets, which then fall, breaking the circuit. The correct potentiometer setting can be obtained by repetition of the process. E.m.f. measurements show that the junction is superior to the free-diffusion and continuous-mixture types. R. S.

Principles of conductometry. J. HARMS and K. F. JAHR (Z. Elektrochem., 1935, 41, 130—136).—A general discussion. Recent work is criticised (cf. this vol., 182). E. S. H.

Dipole apparatus. P. C. HENRIQUEZ (Rec. trav. chim., 1935, 54, 327—333).—The apparatus measures with great ease of working small differences in ϵ with high accuracy, using small quantities of material. Applications to the study of reaction velocity, determination of H_2O content, control of distillation, etc. are pointed out. R. S. B.

High-pressure Wilson cloud chamber. P. KIPFER (Nature, 1935, 135, 431—432).—A Wilson cloud chamber of 2 cm. diameter in which pressure can be increased to 100 atm. has been developed. L. S. T.

Falling cloud-chamber and a radial-expansion chamber. C. T. R. WILSON and J. G. WILSON (Proc. Roy. Soc., 1935, A, 148, 523—533).—The construction and testing of a satisfactory radial-motion expansion apparatus are described. The advantages of removing the cloud-chamber from a confined space, such as that between the poles of a magnet, by letting it fall, and photographing the tracks while the chamber is falling freely, are indicated. The anticipated advantages are confirmed by experiment. L. L. B.

Currents of positive ions produced in a high vacuum. R. PLANIOL (Compt. rend., 1935, 200, 730—731).—Improvements have been made in an apparatus previously described (this vol., 425) for determining the ionisation current in an applied electric field when a beam of electrons of uniform velocity meets an at. stream. Cd is used as the source of the latter and currents of positive ions of 10—30 microamp. have been obtained. M. S. B.

Galvanometer suspension. H. R. JONES (Ind. Eng. Chem. [Anal.], 1935, 7, 136).—A modified device for insulation from mechanical shock is described. E. S. H.

Accuracy of the Curie-Cheneveau magnetic balance. F. WOLFERS (Nature, 1935, 135, 437).—The accuracy of the balance is supported (cf. this vol., 321). L. S. T.

Titration flask facilitating the observation of colour changes. A. DAVIDSOHN (Fettchem. Umschau, 1935, 42, 9—10).—An external, horizontal, concentric tube (5 ± 0.5 mm. internal diameter) is fitted on to the side of an Erlenmeyer flask just above the bottom, so that it encircles about one third of the circumference, and fluid can readily pass through it as the flask is shaken during titration. E. L.

Syringe pipettes. A. KROGH (Ind. Eng. Chem. [Anal.], 1935, 7, 130—131).—The sphere of usefulness of syringe pipettes in the measurement of liquids is discussed. E. S. H.

Gas absorption apparatus based on the dispersion principle. O. LAMM (Kolloid-Z., 1935, 70, 273—275).—The apparatus permits a small quantity of the absorption liquid to be circulated continuously as a spray. E. S. H.

Mercury pump for making and supplying a uniform mixture of gases. L. R. MCKINNON and F. W. ALLEN (Science, 1935, 81, 157). L. S. T.

Study of chemical systems by measurement of the variation of weight with regularly variable temperature. M. GUICHARD (Bull. Soc. chim., 1935, [v], 2, 539—545; cf. A., 1934, 1058).—The method and its application are described. R. S.

Determination of the viscosities of solutions by the Scarpa method. B. K. CHATTERJI and B. L. VAISH (J. Indian Chem. Soc., 1935, 12, 6—15).—Const. times of rise of liquid in the viscosimeter could not be obtained. R. S.

Simple glass connexion. J. B. FICKLEN (Science, 1935, 81, 179—180).—Glass ends are flared, ground square, and kept in position by rubber bands.

The connexions are satisfactory when the increase or reduction in pressure is small. L. S. T.

Direct measurement of low pressures of saturated vapours. G. FOURETIER (Compt. rend., 1935, 200, 667—669).—The apparatus described, capable of measuring v.p. of 10^3 — 10^{-6} mm., is based on the displacement of a light metal piston, against a torsion, when the substance under investigation is arranged on one side of it, the other side being highly evacuated. J. W. S.

Interference extensometer and some observations on the elasticity of lead. B. CHALMERS (Proc. Physical Soc., 1935, 47, 352—370).—An extensometer using interference fringes to measure elastic and plastic extensions in specimens about 3 cm. long to an accuracy of approx. 3×10^{-7} cm. is described. Results for Pb are: a specimen not recently strained obeys Hooke's law within a definite range, and has a definite elastic limit; after severe recent strain a new type of elastic-hysteresis loop is obtained; for stress < elastic limit the whole of the elastic after-effect can be accounted for thermodynamically; the true plastic after-effect (creep) began at > elastic limit. N. M. B.

Application of surface tension to physico-chemical analysis. R. V. MERTZLIN (Ann. Inst. Anal. Phys. Chim., 1935, 7, 265—283).—Theoretical. R. T.

Apparatus for rapid determination of surface tension and effectiveness of capillary-active substances. M. STILLER (Chem.-Ztg., 1935, 59, 208—209).—A capillary apparatus is described. The effectiveness of several capillary-active substances is compared by plotting the surface tensions of dil. aq. solutions (0.1—1.0%) against concn. E. S. H.

Micrometer gas inlet tap. L. SAGGERS (J. Sci. Instr., 1935, 12, 93).—A refined form of needle valve is described. C. W. G.

Six-atmosphere mercury manometer. W. SCHOLL and R. O. E. DAVIS (Ind. Eng. Chem. [Anal.], 1935, 7, 135).—The apparatus described has an accuracy of ± 2 mm. at 5 atm. E. S. H.

Preparation of sintered glass filters. P. L. KIRK (Ind. Eng. Chem. [Anal.], 1935, 7, 135—136).—Practical directions are given. E. S. H.

Use of sintered glass discs in distillations. M. MATTIKOW (Ind. Eng. Chem. [Anal.], 1935, 7, 136).—Bumping is prevented by the presence in the liquid of a sintered glass disc, through which a stream of air or CO₂ is passed. E. S. H.

Psychrometric charts for high and low pressures. D. B. BROOKS (U.S. Bur. Stand. Misc. Publ., 1935, M146, 1—8).—Charts for determining pressure of H₂O vapour, R.H., and dewpoint from psychrometric data in the range 0.125—10 atm. are given. N. M. B.

Heated laboratory press. J. ERDOS (Z. Unters. Lebensm., 1935, 69, 176—177). E. C. S.

Use of crucibles with a porous filtering plate in Allihn's method. P. BALAVOINE (Mitt. Lebensm. Hyg., 1935, 25, 323—324).—Owing to the action of alkali these (Schott No. 4) crucibles (I) may lose

2—3 mg. when used for weighing Cu_2O in Allihn's method for determining sugars. The difficulty is overcome by cleaning (I) in succession with dil. HNO_3 , H_2O , EtOH , and Et_2O after use, and then weighing it and allowing for the loss. J. G.

Micro-extraction apparatus. E. B. COLEGRAVE (Analyst, 1935, 60, 90—91).—The apparatus, of the Soxhlet type, is designed for use with approx. 10 ml. of solvent. E. C. S.

Recording manometer having low inertia. G. ALLSOP and H. LLOYD (Safety in Mines Res. Board, 1935, Paper 91, 3—20).—Two types of electrical manometer are described. C. W. G.

Diffusion pump. P. JOLIBOIS (Compt. rend., 1935, 200, 1020—1022).—A combined form of Sprengel and Hg-vapour pump, specially suited for collection of gases developed during chemical reaction in a vac., is described. J. W. S.

Two-stage oil diffusion pump. J. E. HENDERSON (Rev. Sci. Instr., 1935, [ii], 6, 66—67).—The first stage cannot clog. Pressures of 2×10^{-8} mm. can be obtained using "Apiezon B" oil. C. W. G.

Device for preventing loss of stoppers, taps, etc. B. S. EVANS (Analyst, 1935, 60, 242). E. C. S.

Simple siphoning device. B. S. EVANS (Analyst, 1935, 60, 242). E. C. S.

Adapter collars for use in filtration. B. S. EVANS (Analyst, 1935, 60, 242). E. C. S.

Confining liquids for gas analysis. Solubility of carbon dioxide in salt solutions.—See B., 1935, 258.

New experiments for course in inorganic chemistry. G. LONGINESCU and I. I. PRUNDEANU (Bul. Chim. Soc. Romane, 1934, 37, 1—4).—Modified lecture experiments on oxidation and combustion are described. J. S. A.

Geochemistry.

Vertical distribution of atmospheric ozone in high latitudes. A. R. MEETHAM and G. M. B. DOBSON (Proc. Roy. Soc., 1935, A, 148, 598—603).—The average height of the O_3 in the atm. at Tromsø (N. Norway) is slightly < at Arosa (cf. A., 1934, 1087). L. L. B.

Natural gas in Tyrnava. O. ROUTALA (Suomen Kem., 1935, 8, B, 12).—This gas contains CH_4 93.4, CO , 5.1, O_2 0.2, N_2 1.3%. Its origin is discussed. J. W. S.

Origin of petroleum. B. T. BROOKS (Science, 1935, 81, 176; cf. this vol., 324).—Petroleum has had a low-temp. history and it has not resulted from heat decomp. of org. material. L. S. T.

Are fishes the principal source of petroleum? J. HENDERSON (Science, 1935, 81, 176—177; cf. this vol., 191).—Fish remains are insufficient in amount to account for the large quantities of petroleum occurring in some formations; other plant and animal remains must be taken into consideration. L. S. T.

Distribution of isotopic water in the sea. H. E. WIRTH [with T. G. THOMPSON and C. L. UTTERBACK] (J. Amer. Chem. Soc., 1935, 57, 400—404).—Apparatus for determining small differences of d with a sensitivity of 10^{-8} is described. The mean difference between the d of H_2O distilled from sea- H_2O and that from tap- H_2O is 1.37×10^{-6} in 31 samples. The variation with depth in different oceans is discussed. E. S. H.

Distribution of dissolved oxygen in the north Pacific ocean. T. G. THOMPSON, B. D. THOMAS, and C. A. BARNES (James Thompson Memorial Vol., 1934, 203—234).—Data are recorded and discussed. CH. ABS. (e)

Water from the Dead Sea. B. PANTELEYMONOFF (Rev. Chim. ind., 1934, 43, 118—125; Chem. Zentr., 1934, ii, 3294).—Analytical data are recorded. Separation of carnallite at 20° begins after driving off 60% of the H_2O . H. J. E.

Lakes of the Volga delta. V. I. NIKOLAEV and D. I. KUZNETZOV (Ann. Inst. Anal. Phys. Chim., 1935, 7, 285—294).—Analytical data are given for a no. of salt lakes. R. T.

Analyses of mineral springs of Bad Peterstal from the historical viewpoint. E. REMY (Z. Unters. Lebensm., 1935, 69, 160—169).—Analyses of the H_2O from 1722 to the present date show appreciable changes in $\text{Ca}(\text{HCO}_3)_2$ (I), $\text{Mg}(\text{HCO}_3)_2$ (II), and K_2SO_4 (III) only. (I) and (II) have increased by 43.1 and 35.0%; (III) has decreased by 40.6% since 1891. E. C. S.

Surface waters and deep waters in the canton of Geneva. E. JOUKOVSKY and J. BUFFLE (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 229—233).—The lower a layer of H_2O is in a lake, the more remote is its origin. C. W. G.

Carbon dioxide sorption by natural snow. Y. KAUKO and L. LAITINEN (Suomen Kem., 1935, 8, B, 12; cf. this vol., 190).—The CO_2 content of natural snow in equilibrium with air containing 0.03% varies from 15 to 40 mg. per litre for freshly fallen and old snow, respectively. This is much > the $[\text{CO}_2]$ in H_2O in equilibrium with the atm. J. W. S.

Action of "Erdstrahlen" on the divining rod. M. TRÉNEL (Angew. Chem., 1935, 48, 174—175).—Dobler's results are due to the effect of H_2O on the Al in contact with a photographic plate, and not to γ -rays. R. S.

Meteorite stone of Mangwendi, Southern Rhodesia. B. LIGHTFOOT, A. M. MACGREGOR, and E. GOLDING (Min. Mag., 1935, 24, 1—12).—A stone weighing about 60 lb. ($52\frac{1}{2}$ lb. recovered), which fell in the Mangwendi native reserve on March 7, 1934, is a grey chondritic stone of the Soko-Banja type, consisting of olivine (47.10), enstatite (29.88), feldspar (12.38), chromite and ilmenite (2.50), troilite (4.98),

and metallic Ni-Fe (3.07%); d 3.517. Detailed petrographical description and chemical analyses are given. L. J. S.

Murnpeowie, a granular type of meteoric iron. L. J. SPENCER (Min. Mag., 1935, 24, 13—20).—This mass of 2520 lb. was found in South Australia in 1909. An etched slice shows, at particular inclinations of the reflected light, remnants of an original lamellar octahedral structure from which granular kamacite had been developed by heat-treatment of the mass. The grains of kamacite are irregular in outline and orientation, and they show well-marked Neumann lines. A narrow finely granular zone on the outside of the mass shows the effect of another and later heat-treatment during the flight of the meteorite through the earth's atm. Analysis by M. H. HEY gave Fe 93.88, Ni 6.32, Co 0.32, Cu 0.002, Ge 0.007, Pt 0.07, S 0.006, insol. 0.20%; d 7.78. The amount of Pt is the highest recorded in any meteorite. L. J. S.

Origin of potash-rich rocks. R. D. TERZAGHI (Amer. J. Sci., 1935, [v], 29, 369—380).—The orthoclase-plagioclase equilibrium diagram is no doubt modified by the presence of H_2O and by high pressure, and the liquid may then contain more orthoclase than in a dry melt. Granites and pegmatites may be the result of the squeezing out of such a residual magma rich in H_2O and orthoclase. It is also suggested that rocks similar to granite may be produced by the feldspathisation of metamorphic sedimentary rocks, and by the hydrothermal alteration of igneous rocks when there is an increase in the K : Na ratio.

L. J. S.

Origin of the Solikamsk sulphate-free potassium deposits. V. I. NIKOLAEV (Ann. Inst. Anal. Phys. Chim., 1935, 7, 173—179).—The conditions of evaporation of the Permian Sea to yield the Solikamsk deposits are discussed. It is concluded that the $MgSO_4$ and K_2SO_4 contents of the primæval oceans were < at present.

R. T.

Conditions of formation, and nature, of astrakhanite. V. I. NIKOLAEV, D. I. KUZNETZOV, and G. B. BOKIJ (Ann. Inst. Anal. Phys. Chim., 1935, 7, 159—171).—The conditions of formation of astrakhanite have been studied, and its crystal parameters determined.

R. T.

Incandescence phenomena shown by certain antigorites. (MLLE.) S. CAILLERE (Compt. rend., 1935, 200, 1055—1058; cf. A., 1933, 352; 1934, 628).—X-Ray investigations show that the incandescence observed during the thermal analysis of α -antigorites is due to sudden recrystallisation of the amorphous product of dehydration into a mixture of enstatite and olivine. β -Antigorites recrystallise during dehydration and so do not show the phenomenon.

J. W. S.

Almandine from Botallack, Cornwall. A. R. ALDERMAN (Min. Mag., 1935, 24, 42—48).—Dark red icositetrahedra gave SiO_2 35.58, TiO_2 trace, Al_2O_3 21.94, Fe_2O_3 nil, FeO 38.54, MnO 0.70, MgO 0.68, CaO 1.68, H_2O (<105°) 0.12=99.24%, corresponding with almandine 89.00%; d 4.22, n 1.808. This and other analyses of garnets rich in almandine show an excess of Al_2O_3 over that required

by $3RO.R_2O_3.3SiO_2$, and they are recalcd. to fit $(Fe^{II}, Fe^{III}, Mg, Mn, Ca)_3(Al, Fe^{III}, Ti)_2(Si, Al)_3O_{12}$.

L. J. S.

Synthesis of montmorillonite. W. NOLL (Naturwiss., 1935, 23, 197).—Montmorillonite (I) may be synthesised by heating at 300°, and under a pressure of 87 atm., bohmite or bayerite and amorphous silicic acid in the proportion $Al_2O_3 : SiO_2 = 1 : 4$, in presence of 0.1N-NaOH. X-Ray structure shows identity with natural (I).

A. J. M.

Pneumatolytic augite from lava from the crater of Vesuvius (1929). M. ALFANI (Period. Min., 1934, 5, 77—96; Chem. Zentr., 1934, ii, 2817).—Crystallographic data are recorded. Sb, Cr, As, Pb, and Co, which are hitherto unrecorded constituents, were detected. The composition was (Ca, Mn, Pb, Na, K) : (Mg, Al, Fe, etc.) : (Si, Al) : O = 0.96 : 1.01 : 2 : 6.

H. J. E.

Ginorite, a new calcium borate from Sasso Pisano. G. D'ACHIARDI (Period. Min., 1934, 5, 22—32; Chem. Zentr., 1934, ii, 2817).—The formula assigned is $Ca_2B_{14}O_{23}.8H_2O$ or $H_{12}Ca_2B_{14}O_{29}.2H_2O$.

H. J. E.

Lead thioarsenites. A. FERRARI and R. CURTI (Period. Min., 1934, 5, 155—174; Chem. Zentr., 1934, ii, 2818).—Thioarsenites occurring naturally have $PbS : As_2S_3 = 1.25—2$. Certain minerals (e.g., baumhauerite and rathite) are considered to be solid solutions of As_2S_3 and $Pb_3As_2S_5$. Jordanite and guitermanite have the same lattice.

H. J. E.

Siliceous and micaceous clays. K. ENDELL, U. HOFMANN, and D. WILM (Sprechsaal Keram., 1934, 67, 293—295, 309—311, 325—328; Chem. Zentr. 1934, ii, 2729).— SiO_2 particle size is investigated rontgenographically after heating at 600° to destroy the kaolinite lattice. Cristobalite disappears by reaction with the mica on heating at 1400°.

J. S. A.

Zinc blende deposits at Vallauria (S. Dalmazzo di Tenda). E. SANERO (Period. Min., 1934, 5, 113—122; Chem. Zentr., 1934, ii, 2668—2669).—Crystallographic and analytical data are given.

H. J. E.

Tin deposits of Llallagua, Bolivia. II. F. S. TURNAURE (Econ. Geol., 1935, 30, 170—190; cf. this vol., 469).—The origin of the bonanza ore shoots, hypogene zoning, and the origin of the ore deposit are discussed.

L. S. T.

Reactions of natural natrolites. M. DOMINI-KIEWICZ (Spraw. Prac. dzia. Chem. pańs. Zak. Hig., 1933, No. 1, 116—127; Chem. Zentr., 1934, ii, 2667).—Natrolite (I), $Na_4Al_4Si_6O_{20}.4H_2O$, heated with aq. $AgNO_3$ forms $H_4Ag_4Al_4Si_6O_{22}.2H_2O$. Dehydrated (I) forms $Ag_4Al_4Si_6O_{20}$. Na cannot be replaced by Ag in $Na_4Al_4Si_6O_{24}$ (II), but the replacement occurs readily in $H_4Na_4Al_4Si_6O_{27}$. Al_2O_3 must function in (II) as an acid radical. HCl gas reacts with (I) at 150—160° with separation of SiO_2 . The Ag derivatives react with NH_4Cl , forming AgCl. The NH_4 derivative from (I), $4H_2[H_2(NH_4)_2]Al_4Si_6O_{22}.3NH_3$, loses NH_3 and H_2O when strongly heated, forming $H_4Al_4Si_6O_{20}$, insol. in acids.

H. J. E.

Cyprus salt. S. G. WILLIMOTT (Cyprus Agr. J., 1932, 27, 124—130).—Analytical data for material from salt lakes at Larnaca are recorded.

CH. ABS. (e)

Iron ore deposits of Bihar and Orissa. H. C. JONES (Mem. Geol. Survey India, 1934, 63, Pt. 2, 302 pp.).—Analyses are given. The Fe formations are marine chemical sediments, the porous type arising from leaching out of SiO_2 from banded hematite-quartzite.

CH. ABS. (e)

Chemical-mineralogical investigations of barium aluminate. N. A. TOROPOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 147—151).—The m.p. of the phases produced by mixing varying % BaO and Al_2O_3 are recorded. Three compounds are described: $3\text{BaO} \cdot \text{Al}_2\text{O}_3$, tabular, n 1.735, is readily sol. in H_2O , and is hydrated in air; $\text{BaO} \cdot \text{Al}_2\text{O}_3$, irregular rhombododecahedra, n 1.683, d_{20}^{20} 3.99, m.p. $1820^\circ \pm 20^\circ$, is easily sol. in H_2O , and is not hydrated on exposure to the atm.; $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$, hexagonal, d_{20}^{20} 3.69, is not sol. in conc. HCl or molten NaOH .

W. R. A.

Platinum content of sulphide minerals. O. E. ZVJAGINTSEV and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 136—139).—The Pt content of 11 minerals is recorded. Minerals which contain heavy metals or pyrites do not contain Pt. The greatest Pt content is associated with Pb in galena.

W. R. A.

Occurrence of platinum in sulphide ores. O. E. ZVJAGINTSEV and A. N. FILIPPOV (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 130—135).—The analyses of 17 minerals gave vals. for Pt content varying throughout a wide range, acid magma of eruptive origin giving highest vals.

W. R. A.

Relations of anorthosite to granite. F. F. GROUT and W. W. LONGLEY (J. Geol., 1935, 43, 133—141).

L. S. T.

Cainsmore of Carsphairn igneous complex. W. A. DEER (Quart. J. Geol. Soc., 1935, 91, 47—76).—The intrusion is composite, consisting of a central granite and successive zones of acid hybrid, tonalite, and basic hybrids. The petrology of these zones is described and chemical analyses and variation diagrams are given.

L. S. T.

Pre-Cambrian granites of the Black Hills. G. L. TAYLOR (Amer. J. Sci., 1935, [v], 29, 278—291).—At least two granites have been identified by Pb:U ratios, and microscopic and spectroscopic tests: "Game Lodge" and "Honey Peak fine-grained," with possibly a third, "Little Elk gneissoid."

R. S. B.

Life-history of the Sudbury nickel irruptive. I. Petrogenesis. W. H. COLLINS (Trans. Roy. Soc. Canada, 1934, [iii], 28, IV, 123—177).—A review is given of the history, with many chemical analyses and density determinations, of the Ni-bearing norite and of the transition rocks into the overlying micropegmatite. The whole complex is regarded as a single intrusion with subsequent differentiation of the magma.

L. J. S.

Vein formation at Porcupine, Ontario. M. E. HURST (Econ. Geol., 1935, 30, 103—127).—A study of the mode of formation of the Au-bearing quartz veins and lodes. Mineralisation has been a single, continuous process and the sequence of deposition of the vein minerals is discussed. Au deposition occupied a relatively long interval in this period.

L. S. T.

Spectrographic examination of quartz from some gold-bearing veins. E. L. BRUCE (Trans. Roy. Soc. Canada, 1934, [iii], 28, IV, 7—11).—Grey, black, and bluish quartz from several Canadian localities is often richer in Au than the ordinary white vein quartz. These are decolorised by heating, and the colour is often restored by exposure to X-rays. Since arc spectra of the material give no clue as to the colouring matter (white quartz gave the same lines), it is suggested that the colour may be due to the presence of Si set free by radioactivity. This may perhaps also have given rise to the richer deposition of Au.

L. J. S.

Measurement of thermo-luminescence. H. STEINMETZ (Zentr. Min., 1934, A, 209—218; Chem. Zentr., 1934, ii, 3148—3149).—Measurements on Andreasberg calcite deposits are recorded.

H. J. E.

Pegmatites from Masul (Meran). A. SCHERILLO (Period. Min., 1934, 5, 181—190; Chem. Zentr., 1934, ii, 3105).—Analyses gave: BeO 12.9, Al_2O_3 18.35, SiO_2 64.96, H_2O 2.23%. The beryl separated later than the quartz and albite with which it was associated.

H. J. E.

Artificial preparation of biotite. D. P. GRIGORIEV (Zentr. Min., 1934, A, 219—223; Chem. Zentr., 1934, ii, 3104).—The oxide components were fused together with fluorspar. The identity with phlogopites and anomites was proved by X-ray measurements.

H. J. E.

Pyrite oxidation. G. W. BAIN (Econ. Geol., 1935, 30, 166—169).—The oxidation of at least one variety of pyrite is accelerated by the presence of Na and K salts. The initial alteration is to FeSO_4 , and in building stone this can be arrested by treatment with BaCl_2 . $\text{Fe}_2(\text{SO}_4)_3$ and eventually $\text{Fe}(\text{OH})_3$ are formed if the stone is untreated and the FeSO_4 reaches a heated zone with excess of O_2 present.

L. S. T.

Relations of chalcocite-stromeyerite-argentite. G. M. SCHWARTZ (Econ. Geol., 1935, 30, 128—146).—Synthetic stromeyerite (I), identical with the natural mineral, is easily obtained by compressing powdered Ag_2S and Cu_2S and heating in sealed tubes from 75 to the m.p. of the mixture. Data for numerous artificial mixtures are given. When synthesised at temp. $> 200^\circ$, (I) shows the bladed structure originally described by Guild. Heating and cooling curves show that this is due to an inversion in crystal structure occurring at approx. 93° . (I) forms in rims along the contact by diffusion when Ag_2S and chalcocite are compressed at 16×10^3 lb. per sq. in. for several hr. There is a considerable solubility at both ends of the system Ag_2S — Cu_2S , up to approx. 20% of Cu_2S in Ag_2S and 15% of Ag_2S in Cu_2S . Ag_2S and Cu_2S may be slightly sol. in (I). Jalpaite (II) ($3\text{Ag}_2\text{S} \cdot \text{Cu}_2\text{S}$) is not formed as a compound when

mixtures of the correct composition are compressed and heated. Specimens of this composition are solid solutions of Cu_2S and Ag_2S retaining the crystal structure of argentite. The existence of (II) as a distinct mineral species is doubtful. X-Ray powder diagrams of (I), argentite, chalcocite, and mixtures and the m.-p. curve for the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ are given. L. S. T.

Kaolin in the Whitemud beds of Saskatchewan. F. J. FRASER (Trans. Roy. Soc. Canada, 1934, [iii], 28, IV, 13—16).—The kaolinised sandstones, with the sand grains enveloped in fine clay, contain curved crystals of kaolin, with optical characters distinct from those of dickite (A., 1933, 45, 229). Analyses are given. L. J. S.

Mineralogical methods for the study of silts and clays. C. E. MARSHALL (Z. Krist., 1935, 90, 8—34).—Sedimentation fractionation of small mineral particles is described. By immersion methods the

d , n , and double refraction of particles (1 to 20 μ) are measured. For particles $< 1 \mu$ modified methods are available. A detailed analysis of four clay samples by these methods is given. B. W. R.

Petrology of the Pennsylvanian shales and non-calcareous underclays associated with Illinois coals. R. E. GRIM [with P. F. KERR and O. W. REES] (Bull. Amer. Ceram. Soc., 1935, 14, 113—119).—From petrological and X-ray examination, chemical analysis, and determinations of the dehydration curves of the finest fractions (I) (obtained from suspensions in H_2O) of 59 samples (II) of Pennsylvania shales occurring above the coal, it is concluded that the essential constituent of (I) is a K_2O -bearing clay mineral similar to, but not identical with, sericite, and having a lower K_2O and higher H_2O content. (I) also contain variable quantities of quartz, and probably traces of chloritic material. (II) showed noteworthy uniformity of mineralogical composition. A. L. R.

Organic Chemistry.

Biochemical triangle. M. J. STRITAR (Biochem. Z., 1935, 276, 386—387).—If the formulæ of org. compounds (I) containing only C, H, and O be replaced by formulæ showing the no. of chemical equivs. of each element, (I) can be plotted as points on an equilateral triangular system (II) of co-ordinates, the vertices having the chemical symbols C, H, O. In (II) points corresponding with reactions $A+B \rightarrow C$ lie on the straight "reaction lines" (III) AB , C being between A and B . If C can be produced by two such reactions it occupies the point of intersection of the two (III). All members of homologous series (IV) lie on straight lines (V) which connect the point representing the first member with that representing CH_2 , and each member of (IV) lies at the point of intersection of (V) with appropriate (III). From the point representing H_2O there diverge " H_2O rays" passing through the points representing all substances having the same R.Q. (III) for the most important simple biochemical reactions (hydrogenation, dehydrogenation, addition and elimination of H_2O , decarboxylation) pass respectively through the points representing H, H_2O , and CO_2 .

W. McC.

Free organic radicals in the gaseous state. IV. Synthesis of antimony cacodyl and related substances by the use of free methyl and free ethyl. F. A. PANETH and H. LOLEIT. V. F. A. PANETH, W. HOFEDITZ, and A. WUNSCH. VI. Attempts to prepare various free radicals; existence of free benzyl. F. A. PANETH and W. LAUTSCH (J.C.S., 1935, 366—371, 372—379, 380—383; cf. A., 1932, 40).—IV. Thin films of As, Sb, and Bi react with free Me and Et to give the trialkylarsine, -stibine, and -bismuthine. In addition Me and As yield bisdimethylarsenic and cyclic penta-methylpentarsine (?), b.p. 193—200°/15 mm.; with Me and Sb bisdimethylantimony (I), m.p. 17.5°, is also formed, whilst there is evidence of the formation of

bisdimethylbismuth from Bi. Similarly bisdiethylarsenic, bisdiethylantimony (II), m.p. -61°, and cyclic pentaethylpentarsine (?) are formed. (I) and (II) combine quantitatively with I and Br, and are readily oxidised in air (C_6H_6 solution) to the dialkylantimonic acids. Me and Et react with Be freshly deposited on Au leaf to give dimethyl- (?) and diethyl-beryllium (?), respectively. The v.p. of (I) and (II) have been determined.

V. The method and apparatus previously described for measuring the half-val. period of free Me have been improved and applied to the determination of the conditions under which Me disappears. In H_2 Me disappears according to the equation $\text{Me} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ (A), and partly in the wall reaction $2\text{Me} \rightarrow \text{C}_2\text{H}_6$. Low concn. of Me and low temp. favour (A). Using He as the transport gas, (A) is excluded, C_2H_6 being the main product. The half-val. period of Me in He at 500° can be raised to 0.1 sec.

VI. Decomp. of PbPr_4 and PbBu_4 under conditions described gives products forming Me derivatives only, with films of Pb, Sb, and Zn. No free Ph is obtained by the decomp. of PbPh_4 in H_2 at red heat and 2 mm. pressure, or by the interaction of PhBr and Na vapour. Thermal decomp. of CH_2CO and CH_2N_2 (H_2 and He as transport gas) or the subjection of CH_2N_2 to electric discharge fails to yield free CH_2 , as does the reaction between CH_2Cl_2 and Na vapour in He. Thermal decomp. of $\text{Sn}(\text{CH}_2\text{Ph})_4$ gives dibenzyl (87%) and CH_2Ph which is identified by isolation of $\text{Se}(\text{CH}_2\text{Ph})_2$, $(\text{SeCH}_2\text{Ph})_2$, $\text{Te}(\text{CH}_2\text{Ph})_2$, and $\text{Hg}(\text{CH}_2\text{Ph})_2$. CH_2Ph is also obtained by the action of CH_2N_2 on CH_2PhCl and by the decomp. of $\text{CO}(\text{CH}_2\text{Ph})_2$ at red heat. The half-val. period of CH_2Ph under the conditions of prep. is about 6×10^{-3} sec. F. N. W.

Reaction of bromine with ethylene derivatives in methyl alcohol. II. K. MEINEL (Annalen,

1935, 516, 231—243; cf. A., 1934, 753).—Solutions of MeOBr in MeOH are obtained by shaking Br in MeOH with an excess of very finely-divided AgNO₃, nearly neutralising the liberated HNO₃ with CaCO₃, and rendering harmless the excess of AgNO₃ by KOAc. AgNO₃ cannot be replaced by Na₂CO₃, CaCO₃, BaCO₃, or HgO. From such solutions OMe and Br are rapidly added to the double linkings of substances of which the "Br-binding nos." (A., 1932, 717) are > 50. Thus cyclohexene gives 2-bromo-1-methoxycyclohexane, b.p. 76—77°/10 mm., allylbenzene yields γ -bromo- β -methoxypropylbenzene, and propenylbenzene affords β -bromo- α -methoxypropylbenzene. These compounds are also derived by use of CBr(NO₂)₃, bromoacetamide, or bromophthalimide in MeOH. A further parallelism is found with substances of which the Br-binding no. is < 50. Thus anethole and $\Delta^{1:3}$ -dihydrobenzene do not yield homogeneous Br-OMe-compounds. As the Br-binding no. diminishes the proportion of added Br to added OMe declines until when 0 is reached homogeneous Br-free compounds are formed. Br in MeOH behaves similarly to MeOBr only with substances of which the Br-binding no. is < 50; with compounds in which this factor is > 50 it affords a mixture of Br- and Br-OMe-adducts.

Furfuryl alcohol is converted by 5% Br-MeOH containing CaCO₃ into 4:5-dihydro-4:5-dimethoxyfurfuryl alcohol, b.p. 86—87°/0.4 mm. Similarly, but in absence of CaCO₃, furfuraldehyde affords 4:5-dihydro-4:5-dimethoxyfurfuraldehyde Me₂ acetal, b.p. 80—81°/0.3 mm., hydrogenated (PtO₂) to 4-methoxytetrahydrofurfuraldehyde Me₂ acetal, b.p. 78—80°/0.15 mm. H. W.

Highly polymerised compounds. CIV. Addition of sulphur dioxide to derivatives of ethylene. H. STAUDINGER and B. RITZENTHALER (Ber., 1935, 68, [B], 455—471).—Addition of SO₂ to simple ethylenic compounds occurs slowly; reaction is more rapid with the butadienes, but does not take place with CH₂:CHCl or CH₂:CH·CO₂Alk. The change is hastened by peroxidised Et₂O (I), O₃ in CHCl₃, BzO₂H, and Bz₂O₂, in order of decreasing efficiency. A chain mechanism is suggested. Passage of C₂H₄ or CHMe:CH₂ into boiling SO₂ containing (I) yields cryst. polysulphones which decompose almost completely into their components when heated at 300°. They are insol. in all org. media. The high viscosity of solutions of polypropylenesulphone (II) in conc. H₂SO₄ or conc. HNO₃ indicates a very high degree of polymerisation. They may be formulated as sulphones $\cdots\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdots$ or sulphinic esters $\cdots\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}\cdots$. The stability towards oxidising agents and Br is evidence against the latter view. They are unstable towards alkali and Ba(OH)₂, which affords a mixture of Ba salts of sulphinic acids and the compounds $\text{O}\langle\text{CH}_2\cdot\text{CH}_2\rangle_2$ and $\text{SO}_2\langle\text{CHMe}\cdot\text{CH}_2\rangle_2\text{S}^{\wedge}_2$ m polyethylenesulphone and (II), respectively. Butadiene (III), isoprene (IV), and dimethylbutadiene (V) with SO₂ give mixtures of mono- (VI) and poly- (VII)-sulphones, the proportion of (VI) decreasing in the sequence (V), (IV), (III). The yields of (VII) are

greatest when the reaction occurs most rapidly and greater with mol. proportions of reactants than when SO₂ is in excess. The prep. of (VI) is greatly facilitated by the presence of anticalysts, 1:3:5-C₆H₃(OH)₃ being most efficient, followed by *o*- and *p*-C₆H₄(OH)₂, whereas *m*-C₆H₄(OH)₂ and PhOH have little influence. (VII) are cryst., insol. in organic media, but sol. unchanged in conc. H₂SO₄ and conc. HNO₃ to solutions of eucolloidal character. They are very stable to Br. (VI) are cryst. substances freely sol. in org. media and in H₂O. They dissolve in conc. H₂SO₄ and conc. HNO₃, and may be recovered unchanged by evaporating their solutions in the last-named medium. They do not generally add Br. At somewhat > 100° they decompose smoothly into their components, whereas the corresponding saturated sulphones are far more stable. Monobutadienesulphone, m.p. 65.5°, is oxidised by aq. KMnO₄ to dimethylsulphone, m.p. 109°. With Br in H₂O-AcOH it gives the corresponding dibromide, m.p. 141°, b.p. 204°/15 mm. (decomp.), converted by freshly pptd. Ag₂CO₃ in anhyd. COMe₂ into the compound C₄H₆O₃S. Monoisoprenesulphone, m.p. 64°, and monodimethylbutadienesulphone, m.p. 135°, are described. H. W.

Acetylene series. VI. Oxidation of acetylenic hydrocarbons with permanganate. V. N. KRESTINSKI and M. K. KELBOVSKAJA (Ber., 1934, 68, [B], 512—519; cf. A., 1933, 256).—Neutral products do not appear to be formed during the oxidation of acetylenic hydrocarbons with very dil. KMnO₄ (=10) at 0°. Acids are produced with rupture of the hydrocarbon mol. at the triple linking. C₂H₂ gives HCO₂H and (?) traces of H₂C₂O₄. CPh·CH yields CO₂, BzOH, and traces of HCO₂H. CMe:CEt affords AcOH and EtCO₂H, whilst CBut·CH yields Bu·CO₂H, HCO₂H, and CO₂. The behaviour of the acetylenic linking during oxidation appears to differ completely from that of the ethylenic linking. H. W.

Electrolytic dehalogenation of simple organic compounds. I. C. SANDONNINI and V. N. BORGHELLO (Atti R. Accad. Lincei, 1934, [vi], 20, 334—340).—The anodic liquid was 10% H₂SO₄ and the cathodic liquid a solution of the halogenated compound in H₂O or 10% H₂SO₄, with EtOH added if necessary. The anode was of Pt and the cathode of Pt, Pb, or Cu. The results obtained with CCl₄, CHCl₃, and CH₂Cl₂ show that Cu cathodes are preferable to Pb for the electrolytic prep. of CHCl₃ from CCl₄. With CH₃ derivatives, the halogen is replaced, atom by atom, by H until CH₄ is obtained. With C₂H₆ derivatives, however, the Cl are replaced in pairs—one from each C. T. H. P.

Electrolytic dehalogenation of simple organic substances. II. C. SANDONNINI and V. N. BORGHELLO (Atti R. Accad. Lincei, 1935, [vi], 21, 30—35; cf. preceding abstract).—Electrolytic dehalogenation of mono-, di-, and tri-chloroacetic acids, CCl₃·CH(OH)₂, and CH₂Cl·CH₂·OH at Pt, Cu, and Pb cathodes is easier than in halogen derivatives of CH₄ and C₂H₆, and substitution of Cl by H occurs more readily than the reduction of the ·CO·. O. J. W.

Catalytic decomposition of alkyl chlorides. J. B. SENDERENS (Compt. rend., 1935, 200, 612—615).

—The temp. (varying between 140° and 280°) at which the decomp. $C_nH_{2n+1}Cl$ (I) $\rightarrow HCl + C_nH_{2n}$ is effected by the catalysts (II) Al_2O_3 , ThO_2 , ZrO_2 , kaolin, $Ca_3(PO_4)_2$, anhyd. $BaCl_2$ and $CaCl_2$ are recorded; (I) do not decompose at these temp. in the absence of (II). Pr^oCl , $Pr^{\beta}Cl$, and Bu^oCl all give the olefine, but the $CMe_2:CH_2$ formed from $Bu^{\beta}Cl$ or $Bu^{\gamma}Cl$ recombines with the HCl unless the products are rapidly separated. J. W. B.

Peroxidation of chloroform.—See this vol., 590.

Polychloro-compounds. II. Catalytic action of aluminium chloride in the reaction between chloroform and dichloroethylene. H. J. PRINS and F. J. W. ENGELHARD (Rec. trav. chim., 1935, 54, 307—312).—Equiv. amounts of $CHCl_3$ and $CHCl:CHCl$ containing $AlCl_3$ at 50—55° (cf. A., 1914, i, 648; 1933, 47) give $\alpha\beta\gamma\gamma$ -pentachloropropane (I), which is undecomposed at 60°, and a high-boiling product which inhibits the reaction completely in a concn. of 7% by attacking the catalyst. Neither (I) nor hexachloropentene inhibits the reaction. J. L. D.

Photo-oxidation of liquid carbon tetrachloride.—See this vol., 590.

Preparation of tert.-amyl bromide. Y. F. CHI and C. H. SZE (Trans. Sci. Soc. China, 1934, 8, 85—86).—A colourless product is obtained by washing with 48% HBr instead of H_2SO_4 . CH. ABS. (r)

Isomerides of geraniol and citral. L. RUZICKA and A. ROETHLISBERGER (Helv. Chim. Acta, 1935, 18, 439—444).—Methylheptenone (I), CH_3O , and $Ba(OH)_2$ in aq. $EtOH$ give a mixture, b.p. 122—123°/12 mm., of much ζ -methyl- γ -hydroxymethyl- Δ^6 -hepten- β -one and a little η -methyl- Δ^6 -octen- γ -on- α -ol, which with $MgMeI$ affords a mixture, b.p. 112—113°/1 mm., of $\beta\zeta$ -dimethyl- γ -hydroxymethyl- Δ^6 -hepten- β -ol and $\gamma\eta$ -dimethyl- Δ^6 -octen- $\alpha\gamma$ -diol, dehydrated, best by $o-C_6H_4(CO)_2O$, to much $\beta\zeta$ -dimethyl- γ -hydroxymethyl- Δ^6 -heptadiene (II), b.p. 95—97°/12 mm., with a little geraniol or nerol. (II) and CrO_3 - $AcOH$ give γ -aldehydo- $\beta\zeta$ -dimethyl- Δ^6 -heptadiene (semicarbazone, m.p. 200—201°). (I), iso-amyl formate, and Na in dry Et_2O give a $OH\cdot CH_2$ -derivative, b.p. 90—92°/12 mm., which with $MgMeI$ in C_6H_6 - Et_2O gives probably γ -(α -hydroxyethyl)- ζ -methyl- Δ^6 -hepten- β -one, b.p. 84—85°/0.3 mm., and γ -acetyl- ζ -methyl- Δ^6 -heptadiene, b.p. 96—99°/12 mm., both of which afford the semicarbazone, m.p. 163—164°, of the latter; alternative formulæ are discussed. R. S. C.

Determination of glycerol in presence of sugars by periodic acid. P. FLEURY and M. FATOME (J. Pharm. Chim., 1935, [viii], 21, 247—266).—The following method for the determination of glycerol (I) (0.005—0.02 g.; accuracy 1%) based on its oxidation for 15 min. at room temp. with 5 c.c. of 0.1M- HIO_4 , (I) + $2HIO_4 \rightarrow 2CH_2O + HCO_2H + 2HIO_3$, is described. The excess of HIO_4 is determined (A., 1933, 362) by addition of 0.1N- H_3AsO_3 - $NaHCO_3$, excess of which is titrated with 0.1N-I solution (x c.c.). If a similar blank determination requires y c.c. of 0.1N-I, the amount of (I) present is $2.30(x-y)$ mg. Under the conditions described oxidation is complete in approx. 2 min. Increased acidity has little effect, but in alkaline solution the period necessary for complete

oxidation is greatly increased. In strongly alkaline solution the amount of HIO_4 consumed first increases, then decreases, and again slowly increases (towards the theoretical val.) with time. The decrease in the velocity by lowering the temp. to 0° is also greater in alkaline solution. Application of the method to the determination of (I) in presence of sucrose (> 20 parts) or of glucose (> 10 parts: the permitted amount of sugar approx. \propto its mol. wt.) is described. The sugar is removed by $Ba(OH)_2$ at 0° and pptn. with $EtOH$. Excess of $Ba(OH)_2$ is removed by H_2SO_4 , and excess of $EtOH$ by evaporation from the H_2O solution. With the prescribed technique removal of sugar is complete, only a slight entrainment of (I) being observed. The error is slightly larger in presence of sugars. J. W. B.

Synthesis of a methyl- and a dimethyl-hexitol. J. WIEMANN (Compt. rend., 1935, 200, 840—842).—Vinylpropenyl glycol with $AgClO_3$ and osmic acid (cf. A., 1932, 718; 1933, 47) gives a *hexitol*, $C_7H_{16}O_6$, m.p. 190° (Ac_6 derivative, m.p. 142°), in which the space relationships of two CH_2OH groups are fixed (cf. A., 1929, 293). Charon's dipropenyl glycol similarly gives a *dimethylhexitol* (I), m.p. 250° (decomp.) (Ac_6 derivative, m.p. 160°). *s*-Dipropenyl glycol (A., 1934, 277) does not give (I). J. L. D.

Controlled acetylene-allylene-diene molecular changes of the halogenohydrins. A. FAVORSKY and (MILEE.) T. FAVORSKAJA (Compt. rend., 1935, 200, 839—840).— $OH\cdot CMe_2\cdot C:CH$ (I) with HCl in presence of $CuCl_2$ and NH_4Cl gives β -chloro- β -methyl- Δ^7 -butinene (II), b.p. 76°, which affords a Cl-free substance (III) with aq. NH_3 - $AgOH$, reconverted into (II) as above. Prolonged action of HCl - $CuCl_2$ - NH_4Cl on (III) gives δ -chloro- β -methyl- Δ^8 -butadiene, b.p. 102—103°, which does not react with aq. NH_3 - $AgOH$, but with warm H_2O - $CaCO_3$ it gives (II) and then (I), also $CMe:CH$ and δ -chloro- β -methyl- Δ^7 -butadiene (IV). (IV) is converted into α -chloroisoprene, and with maleic anhydride gives two di-, m.p. 210—211° and 239—241°, and two tetra-carboxylic acids, m.p. 298—299° and 352—353°. J. L. D.

Alkaline hydrolysis of glycerol chlorohydrins. N. S. DROZDOV and O. M. TSCHERNITZOV (J. Gen. Chem. Russ., 1934, 4, 1305—1309).— $\alpha\gamma$ -Dichloro-, α -chloro-, and epichloro-hydrin are readily hydrolysed by dil. aq. $NaOH$ at 50° to yield $OH\cdot CH_2\cdot CH\begin{smallmatrix} \diagup CH_2 \\ \diagdown O \end{smallmatrix}$.

R. T.

Reaction of oxyhalide compounds with unsaturated compounds. A. A. PETROV (J. Gen. Chem. Russ., 1934, 4, 1217—1223).—*n*-Butylene and I in Et_2O at 6° yield, in presence of HgO , β -iodo- γ -hydroxybutane (I) (acetate, b.p. 84—85°/12 mm.). The following ethers of (I) are obtained when the appropriate alcohol is substituted for Et_2O in the above reaction: *Me*, b.p. 53—54°/12 mm., *Et*, b.p. 59—60°/12 mm., *Pr^{\beta}*, b.p. 66—70°/12 mm., and *Bu^{\beta}*, b.p. 79—82°/12 mm. The mechanism of the above reactions is discussed. R. T.

Preparation of ethers in liquid ammonia. T. H. VAUGHN, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 510—512).—*n*- $C_5H_{11}Br$ (I) and *n*- $C_5H_{11}\cdot ONa$ (II) in liquid NH_3 at 1.7 atm. give

Δ^{α} -pentene (III) (7%) and diamyl ether (IV) (31.6%). Similarly $\text{Pr}^{\alpha}\text{ONa}$ and $\text{Pr}^{\alpha}\text{Br}$ (1.5 atm.) give $\text{Pr}^{\alpha}_2\text{O}$ (12%), and $\text{Bu}^{\alpha}\text{ONa}$ and $\text{Bu}^{\alpha}\text{Br}$ give $\text{Bu}^{\alpha}_2\text{O}$ (8% at 1 atm.; 28% at 10 atm.); (II) with (I) and $\text{C}_5\text{H}_{11}\text{Cl}$ at 2.7 atm. gives (IV) (32–33% and 3%, respectively), with $n\text{-C}_5\text{H}_{11}\text{I}$ (IV) (17%) and (III) (13%), with $\text{Bu}^{\alpha}\text{Br}$ and $\text{Bu}^{\alpha}\text{Cl}$ at 3 atm. $\text{Bu}^{\alpha}\text{O}\cdot\text{C}_5\text{H}_{11}$ (28 and 0%, respectively); (I) and NaOPh at 3 atm. give $\text{PhO}\cdot\text{C}_5\text{H}_{11}$ (45%). $\text{C}_5\text{H}_{11}\text{I}$ and liquid NH_3 at 2.7 atm. (without salts) gives 95% of amylamines. Alkyl halides and the Na derivatives of acetylenes give 2–4% yields of dialkyl ethers, due to the presence of traces of H_2O .

R. S. C.

Preparation of α -unsaturated ethers from $\beta\beta$ -dimethoxyalkanes [ketals]. D. B. KILLIAN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 544–545).—Distillation of $\text{CMcBu}(\text{OMe})_2$ (I), $\text{C}_5\text{H}_{11}\cdot\text{CMc}(\text{OMe})_2$ (II), and $\text{CPhMe}(\text{OMe})_2$ with a trace of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ (III) yields β -methoxy- Δ^{α} -hexene, b.p. 119–120°/740 mm., and -heptene, b.p. 142–143°/745 mm., and α -methoxystyrene, b.p. 191–193°/745 mm., which, when distilled with an alcohol, give a mixture of ketals. When distilled with an excess of the appropriate alcohol and a trace of (II), (I) give β -ethoxy-, b.p. 132–133°/745 mm., -propoxy-, b.p. 155–156°/748 mm., -*n*-, b.p. 177–178°/745 mm., and -iso-butoxy- Δ^{α} -hexene, b.p. 166–168°/745 mm. (II) gives similarly β -propoxy- Δ^{α} -heptene, b.p. 181–183°/745 mm. Physical consts. of the products are recorded.

R. S. C.

$\beta\gamma$ -Dihydroxybutane and its derivatives. II. Ethers of ψ -butylene chlorohydrin. M. V. LICHOSCHERSTOV and S. V. ALEXEEV (J. Gen. Chem. Russ., 1934, 4, 1279–1282).—The following ethers of $\text{CHMeCl}\cdot\text{CHMe}\cdot\text{OH}$ have been prepared from ψ -butylene and ROCl in ROH , where R is alkyl: *Me*, b.p. 116°, *Et*, b.p. 122–124°, *Pr* ^{β} , b.p. 130–131°, *Pr* ^{α} , b.p. 136–138°, iso- C_5H_{11} , b.p. 176–178°.

R. T.

Action of ethylene oxide on hydrogen sulphide. A. TSCHITSCHIBABIN and M. BESTOUGEV (Compt. rend., 1935, 200, 242–244).—According to the conditions $(\text{CH}_2)_2\text{O}$ (cryst. monohydrate, m.p. 12°) combines with H_2S in presence of H_2O to give (equimol. quantities at 8–10°) $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, b.p. 54°/12 mm., $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$, b.p. 130°/2 mm., and tri-(β -hydroxyethyl)sulphinium hydroxide, converted by HCl into the known chloride. When no precautions to avoid excessive rise in temp. are taken substances of the type $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ are obtained.

J. W. B.

Preparation of sodium alkylsulphonates. R. M. REED [with H. V. TARTAR] (J. Amer. Chem. Soc., 1935, 57, 570–571).—By the Strecker reaction at 180–200° are obtained *Na n-octyl*-, *n-decyl*-, *lauryl*-, *myristyl*-, *cetyl*-, and *n-octadecyl-sulphonate* in 60–70% yield.

R. S. C.

Relative mobilities of normal primary alkyl radicals from C_1 to C_{16} in their chlorosulphites. P. CARRÉ (Compt. rend., 1935, 200, 555–557; cf. A., 1934, 509).—The temp. of decomp. (*T*) of the *n*-alkyl chlorosulphites (I), C_1 to C_{16} , are determined in $\text{C}_5\text{H}_5\text{N}$. *T* represent, in the inverse order, the relative mobilities of alkyl, which reach a min. at C_7 , increase and “alternate” from C_8 to C_{15} , and finally decrease for

C_{16} . The “alternation” is evidence for a curved or spiral chain structure for (I), for the ease of decomp. of (I) depends partly on the electronic character of alkyl (cf. A., 1933, 806).

J. L. D.

Rare earths. I. J. S. ŠTERBA-BOHM and M. MELICHAR (Coll. Czech. Chem. Comm., 1935, 7, 57–68; cf. A., 1929, 1251).—The following *formates* and *acetates* have been prepared: $(\text{HCO}_2)_3\text{Sc}$, $(\text{HCO}_2)_2\text{Sc}\cdot\text{OH}$, $(\text{HCO}_2)_6\text{LiSc}\cdot 3\text{H}_2\text{O}$, loses $3\text{H}_2\text{O}$ at 100°; $(\text{HCO}_2)_6\text{NaSc}$, slightly hygroscopic; $(\text{HCO}_2)_6\text{K}_3\text{Sc}$; and $\text{Sc}(\text{OAc})_3$, which gives a microcryst. ppt. of $\text{Sc}(\text{OH})(\text{OAc})_2$ when its conc. aq. solution is heated.

M. S. B.

Amphoteric acetates in acetic acid as solvent.—See this vol., 583.

Molecular compounds of trichloroacetic acid with alcohols, phenols, and ethers. N. A. PUSHIN and I. I. RIKOVSKI (Annalen, 1935, 516, 286–295).—The intermediate mol. compounds of $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and alcohols are most stable in the cases of *tert.* alcohols on account of their small rate of esterification. Thermal analysis proves the formation of a compound, $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{EtOH}$, m.p. –38°, formed only in fresh solutions; the equimol. mixture soon becomes cloudy at room temp. and separates H_2O after 24 hr. Bornool and $\text{Bu}^{\alpha}\text{OH}$ yield compounds, $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{C}_{10}\text{H}_{17}\cdot\text{OH}$, and $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{Bu}^{\alpha}\text{OH}$, respectively, whilst pinacol gives the substances $(\text{CMe}_2\cdot\text{OH})_2\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}$ (I), m.p. 44°, and $(\text{CMe}_2\cdot\text{OH})_2\cdot 2\text{CCl}_3\cdot\text{CO}_2\text{H}$, m.p. 26°. (I) shows no external sign of esterification after 2 months at 22–25°. PhOH gives a compound, $\text{PhOH}\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}$, m.p. 38.5°, in which PhOH functions as base; esterification does not appear to have occurred after 2 months. Contrary to Kitran (A., 1925, ii, 533), *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ gives the compound, $\text{C}_6\text{H}_4(\text{OH})_2\cdot 2\text{CCl}_3\cdot\text{CO}_2\text{H}$. *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ yields the substance, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}\cdot 2\text{CCl}_3\cdot\text{CO}_2\text{H}$, stable at > 10.5°. The compound *o*- $\text{C}_6\text{H}_4(\text{OMe})_2\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}$, m.p. 28°, is derived from *o*- $\text{C}_6\text{H}_4(\text{OMe})_2$. A mol. compound is not obtained with *cetyl* alcohol. The behaviour of menthol and mannitol is described.

H. W.

Metabolic products of *Penicillium Charlesii*, G. Smith. Molecular constitution of carlic and carlosic acids.—See this vol., 662.

Preparation of γ -chloro- β -hydroxybutyric acid and $\alpha\delta$ -diphthalimido- γ -hydroxyvaleric acid. M. TOMITA and M. NAKASHIMA (Z. physiol. Chem., 1935, 231, 199–201).—On boiling with conc. HCl γ -chloro- β -hydroxy-*n*-butyronitrile gives γ -chloro- β -hydroxybutyric acid. Et_2 phthalimidohydroxypropylmalonate (A., 1926, 1129) with Br in CHCl_3 affords *Et* α -bromo- δ -phthalimido- γ -hydroxy- α -carbethoxyvalerate (I), m.p. 89°. Hydrolysis of (I) with conc. HBr (saturated at 0°) at 50–55° and decarboxylation at 150–153° yields α -bromo- δ -phthalimido- γ -hydroxyvaleric acid (II), m.p. 191°. With K phthalimide in aq. EtOH , (II) gives $\alpha\delta$ -diphthalimido- γ -hydroxyvaleric acid, m.p. 225–226° (decomp.).

J. H. B.

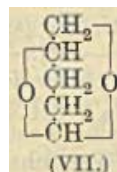
Organic salts containing iron and calcium. T. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 82–83).— Ca lactate and Fe citrate in H_2O give the more sol. salt, $\text{Fe}(\text{C}_6\text{H}_5\text{O}_2)_3\cdot\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_3\cdot\text{OH}$, decomp. > 150°, which at > 100° loses $1\text{H}_2\text{O}$ (? to form a lactone).

R. S. C.

Pyrolysis. I. Pyrolysis of derivatives of α -acetoxypionic acid and related substances. R. BURNS, D. T. JONES, and P. D. RITCHIE (J.C.S., 1935, 400—406).—Pyrolysis (400—600°) of α -OH-acids in which H of OH has been substituted by Ac, Bz, COCl, or α -CO₂·C₆H₄·CO₂Me gives the corresponding Δ^{α} -unsaturated acid with elimination of AcOH; acetylated α -OH-esters can follow two courses: CH₂:CH·CO₂C_nH_{2n+1} + AcOH (I) \leftarrow OAc·CHMe·CO₂C_nH_{2n+1} \rightarrow (II) OAc·CHMe·CO₂H + C_nH_{2n}, (I) predominating when $n=1$ or when C_nH_{2n+1} is replaced by a thermostable radical. Acetylated α -OH-nitriles on pyrolysis up to 450° yield the corresponding unsaturated nitrile principally, but above 450° OAc·CMeR·CN \rightarrow COMeR + HCN (+CH₂:CO?) is involved. Apparatus designed to obviate charring during pyrolysis has been used with the following substances: Me, b.p. 171·5°/760 mm., 76—77°/12 mm. (lit. 168—170°); Et; Bu^u (III), b.p. 105°/15 mm. (obtained from Bu^u lactate, Ac₂O and conc. H₂SO₄ at 40—45° during 12 hr.); and CH₂Ph α -acetoxypionate (IV), b.p. 145—148°/4 mm.; Me α -carbethoxyethylphthalate, b.p. 140°/3 mm. (obtained from Et lactate and α -CO₂H·C₆H₄·CO₂Me in boiling C₆H₆ containing 0·5% of H₂SO₄); α - and β -acetoxypionitrile, b.p. 210—212°/773 mm.; EtOAc; cyclohexyl acetate and 1-cyanocyclohexyl acetate, b.p. 112—113°/15 mm., m.p. 48—49° (by the interaction of cyclohexanone cyanohydrin and Ac₂O). By this means Bu^u acrylate, b.p. 59°/23 mm., is obtained from (III) and CH₂Ph acrylate, b.p. 94°/6 mm., from (IV). F. N. W.

Mechanism of the formation of lævulic acid from hexoses. II. Hydroxyl-free substance resembling glucosan. R. PUMMERER, O. GUYOT, and L. BIRKOFER (Ber., 1935, 68, [B], 480—493; cf. A., 1923, i, 698).—Diminution of the concn. of furfuryl alcohol to 10% and increase in the concn. of HCl-MeOH to 0·6% increases the yield of δ -methoxylævulaldehyde Me₂ acetal (I), b.p. 100—101°/16 mm. (whence the bisdinitrophenylhydrazone of δ -methoxylævulaldehyde, decomp. 192°), to 20%. Under the influence of hot aq. mineral acid the δ -OMe and aldehydic H of (I) interchange positions with production of lævulic acid (II). The conversion of hexoses (particularly fructose) into (II) is considered to proceed through 5-hydroxymethylfurfuraldehyde (III), ϵ -hydroxy- α - δ -diketohexaldehyde, and δ -hydroxylævulaldehyde, which undergoes $\alpha\delta$ -dismutation to (II). The possibility that (III) passes into 5-methylfuran-2-carboxylic acid (IV) is excluded, since (IV) readily and quantitatively loses CO₂ when boiled with 0·5N-H₂SO₄; the presence of Me at 5 greatly facilitates the change, since furan-2-carboxylic acid loses only 5% of its CO₂ under similar conditions. The ability of α -ketoaldehydes to lose HCO₂H under the influence of hot mineral acid is established by the conversion of AcCHO into HCO₂H and MeCHO. The dismutation of (I) does not appear to be due to the \cdot CO \cdot , since (I) is slowly hydrogenated (Pt sponge-H₂O) to γ -hydroxy- δ -methoxylævulaldehyde Me₂ acetal (V), b.p. 102—104°/12 mm., converted by cold acid into the corresponding aldehyde (VI), b.p. 95—96°/16

mm. [yielding the bisdinitrophenylhydrazone of δ -methoxylævulaldehyde with (NO₂)₂C₆H₃·NH·NH₂ in hot 10% H₂SO₄], which is converted by hot acid into γ -valerolactone. (V) and α -C₆H₄(CO₂)₂O afford the compound OR·CH₂:CH< $\begin{array}{c} \text{CH}_2 \\ \text{CH} \\ \text{O} \end{array}$ ·CH·OR (R = CO·C₆H₄·CO₂H). When heated in presence or absence of neutral absorbents of H₂O (VI) passes into the cycloacetal of $\gamma\delta$ -dihydroxyvaleraldehyde (VII), b.p. 91°/16 mm., a model of the glucosan type. (VII) is transformed by boiling 0·5N-H₂SO₄ into γ -valerolactone. Increase in acidity is not observed when glucose, fructose, or rhamnose is boiled with N-AcOH, but the process affords a ready method for the prep. of (III). H. W.



Unsaturated acids of natural oils. I. Highly unsaturated acids from oiticica oil (*Licania rigida*). W. B. BROWN and E. H. FARMER (Biochem. J., 1935, 29, 631—639).—Hydrolysis of the low-melting fat from the disintegrated kernels of *Licania rigida* gives licanic acid (I), C₁₈H₂₈O₂, m.p. 74—75° (yield 33%), hydrogenated to γ -ketostearic (hexahydrolicanic) acid (II), m.p. 96·5° (semicarbazone, m.p. 126°; Me ester, m.p. 49—50°). Oxidation of (I) with KMnO₄ gives H₂C₂O₄, n -valeric acid (III), and γ -ketoazelaic acid (IV), m.p. 108—109° (semicarbazone, m.p. 197°), converted by CrO₃ into adipic acid. (I) is therefore CH₃[CH₂]₃[CH:CH]₃[CH₂]₄·CO·[CH₂]₂·CO₂H. Similar results are recorded with technical oiticica fat, m.p. about 20°, whilst the technical oil (probably obtained by polymerising the fat) yielded 1·3% of isolicanic acid (V), m.p. 96·5°, hydrogenated to (II) and oxidised to H₂C₂O₄, (III), (IV), and $\alpha\beta$ -oxidosuccinic acid, m.p. 205°. W. O. K.

Hydrogenolytic fission of malonic ester and malonic ester derivatives. K. PACKENDORFF and L. LEDER-PACKENDORFF (Ber., 1935, 68, [B], 442—444).—Passage of CH₂(CO₂Et)₂ and H₂ over Pt at 200° gives EtOAc, C₂H₆, and CO₂. Since CH₂(CO₂Et)₂ is stable in CO₂ under similar conditions, reaction consists in addition of H to CO₂Et with production of C₂H₆ + CO₂H·CH₂·CO₂Et, which yields CO₂ + EtOAc. CHMe(CO₂Et)₂ and CMe₂(CO₂Et)₂ similarly yield EtCO₂Et and Pr^uCO₂Et with CO₂ and C₂H₆. In like circumstances the esters of succinic and adipic acids are stable. Hydrogenolytic fission is observed with Et₄ methylenedimalonate but the effects are masked by thermal decomp. H. W.

Peroxide from methyl hydrogen adipate and proof of its formation during electrolysis. F. FICHTER and H. BUSS (Helv. Chim. Acta, 1935, 18, 445—452).— ϵ -Carbethoxy- n -amyl peroxide (I) (90·9% pure) (from CO₂Et·[CH₂]₄·COCl and BaO₂), m.p. 5—13°, when exploded by heat, gives 1·34 mols. of CO₂, Et allylacetate (II), Et n -valerate (III), Et₂ adipate, and Et₂ sebacate (IV) (40·9%), m.p. 1·25°. Electrolysis of K Et adipate in presence of ligroin yields to the ligroin much (IV) with some (I) and CO₂Et·[CH₂]₄·CO₂H (V). It is considered that the side-reactions in the decomp. of (I) by heat or during

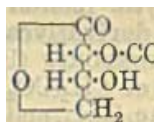
electrolysis are formation of (V) with (a) loss of CO_2 and O_2 to give (III), and (b) loss of CO_2 to form Et δ -hydroxy- n -valerate, which is then dehydrated to (II) R. S. C.

Compounds of bismuth and tartaric acid.
VII. Action of ammonia on monobismuthyl-tartaric acid. V. A. ISMAILSKI and S. S. KAGANOVA [with, in part, S. GORODNEV] (Ber., 1935, 68, [B], 415—421).—Bismuthyltartaric acid is converted by the theoretical quantity of NH_3 into the freely-sol. NH_4 salt $[\text{C}_4\text{H}_4\text{O}_7\text{Bi}]\text{NH}_4$. Excess of NH_3 leads to a sparingly sol. apparently complex salt $[\text{C}_4\text{H}_3\text{O}_6\text{Bi}_2\text{NH}_3]$ (cf. Rosenheim *et al.*, A., 1906, i, 231) accompanied by dibismuthyltartaric acid. Analogous complexes appear to be formed with NH_4Ph and NPhMe_2 , whereas $(\text{CH}_3)_6\text{N}_4$ affords sol. salts. H. W.

Vitamin-C. Synthesis of β -keto- ϵ -methyl-*l*-arabohexonolactone (*l*-rhamnoascorbic acid). T. REICHSTEIN, L. SCHWARZ, and A. GRUSSNER (Helv. Chim. Acta, 1935, 18, 353—354).—Rhamnosone gives, by the KCN method, β -keto- ϵ -methyl-*l*-arabohexonolactone (*l*-rhamnoascorbic acid), m.p. 197—199° (corr.; decomp.), $[\alpha]_D^{25} +27.8 \pm 3^\circ$ in 0.01N-HCl, which is one fifth as potent physiologically as vitamin-C, in accordance with the *d*-configuration of Cy.

R. S. C.

***d*-Glucosaccharosonic acid.** IV. Fission to compounds of the C_4 series. H. ERLBACH (Ber., 1935, 68, [B], 534—539; cf. Ohle, A., 1934, 1333).—The reducing power of Na *d*-glucosaccharosonate (I) towards I disappears during the action of NaOH and $\text{H}_2\text{C}_2\text{O}_4$ is formed, but the fate of the remainder of the mol. remains undecided. Air is involved in the change, which is accelerated by FeCl_3 or $\text{Cu}(\text{OAc})_2$. (I) and PhN_2Cl afford 2-phenylhydrazino-oxalyl-*d*-erythronolactone (II), m.p. 190° (decomp.), $[\alpha]_D^{25} -53.82^\circ$ in CMe_2 , which reduces Fehling's solution, does not react with I in presence of acid, does not condense with CMe , containing H_2SO_4 or anhyd. CuSO_4 is resinified by BzCl in $\text{C}_5\text{H}_5\text{N}$, and gives non-cryst. products with Ac_2O . (II) is converted by NaOH into oxalphenylhydrazide, m.p. 175° (sparingly sol. *Ca* salt), and erythronolactone (III). With HCl -EtOH (II) affords $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, m.p. 118°, the phenylhydrazine salt of phenylhydrazino-oxalic acid, m.p. 180—181°, and erythronophenylhydrazide (IV). With boiling $\text{NHPh}\cdot\text{NH}_2$ (II) gives $(\text{CO}\cdot\text{NH}\cdot\text{NHPh})_2$, m.p. 280°, and (IV), m.p. 127°, $[\alpha]_D^{25} +16.95^\circ$ in H_2O . (III) has m.p. 104°, $[\alpha]_D^{25} -73.05^\circ$ in H_2O . H. W.



(II.)

Derivatives of *d*-galacturonic acid. I. Esterification and acylation of *d*-galacturonic acid. S. MORELL and K. P. LINK (J. Biol. Chem., 1935, 108, 763—771).—Uronic acids can be successfully acylated directly only if CO_2H is protected by esterification or lactonisation. Methyl-*d*-galacturonide Me ester affords, with Ac_2O , 2:3:4-triacetyl- α -methyl-*d*-galacturonide Me ester, m.p. 93.5—94.5°, b.p. 200—210° (bath)/0.05 mm., $[\alpha]_D^{25} +166.0^\circ$ in CHCl_3 , and, with BzCl , 2:3:4-tribenzoyl- α -methyl-*d*-galacturonide Me ester, m.p. 134—135°, $[\alpha]_D^{25} +238^\circ$ in CHCl_3 .

d-Galacturonic acid is best esterified with CH_3N_2 , yielding the α -Me ester (I), m.p. 146—148°, $[\alpha]_D^{25} +75.5^\circ$ to $+38.0^\circ$ in MeOH. (I) affords, with Ac_2O , Me *d*-galacturonate 1:2:3:4-tetra-acetate, m.p. 142—143°, $[\alpha]_D^{25} +143^\circ$ in CHCl_3 , and with BzCl , the corresponding tetra-benzoate, m.p. 181—182°, $[\alpha]_D^{25} +278.5^\circ$ in CHCl_3 . H. N. R.

Sulphoglutaconic acid. J. M. VAN DER ZANDEN (Rec. trav. chim., 1935, 54, 289—293).— β -Chloroglutaconic acid, m.p. 141—142° (lit., 129°) (K salt), with KHSO_3 at 60° gives β -sulphoglutaconic acid [*K*₂ salt (+0.5 H_2O) *Ba* salt (+ H_2O); *Ag* salt (+2 H_2O)], also obtained from glutinic acid (improved prep.), m.p. 158.5° (lit., 145—146°), and KHSO_3 .

J. L. D.

Liquid monomeric formaldehyde. R. SPENCE and W. WILD (J.C.S., 1935, 338—340; cf. A., 1933, 1123).—Liquid monomeric CH_2O (I) is obtained from paraformaldehyde by distillation through a vessel designed to remove impurities which cause polymerisation. (I) thus prepared, although of improved stability, slowly polymerises to a gel (II) if kept above -78° . (II) evolves monomeric gaseous (I) on keeping. F. N. W.

Thermal reaction between formaldehyde and chlorine.—See this vol., 586.

Hydrogenation of a mixture of two α -ethylenic aldehydes. J. WIEMANN (Compt. rend., 1935, 200, 677—678).—Reduction of a mixture of $\text{CH}_2\text{:CH}\cdot\text{CHO}$ (1 mol.) and citral (I) (1 mol.) with $\text{Zn}\cdot\text{Cu}\cdot\text{AcOH}$ in 60—70% EtOH (cf. A., 1934, 898) affords $\zeta\alpha$ -dimethyl- Δ^{101} -*n*-undecatriene- $\gamma\delta$ -diol, $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{CH}\cdot[\text{CH}(\text{OH})]_2\cdot\text{CH}\cdot\text{CHR}$ ($\text{R}=\text{H}$), b.p. 161°/10 mm. (0.13 mol.), $[\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2]_2$ (0—12 mol.), and a substance, $\text{C}_{20}\text{H}_{32}\text{O}$ (II), b.p. 181—182°/9 mm. (0.1 mol.; probably an ether). Similar reduction of a mixture of (I) and $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ gives $\eta\lambda$ -dimethyl- Δ^{1615} -*n*-dodecatriene- $\delta\epsilon$ -diol ($\text{R}=\text{Me}$), b.p. 169—170°/9 mm. (0.32 mol.), $[\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CHMe}]_2$ (0.05 mol.), and a little (II). J. W. B.

Preparation of α -hydroxy-aldehydes. P. FRÉON (Compt. rend., 1935, 200, 464—466).— $\text{CMeEt}\cdot\text{NOH}$ with excess of MgMeI and MgBu^nBr gives, respectively, Me α -hydroxyisopropyl and Me α -hydroxy- α -methylamyl ketoxime (cf. A., 1909, i, 455), which are hydrolysed (dil. $\text{H}_2\text{C}_2\text{O}_4$) to the keto-alcohols (cf. A., 1903, i, 2). Similarly, $\text{CHAc}\cdot\text{NOH}$ with MgBu^nBr gives an oxime, b.p. 105—107°/3.5 mm., which is hydrolysed to α -hydroxy- α -methyl-hexaldehyde, b.p. 86—88°/35 mm. (semicarbazone, m.p. 142—143°), and some α -methyl- Δ^6 -hexenaldehyde, b.p. 72—74°/39 mm. (semicarbazone, m.p. 183—184°; *p*-nitrophenylhydrazone, m.p. 148—149°). J. L. D.

Resolution of *r*-lactaldehyde. R. DWORZAK and W. PRODINGER (Biochem. Z., 1935, 276, 383—385; cf. A., 1929, 297; Betti, A., 1930, 776).—*r*-Lactaldehyde (I) reacts with (+)- β -hydroxynaphthylbenzylamine to give cryst. products (II), m.p. 147°, $[\alpha]_D^{25} -79.92^\circ$ in C_6H_6 , and 138—140°, $[\alpha]_D^{25} -91.8^\circ$ in C_6H_6 . (I) is regenerated from (II) by boiling with 10% aq. $\text{H}_2\text{C}_2\text{O}_4$. W. McC.

Hydroxymethylene ketones and their reaction products. II. Method for removal of water

from readily decomposed *sec.* and *tert.* alcohols. III. Syntheses in the terpene and sesquiterpene series. IV. Action of organomagnesium compounds on salts of hydroxymethylene ketones. R. E. MEYER (Helv. Chim. Acta, 1935, **18**, 279—282, 282—304, 305—307; cf. this vol., 329).—II. Linaloyl acetate is quantitatively decomposed by Cu powder at 135—153° in 1 hr. to AcOH and, probably, myrcene.

III. $\text{Bu}^{\beta}\cdot[\text{CH}_2]_2\cdot\text{COMe}$ gives a $\text{OH}\cdot\text{CH}\cdot$ compound, which with MgMeI gives a $\text{OH}\cdot\text{ketone}$, the *Ac* derivative of which with Cu at 150—160° gives *o*-methyl- Δ^{β} -nonen- δ -one, b.p. 90°/10 mm. (*semicarbazone*, m.p. 143°), oxidised by KMnO_4 to MeCHO , AcOH , and $\text{Bu}^{\beta}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$. This proves that HCO_2Et in alkaline solution condenses with the terminal Me and that mainly 1:4-addition of MgMeI occurs; as formation of the unsaturated ketone is not quant., some β -OH-aldehyde may, however, also be formed. The structures of the following substances follow by analogy. Methylheptenone (I), HCO_2Et , and NaOEt in Et_2O -PhMe give a 60% yield of $\text{OH}\cdot\text{CH}\cdot$ compound (II), m.p. 72°, b.p. 90—98°/8 mm. (much decomp., cf. lit.; 8 inorg. salts, mostly sol. in Et_2O , not very stable in H_2O), which with MgMeI gives CH_4 (1 mol.) and a compound, $\text{C}_{10}\text{H}_{18}\text{O}_2$ (III), an oil, which at 200—250° gives AcOH and (I) (50%), much tar, and *o*-methyl- $\Delta^{\beta\gamma}$ -nonadien- δ -one (IV) (20%), b.p. 90—92°/9 mm. (*oxime*, formed slowly; *semicarbazone*, m.p. 166—167°; slowly decolorises Schiff's reagent and reduces ammoniacal AgNO_3); the oily *Ac* derivative of (III), prepared by AcCl - NPhMe_2 at 25—30°, with Cu in ligroin at 150—160° gives 40% of tar and 47.5% of (IV). With dehydrating agents (III) gives mostly (I) and MeCHO . Hydrogenation (Ni) of ψ -ionone gives mainly the $\gamma\delta$ - H_2 -compound (V), b.p. 131°/13 mm., the $\text{OH}\cdot\text{CH}\cdot$ derivative of which with MgMeI gives 82% of an oily $\text{OH}\cdot\text{ketone}$, which, when heated at 140—150° or at the b.p./14 mm., gives MeCHO and (V), but by acetylation and heating with Cu gives a 25% yield of $\theta\mu$ -dimethyl- $\Delta^{\beta\alpha}$ -tridecatrien- δ -one, b.p. 162°/12 mm. (*semicarbazidosemicarbazone*, m.p. 144°). The $\text{OH}\cdot\text{CH}\cdot$ derivative of β -ionone gives similarly (Cu method in PhOMe) ω -ethylidene- β -ionone, b.p. 126—128°/2 mm., unstable in air [*semicarbazidosemicarbazone*, m.p. 192° (decomp.) after sintering at 182°].

IV. The *Mg* salt of (II) with MgMeI gives the same products as does (II). R. S. C.

Colour reactions of carbazides and carbamides with diacetyl and diacetyldioxime. G. S. SMITH (Analyst, 1935, **60**, 171—172). When $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ (I) is warmed with Ac_2 or $(\text{CMe}\cdot\text{NOH})_2$ and HCl a permanent red colour is produced which, on addition of NH_3 , becomes bluish-violet. Substituted (I) give red to brown colours. $\text{CO}(\text{NH}_2)_2$ and certain other substances also give definite colours. E. C. S.

Application of the double linking rule to questions of sugar chemistry. C. NEUBERG (Ber., 1935, **68**, [B], 505—506; cf. Schmidt, this vol., 329).—The formation of intermediate compounds with double linking between a C_2 and C_3 affords the simplest explanation of the interconversion of *d*-galactose and *l*-sorbose, of the production of furfuraldehyde from

pentoses, of ascorbic acid, and of the degradation of galactose to glycollaldehyde and tetrose. H. W.

d-Xylomethylose (5-deoxyxylose). P. A. LEVENE and J. COMPTON (Science, 1935, **81**, 156).—Non-cryst. *d*-xylomethylose, $[\alpha]_D^{20}$ -2.16° in EtOH , has been synthesised. The *isopropylidene*, b.p. 86—87°/0.2 mm., m.p. 69—70°, $[\alpha]_D$ -20.99° in H_2O , $[\alpha]^{24}$ -18.22° in CHCl_3 , and 3-acetylisopropylidene, b.p. 79—80°/0.2 mm., $[\alpha]^{24}$ $+2.55^\circ$ in CHCl_3 , derivatives, and the *p*-bromophenylhydrazone, m.p. 69—70°, $[\alpha]_D$ -26.05° in $\text{C}_5\text{H}_5\text{N}$, have been prepared.

L. S. T.

Compound of lactose and calcium chloride.—See this vol., 577.

Determination of maltose in the presence of sucrose and monoses. E. SCHAPIRO and M. N. PROFERANSOWA (Z. Wirts. Zuckerind., 1935, **85**, 196—199).—The method is based on the oxidation of maltose to maltobionic acid (I) by alkaline hypiodite (after preliminary hydrolysis of sucrose). The residual solution is heated with NaOH to destroy ketoses. (I) is further hydrolysed with 3% HCl to gluconic acid and glucose, the latter being determined by Bertrand's method. A. G. P.

Rate of hydrolysis of sucrose and the acidity and viscosity of the medium.—See this vol., 587.

Preparation of methylmaltoside hepta-acetate with ortho-ester structure. E. PACSU and F. V. RICH (J. Amer. Chem. Soc., 1935, **57**, 587—588).—Maltose β -octa-acetate and AlCl_3 in cold CHCl_3 give a syrupy chloroacetyl derivative, which in MeOH affords a good yield of methylmaltoside hepta-acetate, $[\alpha]_D$ $+98.8^\circ$, $[\alpha]_D^{20}$ $+79.0^\circ$, $[\alpha]_{\text{H}_2\text{O}}$ $+116.5^\circ$ in CHCl_3 . Lactose and cellobiose octa-acetates do not react. R. S. C.

Configuration and mechanism of hydrolysis of maltose derivatives with ortho-ester structure. E. PACSU (J. Amer. Chem. Soc., 1935, **57**, 537—538).—Methylmaltoside (ortho)acetate (I) in HCl (p_{H} 4) at 23° is hydrolysed (rupture of the linking between Cl and the O of the ortho-ester ring) with subsequent loss of MeOH to give α -maltose 2-acetate, reaction being complete in 2 min. ($[\alpha]_D^{20}$ changes from $+103.7^\circ$ to $+134.6^\circ$); subsequently mutarotation occurs with $k=0.0095$. At p_{H} 4.8 the first reaction requires about 20 min., k being 0.0560. The nature of the hydrolysis and the α -structure of (I) are thus proved. Ortho-ester formation can occur if the OH on C1 and C2 are *cis*. R. S. C.

Biochemical synthesis of β -cyclopentyl- and β -cyclohexyl-glucosides. J. VINTILESCO and C. N. IONESCO (J. Pharm. Chim., 1935, [viii], **21**, 241—246).—By the action of emulsin (I) (10 days) on a cyclopentanol- COMe_2 - H_2O mixture (equal vols.) saturated with glucose is obtained (isolation described) β -cyclopentyl-*d*-glucoside, $[\alpha]_D^{20}$ -40° 30', readily hydrolysed by (I) or by 3% H_2SO_4 at 100°. β -cyclohexyl-*d*-glucoside (Fischer *et al.*, A., 1911, i, 802) is similarly obtained from cyclohexanol. J. W. B.

Cardiac glucosides. X. Hydrogenation of scillarene-*A* and physiological tests of scillarene derivatives. A. STOLL and A. HOFMANN [in part with W. KREIS] (Helv. Chim. Acta, 1935, **18**, 401—

419; cf. this vol., 330).—Hydrogenation (PtO_2) of scillarene-*A* (I) [Ac_6 derivative, m.p. 220—225° (corr.)] in 80% EtOH gives *hexahydrodeoxy-scillarenic-A acid* (II) (53%), $\text{C}_{36}\text{H}_{61}\text{O}_{11}\cdot\text{CO}_2\text{H}$, m.p. about 245—250° (corr.), $[\alpha]_D^{20} -43^\circ$ in EtOH, and *hexahydroscillarene-A* (III), $\text{C}_{37}\text{H}_{60}\text{O}_{13}$, m.p. 197° (corr.), $[\alpha]_D^{20} -49.5^\circ$ in EtOH, neutral. Proscillaridin-*A* (IV) gives similarly *hexahydrodeoxyproscillaridinic-A acid* (45%), $\text{C}_{31}\text{H}_{52}\text{O}_8$, m.p. about 165—175° (corr.), and *hexahydroproscillaridin-A*, $\text{C}_{31}\text{H}_{50}\text{O}_8$, m.p. 243—245° (corr.), neutral. This behaviour is interpreted as due to an ethylenic linking attached to the C carrying the OH involved in the lactone ring; the ring is reductively opened by hydrogenation. (I) and (IV) have three ethylenic linkings, the fourth of scillaridin-*A* (V) being formed by loss of H_2O after hydrolytic removal of the sugar. (I) and (IV), when heated at 150—200°/high vac., give anhydroscillaridin-*A*, the sugar being lost with the H from a neighbouring C, thus forming a new ethylenic linking. Hydrolysis of (I) and (IV) is very slow, 17 hr. with 5% acid being needed to remove the terminal sugar, whilst the rhamnoside linking is still unaffected. The ready hydrolysis of (I), (V), etc. is thus due to lability of the newly-formed OH as well as the nature of the α -deoxy-sugar; the new ethylenic linking is readily formed because it conjugates with other unsaturation already present, but this interpretation is not confirmed by the similarity of the absorption spectra of (I) and (V), which have a max. at 300 μ , due to three conjugated linkings. The colours of (I) and its derivatives with $\text{CCl}_3\cdot\text{CO}_2\text{H}$ resemble those of ergosterol, supporting the view that the former contain sterol structures. Irradiation of (I) and (V) in dioxan or EtOH causes changes in α , but the products have no antirachitic activity. Me scillarenate-*A*-KOPh has 1/18—1/100 of the physiological activity of (I), but (II), (III), methylscillarenic-*A acid* and its Me ester, and *isoscillarenic-A acid* and its Na salt and Me ester are inactive and much less poisonous. The ethylenic linkings, but not the lactone ring, are thus necessary for toxicity. R. S. C.

Ring structure of thymidine. P. A. LEVENE and R. S. TIFSON (Science, 1935, **81**, 98).—Thymine-2-deoxyriboside yields *triphenylmethylthymidine*, m.p. 125°, $[\alpha]_D^{20} +11.4^\circ$ in COMe_2 ; deoxyribose nucleosides have therefore a furanose structure. H. N. R.

Cellulose of native composition from cotton wool. I. E. SCHMIDT, R. SCHNEGG, W. JANDEBEUR, M. HECKER, and W. SIMSON [with J. W. PEDLOW and M. ATTERER] (Ber., 1935, **68**, [B], 542—552).—The sp. criterion of cellulose of native composition is the presence of 0.28% of CO_2H . Higher vals. indicate incomplete removal of fatty and waxy matters, whereas lower vals. show that change in composition has occurred during purification. The following processes are described in detail: (1) treatment with EtOH and C_6H_6 , (2) action of ClO_2 and $\text{C}_5\text{H}_5\text{N}$ in a single stage or of ClO_2 and alkaline materials (e.g., Na_2SO_3 at p_H 6.8—7.0) in a two-stage process at room temp., (3) treatment with ClO_2 and $\text{C}_5\text{H}_5\text{N}$ in a single stage, and after-treatment with 1% $\text{C}_5\text{H}_5\text{N}$. The success of the methods depends somewhat on the type of sample. The preps. contain small amounts of cuticle and PO_4 compounds which

can be removed by pptn. from CuO-NH_3 followed by electro dialysis. Evidence is adduced that the acidity of cellulose is due entirely to CO_2H , since enolic groups, which are reconcilable with the constitution of a polysaccharide, are unstable towards ClO_2 , and that the CO_2H group is not produced or affected in amount by ClO_2 . The isolation of native cellulose from crude cotton wool and crude linters is described in detail. H. W.

Highly polymerised compounds. CVI. "Power of memory" of cellulose acetates. H. STAUDINGER (Ber., 1935, **68**, [B], 474—478).—Mainly a criticism of the work of Hess. If cellulose acetates of differing viscosity are dissolved in AcOH so that, according to Hess, the monose or biose acetate stage is reached, and the solvent is then evaporated in vac., the residual acetates have exactly the same viscosity as previous to dissolution ("memory"). Hess' observations of unusually great depression of the f.p. of AcOH and high osmotic pressures are regarded as abnormal phenomena which cannot be explained at present, but are possibly caused by a reversible change of solvent. H. W.

Sulpholysis of cellulose. G. A. KORSHENIOVSKI (J. Appl. Chem. Russ., 1934, **7**, 1480—1496).—Cellulose is hydrolysed by dissolution in 93% H_2SO_4 (2 pts.); the products consist chiefly of glucose sulphate. The progress of the reaction is conveniently studied by viscosity methods. R. T.

Complex cupric perchlorates and bromates formed with some primary amines.—See this vol., 591.

Salts of γ -amino- β -hydroxybutyric acid. T. FUKAGAWA (Z. physiol. Chem., 1935, **231**, 202—204).— γ -Amino- β -hydroxybutyric acid yields ON-dibenzoyl-, m.p. 162; γ -guanido-, m.p. 250° (decomp.), 2-naphthalenesulphonyl-, m.p. 144° (decomp.), and phenylcarbamido-derivatives and LiI (+ H_2O) and CaI_2 (+2.5 H_2O) salts. J. H. B.

Special reactivity of peptides. B. H. NICOLET (Science, 1935, **81**, 181—182).—Theoretical. The probability that oxidative deamination is a β -oxidation is also discussed. L. S. T.

Synthetic peptide as substrate for tryptic proteinase. M. BERGMANN, L. ZERVAS, and J. S. FRUTON (Science, 1935, **81**, 180).—The peptide substrate $\text{CO}_2\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Ph}$ (I) has been synthesised (cf. A., 1934, 802). It is rapidly split by pancreatin (Merck) and by cryst. trypsin giving carbobenzyloxyglycine and glutamylglycine ester. Tryptic proteinase (II) is thus able to split ordinary peptide linkings if the rest of the mol. fulfils certain structural requirements. In (I), one of these is the presence of the free γ - CO_2H which combines with (II) and enables it to split the peptide. L. S. T.

Ethylenic nitriles. α -Methyl- Δ^8 -hepteno-nitriles and α -amylacrylonitrile. P. CEUTERICK (Bull. Soc. chim. Belg., 1935, **44**, 89—95).— $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ (Na derivative) with Bu^nBr in boiling EtOH gives *Et α -butylacetate*, b.p. 104—104.5°/12 mm., which when boiled with 10% NaOH gives Me

J. L. D.

J. L. D.

R. S. C.

R. T.

H. W.

H. W.

$\text{CH}_2\text{-CMe}_2$
 $\text{CH}_2\text{-CAc} \Rightarrow \text{C}\cdot\text{R}\cdot\text{CO}\cdot\text{NH}_2$ (V), m.p. 215° (5-ring formed by loss of H_2O), identical with a specimen prepared from azafirinone (VI) (A., 1933, 711), by conversion (SOCl_2 followed by NH_3) into its *amide*, m.p. 177—178°, and treatment of this with EtOH-KOH (N_2). The structure assigned to (VI) and to azafrin (VII) is thus confirmed. Oxidation of the Me ester of (VII) in $\text{C}_6\text{H}_6\text{-AcOH}$ with 0.2*N*- CrO_3 (=3 O) affords, in addition to azafirinone Me ester (improved prep.), *azafrinal-I Me ester*, $\text{CHO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$

into a *Cl*-compound, m.p. 65°, which does not lose HCl when heated.

J. L. D.

Conversion of phenylglycinenitrile into its amide by means of hydrogen peroxide. Halogen and acyl derivatives of the amide. L. VON ULLMANN and G. SPECH (Bul. Soc. Chim. Romania, 1934, 16, 157—163).—Anilinoacetonitrile yields anilinoacetamide (I), m.p. 133° (nitrosoamine, m.p. 145°; *Ac*, m.p. 183°, and *Bz* derivative, m.p. 175°), with H₂O₂ and 5% aq. KOH at 80°. Similarly *p*-bromo-, m.p. 91°, and *p*-iodo-anilinoacetonitrile, m.p. 104°, yield *p*-bromo-, m.p. 140°, and *p*-iodo-anilinoacetamide, m.p. 130°, identical with the products of bromination (acid KBr-KBrO₃) and iodination (acid KI-KIO₃) of (I).

F. N. W.

Action of β-aminoethyl alcohol on 2:4:5-trinitrotoluene. G. RACCUI (Atti R. Accad. Sci. Torino, 1934, 69, I, 364—368; Chem. Zentr., 1934, ii, 2823).—β-Aminoethyl alcohol and 2:4:5-C₆H₂Me(NO₂)₃ (I) in COMe₂ solution yield 4:6-dinitro-*N*-β-hydroxyethyl-*m*-toluidine, m.p. 115°. Di- and tri-β-hydroxyethylamines with (I) yield additive compounds: 2C₆H₂Me(NO₂)₃.NH(C₂H₄.OH)₂ and C₆H₂Me(NO₂)₃.2N(C₂H₄.OH)₃ m.p. 171°.

H. N. R.

Rotatory power of α-phenylethylamine and of its halogen salts.—See this vol., 568.

Preparation of dibromodiphenylamine by direct bromination. L. GALATIS and J. MEGALOKONOMOS (Praktika, 1934, 9, 20—21; Chem. Zentr., 1934, ii, 2974).—Bromination of NHPH₂ in 20% EtOH yields 4:4'-dibromodiphenylamine (I), m.p. 107°, together with small amounts of tetrabromodiphenylamine. Conc. HNO₃ displaces the Br in (I).

H. N. R.

Complexes formed between benzidine and metallic salts. J. BARCELO (Anal. Fis. Quim., 1933, 31, 852—860).—The following compounds are described (B=benzidine): [HgB](CN)₂; [CdB]SO₄; [ZnB]SO₄; [AgB]NO₃. Details are given of the prep. of these and other (known) complexes of similar type.

H. F. G.

New derivatives of 2:2'-dinitrobenzidine. II. D. PONTE (Giorn. Farm. Chim., 1934, 83, 185—192; Chem. Zentr., 1934, ii, 3116—3117).—4:4'-Di-iodo-2:2'-dinitrodiphenyl (I), m.p. 187—188°, obtained (Sandmeyer) from 2:2'-dinitrobenzidine, is reduced to 4:4'-di-iodo-2:2'-diaminodiphenyl, m.p. 157—158°, which, by diazotisation and treatment with KI, affords 2:2':4:4'-tetraiododiphenyl, m.p. 125—126°, and some 4:4'-di-iodocarbazole, m.p. 265—266°.

H. N. R.

Preparation of diphenylbenzidine.—See this vol., 462.

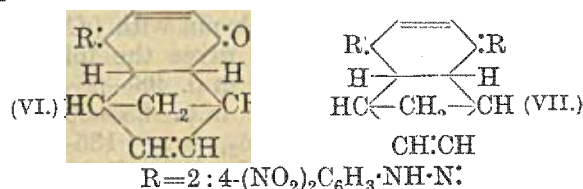
2:4:6-Triaminotoluene hydrochloride. F. HEIN and F. WAGNER (J. pr. Chem., 1935, [ii], 142, 201—204).—Details for the prep. (55% yield) of the above trihydrochloride, +1H₂O and anhyd. (behaviour up to decomp. 320—350° described), by reduction (SnCl₂-AcOH-HCl) of 2:4:6-trinitrotoluene, decomp. of the double Sn salt with H₂S-NaHCO₃ (CO₂ atm.), and saturation of the filtrate with HCl are given.

J. W. B.

Constitution of hydroxyazo-compounds. R. KUHN and F. BAR (Annalen, 1935, 516, 143—155).—The absorption spectrum of 4-benzeneazo-α-naphthol (I) in C₆H₆ shows max. at 410 mμ (corresponding with that of its *O*-Me ether) and at 460 mμ (corresponding with that of the *N*-Me ether of the hydrazone form), and varies greatly according to the solvent. Thus (I) is in tautomeric equilibrium (rapidly established, since all attempts to isolate two forms failed) with its hydrazone form (II). In C₅H₅N it exists almost entirely as (I), and in AcOH or PhNO₂ as (II). The absorption spectra of *o*-, *m*-, and *p*-hydroxyazobenzene (and of azobenzene itself) are essentially the same in AcOH and C₅H₅N, and closely resemble those of the *O*-Me ethers. These are thus true hydroxyazo-compounds. The absorption spectra of 1-benzeneazo-β-naphthol (III) and of 2-benzeneazo-α-naphthol (IV) (both insol. in alkali) are unaffected by the solvent and differ from those of their *Ac* and *Bz* derivatives. (III) and (IV) are thus essentially *o*-quinone hydrazones, but whereas (IV) affords an *O*-Me ether with CH₂N₂-Et₂O only in presence of a trace of EtOH, (III) cannot be so methylated under any conditions. All the chemical and physical properties of these compounds are simply explained on the basis of the (extreme) differences in the position of equilibrium between hydroxyazo- and hydrazone forms. No essential difference is observed in the optical exaltation of 2- and 4-benzeneazo-α-naphthol although the equilibrium position differs greatly.

J. W. B.

Structure of hydroxyazo-compounds. W. M. LAUER and S. E. MILLER (J. Amer. Chem. Soc., 1935, 57, 520—525).—Addition of cyclopentadiene (I) indicates a quinone structure for certain hydroxyazo-compounds, but others do not react. Addition occurs best in acid solution. 2:4-Dinitrophenylhydrazine (II) and benzoquinone or PhOH and (NO₂)₂C₆H₃.N₂Cl give 2:4-dinitrobenzeneazophenol, m.p. 185—186° [*Ac* (III), m.p. 135—136°, and *Bz* (IV) derivative, m.p. 163.5—164.5°; *Me* ether (V), m.p. 176—177°], which with (I) in AcOH gives the adduct (VI), m.p. 166—167° (about 30% yield, changed to 20% and 37—48% by presence of NaOAc and CH₂Cl.CO₂H, respectively). This with (II) gives the bisphenylhydrazone adduct (VII), m.p. 258—260°, also obtained from (II) and the *p*-benzoquinone (I) adduct; it is not obtained as a by-product



with (VI), and the formation of the latter does not, therefore, involve cleavage. 2':4'-Dinitro-4-hydroxy-3-methylazobenzene, m.p. 172.5—173.5° (lit. 127—128°) (*Bz* derivative, m.p. 182—183°), with (I) gives the adduct, m.p. 162—163°, converted by (II) into the bishydrazone adduct, m.p. 252—253° (decomp.), also obtained from (II) and the toluquinone-(I) adduct. Bromobenzoquinone gives 3-bromo-2':4'-dinitro-4-hydroxyazobenzene, m.p. 186—187°, which

with (I) gives the *adduct*, m.p. 176—177°. Benzoquinoneazine in C_6H_6 adds 2 mols. of (I) to give the *adduct*, m.p. 149—150°, thus confirming the nature of the above reactions. (I) does not add to (II), (IV), (V), or the following derivatives of 4-hydroxyazobenzene: 3:5- Br_2 -2':4'-(NO_2)₂-, m.p. 211—212° (*Bz* derivative, m.p. 198—199°), 2- NO_2 -4'- CO_2H -, m.p. 252—254° (*Ac* derivative, m.p. 214—216°), 2':6'- Br_2 -4'- NO_2 -, m.p. 153—153.5°, 2'- NO_2 -, 2'- NO_2 -4'- Br -, 4'- NO_2 -, 2'- CO_2H -, 4'- SO_3H -, 3- CO_2H -, and 4'-OH-. R. S. C.

Phosphoric acid as condensing agent. A. E. TSCHITSCHIRABIN [in part with BESTOUGEY] (Bull. Soc. chim., 1935, [v], 2, 497—520).— H_3PO_4 (usually *d* 1.83—1.85) is used for condensing phenols and ethers with *tert.*- or, less well, *sec.*-alcohols. Ethylenes can also be used, particularly if the chain branches near the ethylenic linking, when the *sec.* or *tert.* C becomes attached to the C_6H_6 ring. Primary alcohols do not condense (unless a temp. is used which causes isomerisation), except $CH_2Ph\cdot OH$, which gives much dibenzyl derivative. Condensation occurs entirely in the *o*-position, except with *sec.*-alcohols, which at high temp. give some *p*-product. Phenols may give a small amount of ethers and unsaturated hydrocarbons. The following are thus prepared. 4-*tert.*-Butyl- (I), hygroscopic, m.p. 23°, b.p. 121—122°/16 mm. (*hydrate*, m.p. 37°; *Me* ether, m.p. 24°), -*tert.*-amyl-, b.p. 119—122°/10 mm., and -*menthyl*-*m*-cresol, b.p. 152—155°/2.5 mm.; 3-*tert.*-butyl-*o*-, hygroscopic, m.p. 27°, b.p. 122.5°/14 mm., and -*p*-cresol, m.p. 44°, b.p. 118—119°/14 mm.; *o*-*tert.*-butyl-, b.p. 125.5—126°/17 mm., and -*isopropyl*-*m*-4-*xylene*ol, b.p. 127—130°/17 mm.; 3-, m.p. 51°, and 5-benzyl-*o*-cresol; 1-*tert.*-butyl- β -naphthol, m.p. 113°, b.p. 186—189°/13 mm.; 4-*tert.*-butyl- (II), b.p. 134—136°/1.5 mm., and + H_2O , *cryst.*, and 4:6-di-*tert.*-butyl-resorcinol (III), anhyd., m.p. 121°, and +2 H_2O , *cryst.*; 4-*n*-octyl-*m*-cresol, b.p. 152—154°/11 mm.; *o*-allylphenol, b.p. 200—205° (polymeride, a resin) (some 2-methylcoumaran is obtained in ligroin solution); *Me* ether of (I), b.p. 95—101°/12 mm., *cryst.*; *Me_2* ethers of (II), b.p. 126—129°/13 mm., m.p. 4°, and (III), m.p. 76°, b.p. 130—146°/13 mm. *m*-Cresol and propylene glycol give a viscous polymeric phenol. R. S. C.

Structure of keten diphenyl acetal. A. C. COPE (J. Amer. Chem. Soc., 1935, 57, 572—574).—The K salt of the appropriate phenol with $(\cdot CH_2Br)_2$ in EtOH or $(\cdot CH_2Cl)_2$ in H_2O gives the following ethylene glycol ethers: Ph_2 (I), m.p. 98—98.5°, (*p*- C_6H_4Br)₂, m.p. 134—135°, *o*-, m.p. 85—86°, *m*-, m.p. 98—99°, and (*p*- C_6H_4Me)₂, m.p. 135—136°, di-6-bromo-*m*-tolyl (II), m.p. 137—138°, di-3-bromo-*p*-tolyl, m.p. 160—161°, and (*o*- $NO_2\cdot C_6H_4$)₂, m.p. 167—168°. These are identical with the corresponding so-called “(tri)aryl orthoacetates” of Heiber (A., 1892, 308), except that Heiber's analogue of (II) has m.p. 151.5—153° (considered to be due to impurity in the *m*-cresol used previously). $CMeCl_3$ and $KOPh$ give *o*- and *p*- $C_6H_4Ac\cdot OH$, but no (I); (I) is formed from a mixture of $CMeCl_3$ and $(\cdot CH_2Cl)_2$, and presence of the latter probably accounts for Biginelli's prep. of (I) (A., 1891, 296), which, how-

ever, he considered erroneously to be “keten Ph_2 acetal” (“diphenylethyldene ether”). Biginelli's “dibromides” and Heiber's “ Br_2 -derivatives” are really the Br-compounds listed above, being obtained either from the bromophenols or by bromination of the ethers. R. S. C.

Constitution of sulphur monochloride, and derivatives of the hypothetical acid $(S\cdot OH)_2$. G. GIACOMELLO (Atti. R. Accad. Lincei, 1935, [vi], 21, 36—42).—By mixing C_6H_6 solutions of $PhOH$ and S_2Cl_2 a compound, m.p. 125°, is obtained with the probable structure $(S\cdot OPh)_2$, i.e., a derivative of $(S\cdot OH)_2$. Similar compounds appear to be formed by the action of S_2Cl_2 on α - and β - $C_{10}H_7\cdot OH$, and on substituted phenols. S_2Cl_2 is considered to be a mixture of the two forms $S\cdots SCl$ and $(\cdot SCl)_2$.

O. J. W.

Oxidation of naphthols by peracetic acid. J. BOESEKEN and J. M. L. VON KONIGSFELDT (Rec. trav. chim., 1935, 54, 313—316; cf. A., 1930, 334).— α - $C_{10}H_7\cdot OH$ in AcOH containing 10% of AcO_2H at < 40° during several days gives *o*-carboxyalloucinamic acid (I), a little coumarin (not isolated), α -naphthaquinone (II), and a hydroxyquinone (?), probably obtained by oxidation of (II). β - $C_{10}H_7\cdot OH$ as above gives mainly (I) (80%) and 2:2':6:6'-tetrahydroxy-1:1'-dinaphthyl (?), m.p. 265—167°.

J. L. D.

Xenyl esters and ethers. C. C. VERNON, E. F. STRUSS, M. A. O'NEIL, and M. A. FORD (J. Amer. Chem. Soc., 1935, 57, 527—528).—Na xenoxide and $POCl_3$ in $PhMe$ give *tri*-*o*-, m.p. 134.5°, and -*p*-xenyl phosphate, m.p. 109°. *o*- and *p*-Xenyl Et, m.p. 68° and 107°, and *Bu* ether, b.p. 137°/18 mm. and m.p. 73°, respectively, are prepared. R. S. C.

Preparation of *p*-substituted dialkylanilines. W. C. DAVIES (Bull. Soc. chim., 1935, [v], 2, 295—296).—The prep. of *p*- $C_6H_4R\cdot NMe_2$ from *p*- $C_6H_4R\cdot NH_2$ - MeI - $NaOH$ - $MeOH$ ($R=NO_2$, OMe , or OEt), of *p*- $NO_2\cdot C_6H_4\cdot NMe_2$ by $KMnO_4$ oxidation of the *p*- NO -compound, and of *p*-methoxydiethylaniline, b.p. 257°/772 mm. (*methiodide*, m.p. 127°; *ethiodide*, m.p. 162°), is described. J. W. B.

Condensation of *p*-phenetidine hydrochloride with epichlorohydrin. I. T. STRUKOV (J. Gen. Chem. Russ., 1934, 4, 1303—1304).—Epichlorohydrin and *p*- $OEt\cdot C_6H_4\cdot NH_2\cdot HCl$ in H_2O at room temp. yield $OH\cdot CH(CH_2Cl)_2$ and *NN*-di-(γ -chloro- β -hydroxy-*n*-propyl)-, m.p. 151°, converted by KOH into *NN*-di-(β - γ -oxido-*n*-propyl)-*p*-phenetidine, b.p. 201—203°/1 mm. R. T.

Ethoxybenzylcarbamides. E. WERTHEIM (J. Amer. Chem. Soc., 1935, 57, 545—546).—*m*- and *p*-Phenetidine yield (diazo-reaction) *m*- (I), b.p. 241—244°, and *p*-ethoxybenzonitrile (II), m.p. 63—65°, respectively; (II) with $Na\cdot MeOH$ gives a poor yield of *p*-ethoxybenzylamine, b.p. 97—102°/3 mm.; (I) with NH_4HS - $EtOH$ at 100—105° gives *m*-ethoxythiobenzamide, m.p. 75—77°, reduced by Zn dust and HCl - $EtOH$ to *m*-ethoxybenzylamine, b.p. 107—110°/5 mm. *o*-Ethoxymethylthiobenzamide is hydrogenated (PtO_2) to *o*-ethoxymethylbenzylamine, b.p. 118—120°/10 mm. [picrate, m.p. 155—157° (lit.

148°)]. The bases with HCl and KCNO afford p., m.p. 163—164°, and m-ethoxy-, m.p. 121—123°, and o-ethoxymethyl-benzylcarbamide, m.p. 116—118°, all tasteless. Sweetness is thus dependent on attachment of the $\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ (III) to the C_6H_5 ring and not on the spatial relationship of (III) to the OEt. R. S. C.

Action of mercuric iodide on phenols in alkaline medium. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 376).—Reduction of HgI_2 to Hg_2I_2 or Hg is effected by various phenols in alkaline solution, with the corresponding formation of the Hg phenoxide. The reaction differentiates α - ($\text{Hg} + \text{Hg}_2\text{I}_2$) and β - [ppt. of $(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{Hg}$] -naphthol, and resorcinol from pyrocatechol and quinol. J. W. B.

Constituents of *Ginkgo biloba*, L., fruit. IV. S. FURUKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 26, 178—185; cf. A., 1934, 1345).—Oxidation of emulsified *Me ginkgolate Me ether*, b.p. 230—233°/2 mm., by KMnO_4 affords 3-methoxyphthalic acid, indicating that the CO_2H is *o* to both the OH and pentadecenyl groups. KMnO_4 oxidation of emulsified bilobol *Me ether* yields α -resorcylic acid *Me*₂ ether (I); hence bilobol is 3:5-dihydroxy-pentadecenylbenzene. The acid chloride of (I) with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ yields Et 3:5-dimethoxybenzoylacetoacetate, partly hydrolysed by aq. NH_3 to the corresponding acetic ester, which, on condensation with tridecenyl iodide and hydrolysis of the 3:5-dimethoxybenzoyltridecenylacetic ester thus formed, affords 3:5-dimethoxyphenyl tetradecenyl ketone, $\text{C}_{23}\text{H}_{36}\text{O}_3$, m.p. 61.5—62.5°, reduced (Clemmensen) to 3:5-dimethoxypentadecylbenzene, m.p. 53.5—54.5°, and demethylated to 3:5-dihydroxypentadecylbenzoic acid [hydrobilobol, isomeric with hydroourushiol (A., 1916, i, 36)]. F. O. H.

Derivatives of 2-methylnaphthalene. F. GIRAL (Anal. Fis. Quim., 1933, 31, 861—881).—2-Methyl- α -naphthaquinone (I) (prep. described) is converted by HNO_3 (*d* 1.51) at room temp. into a substance, m.p. 220° (decomp.), which contains no N. (I) is reduced ($\text{Zn}-\text{H}_2\text{SO}_4$) to 1:4-dihydroxy-2-methylnaphthalene [*Me*₂ ether, m.p. 23—24°, which with oleum gives a disulphonic acid (*Ba* salt), and with HNO_3 (*d* 1.51) gives a NO_2 -compound, m.p. 107°]. 1-Nitro-8-[sulphate, m.p. 175—180° (decomp.)], and -5-amino-2-methylnaphthalene [sulphate, m.p. 270° (decomp.)] [obtained from 1:5-dinitro-2-methylnaphthalene (II) and $\text{SnCl}_2\text{-HCl}$ at 103° (cf. A., 1925, i, 804)] are described. 1:8-Dinitro-2-methylnaphthalene with $\text{PI}_3\text{-H}_2\text{O}$ gives the diamine, m.p. 63° [hydriodide, m.p. 215—220° (decomp.); sulphate, m.p. 197°; Ac_2 , m.p. 136°, and Bz_2 derivative, m.p. about 250°], which is converted by boiling aq. NaHSO_3 into 1-amino-8-hydroxy-2-methylnaphthalene, m.p. 133°. Similarly, (II) gives the $(\text{NH}_2)_2$ -compound, m.p. 136° [hydriodide, m.p. 238—240° (decomp.); diazonium, m.p. about 131°, and Ac_2 derivative, m.p. 202°], which gives no definite substance with NaHSO_3 . J. L. D.

Nitration of 2:2'-dihydroxydiphenyl. F. CALVET and E. SEIGO (Anal. Fis. Quim., 1933, 31, 882—888).—2:2'-Dihydroxydiphenyl with HNO_3 (*d* 1.4) in AcOH gives 3:3'- (Ac_2 derivative, m.p. 103—105°) and 5:5'-dinitro-2:2'-dihydroxydiphenyl (I) (Ac_2

derivative, m.p. 202—204°) different from that of Diels and Bibergeil (A., 1902, i, 219), which is a mixture of (I) and 3:5'-dinitro-2:2'-dihydroxydiphenyl, m.p. 210—211° (dimorphic) (*Me*₂ ether, m.p. 133—135°, Ac_2 derivative, m.p. 122—125°). J. L. D.

Halogenation of diacetyldianisidine. E. HARRISON (Chem. and Ind., 1935, 213—214).—Bromination (Br-AcOH at 20°) of diacetyldianisidine (I) gives 6-bromodiacetyl-, m.p. 223°, hydrolysed to 6-bromo-, m.p. 132°, and further brominated to 6:6'-dibromodiacetyl-dianisidine, m.p. 285°, hydrolysed to the diamine (A., 1929, 1172). (I) on chlorination ($\text{SO}_2\text{Cl}_2\text{-AcOH}$ at 25°) gives 6-chlorodiacetyldianisidine, m.p. 217°, hydrolysed to the diamine, m.p. 127°, and 6:6'-dichlorodiacetyldianisidine (II), m.p. 270°, hydrolysed to the diamine, m.p. 172° (identical with a specimen prepared from 2-nitro-4-chloroanisole through the hydrazo-compound). (I) in AcOH with Cl_2 (gas) gives a Cl_3 -derivative (III), m.p. 285° (decomp.), hydrolysed to the diamine, m.p. 180°. Attempts to prepare (III) from (II) were unsuccessful. H. G. M.

Synthesis of pyrogallol 3:5-dimethyl 1-propyl ether. F. MAUTHNER (J. pr. Chem., 1935, [ii], 142, 152).—Priority is claimed (cf. this vol., 490; A., 1921, i, 726). R. S. C.

Aromatic sulphides. C. LEFEVRE and C. DESGREZ (Compt. rend., 1935, 200, 762—764; cf. A., 1934, 766, 886, 1098).—The presence of S in compounds $(\text{OH}\cdot\text{C}_6\text{H}_4)_2\text{S}$ so increases the acidity of OH that CO_2 is liberated from alkali and alkaline-earth carbonates, that true salts are formed with aq. solutions of Zn, Cu, Pb, and Ag salts, and complex compounds are produced with HgCl_2 and NaOH. In cold solution PhOH with increasing quantities of HgCl_2 and NaOH yields compounds $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{HgCl})_2$, and $\text{OH}\cdot\text{C}_6\text{H}_2(\text{HgCl})_3$, whereas at 70° the products are $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgOH}$, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{HgOH})_2$, and $\text{OH}\cdot\text{C}_6\text{H}_2(\text{HgOH})_3$, from which warm dil. HCl regenerates HgCl_2 . $\text{Hg}(\text{OH})$ is *o* or *p* to OH. Similar substances are derived from $m\text{-C}_6\text{H}_4(\text{OH})_2$. With $\text{Br-H}_2\text{O}$ they give tribromo-phenol and -resorcinol, respectively. The compounds, $[\text{OH}\cdot\text{C}_6\text{H}_3(\text{HgOH})\cdot\text{S}]_n$, $[\text{OH}\cdot\text{C}_6\text{H}_2(\text{HgOH})_2\cdot\text{S}]_2$, $[(\text{OH})_2\text{C}_6\text{H}_3(\text{HgOH})\cdot\text{S}]_2$, and $[(\text{OH})_3\text{C}_6\text{H}_2(\text{HgOH})_2\cdot\text{S}]_2$ are obtained analogously. H. W.

Rearrangement of *o*-benzamido-sulphides. C. F. WIGHT and S. SMILES (J.C.S., 1935, 340—343).—2-Nitro-2'-formamido-diphenyl sulphide, m.p. 143°, with NaOEt-MeI gives 2-*o*-nitrophenylaminophenyl *Me* sulphide, whilst the -benzamido-compound, m.p. 106°, similarly forms 2-*o*-nitrophenylbenzamidophenyl *Me* sulphide, m.p. 206°, oxidised to the sulphone, m.p. 251°. The sulphone is also obtained by rearrangement of 2-nitro-2'-benzamidodiphenylsulphone, m.p. 139°. 2:4-Dinitro-2'-benzamidodiphenyl sulphide, m.p. 178°, obtained from the amine and BzCl , is rearranged to a thiol which could not be isolated owing to formation of a thiazine; 3-nitro-6-benzoylthiodiphenylamine, m.p. 161—162°, is isolated in 25% yield. 2-Benzamidophenylthiol and picryl chloride (cf. Mitsugi *et al.*, A., 1910, i, 337) give a mixture of 2-benzamidophenyl disulphide, 2:4-dinitro-6-benzoylthiodiphenylamine, and 2-benzamidophenyl picryl sulphide, m.p. 213—214° (decomp.); the amine is hydro-

lysed to the 3:5-dinitrothiodiphenylamine obtained by Kehrman (A., 1913, i, 1383) from 2-picramidophenylthiol. 2-Acetamidophenylthiol, picryl chloride, and MgCO_3 afford 2-acetamidophenyl picryl sulphide, m.p. 215—216° (decomp.). F. R. S.

Di-2-hydroxy-1-naphthyl sulphide. A. WAHL and M. RINGEISS (Compt. rend., 1935, 200, 757—759; cf. A., 1934, 999).—Di-2-hydroxy-1-naphthyl sulphide is transformed by boiling NH_2Ph into $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ and $\text{C}_{10}\text{H}_6\text{-}\begin{smallmatrix} \text{S} \\ \text{NH} \end{smallmatrix}\text{-C}_6\text{H}_4$, m.p. 178° (corr.).

H. W.

Dehalogenation of cyclic chlorohydrins with curtailment of the ring. M. GODCHOT, M. MOUSERON, and R. GRANGER (Compt. rend., 1935, 200, 748—750).—The action of HOCl on cyclopentene leads to a little *cis*-2-chlorocyclopentanol (I), b.p. 44°/15 mm. (probably contaminated with 1:2-dichlorocyclopentane), and *trans*-2-chlorocyclopentanol (II), b.p. 84°/15 mm. (I) is unchanged by $\text{EtOH-H}_2\text{O}$ at 90°, whereas (II) is rapidly and completely converted into *trans*-cyclopentane-1:3-diol. Similarly, cyclohexene and HOCl afford *cis*- (III), b.p. 76°/15 mm., and *trans*- (IV), b.p. 87°/15 mm., m.p. 29°, -2-chlorocyclohexanol. (III) is not appreciably changed by $\text{EtOH-H}_2\text{O}$ at 90°, whereas (IV) slowly yields *trans*-cyclohexane-1:2-diol and cyclopentylformaldehyde (semicarbazone, m.p. 123—124°). 1-Methyl- Δ^3 -cyclohexene gives a mixture of four chlorohydrins, two of which (V and VI), b.p. 79°/16 mm. and 101—102°/16 mm., are isolated by distillation. (V) is unchanged by H_2O at 90°, whereas (VI) becomes converted into *trans*-1-methylcyclohexane-3:4-diol, m.p. 63°, and 1-methyl-3-cyclopentylformaldehyde (semicarbazone, m.p. 133°). Only one chlorohydrin, b.p. 98°/16 mm., is isolated from cycloheptene; it is quantitatively converted by $\text{EtOH-H}_2\text{O}$ into cyclohexylformaldehyde (semicarbazone, m.p. 167—168°). 2-Chlorocyclooctanol, b.p. 128—130°/20 mm., is converted by $\text{EtOH-H}_2\text{O}$ at 90° into (?) cyclooctadiene without production of a glycol or of cycloheptylformaldehyde. H. W.

ω -Nitroacetophenones. I. Catalytic hydrogenation of substituted ω -nitroacetophenones. B. REICHERT and W. KOCH (Ber., 1935, 68, [B], 445—453).— ω -Nitroacetophenones can be hydrogenated smoothly (yields about 80%) to β -hydroxy- β -arylethylamines. ω -Nitro-2-methoxystyrene and Br in CHCl_3 afford $\alpha\beta$ -dibromo- α -nitro- β -2-methoxyphenylethane, m.p. 83°, converted by KOAc-EtOH into β -bromo- β -nitro- α -2-methoxyphenylethylene (I), m.p. 70—71°. Under somewhat differing conditions treatment of (I) with boiling KOH-MeOH leads to β -bromo- β -nitro- α -methoxy- α -2-methoxyphenylethane, m.p. 72°, or β -nitro- α -dimethoxy- α -2-methoxyphenylethane, m.p. 82°, hydrolysed by HCl-MeOH to ω -nitro-2-methoxyacetophenone (II), m.p. 118° (with a Br-compound, m.p. 175°). Hydrogenation (PtO_2) of (II) in EtOH containing $\text{H}_2\text{C}_2\text{O}_4$ at 50° gives β -amino- α -2-methoxyphenylethanol oxalate, m.p. 228°. $\alpha\beta$ -Dibromo- β -nitro- α -3:4-dimethoxyphenylethane, m.p. 118°, is converted similarly into β -bromo- β -nitro- α -3:4-dimethoxyphenylethylene, m.p. 139°, and ω -nitro-3:4-dimethoxyacetophenone, m.p. 149°, whence β -amino- α -3:4-dimethoxyphenylethanol oxalate, m.p. 242°. $\alpha\beta$ -Dibromo- β -nitro- α -3:4-methyl-

enedioxyphenylethane, m.p. 83°, affords β -bromo- β -nitro- α -3:4-methylenedioxyphenylethylene, m.p. 99°, converted without apparent formation of intermediate products into ω -nitro-3:4-methylenedioxyacetophenone, m.p. 174°, whence β -amino- α -3:4-methylenedioxyphenylethanol *H* oxalate, m.p. 180°. $\alpha\beta$ -Dibromo- β -nitro- α -4-methoxyphenylethane, m.p. 95°, gives β -bromo- β -nitro- α -4-methoxyphenylethylene, m.p. 68°, transformed by boiling KOH-MeOH into β -nitro- α -methoxy- α -4-methoxyphenylethylene, m.p. 74°, which passes in acid solution immediately into ω -nitro-*p*-methoxyacetophenone, m.p. 156°. In spite of cautious operation HBr is lost during the action of Br on ω -nitro-2:4-dimethoxystyrene and α -bromo- ω -nitro-2:4-dimethoxystyrene (III), m.p. about 174° (decomp.), results. More drastic conditions lead to $\alpha\beta$ -dibromo- β -nitro- α -5-bromo-2:4-dimethoxyphenylethane, m.p. 107°, converted by KOAc into β -bromo- β -nitro- α -5-bromo-2:4-dimethoxyphenylethylene, m.p. 157—158°, from which the corresponding ω - NO_2 -ketone could not be obtained. Oxidation of (III) with KMnO_4 in COMe , affords 5-bromo-2:4-dimethoxybenzaldehyde, m.p. 142° (phenylhydrazone, m.p. 158°), also obtained from Br and 2:4-(OMe) $_2\text{C}_6\text{H}_3\text{:CHO}$ and transformed by MeNO_2 into (III). With excess of $\text{Ca}(\text{MnO}_4)_2$ in COMe , (III) yields 5-bromo-2:4-dimethoxybenzoic acid, m.p. 197°. The non-cryst. dibromide of ω -nitro-2:3:4-trimethoxystyrene is converted by KOAc into β -bromo- β -nitro- α -2:3:4-trimethoxyphenylethylene, m.p. 83°. H. W.

Preparation of coloured hydrocarbons of the rubene type. A. WILLEMART (Compt. rend., 1935, 200, 755—757).— $\alpha\alpha$ -Diphenyl- δ -methyl- Δ^8 -pentin- α -ol (I), from $\text{CBu}^i\text{:C-MgBr}$ and COPh_2 , is converted by PCl_3 into α -chloro- $\alpha\alpha$ -diphenyl- δ -methyl- Δ^8 -pentinene (II), m.p. 53—54° (block), which does not lose HCl when heated. Reconversion of (II) into (I) has not been effected, but both compounds are transformed into $\alpha\alpha$ -diphenyl- δ -methyl- Δ^8 -pentin- γ -one (III), m.p. 66°. (I) and (III) are oxidised by CrO_3 to COPh_2 (yield 80—85%) and (?) $\text{Bu}^i\text{CO}_2\text{H}$. The prep. of a hydrocarbon of the rubene type by thermal decomp. from a substance, $\text{CRR}'\text{Cl:C:CR}''$, does not appear possible if one of the groups is aliphatic. H. W.

Reactions of titanium tetrachloride etherates with benzene. L. I. KASHTANOV (J. Gen. Chem. Russ., 1934, 4, 1204—1205).— $\text{CHPh}_2\text{:OEt}$ and C_6H_6 in presence of TiCl_4 yield CHPh_3 ; under similar conditions, $(\text{CPh}_3)_2\text{O}$ affords $\text{CPh}_3\text{:OH}$, and $(\alpha\text{-C}_{10}\text{H}_7)_2\text{CH:OEt}$ gives $\text{CHPh}(\text{C}_{10}\text{H}_7)_2$. R. T.

Spectrography of cholesterol and its derivatives. A. H. ROFFO, O. CALCAGNO, and A. E. ROFFO (Bull. Soc. Chim. biol., 1935, 17, 203—209).—A no. of spectrograms (I) are given for cholesterol (II) and derivatives in CHCl_3 solution under various conditions of temp., irradiation, etc. The photoactivity of (II) can be precisely stated in terms of (I) provided comparable conditions are used.

P. W. C.

Behaviour of sterol derivatives towards digitonin. E. FERNHOLZ (Z. physiol. Chem., 1935, 232, 97—100).—Sterols with shortened side chain are pptd. by digitonin if they have a free OH in the

position and steric configuration in which it occurs in cholesterol.

J. H. B.

Attempt to ketonise ergosterol. E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 115—116).—Ergosterol refluxed with NH_2OH in EtOH for 3 hr. was recovered unchanged.

F. O. H.

Lumisterol. K. DIMROTH (Ber., 1935, 68, [B], 539—542).—Analyses of perhydrolumisterol and its derivatives indicate the presence of 3 double linkings in lumisterol (I); this is confirmed by measurements of the micro-hydrogenation of lumisteryl and dihydrolumisteryl acetate. Dehydrogenation of (I) with Se affords Diels' methylcyclopentenophenanthrene. The skeleton of ergosterol (II) therefore persists in (I) and the first stage of the action of ultra-violet light on (II) consists in isomerisation and not in fission of a C-C linking.

H. W.

Polyterpenes and polyterpenoids. XCIV. Degradation of sitostanol acetate by chromic acid. L. RUZICKA and E. EICHENBERGER. **XCv. Dehydrogenation products, $\text{C}_{25}\text{H}_{41}$, $\text{C}_{26}\text{H}_{42}$, and $\text{C}_{27}\text{H}_{44}$, from sterols.** L. RUZICKA and M. W. GOLDBERG (Helv. Chim. Acta., 1935, 18, 430—434, 434—438; cf. this vol., 625).—Sitostanol, m.p. 143—143.5°, $[\alpha]_D +18.7^\circ$ in CHCl_3 [from sitosterol (I) of wheat embryos], gives an acetate, m.p. 138—139°, $[\alpha]_D 13^\circ$ in CHCl_3 , which with CrO_3 yields 3-hydroxy- Δ^5 -cholestan-17-one. The OH of (I) thus corresponds with that of cholesterol.

XCv. Purification and analysis of the dehydrogenation products, $\text{C}_{25}\text{H}_{41}$ from cholesterol, $\text{C}_{26}\text{H}_{42}$ from ergosterol, and $\text{C}_{27}\text{H}_{44}$ from phytosterol, m.p. 204—205° (lit. 203—204°), are recorded. The first, prepared by Se, as now obtained, has violet ultra-violet fluorescence and corresponds exactly with the Pd-product in X-ray analysis (powder).

R. S. C.

Olefinic acids. XVI. Additive reactions and tautomeric changes of cyclic unsaturated acids, and analogous observations on α -methylpentenoic acids. E. J. BOORMAN and R. P. LINSTED (J.C.S., 1935, 258—267; cf. A., 1932, 251; 1933, 934).—The prep. of Δ^1 -tetrahydrobenzoic acid (I), m.p. 38° (lit., 29°), and the Δ^2 -acid (II), b.p. 120°/10 mm. (lit., b.p. 234—235°), is described. Dehydration of the cyanohydrin of 3-methylcyclohexanone (cf. A., 1926, 726) gives a mixture of Δ^1 - and Δ^6 -unsaturated nitrile which is hydrolysed (10% $\text{KOH-H}_2\text{O}$) to a mixture of acids (III), which contains about 22% of the Δ^6 -form. Partial esterification gives an ester (IV) and a mixture of acids (Δ^1 and Δ^6), from which 3-methyl- Δ^1 -cyclohexenecarboxylic acid (1:2- Br_2 -derivative, m.p. 119°) is obtained through its Ca salt (cf. J.C.S., 1905, 87, 1085; 1907, 91, 496). Hydrolysis (cf. A., 1932, 251) of (IV) gives an acid, b.p. 123°/7 mm., separated by partial esterification into an ester (V) and an acid, further esterified to (VI). Both (V) and (VI) when hydrolysed give pure 3-methyl- Δ^2 -cyclohexenecarboxylic acid (VII) (J.C.S., 1907, 91, 496). Equilibration of (I) or (II) with hot alkali (cf. A., 1927, 1167) gives a mixture containing 4.1—4.4% of (II). The Δ^6 -acid of the α -methyl series shows little tendency to be trans-

formed into the Δ^5 -acid, not only because the change $\Delta^1 \rightarrow \Delta^2$ is not facile, but also because the 3-Me group greatly favours the formation of (VII). (II) with boiling 50% H_2SO_4 gives *cis*-1:3-cyclohexan-olide (VIII) (cf. J.C.S., 1907, 91, 495). (II) is polymerised by cold acid, and does not give the lactone when boiled alone. (I) is not lactonised to any extent. (VII) with cold H_2SO_4 readily gives 1-methyl-1:3-cyclohexan-olide (IX), also obtained from (III) with H_2SO_4 , which shows (a) the absence of any appreciable amount of the Δ^5 -acid, and (b) the lack of any tendency for the other isomerides to lactonise under these conditions. (VII) lactonises when boiled alone; the reaction is reversible to give 33% of lactone at equilibrium (cf. A., 1933, 934). Lactonisation depends directly on the polarisability of the double linking, if the reacting centres can approach near enough to one another. (I) in AcOH with dry HBr gives *trans*-2-bromocyclohexanecarboxylic acid (X) [*Et* ester (XI) distils with decomp.], whereas (II) with HBr in $\text{AcOH-0.5\% H}_2\text{O}$ gives 18% of (X) and 82% of the 3-Br-isomeride, isolated in its *cis*- (*Et* ester, b.p. 143°/25 mm.) [also prepared from (VIII) and HBr in H_2O] and *trans*-forms. (VII) with HBr affords exclusively 3-bromo-3-methylcyclohexanecarboxylic acid, m.p. 45°, which contains much of the *cis*-acid because hydrolysis (NaOH) converts it into (IX), whereas the Δ^1 -acid gives *trans*(?)-2-bromo-3-methylcyclohexanecarboxylic acid, m.p. 144.5°. The ring has no sp. influence on orientation (cf. A., 1933, 934). (XI) with *Et*, sodiomalonate gives *Et* Δ^2 -tetrahydrobenzoate (cf. A., 1934, 1002), but the isomeric 3-Br-ester is unchanged. (VIII) with H_2O at 100° gives 88% of *cis*-3-hydroxycyclohexanecarboxylic acid, although it is a γ -lactone (cf. A., 1933, 934), whereas the analogous 3-methyl-lactone gives only 28% of OH-acid, because of added stability due to the 3-Me group (cf. A., 1896, i, 598). Δ^4 - α -Methylpentenoic acid with boiling 50% H_2SO_4 gives α -methyl- γ -valerolactone (A., 1928, 1214) (also formed from the Δ^6 -acid, but not when the latter is boiled alone), stable to boiling H_2O , which indicates that the instability of (VIII) and (IX) is due to strain.

J. L. D.

Preparation of phenylacetoneitriles from aromatic aldehydes. A. J. HIGNETT and F. W. KAY (J.S.C.I., 1935, 54, 98r).— $\text{OH}\cdot\text{CHPh}\cdot\text{CN}$, obtained from $\text{OH}\cdot\text{CHPh}\cdot\text{SO}_3\text{Na}$, is converted by SOCl_2 into $\text{CHPhCl}\cdot\text{CN}$, which is reduced to $\text{CH}_2\text{Ph}\cdot\text{CN}$ by Zn-AcOH .

***p*-Phenylcinnamic acid.** D. VORLANDER (Ber., 1935, 68, [B], 453—455).—The *p*-phenylcinnamic acid (I), m.p. II, 224—226°, I, 240°, obtained from $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CHO}$ (II), Ac_2O , and NaOAc at 130—140° or from (II), EtOAc , and Na wire, is identical with the products of Hey (A., 1931, 1293) and von Braun *et al.* (A., 1933, 1291), but differs from that of Knowles (A., 1921, i, 417). The *Me* ester, m.p. 147° (not cryst. liquid), and its *dibromide*, m.p. 147—148° after softening, are described. The *Et* ester, m.p. 86—87°, possibly exists in a second form, m.p. about 65°. $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$ is not a cryst. liquid but can become a monotropic cryst. liquid when mixed with salicylic, anisylidenepropionic, or sorbic

acid. On account of its cryst. liquid properties, (I) is given the *trans*-configuration. H. W.

Reactivity of *peri*-substituted naphthalenes.
III. Further synthetic reactions of 8-halogeno-1-naphthoic acids. H. G. RULE and H. M. TURNER (J.C.S., 1935, 317—319).—8-Bromo-4:5-dinitro-1-naphthoic acid and aq. NH_3 yield 4:5-dinitro-naphthastyril, m.p. 307—308°, and 8-bromo-1-naphthoic acid (I) with sodioanilide gives *N*-phenyl-naphthastyril, m.p. 104—105°, but 8-bromo-1-naphthanilide, m.p. 125—126° and 146—147°, does not react. (I) with $\text{NaHSO}_3\text{-Cu}$, followed by H_2SO_4 , forms naphthalene-1:8-carboxysulphonic anhydride, m.p. 152—153°, and with NaSPh affords *Ph* 8-carboxy-1-naphthyl sulphide, m.p. 131—132°, oxidised (H_2O_2) to the sulphoxide, m.p. 200—201°. 8-Iodo-1-naphthoic acid and *Et* malonate condense (*Cu*) to homonaphthalic acid, m.p. 213—214° (decomp.).

F. R. S.

Optical resolution of phenyl 8-carboxy-1-naphthyl sulphoxide. Prediction of restricted rotation in *peri*-substituted naphthalenes. H. G. RULE and H. M. TURNER (J.C.S., 1935, 319—321).—*Ph* 8-carboxy-1-naphthyl sulphoxide gives a brucine salt, $\alpha_D +9.62^\circ$ in CHCl_3 , decomposed to an acid, $[\alpha]_{405}^{20} +605^\circ$ in COMe_2 , showing no perceptible mutarotation or racemisation in AcOH at 94.5° . The acid shows simple dispersion from λ 6563 to 4358. Restricted rotation of the *peri*-substituents accounts for the asymmetry of the mol.

F. R. S.

Dissociable organic oxides. Photo-oxidation of sodium 1:1':3'-triphenylrubene-3-carboxylate. M. BADOCHÉ (Compt. rend., 1935, 200, 750—753).—Solutions of *Na* 1:1':3'-triphenylrubene-3-carboxylate (I) in EtOH are moderately rapidly decolorised by sunlight, whilst the corresponding acid (II) is much more stable. The residues from the resulting solution are complex and, when heated, evolve mainly CO_2 mixed with 3.7—6.0% of the amount of O_2 expected from a peroxide, $\text{C}_{36}\text{H}_{23}\text{CO}_2\text{Na}(\text{O}_2)$; (II) is produced in small amount. (I) and (II) are very stable when similarly heated. (I) is stable to light in absence of O_2 and to O_2 in absence of light.

H. W.

Muller's lactone from hydrochloroterresantalic acid. Y. ASAHINA, M. ISHIDATE, and T. MOMOSE (Ber., 1935, 68, [B], 559—562).—Terresantalic acid (I) is transformed by HCl in MeOH at 0° into hydrochloroterresantalic acid, m.p. 195° , converted by aq. NaOH , Na_2CO_3 , or NaHCO_3 into Muller's lactone (II), m.p. 103° , $[\alpha]_D -50.00^\circ$ in abs. EtOH . (II) and boiling 10% KOH afford a *OH*-acid (III), $\text{C}_{10}\text{H}_{16}\text{O}_3$, m.p. 185° , $[\alpha]_D -5.83^\circ$ in abs. EtOH , and apocamphenecarboxylic acid (IV), b.p. $156\text{—}157^\circ/23\text{ mm.}$, m.p. 142° , $[\alpha]_D -28.82^\circ$ in C_6H_6 . (IV) is transformed by HCl-MeOH at 0° into hydrochloroapocamphenecarboxylic acid, m.p. 174° (decomp.), $[\alpha]_D -84.32^\circ$ in abs. EtOH , converted by 1% NaOH into (II). (III) is stable towards dil. mineral acids, but is transformed by AcOH containing H_2SO_4 into *l*-cis- π -apoisorborneol-7-carboxylactone, m.p. 191° , $[\alpha]_D -117.9^\circ$ in abs. EtOH , and a little *d*-trans- π -apoacetylisorborneol-7-carboxylic acid, m.p. 122° . The *Me* ester of (III), b.p. $122\text{—}124^\circ/20\text{ mm.}$, passes when heated with

KHSO_4 at 200° and then hydrolysed into a mixture of (I) and isoterresantalic acid. (IV) is not derived from (III), but from a different β -*OH*-acid by loss of H_2O . (II) is regarded as a mixture of two diastereoisomeric β -lactones.

H. W.

Preparation of ethyl benzoylacetate. Y. F. CHI and Y. M. LEE (Trans. Sci. Soc. China, 1934, 8, 87—89).—A modified method of prep. from EtOAc and EtOBz (cf. A., 1913, i, 531) is described, giving a 77% yield.

CH. ABS. (r)

Synthesis of a methoxymethyltetrahydronaphthoic acid, the corresponding naphthoic acid, and of 8-methyl- β -naphthol. G. DARZENS and A. LÉVY (Compt. rend., 1935, 200, 469—471; cf. A., 1932, 941; this vol., 342).—*p*- $\text{OMe-C}_6\text{H}_4\text{-CH}_2\text{Cl}$ with $\text{CHNa}(\text{CO}_2\text{Et})_2$ gives *Et* anisylmalonate, b.p. $178\text{—}180^\circ/3\text{ mm.}$, which with allyl bromide similarly affords *Et* anisylallylmalonate, b.p. $185\text{—}187^\circ/3\text{ mm.}$, hydrolysed and decarboxylated to anisylallylactic acid (I), b.p. $184^\circ/3\text{ mm.}$, which easily isomerises to the lactone (II), b.p. $182^\circ/4\text{ mm.}$, of α -(β -hydroxypropyl)- β -*p*-methoxyphenylpropionic acid. (I) with cold 80% H_2SO_4 gives 6-methoxy-4-methyl-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid (III), m.p. 123° (*Me*, m.p. 53° and *Et* ester, b.p. $185^\circ/11\text{ mm.}$), and a lactone (IV), m.p. 57° , different from, but isomeric with, (II), probably the lactone of β -*p*-methoxyphenyl- α -(γ -hydroxypropyl)propionic acid. With 80% H_2SO_4 , (II) gives (III) and (IV), which is stable to H_2SO_4 . (III) is not dehydrogenated by *S* or *Se* even at 350° , but reaction occurs with its esters at $270\text{—}280^\circ$ to give, after hydrolysis, 6-methoxy-4-methylnaphthalene-2-carboxylic acid (V), m.p. 218° (*Me*, m.p. 94° , and *Et* ester, m.p. 85°), the *Ba* salt of which when heated gives 7-methoxy-1-methylnaphthalene, m.p. 42° , which is demethylated to 8:2- $\text{C}_{10}\text{H}_6\text{Me-OH}$.

J. L. D.

Isomeric forms of complex acetic acid. R. D. DESAI and R. F. HUNTER (Nature, 1935, 135, 434).—The synthesis of 1-carboxy-3-methylcyclohexane-1-acetic acid (I) by Higson and Thorpe's method gives a small quantity of the acid, m.p. 163° , originally obtained by oxidation of α -keto-3-methylcyclohexane-1:1-diacetic acid, accompanied by a gum, of low m.p., resolvable into a mixture of two cryst. isomerides. The application of Lapworth and McRea's synthesis gives a better yield of (I) and only small amounts of the other isomerides. The isolation of three forms of (I) can be explained only on the assumption of a strainless form of the methylcyclohexane ring.

L. S. T.

Diene synthesis with ethyl acetylenedicarboxylate. H. LOHAUS (Annalen, 1935, 516, 295—297).— $(\text{C-CO}_2\text{Et})_2$ and *trans-trans*- α,δ -diphenylbutadiene at $140\text{—}150^\circ$ afford *Et*, 3:6-diphenyldihydrophthalate, m.p. 88° (yield $>90\%$), hydrolysed to 3:6-diphenyldihydrophthalic acid, m.p. 255° (decomp.) (and a substance, m.p. 111°), which is oxidised and decarboxylated to *p*- $\text{C}_6\text{H}_4\text{Ph}_2$. *Me*, 3:6-diphenyldihydrophthalate has m.p. 101° . In this instance $(\text{C-CO}_2\text{Et})_2$ reacts as readily as the *Me* ester.

H. W.

Action of semicarbazides on anhydrides of dibasic acids. B. K. BANERJEE (J. Indian Chem. Soc., 1935, 12, 4—5).—By heating together the acid

anhydride and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ are obtained phthalyl- (benzylidene, m.p. 170—171°, and Ac_3 , m.p. 120—121°, derivatives), diphthalyl-, softens 295°, m.p. 300°, di-camphoryl-, m.p. > 300°, and di(diphenic)-, m.p. 186—187°, -semicarbazide. J. W. B.

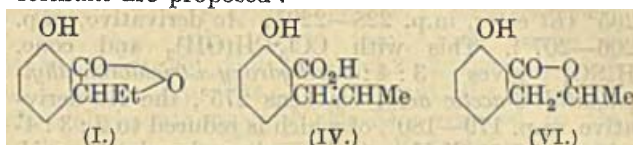
Condensation of phthalic anhydride with amino-alcohols. F. GARELLI and G. RACCIU (Atti R. Accad. Sci. Torino, 1934, 69, I, 358—363; Chem. Zentr., 1934, ii, 2823).—Condensation of $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ with $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ in EtOH yields N- β -hydroxy-ethylphthalimide, m.p. 125—126°. N- γ -Hydroxy-propyl-, m.p. 88°. and N- δ -hydroxybutyl-, m.p. 173°, -phthalimide are prepared similarly. H. N. R.

Isatogens and indoles. XVI. 4:6-Dinitro-isophthalic acid and products of condensation of dinitroxyline and aldehydes. P. RUGGLI and O. SCHMID (Helv. Chim. Acta, 1935, 18, 247—254; cf. this vol., 83).—4:6-Dinitro-*m*-xylene (I) and $\text{CrO}_3\text{-H}_2\text{SO}_4$ at -10° to 20° give a 75% yield of 4:6-dinitro-isophthalic acid (II), m.p. 234—235° (decomp.), stable to hot H_2O [Et_2 ester, m.p. 124°, hydrogenated (Ni) in $\text{EtOAc-EtOH-H}_2\text{O}$ to the $(\text{NH}_2)_2$ -ester; *Et H* ester, impure, m.p. 154°], the dichloride (prep. by SOCl_2), m.p. 106°, of which with $\text{AlCl}_3\text{-C}_6\text{H}_6$ affords 4:6-dibenzoyl-*m*-dinitrobenzene, m.p. 175°. (I) with the appropriate aldehyde and a few drops of piperidine at 140° yields 4:6-di-(4'-hydroxy-3'-methoxystyryl)- (III), m.p. 251° (decomp.), -(3':4'-methylenedioxy-styryl)-, m.p. 215° (decomp.), and -(3'-nitrostyryl)-*m*-dinitrobenzene (prep. at 160°), m.p. 294° (decomp.). 2:4-Dinitrotoluene affords similarly 2:4-dinitro-2'-hydroxy-, m.p. 185—186°, -4'-hydroxy-3'-methoxy-, m.p. 191°, and -3':4'-methylenedioxy-stilbene, m.p. 178—179°. (II) is obtained by oxidation of (III) or, less readily, from the less sol. condensation products of (I) and PhCHO or furfuraldehyde. R. S. C.

Constitution of ochracin (a fermentation product of *Aspergillus ochraceus*). I, II. T. YABUTA and Y. SUMIKI (J. Agric. Chem. Soc. Japan, 1933, 9, 1264—1275; 1934, 10, 703—714).—I. Ochracin (I), $\text{C}_{10}\text{H}_{10}\text{O}_3$, m.p. 58—58.5°, $[\alpha]_D^{25}$ -124.86° [*Me ether* (II), m.p. 88—89°; *Ac* derivative, m.p. 126—127°; *Bz* derivative, m.p. 101—102°; NO_2 -derivative, m.p. 184—185°; $(\text{NO}_2)_2$ -derivative, m.p. 161—162°], is obtained by extraction with Et_2O . Fusion with KOH at 270—280° affords 3-hydroxy-*o*-toluic acid; with 90% KOH at 205—210°, an acid, $\text{C}_9\text{H}_8\text{O}_3$, m.p. 136—137°, is obtained. (II) with KMnO_4 yields 3-methoxyphthalic acid (III).

II. (I) is shown to be identical with mellein (Nishikawa, A., 1934, 810); when heated with KOH it yields melleic acid (IV) [*Me ether* (V), m.p. 130—131°; *Ac* derivative, m.p. 108—109°], which affords dihydromelleic acid (*Me ether*, m.p. 97—98°; *Ac* derivative, m.p. 91—92°) on catalytic hydrogenation. (V) with KMnO_4 yields (III), and, on ozonolysis, MeCHO and 3-methoxy-1-carboxybenzaldehyde, m.p. 152—153° [2:4-dinitrophenylhydrazones, m.p. 245—246° (decomp.)], further oxidised to (III) by Ag_2O . With H_2SO_4 (IV) yields isochracin (VI), $\text{C}_{10}\text{H}_{10}\text{O}_3$, m.p. 78—79°; (VI) contains 1 phenolic OH and 1 lactone group and yields salicylic acid on KOH

fusion (cf. 3-hydroxyphthalic acid). The following formulæ are proposed:



CH. ABS. (r)

Cleavage of organic magnesium compounds.

I. Cleavage of malononitriles. J. L. E. ERICKSON and M. M. BARNETT (J. Amer. Chem. Soc., 1935, 57, 560—562).— $\text{C}(\text{CH}_2\text{Ph})_2(\text{CN})_2$ with MgPhBr in Et_2O gives $\text{MgBr}\cdot\text{N}\cdot\text{CPh}\cdot\text{C}(\text{CN})(\text{CH}_2\text{Ph})_2$, which at once decomposes to PhCN [which reacts further to yield ultimately COPh_2 (100% yield)] and $\text{C}(\text{CH}_2\text{Ph})_2\text{C}\cdot\text{N}\cdot\text{MgBr}$ (I), which with H_2O gives $\text{CH}(\text{CH}_2\text{Ph})_2\text{CN}$ (80% yield), m.p. 92°. In hot C_6H_6 , however, (I) reacts further to give $\text{C}(\text{CH}_2\text{Ph})_2\text{CPh}\cdot\text{N}(\text{MgBr})_2$ and thence $\text{CH}(\text{CH}_2\text{Ph})_2\text{COPh}$. $\text{CMe}_2(\text{CN})_2$ [from $\text{CN}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2$ (modified prep.)] reacts with an excess of MgPhBr in Et_2O with only a little cleavage, giving mainly CMe_2Bz_2 and little COPh_2 ; at -15° with 1 mol. of MgPhBr , $\text{CN}\cdot\text{CMe}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{MgBr}$, initially formed, yields PhCN and $\text{CMe}_2\text{C}\cdot\text{N}\cdot\text{MgBr}$, the latter giving with H_2O Pr^nCN . $\text{CHPh}(\text{CN})_2$ in Et_2O reacts with 1 mol. of reagent, but is recovered unchanged; in C_6H_6 further reaction occurs yielding $\text{MgBr}\cdot\text{N}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{N}(\text{MgBr})_2$, and thence phenyldibenzoylmethane diketimine (α -di-imino- β -triphenylpropane), m.p. 167—168° (decomp.), hydrolysed to CHPhBz_2 . $\text{CH}_2(\text{CN})_2$ forms an insol. MgBr -derivative, which is inert in Et_2O or C_6H_6 .

R. S. C.

β -9-Anthranyl- β -*m*-nitrophenylpropionic acid and its derivatives. J. KANE (Natural. Canad., 1935, 62, 54—76, 83—98).—A more detailed account of work previously summarised (Vachon *et al.*, this vol., 212). By similar methods are obtained *Et*₂ β -9-anthranyl- β -*o*-, m.p. 158—159° (*Me*₂ ester, m.p. 174—175°), and -*p*-nitrophenylethane- α -dicarboxylate, m.p. 153—154°, hydrolysed to β -anthranyl- β -*p*-nitrophenylpropionic acid, m.p. 266—267°: the amide, m.p. 240—242°, anilide, m.p. 110—112°, and *Ag* salt of the corresponding *m*-derivative are described.

J. W. B.

Synthesis of *m*-hemipinic acid. A. N. MELDRUM and P. H. PARIKH (Proc. Indian Acad. Sci., 1935, A, 1, 437—439).—Veratric acid with $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and conc. H_2SO_4 gives 3:4-dimethoxy- α -trichloromethylphthalide, m.p. 146°, hydrolysed by 20% NaOH to 3:4-dimethoxy- α -carboxyphthalide, m.p. 212° (*Na* salt). This is reduced with Zn and AcOH to 3:4-dimethoxy-6- β -dichloroethylbenzoic acid, m.p. 201° (*Ca* salt), oxidised by KMnO_4 in dil. KOH to *m*-hemipinic acid.

F. R. G.

Synthesis of phenylacetic acids from gallic acid and its methyl esters. A. N. MELDRUM and P. H. PARIKH (Proc. Indian Acad. Sci., 1935, A, 1, 431—436; cf. J.C.S., 1920, 117, 964; 1921, 119, 201).—Reduction of 3:4:5-triacetoxy- α -trichloromethylphthalide with Zn and AcOH gives the *Ac* derivative, m.p. 189°, of 3:4:5-trihydroxy-2- β -dichloroethylbenzoic acid, m.p. 178—179° (*Me* ester,

m.p. 131°), which with conc. H_2SO_4 yields 2 : 3 : 4-trihydroxy-6-carboxyphenylacetic acid, blackens 260—265° (*Et* ester, m.p. 228—229°; *Ac* derivative, m.p. 206—207°). This with $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and conc. H_2SO_4 gives 3 : 4 : 5-trihydroxy- α -trichloromethylphthalide-6-acetic acid, blackens 275°, the *Ac* derivative, m.p. 179—180°, of which is reduced to 2 : 3 : 4-triacetoxy-5- β -dichloroethyl-6-carboxyphenylacetic acid, m.p. 220—222°. This with conc. H_2SO_4 gives 2 : 3 : 4-trihydroxy-6-carboxyphenylene-1 : 5-bisacetic acid, blackens 290° [*Ac* derivative, m.p. 239—243° (decomp.)]. 3 : 4 : 5-Trimethoxy- α -trichloromethylphthalide (cf. Bargellini and Molina, A., 1912, i, 773) is reduced to 3 : 4 : 5-trimethoxy-2- β -dichloroethylbenzoic acid, m.p. 124° (*Pb* salt), which with conc. H_2SO_4 gives 2 : 3 : 4-trimethoxy-6-carboxyphenylacetic acid, m.p. 149° (*Me* ester, b.p. 220—225°/23—25 mm.; m.p. 48—50°; *Et* ester, b.p. 225—230°/20 mm.; *Ca* salt; *Pb* salt; anhydride, m.p. 121°), and this with $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and conc. H_2SO_4 yields 3 : 4 : 5-trimethoxy- α -trichloromethylphthalide-6-acetic acid, m.p. 194°. 4-Hydroxy-3 : 5-dimethoxy- α -trichloromethylphthalide similarly gives 4-hydroxy-3 : 5-dimethoxy-2- β -dichloroethylbenzoic acid, m.p. 158° [*Ac* derivative, m.p. 178—179° (decomp.)], and 3-hydroxy-2 : 4-dimethoxy-6-carboxyphenylacetic acid, m.p. 243° (*Ac* derivative, m.p. 189—190°).

F. R. G.

Attempted preparation of 1 : 3-dimethylcyclohexane-1 : 2 : 3-tricarboxylic acid. B. ARBUSOV and O. SCHAPSCHINSKAJA (Ber., 1935, 68, [B], 437—442).—Condensation of $\text{CMeNa}(\text{CO}_2\text{Et})_2$ with $\text{CH}_2(\text{CH}_2\text{Br})_2$ in boiling EtOH affords Et_4 *n*-heptane- $\beta\beta\zeta$ -tetracarboxylate, b.p. 225°/10 mm. (yield 44.9%), hydrolysed and decarboxylated to $\alpha\alpha'$ -dimethylpimelic acid (I). Successive treatment of (I) with Br-red P and EtOH leads to Et_2 $\alpha\alpha'$ -dibromo- $\alpha\alpha'$ -dimethylpimelate, b.p. 182.5—184°/2.5 mm., converted by $\text{CNNa}_2(\text{CO}_2\text{Et})_2$ into Et_4 1 : 3-dimethylcyclohexane-1 : 2 : 3-tetracarboxylate (II), b.p. 206—208°/2 mm., and Et_2 Δ^8 -heptadiene- $\beta\zeta$ -dicarboxylate, b.p. 138—139°/2 mm. (corresponding acid, m.p. 165—168°, probably a mixture of isomerides). (II) is hydrolysed to the corresponding non-cryst. acid, which loses CO_2 when heated and gives 1 : 3-dimethylcyclohexane-1 : 2 : 3-tricarboxylic acid (III) (*Ag* salt) as a rosin-like mass. The b.p. of its *Me*₃ ester (158—162°/7 mm.) is close to that of the corresponding ester obtained by Ruzicka (A., 1933, 820) from the products of the oxidation of abietic acid, but the identity of the compounds remains unestablished.

H. W.

Bile acids. XLV. M. SCHENCK (Z. physiol. Chem., 1935, 232, 87—96; cf. this vol., 213).—The NH_2OH compound of the dioximinohydroxamic acid (I), $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}_3$, is probably a mixture of free (I) with the hydroxylammonium salt or hydroxamoxime hydrate, $\text{C}_{24}\text{H}_{40}\text{O}_9\text{N}_4$, or less probably with the hydroxamoxime, $\text{C}_{24}\text{H}_{38}\text{O}_8\text{N}_4$. If the oximelactamhydroxamic acid (II), $\text{C}_{24}\text{H}_{37}\text{O}_8\text{N}_3$, yields a product with NH_4OH , it is unstable, as only (II) is recovered. With HNO_3 , (I) gives a gel having the same N content as the cryst. NO-compound, $\text{C}_{24}\text{H}_{33}\text{O}_8\text{N}$. With HCl , (I) affords the diketohydroxamic acid, $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}$. With hot HCl , the nitrolactamhydroxamic acid (III),

$\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}_3$, gives the ketolactamtricarboxylic acid, $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}$. The nitroketohydroxamic acid, $\text{C}_{24}\text{H}_{31}\text{O}_9\text{N}_4$, from which (III) is derived, with alkaline KMnO_4 yields the product (IV) $\text{C}_{24}\text{H}_{33}\text{O}_8\text{N}$. Oximation of (IV) gives bilianic acid dioxime.

J. H. B.

Aldehyde-phenylhydrazonesulphonic acids.

I. V. HOPPER, J. T. HENDRY, and R. T. DAWSON (J. Roy. Tech. Coll., 1935, 3, 388—398).— $\text{R}\cdot\text{CHO}$ and $p\text{-NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ with $\text{NH}_2\text{R}'$ or MX in H_2O give a ppt. of $p\text{-R}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{NH}_3\text{R}'$ or $p\text{-R}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{M}$ (R, R' are aryl; MX is a metal salt or hydroxide). The following are described: $\text{CH}_3\text{Ph}\cdot\text{NH}_2$, m.p. 227°, NH_2Ph , m.p. 221°, *o*-, m.p. 213° (decomp.), and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 226°, α -, m.p. 215° (decomp.), and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, *Ba*, *Sr*, *Ca*, *Mg*, *Na*, *K*, *Zn*, *Cd*, Cu^{II} , *Ag*, Fe^{III} , *Co*, *Ni*, and Mn^{II} benzaldehydephenylhydrazone-*p*-sulphonates; NH_2Ph , m.p. 249°, *o*-, m.p. 219°, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 226°, α -, m.p. 209°, and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 230°, *Ca*, *Ba*, *Sr*, and *Ni* salicylaldehydephenylhydrazone-*p*-sulphonates; NH_2Ph , m.p. 215—220°, *o*-, m.p. 196°, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 223°, and *Ba* cinnamaldehydephenylhydrazone-*p*-sulphonates; *Ba* *p*- and *o*-nitrobenzaldehydephenylhydrazone-*p*-sulphonate; NH_2Ph acetophenonephenylhydrazone-*p*-sulphonate, m.p. 215°. *Benz*-, m.p. 233°, *salicyl*-, m.p. 236°, *cinnam*-, *p*-, m.p. 226°, *o*-, m.p. 216°, and *m*-nitrobenzaldehydephenylhydrazone-*p*-sulphonpiperidides, m.p. 217°, are also described. The org. salts are hydrolysed by hot dil. HCl and the metal salts by hot H_2O . The salts crystallise with varying amounts of H_2O . The great solubility of $(p\text{-CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Cu}$ in EtOH enables Cu to be separated from other metals. Aromatic aldehydes may be isolated by pptn. as $(\text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Ca}$ or *Ba*.

F. R. G.

Gattermann hydroxy-aldehyde synthesis. T.

LOVE (J. Roy. Tech. Coll. 1935, 3, 385—387).—*m*-Cresol in C_6H_6 with $\text{Zn}(\text{CN})_2$, AlCl_3 , and HCl gas (modified Gattermann) gives the 6-aldehyde as well as the 4- and a little 2-aldehyde. A compound, $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$, m.p. 235° (decomp.), is also formed. The amount of substitution *o*- to *OH* depends on the concn. of HCN .

F. R. G.

Thermal decomposition of ald-chloroimines.

C. R. HAUSER, A. G. GILLASPIE, and J. W. LEMAISTRE (J. Amer. Chem. Soc., 1935, 57, 567—570).—By NH_2Cl are prepared chloroimines of *o*-, m.p. 48°, and *m*-, bromo-, m.p. 21°, *m*-chloro-, m.p. 15°, *m*-methoxy-, an oil, 3-nitro-4-methoxy- (I), m.p. 86—87°, and *p*-nitro-, m.p. 213° (decomp.), benzaldehyde, *p*-tolualdehyde (II), m.p. 20°, $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ (III), m.p. 52°, *o*- (IV), m.p. 124° (decomp.), *m*- (V), m.p. 140—142° (decomp.), and *p*-nitrocinnamaldehyde (VI), m.p. 153—155° (decomp.). When instantaneously decomposed by heat, *o*- and *m*-nitro-, *p*-methoxy-, *o*- and *m*-chloro-benzalchloroimine give 81—92% of $\text{RCN} + \text{HCl}$, whilst 4-5—8.1% reacts further thus: $\text{CHR}\cdot\text{NCl} + 2\text{HCl} \longrightarrow \text{CHR}\cdot\text{NH}\cdot\text{HCl} + \text{Cl}_2$. The following temp. of instantaneous decomp. are recorded: (I) 168°, 3 : 4- CH_2O_2 -170°, 3-Cl-5- NO_2 -215°, *o*-180—200°, *m*-213°, and *p*- NO_2 -213°, *o*-215°, *m*-215°, and *p*-Cl-195°, *o*-215°, *m*-215°, and *p*-Br-213°, (III) 120°, (IV) 124°, (V) 142°, (VI) 143°, (II) 178°, furfurald-

chloroimine 165°. These temp. accord qualitatively with stabilities in solution. R. S. C.

Free phenolic group in lignin. Evidence from action of chlorine dioxide on aromatic and aliphatic compounds. P. B. SARKAR (Current Sci., 1935, 3, 422—423).—Of 20 aromatic compounds with free phenolic OH, all were readily attacked by ClO_2 . Protection of the phenolic groups by methylation or acetylation reduces but does not completely inhibit the action of ClO_2 . Aliphatic OH in the side-chain is also attacked less vigorously when methylated or acetylated. The CO_2H and CH_2O_2 are resistant. The action of ClO_2 on lignin does not prove the existence in the latter of free phenolic OH. W. O. K.

Colour changes accompanying cyclisation of certain aromatic hydrocarbons, ketones, and alcoholic and phenolic acids. (MME.) RAMART-LUCAS and J. HOCH (Bull. Soc. chim., 1935, [v], 2, 327—344).—To test the validity of the conceptions previously advanced (this vol., 82) the absorption spectra of the following series of compounds are plotted and discussed. The true effect of cyclisation is small and is demonstrated by the series: COEt_2 (I), *cyclopentanone* [differentiated from (I) and (II) by fine bands in C_6H_{12} solution], and *cyclohexanone*; *o*-xylene (III), *indrene* [fine bands absent in (III)], *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}:\text{CH}_2$ (IV) and *indene* (V), the cyclisation of (IV) to (V) producing a hypsochromic effect and a diminution in the intensity of absorption; *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{Et}$, α -hydrindone ($n=1$), 1-ketotetrahydronaphthalene ($n=2$) (position of bands almost unchanged, but the intensity decreases in the order given); *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{Et}$ and the lactones $\text{C}_6\text{H}_4\langle\overset{\text{H}_2}{\text{CO}}\rangle\text{O}$. In general the effect of cyclisation is the greater the greater is the no. of chromophores present in the ring formed, and the smaller is the no. of C atoms in the chain involved in cyclisation. Comparison of the absorption spectra of *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ and of $\text{C}_6\text{H}_4\langle\overset{\text{CH}_2\cdot\text{CH}_2}{\text{O}}\rangle\text{CO}_2\text{H}$, and of *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OAc}$ and *o*-cresol confirms the view that the conversion of a phenolic acid into its lactone is accompanied by a hypsochromic effect and a diminution in intensity, as is also observed in the esterification of a phenol. Improved prep. and purification of materials are given in many cases. J. W. B.

Extinction of ketone reactivity. R. CORNUBERT, C. BORREL, DE DEMO, J. GARNIER, R. HUMEAU, H. le BIHAN, and G. SARKIS (Bull. Soc. chim., 1935, [v], 2, 195—220).—The suppression of CO activity by accumulation of proximate alkyl groups is illustrated with the following ketones, usually prepared by alkylation (NaNH_2) of the parent ketone (A., 1932, 946). 2:2:6:6-Tetramethyl- (I) (yields an oxime; reduced to the cyclohexanol; converted by MgMeI into the methylcarbinol, b.p. $104-109^\circ/22$ mm.), -tetra-*n*-propyl- (II) [converted by MgMeI in boiling Bu_2O into the methylcarbinol, b.p. $172-175^\circ/14$ mm., m.p. $58-59^\circ$, and (with excess of Mg), 2:2:6:6-tetra-*n*-propyl-1-methylenecyclohexane], -tetra-allyl- (III), -tetra-*n*-butyl- (IV) (methylcarbinol, m.p. $151-152^\circ$; cyclohexanol, m.p. $149-150^\circ$), 3- (partly converted, only by excess of MgMeI , into a mixture of

the methylcarbinol and the unsaturated hydrocarbon), and 4-methyl-2:2:6:6-tetra-*n*-propyl- (giving 4-methyl-2:2:6:6-tetra-*n*-propyl-1-methylenecyclohexane, b.p. 161—163°/15 mm., with excess of MgMeI in Bu₂O), and 3-methyl-2:2:6-tri-*n*-propyl-6-isopropyl-, b.p. 173—175°/15 mm. (by reduction of triallylmenthone with H₂-Ni; reduced to the cyclohexanol), -cyclohexanone. Reduction of isopropylidenecyclopentanone affords the Pr⁸ derivative, converted by condensation with COMe₂-NaOMe-MeOH at 0° into isopropylisopropylidenecyclopentanone, b.p. 109—110°/14 mm., reduced (H₂-Ni) to the Pr⁸, derivative, b.p. 102.5°/19 mm. (oxime, m.p. 91°), which with CH₂:CH-CH₂I (V)-NaNH₂ affords its diallyl derivative, b.p. 158°/16 mm., reduced to 2:6-di-*n*-propyl-2:6-diisopropylcyclopentanone (VI), b.p. 161°/23 mm. (reduced to the cyclopentanol, b.p. 163°/17 mm.). Reduction of 3-methyl-5-isopropyl-Δ²-cyclohexenone and repeated action of (V)-NaNH₂ on the product gives a trace of (?) 3-methyl-4-isopropyl-2:2:6-triallylcyclohexanone, b.p. 183—186°/14 mm., m.p. 88°. Reduction (H₂-Ni) of 3:4:5-triphenyl-Δ²-cyclohexenone gives a mixture of triphenylcyclohexanone-*A*, m.p. 178° (semicarbazone, m.p. 174—175°; reduced to the cyclohexanol, m.p. 204°), and -*B*, m.p. 175—176° (oxime, m.p. 125°; semicarbazone, m.p. 180—181°; reduced to the cyclohexanol, m.p. 154—155°), only *B* resulting if H₂-Pt is used. 1:6-Dibenzylcyclohexanone, m.p. 122°, affords an oxime, m.p. 183°, and an oxime, m.p. 91°; and a semicarbazone, m.p. 190—191°. The suppression of CO activity (accompanied by a shift in the max. of the absorption band nearest to the visible in the direction of longer λ) is shown by the observations that an oxime or semicarbazone could be obtained only in the cases noted above; (II), (III), and (IV) react with MgMeI only in boiling Bu₂O, but (VI) does not react at all. Suppression of every CO property except that of reduction to the sec.-alcohol is thus effected, but no definite order of suppression is observed. Suppression of OH-activity in alcohols is much less marked, the following being prepared in this connexion: 2:2:6:6-tetra-*n*-propyl- (*Ac* derivative, b.p. 185—187°/24 mm., phenylurethane, m.p. 98—100°; *H* phthalate, m.p. 124—126°), and 3-methyl-2:2:6:6-tetra-*n*-propyl- (*Ac* derivative, m.p. 63°, phenylurethane, m.p. 76°, incomplete formation of a Me ether; no *H* phthalate), -cyclohexanol. J. W. B.

α -Chlorinated ketones. G. RICHARD (Compt. rend., 1935, 200, 753—755).— α -Chlorobenzyl Me ketone is converted by AlCl_3 in presence of a large excess of C_6H_6 into benzhydryl Me ketone, m.p. 61° (oxime, m.p. 164.5° ; semicarbazone, m.p. 160°). Similarly, α -chlorobenzyl Et ketone, b.p. $117.5\text{--}118.5^\circ/10$ mm., from SO_2Cl_2 and $\text{CH}_2\text{Ph}\cdot\text{COEt}$, affords $\text{CHPh}_2\cdot\text{COEt}$, m.p. 32° (semicarbazone, m.p. 191°), and $\text{HClPh}\cdot\text{COPh}$ gives $\text{CHPh}_2\cdot\text{COPh}$, m.p. 137° (oxime, m.p. 182°). The intermediate formation of a keten is impossible in the first two cases and anomalous behaviour in the Friedel-Crafts reaction (cf. Franke *et al.*, A., 1913, i, 10) is not a general property of α -halogenated CO compounds.

H. W.

Addition of compounds containing a reactive methylene group with phenyl vinyl ketone. S. M. ABDULLAH (J. Indian Chem. Soc., 1935, 12, 62—66).—The following substances are obtained by addition of the appropriate reactive methylene compound to $\text{CH}_2=\text{CH}\cdot\text{COPh}$ (I) in the presence of $\text{NaOEt}\cdot\text{EtOH}$, and subsequent elimination of H_2O . Thus $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (II) gives *Et* 3-phenyl- Δ^2 -cyclohexenone-6-carboxylate, b.p. 200—205°/12 mm., hydrolysed by aq. *N*-KOH to 3-phenyl- Δ^2 -cyclohexenone (III), b.p. 172—173°/12 mm., m.p. 64° (oxime, m.p. 117—118°; semicarbazone, m.p. 222°; *p*-nitrophenylhydrazone, m.p. 184—185°), derived from the initial condensation product *Et* δ -keto- α -acetyl- δ -phenylvalerate, m.p. 120° (monoxime, m.p. 160—161°) [obtained from (II) and $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ with NaOEt ; converted by heating at 200° to (III)]. $\text{COPh}\cdot\text{CH}_2\cdot\text{Ph}$ gives α -diketo- α - δ -triphenyl-*n*-pentane, m.p. 97—98° (monoxime, m.p. 125—126°); $\text{CH}_2\text{Ph}\cdot\text{COMe}$ and $\text{CO}(\text{CH}_2\text{Ph})_2$ afford, respectively, 2:5-di-, m.p. 149—150°, and 2:5:6-tri-phenyl- Δ^5 -cyclohexenone, m.p. 135°. A polymeride, m.p. 108°, of (I) is also obtained in some of the condensations. J. W. B.

Synthesis of phenanthrene derivatives. II. Benzoylphenanthrenes and derivatives. W. E. BACHMANN (J. Amer. Chem. Soc., 1935, 57, 555—559; cf. A., 1934, 893).—Phenanthrene (modified purification) and BzCl in CS_2 or by the Perrier method give 1-benzoylphenanthrene (I), m.p. 148.5—149.5° (cf. A., 1911, ii, 882), but in PhNO_2 afford 1- (6%), 2- (II) (3%), dimorphic, m.p. 117—118° and 108—109°, and 3-benzoylphenanthrene (III) (20%), dimorphic, m.p. 111—112° and 107—108°. 2- and 3-Phenanthroic acid, by way of the chloride (PCl_5), give the amides, which with P_2O_5 yield the nitriles, m.p. 108—109.5° and 102°, in 77 and 62% yield, respectively, whence (MgPhBr) (II) and (III) are obtained. (I) and hot KOH give a little 1-phenanthroic acid, m.p. 228° (Me ester, m.p. 55.5—56°), which was reconverted into (I) by way of the chloride, amide, m.p. 274°, and nitrile, dimorphic, m.p. 130—130.2° and 125.5°. 1-Keto-1:2:3:4-tetrahydrophenanthrene and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ in Et_2O give 1-hydroxy-1-benzyl-1:2:3:4-tetrahydrophenanthrene, which is dehydrated by HCO_2H ; the product with Se at 300° gives (I) and with S at 250° 1-benzylphenanthrene, m.p. 107—108°. (I), (II), and (III) with $\text{Na}\cdot\text{Hg}$ afford phenylphenanthryl-1-, m.p. 125—126°, -2- (IV), m.p. 110—111°, and -3-carbinol (V), m.p. 128—129°, reduced by *I*-red P to 1-, 2-, dimorphic, m.p. 107—108° and 95—96°, and 3-benzylphenanthrene, m.p. 79—80°. 2-, m.p. 217—218°, and 3-Phenanthroanilide, m.p. 216—217°, give by Shoppee's method 58% yields of 2- and 3-phenanthraldehyde, which with MgPhBr give (IV) and (V). (I), (II), and (III) with CrO_3 yield 1-, m.p. 268—269°, 2-, m.p. 218—218.5°, and 3-benzoylphenanthrene-9:10-quinone, m.p. 209—210° (lit. 205—206°). (II) and (III) with MgPhBr give diphenylphenanthryl-2-, m.p. 175—175.5°, and -3-carbinol, m.p. 143.5—144.5°, converted by AcBr into the bromides, m.p. 148—149° and 155—156°, respectively, which with Ag afford diphenylphenanthryl-2- and -3-methyl (cherry-red and dark red, respectively, in C_6H_6), oxidised by air to diphenylphenanthryl-2-, m.p. 190—191°, and -3-methyl peroxide, m.p. 195—

196°. 9-Benzoylphenanthrene is dimorphic, m.p. 89.5—90° and 80—81°. R. S. C.

Condensation of formaldehyde and mono-ketones. II. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 496—497; cf. A., 1931, 471).—40% aq. CH_2O and *p*- $\text{C}_6\text{H}_4\text{Ac}\cdot\text{NH}_2$ at 100° give *p*-methylideneaminoacetophenone, m.p. 192—193°, and its ω -OH-derivative, m.p. 218—219° (*Ac* derivative, m.p. 167°). *p*-Dimethylamino- α - and - β -deoxybenzoin give 4-dimethylamino- α -hydroxymethyl- α -, m.p. 110—111° (*Bz* derivative, m.p. 135—136°), and - β -deoxybenzoin, m.p. 132—133°, respectively; the latter product or its *Bz* derivative, m.p. 176—177°, with hot $\text{KOH}\cdot\text{EtOH}$ gives a compound, m.p. 252°. 8-Hydroxy-5-propionylquinoline gives α -methylenebis-8-hydroxy-5-propionylquinoline, m.p. 166—267° [oxime, m.p. 246—248° (decomp.); dioxime, m.p. 266—267° (decomp.); hydrochloride, $\text{B}, 1\cdot5\text{HCl}, 1\cdot5\text{H}_2\text{O}$, decomp. 150—160°, hydrolysed by H_2O]. R. S. C.

Influence of light on the formation of benzoin. R. BOUSSET (Bull. Soc. chim., 1935, [v], 2, 309—311).—Absorption of KCN by PhCHO in the benzoin (I) condensation is rapid and is unaffected by irradiation, which, however, converts (I) into a viscous resin (II). Resinification is increased by rise in temp. and by extended irradiation. An Et_2O -insol. substance, not melting at 250°, is isolated from (II). J. W. B.

Inter-relationship of acetylphenylcarbinol and benzoylmethylcarbinol: new type of tautomerism. A. E. FAVORSKI and (MME.) T. I. TEMNIKOVA (Bull. Soc. chim., 1935, [v], 2, 253—272).—Pure $\text{OH}\cdot\text{CHMe}\cdot\text{COPh}$ (I) (prep. and purification through its acetate described) and $\text{OH}\cdot\text{CHPh}\cdot\text{COMe}$ (II) (prep. described) give only one semicarbazone, m.p. 193°, and one phenylurethane, m.p. 143—144°, but with MgMeBr at 0° (I) affords a mixture, b.p. 154.5—155°/17.5 mm., m.p. 35—44°, of the glycols $\text{OH}\cdot\text{CHMe}\cdot\text{CPhMe}\cdot\text{OH}$ (III) (2 parts) and $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{OH}$ (IV) (1 part) (the composition of the mixture being determined by CrO_3 oxidation to give COMe_2 , COPhMe , AcOH , and BzOH), whereas (II) affords a similar mixture of 2 parts of (III) and 3 parts of (IV). Similarly (I) and MgPhBr afford a mixture of $\text{OH}\cdot\text{CHPh}\cdot\text{CPhMe}\cdot\text{OH}$ (V) (2 parts) and $\text{OH}\cdot\text{CHMe}\cdot\text{CPh}_2\cdot\text{OH}$ (1 part), but (II) gives only the α -form, m.p. 97.5°, of (V). With $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$ (I) gives a mixture of $\text{OBz}\cdot\text{CHMe}\cdot\text{COPh}$ (VI), m.p. 109° (7) (converted by MgMeBr into β -phenyl-*n*-butane- β -diol, b.p. 146—147°/11 mm.), and $\text{OBz}\cdot\text{CHPh}\cdot\text{COMe}$ (VII), m.p. 51.5—52.5° (2); (II) also gives (VI) and (VII), but in the ratio 1:5. (I) and (II) are thus separate entities, but are interconvertible by a type of keto-enol tautomerism involving the migration of two H, for which the name keto-anolic (carbinolic) is proposed. α -Ketols of the type (I) containing *Bz* and an alkyl $> \text{Me}$ possess the structure $\text{O} < \text{CPh}\cdot\text{OH}$, since they do not yield normal semicarbazones, but by prolonged action of 2 mols. of $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ give derivatives of the type $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CPh}\cdot\text{CHR}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$. The contradictory lit. relative to (I) and (II) is discussed.

J. W. B.

Alkylation of bindone. G. WANAG (Ber., 1935, 68, [B], 408—414).—The yield of methylbindone (I), $C_6H_4<\overset{CO}{\underset{CO}{C}}C<\overset{C_6H_5}{\underset{CXR}{C}}CO$ ($X=H$, $R=Me$), m.p. 176°, is greatly increased by condensing bindone with MeI and MeOH in presence of K_2CO_3 instead of NaOMe (Hantzsch *et al.*, A., 1912, i, 872); isobindone, $C_6H_3Bz_3$, and a brownish-yellow substance are obtained as by-products. (I) and Br in boiling $CHCl_3$ afford bromomethylbindone ($X=Br$; $R=Me$), m.p. 183—184°, whilst chloro(chloromethyl)bindone, m.p. 152°, is derived from (I) and Cl_2 in hot $CHCl_3$. (I) and boiling Ac_2O give acetylmethylbindone ($X=Ac$; $R=Me$), m.p. 219—220°. Nitromethylbindone ($X=NO_2$; $R=Me$), m.p. 220°, is derived from (I) and fuming HNO_3 in hot $AcOH$. Ethylbindone, m.p. 166°, bromoethylbindone ($X=Br$; $R=Et$), m.p. 177°, and nitroethylbindone, ($X=NO_2$; $R=Et$), m.p. 191°, are analogously obtained. The following bindones are described: n-propyl-, m.p. 169°; nitro-n-propyl-, m.p. 184—185°; isoamyl-, m.p. 151°; nitroisoamyl-, m.p. 177—178°; allyl-, m.p. 162°; diallyl-, m.p. 114—115°; bromo- β -dibromo-n-propyl-, m.p. 82°; trinitroallyl-, m.p. 164°; benzyl-, m.p. 178°; bromobenzyl- ($X=Br$; $R=CH_2Ph$) and nitrobenzyl-, m.p. 194—195°. H. W.

Formoins. P. KARRER and A. VON SEGESSER (Helv. Chim. Acta, 1935, 18, 273—275).— p - C_6H_4AcOMe and SeO_2 in hot EtOH give *p*-anisylglyoxal, b.p. 170—180°/10 mm., cryst. (hydrate, cryst.), which with KCN in 50% EtOH gives dianisoylformoin (α -hydroxy- $\beta\gamma\delta$ -triketo- $\alpha\delta$ -di-*p*-anisyl-n-butane), m.p. 151—152°. This and dibenzoylformoin show 40 and 50% of the dienolic form and give 100 and 95% yields, respectively, of Cu_2O with hot $Cu(OAc)_2$.

R. S. C.

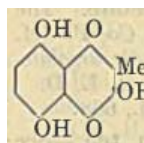
Preparation of aromatic hydroxy-ketones.—See B., 1935, 348.

Reduction potentials of naphthaquinones.—See this vol., 585.

Colouring matters of *Drösera Whittakeri*. I. Absorption spectra and colour reactions of hydroxynaphthaquinones. A. K. MACBETH, J. R. PRICE, and F. L. WINZOR. II. A. K. MACBETH and F. L. WINZOR. III. Synthesis of hydroxydroserone. F. L. WINZOR (J.C.S., 1935, 325—333, 334—336, 336—338).—I. The bulb of *D. Whittakeri* contains two colouring matters, droserone (I), $C_{11}H_8O_4$, m.p. 178°, and hydroxydroserone (3:5:8-trihydroxy-2-methyl-1:4-naphthaquinone) (II), $C_{11}H_8O_5$, m.p. 192—193°. The absorption spectra of typical 1:2- and 1:4-naphthaquinones and a series of hydroxy-1:4-naphthaquinones and their acetates have been examined. The introduction of OH alters the absorption typical of simple 1:4-compounds; the curves for the Ac derivatives revert to the simple type. The Ac_3 derivative of (II) indicates a 1:4-naphthaquinone compound, and comparison of the curves of (II) with those of naphthazarin, methyl-naphthazarin, and naphthopurpurin suggests that (II) has two OH in the *peri*-positions and the quinone ring is fully substituted. Colour reactions of hydroxynaphthaquinones with $CN\cdot CH_2\cdot CO_2Et$ and similar substances show that the presence of one OH in the quinone ring inhibits colour production apart from that of the quinone salt. (I)

and (II) give negative results in such colour tests. Methyl-naphthazarin, m.p. 171° (diacetate, m.p. 168°), is prepared from maleic anhydride and toluquinol or from citraconic anhydride and quinol.

II. Boroacetic anhydride, used as a reagent for *peri*-OH groups, gives methyl-naphthazarin and hydroxydroserone diboroacetates, whilst (I) gives a monoboroacetate [(I) is probably 3:5(or 3:8)-dihydroxy-2-methyl-1:4-naphthaquinone]. 2-Hydroxy-1:4-



naphthaquinone forms a $SnCl_3$ compound and a pyridine salt; 2:3-dihydroxy-1:4-naphthaquinone gives a Sn complex and a pyridine salt. (I) and (II) also yield pyridine salts. The formation of C_5H_5N salts supports the formulae given. CH_2N_2 methylates 2-hydroxy- and 2:3-dihydroxy-1:4-naphthaquinones, but condenses with (II). The bearing of this reaction on the structure and tautomerisation of (II) is discussed.

III. 3:6-Dihydroxy-2-methoxytoluene and maleic anhydride condense ($AlCl_3$) to 3:5:8-trihydroxy-2-methyl-1:4-naphthaquinone, m.p. 192—193°, identical with (II) obtained from natural sources, confirmed by the identity of the Ac_3 compound. The formula (II) is preferred. F. R. S.

Dynamics of acid hydrolysis of benzoyl derivatives of aminoanthraquinones. M. A. ILJINSKI and A. A. ZAJKIN (J. Gen. Chem. Russ., 1934, 4, 1294—1302).—1:5- (I) and 1:8-dibenzamidoanthraquinone (II) are completely hydrolysed by 88.3% H_2SO_4 at 70° (2 hr.); < 80% H_2SO_4 has no effect even after 5 hr., whilst with conc. H_2SO_4 at 0° the 8-OH-derivative of (I), but not of (II), is obtained. The corresponding 1:4-isomeride, m.p. 283°, is completely hydrolysed by 90% H_2SO_4 at 70° after 1 hr., whilst 95.6—100% H_2SO_4 at 0° yields a monobenzoyldiamine, m.p. 278°. 1- and 2-Benzamidoanthraquinone are completely hydrolysed by 90% H_2SO_4 after 1 hr. at 70°. R. T.

Constituents of resins. I. Lactone of sulphite waste and tsugaresinol. H. EMDE and H. SCHARFNER (Helv. Chim. Acta, 1935, 18, 344—352).—The Me_2 ether of the lactone (I) (modified prep.) from sulphite waste has the formula given by Erdtmann (this vol., 218), but according to analyses (I) contains an impurity richer in C. (I) is obtained also from naturally aged pine resin and is identical with tsugaresinol (A., 1932, 275). The names, tsuga-lactone and -acid, are proposed for (I) and the corresponding acid. R. S. C.

Lignin and related compounds. XI. Nature of lignite humic acid and of the so-called "humic acid" from sucrose. M. PLUNGUAN and H. HIBBERT (J. Amer. Chem. Soc., 1935, 57, 528—536; cf. A., 1934, 74).—By analysis of the products of methylation (Me_2SO_4 and CH_2N_2) and acetylation, hydrolysis of the latter, and re-methylation or re-acetylation, lignite humic acid is shown to be $[C_{77}H_{54}O_{11}(OMe)(OH)_8(CO_2H)_2]_x$, 6 OH being probably phenolic and 2 enolic. Similarly it is shown that "humic acid," produced from sucrose by 72% H_2SO_4 , is $[C_{55}H_{41}O_{11}(OH)_4(CO_2H)_4]_x$, 3 OH being aliphatic and 1 more acidic. R. S. C.

Constituents of *Lecanora gangleoides*.—See this vol., 550.

Pigment of red cabbage.—See this vol., 674.

Metallic salts of ursolic acid. H. M. SELL and R. E. KREMERS (Ind. Eng. Chem. [Anal.], 1935, 7, 105—106).—Na ursolate (cf. Sando, A., 1923, i, 990) with many salts in 50% EtOH-H₂O gives metal ursolates which are insol. in hexane and glycerol, but sol. in dioxan, butyl alcohol and acetate. The following are prepared: *Al, Ba, Ca, Cd, Co, Pb* (cf. B., 1934, 939), *Li, Mg, Mn, Ni, Ag*, and *Sr ursolate*. J. L. D.

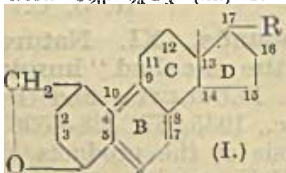
Crystalline vitamin-B₁.—See this vol., 668.

Crystalline tea-tannin from green tea.—See this vol., 673.

Sapogenins from *Chlorogalum pomeridianum*.—See this vol., 673.

Vegetable heart poisons. VI. Genins of the heart poisons of a species of *Strophanthus hispidus*. R. TSCHESCHE (Ber., 1935, 68, [B], 423—426).—Extraction of the crushed seeds of *Strophanthus hispidus* with MeOH and hydrolysis of the non-cryst. glucosides leads to α -monoanhydrohispidogenin-A (I), C₂₃H₃₂O₄, m.p. 208°, [α]_D²⁰ -27.7° in CHCl₃ (Ac₂ derivative, m.p. about 203°, [α]_D²⁰ -44.0° in CHCl₃), and dianhydrohispidogenin-B (II), C₂₃H₃₀O₆, m.p. 262—264° (diacetate, m.p. 284°). (I) contains 2 (?) sec. OH and 2 double linkings (PtO₂). One of the latter probably arises by elimination of a *tert*-OH during fission, so that the original genin is C₂₃H₃₄O₅ and is isomeric with sarmentogenin. (II) contains 2 sec.-OH, 2 O in lactone groups, and probably 2 *tert*-OH. Of its 3 double linkings, 2 probably arise during hydrolysis by loss of 2 *tert*-OH, so that the original genin is C₂₃H₃₄O₈ and is isomeric or identical with ouabagenin. (I) is transformed by conc. HCl into β -anhydrohispidogenin-A, C₂₃H₃₂O₄, m.p. 222—224°, [α]_D¹⁹ +36.0° in CHCl₃, which contains 2 double linkings (PtO₂). H. W.

Strophanthin. XXXII. Anhydrostrophanthidins. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1935, 108, 693—702; cf. A., 1934, 1359).—In consequence of the new structure for strophanthidin (this vol., 218) trianhydrostrophanthidin is now represented as (I) (R= $\text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{O} \end{smallmatrix}$), the acid C₂₃H₂₄O₆ derived from it being produced by oxidative fission of the C₃-C₄ linking, whilst the acid C₂₀H₁₆O₃ (II) is regarded as (I) (R=CO₂H).



(II) by the Curtius degradation yields an amine, C₁₉H₂₅ON (hydrochloride, m.p. 248—250°), which is not aromatic in character. Comparative experiments show that the *Me* ester (III), m.p.

88°, of (II) resembles MeOBz and *Me o*-toluate, but differs from *Me 2:4:6*-trimethylbenzoate in being readily hydrolysed by 0.1*N*-NaOH. (III) with MgPhBr affords a *diphenylcarbinol*, C₃₂H₃₄O₂, m.p. 127—128° (decomp.), which with CrO₃ yields a *lactone*, C₃₂H₃₀O₄, m.p. 288°. Treatment of monoanhydrostrophanthidin with KOH-MeOH, followed by relactonisation, yields

isomonoanhydrostrophanthidin (IV), C₂₃H₃₀O₅, [α]_D²⁰ -178° in CHCl₃ [oxime, m.p. 266—270° (decomp.)] (also obtained by hydrolysis of the ethylal of oxidoanhydrostrophanthidinic acid). (IV) gives a negative nitroprusside test and the erstwhile lactone-ring double linking is probably conjugated with that in ring D. Similar tautomeric changes are suggested in other strophanthidin derivatives. (IV) with KMnO₄ yields a *lactonic acid*, C₂₃H₃₀O₆, m.p. 287° (decomp.).

H. N. R.
Reduction of pulegone: pulegol. J. DÆUVRE and H. PERRET (Bull. Soc. chim., 1935, [v], 2, 298—305).—Reduction of pulegone (I) with Al(OPr^{*i*})₃ in boiling Pr^{*i*}OH affords a mixture, b.p. 184° (corr.)/731 mm., of $\Delta^2:4^{(8)}$ - (27% COMe₂ on ozonolysis) and $\Delta^3:8^{(9)}$ -*p*-menthadiene (83% of CH₂O and HCO₂H with O₃; affords β -methyladipic acid with CrO₃-AcOH), unchanged (I) (separated with NaHSO₃), and *d*-pulegol (II), b.p. 91.5°/12 mm., which is probably moderately pure, although ozonolysis affords only 38% of the theoretical amount of COMe₂, and 6% of CH₂O (terminal :CH₂). (II) undergoes dehydration very readily. J. W. B.

Oxidation of carvomenthene by selenium dioxide. Synthesis of carvotanacetol. J. TABUTEAU (Compt. rend., 1935, 200, 244—245).—Treatment of the product of oxidation of carvomenthene with SeO₂ in boiling AcOH with NaHSO₃ effects the isolation of carvotanacetone, the non-CO portion (containing 70% EtOAc), after hydrolysis, affording carvotanacetol, b.p. 86°/3 mm. (probably a mixture of *cis*- and *trans*-), reduced by H₂-PtO₅ (Adams) to a mixture of stereoisomeric carvomenthols.

J. W. B.
Synthesis of myrtenol. G. DUPONT and W. ZACHAREWICZ (Bull. Soc. chim., 1935, [v], 2, 533—539).—Pinene and SeO₂ in EtOH give myrtenol (I), b.p. 106—107°, *dl*- and *d*-, [α]_D²⁰ +44.11° (benzoate, b.p. 102.5—104°/9 mm., *d*-, [α]_D²⁰ +45.32°; H phthalate, *dl*-, m.p. 120—120.5°, *d*-, m.p. 113.5—114.5°, [α]_D²⁰ +21.25° in EtOH), myrtenal (II), b.p. 99—100°/15 mm., *d*-, [α]_D²⁰ +14.75° (semicarbazone, *d*-, dimorphic, m.p. 225° and 216°, *dl*-, m.p. 200.5°; oxime, *dl*-, m.p. 101°, *d*-, m.p. 70.5—71.5°, [α]_D²⁰ +16.25°, gives the *d*-nitrile, and thence *d*-myrtenic acid, m.p. 53—54°, and pinic acid) [also obtained from (I) and CrO₃], and a hydrocarbon, b.p. 54—95°/20 mm. (cf. A., 1933, 1166). Verbenone is readily obtained pure from Aleppo pine oil and air by Co abietate, but that from enfleurage oil contains (II), which caused the error in previous work. Raman spectra are given. R. S. C.

Synthesis of nopinene and $\Delta^{1:5}$ -pinadiene from pinene. G. DUPONT and W. ZACHAREWICZ (Compt. rend., 1935, 200, 759—762; cf. A., 1934, 1106).—The hydrocarbons formed in addition to myrtenol (I) and myrtenal (II) by the oxidation of pinene (III) with SeO₂ consist almost exclusively of nopinene (IV) and $\Delta^{1:5}$ -pinadiene (V). [α]_D²⁰ of (IV) is of the same sign as that of the (III) from which it is obtained. The constitution of (V) rests mainly on its oxidation to a diketodicarboxylic acid, C₁₀H₁₄O₆, m.p. 225°, apparently produced by rupture of the double

linkings of (V). (I) or (II) could not be transformed into (III) or (IV). H. W.

Configuration of borneol and isoborneol. Y. ASAHINA and M. ISHIDATE (Ber., 1935, 68, [B], 555—558).—Reduction of *l*-cis- π -apocamphor-7-carboxylic acid gives a OH-acid (I), m.p. 196°, corresponding with the Semmler-Bartelt lactone (II); since the latter is obtained by hydration of apocamphenecarboxylic acid. (I) has the isoborneol configuration. Reduction of *d*-ketodihydroteresanalic acid by Na in boiling EtOH gives *d*-cis- π -apoborneol-7-carboxylic acid (III), m.p. 278°, $[\alpha]_D^{25} +47.52^\circ$ in abs. EtOH. In contrast with (I), (III), which from its mode of formation belongs to the borneol type, is remarkably stable. With AcCl (III) affords *d*-cis- π -apobornyl acetate 7-carboxyanhydride, m.p. 138—139°, $[\alpha]_D^{25} +71.02^\circ$ in EtOH, reconverted into (III) by 10% KOH. OH of (I) by reason of the ready formation of a lactone with the *cis*-7-CO₂H is to be regarded as the *exo*-form, whereas that of (II) occupies the *endo*-position. (II) is converted by HCl-AcOH at 80° or by PBr₅ in light petroleum into the corresponding lactone [optical antipode of (II)], m.p. 191°, $[\alpha]_D^{25} +115.5^\circ$ in abs. EtOH, hydrolysed by KOH to *d*-cis- π -apoisoborneol-7-carboxylic acid, m.p. 196°, $[\alpha]_D^{25} -24.05^\circ$ in abs. EtOH. *d*-trans- π -apobornyl acetate 7-carboxylic acid, m.p. 106—107°, b.p. 185—186°/17 mm. (*Me* ester, b.p. 139—140°/17 mm.), and *Me d*-trans- π -apoisobornyl acetate 7-carboxylate, b.p. 137—138°/16 mm., 266°/760 mm., are described. H. W.

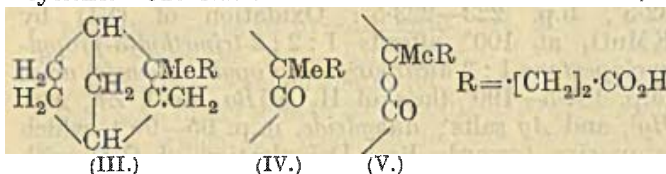
New homologues of the camphor group. Propylcamphor and its derivatives. S. S. NAMETKIN and A. I. SCHAVRIGIN (Annalen, 1935, 516, 199—217; cf. A., 1927, 249).—Treatment of (+)-camphor with CH₂:CH·CH₂Br and activated Mg affords (85—95% yield) *tert*-allylboryl alcohol, b.p. 118—121°/18 mm., $[\alpha]_D^{25} -15.14^\circ$ in EtOH, reduced (Pt-black in EtOH) to *tert*-propylbornyl alcohol (I), m.p. 30—32°, $[\alpha]_D^{25} -7.19^\circ$ in EtOH. (I) is dehydrated by NaHSO₄ at 120—125° to a mixture (II), b.p. 86—87°/12 mm., $[\alpha]_D^{25} -36.71^\circ$, of propylidenecamphane (III) and propylcamphene (IV), hydrogenated (Pt-black in AcOH) to the hydrocarbon C₁₃H₂₄, b.p. 93.5—94°/14 mm. Treatment of (II) with AcOH-dil. H₂SO₄ at 50—60° leads to propylisobornyl acetate (V), b.p. 123—124°/6.5 mm., the yield of which is very greatly increased by subjecting the unattacked hydrocarbon to repeated treatment. Since each treatment affects only about 25% of the initial material and the yields of (V) remain const., whilst the unattacked material retains its original properties with the exception of $[\alpha]_D$, it appears that hydration is accompanied by isomerisation of (III) to (IV). Oxidation of (II) affords camphoric acid (anhydride, m.p. 222—223°). Treatment of (II) in ligroin with nitrous fumes and of the product with KOH-EtOH-H₂O gives inactive camphor, m.p. 173—174° (semicarbazone, m.p. 236—237°), and α -propylcamphenilone, b.p. 114—115°/9 mm. [semicarbazone, m.p. 196—198° (decomp.)]. Hydrolysis of (V) gives 4-propylisoborneol (VI), m.p. 57—58°, $[\alpha]_D^{25} +6.20^\circ$ in EtOH. 4-Propylcamphor (VII), m.p. 62°, $[\alpha] \pm 0^\circ$ (semicarbazone, m.p. 202°;

oxime, m.p. 114.5—115°), is reduced by Na and EtOH to propylborneol, m.p. 50—51°. The hydrazone, m.p. 108—110°, of (VII) is transformed by NaOEt-EtOH at 195—205° into propylcamphane, m.p. 32—32.5°, b.p. 223—223.5°. Oxidation of (VI) by KMnO₄ at 100° affords 1:2:2-trimethyl-3-propylcyclopentane-1:3-dicarboxylic (propylcamphoric) acid, m.p. 189.5—190° (loss of H₂O) [Ba, Fe^{III}, Zn, Mn, Hg^I, and Ag salts; anhydride, m.p. 95—96°], which is passive towards Br. Dehydration of (VI) with NaHSO₄ affords β -propylcamphene, (VIII), b.p. 92—93°/16 mm., which is not hydrogenated in presence of Pt-black, yields ill-defined products when oxidised, and is converted by successive treatments with AcOH-H₂SO₄ and KOH-EtOH-H₂O into (VI). (VIII) is transformed by nitrous fumes followed by alkali into β -propylcamphenilone, b.p. 124—125°/22 mm. (semicarbazone, m.p. 224—225°), converted by NaNH₂ into 3-propyl-3-isopropylcyclopentanecarboxylamide, m.p. 79—81°. H. W.

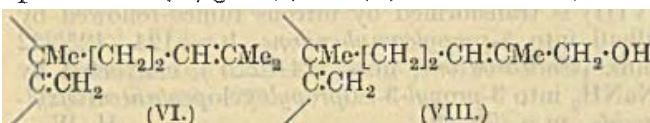
Catalytic reduction of both hydroxymethylene-camphor benzoates; second camphorylcarbinol. H. RUPE and M. LENZLINGER [with, in part, H. MARTIN] (Helv. Chim. Acta, 1935, 18, 255—265).—Hydrogenation (Ni) of hydroxymethylenecamphor (I) α -benzoate (trans-isomeride) in EtOAc-EtOH-H₂O gives α -methylcamphor (II) [oxime, m.p. 59.5—60.5°, with hot dil. HCl gives methylcampholenonitrile (III); semicarbazone, m.p. 229.5—230°] and an isomeride [oxime (IV), m.p. 80°, $[\alpha]_D^{25} -11.45^\circ$, with hot 20% HCl gives (III)], a small amount of a strongly dextrorotatory substance (possibly an oxide), and much BzOH. It is probable that hydrolysis does not occur, but rather fission into BzOH and methylenecamphor (V). The β -(*cis*-)benzoate of (I) with H₂-Pd black in dry EtOH gives BzOH, (V), and β -camphorylcarbinol benzoate, m.p. 42—43°, $[\alpha]_D^{25} +58.8^\circ$, $[\alpha]_{540}^{25} +70.46^\circ$ in C₆H₆ (10%), hydrolysed by H₂SO₄-EtOH to the β -carbinol (VI), b.p. 146.5—147.5°/13 mm., $[\alpha]_D^{25} +35.93^\circ$, $[\alpha]_{540}^{25} +45.01^\circ$. The known (α -)isomeride (VII) of (VI), previously called camphylcarbinol, prepared from (I) by Ni-H₂, contains about 1% of (VI). Pd-hydrogenation of the α -benzoate of (I) is slower, in accordance with analogies, and affords much (VI) with 3—4% of (VII). α for (II) and *Me* camphorcarboxylate changes sign with λ in C₆H₆, giving $[\alpha]_{589}^{25} -2.49^\circ$ and -4.5° , $[\alpha]_{541}^{25} +10.76^\circ$ and $+6.5^\circ$, respectively; (II) is, however, dextrorotatory over this range in cyclohexane (+20.55° to +62.35°) and EtOH (+19.44° to +55.61°). Hydrolysis of (IV) by 20% HCl gives (III) with a high $[\alpha]$ (+45°). R. S. C.

Polyterpenes and polyterpenoids. XCIII. Constitution of β -santalol and β -santalene. L. RUZICKA and G. THOMANN (Helv. Chim. Acta, 1935, 18, 355—362; cf. this vol., 351).—The prep. of tricycloeksantalic acid (I) from α -santalol (II), $\alpha_D +1.5^\circ$, is modified (22 g. from 100 g.). dicycloeksantalic acid (III) with O₃ in AcOH or, better, CCl₄ gives camphenilonylacetic acid (IV), b.p. 149°/0.1 mm. [*Me* ester, m.p. 76—77° (semicarbazone, m.p. 192°)], and β -methylnorcampholidylpropionic acid (V), b.p. about 180°/0.1 mm. (decomp.) (*Me* ester, b.p. 132°/0.1 mm.). By analogy with Harries' ozonisation

of camphene it is thus proved that β -santalene (VI) and (III) have the formulæ given and that (VI) is related to α -santalene (VII) as camphene is to tricyclene. Ozonisation of santalene and santalol,



$\alpha_D - 57^\circ$, rich in β -forms, gives (V) [(IV) could not be isolated], thus proving the relationship of (V) to β -santalol, which is probably (VIII). The purest specimens of (II) give (I) and (V), and those of (VII)



afford (I), (V), and teresantallic acid (IX). (VI) gives (IX) and a substance, $C_{11}H_{16}O$, m.p. 180° , b.p. $115-116^\circ/2$ mm., possibly an oxide. It follows that none of these substances has been obtained free from their isomerides. (I) and (III) with hot 100% HCO_2H give the lactone, $C_{12}H_{18}O_2$, m.p. 102° (A., 1908, i, 434). R. S. C.

Halochromy of compounds with a furan nucleus. N. MAXIM and S. POPESCO (Bul. Soc. Chim. Romania, 1934, 16, 89-116).—2-Furoyl chloride undergoes the Friedel-Crafts reaction with benzene derivatives. Thus the following 2-furyl ketones are prepared: *p*-chlorophenyl (I), m.p. 42° , b.p. $182^\circ/14$ mm. (semicarbazone, m.p. 74°); *p*-tolyl (II), b.p. $191^\circ/30$ mm., $161^\circ/14$ mm. (semicarbazone, m.p. 66°); *p*-bromophenyl (III), m.p. 51° , b.p. $197^\circ/14$ mm. (semicarbazone, m.p. 84°); *p*-methoxyphenyl (IV), m.p. 64° . Similarly β -2-furylacrylyl chloride yields furfurylidene-*p*-methyl-, *p*-chloro-, *p*-bromo-, and *p*-methoxy-acetophenone (cf. A., 1933, 281; 1934, 1361). Addition of Grignard reagent to Ph 2-furyl ketone and to (I), (II), (III), and (IV) yields the following carbinols: phenyl-2-furyl-ethyl-, b.p. $128^\circ/13$ mm., *n*-propyl-, b.p. $134^\circ/12$ mm., and *isobutyl*-, b.p. $138^\circ/12$ mm.; *p*-tolyl-2-furyl-ethyl-, b.p. $136^\circ/12$ mm., (benzoate, b.p. $148^\circ/12$ mm.), *n*-propyl-, b.p. $140^\circ/12$ mm., and *isobutyl*-, b.p. $145^\circ/13$ mm.; *p*-chlorophenyl-2-furyl-ethyl-, b.p. $146^\circ/12$ mm. (benzoate, b.p. $159^\circ/12$ mm.), *n*-propyl-, b.p. $150^\circ/11$ mm., and *isobutyl*-, b.p. $156^\circ/11$ mm.; *p*-bromophenyl-2-furyl-ethyl-, b.p. $169^\circ/13$ mm., *n*-propyl-, b.p. $173^\circ/12$ mm., and *isobutyl*-, b.p. $176^\circ/12$ mm.; diphenyl-2-furyl-, m.p. 90° ; phenyl-*p*-tolyl-2-furyl- (decomp.); phenyl-*p*-chloro- (decomp.), *p*-bromo- (decomp.), and *p*-anisyl-2-furyl-carbinol, m.p. 129° . The following highly coloured, cryst. salts are prepared by the action of dry HCl on a C_6H_6 solution of the ketone: furfurylidene-, m.p. 46° ; furfurylidene-*p*-methyl-, m.p. 36° ; *p*-chloro-, m.p. 81° ; *p*-bromo-, m.p. 91° , and *p*-methoxy-acetophenonehydrochloride, m.p. 83° . The halochromic properties of the compounds described are compared with those of the corresponding aryl compounds whilst the absorption spectra in $CHCl_3$ and H_2SO_4 solution show

that the latter modifies the structure of the carbinols and the ketones. F. N. W.

Unsaturated furan ketone derivatives. N. MAXIM and COPUZEANU (Bul. Soc. Chim. Romania, 1934, 16, 117-120).—Furfurylideneacetone condenses with the appropriate aldehyde in presence of $EtOH-NaOH$ to give difurfurylidene-, m.p. $57-5^\circ$; furfurylidene-anisylidene-, m.p. 84° ; *p*-piperonylidene-, m.p. 132° , and *p*-dimethylaminobenzylidene-acetone, m.p. 178° . F. N. W.

Hydropyran nucleus. Preparation of 2-alkyl-tetrahydropyrans. α -Dibromides and diols. R. PAUL (Bull. Soc. chim., 1935, [v], 2, 311-322).—2-Hydroxytetrahydropyran [from dihydropyran (I) and dil. HCl] reacts in an open-chain form $HO[CH_2]_4CHO$ with $MgRI$ to give good yields [33% calc. on (I)] of α -diols (II); thus are obtained: *n*-heptane- α -diol, b.p. $135-136^\circ/11$ mm., and *n*-octane- α -diol, b.p. $144-146^\circ/11$ mm. Dehydration of (II) (mechanism discussed) to 2-alkyltetrahydropyrans (III) is unsatisfactory, and (III) are best prepared by the action of $MgRX$ on 2-bromotetrahydropyran (this vol., 220) [prepared *in situ* from (I)]; thus are obtained 2-ethyl-, b.p. $128-129^\circ/770$ mm. [76% yield calc. on (I)], 2-*n*-propyl-, b.p. $152-153^\circ/760$ mm. (86%), and 2-phenyl- (IV), b.p. $113^\circ/11$ mm. (74%), tetrahydropyran. These are converted by $HBr-AcOH$ at $150-160^\circ$ into α -dibromoparaffins, and thus are prepared α -dibromo-*n*-heptane, b.p. $113-115^\circ/11$ mm., and *n*-octane, b.p. $127-128^\circ/11$ mm., but (IV) gives ϵ -bromo- α -phenyl- Δ^2 -pentene, b.p. $164-166^\circ/11$ mm., converted by Br at -5° into $\alpha\beta$ -tribromo- α -phenyl-*n*-pentane, m.p. 72° . By similar action of the appropriate Grignard reagent on 2:3-dibromotetrahydropyran [prepared *in situ* from (I) and Br] are obtained 3-bromo-2-ethyl-, b.p. $71-72^\circ/12$ mm., and 2-phenyl-, b.p. $160-162^\circ/15$ mm., m.p. 38° , tetrahydropyran. J. W. B.

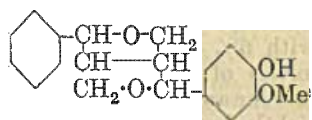
Condensation of aldehydes with malonic acid in presence of organic bases. II. Condensation of salicylaldehyde. A. A. KHAN, P. N. KURIEN, and K. C. PANDYA (Proc. Indian Acad. Sci., 1935, A, 1, 440-445; cf. this vol., 353).—The yields of coumarincarboxylic acid from $CH_2(CO_2H)_2$ and *o*-OH- C_6H_4 -CHO with differing amounts of added org. bases and differing experimental conditions are tabulated. F. R. G.

Toddalia aculeata (Pers.). II. Toddalolactone. B. B. DEY and P. P. PILLAY (Arch. Pharm., 1935, 273, 223-232; cf. A., 1934, 88).—Toddalolactone (I), $C_{14}H_{14}O_2(OMe)_2(OH)_2$, dimorphic, m.p. $132-5^\circ$, b.p. $230-235^\circ/8$ mm., $[\alpha]_D^{20} + 55.9^\circ$ in $CHCl_3$ [Ac_2 , m.p. $111-113^\circ$, and NO_2 -derivative, m.p. $186-187^\circ$; *H* phthalate, m.p. $180-181^\circ$ (*Ag* salt, m.p. $174-177^\circ$)], with cold conc. H_2SO_4 or, better, 2% HCl at 140° gives H_2O and a ketone, $C_{16}H_{18}O_5$, m.p. $120-121^\circ$ (semicarbazone, m.p. $204-210^\circ$; phenylhydrazone, m.p. $171-172^\circ$). It slowly dissolves in cold dil. NaOH and is pptd. therefrom unchanged. With hot 0.2N-NaOH, best with a trace of HgO , it gives the trans-coumaric acid (II), $C_{18}H_{22}O_7$, m.p. $178-179^\circ$, $[\alpha]_D + 36.1^\circ$ in MeOH (*Ag* salt), converted by H_2O at 100° or at the m.p. into an amorphous, unsaturated phenol, $C_{15}H_{22}O_5$. The *Ac* derivative, m.p. 168° (de-

comp.), of (II) with Br-MeOH in sunlight gives (I). (I) and alkaline KMnO_4 gives $\text{H}_2\text{C}_2\text{O}_4$ and a substance, m.p. $> 250^\circ$. With conc. HNO_3 at 100° (I) gives a *nitrodimethoxycoumarincarboxylic acid*, $\text{C}_{12}\text{H}_8\text{O}_9\text{N}$, m.p. $248-250^\circ$ (Me ester, m.p. 202°). (I) is therefore a dimethoxycoumarin with a $\text{C}_5\text{H}_{11}\text{O}_2$ side-chain, which is probably $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot$ or $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}(\text{OH})\cdot$. R. S. C.

1:3-Dioxins. IV. Condensation of 3:3', 3:5', and 5:5'-dinitro-2:2'-dihydroxydiphenyl with formaldehyde. F. CALVET and E. SEIGO (Anal. Fis. Quim., 1933, 31, 889-895; cf. A., 1933, 163).—3:3'-Dinitro-2:2'-dihydroxydiphenyl with conc. H_2SO_4 containing CH_2O at room temp. gives 3:3'-dinitro-2:2'-dihydroxydiphenyl-5:5'-dialdehyde, m.p. $288-290^\circ$ (decomp.) [monoxime, m.p. 215° (decomp.)], oxidised (KMnO_4) to the dicarboxylic acid, m.p. $310-315^\circ$ (decomp.), which is converted by CH_2N_2 into Me 3:3'-dinitro-2:2'-dimethoxydiphenyl-5:5'-dicarboxylate, m.p. $180-182^\circ$. 3:5'-Dinitro-2:2'-dihydroxydiphenyl with conc. H_2SO_4 and CH_2O affords 6-nitro-8-(3'-nitro-2'-hydroxy-5'-aldehydophenyl)-1:3-benzodioxin, m.p. 245° (decomp.) [oxime, m.p. $248-250^\circ$ (decomp.)], whereas 5:5'-dinitro-2:2'-dihydroxydiphenyl gives 8:8'-bis-6-nitro-1:3-benzodioxin, m.p. $> 310^\circ$. J. L. D.

Constitution of resin phenols and their biogenetic relationships. II. Pinoresinol and its relationship to eudesmin. H. ERDTMANN (Annalen, 1935, 516, 162-176).—Pinoresinol Me_2 ether (I), m.p. $107-108^\circ$, $[\alpha]_D^{25} + 64.5^\circ$ in CHCl_3 (this vol., 218), is the optical antipode of eudesmin (Robinson *et al.*, A., 1915, i, 890). A true racemate could not be obtained from these, but di-dinitroeudesmin, m.p. $241-242^\circ$ (decomp.), is obtained from the $(\text{NO}_2)_2$ -derivative (II) of (I), m.p. $212-213^\circ$, $[\alpha]_D^{25} - 124.7^\circ$ in CHCl_3 [obtained with 4-nitroveratrole by the action of $\text{HNO}_3\text{-AcOH}$ at $< 10^\circ$ on (I)], and dinitroeudesmin, $[\alpha]_D^{25} + 124^\circ$ in CHCl_3 , and di-dibromoeudesmin, m.p. $177-178^\circ$, from the Br_2 -derivative (III) of (I), m.p. 173° , $[\alpha]_D^{25} - 69.1^\circ$ in CHCl_3 , and dibromoeudesmin, $[\alpha]_D^{25} + 69.4^\circ$. When heated with HNO_3 (*d* 1.41) (II) gives 4:5-dinitro-, and (I) with HNO_3 (*d* 1.52) at -10° and then heated to 55° gives trinitro-veratrole. Similarly (III) with HNO_3 affords 4-bromo-5-nitro-veratrole, and with KMnO_4 it gives 6-bromoveratric acid. Oxidation of the Bz_2 derivative of pinoresinol (IV) with $\text{CrO}_3\text{-AcOH}$ gives a substance, m.p. $228-229^\circ$ (decomp.), $[\alpha]_D^{25} + 170^\circ$ in CHCl_3 , which, contrary



to Zinke *et al.* (A., 1924, i, 1088), is insol. in alkali and has quinone-like properties. On the basis of

these results and arguments based on biogenetic relationships, the annexed structure is suggested (amongst others) for (IV).

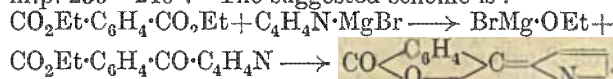
J. W. B.

Constitution of mono- and di-substituted derivatives of diphenylene sulphide. M. CHAIX and DE ROCHEBOUET (Bull. Soc. chim., 1935, [v], 2, 272-281).—Details of the proof that substitution in diphenylene sulphide occurs in the 3 and 6 positions. Courtot, A., 1934, 1109) are given. The following appear to be new: di-(5-bromo-2-diphenyl) disulphide,

m.p. 159° ; 5-bromo-, m.p. $118-119^\circ$ (corr.), and 5-chloro-diphenyl-2-sulphonyl chloride, m.p. 102° (*loc. cit.*, given as m.p. of the acid) [*Na* salt of acid, m.p. 285° (corr.)]. J. W. B.

Catalytic hydrogenation of pyrrole homologues, and the dehydrogenation of their tetrahydro-derivatives. J. K. JURIEV and F. F. SCHENJAN (J. Gen. Chem. Russ., 1934, 4, 1258-1261).—*N*-Methyl-, ethyl-, and -propyl-pyrrolidine are obtained by catalytic (Pd) hydrogenation at 160° of the corresponding pyrroles, whilst *NN'*-dipyrrolylmethane yields a mixture of pyrrole, *N*-methylpyrrole, NHet_2 , NH_2Bu , and NIMeBu . The above pyrrolidines are readily dehydrogenated at 275° (Pd catalyst). R. T.

Mechanism of the reaction between magnesiopyrrole and ethyl phthalate. T. N. GODNEV (Ber., 1935, 68, [B], 422-423).—Mg pyrrolyl bromide and *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Et})_2$ in Et_2O afford pyrrolenephthalide, m.p. $239-240^\circ$. The suggested scheme is:



H. W.

Sulphur derivatives of pyrroles. P. PRATESI (Gazzetta, 1935, 65, 43-50).—Et 5-thiocyano-2:4-dimethylpyrrole-3-carboxylate (A., 1933, 282) treated with Zn and NaOAc in $\text{AcOH} + \text{Ac}_2\text{O}$ yields Et 5-acetylthiol-2:4-dimethylpyrrole-3-carboxylate, m.p. $103-104^\circ$. Et 2:4-dimethylpyrrole-3-carboxylate with ClSO_3H in CHCl_3 gives 5-carbethoxy-2:4-dimethylpyrrole-3-sulphonic acid, m.p. 112° (K salt). 2:4-Dimethylpyrrole-5-aldehyde similarly treated yields a substance, $\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_2\text{S}$ or $\text{C}_{14}\text{H}_{18}\text{O}_5\text{N}_2\text{S}$ (?), m.p. 160° . E. W. W.

[Thiopyrrolecarboxylic acids.] K. NEISSER (Ber., 1935, 68, [B], 563; cf. this vol., 221).—Thiocyanation by NH_4CNS and Br was introduced by Kaufmann (A., 1926, 392). H. W.

Organic vanadium compounds. J. MEYER and W. TAUBE (Z. anorg. Chem., 1935, 222, 167-176).—Attempts to prepare org. V compounds (other than esters) from VCl_4 and C_6H_6 , PhMe , C_{10}H_8 , PhOH , $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, MgPhBr , or HgPh_2 resulted in the formation of amorphous products of indefinite composition. VCl_3 and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ gave the compound $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O})_3\text{V}$, and VCl_4 and $\text{C}_5\text{H}_5\text{N}$ the compound $[\text{VOCl}_2\cdot 2\text{C}_5\text{H}_5\text{N}]\cdot 3\text{C}_5\text{H}_5\text{N}$. F. L. U.

Condensations of aliphatic oxides with 2-aminopyridine. I. L. KNUNJANZ (Ber., 1935, 68, [B], 397-399).—Treatment of 2-aminopyridine (I) with $(\text{CH}_2)_2\text{O}$ in MeOH at $15-20^\circ$ leads to 1-β-hydroxyethylpyridoneimine, b.p. $184-185^\circ/17\text{ mm.}$, m.p. $112-113^\circ$, hydrolysed by boiling 10% NaOH to 1-β-hydroxyethylpyridone, b.p. $185^\circ/9\text{ mm.}$, m.p. 100° . (I) and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ in EtOH afford 5-hydroxy-1:2-divinylenetetrahydropyrimidine hydrochloride, m.p. 190° [corresponding platinichloride, m.p. 215° (decomp.)]; the non-cryst. base does not evolve NH_3 when boiled with alkali. (I) is considered to react in the pyridoneimine form. H. W.

Tschitschibabin condensation of butaldehyde and ammonia. L. HASKELBERG (Chem. and Ind.,

1935, 261—262).—Prolonged heating of $\text{OH}\cdot\text{CHPr}\cdot\text{NH}_2$ at 150—160° yields 3:5-diethyl-2-*n*-propylpyridine (I) (mercurichloride; picrate, m.p. 125—126°) (cf. Tschitschibabin, A., 1906, i, 451) and 3:5-diethyl-2- β -hydroxy- α -ethyl-*n*-amylpyridine, b.p. 164—170°/26 mm., also obtained from the product (II) from (I) and LiPh when treated with $\text{Pr}\cdot\text{CHO}$. (II) with CH_2PhCl and PhCHO gives, respectively, 2- α -benzyl-*n*-propyl-3:5-diethylpyridine, b.p. 185°/26 mm., and 3:5-diethyl-2- α -benzyloxypropylpyridine, b.p. 180—185°/26 mm. F. R. G.

Synthesis of indole-3-aldehyde and its homologues. W. J. BOYD and W. ROBSON (Biochem. J., 1935, 29, 555—561).—The yields of indole-3-aldehyde (I), 2- and 5-methylindole-3-aldehyde from the appropriate indole, CHCl_3 , and KOH (A., 1906, i, 696) are improved by the use of a larger quantity of KOH. 7-Methylindole-3-aldehyde (II), m.p. 202° [anil, m.p. 128°], has been prepared by this method and is formed together with some 3-chloro-8-methylquinoline, m.p. 55°. (I) is also obtained from Et indole-2-carboxylate and $\text{Zn}(\text{CN})_2\cdot\text{HCl}$ by Adams and Levine's method (A., 1924, i, 51); the resulting indole-3-aldehyde-2-carboxylate is decarboxylated by heating the acid of the acid, m.p. 244—245°, in paraffin at 210°. The anil of (I), m.p. 123° (lit. 126—127°), is hydrolysed to (I) with dil. AcOH . (II) was prepared by a similar method. Et 7-methylindole-3-aldehyde-2-carboxylate, m.p. 189°, with NaOH and NH_2Ph gives the anil of the corresponding acid, m.p. 255°, and a substance, m.p. 245°. An improved prep. (cf. A., 1927, 157) of 7-methylindole, m.p. 82° (lit. 85°) [picrate, m.p. 172° (lit. 175°)], is described. Treatment of pyruvic acid-*o*-tolylhydrazone with hot $\text{EtOH}\cdot\text{HCl}$ gives 7-methylindole-2-carboxylic acid (III) and an amide, $\text{C}_{25}\text{H}_{20}\text{O}_7\text{N}_3$, m.p. 283° (decomp.), hydrolysed to the acid, $\text{C}_{25}\text{H}_{19}\text{O}_8\text{N}_2$, m.p. 235°. (III) is decarboxylated by heating the NH_4 salt.

H. G. M.

Syntheses of Bz-tetrahydroisoquinolines. U. BASU and B. BANERJEE (Annalen, 1935, 516, 243—248; cf. A., 1934, 1111).—2-Hydroxymethylenecyclohexanone is transformed by NH_3 in CHCl_3 into 2-aminomethylenecyclohexanone, m.p. 110—111°, converted by the successive action of Na and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in C_6H_6 into 3-keto-4-cyano-2:3:5:6:7:8-hexahydroisoquinoline (I), m.p. 223° (*Me* derivative, m.p. 185°, prepared with $\text{Me}_2\text{SO}_4\cdot\text{KOH}$). (I) is hydrolysed by boiling 75% H_2SO_4 to 3-keto-2:3:5:6:7:8-hexahydroisoquinoline-4-carboxylic acid, m.p. 224° (decomp.), which passes when heated into 3-hydroxy-5:6:7:8-tetrahydroisoquinoline, m.p. 197—198°, converted by the successive action of Zn dust and PbO into isoquinoline. The following compounds are analogously obtained: 5-methyl-2-aminomethylenecyclohexanone, m.p. 112—115°; 3-keto-4-cyano-6-methyl-2:3:5:6:7:8-hexahydroisoquinoline, m.p. 228° (*Me* derivative, m.p. 137°); 3-keto-6-methyl-2:3:5:6:7:8-hexahydroisoquinoline-4-carboxylic acid, m.p. 235° (decomp.), and 3-hydroxy-6-methyl-5:6:7:8-tetrahydroisoquinoline, m.p. 178°; 4-methyl-2-aminomethylenecyclohexanone, m.p. 119°, 3-keto-4-cyano-7-methyl-2:3:5:6:7:8-hexahydroisoquinoline, m.p. 233°

(*Me* derivative, m.p. 222°), 3-keto-7-methyl-2:3:5:6:7:8-hexahydroisoquinoline-4-carboxylic acid, m.p. 216° (decomp.), and 3-hydroxy-7-methyl-5:6:7:8-tetrahydroisoquinoline, m.p. 169°; 6-methyl-2-hydroxymethylenecyclohexanone, b.p. 140°/14 mm., 3-keto-4-cyano-5-methyl-2:3:5:6:7:8-hexahydroisoquinoline, m.p. 212° (*Me* derivative, m.p. 118°), and 3-keto-5-methyl-2:3:5:6:7:8-hexahydroisoquinoline-4-carboxylic acid, m.p. 284° (decomp.). H. W.

Reaction between diarylthiocarbamides and alicyclic ketones. K. DZIEWONSKI and J. SCHOEN (Bull. Acad. Polonaise, 1934, A, 448—454).—cyclo-Hexanone heated with $\text{CS}(\text{NHPh})_2$ (I) yields 9-anilino-1:2:3:4-tetrahydroacridine, m.p. 235—236° (picrate, m.p. 245—246°; *NO*-derivative, m.p. 130°), which with 50% $\text{EtOH}\cdot\text{KOH}$ gives 1:2:3:4-tetrahydroacridone, m.p. 361—362°. Similarly 1-keto-1:2:3:4-tetrahydronaphthalene and (I) give 9-anilino-1:2-dihydro-3:4-benzacridine, m.p. 188—189° (picrate, m.p. 227—228°; *NO*-derivative, m.p. 126°), which with (II) yields 1:2-dihydro-3:4-benzacridone, m.p. 308—310°, transformed by Zn dust into 3:4-benzacridone. F. N. W.

Synthesis of pinacryptol-yellow.—See B., 1935, 298.

Synthesis of amino-acids. I. Piperidine and diethylamine as catalysts in the condensation of aromatic aldehydes with hydantoins. II. Sulphides as reducing and hydrolytic agents in the hydantoin synthesis of amino-acids. W. J. BOYD and W. ROBSON (Biochem. J., 1935, 29, 542—545, 546—554).—I. Nearly quant. yields of benzylidenethiohydantoin, of the *p*-OMe- and *p*-OH-derivatives, are obtained by condensing acetylthiohydantoin with the requisite aldehyde at 100° in presence of $\text{C}_5\text{H}_5\text{N}$ and piperidine. The product can be readily converted into the corresponding hydantoin by heating with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. The corresponding condensations (cf. A., 1911, i, 498) with hydantoin gave poor yields with this catalyst, but good yields with a mixture of $\text{C}_5\text{H}_5\text{N}$ and NH_4Et , as catalyst.

II. Benzylidenethiohydantoin when heated with aq. $(\text{NH}_4)_2\text{S}$ (16%) is reduced and hydrolysed to benzylhydantoin (I) and phenylalanine. *p*-Methoxy- and *p*-hydroxy-benzylidenethiohydantoin and the corresponding thiohydantoins give similar results. Unsaturated hydantoins are reduced quantitatively by heating with $\text{EtOH}\cdot(\text{NH}_4)_2\text{S}$ at 100°, with sulphides of org. bases, or with NaHS . Saturated hydantoins are hydrolysed quantitatively to the corresponding NH_2 -acid by heating with 6% aq. $(\text{NH}_4)_2\text{S}$ at 100° during 120 hr. Hydrolysis of (I) by this method gave also a little phenylalanine anhydride. Hydrolysis by 3% aq. NH_3 gave slightly less satisfactory results.

Synthesis of carnosine. Splitting of the benzyl group from carbobenzyloxy-derivatives and from benzylothio-ethers. R. H. SIFFERD and V. DU VIGNEAUD (J. Biol. Chem., 1935, 108, 753—761).—The following improved synthesis gives a 65% yield on the histidine used. Carbobenzyloxy- β -alanine (I), m.p. 106° (corr.), is prepared directly from succinimide by the Hofmann reaction and converted, through the acid chloride and *Me* ester, into carbo-

benzyloxy-β-alanyl hydrazide, m.p. 143° (corr.). This with HNO_2 yields the *azide*, which with *L*-histidine Me ester yields *carbobenzyloxycarnosine* (II), m.p. 160—161° (corr.), hydrogenated (Pd in H_2O) to *carnosine* (III), m.p. 260° (tube), 308—309° (Dennis bar), $[\alpha]_D^{20} +20.5^\circ$ in H_2O , identical with natural (III). (II) was also obtained, in poor yield, by condensing carbobenzyloxy-β-alanyl chloride with the Na salt of histidine. (I) with Na in liquid NH_3 (cf. A., 1931, 76) yields β-alanine and $(\cdot\text{CH}_2\text{Ph})_2$; (II) similarly affords an 80% yield of (III); carbobenzyloxycystine gives cystine after oxidation of the cysteine formed and benzylocystine behaves similarly. During the prep. of (III) from sheep-muscle tyrosine was isolated and identified.

H. N. R.

Bis-β-halogenoethylamines. VII. Synthesis of *N*-monoalkylated piperazines. V. PRELOG and V. STEPAN (Coll. Czech. Chem. Comm., 1935, 7, 93—102).—The *hydrobromide*, m.p. 151—152°, of $\text{NMe}(\text{CH}_2\cdot\text{CH}_2\text{Br})_2$ (*picrate*, m.p. 121—122°) or the *hydrochloride*, m.p. 116—117°, of $\text{NMe}(\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$ and NH_2Ph in hot MeOH give 4-phenyl-1-methylpiperazine, b.p. 140—142°/3 mm. (*monohydrochloride*, m.p. 233.5°; *methochloride hydrochloride*, decomp. 215°), which with NaNO_2 in aq. HCl followed by SO_2 in aq. Na_2CO_3 yields 1-methylpiperazine, b.p. 134—136° (*dihydrochloride*, m.p. 242—243°; *dihydrochloride monohydrate*, m.p. 90—91°; *diplatinichloride*; *dipicrate*, decomp. 272°; 4-dithiocarboxylic acid, sublimes 180°; Bz derivative, m.p. 240°). Similarly the *hydrobromide*, m.p. 170°, of $\text{NEt}(\text{CH}_2\cdot\text{CH}_2\text{Br})_2$ (*picrate*, m.p. 120.5°) gives 4-phenyl-1-ethylpiperazine, m.p. 50—51°, which with NaNO_2 in aq. HCl yields 4-p-nitrosophenyl-1-ethylpiperazine *dihydrochloride*, decomp. 210°, and this with SO_2 gives 1-ethylpiperazine (*dihydrochloride*, m.p. 210—211°; *dipicrate*, decomp. 257°) (cf. Moore *et al.*, A., 1929, 331). The *hydrobromide*, m.p. 157°, of $\text{NPr}(\text{CH}_2\cdot\text{CH}_2\text{Br})_2$ (*picrate*, m.p. 101—102°) gives similarly 4-phenyl-1-n-propylpiperazine, b.p. 102—103°/<0.1 mm. (*monohydrobromide*, m.p. 231—232°), 1-n-propylpiperazine *dipicrate*, m.p. 241—242° (decomp.), and *dihydrochloride*, decomp. 256°.

F. R. G.

Hydrolysis of diketopiperazine and of glycylglycine.—See this vol., 587.

Action of alkali on 2:4-diethoxypyrimidine: application to a synthesis of cytosine. G. E. HILBERT and E. F. JANSEN. **Refractive indices of some pyrimidines.** S. B. HENDRICKS (J. Amer. Chem. Soc., 1935, 57, 552—554).—2:4-Diethoxypyrimidine (modified prep.) and NaOH in hot 96% EtOH give 1:2-dihydro-4-keto-2-, m.p. 167—167.5° [*Na* salt, m.p. 305° (decomp.)], and 3:4-dihydro-2-keto-4-ethoxypyrimidine, m.p. 127.5—129° [*Na* salt, hygroscopic, m.p. 225° (decomp.)], which with dry NH_3 -EtOH at 120° yield cytosine (50% formed at 80°) and isocytosine (none formed at 80°), respectively. Optical data are recorded for these compounds, which have large birefringence, suggesting structural relationship with C_6H_6 . M.p. are corr.

R. S. C.

Preparation of 6-thiocyano-2-ethylthiol-5-phenylpyrimidine. Y. F. CHI and T. Y. HO (Trans. Sci. Soc. China, 1934, 8, 69—72; cf. A., 1932,

755).—2-Ethylthiol-5-phenyluracil (modified prep.; cf. A., 1905, i, 483) and POCl_3 yield 6-chloro-2-ethylthiol-5-phenylpyrimidine, b.p. 218°/10 mm., m.p. 38—39°; this, with KCNS, affords 6-thiocyano-2-ethylthiol-5-phenylpyrimidine, m.p. 90—91°.

CH. ABS. (r)

Preparation of ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate. Y. F. CHI and F. SZE (Trans. Sci. Soc. China, 1934, 8, 73—76).—*Et* 6-chloro-2-ethylthiolpyrimidine-5-acetate, b.p. 172—174°/4 mm., is obtained from the corresponding OH-compound with POCl_3 .

CH. ABS. (r)

Action of potassium cyanate on 6-chloro-2-ethylthiol-5-carbethoxypyrimidine. Y. F. CHI and S. Y. MING (Trans. Sci. Soc. China, 1934, 8, 77—80).—The product from the above reaction yields, with NH_3 , *Et* 6-carbamido-2-ethylthiolpyrimidine-5-carboxylate, m.p. 140—141°, and, with NH_2Ph *Et* 6-phenylcarbamido-2-ethylthiolpyrimidine-5-carboxylate, m.p. 195°.

CH. ABS. (r)

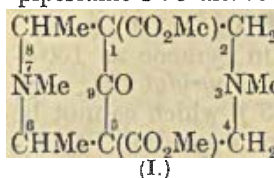
Preparation of uracil. Y. F. CHI and Y. H. CHEN (Trans. Sci. Soc. China, 1934, 8, 83—84).—A modification of the method of Davidson and Baudisch (A., 1926, 1154) giving a 58% yield is described.

CH. ABS. (r)

Rearrangement of ethyl 6-thiocyano-2-ethylthiolpyrimidine-5-acetate into its thiocarbimide modification. Y. F. CHI and C. M. MA (Trans. Sci. Soc. China, 1934, 8, 91—96).—Further details of work already reported (A., 1934, 85).

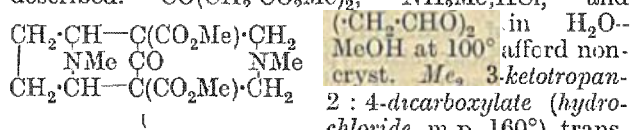
CH. ABS. (r)

Derivatives of dipidine. C. MANNICH and F. VERT (Ber., 1935, 68, [B], 506—512; cf. A., 1930, 618).—Treatment of Me_2 4-keto-1:2:6-trimethylpiperidine-3:5-dicarboxylate with CH_2O and NH_2Me .HCl leads to Me_2 9-keto-3:6:7:8-tetramethyl-dipidine-1:5-dicarboxylate (I), m.p. 112° (decomp.) [*monohydrochloride*, m.p. 112° (decomp.)]; *monoperchlorate*, m.p. 137° (decomp.); *monomethiodide*, m.p. 95°]. The *Et*₂ ester has m.p. 89°.



The substances behave as monacidic bases in presence of Me-red. They do not give derivatives with ketonic reagents. They behave as if saturated towards H_2 (Pd or Pt-sponge) in Et_2O , whereas in MeOH (Pd-C) the gas is absorbed with fission of the basic mol. and production of NH_2Me and MeCHO . They are readily hydrolysed by acids. Thus when gently heated with 25% HCl (I) loses NH_2Me and MeCHO with formation of Me_2 4-keto-1-methylpiperidine-3:5-dicarboxylate, m.p. 87° (corresponding *Et*₂ ester, m.p. 115°), whilst more drastic treatment results in CO_2 and *Me* 4-keto-1-methylpiperidine-3-carboxylate (II) (*hydrochloride*, m.p. 173°) (corresponding *Et* ester, b.p. 130°/12 mm., and its *hydrochloride*, m.p. 129°). Hydrogenation of (II) (PtO_2 in 50% MeOH) yields *Me* 4-hydroxy-1-methylpiperidine-3-carboxylate (? mixture of stereoisomerides), the non-cryst. *hydrochloride* of which is transformed by BzCl at 140° into the corresponding benzoate (non-cryst. *hydrochloride*; *perchlorate*, m.p. 174°) and by $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ at 160° into the *p*-nitrobenzoate (*hydrochloride*, m.p. 192°),

reduced (PtO₂) to the *p*-aminobenzoate (dihydrochloride, m.p. 208°). Me₂ 9-keto-6:7:8-trimethyl-3-allyldipidone-1:5-dicarboxylate, Me₂ 4-keto-1-allylpiperidine-3:5-dicarboxylate (hydrochloride, m.p. 134°), Me₂ 9-keto-6:7:8-trimethyl-3-β-phenylethylpiperidine-1:5-dicarboxylate, m.p. 102°, Me₂ 4-keto-1-β-phenylethylpiperidine-3:5-dicarboxylate (hydrobromide, m.p. 130°), Me₂ 9-keto-6:7:8-trimethyl-3-β-chloroethylpiperidine-1:5-dicarboxylate [nitrate (+H₂O), decomp. 132—133°], and Me₂ 4-keto-1-β-chloroethylpiperidine-3:5-dicarboxylate [nitrate, m.p. 135° (decomp.)], are described. CO(CH₂·CO₂Me)₂, NH₂Me, HCl, and



formed by NH₂Me and CH₂O into Me₂ 9-keto-3:7-dimethyl-6:8-ethylenedipidone-1:5-dicarboxylate (III), m.p. 113° (hydrobromide; perchlorate). H. W.

Preparation of 2:2'-dipyridyl and some of its derivatives. H. D. T. WILLINK, jun., and J. P. WIBAUT (Rec. trav. chim., 1935, 54, 275—283; cf. A., 1934, 763).—C₅H₅N containing 2—16% of I at 320° gives 2:2'-dipyridyl (I). 2-Methylpyridine (II) with Ni (but not with I) at 325° under pressure gives 6:6'-dimethyl-2:2'-dipyridyl (III) (picrate, m.p. 170—171°; +HgCl₂ m.p. 237—238°) (also obtained by boiling 6-bromo-2-methylpyridine with Cu), which gives no colour with Fe^{II} salts, and an oil which affords *monopicates*, m.p. 154—155° and 237—238° (base+AuCl₃, m.p. 204—205.5°), and a *dipicrate*, m.p. 200—201° (decomp.) (+HgCl₂, m.p. 201—202°). 2:3:5-Tribromo-, 2:5- and 2:6-dibromo-, 6-bromo-2-ethoxy-, and 6-bromo-2-amino-pyridine give no dipyridyl compounds with Cu. (I) does not react with H₂SO₄-KNO₃-conc. HNO₃ at 290° (cf. A., 1925, i, 697), but with NaNH₂ in cymene at 150—160° it gives 6:6'-diamino-2:2'-dipyridyl (?), m.p. 185—186° (picrate, m.p. 254—255°), which cannot be synthesised from 2-bromo-6-aminopyridine. 2:2'-Dipyridyl-3:3'-dicarboxylic acid could not be resolved. J. L. D.

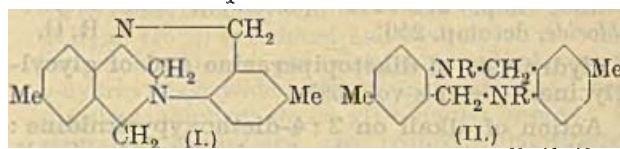
Synthesis of 1-methylphenazine. C. MERMOD (Helv. Chim. Acta, 1935, 18, 362—363).—3-Methyl-*o*-benzoquinone and *o*-C₆H₄(NH₂)₂ in Et₂O give 1-methylphenazine. R. S. C.

Derivatives of 4-hydroxy-2-thion-1:2:3:4-tetrahydroquinazoline and the phenomenon of their colour. C. V. GHEORGHIU (Bull. Soc. chim., 1935, [v], 2, 223—239).—A detailed account of work briefly summarised previously (A., 1934, 1011). The following are prepared by condensation of the *o*-NH₂·C₆H₄·CHO and PhNCS: 4-ethoxy-6:7-methylenedioxy-2-thion-3-phenyl-1:2:3:4-tetrahydro- (I), readily converted (e.g., H₂O to its solution in C₅H₅N) into 6:7-methylenedioxy-2-thion-3-phenyl-2:3-dihydro-quinazoline (II), reconverted by hot EtOH into (I) and by hot PrOH into the analogous 4-*n*-propoxy-derivative. With HClO₄ (d 1.7) a suspension of (I) in 96% EtOH affords its carbonium perchlorate, and with HgO (I) gives a substance, m.p. 137—138°, possibly 2:4-diketo-6:7-methylenedioxy-3-phenyl-1:2:3:4-tetrahydroquinazoline. Similarly are ob-

tained 4-acetoxy-6:7-methylenedioxy-2-thion-3-phenyl-, m.p. 198—200°, 4-ethoxy-6:7-methylenedioxy-2-thion-3-*o*-, m.p. 233—235° (carbonium perchlorate), and -3-*p*-tolyl-, m.p. 215° (HClO₄ gives the perchlorate of the 4-OH-derivative), -1:2:3:4-tetrahydroquinazoline; 6:7-methylenedioxy-2-thion-3-*o*- and -3-*p*-tolyl-2:3-dihydroquinazoline. 4-Ethoxy-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline with EtI-KOH-aq. EtOH (or EtBr at 100°) affords 4-hydroxy-2-ethylthiol-3-phenyl-3:4-dihydroquinazoline, sinters 155°, m.p. 162° (perchlorate, m.p. 210°), which does not give intensely coloured derivatives since the formation of an internal dipole is impossible. Condensation of isatin and allylthiocarbimide in aq. EtOH-NaOH affords the 4-carboxylic acid, m.p. 145—147°, decarboxylated in boiling MeOBz to 4-hydroxy-2-thion-3-allyl-1:2:3:4-tetrahydroquinazoline, m.p. 164° (perchlorate, m.p. 138—145°), or by boiling EtOH to the corresponding 4-OEt-derivative, m.p. 125°. The carbonium perchlorates of 4-hydroxy-2-thion-3-phenyl-, m.p. 234°, and -3-*o*-tolyl-, m.p. 252°, -1:2:3:4-tetrahydroquinazoline are prepared (HClO₄ on the 4-OEt-compound) and the constitution of these coloured derivatives is fully discussed.

J. W. B.

Structure of Troeger's base. M. A. SPIELMAN (J. Amer. Chem. Soc., 1935, 57, 583—585).—Troeger's base, m.p. 135—136° (hydrochloride, +H₂O, m.p. 213°; picrate, m.p. 188—189°), formed from *p*-C₆H₄Me·NH₂ and CH₂O, is proved by degradation and synthesis to be (I). It cannot have previously described formulae because of analysis and indifference to PhNCO, PhNCS, Na-EtOH, Sn-HCl, HgO, NH₃-AgNO₃, and *p*-C₆H₄Me·N₂Cl. With hot Ac₂O it gives CH₂O and the Ac₂ (II; R=Ac), m.p. 286—288°, with BzCl-C₅H₅N the Bz₂ (II; R=Bz), m.p. 290—291°, and with HNO₃ the (NO)₂-compound (II; R=NO), m.p. 246—247°, 254—255° (corr.). With HI and red P at 200° it gives 1 mol. of *m*-4-xylidine. It is prepared from CH₂O, 6-methyl-3-*p*-tolyl-1:2:3:4-tetrahydroquinazoline, and HCl in EtOH at room temp.



R. S. C.

Cyanine dye series. I. Method of preparing certain carbocyanines. L. G. S. BROOKER and F. L. WHITE (J. Amer. Chem. Soc., 1935, 57, 547—551).—8-Me derivatives of carbocyanines of the type C₆H₄< $\begin{smallmatrix} \text{R} \\ \text{NET} \end{smallmatrix}\right>\text{C}:\text{CH}\cdot\text{CMe}:\text{CH}\cdot\text{C}<\begin{smallmatrix} \text{R} \\ \text{NET} \end{smallmatrix}\right>\text{C}_6\text{H}_4$ (A) (R=S, Se, or O) are obtained in good yields by heating the quaternary salt (1 mol.) of heterocyclic bases containing a reactive Me, often with NEt₃, in C₅H₅N (or, in one case, PrOH). Part of the salt is decomposed to give the :CMe needed for condensation. The absorption max., given in parentheses below, are usually shifted by the Me towards the blue (up to 200 Å. shift) if R=S or Se, but towards the red if R=O (one case only examined). 1-Methylbenzthiazole ethiodide with NEt₃ in hot C₅H₅N (0.5 hr.)

gives a 56% yield of 8-methyl-2 : 2'-diethylthiacarbocyanine iodide (*A*; *R*=S), m.p. 286—287° (decomp.) (5430 Å.); a 4% yield is obtained without NEt_3 in 6 hr., and a 17% yield from the *etho-p-toluenesulphonate*, m.p. 163.5—164.5°, in $\text{C}_5\text{H}_5\text{N}$ in 3 hr. 2 : 2'-Diethylthiacarbocyanine iodide has m.p. 270—271° (decomp.) (5575 Å.). 1-Methylbenzthiazole methiodide and NEt_3 in $\text{C}_5\text{H}_5\text{N}$ give 2 : 2' : 8-trimethylthiacarbocyanine iodide (38%), m.p. 299° (decomp.) (5380 Å.); the 2 : 2'- Me_2 dye has m.p. 287° (decomp.) (5550 Å.). 1-Methyl- α -naphthothiazole *etho-p-toluenesulphonate*, m.p. 200—206° (softens at 190°), and NEt_3 in $\text{C}_5\text{H}_5\text{N}$ (15 min.) give 8-methyl-2 : 2'-diethyl-5 : 6 : 5' : 6'-dibenzothiacarbocyanine iodide (7.5%), m.p. 297° (decomp.) (5725 Å.); the Me-free homologue has m.p. 295° (decomp.) (5925 Å.). 1-Methyl- β -naphthothiazole *etho-p-toluenesulphonate*, m.p. 151—154° (softens at 140°), leads (*a*) similarly (6%) or (*b*) when heated (1 hr.) with $\text{CMe}(\text{OEt})_3$ (I) (1.5 mol.) in $\text{C}_5\text{H}_5\text{N}$ (36% yield) to 8-methyl-2 : 2'-diethyl-3 : 4 : 3' : 4'-dibenzothiacyanine bromide, m.p. 240° (decomp.) [5750 and 5350 Å. (*sec.*); max. sensitisation 6600 and 5500 Å. (*sec.*); the bromide of the Me-free homologue, prepared by method (*b*) (84% yield), has m.p. 268° (decomp.) [5950 Å.; sensitisation max. 6400 and 5600 Å. (*sec.*)]. 1-Methylbenz-selenazole *etho-p-toluenesulphonate* with (I) (36%) or NEt_3 (32%) in $\text{C}_5\text{H}_5\text{N}$ gives 8-methyl-2 : 2'-diethyl-selenacarbocyanine iodide (*A*; *R*=Se), m.p. 296° (decomp.) (5525 and ? 5200 Å.; sensitisation max. 6100 and 5350 Å.); the absorption max. of the Me-free homologue is 5675 Å. 1-Methylbenzoxazole ethiodide with (I) (2 mols.) and NEt_3 (0.5 mol.) in $\text{C}_5\text{H}_5\text{N}$ (12%) or NEt_3 in PrOH (6% yield) give 8-methyl-2 : 2'-diethylloxacarbocyanine iodide (*A*; *R*=O), m.p. 274° (decomp.) [4885 and 4650 Å. (*sec.*); sensitisation max. 5100 Å.]; the Me-free homologue has m.p. 285° (decomp.) (4825 Å.). R. S. C.

Tetrahydro-*p*-phenanthroline. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 495).—*p*-Phenanthroline with $\text{Na-C}_5\text{H}_{11}\text{OH}$ or Sn-HCl gives only the H_4 -compound, m.p. 152—152.5° [*picrate*, m.p. 220.5°; *platinichloride*, m.p. > 310.5°; *hydrochloride*, red, and *dihydrochloride* (1 HCl lost at 100°), colourless, m.p. 241°]. R. S. C.

2-Aminobenziminazole. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1935, 65, 38—43).—2-Aminobenziminazole (I) condenses in $\text{C}_5\text{H}_5\text{N}$ with $\text{CET}_2(\text{COCl})_2$ to form 1 : 2-diethylmalonylamidobenziminazole $\text{C}_6\text{H}_4\text{N-CO-CET}$, m.p. 243°, with its hydrolysis product, *N*-(2-benziminazolyl)diethylmalonamidic acid, m.p. 214° (*Me ester*, m.p. 116°). With CS_2 , (I) yields *di*-(2 : 2'-benziminazolyl)thiocarbamide, m.p. 208°. E. W. W.

Photo-decomposition of flavins. P. KARRER, T. KOBNER, H. SALOMON, and F. ZEHENDER (Helv. Chim. Acta, 1935, 18, 266—272).—Illumination of 9- β -hydroxyethyl- (I) and 9- β -dihydroxy-*n*-propylisalloxazine in H_2O or MeOH at 0.2 mm. or in N_2 gives alloxazine (II). Under similar conditions lactoflavin (III) is almost decolorised and affords (after admission of air) a trave of flavin and 16—33% of lumichrome (IV). (I) in 75% aq. MeOH is de-

colorised [to give (II)] by daylight in 1 day, but 9- γ -hydroxy-*n*-propylisalloxazine (V) gives no (II) after 14 days (a small amount of flavin, possibly isalloxazine-9-propionic acid, is formed). It is concluded that decomp. to lumichrome derivatives in neutral solution is a dehydration commencing by oxidation of the $\beta\text{-CH-OH}$ to CO . In alkaline solution (V) is rapidly decomposed to (II), so that a different mechanism must be postulated. The prep. of (IV) from (III) is described. $\text{OH}[\text{CH}_2]_3\text{NH}_2$, b.p. 82°/16 mm. [from γ -bromopropylphthalimide and H_2SO_4 at 200° (autoclave); 32% yield], and *o*- $\text{C}_6\text{H}_4\text{Cl-NO}_2$ in $\text{C}_5\text{H}_5\text{N}$ afford *N*- γ -hydroxypropyl-*o*-nitroaniline, m.p. 65°, which by hydrogenation (Pt) in EtOH and condensation affords (V), decomp. 297°. R. S. C.

Synthesis of flavins. IV. P. KARRER, K. SCHÖPP, and F. BENZ (Helv. Chim. Acta, 1935, 18, 426—429; cf. this vol., 359).—*N*-2-Carbethoxy-amino-4 : 5-dimethylphenyl-*d*-xylamine and alloxan give 6 : 7-dimethyl-9-*d*-1'-xylitylisoalloxazine, m.p. 278—280°, $[\alpha]_D^{20} -82.2 \pm 7^\circ$ in 0.05*N*- NaOH (Ac_4 derivative, m.p. 216°). *N*-2-Carbethoxyamino-4 : 5-dimethylphenyl-*d*-ribamine, m.p. 170°, $[\alpha]_D^{20} -13 \pm 2^\circ$ in H_2O , affords similarly 6 : 7-dimethyl-9-*d*-1'-ribitylisoalloxazine, m.p. 278—280°, $[\alpha]_D^{20} -92.6 \pm 7^\circ$ in 0.05*N*- NaOH (Ac_4 derivative, m.p. 236°), possibly identical with the less sol. lactoflavin fraction. 7-Methyl-9-*d*-1'-dulcetyl- and -mannityl-isoalloxazine and 6 : 7-dimethyl-9-*d*-1'-arabitylisoalloxazine tetra-acetate, m.p. 213—215°, are also prepared. R. S. C.

Constitution of bile pigment. XI. Syntheses of neo- and isoneo-xanthobilirubic acid. W. SIEDEL (Z. physiol. Chem., 1935, 231, 167—198; cf. A., 1933, 404).—Reduction of 5-carbethoxy-3-acetyl-2 : 4-dimethylpyrrole with NaOEt and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 185° for 6—8 hr. gives cryptopyrrole (I). $\text{CH}_2\text{Ac-CO}_2\text{Bu}$ in AcOH , treated with NaNO_2 and then with CH_2Ac_2 and reduced with Zn , affords *Bu* 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate, m.p. 75°, which may be used for prep. of (I). The product of the Grignard reaction on (I), when heated with ClCO_2Et , affords *Et* 2 : 4-dimethyl-3-ethylpyrrole-1- and -5-carboxylate (II), m.p. 96°. (II) is quantitatively reconverted into (I) by aq. KOH . ClCO_2Et and the Grignard compound of dimethylpyrrole afford *Et* 2 : 4-dimethylpyrrole-1-carboxylate, b.p. 101°/12 mm. *Et* 2 : 3-dimethyl-4-ethylpyrrole-1-carboxylate, b.p. 129—130°/10 mm., and *Et* 2 : 3-dimethyl-3-propylpyrrole-1-carboxylate, b.p. 165—170°/12 mm., are similarly obtained. Treatment of $\text{CH}_2(\text{CO}_2\text{Et})_2$ with NaNO_2 and then with $\text{CH}_2\text{Ac-CO}_2\text{H}$ and Zn gives *Et* 5-propionyl-2-methyl-4-ethylpyrrole-3-carboxylate, m.p. 156° [free acid (III), decomp. 253°]. On heating, (III) gives 5-propionyl-2-methyl-4-ethylpyrrole (IV), m.p. 115.5°, b.p. 226°/720 mm. With HCl-HCN in Et_2O , (IV) yields the aldimine hydrochloride, which with NH_3 affords non-cryst. 3-aldehydo-5-propionyl-2-methyl-4-ethylpyrrole, which by Wolff-Kishner reduction gives 2 : 3-dimethyl-4-ethylpyrrole (hæmopyrrole). *Opsopyrrole* (V) aldehyde, sinters at 210—215°, obtained by the same method, gives (Wolff-Kishner) cryptopyrrole (VI). 3 : 5-Dicarbethoxy-2 : 4-dimethylpyrrole with SO_2Cl_2 and then with $\text{EtOH-H}_2\text{O}$ gives 5-aldehydo-2 : 4-dicarbethoxy-

3-methylpyrrole, m.p. 127—128°. 3-Methylpyrrole by Fischer-Zerrweck synthesis (A., 1922, i, 758) affords 5-aldehydo-3-methylpyrrole, sinters 119—121°, yielding on reduction 2:4-dimethylpyrrole. (VI) with Cu powder and Et diazoacetate gives 2:4-dimethyl-3-ethyl-5-carbomethoxymethylpyrrole, b.p. 149°/11 mm., which on hydrolysis (KOH-EtOH) and acidification affords 2:3:5-trimethyl-4-ethylpyrrole (phyllopyrrole). By similar reactions (V) gives 5-carbomethoxymethyl-, b.p. 143—145°/11 mm., 2-carbomethoxymethyl-, b.p. 146—149°/11 mm., and 2:5-di(carbomethoxymethyl)-3-methyl-4-ethylpyrrole, b.p. 180°/11 mm. Treatment of 5-carbomethoxy-2:3-dimethyl-4-ethylpyrrole with 3 mols. of SO_2Cl_2 and subsequently with H_2O at 100° affords Et 2-carboxy-3-methyl-4-ethylpyrrole-5-carboxylate, m.p. 218—219°, yielding on heating at 220—230°, Et 3-methyl-4-ethylpyrrole-5-carboxylate (VII), m.p. 76°, b.p. 136—137°/11 mm. With HCN-HCl in $\text{Et}_2\text{O}-\text{CHCl}_3$, (VII) gives the aldimine hydrochloride, which in H_2O yields Et 2-aldehydo-3-methyl-4-ethylpyrrole-5-carboxylate (VIII), m.p. 68° (hydrazone, m.p. 72°; aldazine, m.p. 248—249°; free acid, m.p. 174°). Bromination of (VIII) was unsuccessful. With MgEtBr and AcCl , (V) affords 2-acetyl-3-methyl-4-ethylpyrrole (IX), m.p. 92.5—93°. Wolff-Kishner reduction of (IX) gives 3-methyl-2:4-diethylpyrrole. With $\text{Br}-\text{AcOH}$, (IX) yields o-bromo-2-acetyl-3-methyl-4-ethylpyrrole, m.p. 125—126°. (V) similarly affords 2-propionyl-, m.p. 101°, b.p. 146—150°/11 mm., 5-bromo-2-propionyl-, m.p. 152—153°, 2-benzoyl-, m.p. 78°, b.p. 145°/11 mm., 207—210°/730 mm., and 5-bromo-2-benzoyl-3-methyl-4-ethylpyrrole, m.p. 123°. Similarly (I) gives 5-acetyl- (X), m.p. 114—115°, 5-propionyl- m.p. 139°, 5-butyryl- (XI), m.p. 136—137°, and 5-benzoyl-2:4-dimethyl-3-ethylpyrrole, m.p. 143°. Heating after addition of AcCl in the prep. of (X) yields 3:3':5:5'-tetramethyl-4:4'-diethyl-ms-methylpyrromethene hydrochloride, m.p. 192° (Zn complex salt of methene, m.p. 248—249°). Similarly heating in the prep. of (XI) gives the -ms-propylpyrromethene hydrochloride, m.p. 218° (Zn complex salt of methene, m.p. 153°). 3-Methyl-4-ethylpyrrole-2-carboxylic acid (XII), m.p. 205—206° (Me ester, m.p. 70°), is obtained from the Et ester by hydrolysis with KOH in aq. MeOH, also (in 50% yield) by direct action of CO_2 on the Grignard compound of (V). By the same method, (I) gives the α -carboxylic acid, m.p. 95° (Me ester, m.p. 115—116°). Hæmopyrrole likewise gives the α -carboxylic acid, m.p. 124° (decomp.) (Me ester, m.p. 129°). A β -Me group renders the adjacent α - CO_2H more labile than a β -Et group. With Br in CCl_4 , (XII) gives 5-bromo-3-methyl-4-ethylpyrrole-2-carboxylic acid (XIII), m.p. 76°, decomp. 81—82°. Attempts to decarboxylate (XIII) led to complete decomp. Condensation of (XIII) with 2-aldehydo-3-methyl-4- β -carboxyethylpyrrole in MeOH by 48% HBr affords as the hydrobromide (XIV), m.p. 210°, 5-bromo-3:3'-dimethyl-4-ethyl-4'- β -carbomethoxyethylpyrromethene, m.p. 106—107° (picrate, m.p. 178—179°). With NaOMe in aq. MeOH at 150—153°, (XIV) yields isoneoxanthobilirubic acid. By similar methods, (VII) gives successively 3-methyl-4-ethylpyrrole-5-carboxylic acid, m.p. 210—211° (Me ester, m.p. 62—63°), 2-bromo-3-methyl-4-ethylpyrrole-5-

carboxylic acid, 5-bromo-4:3'-dimethyl-3-ethyl-4'- β -carbomethoxyethylpyrromethene, m.p. 105° (hydrobromide, m.p. 201°; picrate, m.p. 185°), neoxanthobilirubic acid. The following (V) esters were prepared from the corresponding 5-carboxylic acids: 5-carbomethoxy-2-carbomethoxy-, m.p. 68°, and 2:5-dicarbomethoxy-, m.p. 97°, and from the 2-carboxylic acid 2-carbomethoxy-5-carbomethoxy-, m.p. 80°, 3-methyl-4-ethylpyrrole (all m.p. corr.). J. H. B.

Bile pigments. XII. Synthesis of acetylpyrromethenes and bilirubinoids. H. FISCHER and G. FRIES (Z. physiol. Chem., 1935, 231, 231—258).—With aq. NaOH, Et 2-aldehydo-3-acetyl-4-methylpyrrole-5-carboxylate (I) gives the 5-carboxylic acid, m.p. < 360° (phenylhydrazone, m.p. 240°; diphenylhydrazone, m.p. 220°). The CHO of (I) condenses with $\text{CN}-\text{CH}_2-\text{CO}_2\text{Et}$ and with malonodinitrile yielding products, m.p. 127° and 96°, respectively. With 2:4-dimethyl-3- β -carboxyethylpyrrole (II) and HBr, (I) affords 5-carbomethoxy-3-acetyl-4:3':5'-trimethyl-4'- β -carboxyethylpyrromethene hydrobromide, m.p. 220° (decomp.), and with 2:4-dimethyl-3-ethylpyrrole (III) and HBr 5-carbomethoxy-3-acetyl-4:3':5'-trimethyl-4'-ethylpyrromethene hydrobromide (IV), m.p. 258° (decomp.) (picrate of base, m.p. 200°). With NH_4OH (IV) gives (probably) 5-carbomethoxy-3-acetyl-4:3':5'-trimethyl-4'-ethylpyrromethane ketoxime hydrobromide (V), m.p. 260°, which on hydrolysis with NaOH affords the 5-carboxylic acid (?), $\text{C}_{17}\text{H}_{24}\text{O}_4\text{N}_3\text{Br}$, m.p. 229°. Condensation of (I) with 3-methyl-4- β -carboxyethylpyrrole in EtOH yields a non-cryst. product (VI), decomp. 232°, giving with $\text{Br}-\text{HCO}_2\text{H}$ a violet amorphous product, $\text{C}_{16}\text{H}_{21}\text{O}_5\text{N}_2\text{Br}$, m.p. < 350°. With aq. NaOH at 100°, (VI) gives an amorphous product, $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_2$, m.p. < 350°. With 3-acetyl-2:4-dimethylpyrrole (VII) in EtOH, (I) affords the pyrromethane, $\text{C}_{19}\text{H}_{34}\text{O}_4\text{N}_2$, m.p. 229° (dioxime, decomp. 159°, m.p. 219°), and with (III) in EtOH the carbinol (VIII), m.p. 145°, of (IV). With $\text{NH}_4\text{OH}, \text{HCl}$, (VIII) gives (V). 5-Bromo-2-aldehydo-3-methyl-4- β -carboxyethylpyrrole (IX) with (VII) in MeOH affords the carbinol base, which with HBr gives 5-bromo-4'-acetyl-3:3':5'-trimethyl-4- β -carboxyethylpyrromethene hydrobromide (X). With AgOAc in AcOH, (X) yields the 5-hydroxy-base (XI), $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2$, m.p. 312° (Me ester, m.p. 252—253°). With 10% NaOMe in MeOH, (X) gives the 5-methoxy-base, $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_2$, m.p. 230°. 2-Aldehydo-3-methyl-4- β -carboxyethylpyrrole and 3- β -methoxyacetyl-2:4-dimethylpyrrole with 48% HBr in EtOH yield the pyrromethene hydrobromide, m.p. 195°, giving with $\text{Br}-\text{HCO}_2\text{H}$, 5-bromo-4'- β -methoxyacetyl-3:3':5'-trimethyl-4- β -carboxyethylpyrrole hydrobromide (XII), m.p. < 280°. (XI) is also obtained by direct condensation of the appropriate pyrroles in MeOH-48% HBr. With AgOAc in AcOH (XII) affords 5-hydroxy-4'- β -methoxyacetyl-3:3':5'-trimethyl-4- β -carboxyethylpyrromethene, m.p. < 290°. (IX) and the ketoxime of (VII) in MeOH-HBr give o-bromo-4'-acetyl-3:3':5'-trimethyl-4- β -carboxyethylpyrromethene hydrobromide ketoxime hydrobromide, becomes green at 180°, yielding with KOH-MeOH 4'-acetyl-5-methoxy-3:3':5'-trimethyl-4- β -carboxyethylpyrromethene ketoxime, m.p. 212°. With

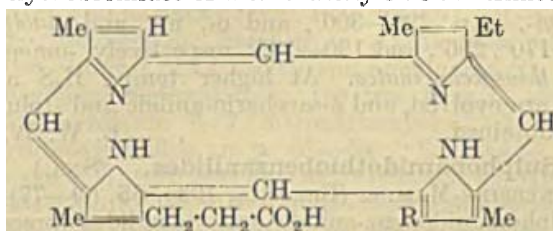
Br-AcOH, (XI) gives a cryst. substitution product, blackens at 240°, which on treatment with COMe₂ yields bromoacetone. 3-Methylpyrrole with (IX) and HBr-AcOH affords 5-bromo-3:3'-dimethyl-4-β-carboxyethylpyrromethene hydrobromide, m.p. < 290°, which with KOH-MeOH yields the 5-methoxymethene (XIII), m.p. 161°. With CH₂O-HCl and treatment with CH₂N₂, (XIII) gives di-(5-methoxy-3:3'-dimethyl-4-β-carboxyethylpyrromethene)methane (Me₂ ester of deuterobilirubin Me₂ ether IIIγ), m.p. 113°. In like manner (IX) with 3-ethylpyrrole yields successively 5-bromo-3-methyl-3'-ethyl-4-β-carboxyethylpyrromethene hydrobromide, m.p. < 290°, the 5-methoxy-pyrromethene, m.p. 115°, and the corresponding methane (Me₂ ester of ethyldeuterobilirubin Me₂ ether IIIγ), m.p. 282—285°; with 3-methyl-4-β-carboxyethylpyrrole, 5-bromo-3:3'-dimethyl-4:β-carboxyethylpyrromethene hydrobromide, m.p. 212° (decomp.), the 5-methoxy-methene, m.p. 238—241° (decomp.), and the corresponding methane (dimethoxycoprobilirubin dihydrochloride IIγ), m.p. 282° (Me₂ ester, m.p. 256°); and with 3-methyl-4-ethylpyrrole, 5-bromo-3:3'-dimethyl-4-ethyl-4-β-carboxyethylpyrromethene hydrobromide, blackens at 220°, 5-methoxy-3:3'-dimethyl-4'-ethyl-4-β-carboxyethylpyrromethene, m.p. 144°, di-(5-methoxy-3:3'-dimethyl-4-ethyl-4-β-carboxyethyl)methane (mesobilirubin Me₂ ether dihydrochloride IIIγ), m.p. 198—200°, giving mesobilirubin Me₂ ether IIIγ, m.p. 212° (Me₂ ester, m.p. 164°). With 5-bromo-2-aldehydo-4-methyl-3-ethylpyrrole, (II) affords 5-bromo-4'-carbethoxy-4:3':5'-trimethyl-3-ethylpyrromethene hydrobromide, m.p. 205° (decomp.). With (IX), 2:4-dimethylpyrrole in HBr gives, after esterification with HBr-MeOH, 5-bromo-3:3':5'-trimethyl-4'-β-carboxyethylpyrromethene hydrobromide (XIV), m.p. 205°. With 15% KOH in aq. MeOH, (XIV) yields 5-hydroxy-3:3':5'-trimethyl-4-β-carboxyethylpyrromethene, m.p. 275°. With Et-3-methylpyrrole-4-carboxylate, (IX) affords 5-bromo-4'-carbethoxy-3:3'-dimethyl-4-β-carboxyethylpyrromethene hydrobromide, blackens at 210°. 2-Aldehydo-3-methylpyrrole-4-carboxylic acid and 3-methyl-4-β-carboxyethylpyrrole gives 4-carboxy-3:3'-dimethyl-4'-β-carboxyethylpyrromethene hydrobromide, m.p. < 300°.

J. H. B.

Synthesis of several chlorophyll porphyrins.

H. FISCHER and S. BÖCKH (Annalen, 1935, 516, 177—198).—3-Bromo-2-aldehydo-4-methylpyrrole-5-carboxylic acid and hæmopyrrole with AcOH-HBr afford the hydrobromide (A), m.p. 134°, of 3'-bromo-, converted by Br-HCO₂H into 3':5'-dibromo-, m.p. 165° [hydrobromide (B), m.p. 176°], converted by AcOH-KOAc into 3'-bromo-5'-hydroxy-, and by MeOH-KOH into 3'-bromo-5-methoxy-, m.p. 133°, -4:5:4'-trimethyl-3-ethylpyrromethene. Succinic acid fusion at 160—180° of a mixture of (A) and 5-bromo-4:3':5'-trimethyl-3:4'-diethylpyrromethene hydrobromide affords pyroætioporphyrin V (C) (1:3:6:8-tetramethyl-2:5:7-triethylporphin), m.p. 284° [also from (B) and (E)], bromopyroætioporphyrin V [also from (C) and Br-AcOH: debrominated by 1% Pd-CaCO₃-N₂H₄-H₂O-10% MeOH-KOH to (C)], and ætioporphyrin I (separated by extraction with various concns. of HCl). Fusion of (B) with succinic acid gives

deuteroætioporphyrin V, not melting at 300°, and its Br₁- and Br₂-derivatives. From 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid and 2:3-dimethylpyrrole (D) in AcOH-HBr is obtained the hydrobromide (E), m.p. 170° (decomp.), of 4:4':5'-trimethyl-3-ethylpyrromethene-5-carboxylic acid, converted by AcOH-Br into the hydrobromide, not melting at 250°, of 5:3'-dibromo-, m.p. 153°, converted by AcOH-AgOAc into 3'-bromo-5-hydroxy-, not melting at 250°, and by MeOH-KOH into 3'-bromo-5-methoxy-, m.p. 130°, -4:4':5'-trimethyl-3-ethylpyrromethene. Hæmin is converted by Ac₂O-SnCl₄ into acetyl-, not melting at 290°, and by CH₂Cl-OMe-SnCl₄ (after demethylation with HBr-AcOH) into hydroxymethylpyroætioporphyrin, not melting at 300° (converted by 50% oleum into a substance C₃₁H₃₄N₄O₃S). From the hydrobromide of 4:3':5'-trimethyl-3-ethylpyrromethene-5-carboxylic acid [from 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid and (D)] is obtained 5:4'-dibromo-4:5:3'-trimethyl-3-ethylpyrromethene hydrobromide, fusion of which with succinic acid and the hydrobromide of 4:5'-dibromo-3:5:3'-trimethylpyrromethene-4-propionic acid (F) affords a mixture (separation described) of deuteroætioporphyrin II (and its Br₁- and Br₂-derivatives) and V, and 2-de-ethylpyroporphyrin (G) (annexed formula, R=H) (and its Br₁- and Br₂-derivatives), converted by CH₂N₂ into its Me ester (Cu salt, m.p. 165°; Br₁-, m.p. 235°, and Br₂-, m.p. 270°, -derivatives), identical with an "analytical" specimen from chlorophyll-a, which thus, as suggested, must have the unsaturated side-chain in position 2. Succinic acid fusion of the hydrobromides of 4-carbethoxy-3:5:4'-trimethyl-3'-



ethylpyrromethene-5'-carboxylic acid and (F) affords deuteroporphyrin V, (G), and the Et₂ ester of 2-de-ethylrhodoporphyrin (annexed formula, R=CO₂H), converted by hydrolysis and CH₂N₂ into its Me₂ ester, identical in all respects with an "analytical" specimen.

J. W. B.

Fluorescence of the porphyrins. IV. H. FINK and W. HOERBURGER (Z. physiol. Chem., 1935, 232, 28—35; cf. A., 1934, 1012).—Even at very low porphyrin concns. the specificity of the *p_H*-fluorescence curves is retained for the isomeric coproporphyrins I and III.

J. H. B.

Preparation and reactions of naphthaphenoxazines. R. LANTZ and A. WAHL (Bull. Soc. chim., 1935, [v], 2, 488—494).—1:2-Naphthaquinone-1-phenylimine, alone at 60—70° or in hot C₆H₆, gives ang-naphthaphenoxazine (I), but in hot COMe₂ 1-anilino-β-naphthol is also formed. (I) and Fe(ClO₄)₃ in EtOH give the 6-keto-derivative (II), whilst with NH₂Ph or *p*-toluidine, a little hydrochloride, and air at 90—130° the 6-anilo- (III) and 6-*p*-tolylimino-derivatives are obtained. (III) and 99% H₂SO₄ at

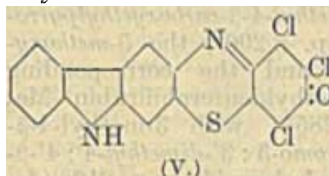
100° give the 6-sulphoanilo-derivative (Na and NH_4 salts), hydrolysed by hot, very dil. H_2SO_4 to (II); the presence of a little SO_3 leads to a disulphonic acid (Na and NH_4 salts), hydrolysed by hot 20% H_2SO_4 to 2-anilino-1 : 2-naphthaquinone. R. S. C.

Action of anilines on saccharin and thio-saccharin. (SNA.) A. MANNESSIER-MAMELI (Gazzetta, 1935, 65, 51—69).—The products of action of anilines on saccharin (I) are, in the cold, aryl-ammonium saccharinates (II); at higher temp., o-sulphonamidobenzanilides, $NH_2 \cdot SO_2 \cdot C_6H_4 \cdot CO \cdot NHR$ (III), also obtained by heating (II), and, on prolonged heating, ψ -saccharinanilides, $SO_2 \langle \text{C}_6H_4 \rangle_N \text{C} \cdot NHR$ (IV), also obtained by heating (III), either alone or with the aniline. The following are described. (II): *phenyl*-, m.p. 90°; o-, m-, and p-*tolyl*-, m.p. 141°, 126°, and 128°, respectively; *acetyl-p-tolyl*-, m.p. 195° [from *acet-p-toluidide* (V)]; *phenylmethyl*-, m.p. 37°; and *phenyldimethyl*-, m.p. 125°, -*ammonium saccharinates*. (III): o-sulphonamidobenz-anilide (VI), new m.p. 195°; -o- and -p-*toluidides*, new m.p. 203° and 213°, respectively; -m-*toluidide*, m.p. 170°; and -*acet-p-toluidide* (VII), m.p. 135—136° [from (V)]. (IV) ψ -saccharin-anilide (VIII), new m.p. 315—317° (cf. A., 1893, i, 715), -o-, m.p. 276°, -m-, m.p. 296—297°, and -p-*toluidide*, m.p. 285° [obtained from (I) and (V), or from (VII)]. With (VIII), a substance, m.p. 185.5°, is also obtained. The action of $NHPhMe$ on (I) yields o-sulphonamidobenzmethyl-anilide, m.p. 182°, with *N*-methylsaccharin, which is the sole product from (I) and $NPhMe_2$ (cf. A., 1930, 1452). Thiosaccharin similarly gives, in the cold, *phenyl*-, m.p. 290—300°, and o-, m-, and p-*tolyl*-, m.p. 170°, 296°, and 130—132°, respectively, -*ammonium thiosaccharinates*. At higher temp., H_2S and NH_3 are evolved, and ψ -saccharin-anilide and -*toluidides* obtained. E. W. W.

o-Sulphonamidothiobenzanilides. (SNA.) A. MANNESSIER-MAMELI (Gazzetta, 1935, 65, 69—77).—o-Sulphonamidobenz-anilide and -*toluidides* (preceding abstract) with P_2S_5 at 180° yield dithiosulphindene, the corresponding ψ -saccharin-anilide or -*toluidide*, and the following: o-sulphonamidothiobenz-anilide, $NH_2 \cdot SO_2 \cdot C_6H_4 \cdot CS \cdot NHPh$, m.p. 280—290° (converted by alkali into o-sulphonamidobenzoic acid, and by heating into ψ -saccharinanilide), and -o-, -m-, and -p-*toluidides*, m.p. 255—260°, 270°, and 265—260°, respectively. E. W. W.

Synthesis of blue sulphur dyes. R. SIBATA and T. NISI (J. Soc. Chem. Ind. Japan, 1935, 38, 41—47B).—Products (I) identical with Hydron Blue R in every respect are obtained by condensing 3-amino-9-benzoyl- (II), m.p. 142° (+1HCl) or 3-amino-9-acetyl-carbazole (III), m.p. 122—123° (+1HCl, m.p.

the resulting 3-amino-2-thiolcarbazole (IV) (Zn salt) with chloranil, and finally fusing the resulting trichlorothiazine (V) with Na_2S_n in EtOH. (II) and (III) are prepared by nitrating the corresponding acylcarbazole (HNO_3 -AcOH) and reducing the NO_2 -compounds thus formed, m.p. 185°, and 235—237° (also obtained from 3-nitrocarbazole and Ac_2O). A trinitro-9-acetylcarbazole, m.p. 285—287°, is described. Carbazole reacts vigorously with S_2Cl_2 in C_6H_6 to form a 9 : 9'-disulphide, $C_{12}H_{16}N_2S_2$, converted by crystallisation from $PhNO_2$ into the monosulphide,

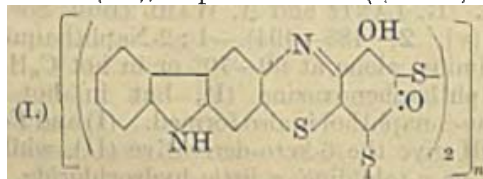


m.p. 360° (decomp.). The reported synthesis of Hydron Blue by the above route from 3-aminocarbazole (von Weinberg, Ber., 1930, 63, [4], 123) must therefore have resulted in products substituted in position 9. Interaction of (IV) with $CH_2Cl \cdot CO_2H$ in aq. alkali gives the lactam, m.p. 225° (decomp.), of 3-amino-2-carbazolylthioglycollic acid. H. A. P.

New sensitisers for the photography of the infra-red. Tetra- and penta-carbocyanines. L. G. S. BROOKER and G. H. KEYES (J. Franklin Inst., 1935, 219, 255—261).—Condensation of König's acetoxypolymethine dyes (A., 1934, 898) with quaternary heterocyclic NH_4 salts containing a reactive Me yields tetra- and penta-carbocyanines, which are infra-red sensitisers. They are unstable and difficult to purify. Thus from 4-acetoxy- $\Delta^3:5$ -heptatriene-1 : 2-dial ditetrahydroquinolide perchlorate are obtained 11-acetoxy-2 : 2'-diethyl- (I), 11-acetoxy-2 : 2'-diethyl-5 : 6 : 5' : 6'-dibenz- (II), and 11-acetoxy-2 : 2'-diethyl-3 : 4 : 3' : 4'-dibenz-thiatetracarbo-cyanine perchlorate (III), also 13-acetoxy-1 : 1'-diethyl-2 : 2'-tetracarbo-cyanine perchlorate (IV). From 4-acetoxy- $\Delta^3:5:7$ -nonatriene-1 : 9-dial ditetrahydroquinolide perchlorate are obtained 11-acetoxy-2 : 2'-diethyl- (V), 11-acetoxy-2 : 2'-diethyl-5 : 6 : 5' : 6'-dibenz- (VI), and 11-acetoxy-2 : 2'-diethyl-3 : 4 : 3' : 4'-dibenz-thiapentacarbo-cyanine perchlorate (VII), also 13-acetoxy-1 : 1'-diethyl-2 : 2'-pentacarbo-cyanine perchlorate (VIII). (I) sensitises from 7600 to 10,000 with a max. at 9400 Å.; for (II) and (III) the max. is at 9600, for (IV) at 9900, for (V) at 10,500, for (VI) and (VII) at 10,900, and for (VIII) at 11,200 Å. F. M. H.

Alkaloids of Arundo donax. L. A. OREKHOV and S. NORKINA [with T. MAXIMOVA] (Ber., 1935, 68, [B], 436—437).—Extraction of the leaves of *A. donax* with $C_6H_4Cl_2$ affords donaxine (I), $C_{11}H_{14}N$, m.p. 138—139°, $[\alpha] \pm 0^\circ$ in EtOH. (I) is a moderately strong, monacid base, contains 1 active H, and is markedly unsaturated. It gives a picrate, m.p. 144—145°, perchlorate, m.p. 150—151°, platinichloride, m.p. 180—181° (decomp.), and methiodide, m.p. 176—177°. H. W.

Ester of p-aminobenzoic acid and lupinine. M. M. KATZNELSON and M. I. KABATSCNIK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 125—127).—p-Nitrobenzoyl-lupinine, m.p. 95 (hydrochloride, m.p. 229—231°), is reduced by $Sn-HCl$ to p-aminobenzoyl-lupinine, m.p. 162—163° (hydrochloride, very hygroscopic). P. W. C.



253—254°), with S_2Cl_2 , hydrolysing the brown thio-thionium chloride by vatting in aq. EtOH, condensing

Structure of the isomeric chloroanabasines.

M. J. KABATSCHNIK and M. M. KATZNELSON (Ber., 1935, 68, [B], 399—402; cf. A., 1934, 538; this vol., 223).—Direct comparison of the chloropyridine-3-carboxylic acids obtained by oxidising the isomeric chloroanabasines (I) with synthetic specimens shows that (I), b.p. 126°/1 mm., m.p. 58.5—59.5°, is 2-2'-chloro- and (I), b.p. 99.5—100°, is 2-6'-chloro-3'-pyridylpiperidine (II). The chloroanabasine of Menschikov *et al.* (A., 1934, 1014) is (II). Treatment of (II) with aq. CH_2O and HCO_2H affords 6'-chloro-1-methylanabasine, m.p. 46—47°; the identity of the compound with that of Menschikov (*loc. cit.*) is uncertain.

H. W.

Introduction of amino-groups into alkaloids by sodamide and potassamide. α -Aminoanabasine.

I. M. M. KATZNELSON and M. J. KABATSCHNIK (Bull. Soc. chim., 1935, [v], 2, 521—525).—Anabasine (modified purification) and NaNH_2 , best in NPhMe_2 , give α -aminoanabasine (2- or 6-amino-3-2'-piperidylpyridine) (30% yield), b.p. 174—186°/7 mm., m.p. 109° [platinichloride, m.p. > 255°; dipicrate, m.p. 233—233.5° (decomp.); hydrochloride, m.p. 251.5—252.5°], possibly also obtained impure in 5% yield from benzoylanabasine.

R. S. C.

Tobacco bases. II. Simplification of Pictet's synthesis of nicotine.

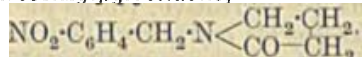
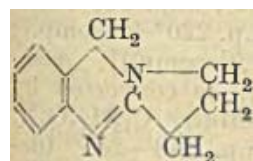
E. SPATH and F. KUFFNER (Ber., 1935, 68, [B], 494—497).—Selective hydrogenation (Pd-C) of nicotyrine affords *dl*-nicotine, the identity of which with the racemised natural base is established by comparison of the picrates, trinitro-*m*-tolylloxides, and picrolonates.

H. W.

Constitution of peganine (vasicine).

E. SPATH, F. KUFFNER, and N. PLATZER (Ber., 1935, 68, [B], 497—501).—After sublimation in a high vac. an original sample of vasicine (Krishna *et al.*, A., 1933, 87) and peganine (I), singly or mixed, have m.p. 211—212° after softening at 210°; they are therefore regarded as identical.

$\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ is condensed with Me γ -aminobutyrate to the *o*-nitrobenzylpyrrolidone,



m.p. 102—103°, reduced ($\text{SnCl}_2\text{-HCl}$) to 1-*o*-aminobenzylpyrrolid-2-one, m.p. 74.5—75.5°, which is transformed by POCl_3 into the base (II), m.p. 99—100°, also

obtained by reduction of chlorodeoxypeganine. (I) is therefore a OH-derivative of (II).

H. W.

Sophora alkaloids. VII. Alkaloids of *S. flavescent* and the identity of sophocarpidine with matrine.

A. OREKHOV and N. PROSKURNINA. VIII. Alkaloids from the seeds and the foliage of *S. alopecuroides*. A. OREKHOV, N. PROSKURNINA, and R. KONOVALOVA (Ber., 1935, 68, [B], 429—431, 431—436; cf. this vol., 97).—VII. The isolation of matrine (I) and sophocarpine (II) from the roots of *S. flavescent* is described. The differences in the m.p. of matric acid (III) and K matrate (IV) obtained from (I) and sophocarpidine (V), respectively, are shown to be due to the firmness with which these products retain H_2O . After exhaustive desiccation

(III) and (IV) from (I) and (V) are identical with one another and with Kondo's preps. (V) and (I) are therefore identical and the name "sophocarpidine" is superfluous.

VIII. Further examination (cf. A., 1933, 840) of the alkaloids of the foliage of *S. alopecuroides* establishes the presence of (I), (II), and *aloperine* (VI), $\text{C}_{15}\text{H}_{21}\text{N}_2$, m.p. 73—75°, $[\alpha]_D^{20} + 85.90^\circ$ in EtOH, in addition to sophoridine (VII) and sophoramine (VIII). (VI) affords a hydrochloride, m.p. 261—263°, $[\alpha]_D^{20} + 92.40^\circ$ in H_2O , hydriodide, m.p. 242—244°, picrate, decomp. about 235°, picrolonate, m.p. 190—195° (decomp.), and aurichloride, m.p. 204—206°. 1 N is *sec.* since (VI) yields a Bz derivative, m.p. 161—162°. With MeI (VI) affords the methiodide of N-methylaloperine hydriodide, m.p. 247—249°, converted by aq. NaOH into N-methylaloperine methiodide, m.p. 190—195°.

[With S. YUNUSOV.] The seeds of *S. alopecuroides* contain (I), (II), (VI), and (VII) in about the same amount as does the foliage, but (VIII) is absent.

H. W.

Nymphæine. E. BURES and M. HOFFMANN (Časopis českoslov. Lek., 1934, 14, 129—136; Chem. Zentr., 1934, ii, 2834—2835).—The isolation of an amorphous, optically inactive alkaloid, *nymphæine* (I), $\text{C}_{14}\text{H}_{23}\text{O}_2\text{N}$, m.p. 76—77° (yellow hydrochloride, decomp. 230°), from the roots of *Nymphæa alba* and a no. of colour reactions for (I) are described. (I) is toxic to frogs, producing tetanus-like symptoms.

H. N. R.

Cactus alkaloids. XIII. New cactus alkaloid, anhalinine, and constitution of anhalonine.

E. SPATH and F. BECKE (Ber., 1935, 68, [B], 501—505).—The non-phenolic bases from *Anhalonium Lewinii*, after removal of mezcaline and anhalonine (I), afford *anhalinine hydrochloride*; the free base is identical with synthetic 6:7:8-trimethoxy-1:2:3:4-tetrahydroisoquinoline, m.p. 61—63°. Successive treatments of (I) with MeI and Ag_2O followed by oxidation with KMnO_4 lead to 5-methoxy-3:4-methylenedioxy-*o*-phthalic acid, identified as the anhydride, m.p. 190—193°, thus confirming the constitution assigned to (I) (A., 1924, i, 69).

H. W.

Indole series. III. Synthesis of [substances containing the ring-system of] physostigmine.

IV. Synthesis of *dl*-eserethole. P. L. JULIAN and J. PIKL (J. Amer. Chem. Soc., 1935, 57, 539—544, 563—566; cf. A., 1934, 1116).—III. The Na derivative of 1:3-dimethylindole (I) and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ in Et_2O give a little 1:3-dimethylindoxindole, m.p. 152°, and a 73% yield of 1:3-dimethyl-3- β -phthalimidoethyloxindole, m.p. 146°, hydrolysed (80% yield) by N_2H_4 to 1:3-dimethyl-3- β -aminoethyloxindole (II), b.p. 192—194°/18 mm. (picrate, m.p. 186°, not identical with the salt previously given this structure), also obtained (75% yield) by hydrogenation (Pd) of 1:3-dimethyl-oxindolyl-3-acetonitrile in AcOH containing a little H_2SO_4 . (II) with Na-EtOH or Na-amyl alcohol gives *dl*-deoxynoreseroline (III) [no carbylamine reaction; contains one and its Bz derivative no active H (Grignard); *p*-toluenesulphonyl derivative, m.p. 114°, does not react with Na], which is hydrogenated

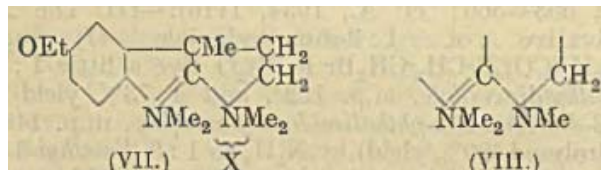
to 1 : 3-dimethyl-3- β -aminoethyl-dihydroindole [picrate, m.p. 136°; dipicrate, m.p. 179° (decomp.)]. (III) and p -C₆H₄Me·SO₃Me give a mixture. The benzylidene derivative, m.p. 102°, of (II) with MeI at 100° gives 1 : 3-dimethyl-3- β -methylaminoethylloxindole, m.p. 87° (picrate, m.p. 227°), reduced (Na) to *dl*-deoxyseroline (picrate, m.p. 179—180°; contains no active H), the methiodide of which at 180—200° gives 1 : 3-dimethylindole and with aq. NaOH the methine, converted by K₃Fe(CN)₆ into 1 : 3-dimethyl-3- β -dimethylaminoethylloxindole (IV), b.p. 167—173°/14 mm. (picrate, m.p. 132°; picrolonate, m.p. 192°), also obtained by treating (I) with a large excess of (·CH₂Br)₂ and heating the resulting crude 1 : 3-dimethyl-3- β -bromoethylloxindole, b.p. 150—160°/1 mm., with NHMe₂ at 100°. Hydrogenation of (IV) gives 1 : 3-dimethyl-3- β -methylaminoethyl-dihydroindole (picrate, m.p. 129°; dipicrate, m.p. 153°). The relations of the eseroline derivatives to eserine are thus proved.

IV. *dl*-Eserethole is synthesised for the first time. All stages give good yields. Sodiaoacet-*p*-phenetidine and Me₂SO₄ in hot xylene give a 96% yield of *N*-methyl-*p*-phenetidine, b.p. 138°/18 mm., the *N*- α -bromopropionyl derivative of which with AlCl₃ at 180—185° gives in 92% yield 5-hydroxy-1 : 3-dimethylloxindole, m.p. 219°. The *Et* ether, m.p. 78°, b.p. 192—194°/18 mm., thereof (prepared by Et₂SO₄) with NaOEt and CH₂Cl·CN in Et₂O gives 5-ethoxy-1 : 3-dimethylloxindolyl-3-acetonitrile (84% yield), b.p. 226—228°/17 mm., m.p. 109°, hydrogenated (Pd) to 1 : 3-dimethyl-3- β -aminoethylloxindole (V) (91% yield), b.p. 216°/13 mm. (picrate, m.p. 184°). The benzylidene derivative, m.p. 81°, of (V) with MeI gives 1 : 3-dimethyl-3- β -methylaminoethylloxindole, b.p. 212—213°/14.5 mm. (hydriodide, m.p. 188°), reduced (Na) to *dl*-eserethole (VI), b.p. 181—183°/12 mm., m.p. 38° (picrate, m.p. 155°). Na-reduction of (V) gives *dl*-noreserethole, b.p. 187—192°/12 mm. (picrate, m.p. 182—183°; picrolonate, m.p. 221°; *Bz* derivative, m.p. 108°; contains 1 active H). (VI) and MeI give a (di)methiodide, which is converted by distillation/high vac. into 5-ethoxy-1 : 3-dimethylindole (identical with the product obtained from *l*-eserethole), and with picric acid gives a dimethopicate, m.p. 169—171°, readily converted by hot EtOH into the picrate [VII; X = C₆H₂(NO₂)₃·O], m.p. 194° (decomp.). Robinson's compound, stated to be (VI), is probably (VIII). Hydrogenation of (VI) affords 5-ethoxy-1 : 3-dimethyl-

dihydrocupreine, and NaOEt in EtOH at 92—94° give a substance, hydrolysed to β -hydroxyethyl-dihydrocupreine (I), m.p. 165° after softening at 105—112°, [α]_D —132.1° in EtOH [dihydrochloride, m.p. 234° (decomp.), [α]_D —177° in H₂O; *Bz* derivative (II), m.p. 231° (decomp.), [α]_D —105.4° in EtOH]. (·CH₂·OH)₂ and p -C₆H₄Me·SO₃Cl in C₆H₅N give ethylene glycol *p*-toluenesulphonate, an oil (changed rapidly, when kept, into the *di*-*p*-toluenesulphonate, m.p. 126°), which yields (I). OBz·[CH₂]₂·OH affords benzoyloxyethyl *p*-toluenesulphonate, m.p. 74—75°, which yields (II). Chloroethyl-dihydrocupreine has [α]_D —125.1° in EtOH; its hydrochloride, [α]_D —163.3° in H₂O, with NaOEt gives vinyl-dihydrocupreine (dihydrochloride, [α]_D —174° in H₂O). β -Ethoxyethyl *p*-toluenesulphonate, b.p. 186—187°/3 mm., gives β -ethoxyethyl-dihydrocupreine (dihydrochloride, amorphous, [α]_D —149°). The above and other quinine derivatives are of little val. against *Pneumococcus*, except (I), which sterilises cultures *in vitro* at 1 : 200,000, affords considerable protection to mice in 2-mg. doses, and is only slightly toxic in 5-mg. doses. R. S. C.

Alkaloids of *Rauwolfia serpentina*. Benth.

II. Ajmaline series. S. SIDDIQUI and R. H. SIDDIQUI (J. Indian Chem. Soc., 1935, 12, 37—47).—New analyses of ajmaline (I) (A., 1933, 289) show that it is correctly represented by C₂₀H₂₈O₂N₂ (full dehydration only at 200°). With Br·CHCl₃ it gives dibromo-ajmaline, C₂₀H₂₆O₂N₂Br₂, m.p. 230° (decomp.), with conc. HNO₃ an amorphous (NO₂)₃-derivative, m.p. 238—258° (decomp.), and with H₂SO₄ (*d* 1.84) at 100°, a monosulphonic acid, softens 310°, m.p. 319—320° (decomp.) [NH₄, shrinks at 262°, m.p. 319—320° (decomp.)], *Ba*, m.p. 322—324° (decomp.), *Ca*, *K*, and *Na* salts]. Repeated crystallisation of pyroajmaline (*loc. cit.*) from EtOAc separates it into (I) and the isomeric (diacid) isoajmaline (II), m.p. 265—266°, [α]_D²⁵ +72.8° in EtOH [hydrochloride, [α]_D²⁵ +98.7° in H₂O; platinichloride, m.p. 227—228° (decomp.)]; picrate, softens 150—160°, chars at 180—200°. Ajmalinine (III), revised formula C₂₀H₂₆O₃N₂ {amorphous *Bz* derivative, froths at 100°, m.p. 140—150° [hydrochloride and picrate, both m.p. 220° (decomp.)]; platinichloride, m.p. 242—245° (decomp.)]; methiodide, m.p. 233—234° (decomp.)}, is converted by heating at 210° (in H₂) into apoajmalinine, C₁₃H₁₇O₃N, m.p. 270—272° [hydrochloride, m.p. 243—244° (decomp.)]; picrate, m.p. 231—232°. Serpentine (IV) C₂₀H₂₀O₃N₂ (1 OH, 1 OMe) [methiodide, m.p. 271—272° (decomp.)], is a *tert*-base since the substance obtained by the action of HNO₂ is the nitrite, m.p. 165—166° (decomp.). With Br·CHCl₃ (IV) gives bromoserpentine hydrobromide, m.p. 257—258° (decomp.). When heated at 210° (H₂) (IV) isomerises to isoserpentine, m.p. 230—232° [hydrochloride, m.p. 271—272°, [α]_D +168.08° in H₂O; platinichloride, m.p. 248—249° (decomp.)]; aurichloride, softens 174°, m.p. 194—195° (decomp.); picrate, m.p. 263—264° (decomp.). Serpentinine, C₂₀H₂₀O₅N₂ + 1.5H₂O, not lost completely until 150° [hydrochloride, m.p. 271—272° (decomp.)], and picrate, m.p. 263—264°, now both obtained cryst.; aurichloride, m.p. 194—195° (decomp.); hydrobromide, m.p. 271—272° (decomp.); hydriodide, m.p. 271—272° (decomp.)], is a *sec*-base



3- β -methylaminoethyl-dihydroindole (picrate, m.p. 140°; dipicrate, m.p. 166°). Since (VI) readily yields physostigmine, this constitutes a synthesis of the latter.

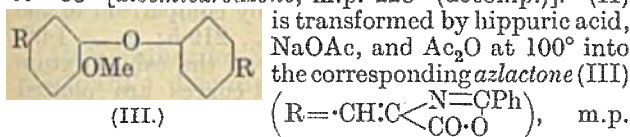
R. S. C.

Cinchona alkaloids in pneumonia. I. Miscellaneous alkaloids and some hydrocupreine ethers. C. L. BUTLER, W. L. NELSON, (Miss) A. G. RENFREW, and L. H. CRETCHER (J. Amer. Chem. Soc., 1935, 57, 575—578).—Et chlorovinyl ether,

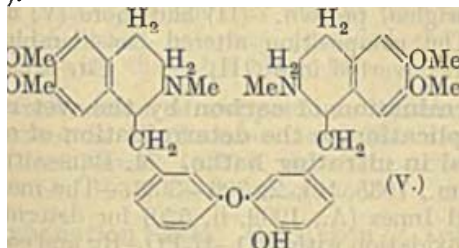
since it gives a *NO*-derivative + 1.5H₂O and anhyd., m.p. 159—160°. Partial formulæ containing a betaine grouping are suggested for (I), (II), and (III), which possibly contain a C₁₉ ring system similar to that (C₂₁) in strychnine. J. W. B.

Effect of boric acid on the properties of apomorphine hydrochloride solutions. S. WITTEBOON (Pharm. Weekblad, 1935, 72, 350—354).—When a 1% solution of apomorphine (I) hydrochloride is mixed with a 2% solution of H₃BO₃, HCl is slowly liberated, *p_H* falls to 2.0, and a gelatinous *boryl* derivative of (I) is formed, which probably contains 2 mols. of (I) to 1 mol. of B. S. C.

Alkaloids of *Sinomenium* and *Cocculus*.
XXXIX. Constitution of dauricine. H. KONDO, Z. NARITA, and S. UYEO (Ber., 1935, 68, [B], 519—528; cf. A., 1931, 243).—The m.p. of α-methylauricinemethine (I) is 127—128° (not 108°). The corresponding methiodide, m.p. 207—208° to a turbid liquid after softening at 200°, contains 1.5H₂O. 6-Methoxy-3:4'-ditolyl ether, b.p. 170°/8 mm., from *p*-cresol, C₆H₅MeBr·OMe, KOH, and Cu powder at 210°, is oxidised by KMnO₄ to 6-methoxy-3:4'-dicarboxydiphenyl ether, m.p. 312—313° (Me₂ ester, m.p. 96—97°), in 69% yield. The corresponding acid chloride, m.p. 85—86°, is reduced (Pd-BaSO₄ in xylene) to 3:4'-dialdehyde-6-methoxydiphenyl ether (II), m.p. 80—83° [disemicarbazone, m.p. 228° (decomp.)]. (II)



is transformed by hippuric acid, NaOAc, and Ac₂O at 100° into the corresponding azlactone (III) (R=·CH:C<N=CPh>CO·O), m.p. 257—258°, from which the acid [R=·CH:C(CO₂H)·NHBz], m.p. 248—249° (decomp.), and the *keto-acid* (R=·CH₂·CO·CO₂H), m.p. 198.5° (decomp.), are derived. Treatment of (III) with Ba(OH)₂ in boiling aq. EtOH leads to 6-methoxy-3:4'-di(carboxymethyl)diphenyl ether (IV), m.p. 174—176° (Me₂ ester, m.p. 52—53°). Homoveratrylamine (prep. by reduction of the corresponding nitrostyrene at a Pb cathode described) and (IV) in boiling tetrahydronaphthalene yield 6-methoxydiphenyl ether 3:4'-diacetidihomoveratrylamide [cf. III; R=CH₂·CO·NH·CH₂·CH₂·C₆H₅(OMe)₂], m.p. 139—140°, converted by the successive action of PCl₅, H₂ (PtO₂), Me₂SO₄, and alkali into (I). Dauricine is therefore (V).



H. W.

Cyclic polymethylene arsenic derivatives. I—II. I. M. GORSKI and V. A. SCHPANSKI (J. Gen. Chem. Russ., 1934, 4, 1270—1273, 1283—1285).—I. [With L. I. MULJAR] CH₂<[CH₂]₂>As·CH·CHCl (I), b.p. 89—91°/5 mm., prepared from α-dibromo-

pentane, Mg, and CHCl·CH·AsCl₂ (II) in Et₂O, affords the *dichloride* (III), m.p. 121°, with Cl₂ in CCl₄. (III) decomposes when heated to yield (I), ε-chloroamyl-6-chlorovinylchloroarsine (IV), b.p. 151—152°/5 mm., αε-dichloropentane (V), and (II); the last two products are also obtained by heating (IV).

II. CH₂<[CH₂]₂>AsMe, b.p. 57—58°/20 mm. [*di-chloride* (VI), m.p. 133°], is prepared from (V), Mg, and AsMeCl, in Et₂O. (VI) yields cyclopentamethyl-enochloroarsine (VII), m.p. 26—27°, when vac.-distilled. (VII), when heated at 100° with NaOMe in MeOH, affords the corresponding *oxide*, b.p. 118°/2 mm., converted by H₂O₂ into cyclopentylarsinic acid, m.p. 200.5—202°. R. T.

Reactivity of nuclear chlorine in 5-substituted derivatives of 2-chlorophenylarsinic acid. W. E. CRAIG and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 578—580).—2-Chloro-5-carboxyphenylarsinic acid (I) undergoes the Ullmann reaction with NH₂·[CH₂]₂·OH, glycine, and PhOH as readily as does 2-chlorophenylarsinic acid (II). 2-Chloro-5-cyanophenylarsinic acid (III) condenses with PhOH, but with greater difficulty. *op*-Directing groups (NH₂, NHAc, OH) in the 5-position in (II) prevent condensation. 2-Chloro-5-aminophenylarsinic acid (IV) [Ac derivative, anhyd. and +H₂O (lost at 160°), m.p. 225—227°] with H₃PO₂ gives 2:2'-dichloro-5:5'-diaminoarsenobenzene, with N₂O₃·HCl 4-chloro-3-arsinobenzene diazonium chloride [with MeOH gives (II)], and (diazo-reaction) 2-chloro-5-hydroxyphenylarsinic acid, anhyd. and + about 1H₂O; the OH-acid with ClCO₂Et and a little C₅H₅N gives 2-chloro-5-carbethoxyphenylarsinic acid, and with H₃PO₂ 2:2'-dichloro-5:5'-dihydroxyarsenobenzene, anhyd. and + about 1H₂O. (IV) yields (diazo-reaction) (III), decomp. 200°, and (I). By condensation of the above with the appropriate reagents, K₂CO₃, and a trace of CuI in amyl alcohol are obtained *Ph* 4-cyano- and 4-carboxy-2-arsinophenyl ether, 2-3-hydroxyethylamino-5-carboxyphenylarsinic acid, m.p. 240—243° (decomp.), 4-carboxy- and 4-nitro-2-arsinophenylglycine, m.p. 208°, hydrogenated (Ni) to the 4-NH₂-acid, m.p. 210° (decomp.). R. S. C.

Acridylarsinic acids and their derivatives. S. M. SCHERLIN, G. J. BRAS, A. J. JAKUBOVITSCH, E. I. VOROBYOVA, and A. P. SERGEEV (Annalen, 1935, 516, 218—230).—Addition of NaNO₂ to 1-amino-acridine sulphate in AcOH containing AsCl₃ and Cu₂Cl₂ and subsequent boiling of the mixture leads to 1-acridylarsinic acid (I), also obtained directly from 1-amino-9:10-dihydroacridine; the *hydrochloride*, m.p. 302—303° (decomp.) after becoming red at 180—190° and black at 290°, readily hydrolysed *sulphate* and *perchlorate*, m.p. 207—215°, are described. Reduction of (I) with SO₂ in presence of I gives 1-acridyldichloroarsine (*hydrochloride*, m.p. 221—221.6° when rapidly heated), transformed by NH₃·H₂O into 1-acridylarsine *oxide*, m.p. (indef.) 248—261° (decomp.) after darkening at 180° and softening at 236°. 2-Nitroacridone is reduced by Na-Hg to 2-amino-9:10-dihydroacridine (II), m.p. 193—196° or m.p. 206—207° in a sealed capillary, transformed by acetylation, oxidation with NaNO₂, and sub-

sequent hydrolysis into 2-aminoacridine, m.p. 221—222° (sealed tube). (II) is diazotised in presence of AsCl_3 to 2-acridylarsinic acid hydrochloride, m.p. 223.5—224.5° (sealed tube), whence 2-acridyldichloroarsine hydrochloride, m.p. 263—264° (slight decomp.) in a bath pre-heated to 250°. Reduction of 3-nitroacridone, from 4-nitrodiphenylamine-2-carboxylic acid (improved method), yields 3-amino-9:10-dihydroacridine, m.p. 191—192° in bath pre-heated to 190°, and 3-aminoacridine, m.p. 211—214° in bath pre-heated to 205°, apparently identical with Anschütz' " α -aminoacridine." The product of the reduction of 2-nitroacridone obtained by nitration of acridone (Lehmstedt, A., 1931, 1431) is contaminated with 3:8-diaminoacridine, m.p. 303—305° in bath pre-heated to 290°. 3-Acridylarsinic acid hydrochloride, m.p. 229—230° in bath pre-heated to 225°, is reduced to 3-acridyldichloroarsine hydrochloride, decomp. 245—248° when rapidly heated. 2:9-Diaminoacridine, m.p. 270—278° (purification described) [hydrochloride (+1H₂O), m.p. > 310°], yields 3-aminoacridyl-9-arsinic acid, m.p. > 250° (hydrochloride; Na salt; sulphate, m.p. > 290°).

H. W.

Dioximes. CV. G. LONGO (Gazzetta, 1935, 65, 84—88).—Glyoxime and methyl-, dimethyl-, methyl-ethyl-, α - and β -phenyl-, and α - and β -*p*-tolyl-glyoxime react with MgMeI to give compounds (I) of type $\text{IMg}\cdot\text{O}\cdot\text{N}\cdot\text{CR}\cdot\text{CR}\cdot\text{N}\cdot\text{O}\cdot\text{MgI}$; the C:N linking does not react, and α - and β -forms of the same dioxime do not differ in reactivity. (I) is hydrolysed to the original glyoxime in its same form. β -Aminophenylglyoxime gives a compound $\text{IMg}\cdot\text{O}\cdot\text{N}\cdot\text{CPh}\cdot\text{C}(\text{N}\cdot\text{O}\cdot\text{MgI})\cdot\text{NH}\cdot\text{MgI}$; the α -form, and the α - and β -forms of the *p*-tolyl analogue, react similarly.

E. W. W.

Organic compounds of thallium. S. S. NAMETKIN and N. N. MELNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 228—234).—The following compounds have been obtained from the corresponding diazonium chlorides and TiCl_3 : $\text{Ph}\cdot\text{N}_2\cdot\text{TiCl}_4$ (I), m.p. 68—69°; $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{TiCl}_4$, m.p. 59°; $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{TiCl}_4$, m.p. 93°; $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{TiCl}_4$, m.p. 66°; p -, m.p. 91°, and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{TiCl}_4$, m.p. 111—112.5°; $o\text{-[NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2]\cdot\text{TiCl}_5$, m.p. 98—98.5°; $\alpha\text{-C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{TiCl}_4$, m.p. 71—72.5°. The NO_2 -compounds have three and the other compounds two ionisable Cl atoms. (I) decomposes with the formation of Ph_2 , PhCl , TiCl , and (in presence of H_2O) PhOH . A method for the determination of Ti is described, depending on the oxidation of the org. compound by KMnO_4 and H_2SO_4 followed by iodometric titration.

W. O. K.

Refractivity of protein solutions. D. B. HAND (J. Biol. Chem., 1935, 108, 703—707).—A method for determination and comparison of the refractivity of proteins is described and vals. for 13 proteins are tabulated.

M. S.

Protein problem. II. Detection of the free amino-group of terminal glycine. W. ZIMMERMANN. III. Methylation and enzymic fission of gelatin. W. ZIMMERMANN, M. K. MCPHAIL, and A. CANZANELLI (Z. physiol. Chem., 1935, 231, 19—24, 25—28; cf. A., 1933, 1148).—II. Glycine with

free NH_2 at the end of a polypeptide chain is detected by the formation of glycine betaine (I) on methylation. (I) is isolated as the chloride, which is almost insol. in abs. EtOH. Thus glycylglycine affords (I) (in yield much < calc.). (I) is also given by the proline-glycine peptide mixture from goose feathers and by glutokyrin, but not by glutathione or insulin.

III. Gelatin gives no (I) until after tryptic or mild acid hydrolysis. Witte's glutin peptone (but not bacteriological peptone) gives (I). None is given by fibrin, albumin, or their enzymic fission products.

J. H. B.

Effect of temperature on the products of hydrolysis of proteins. V. S. SADIKOV, R. G. KRISTALLINSKAJA, S. V. LINDKVIST-RISAKOVA, and V. N. MENSCHIKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 458—462).—An investigation into the optimum conditions for cyclopeptide formation from proteins. The protein is heated at 220° for 10 min. in an autoclave with 4% aq. mineral acid, when about 20% of the total protein is converted into cyclopeptide.

E. A. H. R.

Casein. T. GIZA (Bull. Acad. Polonaise, 1934, A, 421—447).—Cow's milk casein (I) fractionated by Linderström-Lang's method (A., 1929, 1093) gives six fractions (II) having approx. identical N but varying P content. An indirect check of Linderström-Lang's determination of tryptophan (III) and tyrosine (IV) in (I) is obtained by comparison of the absorption spectra of (II), ($\lambda_{\text{max.}}$, 219.5; $\epsilon_{\text{max.}}$, 1.06, 1.07, 0.85, 0.89, 1.13) with that of the calc. mixture of (III) and (IV). p_{H} -conc'n. curves are plotted and show that the buffer capacity (B) of (II) in NaOH aq. increases with increasing P content, but is not due entirely to H_3PO_4 or KH_2PO_4 . The (B) of milk from different sources varies with the casein (III) content; (B) of cow's [2.9% (III)], goat's, and human milk [0.8% (III)] decreases in that order.

F. N. W.

Proteins. XIV. Action of superheated water on glycinin from soya beans. S. KOMATSU, T. HIBINO, and S. YAMAGUCHI (J. Chem. Soc. Japan, 1934, 55, 791—801).—Hydrolysis of glycinin at 120—150° yielded meta-protein (I), proteose (II), peptone (III), and polypeptide, the proportion of sol. products increasing with rise of temp. At 150° part of the NH_2 - and $(\text{NH}_2)_2\text{-N}$ (IV) changed to amide-N (V). The N distribution of (I) and (II) resembled that of the original protein. (II) had more (V) and less (IV). The composition altered considerably when (II) was converted into (III).

CH. ABS. (p)

Determination of carbon by the wet method and application to the determination of organic material in nitrating baths. M. BRISSAUD (Bull. Soc. chim., 1935, [v], 2, 306—309).—The method of Berl and Innes (A., 1909, ii, 520) for determination of C by oxidation with $\text{CrO}_3\text{-H}_3\text{PO}_4\text{-Hg}$ and collection of CO_2 is modified, mainly by final addition of NaBO_3 to generate O_2 to sweep over the last traces of CO_2 ; details of apparatus and technique are given. The method is accurate (approx. $\pm 1\%$) for determination of C in nitrating mixtures, but is untrustworthy for cellulose nitrate powders (error $\pm 2.5\%$, but is dependent on the wt. of powder used).

J. W. B.

Simple semi-micro-method for determination of carbon and hydrogen in organic compounds. R. ROGER and W. B. MACKAY (J.S.C.I., 1935, 54, 46—48T).—By modification of the usual macro-combustion tube filling and absorption tube design, the method is made applicable to 25—50 mg. of material. J. S. A.

Modified chromic acid method for determination of carbon. I. M. ROBERTSON and J. M. SHEWAN (J.S.C.I., 1935, 54, 35—36T).—The material is heated with $\text{CrO}_3\text{--H}_2\text{SO}_4$ and the gases evolved are passed through a heated combustion tube containing CuO and PbCrO_4 . Halogens, S, etc. are removed and complete combustion of the C compounds is obtained, after which the CO_2 is absorbed in KOH and soda-lime, and weighed.

Benzoylauramine G. New indicator for Kjeldahl nitrogen determinations. J. T. SCANLAN and J. D. REID (Ind. Eng. Chem. [Anal.], 1935, 7, 125—126).—*Benzoylauramine G* (I) (4:4'-dimethyldiamino-3:3'-dimethylbenzophenonebenzoylimine), m.p. 176—177° (obtained from auramine G and Bz_2O), changes sharply (p_H 5—5.6) in MeOH from a pale yellow to a violet-coloured compound which is dichroic. (I) is fairly easily hydrolysed (cf. A., 1895, i, 184) in acid or alkaline solution, so is added as an indicator near the neutral point. The end-point is more satisfactory than that of Me-red in presence of NH_4Cl . J. L. D.

Determination of nitrogen and phosphorus in Kjeldahl's decomposition using selenium.—See this vol., 595.

Determination of small amounts of sulphur in certain organic compounds. N. STRAFFORD and H. CROSSLEY (Analyst, 1935, 60, 163—169).—Apparatus is described in which PhNO_2 and similar liquids (I) are aspirated in a fine spray through an incandescent combustion tube in which S is oxidised. (I) not containing -NO_2 and solids are dissolved in PhNO_2 of known S content. E. C. S.

Tests for elements in organic compounds. H. MIDDLETON (Analyst, 1935, 60, 154—157).—For the detection of S and halogens the substance (I) is heated with Na_2CO_3 and sucrose; a positive test for N is given by a limited no. of N compounds only. For the detection of N, (I) is heated with Zn and Na_2CO_3 , which may also be used for the detection of S and halogens, provided the result is compared with that of a blank test. E. C. S.

Determination of copper in organic matter. O. SHEETS, R. W. PEARSON, and M. GIEGER (Ind. Eng. Chem. [Anal.], 1935, 7, 109—110).—Ansbacher's method (A., 1931, 1202) is modified. J. L. D.

Sulphonation flask. H. BARSCH (Z. anal. Chem., 1935, 100, 280—281).—The neck is graduated in c.c., enabling the contraction during sulphonation to be read directly without transference. J. S. A.

Use of crucibles with a porous filtering plate in Allihn's method [for determining sugars].—See this vol., 599.

Micro-determination of lactose. J. M. CLAVERA and F. M. MARTIN (Anal. Fis. Quím., 1933, 31, 905—906).—A claim for priority (cf. A., 1933, 732).

J. L. D.

Micro-detection of volatile amines and their influence on the permeability of animal membranes. A. VON WACEK (Klin. Woch., 1934, 13, 1147—1148; Chem. Zentr., 1934, ii, 2868).—The slightly acid or neutral solution to be tested is absorbed with HgO and covered with a layer of HgO . On making alkaline, NH_3 is retained by the HgO and the amines pass off. By controlled addition of alkali a fractional liberation of amines from a mixture is possible. Results with animal materials are recorded.

H. J. E.

Identification of flavianates of various organic bases. W. D. LANGLEY and A. J. ALBRECHT (J. Biol. Chem., 1935, 108, 729—739).—Flavianic acid (I) is recommended for the isolation and identification of bases. A micro-colorimetric method for the determination of (I) is described and the crystallographic and optical characteristics of the following are given in detail: flavianic acid, m.p. 150°; NH_4 , m.p. 291—292° and 292—293°; *ergamine*, m.p. > 300°; *NMe₃O*, m.p. 218°; *NH₂OH*, m.p. 216.5—218°; *methylglyoxaline*, m.p. 217—218°; *putrescine mono-*, m.p. 285°; *acetylcholine*, m.p. 222.5—225°; *betaine*, m.p. 242—243°; *glyoxaline*, m.p. 224—226°; *histidine di-*, m.p. 237—238°; *NH₂Me*, m.p. 262.5°; *OH-[CH₂]₂NH₂*, m.p. 211—212°; *methylcarbamide*, m.p. 201—202°; *histidine mono-*, m.p. 212—214° (+3H₂O); *histamine mono-*, m.p. 260°; *nicotinic acid*, m.p. 250—251°; *NMe₃*, m.p. 239°; *CO(NH₂)₂*, m.p. 289°; *guanidine mono-*, m.p. 279.5—280°; *as-dimethylguanidine*, m.p. 265—266°; *choline*, m.p. 162°; *methylguanidine mono-*, m.p. 227° and 230°; *K*, m.p. > 300°; *NHMe₂*, m.p. 234—236°; *NMe₄*, m.p. 273—274°; *nicotine*, m.p. 245.5—246.5°; *creatine*, m.p. 231°; *carnosine mono-*, m.p. 110° (anhyd.; cryst. with 3H₂O); *anserine di-*, decomp. 200—205°; *hydroxymethylglyoxaline*, m.p. 216°; *piperidine*, m.p. 248.5°; *trigonelline*, m.p. 236.8°; *hypoxanthine*, m.p. 282°; *creatinine*, m.p. 246°; *tyramine*, m.p. 235°, and arginine flavianates.

H. N. R.

Potentiometric titration of organic precipitates. I. Determination of 8-hydroxyquinoline, anthranilic acid, and the metals precipitable by these two compounds. I. KITAJIMA (J. Chem. Soc. Japan, 1934, 55, 884—886).—8-Hydroxyquinoline and anthranilic acid may be determined potentiometrically with HBrO_3 . The method is applicable to the indirect determination of Cu, Cd, Al, Mn, Zn, Fe, Ni, Co, Ca, Mg, and U. CH. ABS. (e)

Colorimetric determination of urinary indican by means of ninhydrin.—See this vol., 648.

Tryptophan reaction and detection of hetero-auxin. S. WINKLER and S. PETERSEN (Z. physiol. Chem., 1935, 231, 210—212).—3-Indolylacetic acid (I) gives a reddish-violet coloration with the modified (A., 1934, 1376) Adamkiewicz-Hopkins reaction. The best ratio of the reagents is 2 mols. of Cu, 1 mol. of $\text{CHO}\cdot\text{CO}_2\text{H}$, and 1 mol. of (I). The reaction is used for colorimetric determination of (I). (I) is

distinguished from tryptophan by its positive FeCl_3 reaction. J. H. B.

Determination of small quantities of morphine. C. G. VAN ARKEL (Pharm. Weekblad, 1935, 72, 366—369).—The solution (20 c.c.), containing approx. 5 mg. of morphine (I), is treated with 1 c.c.

of AcOH , and 1 c.c. of 10% aq. NaNO_2 for 5 min. and then with 3 c.c. of 15% aq. NH_3 . The orange-coloured nitrosomorphine solution is measured colorimetrically, preferably in a Zeiss step-photometer. The colour is not \propto the concn. The method can also be used for determining (I) in small amounts of opium. S. C.

Biochemistry.

New measurement of "oxygen-absorbing power." E. E. ZIEGLER (Med. Ann. Dist. Columbia, 1933, 2, 225—230).—The " O_2 -absorbing power" is the ratio of absorbed to respired O_2 , and represents the ability of the system to absorb O_2 from each unit of gas available. The val. is important in cardiac and metabolic diseases. CH. ABS. (p)

Role of carbamino-compounds in the transport of carbon dioxide by the blood. W. C. STADIE (Science, 1935, 81, 207—208).—Meldrum and Rough-ton's conclusion (J. Physiol., 1933, 80, 143) that carbaminohæmoglobin plays an important role as a CO_2 carrier in blood is criticised. Evidence is advanced that only the equilibrium $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ is of physiological significance. L. S. T.

Acid-base equilibrium and the Henderson formula. R. REDING, N. JOUKOVSKY, and R. GOFFINET (Bull. Soc. Chim. biol., 1935, 17, 156—168).—The formula of Van Slyke for the calculation of free CO_2 (I) is shown to have a min. error of 24%, and, unlike that of Henderson and Hasselbalch, may not therefore be used to prove the existence or absence of parallel behaviour in the variations of (I) and HCO_3^- . A. L.

Electric impedance of suspensions of leucocytes. H. FRICKE and H. J. CURTIS (Nature, 1935, 135, 436).—Curves for white cells of the rabbit are discussed. L. S. T.

A. Viscosity of suspensions of blood-corpuscles at small concentrations. B. Properties of suspensions of blood-corpuscles at various p_{H} values. G. ACHARD (Compt. rend. Soc. Biol., 1935, 118, 676—679, 679—682).—A. Examination of ox- and pig-blood in low concn. (0.01 — 0.4×10^6 corpuscles per cu. mm.) shows that there is a rapid increase in viscosity as the concn. increases, and loss of protein and salts to the serum as the concn. falls.

B. A study of the increase with time in the p_{H} of blood brought to various initial p_{H} vals. A. L.

Phagocytosis of silica by surviving leucocytes. W. R. FRANKS and A. J. WATT (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 43—46).—*In vitro* blood-monocytes (I) transport added particles (II) of SiO_2 , but lose motility when engorged with (II). Absorption of fine quartz (II) by (I) continues until (I) are turgid and rounded, with resulting delay in appearance of fat. W. McC.

Mechanism of the aerobic resynthesis of adenylypyrophosphoric acid in bird erythrocytes. A. E. BRAUNSTEIN and B. A. SEVERIN (Biochem. Z., 1935, 276, 359—367).— AcCO_2H is oxidised by intact

pigeon erythrocytes in presence of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ with accompanying resynthesis (I) of adenyly pyrophosphate. This process and the naturally occurring (I) are not connected with carbohydrate degradation. Possibly the AcCO_2H is first phosphorylated. If so, the results indicate that the glycolytic and oxidative mechanisms of (I) are identical. W. McC.

Protein substances of disequilibrium and leucocytosis. R. LECOQ (Compt. rend. Soc. Biol., 1935, 118, 869—871).—Ingestion of fibrin (I) or muscle (II) produces increased leucocyte content (III), whilst ovalbumin (IV) decreases (III). On the other hand, (III) is decreased by peptones of (I) and (II) and increased by that of (IV). R. N. C.

Composition and specificity of hæmoglobins. J. ROCHE and G. JEAN (Compt. rend. Soc. Biol., 1935, 118, 174—176).—The arginine (I) and S of different globins of the same species are const., but the (I)/S ratio (II) shows small variations. In different species, (I) is fairly const., but S shows variations reaching 30% in extreme cases; hence (II) also varies, its val. being characteristic of the specificity of the hæmoglobin. R. N. C.

Spectral characters and specificity of hæmoglobins. J. ROCHE (Compt. rend. Soc. Biol., 1935, 118, 172—174).—The spectra of cryst. human, rabbit, horse, pig, and sheep hæmoglobins are identical, and are not altered by the addition of glutathione to their solutions. R. N. C.

Varying behaviour of the blood of different animal species as regards crystallisation of carboxyhæmoglobin. E. BROCCA (Atti R. Accad. Lincei, 1934, [vi], 20, 474—479).—When blood is treated by Amantea's saponin method, crystallisation of the carboxyhæmoglobin (I) occurs only with those bloods which, when examined under ordinary conditions (no treatment with CO), are able to yield cryst. oxyhæmoglobin (II) [with or without cryst. reduced hæmoglobin (III)]. Human blood treated by the saponin method gives cryst. (III), but never cryst. (II). T. H. P.

Microcrystallographic examination of blood in forensic medicine. M. BORNAND (Mitt. Lebensm. Hyg., 1935, 26, 15—18).—For the identification of blood the methods of Takayama and Bertrand (A. 1932, 292) are equally trustworthy. Comparative results are given for 13 vertebrates. E. C. S.

Oxalic acid in blood. (A) Effect of injection of sodium oxalate. (B) Effect of administration of adrenaline and insulin. (C) Effect of administration of colloidal sulphur and colloidal silver. (D) Effect of physiological and patho-

logical conditions. (E) Effect of administration of thyroxine. (F) Effect of body-temperature. (G) During hibernation. S. SUZUKI (Japan. J. Med. Sci., 1935, II, 3, 19—22, 23—31, 33—35, 37—39, 41—44, 45—50, 51—52; cf. A., 1934, 1122).—(A) Only part of the $H_2C_2O_4$ of ox-blood is diffusible. $Na_2C_2O_4$, intravenously injected into rabbits, disappears from the blood in a few hr. After subcutaneous injection the max. concn. is attained in the blood in 1 hr.

(B) Administration of adrenaline (I) to rabbits causes increase (lasting 4—5 hr.) in the $H_2C_2O_4$ content (II) of their blood. The max. (II) is reached in 1.5—3.0 hr. Slight reduction in (II) follows small doses of insulin (III), whilst large doses usually cause rapid transient reduction. (II) increases considerably during convulsions following (III) administration. (I) and (III) given simultaneously act antagonistically on (II).

(C) (II) of rabbit's blood is increased by injecting S or Ag.

(D) (II) of children's blood is < that of adults'. In women (II) of the blood increases slightly in the menstrual period and greatly (occasionally) during pregnancy. (II) of the blood decreases slightly in leucæmia, but is unaltered in anæmia, sciatica, apoplexy, and hypertony.

(E) In rabbits injection of thyroxine (IV) produces a gradual increase, thyroidectomy (V) a temporary decrease, in (II) of the blood. After (V), the increase in (II) following administration of glucose or fructose is < normal. Probably the effect of (IV) on (II) is indirect.

(F) In rabbits (II) of the blood is unaffected by severe rapid reduction (VI) (to 25°) of body-temp., but is increased by gradual, less severe (VI). (II) decreases slightly in fever produced by injection of typhoid vaccine, but increases strikingly following injection of tetrahydroxy- β -naphthylamine.

(G) (II) of the blood of the bull-frog decreases slightly during hibernation. W. McC.

Normal urea concentration in blood and cerebrospinal fluid. G. STRAUBE and R. HOFMANN (Klin. Woch., 1934, 13, 1377—1381; Chem. Zentr., 1934, ii, 3137).—Urea is determined in the protein-free fluids by a semi-micro-urease method. Vals. varied considerably with individuals, but in no case did those for cerebrospinal fluid exceed those for whole blood or serum (I). Vals. for corpuscles were < those for (I). A. G. P.

Urea ratio as a measure of renal function. H. O. MOSETHAL and M. BRUGER (Arch. Int. Med., 1935, 55, 411—419).—The urea ratio (% of urea-N in the total non-protein-N of the blood) is a trustworthy numerical index of renal efficiency. The normal val. is ≥ 44 , which rises to ≤ 80 with max. impairment of the function. H. G. R.

Modifications produced in rabbit serum by repeated bleeding. P. VALLERY-RADOT, G. MAURIC, A. HUGO, and P. GAUTHIER-VILLARS (Compt. rend. Soc. Biol., 1935, 118, 1185—1188).—Blood-urea and -cholesterol are generally increased by repeated bleeding. Albumin falls at first, this being followed

in some cases by return to the initial val. or by fluctuations. The opacifying power varies. R. N. C.

Experimental hyperglycæmia in individuals of different physical character. A. Individual variations. B. Variation in blood-sugar following injections of insulin and adrenaline. H. HIRSCH (Compt. rend. Soc. Biol., 1935, 118, 704—705, 706—707).—A. The variations with time in the blood-sugar following ingestion of glucose after fasting by thick-set (I), athletic (II), and thin (III) individuals are studied. With (I) there is a sharp rise and a slow decrease, whereas with (III) the max. is lower, and the decrease more rapid, (II) being intermediate.

B. The effects on the blood-sugar after separate injections of insulin (10 units) and adrenaline (1 mg.) are considerably greater in (III) than in (I). A. L.

Hyperglycæmia following excitation of the Cyon-Ludwig depressor nerve in the rabbit. J. MALMEJAC, E. DONNET, and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 118, 895—898).—Excitation of the depressor nerves does not increase blood-sugar if the animal has been anæsthetised. R. N. C.

Hyperglycæmic effect of section of the depressor nerves in the dog. J. MALMEJAC, E. DESANTI, and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 118, 892—894).—The hyperglycæmic effect of section of the depressor nerves is parallel with the pressor effect, and is due to increased adrenal secretion. R. N. C.

Differentiation and classification, by means of sparteine, of some hyperglycæmias provoked in the rabbit. R. HAZARD and C. VAILLE (Compt. rend. Soc. Biol., 1935, 118, 864—866).—Sparteine suppresses completely the hyperglycæmic effects of nicotine, posterior pituitary extract, and papaverine, partly those of morphine, its derivatives, and Na salicylate, and does not affect that of adrenaline. R. N. C.

Hypoglycæmic action of testicular extract in sugar diabetes. L. CORNIL and J. E. PAILLAS (Compt. rend. Soc. Biol., 1935, 118, 406—408).—Intravenous injection in diabetics of an aq. extract of 10 g. of fresh bull's testis decreases blood-sugar for ≥ 3 hr. A. L.

Influence of substances of the pilocarpine group (pilocarpine, arecoline, physostigmine) on the alkali reserve and blood-sugar [of dogs]. A. M. PREOBRAZHENSKI (J. Physiol. U.S.S.R., 1934, 17, 886—895).—The blood-sugar rises, and the alkali reserve falls, after administration of physostigmine, pilocarpine, or arecoline, to an extent \propto the dose; the activity of these substances diminishes in the order given. R. T.

Influence of sodium bicarbonate on adrenaline glycæmia. V. PAPILLAN and V. PREDA (Compt. rend. Soc. Biol., 1935, 118, 472—473).—The slight increase in blood-sugar (I) of dogs caused by intravenous injection of aq. $NaHCO_3$ was unchanged by a following injection of adrenaline. With simultaneous injection there was a slight increase in (I). A. L.

Effect of slow and continuous injection of adrenaline on the blood-sugar. A. BOUDOUIN, H. BENARD, J. LEWIN, and J. SALLET (Compt. rend.

Soc. Biol., 1935, 118, 529—531).—With continuous injection of adrenaline (I) at varying rates into dogs under chloralose anaesthesia the increase in blood-sugar is not \propto the amount of (I) injected. (I) injected at a rate of 0.05 and 0.6 mg. per kg. per hr. caused an average increase of 0.06 and 0.08 g. per 100 c.c., respectively. A. L.

Papaverine and blood-sugar. F. MERCIER and J. DELPHANT (Compt. rend. Soc. Biol., 1935, 118, 572—573).—The blood-sugar of dogs under chloralose anaesthesia may increase 64% five min. after the injection of 10 mg. of papaverine per kg., possibly owing to the discharge of adrenaline. A. L.

Iodometric micro-determination of blood-sugar. C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 118, 570—572; cf. A., 1934, 992).—The serum or blood is deproteinised with $\text{Hg}(\text{NO}_3)_2$ and the sugar determined iodometrically. The error is 2%. A. L.

Determination of adrenaline in blood. J. C. WHITEHORN (J. Biol. Chem., 1935, 108, 633—643).—Adrenaline (I) in concns. > 0.02 p.p.m. is determined colorimetrically in blood with arsenomolybdic acid after pptn. of proteins with $\text{CCl}_3\cdot\text{CO}_2\text{H}$, adsorption of (I) from the filtrate at p_H 7 by SiO_2 , and elution with $0.6N\text{-H}_2\text{SO}_4$. A solution of pyrocatechol is used as a standard. H. D.

Creatinine in blood. J. M. HAYMAN, jun., S. M. JOHNSTON, and J. A. BENDER (J. Biol. Chem., 1935, 108, 675—691).—Creatinine (I) is determined by the method of Rehberg. Adsorption of (I) by kaolin (II) and Lloyd's reagent (III) from $\text{CCl}_3\cdot\text{CO}_2\text{H}$ serum filtrates (IV) was $>$ from picric acid (V) filtrates. Shaking a solution of (V) with (II) or (III) gave a deeper colour on addition of NaOH and (I). (IV), shaken with (II), show a deeper colour on addition of (V) and NaOH; no difference is observed with (III). The plots of colour development against time are similar for solutions of pure (I) and the eluted (III) after adsorption of (I) from the (IV); untreated (IV) shows a continuous increase in colour; (IV) after shaking with (III) shows a rapid but small colour development. A high degree of correlation was observed between the apparent (I) vals. obtained by the Rehberg method and those obtained using (III) for normal and pathological serum, and for serum drawn before and after ingestion of (I). H. D.

Effect of diet on the blood-thioneine of the albino rat. V. R. POTTER and K. W. FRANKE (J. Nutrition, 1935, 9, 1—10).—Modified methods for determining uric acid and thioneine (I) in blood are described. Vals. obtained with many samples of rats' blood are recorded. The precursor of (I) is probably not methionine, glutathione, or thiohistidine. A. G. P.

Blood-cholesterol in Koreans on ordinary diet. M. S. KIM (J. Chosen Med. Assoc., 1934, 24, 490—493).—Whole blood contained (male) 141—250, (female) 143—243 mg. per 100 c.c. CH. ABS.

Influence of age on the variations in cholesterol content and cholesterololytic power of the blood. M. ECK and J. DESBORDES (Compt. rend. Soc. Biol., 1935, 118, 498—501).—The average cholesterol

content of the blood of healthy human subjects of 6—15, 20—40, and 60—80 years of age is 1.46, 1.76, and 1.77 g. per kg., the cholesterololytic power (Loeper, A., 1929, 88) being +1, +4.8, and —15, respectively. A. L.

Modifications in the composition of the blood of healthy individuals through the suppression or addition of salt in the food. E. LEVY-SOLAL and M. LAUDAT (Compt. rend. Soc. Biol., 1935, 118, 851—854).—Suppression of NaCl in the diet causes a steady rise of blood-protein and -fat, and a corresponding fall of plasma- and corpuscle-Cl, all returning to normal when NaCl is replaced. Blood-sugar and -urea are unaffected. R. N. C.

Comparative investigations of blood. VII. Cat and horse. H. VAULONT (Z. Biol., 1935, 96, 241—252).—Data are given for erythrocyte count, hæmoglobin content, total and differential counts of leucocytes, and plasma-*n* and -proteins. F. O. H.

Importance of the relationship between blood-protein concentration and the so-called colloidal osmotic pressure. A. GRÖNWALL (Biochem. Z., 1935, 276, 223—233).—The colloid pressure (I) (this term replaces the term colloidal osmotic pressure) in dil., conc., and normal sera (II) is determined. In conc. (II), (I) increases with increasing protein content but more rapidly than with dil. (II). The results are discussed in relation to kidney function. P. W. C.

Organic phosphorus of the blood, studied through prolonged spontaneous hydrolysis in the human subject and in some domestic animals, both adult and infantile. G. DE TONI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1258—1261).—Autolysis of org. PO_4 is rapid in the first 24 hr., and then becomes slower, suggesting that rapidly- (I) and slowly-autolysing esters (II) of H_3PO_4 are present. In infants (I) predominates, decreasing during growth to a val. approx. that of (II) in adults. Autolysable org. PO_4 is low in the blood of ruminants, but high in that of horses and rabbits. R. N. C.

Distribution of normal phosphorus in Uruguay cattle. L. ECHENIQUE (Compt. rend. Soc. Biol., 1935, 118, 931—932).—Vals. are given for inorg., acid-sol., org., lipid, and total P in the blood of steers and lactating cows. P in steers increases in spring. R. N. C.

Origin of blood-ammonia. G. POPOVICIU and C. OPRISIU (Compt. rend. Soc. Biol., 1935, 118, 473—475).—In dogs intravenous injection of $\text{PO}_4^{'''}$ (I) and lactate (II) increased the blood- NH_3 (III), the increase at p_H 5.8 being $>$ that at p_H 7.5 in the case of (I), and the reverse with (II). Separate injection of alanine, guanidine, and Na nucleate (IV) with (I) resulted in an increase which was, however, $<$ that caused by (I) alone. (IV) injected with (II) caused a decrease in (III). A. L.

Eosin and neutral sulphur. F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1934, 9, 1210—1211).—Rabbits injected with eosin show an increase in the neutral S of the blood \propto the amount injected. R. N. C.

Comparison of copper extracted from the blood of the horseshoe crab (*Limulus polyphemus*) with common copper. G. P. BAXTER and J. S. THOMAS (J. Amer. Chem. Soc., 1935, 57, 465—467).—No difference could be detected. E. S. H.

Biochemistry of copper. VI. Copper in relation to menstruation and pregnancy. Copper in men's blood. VII. Blood-copper in anæmia in men and horses. Blood-copper in children. VIII. Effect of gradual loss of blood on blood-copper. Copper content of bone-marrow. U. SARATA. IX. Effect of rapid loss of blood followed by injection of salt solution on blood-copper. M. ITIZYO. X. Effect of fasting and diet on blood-copper. U. SARATA (Japan. J. Med. Sci., 1935, II, 3, 1—8, 55—62, 63—66, 67—72, 73—77; cf. A., 1934, 1123).—VI. In men whole-blood-Cu (I) remains practically const. at 0.089—0.110 mg. per 100 c.c., limited fluctuations occurring in the plasma. In women (II), (I) increases before menstruation and decreases during the flow. In the early stages of pregnancy (III) in (II) plasma-Cu (IV) increases but falls to near the normal val. at the end. Corpuscular Cu (V) is also increased, but to a smaller extent, at the beginning of (III).

VII. In children (I) is high (0.10—0.12 mg. per 100 c.c.), most of the Cu being (V). In man (I) is high in anæmia (VI), leucæmia, and paroxysmal hæmoglobinuria (but not in purpura), the increase generally being in (IV). In infectious (VI) in horses (I) is markedly decreased, the decrease in (IV) being > in (V).

VIII. In rabbits (V) increases following gradual bleeding (VII), the decrease being < that following rapid (VII). (IV) remains unchanged. Repeated (VII) leads to increase in the Cu content of bone-marrow which normally contains, per 100 g. (fresh), 0.20—0.36 mg. and 0.07—0.09 mg. of Cu in the red and fatty parts, respectively.

IX. Injection of Ringer's solution into rabbits immediately after large (VII) checks the increase in (I) which otherwise occurs. Early in the recovery (V) rises above the normal val., (IV) remaining unaffected. Cu is an essential constituent of the corpuscles.

X. Fasting in rabbits causes a 20% decrease in (IV) mostly on the first day. The subsequent decrease is very slow. In chickens, no appreciable change in (I) follows change of diet, season, or environment. W. McC.

Micro-determination of bromine in blood. A. A. DIAS (Compt. rend. Soc. Biol., 1935, 118, 1115—1117).—The method of Pincussen and Roman (A., 1929, 713) is inaccurate. F. O. H.

Pituitary and the mineral substances of the blood. A. D. MARENZI and R. GERSCHMAN (Compt. rend. Soc. Biol., 1935, 118, 488—489).—In hypophysectomised dogs there is a considerable decrease in blood-plasma-K. Injection of anterior pituitary extract increases blood-sugar, protein, CO_2 , P, Ca, and Mg and decreases Na and Cl. A. L.

Relation of plasma-proteins to ascites and oedema in cirrhosis of the liver. W. K. MYERS

and C. S. KEEFER [with A. B. GRINNAN] (Arch. Int. Med., 1935, 55, 349—359).—Cirrhosis of the liver is characterised by a decrease in plasma (I)-protein (II), particularly in the albumin (III) fraction, with an inversion of the (III)-globulin ratio. (II) of the ascitic fluid (IV) varies between 0.1 and 1.7 g. per 100 c.c., (III) being > that of (I). This is probably due to defective formation of (II) and a loss into (IV). H. G. R.

Protein content of the blood-plasma of insects. M. FLORKIN (Compt. rend. Soc. Biol., 1935, 118, 1224—1226).—The protein contents (I) of the plasmas of a no. of insects and larvæ are given. In larvæ (I) increases with age. R. N. C.

Mercury-precipitating reaction of serum from hepatic affections. H. UCKO (Compt. rend. Soc. Biol., 1935, 118, 534—536).—A modification of the reaction of Takata in which an immediate ppt. on adding 0.5% aq. HgCl_2 to the serum made alkaline with 0.36% aq. Na_2CO_3 indicates hepatic affections. A. L.

Osmotic pressure and molecular weight of serum-albumin. A. ROCHE and F. MARQUET (Compt. rend. Soc. Biol., 1935, 118, 898—900).—The osmotic pressure and mol. wt. are not altered by keeping under aseptic conditions at room temp., 37°, or 0°. R. N. C.

"Anti-embryonic" sensitiser in rabbit serum. L. NATAN-LARRIER and L. GRIMARD (Compt. rend. Soc. Biol., 1935, 118, 1128—1130).—The sera of adult rabbits fix alexin in presence of extract of chick embryo. R. N. C.

Physico-chemical study of the blood of fish. Isoelectric points. G. FLORENCE and A. DRILHON (Compt. rend. Soc. Biol., 1935, 118, 1200—1202).—The normal serum of the carp has an isoelectric point at p_H 7.5, which is shifted towards the alkaline side as the salinity of the medium increases. The "β-point" at p_H 5.5 is not shifted, but becomes more perceptible. R. N. C.

"Non-solvent volume" of albuminous liquids. L. AMBARD and C. DEVILLER (Compt. rend. Soc. Biol., 1935, 118, 674—676).—The increase in the "non-solvent" vol. of albuminous liquids caused by addition of alkali or by reducing the concn. of electrolytes is explained by the repellent action of Na^+ of the plasma-protein on the crystalloids of the surrounding aq. zone. A. L.

Splenic derivatives and erythrocyte fragility. M. H. ELLIS, H. L. MOTLEY, and M. D. ELLIS (J. Pharm. Exp. Ther., 1935, 52, 273—294).—Aq. NaCl and EtOH extracts (I) of spleen were hæmolytic to erythrocytes (II) in small concns. (I) protected (II) from the action of saponin and dog serum. The EtOH extract was separated into a hæmolytic (COME_2 -sol.) and an anti-hæmolytic (COME_2 -insol.) fraction (III). (III) occurs in blood and liver, but not in striated muscle, fat, and cerebrum; it gives a negative sterol test. Pigeon, turtle, and frog (II) increase the effect of (III). H. D.

Action of potassium cyanide on photodynamic hæmolysis. O. BIER and M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1935, 118, 911—913).—KCN (0.007—

0.031*M*) increases considerably the hæmolytic and fixative action of irradiated eosin. R. N. C.

Action of concentrated sodium chloride solutions on hæmolysis and fixation of erythrocytes by irradiated eosin. O. BIER and M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1935, 118, 914—915).—Hypertonic NaCl solutions inhibit hæmolysis and assist fixation. R. N. C.

Blood coagulant from ox-lung. A. F. CHARLES, A. M. FISHER, and D. A. SCOTT (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 49—54).—100 lb. of lung yield 7.5 g. of coagulant (I) stable to heat (200° for 30 min.) and oxidising agents. (I) is sol. in fat solvents and appears to be closely related to the fatty acids. W. McC.

Flocculation of animal sera by the action of orthophosphoric acid solutions. P. GORI (Arch. Ist. Biochim. Ital., 1935, 7, 61—68).—Normal sera are flocculated by H_3PO_4 at 80°; the flocculation is determined by the serum : H_3PO_4 ratio, the optimum val. of which varies with the species. R. N. C.

Arrest of heavy bleeding in all forms of hæmorrhagic diathesis and of hæmophilia by administration of vitamin-C ("Cebion Merck"). A. BOGER and H. SCHRODER (Münch. med. Woch., 1934, 81, 1335—1337; Chem. Zentr., 1934, ii, 2706).—Incipient bleeding in a severe case was checked in 4 days by daily intravenous injection of 150 mg. of "Cebion." Increase in thrombocytes occurred 2 days later. R. N. C.

Relation between serum-polypeptides in general paralysis and the Wassermann and Kahn reactions. A. PRUNELL (Compt. rend. Soc. Biol., 1935, 118, 479—481).—Sera of general paralysis cases usually show normal polypeptide content, and positive Wassermann and Kahn reactions. A. L.

Anti-toxin content of human serum in relation to the Dick reaction. H. PLUMMER (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 97—100).—Skin reactions in chinchilla rabbits produced by mixtures of toxin with serum are compared with those produced by the same amount of toxin plus streptococcal anti-toxin (I) of known strength, those injections which produce marks equal in size being presumed to be due to the same amount of unneutralised serum. The (I) content of human blood-serum (II) is closely related to the interpretation of the Dick test (III), but there is no direct relation between the size of the marks produced in (III) and the quantity of (I) in (II). W. McC.

Complement fixation reaction with elementary bodies of vaccinia and specific precipitable substance of vaccinia. J. CRAIGIE and F. O. WISHART (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 91—96).—In presence of immune serum sp. fixation of complement (guinea-pig serum) occurs with the elementary bodies and with filtered extracts (containing the sp. precipitable substance) of skin infected with vaccinia. W. McC.

Colloidal characteristics of serum after contact with starch. A. LUMIERE and P. MEYER (Compt. rend. Soc. Biol., 1935, 118, 884—885).—The

appearance of anaphylactic properties in serum after contact with starch is accompanied by increases in viscosity and surface tension \propto the anaphylactic power. The activity of the starch inversely \propto the size of the grains. R. N. C.

Colloidal nature of anaphylactic precipitates. W. KOPACZEWSKI (Bull. Soc. Chim. biol., 1935, 17, 180—183).—A criticism of the work of Lumiere and Meyer (this vol., 116). A. L.

Colloidal nature of anaphylactic precipitates. A. LUMIERE and P. MEYER (Bull. Soc. Chim. biol., 1935, 17, 184—186).—A reply to Kopaczewski (above). A. L.

Antibody content of animal tissues after treatment with thymus extract. A. WASITZKY-STROBL and A. WASITZKY (Klin. Woch., 1934, 13, 797—798; Chem. Zentr., 1934, ii, 2701).—Injection of thymus extract in guinea-pigs and rabbits increases the antibody content of the organs, particularly of the lymphoid organs, and lowers that of the blood. R. N. C.

Lipase-inhibiting action induced in rabbit serum. G. BENETATO (Compt. rend. Soc. Biol., 1935, 118, 476—478).—Rabbit serum from animals injected with impure lipase, when added to normal serum (I) *in vitro*, inhibits considerably the lipase action of (I). A. L.

Action of aldehydes on antibodies. L. OLITZKI (Compt. rend. Soc. Biol., 1935, 118, 139—140).—Somatoc agglutinins (I) are converted into agglutinoids in 2—3 weeks by 1% solutions of CH_2O or $MeCHO$. Hæmo- and bacterio-lysins are also destroyed. The action of CH_2O is inhibited by 2% of glycine, saturation with sucrose, or 50% of glycerol. CH_2O is without effect on sera diluted $< 1/10$, or on elutions with negative protein reaction. The activity of (I) destroyed by CH_2O can be partly restored by pepsin. It is concluded that CH_2O attacks not (I), but their associated proteins. R. N. C.

Preparation of an anti-embryonic antibody. L. NATTAN-LARRIER and L. GRIMARD (Compt. rend. Soc. Biol., 1935, 118, 638—641).—There is produced in tissue cultures of chicken embryo heart an antibody which fixes the complement in the presence of chicken embryo extract. A. L.

Isoantigenic power of ovalbumin. G. BRUYNOCHE (Compt. rend. Soc. Biol., 1935, 118, 1260—1262).—Ovalbumin causes formation of antibodies and isoprecipitins when injected into fowls. R. N. C.

Influence of sodium caseinate on the iron content of dog's spleen and liver. C. ACHARD, M. BARIETY and F. GALLAIS (Compt. rend. Soc. biol., 1935, 118, 408—409).—The Fe content of the liver and spleen of normal dogs varies within wide limits. The mean vals. are 0.040 and 0.084%, respectively. Intravenous injection of Na caseinate doubles these vals. but the H_2O content remains const. A. L.

Seasonal variations in the muscle- and hepatic nitrogen of the green frog (*Rana esculenta*). A. GRADINESCO and C. DEGAN (Compt. rend. Soc. Biol., 1935, 118, 465—468).—The N contents of the muscle and liver of the female green frog decrease by

7 and 25%, respectively, in the post-hibernation period. In the male the variations are not so marked. A. L.

Influence of extirpation of the motility region of the brain on chemical changes in the muscles. S. FOMIN and S. EPELBAUM (Bull. Soc. Chim. biol., 1935, 17, 128—135).—Extirpation of one side of the mobility region (I) of the surface of the brain of the dog causes an increase in creatinephosphoric acid (II) and a decrease in inorg. P (III) in the paw muscle of the opposite side, although (II)+(III) remains unchanged. Proteolysis on the other side of (I) is the same before and after the operation.

A. L.

Component glycerides of hen body-fats. T. P. HILDITCH and W. J. STAINSBY (Biochem. J., 1935, 29, 599—605; cf. A., 1934, 913).—The component glycerides of the abdominal and gizzard fats of the hen (I) were studied by the methods previously described (this vol., 233). 40% (mol.) were monopalmitodioleins (II), 30% unsaturated tri- C_{18} -glycerides (III), and 30% di- C_{16} -mono- C_{18} -glycerides (IV). (II) consisted of β -monopalmitodioleins, (IV) largely of α -palmito-derivatives with 8% of palmitoleic acid. (I) fats are differentiated from those of the pig, sheep, and cow by their large proportion of (III) and (IV); these differences are reflected in the physical consistency of the fats.

H. D.

Phosphatides. XI. Fatty acids of the liver-phosphatides and of the liver-oil of the Greek tortoise (*Testudo graeca*). E. KLENK (Z. physiol. Chem., 1935, 232, 47—53; cf. this vol., 384).—The fatty acids of the liver-phosphatides consist of: saturated acids; C_{16} 15, C_{18} 10; unsaturated acids C_{16} 10, C_{18} 48, C_{20-22} 17% (mean degree of unsaturation C_{16} 2.0, C_{18} 2.8, C_{20-22} 5.7—6.5 H atoms). The vals. for the liver-oil are: saturated acids C_{14} 1, C_{16} 11, C_{18} 4; unsaturated C_{16} 9, C_{18} 66, C_{20-22} 3% (mean degree of unsaturation C_{16} 2.0, C_{18} 2.1, C_{20-22} 2.7—4.5 H).

J. H. B.

Depôt-fat of vertebrates. E. KLENK, F. DITT, and W. DIEBOLD (Z. physiol. Chem., 1935, 232, 54—63).—The depôt-fat of the Greek tortoise contains: saturated fatty acids (I) C_{14} 1, C_{16} 14, C_{18} 4; unsaturated (II) C_{16} 9, C_{18} 65, C_{20-22} 7% (mean degree of unsaturation C_{16} 2.0, C_{18} 2.4, C_{20-22} 3.2—5.3 H). The vals. for the lizard (*Varanus salvator*, Laurenti) are: (I) C_{14} 4, C_{16} 18, C_{18} 7; (II) C_{16} 10, C_{18} 56, C_{20-22} 5% (mean degree of unsaturation C_{16} 2.0, C_{18} 2.4, C_{20-22} 3.6—5.5 H), and for the rat: (I) C_{14} 2, C_{16} 25, C_{18} 3.5; (II) C_{16} 13, C_{18} 55, C_{20-22} 5% (?) [mean degree of unsaturation C_{16} 2.0, C_{18} 2.6, C_{20-22} 2.9(?)]. Thus the content of (II) C_{20-22} dependent on body-temp.

J. H. B.

Blood-cholesterol and fat and lipin contents of the adrenal cortex during pregnancy and after parturition. M. COPPOLA (Arch. Farm. sperim., 1935, 59, 232—244).—The variations in the blood-cholesterol (I) and in the wt. and ability (II) to stain with Sudan III of the adrenal cortex were followed in rabbits during pregnancy and *post partum*. (I) varies inversely to the wt. and (II).

F. O. H.

Blood-cholesterol and fat and lipin contents of the adrenal cortex of splenectomised animals.

A. LIGAS (Arch. Farm. sperim., 1935, 59, 210—219).—Splenectomy in rabbits produces a hypercholesterolaemia followed by increases in the content of substances stained by Sudan III, wt., and vol. of the adrenal cortex.

F. O. H.

Relation of lipin composition to physiological activity in ovaries of pregnant and pseudo-pregnant rabbits. E. M. BOYD (J. Biol. Chem., 1935, 108, 607—617).—The phospholipins (I), free cholesterol (II), and neutral fat (III) in the $EtOH-Et_2O$ extract of pregnant rabbits' ovaries attained a max. about 15 days after conception; the ester cholesterol (IV) at about the 25th day. (I), (II), and (IV) had dropped to their normal vals. at parturition, whilst (III) remained high. During pseudo-pregnancy similar changes occur.

H. D.

Liver-glycogen from derivatives of glucose. W. T. SALTER, P. D. ROBB, and F. H. SCHARLES (J. Nutrition, 1935, 9, 11—23).—Administration of glucose (I) to fasting mice is followed by storage in the liver of glycogen (II) in amounts \propto the quantity of (I) supplied. Stored (II) is utilised as fasting proceeds. Temporarily increased (II) contents were also observed after feeding sorbitol, Ca gluconate, glucosamine, methyl- and ethyl-glucosides, and propylene glycol.

A. G. P.

Isolation of components of human lipochrome. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1935, 231, 259—264).—The carotenoid pigments of human fat were separated by chromatographic analysis and determined by colorimeter. 1 kg. of depôt-fat (10% of H_2O) contained carotene 0.53, lycopene 0.24, xanthophyll 0.57, capsanthin 0.17 mg. β -Carotene was isolated.

J. H. B.

Influence of sympathetic stimulation on the chemical composition and physico-chemical properties of striated muscle. V. BORSUK, N. VERSHBINSKAJA, E. KREPS, N. MICHELSON, and V. STRELTZOV (J. Physiol. U.S.S.R., 1934, 17, 474—486).—The lactic acid, phosphocreatine, inorg. PO_4''' , hexose monophosphate, and adenylic acid contents of muscle are unaffected, and the P_2O_7''' content is increased at the expense of PO_4''' , by application of nicotine to the sympathetic ganglia of frogs during the isometric contraction of their leg muscles. Titration of suspensions of muscle indicated a rise in their buffer content.

R. T.

Glutathione in endocrine glands. M. T. REGNIER (Compt. rend. Soc. Biol., 1935, 118, 1060—1062).—The glutathione contents (determined as $\cdot SH$ compounds) of adrenal and pituitary glands (horse, ox) are high, those of the cortex and anterior lobe being $>$ those of the medulla and posterior lobe, respectively. Data are also given for thyroid, pancreas, testis, and muscle.

F. O. H.

Glutathione content and exercising capability of the muscles. K. WACHHOLDER and W. QUENSEL (Pflüger's Archiv, 1934, 235, 70—88).—The glutathione content (I) of resting human and animal muscles is highest in those muscles which are most often required for prolonged exercise; the single-jointed extensors for maintenance of posture contain more glutathione than the double-jointed extensors

used for movements of short duration. (I) is not associated with red coloration in muscles. (I) is high in all skeletal muscles of rabbits in the embryonic stage and during the first week of life, but falls in the less-used muscles during the second week.

R. N. C.

Influence of the sulphur mineral water of Tivoli (Acque Albule) on the content and distribution of glutathione in the organs. P. TESTONI (Annali Chim. Appl., 1935, 25, 81—93).—Gastric administration of this H_2O to rabbits for 60 days in 5 c.c. daily doses (corresponding with those prescribed for man) increases the glutathione (I) content of the adrenals, alters slightly that of the blood, lungs, liver, spleen, and muscles, and greatly diminishes that of the thyroid and kidneys, with a slight increase overall. When 10 c.c. daily doses were given, (I) decreased slightly in the liver, more in the thyroid, greatly in the kidneys, spleen, adrenals, and muscles, and still more greatly in the lungs and blood. Thus small doses of the H_2O slightly, and larger doses greatly, accelerate the oxidation-reduction processes in the various organs, with excessive consumption of (I), especially in organs which normally fix it in large amounts.

T. H. P.

Influence of the sulphur mineral water of Tivoli (Acque Albule) on the glutathione content of certain organs. A. SALAROLI (Annali Chim. Appl., 1935, 25, 93—110).—Rabbits tolerate this H_2O , even in large doses, and usually increase in wt. The glutathione content (I) of the blood is always reduced, but that of the tissues may increase. The liver (II) is affected little, but spleen (III) and adrenals (IV) show decrease in (I), when the H_2O is ingested in moderate doses (5—8 c.c.) over a long period (a month). Increases of (I) in (III) and especially in (IV), with little change in (II), are produced when the H_2O is given in (1) small doses over a short period, (2) increasing and then decreasing doses, or (3) doses at first large and afterwards decreasing.

T. H. P.

Nucleic acids of the pancreas. I. Thymonucleic acid. H. STEUDEL (Z. physiol. Chem., 1935, 231, 273—278).—The products of hydrolysis of the nucleic acid obtained from the residues from the prep. of pancreatic protein indicate that it is identical with thymonucleic acid.

J. H. B.

Heparin, a chondroitinpolysulphuric acid. E. JORPES (Naturwiss., 1935, 23, 196—197).—An air-dried heparin prep. (cf. A., 1933, 1317) contained 17—19% of hexuronic acid, 10—14% of hexosamine, 5.35—6.0% of Ac, 11.2% of S (3.3—3.6% directly pptd. by $BaCl_2$ in acid solution and 7.9—7.6% of org. S), 1.6—1.9% of N, and 40% of ash. The bound SO_4 was hydrolysed by $N-HCl$ at the b.p., but not at room temp. for 24 hr. The prep. was pptd. by basic, but not normal, Pb acetate or by $CdCl_2$, contained 500 Toronto units (*ibid.*) per mg., and was not replaceable by normal chondroitinsulphuric acid.

F. O. H.

Preparation of heparin from ox-lung. A. F. CHARLES and D. A. SCOTT (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 55—58).—For the prep. of heparin (I) from large amounts of material by the process described lung is better than liver. The average

yield of (I) is 2800 units per lb. Increased purity (15 units per mg.) of (I) is attained by fractional pptn. with EtOH followed by treatment with Lloyd's reagent in dil. AcOH.

W. McC.

Biochemistry of two Lepidoptera: the hive-mite, *Galleria mellonella*, and the silk-worm, *Bombyx mori*. C. MANUNTA (Mem. R. Accad. Lincei, 1935, 6, 75—161).—The oil of the chrysalis of *G. mellonella* consists chiefly of triglycerides (I); they are formed by the organism from constituents of the wax that cannot be utilised without undergoing profound modifications. Analytical vals. for the (I) and fatty acids of the oil are given. The hæmolymph of the yellow-blooded species of *B. mori* contains 100—150 times as much carotenoid (II) as that of the white species. Blood-carotenes (III) are always < xanthophylls (IV). At metamorphosis the pigments pass from the blood to the silk glands; the absorption is easily followed by studying their distribution in the cocoon. (III) and (IV) show distinct velocities of migration, which vary with the species. The (II) content of the ovular vitellus also varies with the species; (IV) are always present, but not necessarily (III) or flavones. In crossed species the egg-, blood-, and cocoon-pigments are all clearly influenced by both parents.

R. N. C.

Chemistry of insects. I. Wax of the felted beech coccus. B. K. BLOUNT (J.C.S., 1935, 391—393).—The wax $C_{52}H_{104}O_2$, m.p. 81—81.5°, excreted by *Cryptococcus fagi*, Barendsprung, on hydrolysis gave an alcohol (I), m.p. 77.5—78°, consisting of about 80% of the C_{26} with 20% of the C_{24} and C_{28} straight-chain alcohols and an acid (II), m.p. 81.1—82° (Et ester, m.p. 60.4—60.8°), consisting of 70—80% of the C_{26} and 30—20% of the C_{24} and C_{28} straight-chain acids. (I) on oxidation with CrO_3 -AcOH gave an acid, m.p. 81.5—82.3°, mixed m.p. with (II) 81.2—82°.

P. W. C.

3:4-Dihydroxyphenylacetic acid, a metabolic product of the meal-worm (*Tenebrio molitor*, L.) and its detection. H. SCHMALFUSS and G. BUSSMANN (Z. physiol. Chem., 1935, 231, 161—166).—The method permits the isolation of 0.01 mg. of 3:4-dihydroxyphenylacetic acid (I). (I) is found in the wing-covers of the living beetle (II) and in the pro-thorax of the dead (II).

J. H. B.

Chemistry of helminths. II. Chemical composition of *Taenia saginata*. I. A. SMORODINCEV and K. V. BEBESCHIN (Biochem. Z., 1935, 276, 271—273).—Tables show the H_2O , dry wt., ash, total N, and lipid contents of the head, middle, and tail portions of *T. saginata* and the normal variations in these vals. The head portion is characterised by high lipid- and total N and the tail portion by high ash.

P. W. C.

Red pigment in the skin of goldfish. E. LEDERER (Compt. rend. Soc. Biol., 1935, 118, 542—544).—Astacene is isolated from the skin of *Beryx decadactylus* and *Carassius auratus* by extraction with $COMe_2$ followed by alkaline hydrolysis and extraction with EtOH.

A. L.

Cetacea. XLV. Nitrogenous compound from the muscle of the finback whale. T. YAZAWA

(Japan. J. Med. Sci., 1935, II, 3, 15—17; cf. A., 1933, 736).—The base (I) related to lysine is $C_{10}H_{17}O_2N_3(NH_2) \cdot CO_2H$, m.p. 261—263°, $[\alpha]_D^{20} +30.7^\circ$ (platinchloride, decomp. 230—232°; Cu salt, decomp. 202—205°). (I) is pptd. from hot H_2O by EtOH.

W. McC.

Detoxication of isotonic sodium chloride solutions by potassium (but not by calcium) in certain marine Crustacea. A. BETHE (Pflüger's Archiv, 1934, 234, 645—647; Chem. Zentr., 1934, ii, 2735).—The antagonism of K towards Na in respect of Crustacea is much $>$ that of Ca. In fish the reverse is the case.

A. G. P.

Acetone and β -hydroxybutyric acid content of the tissues after injection of acetone in healthy animals. P. VALDIGUIE (Compt. rend. Soc. Biol., 1935, 118, 858—860).— $COMe_2$ accumulates in the kidneys, lungs, liver, spleen, pancreas, brain, blood, and cerebrospinal fluid, but is almost absent from muscles. β -Hydroxybutyric acid rises in all tissues after injection of $COMe_2$, the increase being $>$ that of $COMe_2$ in the tissues, but $<$ that of $COMe_2$ in the serum.

R. N. C.

Staining of recently deposited calcium by alizarin-red. N. B. TAYLOR, H. D. BRANON, and W. R. GRAHAM (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 29—31).—Subcutaneous or oral administration of Na alizarin-red sulphionate (I) to growing rats, rabbits, chickens (II), and dogs results in staining of recently deposited bone. The shells of the eggs of hens receiving (I) are not stained. Trypan-blue injected into young (II) does not produce sp. staining of bone. Possibly presence of P is essential for intravital staining of Ca.

W. McC.

Phosphovanillic reaction. (A) With lung. (B) With other tissues. E. CHABROL, R. CHARONNAT, and J. COTTET (Compt. rend. Soc. Biol., 1935, 118, 980—982, 982—983).—(A) Bile acids (cholic) on heating at 100° with H_3PO_4 and adding vanillin (6:1000) give a pink colour (I) which subsequently becomes yellow and then violet. The time required to reach max. (I) \propto the amount of H_2O present. (I) is destroyed by addition of 2—3 vols. of H_2O , and is not given by indole or pyrrole or their derivatives (tryptophan), phenols, or aromatic amines. Extracts of dogs' lungs always give (I).

(B) Extracts of many other tissues (e.g., liver, pancreas, spleen, small intestine, but not adrenals) react positively to the test.

W. McC.

Influence of electrolytes on the physico-chemical properties of colloidal systems comparable with cytoplasm. II. Influence of salts on the viscosity of egg-yolk solutions of different concentration. B. ZAWADZKI (Protoplasma, 1935, 22, 616—628; cf. A., 1934, 327).—The action of NaCl, KCl, and $CaCl_2$ in increasing the viscosity of egg-yolk (I) persists in 20—70% solutions of (I). Max. vals. are obtained with 0.2M-NaCl and -KCl and with 0.1M- $CaCl_2$, min. vals. being reached with 0.4M for all salts. Viscosity of undiluted yolk is probably affected considerably by very small alterations in H_2O or salt contents.

A. G. P.

Absorption spectra of acids from fish-liver oils. J. R. EDISBURY, R. A. MORTON, and J. A. LOVERN (Biochem. J., 1935, 29, 899—908).—Partly successful attempts have been made to isolate and identify the unsaturated C_{22} and C_{20} acids which show a highly selective absorption. Changes in absorption may be due to cyclisation of the acids to give hydroaromatic polycyclic derivatives.

H. T.

"Menstruation poisons." H. MOMMSEN (Münch. med. Woch., 1934, 81, 1458—1460; Chem. Zentr., 1934, ii, 3133).—The "menstruation poison" is present in human milk, and is eliminated by the thymus at intervals of 3—4 weeks after birth. It is probably a biogenic amine resulting from lipin metabolism.

R. N. C.

Relation of sodium to chlorine in the milk of shorthorn and Guernsey cows. T. S. G. JONES and W. L. DAVIES (Biochem. J., 1935, 29, 978—981).—Na should be determined by the "triple acetate" gravimetric method. The relation between Na and Cl in the milk of shorthorn and Guernsey cows is given by the equation $Cl \text{ (mg. per 100 ml.)} = 1.24 \times Na \text{ (mg. per 100 ml.)} + 18.09$.

A. E. O.

Iodine content of milk as affected by feeding iodised dry milk. Z. M. HANFORD, G. C. SUPPLEE, and L. T. WILSON (J. Dairy Sci., 1934, 17, 771—780).—Seasonal variations in I content of milks are recorded. The % I recovery in milk at comparable periods is of the same magnitude, irrespective of the form in which it is supplied. The % and total output of I in milk are increased by feeding org. I, e.g., iodised dry milk. No parallelism is apparent between the total I output, % I recovery, and the I ingested.

A. G.

Milk and butter-fat yields of Jersey cows as affected by frequency of milking. L. COPELAND (J. Dairy Sci., 1934, 17, 815—821).—Increasing the no. of milkings from 2 to 3 daily increased the yields of milk and of butter-fat.

A. G. P.

Biological food value of milk. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 138—140).—The power of milk to reduce methylene-blue is lost on diluting with H_2O . Addition of 1 c.c. of broth (itself non-reducing) to 5 c.c. of this dil. milk restores the reducing power completely. Peptone and beef-albumin do not possess this action.

P. W. C.

Electrokinetics in relation to dairy phenomena.

I. Theory and method. G. C. NORTH and H. H. SOMMER (J. Dairy Sci., 1935, 18, 21—43).—The electrical condition of the fat-serum interface is examined by a method based on the theory of streaming potentials. The isoelectric point of the interface is p_H 4.3 approx. The effects on the electrokinetic potential of additions of chlorides of K, Ca, Fe, and Th, of Na_2HPO_4 , and Na citrate are examined.

A. G. P.

Increase of milk secretion by antithyroid protector. H. KUSTNER (Münch. med. Woch., 1934, 81, 1261—1262; Chem. Zentr., 1934, ii, 2701).—Lactation, inhibited by thyroxine, is restored by antithyroidin, which weakens the thyroid function.

R. N. C.

Calcium and phosphorus in human cerebrospinal fluid. W. L. DULIERE and R. MINNE (Compt. rend. Soc. Biol., 1935, 118, 1262—1264).—The Ca and free H_2PO_4 contents of the fluid (I) are 60% and 26%, respectively, of those of serum. (I) cannot be considered as an ultrafiltrate from plasma; it contains no phosphatase. R. N. C.

Prolan content of cerebrospinal fluid, particularly in essential hypertonia. T. KJELLIN and E. KYLIN (Deut. Arch. klin. Med., 1934, 176, 683—689; Chem. Zentr., 1934, ii, 3134—3135).—The prolane content is increased in essential hypertonia and nephropathia gravidarum. R. N. C.

Detoxifying action of ox-bile. M. D. SMITH and P. J. MOLONEY (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 111—118; cf. A., 1934, 454).—The heat-labile component (I) of the detoxifying agent is destroyed by heating at 100° for 20 min. (p_H 2—8), but is unaffected by freezing and only partly destroyed by drying in vac. (I) is completely pptd. from aq. solution at p_H 5.5 by EtOH (5 vols.), but not by $Pb(OAc)_2$. C adsorbs (I), which does not give the biuret, xanthoproteic, Millon, or Molisch reactions. $Pb(OAc)_2$ and $FeCl_3$ ppt. the heat-stable component (II) from aq. solution. (II) withstands treatment with conc. acid or conc. alkali; it is sol. in EtOH, $C_5H_{11}OH$, and PhOH. Diphtheria toxin (III) removes (I) and (II) from adsorption on $FeCl_3$ and (II) from adsorption on gelatin. (I)+(II) administered to guinea-pigs (IV) after or before they receive injections of (III) have no detoxifying effect. Horse-serum (IV)-serum inhibits detoxification. W. McC.

Histamine and the bile secretion. G. BALTA-CEANO and C. VASILIU (Compt. rend. Soc. Biol., 1935, 118, 599—603).—Subcutaneous injection in the dog of small doses (1 mg.) of histamine causes little change in the quantity and constituents of the bile (I). Larger doses (5 mg.) increase both the quantity of (I) and that of the (I) salts, but the cholesterol decreases. A. L.

Effect of colloids on formation of calculi.—See this vol., 580.

Secretion of mucus and acid by the stomach in healthy persons and in persons with peptic ulcer. H. NÉCHELES and A. COYNE [with H. GROSS] (Arch. Int. Med., 1935, 55, 395—402).—Injection of pilocarpine (I) causes an increased secretion of mucus in normal persons but not in cases of ulcer (II); a decreased secretion is obtained in persons who drink alcohol. Gastric resting acidity (III) does not vary with age, but, in cases of (II), the acid content above 40 years is > that below. After (I), (III) of normal persons above 40 years was the only group to show a decrease. H. G. R.

Extrapalleal liquid of *Anodonta* is not identical with the blood of this animal. M. FLOKIN and G. BESSON (Compt. rend. Soc. Biol., 1935, 118, 1222—1224).—The catalase of the extrapalleal liquid of *Anodonta cygnea* is not present in the plasma. R. N. C.

Products of partial hydrolysis of silk fibroin. R. L. GRANT and H. B. LEWIS (J. Biol. Chem., 1935, 108, 667—673).—Changes in the total, NH_2 , and

tyrosine-N (I) in silk fibroin with varying times of hydrolysis with 70% H_2SO_4 were determined. After 75 min. at 30° the product on removal of H_2SO_4 was separated into H_2O -insol. and -sol. fractions containing different amounts of NH_2 -N and (I). H. D.

Human tyrosinuria. M. MITOLO (Atti R. Accad. Lincei, 1934, [vi], 20, 472—474).—Under normal conditions a minute amount of tyrosine is excreted in the urine. T. H. P.

Determination of urinary phenols, particularly in *post-partum* and cancerous states. L. SERVANTIE and A. BARON (Compt. rend. Soc. Biol., 1935, 118, 147—149).—Urinary phenols (I) are determined by Marenzi's colorimetric method. The ratio conjugated/total (I) falls rapidly during the first few days of puerperium, rising again after the 7th. In untreated cancer the ratio is almost always > 30%. R. N. C.

Colorimetric determination of urinary indican by means of ninhydrin. T. KUMON (Z. physiol. Chem., 1935, 231, 205—207).—With indoxyl, ninhydrin yields a violet-red compound, $C_{11}H_9O_3N$, m.p. 240° (decomp.). The reaction may be employed in the colorimetric determination of urinary indican. J. H. B.

Acid-base balance of the body. Determination by analysis of urine and an interpretation of variants in analytical data. G. RODILLON (Bull. biol. Pharm., 1934, 253—290).—Analyses of urinary constituents permit calculation of acid-base balance of the body. CH. ABS. (p)

Post-operative variations of urinary sulphur. S. DELAUNEY and J. GOSSET (Compt. rend. Soc. Biol., 1935, 118, 843—845).—Urinary S increases considerably during the first few days after operation, and blood-S is also disturbed. R. N. C.

Interpretation of urine analysis in diagnosis. G. F. BODDIE (Vet. Rec., 1935, 15, 219—222).—Descriptive. R. N. C.

Determination of uric acid in the mixed excrement of birds. J. C. FRITZ (Ind. Eng. Chem. [Anal.], 1935, 7, 123—124).—A method is described in which the difference in total N between two identical samples, one extracted with piperidine and the other not, measures the uric acid content. This and Suzuki's method (A., 1932, 1156) are the most accurate of many which were tried. J. L. D.

Determination of indigestible residue (crude fibre) in faeces: lignin, cellulose, and non-water-soluble hemicelluloses. R. D. WILLIAMS and W. H. OLMSTED (J. Biol. Chem., 1935, 108, 653—666).—Remy's enzymic digestion (A., 1931, 1198) and taka-diastase digest the hemicelluloses (I) of faeces. Pancreatin (II) removes the starch without loss of (I). Faeces treated with (II) are extracted with 21.4N- H_2SO_4 at 6—10°; lignin is pptd. and (I) and cellulose (III) are converted into sugars by boiling the diluted extract. Lignin is weighed, and (I) and (III) are determined with the Shaffer-Somogyi reagent (A., 1933, 699) before and after fermentation (A., 1928, 912). The Weende technique gives variable losses of (I), (III), and lignin. H. D.

Distribution of organic acids in human sweat. J. COURAUD (Compt. rend. Soc. Biol., 1935, 118, 155—156).—The total Et_2O -sol. org. acids of the sweat are equiv. to 12—40 c.c. of 0.1N-acid per 100 c.c. The average volatile acid (I) content is 15%, and average lactic acid (II) 75%, of the total acid. Sweats from the trunk contain considerable quantities of acids other than (I) and (II).

R. N. C.

Effect of yeast extract in anæmias. II. Nature of the hæmopoietic factor in yeast effective in pernicious anæmia. C. C. UNGLEY and G. V. JAMES (Quart. Med. J. [N.S.], 1934, 3, 523—548).—The factor was present in the 65% EtOH -sol. extract of fresh yeast. Its potency did not increase with autolysis. Many cases of pernicious anæmia retain the power to secrete the intrinsic factor (I) and the response to yeast is a measure of this activity. No parallelism exists between vitamin- B_2 potency and (I). There is no correlation between the secretion of (I) and that of acid, pepsin, or Cl^- .

CH. ABS. (p)

Atherosclerosis, chemical, experimental, and morphologic: rôles of cholesterol metabolism, blood-pressure, and structure of the aorta; fat angle of the aorta (F.A.A.) and the infiltration-expression theory of lipin deposit. S. R. ROSENTHAL (Arch. Path., 1934, 18, 473—506, 660—698).—The fat content of aortas increased \propto age and severity of atherosclerosis (I). A mathematical relationship is established. Cholesterol metabolism is concerned in the production of (I).

CH. ABS. (p)

Iodine treatment in Basedow's disease. H. DENNIG and E. SCHUELKE (Münch. med. Woch., 1934, 81, 1263—1265; Chem. Zentr., 1934, ii, 2998—2999).—I is most effective administered intermittently; di-iodotyrosine is effective \propto its I content.

R. N. C.

Vitamin- B_2 and canine black tongue. C. P. RHOADS and D. K. MILLER (Science, 1935, 81, 159).—Autoclaved yeast extract, but not Fe or carotene, is an effective preventive. The disease is due to a deficiency not of vitamin- B_2 but of an unidentified factor.

L. S. T.

Effect on experimental tumours of the product obtained by the action of ferric chloride on ascorbic acid. F. ARLOING, A. MOREL, and A. JOSSERAND (Compt. rend. Soc. Biol., 1935, 118, 551—554).—Ascorboferrin, the violet-coloured substance obtained by adding FeCl_3 to ascorbic acid, injected subcutaneously into mice suffering from experimental epithelioma, and intravenously into rabbits having experimental testicular cancer, caused in both cases a progressive regression of the tumours.

A. L.

Production of uterine tumours in rabbits by ovarian hormone. H. PIERSON (Z. Krebsforsch., 1934, 41, 103—138; Chem. Zentr., 1934, ii, 3134).—The cancer-like tumours produced by brushing with tar and injection of folliculin are described.

R. N. C.

Deposition of magnesium compounds in tumours. F. EICHHOLTZ and W. KAUDERER (Biochem. Z., 1935, 276, 326—330; cf. Kluge, A., 1932,

80).—After subcutaneous injection into rats of MgCl_2 or MgSO_4 the Mg content of multiple inoculation sarcoma (I) increases (max. reached in 4 hr.) and then falls to the original val. after 8 hr. Mg pyrocatechol-disulphonate produces no increase. The amount of Mg which penetrated to (I) is only about a quarter of the corresponding Ca penetration following Ca injection. Mg injection affects neither the Ca content of (I) nor the sensitivity of (I) to X-ray irradiation (II). The increase in the sensitivity of (I) to (II) produced by injection of Ca salts reaches its max. in 15 min. and is independent of the amount of Ca which reaches (I).

W. McC.

Effect of X-ray irradiation on the colloidal state and amino-acid content of rat sarcoma. P. SZENDRO, E. SCHLEICHER, and L. KLUGE (Biochem. Z., 1935, 276, 331—335; cf. Eichholtz, A., 1931, 976).—Periods of irradiation (I) with X-rays sufficient greatly to restrict growth have no effect on the iso-electric point or N content of extracts of rat sarcoma (II). The tyrosine, tryptophan, and cystine contents of (II) are not affected by (I). The NH_2 -acid content of the non-coagulable proteins of (II) is also unaffected by (I).

W. McC.

[Blood-sugar and reducing power in] blood of cancerous subjects during treatment with radium. C. GRANDCLAUDE, M. POLONOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 118, 987—989).—Repeated exposure to Ra (I) produces progressive great (to 50%) decrease in the blood-sugar of cancer patients. If these have not previously undergone physical treatment the reducing power ($\text{K}_2\text{Cr}_2\text{O}_7$) of the deproteinised blood is rapidly decreased by (I) and frequently remains low after (I).

W. McC.

Surface tensions of carcinogenic substances. W. KOPACZEWSKI (Compt. rend. Soc. Biol., 1935, 118, 1142—1145).—Addition of most carcinogenic substances to serum (I) produces a lowering of σ ; salts of multivalent cations are an exception. Hydrocarbons insol. in (I) exert their effect by dissolving out the (I)-lipins.

R. N. C.

Action of some normal or pathological liquids and therapeutic products on the fluorescence of uranin solutions. A. BOUTARIC and J. BOUCHARD (Compt. rend. Soc. Biol., 1935, 118, 1188—1189).—Fluorescence of uranin is reduced by cancerous sera, but not by other pathological, normal, or therapeutic sera, ascitic fluid, pleural effusions, or diphtheria toxin. The action appears to be one of retardation of cellular oxidation.

R. N. C.

Cataract in rats fed on high-lactose rations. H. S. MITCHELL and W. M. DODGE (J. Nutrition, 1935, 9, 37—49).—Mature bilateral cataract occurred in rats receiving a high-lactose ration, but not when starch, maltose, dextrin, or sucrose was supplied as sole source of carbohydrate (I). Affected animals showed disturbance of (I) and mineral metabolism with a loss of galactose in urine. The Ca content of the eyes was twice normal, but serum-Ca was not appreciably altered.

A. G. P.

Diabetes and hyperthyroidism. E. P. JOSLIN and F. H. LAHEY (Ann. Surgery, 1934, 100, 629—

637).—After surgical relief of hyperthyroidism there is an increase in carbohydrate tolerance of ± 30 g., and a marked diminution in the need for insulin.

CH. ABS. (p)

Blood-cholesterol and creatinine excretion in the urine as aids to diagnosis and treatment of hypothyroidism. J. H. HESS (Ann. Int. Med., 1934, 8, 607—611).—Thyroid medication reduces the high blood-cholesterol in children with hypothyroidism (I). From infancy to puberty creatinuria is physiological. (I) causes reduction of creatinine excretion which is restored by administration of thyroid extract.

CH. ABS. (p)

Toxic diphtheria : significance of sugar-tolerance curves and the value of insulin. N. D. BEGG (Lancet, 1935, 228, 480—484).—In diphtheria (I) the response of the body to intravenous glucose is always abnormal and results in higher vals. for blood-sugar. The degree of variation is a trustworthy guide to the progress of (I). Insulin has no effect on the abnormal sugar-tolerance curves or on the course of (I).

L. S. T.

Role of histamine in inflammation. J. R. E. MORGAN (Arch. Path., 1934, 18, 516—523).—Histamine (I) acts on the skin capillaries causing dilatation and engorgement with a slowing of the bloodstream and exudation of fluid. The part played by (I) in inflammation is limited to this effect.

CH. ABS. (p)

[Direct and indirect] bilirubin in catarrhal icterus. B. VARELA-FUENTES and C. VIANA (Compt. rend. Soc. Biol., 1935, 118, 927—930).—Both direct and indirect bilirubin rise rapidly in the first few days of catarrhal icterus, afterwards falling more slowly. Anomalies occur in grave icterus.

R. N. C.

Lactic acid and glucose in the blood during Addison's disease as influenced by cortical hormone. J. A. COLLAZO and J. BARBUDO (Arch. med. chirurg. esp., 1933, 36, No. 18).—The basal lactic acid content averaged 25 mg. in diseased and 14 mg. per 100 c.c. in normal cases. Cortical hormone treatment caused this val. and the blood-sugar content to approach normal.

CH. ABS. (p)

Nitrogen and sulphur metabolism in Bright's disease. VI. Effect of diets low in sulphur on excretion of sulphur. G. P. GRABFIELD and L. G. ADAMS (Arch. Int. Med., 1935, 55, 360—370).—The diminution of the excretion of S in cases of Bright's disease with low serum-protein vals., on a low-S diet, was $>$ normal.

H. G. R.

Secretion of ammonia in experimental nephritis. M. POLONOVSKI, G. BIZARD, and P. BOULANGER (Compt. rend. Soc. Biol., 1935, 118, 989—990).—In dogs suffering from acute $\text{UO}_2(\text{NO}_3)_2$ nephritis (I) the NH_3 contents of the blood (renal and femoral vein and artery) and urine before and after intravenous injection of $(\text{NH}_4)_2\text{CO}_3$ or alanine show that (I) greatly diminishes excretion but does not affect secretion of NH_3 .

W. McC.

Diazo-values of blood and urine in acute uranium nephritis in the dog. G. BARAC (Compt. rend. Soc. Biol., 1935, 118, 1250—1251).—The

diazo-vals. increase considerably, indicating an increased formation of substances giving the diazo-reaction in alkaline solution.

R. N. C.

Uranium glycosuria : its modifications in experimental hypoglycæmia from insulin. R. WEEKERS (Compt. rend. Soc. Biol., 1935, 118, 1252—1253).—Injection of insulin in dogs with $\text{UO}_2(\text{NO}_3)_2$ nephritis lessens glycosuria (I) or the fall in blood-sugar (II). A large fall in (II) does not abolish (I) entirely. Injection of phloridzin causes a rise of (I) in spite of the low (II).

R. N. C.

Sugar metabolism in experimental nephritis from uranium nitrate. R. WEEKERS (Compt. rend. Soc. Biol., 1935, 118, 1254—1255).—The distribution of glucose between plasma and corpuscles is not altered in the course of $\text{UO}_2(\text{NO}_3)_2$ glycosuria, nor is the permeability of the corpuscular membrane to glucose.

R. N. C.

Ochronosis of cattle. III. H. FINK and W. HOERBURGER (Z. physiol. Chem., 1935, 232, 77—78; cf. A., 1932, 81).—In an ox with ochronosis a section of the tubular bone of the fore-leg showed concentric bands, indicating deposition of the pigment in layers.

J. H. B.

Plasma-proteins and cardiac œdema. W. A. R. THOMPSON (Quart. J. Med., 1934, [ii], 3, 587—601).—Cardiac œdema causes a decrease in plasma-protein.

CH. ABS. (p)

Differentiation of normal and paludic serum-globulin by the serum-flocculation reaction of Henry for paludism. F. TRENSZ (Compt. rend. Soc. Biol., 1935, 118, 1076—1077).—The euglobulin of paludic sera differs from that of normal sera by its flocculation reactions (in which only a part of the euglobulin participates) with melanin, especially when the latter is purified.

F. O. H.

Cinchona alkaloids in pneumonia. I. Miscellaneous alkaloids and some hydrocupreine ethers.—See this vol., 636.

Salt metabolism in pregnant women. E. LEVY-SOLAL and M. LAUDAT (Compt. rend. Soc. Biol., 1935, 118, 977—980).—Removal (I) of NaCl from the diet of pregnant (6—9 months) women causes increase in urinary vol. with continued excretion of NaCl, the effects being more marked than in non-pregnant women (II) similarly treated. (I) causes increase in the protein and alteration in the globulin/albumin ratio in the blood, the alterations being less regular than in (II). Restoration of NaCl to the diet re-establishes the original conditions.

W. McC.

Weight curve and Benedict test during pregnancy. H. W. LAWSON (Med. Ann. Dist. Columbia, 1934, 3, 153—155).—Positive tests for sugar in pregnancy urine were obtained in 47% of first-month tests, 12% in second-month, and up to 54% at later stages.

CH. ABS. (p)

Phosphorus and rickets. IV. Elementary phosphorus and experimental rickets. R. LECOQ and R. GALLIER (J. Pharm. Chim., 1935, [viii], 21, 211—215).—Yellow P, when fed to rats in dil. solution in certain vegetable oils, has no antirachitic power.

A. E. O.

Experimental rickets. VI. Influence of magnesium salts. F. ROGOZIŃSKI and Z. GŁÓWCZYŃSKI (Bull. Acad. Polonaise, 1934, B, 197—208, and Bull. Soc. Chim. biol., 1935, 17, 88—95).—Partial substitution of Ca by Mg in the diet exerts a favourable influence on the calcification of the bones of rats fed on a rachitogenic diet poor in P and rich in Ca. Total substitution of Ca by Mg or addition of excess of Mg has no such effect and growth is arrested. Addition of excess of Mg has no effect on growth or calcification with rats fed on a diet adequate in both Ca and P, or rich in P and poor in Ca. A. E. O.

Influence of a local excess of calcium and phosphorus on the healing of fractures. K. O. HALDEMAN and J. M. MOORE (Arch. Surgery, 1934, 29, 385—396).—In normal healing excess of Ca or P did not effect or retard union. In delayed healing $\text{Ca}_3(\text{PO}_4)_2$ at the site favoured union. CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and Ca glycerophosphate had no favourable influence. CH. ABS. (p)

Vasodilatation and local liberation of histamine-like substances. J. TINEL and G. UNGAR (Compt. rend. Soc. Biol., 1935, 118, 1148—1149).—Local vasodilatation is accompanied by an increase in gastric secretion through liberation of histamine-like substances, which is controlled by certain nerve-elements. R. N. C.

Liberation of histamine-like substances in states of shock. J. TINEL, G. UNGAR, and M. R. ZERLING (Compt. rend. Soc. Biol., 1935, 118, 1150).—Colloidal and anaphylactic shock are accompanied by increased gastric secretion. R. N. C.

Acute silicosis. R. POMERANZ (J. Med. Soc. New Jersey, 1933, 30, 320—323).—Progressive fibrosis occurs even after removal from exposure to SiO_2 , and is a defence action against the toxic chemical and colloidal effects on the cells. CH. ABS. (p)

Calcium in tuberculosis. G. CAPUANI (Arch. Ist. Biochim. Ital., 1935, 7, 69—122).—Protein-Ca, the total : diffusible Ca ratio, and $[\text{Ca}] \times [\text{P}]$ are all decreased in tuberculosis in man. Injection of Ca decreases the time of coagulation of blood and the velocity of sedimentation of the red corpuscles, the effect of CaCl_2 being $>$ that of Ca gluconate (I). Whilst total blood-Ca (II) is increased by all Ca salts, diffusible Ca (III) shows a small transient increase with CaCl_2 , and is unaffected by (I). Ca excretion in the urine \propto the quantity of sol. Ca, and hence is greater with CaCl_2 . (II) remains high for a considerable period after cessation of Ca therapy, and then falls slowly to normal; (III) behaves similarly, whilst P shows a slight rise when Ca begins to fall. Results are given for other applications of Ca therapy, including its association with Ca-fixing agents. R. N. C.

Borders of physics and biology. C. E. GUYE (Arch. Sci. phys. nat., 1935, [v], 17, 5—33).—Philosophical. A general discussion of the temp. limits of survival of living matter, and of probabilities in relation to the asymmetry of complex systems (e.g., mols. of high mol. wt.). F. A. A.

Growth and development. XXXIV. Basal metabolism, endogenous nitrogen, creatinine,

and neutral sulphur excretions as functions of the body-weight. S. BRODY, R. C. PROCTER, and U. S. ASHWORTH (Missouri Agric. Exp. Sta. Res. Bull., 1934, No. 220, 40 pp.; cf. A., 1934, 212).—Among animals of different species and widely varying body-wt. (W), the basal metabolism, endogenous N and neutral S excretions $\propto W^{0.75}$. Creatinine excretion $\propto W^{0.90}$. Prediction tables and maintenance ration standards based on these findings are given. A. G. P.

Basal metabolism and diet of normal young college women in Florida. J. TILT and C. F. WALTERS (J. Nutrition, 1935, 9, 109—117).—Data obtained show no consistent relationship between basal metabolism and protein or caloric intake. A. G. P.

Basal metabolism as a function of corpulence. R. FAILLIE and W. LIBERSON (Compt. rend. Soc. Biol., 1935, 118, 1151—1153).—The basal metabolism in a no. of cases of "gabarit" was independent of age, wt., and size. R. N. C.

Influence of nutrition on working metabolism. II. Action of various proteins. F. BRUMAN and O. BAUMGARTNER (Deut. Arch. klin. Med., 1934, 176, 519—525).—Resting O_2 consumption is the same whether the diet is rich in meat-protein (I) or in caseinogen. Vals. during work and in subsequent recovery are higher for (I). A. G. P.

Energy metabolism of the albino rat in relation to the plane of nutrition. E. B. FORBES, M. KRISS, and R. C. MILLER (J. Nutrition, 1934, 8, 535—552).—Increments in heat production with rising levels of feeding became progressively greater between the planes of basal and full rations. A. G. P.

Specific dynamic effects of protein, fat, and carbohydrate as determined with the albino rat on different planes of nutrition. M. KRISS, E. B. FORBES, and R. C. MILLER (J. Nutrition, 1934, 8, 509—534).—The sp. dynamic effects resulting from additions to a basal ration of caseinogen, starch, and olive oil were $>$ the corresponding increases in heat production over the fasting metabolism. Heat-increment vals. corr. for the sparing of body-protein (I) and -fat agreed with the corresponding vals. obtained at $>$ maintenance level. Heat produced by catabolism of (I) includes a factor of waste heat of utilisation. A. G. P.

Effect of thyroxine on the basal metabolic rate. (A) Adult rabbit. (B) Growing rabbit. E. LE BRETON and G. SHAEFFER (Compt. rend. Soc. Biol., 1935, 118, 445—448, 448—450).—(A) By subcutaneous injection of thyroxine (I) in adult rabbits it is possible to increase the basal metabolic rate (II) threefold. In one case a val. of 6 g.-cal. per kg. per hr. was reached.

(B) The increase (III) in the (II) of growing rabbits after (I) injection depends on the initial (II). When (II) is > 4 , between 3.5 and 4.0, and between 3.0 and 3.5, (III) is nil, 25, and 70%, respectively. A. L.

Variations of p_{H} and alkaline reserve in the course of intoxication by water (alone or associated with posterior pituitary extract) and by

guanidine. J. L. WODON and J. LEDRUT (Compt. rend. Soc. Biol., 1935, **118**, 1212—1214).—The alkaline reserve (I) and p_H are only slightly altered by ingestion of large quantities of H_2O , with or without posterior pituitary extract. Guanidine causes a fall in (I) and p_H . R. N. C.

Water exchange. VII. Effect of acids and alkalis on diuresis, when administered orally in starvation. VIII. Importance of acidogenic or alkaligenic character of the diet on hydration of the tissues. M. SAVIANO (Boll. Soc. ital. Biol. sperim., 1934, **9**, 1272—1273, 1273—1276).

R. N. C.

Alkaline reserve, p_H , and shell-casting of brachyural Crustacea. A. DRILHON (Compt. rend., 1935, **200**, 1150—1152).—The alkaline reserve shows a rapid increase to a max. at the moment of shell-casting, followed by a slow diminution. The p_H also rises to a max. at the same instant. R. N. C.

Effect of traumatism on the distribution of chlorine and sodium between the blood and the tissues, and on acid-base equilibrium. H. CIABANIER, C. LOBO-ONELL, A. DE CASTRO-GALHARDO, and E. LELU (Compt. rend. Soc. Biol., 1935, **118**, 1196—1198).—Muscle-Cl and -Na increase steadily after 1—2 hr. of trauma; at 24—48 hr. Cl increases more rapidly than Na. Plasma- and corpuscle-Cl and the corpuscle: plasma-Cl ratio increase after 1—2 hr., but fall after 24—48 hr. Blood-Na increases more rapidly than Cl, and continues to rise when Cl falls. The alkaline reserve and plasma p_H fall after 2 hr., rising again after 24 hr. to vals. > the initial val.; acid-base equilibrium is thus shifted in turn towards acidosis and alkalosis. R. N. C.

Alkaline reserve during metamorphosis of *Lepidoptera*. A. DRILHON (Compt. rend. Soc. Biol., 1935, **118**, 131—132).—During metamorphosis (I) CO_2 content rises steadily to a max. at 48 hr. after enclosure of the larva, afterwards falling progressively as (I) proceeds; it is concluded that the CO_2 is utilised for the purposes of (I). R. N. C.

Water content of the bio-plasma and the thermal coefficient of oxidation. J. BLEHRADSKÝ and J. MLADEK (Protoplasma, 1934, **21**, 335—339; Chem. Zentr., 1934, ii, 3127).—Examination of the O_2 consumption of larvæ of *Tenebrio molitor* shows a higher thermal coeff. of oxidation with lower H_2O content. A. G. P.

Effect of potassium and calcium chlorides on the respiratory metabolism of nerve. S. N. KAGANOVSKAJA and A. G. SCHLIKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 256—261).—The O_2 uptake of the isolated frog's ischiadicus is decreased by about 30% in presence of KCl, whilst CaCl₂ has either no action or increases it by about 40%. W. O. K.

Oxygen consumption of the cockroach in relation to moulting. D. L. GUNN (Nature, 1935, **135**, 434—435).— O_2 consumption increases just after moulting. L. S. T.

Apparatus for determining the gaseous metabolism of small animals. J. PELYI (Biochem. Z., 1935, **276**, 376—382).—Increased accuracy is attained

in the simple apparatus described because the O_2 consumption is directly determined. W. McC.

Indicator for the passage of food through the alimentary tract of animals. E. L. TAYLOR (Nature, 1935, **135**, 434).—Lycopodium powder is satisfactory. L. S. T.

Utilisation of meat by human subjects. I. Utilisation of the nitrogen and phosphorus of loin and heel cuts of beef. M. S. PITTMAN, R. B. McCAMMON, and M. HOLMAN (J. Nutrition, 1934, **8**, 503—507).—Loin is a slightly better source of N and P than heel. Differences in utilisation are more marked in the case of N. A. G. P.

Protein requirement of pre-school children. A. L. DANIELS, M. K. HUTTON, E. M. KNOTT, O. E. WRIGHT, G. J. EVERSON, and F. SCOLLAR (J. Nutrition, 1935, **9**, 91—107).—Elimination of creatinine, taken as a measure of muscle requirement, gives more consistent data than other methods for the protein (I) demand. For children from 37 to 66 months old vals. approximate to 3.2 g. of (I) per kg., of which < 50% should be from animal sources. A. G. P.

Nutritive value of various proteinaceous food-stuffs. M. KASPER (Biochem. Z., 1935, **276**, 215—222).—In rats the dry wt., carbohydrate content, and vacate-O of the faeces (I) and the C : N and vacate-O : N ratios of the urine are usually greater on a vegetable than on an animal protein (II) diet, whilst the N content of (I) with lentil- and bean-meal protein was > and with pea-meal protein the same as with (II). P. W. C.

Nutritive value of winter-wheat straw. J. SOTOLA (Rec. Proc. XXVI Ann. Mtg. Amer. Soc. Animal Prod., 1933, 189—192).—Analytical data are given. CH. ABS.

Amino-acid composition of the more important dietary proteins. IV. Hen's eggs. V. Optimum amino-acid composition of dietary protein. A. E. SCHARPENAK, O. N. BALASCHOVA, and E. M. SOLOVIEVA (J. Physiol. U.S.S.R., 1934, **17**, 788—798, 799—804).—IV. The white and yolk of 2-day-old eggs (from 2-year-old White Leghorns) contain respectively: glycine+alanine 0.406, 0.710, valine 0.602, 0.797, leucine 1.232, 1.415, phenylalanine 0.464, 0.571, glutamic acid 3.643, 5.046, aspartic acid 1.042, 1.208, arginine 0.782, 1.339, histidine 0.191, 0.332, lysine 0.416, 0.825, cystine 0.279, 0.302, tyrosine 0.421, 0.723, tryptophan 0.276, 0.408, and NH_3 0.175, 0.273%.

V. The individual NH_2 -acid contents (I) of milk- and pea-proteins are compared with those of an egg-meat mixture, considered to have an optimum (I). R. T.

Blood transfusion. I. Biological value of the proteins of homologous transfused blood in endogenous nitrogen metabolism. U. LOMBROSO and C. ZUMMO (Boll. Soc. ital. Biol. sperim., 1934, **9**, 1253—1255).—Introduction of blood with a N content > that of the normal blood in animals in the condition of min. N metabolism leads to increased N excretion during and after transfusion; the proteins of the transfused blood are hence utilised. R. N. C.

Gastric and pancreatic digestion of lecithin. C. JANDOLO (Boll. Soc. ital. Biol. sperim., 1934, 9, 1265—1267).—Gastric juice hydrolyses lecithin slightly by reason of its acidity, the hydrolysis liberating the fatty acids. The hydrolytic action of pancreatic juice is due to an enzyme which is activated by bile and inhibited by NaF. R. N. C.

Indole. I. Behaviour when introduced into the blood and its route of elimination. E. MACCHIA (Boll. Soc. ital. Biol. sperim., 1934, 9, 1213—1215).—Indole injected intravenously in the dog is excreted in the urine, bile, and saliva, but can still be detected in the blood $3\frac{1}{2}$ hr. after injection. Blood-indican reaches its max. 2 hr. after the injection. R. N. C.

Relationship between absorption and nutritive value of fats. U. TANGE (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 133—138).—With yeast-free diets, addition of butter produces more rapid growth (of rats) than that of lard and coconut oil; absence of fat causes an even smaller growth. With diets containing 2% of yeast, absence of fat produces growth equal to that when butter is present. An increased fat content produces increased absorption but not necessarily increased growth. F. O. H.

Nutritive value of butter and margarine. U. TANGE (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 125—132).—The inferiority of the nutritive val. (I) (in rats) of margarine to that of butter is probably due to a deficiency in vitamin-A (II). (I) of hydrogenated vegetable oils is $>$ that of hydrogenated fish oils. (II) is stored in the body of rats (especially when young) for lengthy periods. F. O. H.

Fat and lipin contents of the blood in the right and left heart. T. KURIYAGAWA, H. ÔKAWA, K. TAJIMA, T. HATAKEYAMA, and S. KATSURA (Biochem. Z., 1935, 276, 336—342; cf. Oliaro, A., 1934, 920).—Blood (rabbit, dog) from the right heart (I) does not differ from that of the left as regards fat and lipin contents but in alimentary hyperlipæmia the blood of the superior vena cava contains more total lipin and neutral fat than that from the left heart. Intravenous injection of fat emulsion causes mechanical increase of the serum-lipin of (I). The lungs probably play no sp. part in normal fat and lipin metabolism. W. McC.

Alimentary hyperlipæmia. K. TAJIMA (Biochem. Z., 1935, 276, 343—351).—In man, oral administration of < 0.2 c.c. of olive oil per kg. causes an increase in the lipin content of the blood-plasma (no increase in the corpuscles); greater amounts cause increase in the contents of neutral fat (I), phosphatide (II), and cholesteryl ester. Free cholesterol is not increased. In rabbits, after 7—8 hr., alimentary hyperlipæmia [increase of (I) and (II)] follows oral administration of fat emulsion. W. McC.

Fat metabolism in fishes. VI. Fats of some plankton Crustacea. J. A. LOVERN (Biochem. J., 1935, 29, 847—849).—The differences observed previously (A., 1933, 183) between the fat contents of fish from fresh and sea- H_2O occur in the planktons *Calanus finmarchicus*, *Cyclops strenuus*, *Daphnia*

galeata, and *Diaptomus gracilis*. The fat ingested by the fish is probably deposited mainly unchanged. H. D.

Dissolution of fats and fatty acids by the gastric juices of *Potamobius leptodactylus*. H. J. VONK (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 210—215).—The digestive juice (I) of crayfish is very surface-active ($\sigma=42$ dynes per cm. at 18°) and contains 4.5—5.5% of EtOH-pptd. proteins (approx. 2.8% true proteins and approx. 2.5% albumoses and peptones). When milk or oleic acid suspensions in H_2O or buffer at p_H 5 [the average p_H of (I)] are treated with (I), the fat globules disappear and the liquids clear. The bearing of the phenomenon on fat digestion is discussed. F. O. H.

Balance experiments with dihydrocholesterol in rats. H. DAM and G. C. BRUN (Biochem. Z., 1935, 276, 274—276).—After administration of dihydrocholesterol (I) to rats, less (I) was excreted than was fed and the degree of saturation of the total body-sterol was increased. P. W. C.

Stool volatile fatty acids. IV. Influence of feeding bran-pentosan and -fibre to man. W. H. OLMSTED, G. CURTIS, and O. K. TIMM (J. Biol. Chem., 1935, 108, 645—652; cf. A., 1930, 240).—Pentosan, extracted from washed bran with 7% aq. NaOH, pptd. with EtOH, and fed to man, was mostly absorbed from the intestinal tract (I); it produced no increase in the volatile fatty acids (II) excreted and was not laxative. Acid-extracted bran was not broken down in (I), was laxative, and increased the excretion of (II). H. D.

Liver and theory of fatty acid desaturation. H. H. WILLIAMS and W. E. ANDERSON (Oil and Soap, 1935, 12, 42—44).—A review. G. H. C.

Oxidative disappearance of lactic acid from brain and the Pasteur reaction. K. C. DIXON (Biochem. J., 1935, 29, 973—977).—Previous results (this vol., 251) are confirmed. In O_2 , lactic acid (I), if formed at all from glucose, is produced very much more slowly than in N_2 , and is completely oxidised. No aerobic formation of (I) occurs with fructose, even in presence of KCl, which can be used as an indicator for the presence of (I)-forming substances. A. E. O.

Presence of acetaldehyde in living creatures. D. GANASSINI (Arch. Ist. Biochim. Ital., 1935, 7, 19—26).—MeCHO is distributed widely in plant and animal tissues; in plants it is probably formed by photochemical decomp. of org. substances. MeCHO condenses readily *in vitro* with asparagine to a colloidal complex; this reaction possibly plays a part in protein synthesis. Minced animal tissues *in vitro* partly convert MeCHO into EtOAc or CH_3AcCO_2H , and such reactions are possibly involved in fat synthesis. R. N. C.

Phloridzin and muscles of the dog *in vivo* and *in vitro*. A. LAMBRECHTS (Compt. rend. Soc. Biol., 1935, 118, 1248—1250).—Phloridzin can be recovered from the plasma, liver, and kidneys of dogs injected with it, but not from the muscles. Excised muscles destroy it to a considerable extent *in vitro*. R. N. C.

Absorption of glucose and water by the small intestine and colon. R. A. CUTTING (Arch. Surgery, 1934, 29, 643—660).—Increases in blood-sugar may not be \propto intestinal absorption of glucose (I). Other factors, e.g., administration of Na barbital or surgical treatment, are influential. Vals. for portal blood may be even less significant since absorption rates of H_2O and (I) may diverge. Absorption of H_2O in the colon is $>$ that in the ileum. The R.Q. is not a measure of intestinal absorption of (I). In the jejunum the latter is $>$ in the lower bowel.

CH. ABS. (p)

Dependence of glucose consumption of the surviving frog's heart on the output and accompanying factors of the work performance. N. SCHEINFINKEL (Z. Biol., 1935, 96, 178—184).—Optical recording of the changes in vol. and pressure of the heart together with determinations of the glucose consumption (I) indicate the validity of the "all-or-none law" even for (I) and a new aspect of differentiation between skeletal and cardiac muscle.

F. O. H.

Relative food values of glucose and sucrose. S. W. COLE (Lancet, 1935, 228, 431—432).—A discussion.

L. S. T.

Effect of supplementary iodine on the nutritive value of chick rations. A. D. HOLMES, M. G. PIGOTT, and W. H. PACKARD (J. Nutrition, 1934, 8, 583—595).—Supplementary feeding with KI produced no significant improvement in nutrient efficiency, bone deposition, or blood-haemoglobin.

A. G. P.

Iron metabolism of normal women. M. A. OHLSON and K. DAUM (J. Nutrition, 1935, 9, 75—89).—Data for Fe balances are given. Negative balances are associated with increased faecal N. No relationship was observed between Fe retained and that lost in menstruation, or between the Fe balance and that of N or Cu. Cu was excreted in faeces.

A. G. P.

Electric charge and fixation of colloids injected into the trachea. III. Colloidal ferric hydroxide. A. CESTARI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1276—1278).—Colloidal $Fe(OH)_3$, injected intratracheally, passes through the alveoli (I) and is fixed by the reticulo-endothelial tissue. A small proportion is retained in granular form in (I), its charge being reversed.

R. N. C.

Rock phosphate as mineral feed for swine. J. M. FARGO, G. BOHSTEDT, E. B. HART, and P. H. PHILLIPS (Rec. Proc. XXVI Ann. Mtg. Amer. Soc. Animal Prod., 1933, 138—141).—0.4% gave normal growth and reproduction; 0.8% was harmful except to animals on pasture, and 1.6% was harmful under all conditions, owing to the F content. CH. ABS.

Phosphorus supplements in beet by-product rations. E. J. MAYNARD (Rec. Proc. XXVI Ann. Mtg. Amer. Soc. Animal Prod., 1933, 86—89).—Blood-P was increased and -Ca decreased by addition of P supplements.

CH. ABS.

Comparative efficacy of "dicapho," bone-meal, and limestone when fed as mineral supplements to rations for pigs. B. H. THOMAS, C. C.

CULBERTSON, J. M. RAMSBOTTOM, and W. E. HAMMOND (Rec. Proc. XXVI Ann. Mtg. Amer. Soc. Animal Prod., 1933, 142—144).—In general there were no significant differences in Ca and P retention if equiv. quantities of Ca were employed.

CH. ABS.

Importance of manganese for animals. G. BERTRAND and H. NAKAMURA (Bull. Soc. Chim. biol., 1935, 17, 81—87).—Mice fed on a diet containing Mn survived longer than control animals receiving no Mn.

A. L.

Manganese retention in children. G. J. EVERSON and A. L. DANIELS (J. Nutrition, 1934, 8, 497—502).—The amount of Mn retained \propto that ingested. Diet for children should contain 0.2—0.3 mg. of Mn per kg.

A. G. P.

Rôle of ammonia in the animal organism. J. M. HEFTER (J. Physiol. U.S.S.R., 1934, 17, 446—456).—A review.

R. T.

Control of hepatic function by pre-formed ammonia of blood. J. MONGUIO (Compt. rend. Soc. Biol., 1935, 118, 1014—1016).—In normal dogs (I) a meat diet or administration of urea alters blood- NH_3 (II), whilst in Eck fistula dogs (III) carbohydrate diet slightly diminishes and meat diet increases (II). Peritoneal administration of NH_4 lactate or citrate does not affect (II) in (I), very slightly increases it in dogs with the bile duct ligatured, and rapidly increases it in (III). Intravenous administration of glycine increases (II) and the effect persists longer in (III) than in (I). Intravenous administration of urease with or without preceding injection of urea increases (II) in (I) and (III). Intravenous injection of glucose decreases (II).

W. McC.

Behaviour of racemic amino-acids in the animal organism. E. ABDERHALDEN and E. TETZNER (Z. physiol. Chem., 1935, 232, 79—86).—Administration of *dl*-alanine to man, dog, rabbit, or rat leads to excretion of *d*(—)-alanine in the urine. Krebs found the *d*- more rapidly deaminated than the *l*-component in the isolated rat's kidney (A., 1933, 856). Parenteral administration of -alanine to pigeons produces serious disturbances.

J. H. B.

Creatine and creatinine metabolism. III. Creatinine determination. H. LIEB and M. K. ZACHERL (Z. physiol. Chem., 1935, 232, 41—46; cf. A., 1934, 543).—Folin's criticisms (this vol., 103) are rebutted.

J. H. B.

Effect of ephedrine on the respiratory exchange. G. ORESTANO (Arch. Farm. sperim., 1935, 59, 220—231).—Ephedrine (I), like adrenaline (II), has a marked action on the gaseous metabolism of rats, but not rabbits or pigeons; in no case is the R.Q. appreciably influenced. With rats the duration of action of (I) is somewhat $>$ that of (II) but the doses for max. effect are approx. 900 : 1, respectively. The mechanism of the action of (I) and (II) is discussed.

F. O. H.

Influence of the reaction of the medium on the action of poisons. N. V. GOLJACHOVSKI (J. Physiol. U.S.S.R., 1934, 17, 878—885).—The depressant action on an isolated frog's heart of quinine rises, and of Na salicylate diminishes, with increasing p_H from 6.5 to

8.3. The effects are ascribed to changes in the binding power of the tissues for the above poisons. R. T.

Detection and determination of atebirin in urine. R. C. WATS and B. N. GHOSH (Rec. Malaria Surv. India, 1934, 4, 367—370).—Atebrin is extracted from alkalised urine with $C_5H_{11}OH$, the alkaline solution is washed with K_2CO_3 , centrifuged, acidified with $AcOH$, and compared colorimetrically with a standard. The test is sensitive to 1 in 10^6 . H. T.

Curare. H. KING (Nature, 1935, 135, 469—470).—Of the several *Strychnos* species examined only one, *S. toxifera*, contains an amorphous quaternary alkaloid indistinguishable chemically and pharmacologically from the paralyzing principle curarine (I) isolated from calabash or gourd curare from various sources. *Guettarda acreana*, although rich in alkaloids, does not contain a paralyzing principle. The quaternary alkaloid tubocurarine (II) from native preps. of tubocurare has now been crystallised; it has a paralyzing effect on the frog slightly < that of (I) from *S. toxifera*. O-Methylation supports a formula $C_{38}H_{44}O_6N_2Cl_2$ for (II), making it isomeric with bebeerine methochloride (III). d-(III) is similar to but not identical with d-(II) chloride and has a paralyzing effect on the frog much < that of d-(II) chloride. L. S. T.

Substance responsible for the traditional clinical effect of ergot. H. W. DUDLEY and C. MOIR (Brit. Med. J., 1935, i, 520—530).—The characteristic oxytocic effect of ergot is not due to ergotamine, ergotamine, tyramine, or histamine, but to a previously unidentified alkaloid, *ergometrine*, decomp. 150—152°, $[\alpha]_D -45^\circ$ in $CHCl_3$. Methods of its prep. in cryst. form and of testing its activity are described. P. W. C.

Pharmacology of *Galinsoga*. M. A. YAVORSKY and E. C. REIF (J. Amer. Pharm. Assoc., 1935, 24, 108—113).—The O_2 consumption of minced guinea-pig's heart is increased by extracts (hot H_2O) of *Galinsoga parviflora*, the action decreasing with keeping of the extract. The principles concerned are insol. in cold H_2O . F. O. H.

Cardiac glucosides.—See this vol., 609.

Clinical observations on two pure glucosides of digitalis, digoxin and digitalinum. E. J. WAYNE (Clin. Sci., 1933, 1, 63—76). CH. ABS. (p)

Pharmacological action of sulphurated oil. G. SPAGNOL (Rev. Sudamer. Endocrinol., 1934, 17, 91—111).—Lethal and sublethal effects of injections of a solution of S in olive oil are examined. CH. ABS. (p)

Dangers of the therapeutic application of α -dinitrophenol. A. DE CHATEL and J. MOTIKA (Deut. Arch. klin. Med., 1934, 176, 700—705; Chem. Zentr., 1934, ii, 3142—4143).—2 : 4-Dinitrophenol in therapeutic doses produces symptoms of damaging of the kidneys and cardiac sac. R. N. C.

Metabolic stimulants with special reference to sodium dinitrophenoxide. E. L. BORTZ (Ann. Int. Med., 1934, 8, 599—606).—2 : 4-Dinitrophenol is effective in exogenous obesity and is not a substitute for thyroid. Toxic effects may be produced. CH. ABS. (p)

Effect of dinitrophenol on the velocity of metabolism of ethyl alcohol. E. M. P. WIDMARK (Biochem. Z., 1935, 276, 268—270).—2 : 4-Dinitrophenol and dinitro-*o*-cresol on oral administration to dogs cause a considerable increase in the rate of disappearance of EtOH from the blood; 2 : 5- and 2 : 6-dinitrophenol are inactive. P. W. C.

Comparative value of intravenous sclerosing substances. A. OCHSNER and H. MAHORNER (Arch. Surgery, 1934, 29, 397—416).—Of nine substances tested Na morrhuate was the most effective. CH. ABS. (p)

Calcium gluconate as a local anæsthetic. G. TAVARES (Munch. med. Woch., 1934, 81, 1543—1544; Chem. Zentr., 1934, ii, 3142).—Ca gluconate acts as a local anæsthetic in 3—10% solution. R. N. C.

Ether anæsthesia : concentration in inspired air and blood required for anæsthesia, loss of reflexes, and death. B. H. ROBBINS (J. Pharm. Exp. Ther., 1935, 53, 251—263).— Et_2O -air mixtures (I) were determined by thermal conductivity measurements. The blood- Et_2O (II) for a given (I) reached a max. in 30—60 min. Anæsthesia was induced and maintained in dogs with 3.7—4.5% (I) and a (II) of 100—120 mg. per 100 c.c. Respiratory failure occurred with 6.7—8% (I) and a (II) of 170—190 mg. per 100 c.c. Distribution ratios were 1 : 10. With an initially strong followed by a weaker (I) a ratio of 1 : 14 was obtained, and the maintenance mixture was 3—3.5%. H. D.

Dependence of the action of volatile narcotics on duration of exposure and concentration. N. V. LAZAREV and A. I. BRUSILOVSKAJA (J. Physiol. U.S.S.R., 1934, 17, 611—619).—Haber's toxicity coeff., $g-clA$ (c =concn., t =time of exposure, A =min. respiratory vol.), is, within certain limits, applicable to MeOH, EtOH, CO_2 , and xylene; for many other poisons (heptane, benzene, *cyclo*-hexane and -hexene, C_6H_6 , PhMe, PhEt, CS_2 , $CHCl_3$, $C_2H_2Cl_2$, $CMeCl_3$, $CH_2Cl-CHCl_2$) the val. of g rises with increasing dilution. R. T.

Effect of hypnotics on glucose tolerance. H. TOD (Biochem. J., 1935, 29, 914—918).—Hypnotics (nembutal, veronal, chloral, morphine) in clinical doses produce a marked decrease in hyperglycæmic area after ingestion of glucose with lowered max. and/or shortened hyperglycæmia. H. T.

Depth of avertin narcosis in animal experiments after preparatory therapeutic measures. L. LENDLE (Schmerz, Narkose, Anæsthesie, 1934, 7, 20—26; Chem. Zentr., 1934, ii, 3142).—Conditions of action of avertin are not improved by treatment for collapse. R. N. C.

Detection of ethyl alcohol in organs. B. B. OLSZEWSKI (Rocz. Farm., 1934, 10, 10—48; Chem. Zentr., 1934, ii, 3016—3017). H. N. R.

Effect of methyl and ethyl alcohols on blood-pressure. A. GRADINESCO, C. DEGAN, and H. PALMHERT (Bul. Soc. Stiinte Cluj, 1934, 7, 542—548; Chem. Zentr., 1934, ii, 2853).—Small quantities of EtOH and MeOH in dogs act as pressors, and larger quantities as depressors, which prove fatal. A 1 : 1

mixture is without action in small doses, and increases pressure in larger quantities.

R. N. C.

Effect of ethyl and methyl alcohols in artificial perfusion. A. GRADINESCO, C. DEGAN, and H. PALMHERT (Bul. Soc. Stiinte Cluj, 1934, 7, 549—551; Chem. Zentr., 1934, ii, 2853).—Perfusion of the Lawen-Trendelenburg frog prep. with EtOH at various dilutions gives contradictory results.

R. N. C.

Experimental tolerance to poisons. I. Alcoholism. II. Fixation of alcohol in the tissues of animals rendered tolerant. III. Can tolerance to alcohol be considered due to reduced cellular sensitivity? IV. Tolerance of carp to tribromoethyl alcohol. J. LÉVY (Bull. Soc. Chim. biol., 1935, 17, 13—26, 27—46, 47—59, 60—66; cf. this vol., 117).—I. With rats accustomed to daily doses of EtOH, the anaesthetic and the min. lethal dose were 25% and 10%, respectively, > the corresponding vals. for normal animals (I). The resistance of animals rendered tolerant to EtOH was slightly more towards $\text{CBr}_3\cdot\text{CH}_2\cdot\text{OH}$ (II), unchanged towards butylmalonylcarbamide, and less towards chloralose. These facts do not support the theory of increased oxidation to account for tolerance.

II. The EtOH contents of the blood, brain, kidney, and liver of, and the rate of oxidation of EtOH by, rats rendered tolerant to EtOH injected with the min. anaesthetic dose were the same as the corresponding vals. for (I).

III. EtOH content of the brain of rats tolerant to and anaesthetised with EtOH was > that of (I) under the same degree of anaesthesia. The process of rendering the animals tolerant is therefore associated with a reduced sensitivity of the cells.

IV. In carp rendered tolerant to (II) by being passed through progressively more conc. solutions and immersed in aq. (II) until anaesthesia was produced the Br content of the brain was four times that of (I) under the same degree of anaesthesia, and the same as that of (I) immersed for the same period.

A. L.

Action of bromoacetic acid on the sexual functions of the rat. M. BRANDONSHILLER (Compt. rend. Soc. Biol., 1935, 118, 1198—1200).— $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ causes reversible degeneration of the sex organs in males, and suspension of the oestrous cycle in females.

R. N. C.

Poisoning by barbituric acid derivatives. A. BUZZO and R. E. CARRATALA (Rev. Assoc. Med. Argentina, 1932, 40, 104—111).—*Post-mortem* examination in cases of barbituromania shows conversion of barbituric into HCN derivatives. CH. ABS. (p)

Oral toxicity of 6-alkyl-*m*-cresols. H. W. BROWN and P. D. LAMSON (J. Pharm. Exp. Ther., 1935, 53, 264—272).—The toxicity of the compounds when fed to rats decreases with the length of the alkyl chain. The toxicity of 6-hexyl-*m*-cresol to man is > that of hexylresorcinol.

H. D.

Influence of chain-length on the taste of aliphatic ω -betaines. R. KUHN and F. GIRAL (Z. physiol. Chem., 1935, 231, 208—209).—The betaine

$\text{NMe}_3\text{[CH]}>\text{CO}$ is bitter or tasteless according

as to n is 14 or 16. The corresponding NH_2 -acids are tasteless but their Me esters show the same difference as the betaines.

J. H. B.

Preparation of cryptotoxic agents from inactive compounds, particularly amino-acids. L. VELLUZ (Compt. rend. Soc. Biol., 1935, 118, 872—874).— NH_2 -acids are rendered cryptotoxic by conversion into their phenylcarbamido-derivatives

R. N. C.

Toxic action of glyoxalines. M. LOEPER, A. MONGEOT, and J. PARROD (Compt. rend. Soc. Biol., 1935, 118, 405—406).—Diarabino- and hydroxy-methyl-glyoxaline are equally toxic to mice; subcutaneously 0.05 g. and peritoneally 0.025 g. cause death in 18 and 3 hr., respectively. Methylglyoxaline is more toxic, 5 mg. intraperitoneally being fatal in 5 min. These substances appear to act on the nervous system.

A. L.

Hydropigenic action of glyoxalines. M. LOEPER and A. MONGEOT (Compt. rend. Soc. Biol., 1935, 118, 510—511).—Hydroxymethylglyoxaline (I) injected into the feet of mice causes a considerable hydration of the tissue. Diarabinoglyoxaline and (I), but not 4-methylglyoxaline or $\text{HCO}\cdot\text{NH}_2$, showed a hydropigenic action when injected into the peritoneum of guinea-pigs.

A. L.

Heat regulation and water exchange. XIX. Reversal of febrile liver hydration with amidopyrine antipyresis. H. SHERMAN and H. G. BARBOUR (J. Pharm. Exp. Ther., 1935, 53, 350—357).—Amidopyrine inhibits the increased liver hydration in dogs produced by *B. dysenteriae*, Shiga. H. D.

Melanin and melano-ferric reactants in solution and in suspensions. A. F. X. HENRY (Compt. rend. Soc. Biol., 1935, 118, 501—504).—The melanin (I) obtained from beef choroid made sol. by treatment with antiformin is less effective in the diagnosis of paludism than (I) in suspension.

A. L.

Physiological action of salts of complex thioacids containing gold. M. PICON (J. Pharm. Chim., 1935, [viii], 21, 215—225).—The effect of the following compounds on guinea-pigs and rabbits is described: Na, Ca, and quinine aurothiosulphates (I), colloidal Au sulphide, aurothioglucose, Na aurothiopropionolsulphonate, aurothiomalate, and aurothiolactate. Retention of Au in the kidneys [with (I)], and local reactions are observed after injection of certain of the above.

A. E. O.

Acetylcholine-sensitising substance, formed in the trunk of the pneumogastric nerve in the course of indirect excitation. L. BINET and B. MINZ (Compt. rend. Soc. Biol., 1935, 118, 1130—1132).—Extract of the indirectly-excited nerve sensitises the leech muscle to acetylcholine.

R. N. C.

Uptake of nicotine by the human organism during smoking. Fate of the nicotine. J. BODNAR, V. L. NAGY, and A. DICKMANN (Biochem. Z., 1935, 276, 317—322).—From 60 [without inhaling (I)] to 93% [with (I)] [equiv. to 34 and 79 mg. of nicotine (II) from 10 cigarettes] of the (II) of tobacco smoke is retained in the organism. With (I) only 1.7% of (II), without (I) no (II), is excreted in the

urine. (II) taken in with (I) and not subsequently excreted unchanged is rendered non-toxic in the liver.

W. McC.

Toxicity of certain species of *Crotalaria* seed for chicken, quail, turkey, and dove. E. F. THOMAS (J. Amer. Vet. Med. Assoc., 1934, 85, 617—622).—Data are given for *C. spectabilis*, *C. striata*, *C. grantiana*, *C. incana*, and *C. intermedia*. CH. ABS. (p)

Toxic substance occurring naturally in certain samples of plant foodstuffs. I. Feeding trials. II. Occurrence in the protein fraction. K. W. FRANKE (J. Nutrition, 1934, 8, 597—608, 609—613).—I. Samples of various grains from certain localities had a toxic effect on rats.

II. Toxic properties are associated with the protein fraction. A. G. P.

Plant poisoning in stock and the development of tolerance. D. W. STEYN (Onderstepoort J. Vet. Sci., 1934, 3, 119—123).—Continuous ingestion of leaves or underground stems of *Dichapetalum cymosum*, Hook., did not induce development of tolerance in rabbits. The active principle was either inactivated in the body or excreted slowly. CH. ABS. (p)

Comparison of natural and synthetic poisons. K. A. HOFFMANN (Oesterr. Chem.-Ztg., 1935, 38, 41—42).—The irritant and lethal action of synthetic poisons is of the same order as that of natural poisons. There is no indication of the possibility of synthesising "ultra-poisons." M. S. B.

Modern chemotherapy of antimony and the biological problems of specificity and resistance. E. MENEGETTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1122—1181).—A dissertation. R. N. C.

The antimony test and its prognostic value during and after kala-azar therapy. M. BERGONZINI and Y. LI-JEN (Boll. Soc. ital. Biol. sperim., 1934, 9, 1208—1210).—The intensity of the reaction decreases as the therapeutic action of Sb proceeds. R. N. C.

Effect of arsenic therapy on nitrogen and carbohydrate metabolism. F. RATHERY, R. WOLFF, and S. MANJEAN (Bull. Acad. Med., 1934, 112, 74—86; Chem. Zentr., 1934, ii, 2706).—Administration of mineral-H₂O containing As to severe diabetics with insulin and to normal dogs produces a slight fall of blood-sugar and of glycosuria during the cure. There is no noticeable alteration in protein metabolism or protein retention. Blood-cholesterol and -glutathione are unchanged. R. N. C.

Resorption of bismuth from the gastrointestinal canal. S. SEREFIS (Deut. med. Woch., 1934, 60, 1237—1240; Chem. Zentr., 1934, ii, 2858; cf. this vol., p. 398).—Oral administration of H₂O-insol., -sol., and fat-sol. Bi salts has no effect on experimental syphilis in animals. BiCl₃ in acid solution together with glycerol exerts a healing effect. R. N. C.

Lead absorption and lead poisoning. Clinical and pathological analysis of 100 cases. O. LOWY and L. L. LEVISON (J. Med. Soc. New Jersey, 1933, 30, 849—852).—In Pb absorption renal impairment was rare. CH. ABS. (p)

Blood-carbon monoxide in oxalæmia. M. LOEPER and J. TONNET (Compt. rend. Soc. Biol., 1935, 118, 1064—1065).—With oxalæmia the blood-CO is increased > 10-fold (cf. A., 1925, i, 321); hence it probably originates from H₂C₂O₄. F. O. H.

Chronic copper poisoning in sheep. N. BISSET (Vet. J., 1934, 90, 405—407).—Poisoning occurred in sheep grazing near a Ni-smelting works, Cu being found in grass and grain growing in the area.

CH. ABS. (e)

Intrapulmonic absorption of iodine. V. V. COLE, R. H. DUNN, and G. M. CURTIS (J. Pharm. Exp. Ther., 1935, 53, 327—330).—I is injected into the bronchi of dogs and the changes in blood-I (I) are determined. KI produces a large rise in (I), whereas I combined with lipins has little influence. Nembutal and amytal were without influence on (I), whilst Na amytal lowered it. H. D.

Absorption of hydrocyanic acid vapour through the skin: acute cyanide poisoning. A. FAIRLEY, E. C. LINTON, and F. E. WILD (J. Hyg., 1934, 34, 283—294).—From a saturated atm. HCN is readily absorbed through the skin. Na₂S₂O₃ affords limited protection. CH. ABS. (p)

Effect of open and closed carbohydrate chains on the antirachitic activity of orthophosphoric acid. R. LECOQ and M. L. BARBAN (Compt. rend. Soc. Biol., 1935, 118, 867—868).—Na nucleates show low antirachitic activity, but in Ca and Mg inositol phosphates the activity is increased 2—3 times.

R. N. C.

Influence of heavy water of low concentration on *Spirogyra*, *Planaria*, and on enzyme action. T. C. BARNES and E. J. LARSON (Protoplasma, 1934, 22, 431—443).—The survival period of sections of *Spirogyra* filaments and the maintenance of body-wt. of *Planaria* in small concns. of H₂O was > in H₂O, probably as a result of lowered enzymic hydrolysis. Physiological effects of H₂O are more significant in low than in high concns. A. G. P.

Chemical basis for some biological effects of heavy water. T. C. BARNES and H. Z. GAW (J. Amer. Chem. Soc., 1935, 57, 590—591).—The Arrhenius equation, applied to the rate of contraction of the vacuole of *Paramecium caudatum*, gives the following energies of activation, *E* g.-cal., for the controlling catalyst: 24,000 at < 16°, 17,000 at 16—22°, 14,000 at > 22°. In 30% H₂O *E* is 22,000 at all temp. examined. Thus, the catalyst of the catenary chain, which in H₂O is in control only at low temp., is so slowed down by H₂O that it then controls the contractions at all temp. In accordance with predictions H₂O thus has the effect of low temp. Cells of *Spirogyra* survive better in 0.47% H₂O than in ordinary H₂O, particularly when illuminated (72% as against 32% after 2 days), suggesting that the stronger C-H² linking stabilises the photosynthetic intermediate (?CH₂O) and possibly also strengthens the C-C linking. R. S. C.

Analysis of physiological states responsible for antero-posterior disintegration in *Planaria dorotocephala*. J. W. BUCHANAN (Protoplasma, 1935, 22, 497—512).—Cytolysis in H₂O and in various

solutions is examined. The antero-posterior gradient in cytolytic disintegration represents a differential sensitivity to disturbance of the Ca-lipin- H_2O relations of the organism. A. G. P.

Necrosis of the myocardium induced by the orthophosphates. F. A. MCJUNKIN, W. R. TWEEDY, and W. J. MENCKY (Arch. Path., 1934, 18, 626—634).—Myocardial necrosis is induced by injection of Na_2HPO_4 into nephrectomised rats and similar lesions are produced by Ca gluconate. Both tend to produce early calcification. CH. ABS. (p)

Hyperglycaemia due to electrical stimulation of the hypothalamus. M. DE JAEGER and A. VAN BOGAERT (Compt. rend. Soc. Biol., 1935, 118, 1035—1037).—Electrical stimulation of the floor of the third ventricle in normal but not adrenalectomised dogs produces a marked hyperglycaemia. This is correlated with the sympathetic vasomotor centre of the hypothalamic region. F. O. H.

Components of the dehydrogenase system. II. E. ADLER and H. VON EULER. III, IV. H. VON EULER and E. ADLER (Z. physiol. Chem., 1935, 232, 6—9, 10—16, 16—27; cf. A., 1934, 1257).—II. O_2 can act as acceptor for the glucose-dehydrogenase (I) system. (I) and EtOH. (II) or hexose monophosphate-dehydrogenase (III) are different enzymes. (II) and (III) may also differ.

III. Cu even in low concn. inhibits the systems (I), (II), and (III); (II) is inhibited strongly by Ag and Hg, much less by Fe^{III} and Zn. KCN removes the inhibition by Cu. NaF does not inhibit (II) or (III); $CH_2Br\cdot CO_2H$ inhibits (III) strongly, (II) to a smaller extent.

IV. In white or red light (675—645 $m\mu$, corresponding with the absorption max. of methylene-blue) the system (II) is still active even in absence of the flavin. The inhibition by heavy metals and $CH_2Br\cdot CO_2H$ is unchanged, showing that these substances act directly on the enzyme or co-enzyme, not on the flavin. The cozymase is indispensable. J. H. B.

Reversibility of oxidations in presence of alcohol-dehydrogenase. R. WURMSER and S. FILITTI (Compt. rend. Soc. Biol., 1935, 118, 1027—1029).—The technique and electrometric data are given for the reduction of $COMe_2$ to Pr^oOH by leucomethylviologen in presence of an alcohol-dehydrogenase from Lebedev's maceration extract of bottom yeast (A., 1933, 982). F. O. H.

Dehydrogenases and hydrogen donors in the brains of animals when narcotised, hypnotised, and poisoned with monoiodoacetic acid. H. WAELSCH and G. KLEPETAR (Pflüger's Archiv, 1934, 235, 60—69).—The brains of narcotised and hypnotised fowls and guinea-pigs decolorise methylene-blue more rapidly than those of normal animals, the decrease in time being probably due to increased lactic acid in the brain. The rate of decolorisation (I) is independent of the blood-sugar, and is unaffected by keeping the brain for 2 hr. at 37° . Frogs' brains show the same effect, either normal or when poisoned with $CH_2I\cdot CO_2H$. (I) by guinea-pig liver is increased by narcosis with Et_2O or avertin, but decreased by $CHCl_3$ narcosis. The narcotic and enzyme-inhibitory

effects of avertin solutions are closely related to the concn. and to one another. R. N. C.

Inositol. I. Oxidation by rat-tissue. N. DAS and B. C. GUHA (Z. physiol. Chem., 1935, 231, 157—160).—Inositol is oxidised in presence of brain-, heart-, kidney-, and liver-tissue of rats. The oxidation is least with liver. J. H. B.

Catalase action of the various component parts of erythrocytes, and certain artificial catalase systems. M. J. GALVIALO and L. P. SUTSCHKOVA-NETSCHAEVA (J. Physiol. U.S.S.R., 1934, 17, 577—588).—The entire catalase (I) content of blood is associated with the plasma of the erythrocytes. Extremely active preps. are obtained by modifications of Tsuchiaschi's method (A., 1923, i, 1147), viz., the duration of shaking with $CHCl_3$ is increased, and the pptd. hæmoglobin removed by repeated centrifuging, NaH_2PO_4 is used for elution of (I) from $Ca_3(PO_4)_2$; the ppt. obtained on dialysing the eluate contains practically all the blood-(I). Artificial (I) systems of an activity comparable with that of whole blood are obtained by adding $FeCl_3$ to plasma or serum. R. T.

Enzymic activity as a characteristic of [plant] variety. B. A. RUBIN and L. I. NAUMOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 4, 486—492).—Early radishes have a greater catalase activity (I) than the late variety, in both leaf and root. At the first appearance of the leaf (I) may be used to characterise the variety of radish. Both early and late varieties have about the same amylase activity. The root of the late variety when it first appears has a greater invertase activity (II) than that of the early, but when the radish is "market-ripe" (II) is greater in the early variety. E. A. H. R.

Biological action of iodoacetic acid and fluoride. Fumarase. K. P. JACOBSON and J. TAPADINHAS (Compt. rend. Soc. Biol., 1935, 118, 1110—1113).— $CH_2I\cdot CO_2H$ and, to a smaller extent, F^- in concns. of 0.2% partly inhibit the action of pig's liver-fumarase; at concns. of 0.02% no inhibition occurs. F. O. H.

Action on fumarase of substances capable of complex salt formation. A. DA CRUZ (Compt. rend. Soc. Biol., 1935, 118, 1113—1115).—Small concns. of KCN do not inhibit the action of pig's liver-fumarase (I); with 0.03% an inhibition occurs (cf. A., 1927, 693). The inhibition due to Ag^+ is not influenced by KCN. Normal, but not Ag^+ -inhibited, (I) is inhibited by SCN^- , whilst $SCN^- + AgNO_3$ is without action (cf. A., 1933, 535, 865). F. O. H.

[Enzyme from] Acer saccharum. E. BOIS and A. NADEAU (Natural. Canad., 1935, 62, 106—112).—The sap contains an amylase (I) which hydrolyses starch to sucrose and cellobiose. Enzymolysis occurs at 8° and increases rapidly with rise in temp. (to 37°), the optimum p_H being 6.8. J. W. B.

(A) **Post-mortem breakdown of glycogen and accumulation of lactic acid in fish-muscle at low temperatures.** (B) **Glycogenolysis in fish-liver at low temperatures.** J. G. SHARP (Biochem. J., 1935, 29, 850—853, 854—859).—(A) Between -3.2° and -3.7° the max. rate of glycogenolysis (I) occurs

in frozen fish-muscle (II). Between -1.6° and -2° there is a crit. temp. below which (II) loses its power of synthesising glycogen (III) from lactic acid (IV) on thawing, and a rapid formation of (IV) continues.

(B) In fish-liver at 0° an initial rapid increase in (I) occurs whilst the sugar and (IV) concns. increased only slowly and the total carbohydrate content remained const. until most of the (III) had been destroyed. The process is independent of the presence of O_2 . Below 0° (I) decreases. H. D.

Enzyme preparation. M. SRINIVASAN and M. SREENIVASAYA (J. Indian Inst. Sci., 1935, 18, A, 1—5).—Diastase (I) and emulsin adsorbed on filter-paper are as active as when applied in the free state. Invertase similarly adsorbed was less active, but this is attributed to the presence of yeast-gum preventing elution. The (I) preps. retained their activity unimpaired over a year. W. O. K.

Enzymic fission of salicin by emulsin in heavy water.—See this vol., 588.

Determination of invertase activity. W. R. JOHNSTON, S. REDFERN, and G. E. MILLER (Ind. Eng. Chem. [Anal.], 1935, 7, 82—86).—The rate of inversion of 5% aq. sucrose at 25° during 10 min. \propto the concn. of invertase (2.5—10 mg. per c.c.) (cf. A., 1913, i, 540; 1922, i, 388), and is a measure of the no. of "inverton" units (I) (defined, and calc. from an empirical expression) contained in the sample (II). A nomogram to read off the (I) content of (II) is constructed. J. L. D.

Fractional ultrafiltration of invertase from the intestinal juice of the dog. P. GRABAR (Compt. rend. Soc. Biol., 1935, 118, 455—456).—The invertase mol. has a diameter slightly $>$ that of serum-albumin, being retained by membranes of porosity 10 μ . A. L.

Enzymic synthesis of sucrose. A. LEBEDEV and A. DIKANOVA (Z. physiol. Chem., 1935, 231, 271—272).—The statement of Oparin and Kurssanov (A., 1931, 1193) that sucrose is synthesised from invert sugar in presence of invertase could not be confirmed. J. H. B.

Induction of glycolysis. F. LIPMANN (Biochem. Z., 1935, 276, 234—238).—An induction period corresponding with the initial stages of fermentation precedes glycolysis of glucose (I) in Meyerhof's muscle extract + activator (from yeast) in the absence of substances shortening the induction period (II). (II) is removed by addition of hexose diphosphate and $AcCO_2H$ ($10^{-5}M$). Both substances in NaF -muscle extract-activator solution bring about esterification of (I). P. W. C.

Isolation of isomeric phosphoglyceric acids (glyceric acid-2- and -3-phosphoric acid) from fermentation solutions and their enzymic equilibrium. O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 276, 239—253).—Natural phosphoglyceric acid from yeast maceration extract can be separated into two isomerides, *l*-glyceric acid-3- (I), $[\alpha]_D^{20} -14.5^{\circ}$, and *d*-glyceric acid-2-phosphoric acid (II), $[\alpha]_D^{20} +24.5^{\circ}$. (I) and (II) in dialysed muscle and yeast extracts exist in an equilibrium (III) attained from either side in a few min., K for (I)/(II) being 7.3—2.3

with temp. from 60° to 0° . (III) is independent of the simultaneous production of phosphopyruvic acid, production of which can be inhibited by NaF . The same (III) is obtained using racemic (I) and (II), a half (*i.e.*, one optical isomeride) of each acid being attacked and optically active products resulting. By acid hydrolysis of natural diphosphoglyceric acid (from pig's blood) a mixture of (I) and (II) is obtained.

P. W. C.

Biochemical degradation of diphosphoglyceric acid. W. SCHUCHARDT and A. VERCELLONE (Biochem. Z., 1935, 276, 280—288).—Horse, pig, and rabbit muscle, kidney, and intestinal cells can convert diphosphoglyceric acid into $AcCO_2H$. The liver has little power to effect this reaction but Jensen sarcoma tissue is strongly active. The fact is confirmed that erythrocytes have usually only a slight action on monophosphoglyceric acid. P. W. C.

Glucosulphatase. XI. Mode of reaction. Expression of enzyme concentration. T. SODA and F. EGAMI (J. Chem. Soc. Japan, 1934, 55, 914—927).—The concn. of the enzyme cannot be expressed by using const. of a reaction of the first order. A suitable formula is developed and the S-form of the velocity curve explained. CH. ABS. (p)

Esterase models. S. C. J. OLIVIER (Rec. trav. chim., 1935, 54, 322—326).—Partly a criticism of Langenbeck and Baltes (cf. A., 1934, 509). The small apparent increase due to $CH_2Bz\cdot OH$ (I) in the rate of hydrolysis of $Bu\cdot OMe$ by $Ba(OH)_2$ at 30° in CO_2 -free H_2O is due to interaction of (I) with $Ba(OH)_2$. J. L. D.

Activity of arginase during the development of the hen embryo. J. BRACHET and J. NEEDHAM (Compt. rend. Soc. Biol., 1935, 118, 840—842).—Arginase falls rapidly during the first week of development to reach a steady min. val. at the 10th day. R. N. C.

Histaminase. IV. Purification. V. Source of ammonia formed in the histamine-histaminase reaction. E. W. MCHENRY and G. GAVIN (Biochem. J., 1935, 29, 622—624, 624—625; cf. A., 1932, 1166).—IV. The increased activity of histaminase (I) produced by PO_4''' is similar to that by C_2O_4'' and is due to the pptn. of Ca'' . Pptn. of (I) with 0.5% tannic acid and removal of the latter with $COMe_2$ gives a more conc. prep. (I), pptd. by $(NH_4)_2SO_4$ and redissolved in H_2O , is pptd. with $COMe_2$ giving a four-fold increase in activity. (I) is adsorbed by the $Al(OH)_3$ procedure (A., 1930, 1316) and eluted with HPO_4'' buffer.

V. Histamine, freed from proteins with $CCl_3\cdot CO_2H$, shows a decrease in $NH_2\cdot N$ on treatment with (I). H. D.

Localisation of kidney-deaminase. F. VON LEOVEY (Biochem. Z., 1935, 276, 265—267).—Histological and chemical examination shows that kidney-deaminase occurs chiefly in the epithelial cells of the tubuli contorti and to a small extent in the cells of the tubuli recti. P. W. C.

Reversibility of the action of histozyyme. A. V. BLAGOVESTSCHENSKI and K. A. NIKOLAEV (Biochem. Z., 1935, 276, 368—375).—Phosphate-buffered extracts of dried taka-diastase (I) contain all the

histozone (II) of (I) and hydrolyse hippuric acid (III). Cysteine restricts the activity of (II) and activity is not restored by addition of FeSO_4 . O_2 , H_2O_2 , and benzoquinone also restrict activity of (I). In presence of oxidising agents (e.g., H_2O_2) and systems which supply energy (I) synthesises (III) from $\text{CH}_3\text{Ph}\cdot\text{OH}$ (but not BzOH) and glycine.

W. McC.

Activation of trypsinogen by enterokinase. M. GUILLAUMIE (Compt. rend. Soc. Biol., 1935, 118, 1049—1052).—The rapidity of activation of trypsinogen (I) by enterokinase (II) and the max. tryptic activity attained are dependent only on the amount of (II) added. In the absence of (II), preps. of (I) purified by $(\text{NH}_4)_2\text{SO}_4$ pptn. have no proteolytic or curdling activities, whilst on subsequent activation they are not produced proportionately. F. O. H.

Evaluation of pepsin by the coagulation method. K. SCHULZE (Apoth.-Ztg., 1934, 49, 1039—1040; Chem. Zentr., 1934, ii, 2719).—Munro and Seifert's method (cf. B., 1933, 651) is unsuitable, as it measures only the action of the protease pepsin, not that of the chymase.

H. J. E.

Influence of temperature on the activation and inactivation of yeast-proteinase in relation to the conditions of the medium. A. V. BLAGOVESHCHENSKI and G. D. VOVTSCHENKO (Biochem. Z., 1935, 276, 289—296).—The influence of temp. on the activation of yeast-proteinase (I) by KCN and $\cdot\text{SH}$ compounds and on the inactivation by heat is investigated particularly in relation to the time of activation and amount of activator. The temp. optimum for (I) is $40\text{--}45^\circ$ corresponding with the optimum for proteinase. Inactivation proceeds slowly and is complete at 65° . With an excess of activator (cysteine) (I) is inactivated. The activated enzyme is more readily destroyed by heat than the non-activated.

P. W. C.

Function of an enzyme, endosomase, in cell division. G. VAN CAMP (Bull. Soc. Chim. biol., 1935, 17, 169—179).—The failure of nucleoproteins to give the Foulgen reaction may be avoided by a preliminary treatment with an extract (I) of the lymphatic ganglia, which brings about degradation to nuclein or nucleic acid. The enzyme responsible for the action of (I) may take part in cell division. A. L.

Interferometry of Hirsch. Non-specific concentrating power of opzims. (Non-specific value of Durupt.) I. By exhaustion of the enzymic power of the serum. A. LIENGME and J. PIQUET (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 127—131).—The mol. concn. of serum increases to a const. val. after 4 successive treatments with opzim (from thymus). Further increase does not occur owing to gradual exhaustion of the serum-enzymes. The increase of mol. concn. is therefore due to enzymic action and is not a non-sp. concn. due to removal of H_2O by opzim.

P. W. C.

Importance of technique in the study of the protective enzymes of serum. C. O. GUILLAUMIN (Compt. rend. Soc. Biol., 1935, 118, 632—634).—The use of the interferometric method is described.

A. L.

Existence of specific defence enzymes in the organism, and their measurement by the interferometric method. P. LAURENT-GERARD and H. SIMONNET (Compt. rend. Soc. Biol., 1935, 118, 1171—1175).—Injection of P oil in dogs destroys the organs, but the blood shows no trace of defence enzymes, which also cannot be detected in blood from rat tumours.

R. N. C.

Phosphatases. II. Inactivation and reactivation of phosphatases of animal organs. S. BELFANTI, A. CONTARDI, and A. ERCOLI (Biochem. J., 1935, 29, 842—846; cf. this vol., 534).—The time of contact of rabbit-liver extracts with $\text{Na}_2\text{C}_2\text{O}_4$ has no influence on the acid-phosphatase (I) deactivation; addition of CaCl_2 or dialysis reactivates (I) after treatment with $\text{Na}_2\text{C}_2\text{O}_4$. NaF in time irreversibly inactivates (I). At p_{H} 4.5 alkaline-phosphatase extracts from kidney and liver are inactivated with time. NaF at this p_{H} increases the effect. The effect is more marked with bone-phosphatases.

H. D.

Hydrolysis of hexose diphosphoric ester by bone-phosphatase. II. (a) Participation of phosphohexokinase. (b) Isolation of fructose 1-phosphate. B. TANKÓ and R. ROBISON (Biochem. J., 1935, 29, 961—972).—Highly purified bone-phosphatase (I) converts fructose 1:6-diphosphate (II) into fructose 1- (III) and 6-phosphate (IV) in approx. equal amounts. The production of aldo-derivatives previously observed (A., 1933, 534) is due to the presence of a phosphohexokinase (V) in (I) preps. pptd. by EtOH and Et_2O and not further purified. (V) is present also in marrow extracts and is probably identical with an enzyme found in muscle, kidney, liver, brain, and yeast (A., 1933, 863). It converts (IV) and glucose 6-phosphate into equilibrium mixtures of aldo- and keto-esters, but has no action on (III), nor on (II) in absence of (I). (III) is best separated from (IV) by fractional crystallisation of the brucine salts from H_2O . It has $[\alpha]_{5461} -64.2^\circ$ (Ba salt, $[\alpha]_{5461} -39.0^\circ$), yields glucosazone on treatment with $\text{NHPh}\cdot\text{NH}_2$, and is probably 1-phosphofructopyranose. The rates of hydrolysis of the free ester in 0.01M aq. solution and in 0.1N- and N-HCl at 100° have been determined.

A. E. O.

Phosphatases of marine invertebrates. E. R. NORRIS and D. A. R. RAO (J. Biol. Chem., 1935, 108, 783—790).—The phosphatase (I) activity, of tissue extracts of invertebrates (II) has been investigated. Many (II) have an acid and an alkaline optimum of (I) activity; some (II) require Mg' and others are inactivated above 30° .

M. S.

Action of animal phosphatases on the mono- and di-esters of phosphoric acid. J. ROCHE and M. LATREILLE (Compt. rend. Soc. Biol., 1935, 118, 900—902).—Mono-esters are hydrolysed more readily than di-esters, and phenolic than alcoholic esters.

R. N. C.

Enzymic determination of α -glycerophosphate in admixture with β -glycerophosphate. A. SCHAFFNER and E. BAUER (Z. physiol. Chem., 1935, 232, 64—65).—The fact that yeast-phosphatase hydrolyses α - (I) readily but β -glycerophosphate (II)

only slightly affords a ready method of determination of (I) and (II) in mixtures. J. H. B.

Fermentative enzymes. I. Yeast-phosphatase. A. SCHAFFNER and E. BAUER (Z. physiol. Chem., 1935, 232, 66—76).—Yeast-phosphatase (I) is separated from the oxido-reduction system by extracting dried yeast with glycerol (II) and subsequent dialysis. Zymohexase is removed by adsorption on $\text{Al}(\text{OH})_3\text{-C}_7$. The optimum p_{H} of (I) is 6.4, the optimum $[\text{Mg}]$ 0.01M. H_3PO_4 inhibits markedly, (II) only slightly. (I) is strictly an α -glycerophosphatase, thus differing from phosphatase preps. from other sources, some of which hydrolyse β - more rapidly than α -glycerophosphate; it is also a monoesterase, Ph_2HPO_4 not being attacked. Hexosephosphoric acids are hydrolysed much more slowly than is glycerophosphoric acid. The determination of (I) is described. J. H. B.

Yeast-phosphatase. C. HOMMERBERG (Svensk Kem. Tidskr., 1935, 47, 63—75).—The prep. of phosphatase (I) from baker's yeast autolysate is described. Autolysis for 1 week yields the most active prep. The hydrolysis of β -glycerophosphate (II) and sucrose phosphate by (I) is activated by Mg^{++} . A definite p_{H} optimum for (I) cannot be determined, as it decreases with increasing duration of the experiment due to a gradual destruction of (I) in slightly alkaline solution. This destruction is more marked with yeast- than with animal (I). AsO_4''' inhibits the hydrolysis of (II) but in non-buffered solutions addition of AsO_4''' may produce an apparent activation by shifting the p_{H} nearer the optimum. Cozymase, AcCO_3H , and MeCHO do not activate yeast- or animal (I). There is no general parallelism between (I)- and sulphatase-activity in animal organs. E. A. H. R.

Degradation of lactic acid by yeast enzymes. IV. A. HAHN, H. NIEMER, and B. FREYTAG (Z. Biol., 1935, 96, 253—260; cf. A., 1933, 1204).—Yeast extracts containing lactic acid (I)-dehydrase do not aerobically decompose (I) except in the presence of methylene-blue, which functions as O_2 -carrier. The data from both normal and washed yeast refute the alleged participation of the yellow respiratory enzyme in the aerobic decomp. of (I). F. O. H.

Kinetics of alcoholic fermentation of sugars by brewer's yeast. I. Effect of concentrations of yeast and sugar. II. Relative rates of fermentation of glucose and fructose. R. H. HOPKINS and R. H. ROBERTS (Biochem. J., 1935, 29, 919—930, 931—936).—Alcoholic fermentation of glucose by yeast follows the ordinary enzymic reaction course. The rate of fermentation (I) is dependent on the nature of the stirring and \propto yeast concn. (II).

II. (I) of fructose \propto (II) to a limit. With glucose (I) \propto (II) to higher (II). Under the same conditions glucose is fermented at the same rate from 1 to 10% and fructose from 2 to 8%. (I) for fructose is $<$ for glucose. The dissociation consts. K_m of enzyme and substrate for glucose and fructose are deduced and the selectivity const. $K_{G/F}$ is calc. H. T.

Effect of acetic acid on fermentation of sugar by yeasts in presence of alcohol. B. PORCHET (Mitt. Lebensm. Hyg., 1935, 26, 18—28).—The limiting $[\text{EtOH}]$ and $[\text{AcOH}]$ for growth and survival

of species of *Saccharomyces* and *Torula* and of *Mycoderma vini* (I) have been determined. *S. ellipsoideus* (II) is more resistant than *S. apiculatus* to both EtOH and AcOH . (II) will grow in must containing 0.8 vol.-% of AcOH and will survive several days in 2%, but is killed after 2 months in 1%. When the limit of either $[\text{EtOH}]$ or $[\text{AcOH}]$ is approached, sugar has a slightly inhibitory action on (II). (I) grown in wine containing 6 vol.-% of EtOH develops in presence of 1 vol.-% of AcOH . In practice 0.5 vol.-% AcOH , 5 vol.-% EtOH , and 5—10% sugar are the max. allowable concns. E. C. S.

Action of 2:6- and 2:5-dinitrophenol and of the mononitrophenols on yeast respiration. J. FIELD, jun., A. W. MARTIN, and S. M. FIELD (J. Pharm. Exp. Ther., 1935, 53, 314—326).—2:6- and 2:5-Dinitro- and *m*- and *p*-nitro-phenol stimulate the respiration of yeast. Added glucose decreases the effect. H. D.

Ergosterol and fat increase in brewer's yeast. W. HALDEN (Fettchem. Umschau, 1935, 42, 29—32).—A discussion (cf. A., 1933, 1205; 1934, 1035). H. G. M.

Separation of Greek strains of *Saccharomyces* from Cyprus and Santorin in over-acid media of tartaric acid in presence of ethyl alcohol and magnesium sulphate. G. KELAIDITIS (Praktika, 1933, 8, 385—389; Chem. Zentr., 1934, ii, 2915). H. J. E.

Algæ of Manitoba soils. C. W. LOWE and A. V. MOYSE (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 119—152).—Resting and vegetating algæ (I) belonging to > 27 species inhabit the soils, *Isokontæ* being more widely distributed than *Myxophyceæ* (II) or *Bacillariales*. (II) grow more in cultivated than in uncultivated soils. *Chlorococcum humicola* is very widely distributed. The distribution of (I) is wider in heavy than in light soils. W. McC.

Incorporation of heavy hydrogen into growing organisms. O. REITZ and K. F. BONHOEFFER (Z. physikal. Chem., 1935, 172, 369—388; cf. this vol., 132).—A micro-method has been developed for the determination of H^2 in a few mg. of an org. compound. If yeast is shaken with H_2O containing 12 at.-% H^2 or grown in a solution of sucrose in such H_2O its dry substance takes up about 3 at.-% H^2 , but this is only loosely bound and can be washed out with ordinary H_2O . There is thus no incorporation of H^2 in the C compounds of the organism. Algæ, *Chlamydomonas* and *Scenedesmus* grown in H_2O of high H^2 content contain in their dry substance $>$ half as much H^2 as the culture solution. Of this only 20—25% can be washed out with ordinary H_2O . R. C.

Periodic analysis of mineral waters and *Spirogyra borgeana*. R. RETROVSKY (Bull. Soc. Chim. biol., 1935, 17, 96—105).—The sterility of *S. borgeana* present in a Slovakian spring- H_2O is probably due to the low p_{H} (6.2) and the presence of $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$ in large amount. A. L.

Stability of strains of *Aspergillus niger* as regards acid production. E. I. SOTNIKOV and T. J. PALEI (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 139—146).—The ability to produce citric acid by *A.*

niger energetically and without diminution is a physiological character of individual strains of these organisms.

P. W. C.

Citric fermentation. M. GIORDANI (Chimica e l'Ind., 1935, 17, 77—81).—The properties of a culture of *Aspergillus niger* (I) depend mainly on the method of seeding the nutrient solution with the spores, max. yields of citric acid being obtained on prolonged immersion of the spores in H₂O or other liquid. Cultivation of (I) in media containing invert sugar gives growths which develop more rapidly and are more robust and of higher acidifying power than when sucrose is used. Fe aids development of mycelia but accelerates oxidation of the citric acid and should be excluded.

T. H. P.

Respiratory pigment of *Aspergillus niger*. M. GIORDANI (Atti R. Accad. Lincei, 1934, [vi], 20, 340—342).—An alkaline extract of *A. niger* spores displays max. absorptions at 2840, 4300, and 4500 Å., probably due to the presence of a respiratory flavin-like pigment.

T. H. P.

Constitution of ochracin.—See this vol., 619.

Biochemistry of micro-organisms. XLII. Metabolic products of *Aspergillus terreus*, Thom. Terrein. H. RAISTRICK and G. SMITH (Biochem. J., 1935, 29, 606—611).—Of 5 strains of *A. terreus*, grown on Czapek-Dox solution with 5% glucose as sole source of C, two produce terrein (I), C₈H₁₀O₃, m.p. 127°, [α]_D²⁰ +185° in H₂O; the others only gave succinic acid and H₂C₂O₄. (I) is isolated by acidifying the metabolism solution, filtering from the ppt., concn. of the filtrate, and extraction with Et₂O. On concn. (I) separates. A strain producing (I) also produced citrinin.

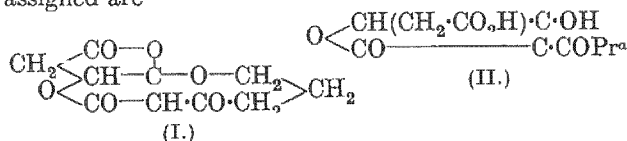
H. D.

Production of fat from glucose by moulds. Cultivation of *Penicillium javanicum*, van Beijma, in large-scale laboratory apparatus. G. E. WARD, L. B. LOCKWOOD, O. E. MAY, and H. T. HERRICK (Ind. Eng. Chem., 1935, 27, 318—322).—Of 61 species of *Penicillium* and *Aspergillus* examined, the mycelium (I) of 10 only contained > 15% of fat (II). The (I) of *P. javanicum* contained up to 41.5% of (II), media containing 40% of glucose (III) giving the highest yield. A cabinet for shallow-pan fermentations is described. In such cultures increase in (III) does not cause increase in (II). The constns. of (II) are given, and a carbohydrate and a chitinous complex isolated from (I) are described (cf. A., 1934, 1035).

E. C. S.

Biochemistry of micro-organisms. XLIII. Metabolic products of *Penicillium Charlesii*, G. Smith. III. Molecular constitution of carlic and carlosic acids. P. W. CLUTTERBUCK, H. RAISTRICK, and F. REUTER (Biochem. J., 1935, 29, 871—883).—Carlic acid (I) (A., 1934, 452), C₁₀H₁₀O₆, m.p. 176°, [α]_D²⁰ -160° in H₂O, dibasic and acid to Congo-red, containing no active H in anisole and 2 active H in C₅H₅N, and carlosic acid (II), C₁₀H₁₂O₆, m.p. 181°, [α]_D²⁰ -160° in H₂O, dibasic and containing 2.1 active H in anisole at 18°, on bromination in dil. AcOH both give the same 1-α-bromo-γ-carboxymethyltetronic acid, C₆H₅O₅Br, m.p. 194°, [α]_D²⁰ -117° in H₂O, dibasic, which on reduction with Pd-C-H,

gives 1-γ-carboxymethyltetronic acid, C₆H₆O₅, m.p. 182°, [α]_D²⁰ -52° in H₂O, dibasic, red FeCl₃ and violet NaNO₂ colours, hydrolysis products 1 mol. of acetoin and 2 mols. of CO₂ (1 mol. readily, 1 mol. slowly). On hydrolysis (I) gives 1 mol. each of butyrolactone and acetoin and 2 mols. of CO₂ (1 mol. readily, 1 mol. slowly) whilst (II) gives 1 mol. each of n-butyric acid and acetoin and 2 mols. of CO₂ (1 mol. readily, 1 mol. slowly). On reduction with Pd-C-H₂, (I) gives an acid, C₁₀H₁₄O₆, m.p. 157.5°, dibasic, red FeCl₃ colour, whilst (II) gives an acid, C₁₀H₁₄O₅, m.p. 217°, dibasic, red FeCl₃ colour. Both (I) and (II) react with 2:4-dinitrophenylhydrazine, the dinitrophenylhydrazone of (II) having m.p. 182°. Both (I) and (II) with CH₂N₂ give Me₁ ether Me₁ esters. The structures assigned are



A complete analogy is obtained between all the reactions of these acids and of carolic, carolinic, and α-acetyltetronic acids (this vol., 327) and attention is directed also to the close structural relationship with ascorbic acid (III), a fact borne out by the close similarity of their absorption spectra with that of (III).

P. W. C.

Properties of a bacterial inhibitory substance produced by a mould. R. D. REID (J. Bact., 1935, 29, 215—221).—Inhibitory material obtained from cultures of *Penicillium rubrum* is sp. in its action on bacteria and is not identical with the pigment produced by the fungus. It is relatively thermostable and cannot be separated by dialysis, adsorption, or distillation. It is destroyed, or its formation is prevented, by exposure to light, O₂, H₂, or CO₂.

A. G. P.

Possibilities of development of micro-organisms in an unfavourable medium. G. DUCCELLIER (Bull. Assoc. Chim. Suor., 1935, 52, 201—211).—The progress of fermentation (I) with yeast is followed by using a self-recording "activograph" (II) operated by the CO₂ pressure developed, a hydraulic valve allowing intermittent escape of gas whenever a certain CO₂ pressure is attained. Each curve of the record represents a definite vol. of CO₂, and the closeness of the curves shows the (I) activity. The unfavourable influence of sulphites and added EtOH is most marked when sugar concn. is low [i.e., at the end of (I)] and seeding rate small. The effect of sudden fall of temp. is also greatest towards the end of (I). When (I) ceases, gaseous absorption occurs. A formula is proposed for calculating the relative receptibility for yeast transferred from one medium to another. (II) may be modified to register respiration or the O₂ absorption during acetification, or for use with open vessels.

I. A. P.

Factors influencing the size of bacterial populations. J. P. CLEARY, P. J. BEARD, and C. E. CLIFTON (J. Bact., 1935, 29, 205—213).—Bacterial growth is not appreciably restricted by physical crowding or by the formation in cultures of sp. growth-inhibiting substances. The effect of meta-

bolites varies with their nature and influence on the enzymic activity of the cells. The limit of growth is set by the reduction in the energy available per cell, by changes in the availability of nutrients, and the energy demand. A. G. P.

Preparation of wheat extracts containing a growth-factor for micro-organisms. W. H. SCHOPFER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 47—49).—The prep. of an extract of wheat-germ containing a thermostable factor activating the growth of *Phycomyces* is described. Since extracts of polished rice are equally active, the factor cannot be restricted to the germ. P. W. C.

Preparation by dialysis of the growth-factor for micro-organisms. Its existence in the anther of various flowers. W. H. SCHOPFER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 169—171).—By placing wheat-germ or the stamens of various flowers in distilled H_2O at a low temp. for 24 hr. and filtering, a solution is obtained which can bring about growth of *Phycomyces blakesleeana* in media on which this organism will not normally develop. P. W. C.

Nature of the growth-factor for micro-organisms. W. H. SCHOPFER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 165—169).—Extracts of wheat-germ contain a growth-factor *M* for *Phycomyces* and for *S. cerevisiae*. Vitamin- B_1 and - B_2 catalyse the growth of *Phycomyces* but have no action on the development of yeast. *M* resembles but is not identical with bios. P. W. C.

Medium suitable for obtaining homogeneous cultures of streptococci. F. NITTI (Compt. rend. Soc. Biol., 1935, 118, 504—506).—A peptone-meat-juice-Na phosphate-starch medium for the culture of streptococci for sp. agglutination work is described. A. L.

Technique for the examination of butter for typhoid and paratyphoid bacteria. J. BRISOU (Compt. rend. Soc. Biol., 1935, 118, 711—712).—A malachite-green-PbO-Pb(OAc) $_2$ medium is used for plating. A. L.

Isolation of streptococci from milk. W. M. GROESBECK (Amer. J. Publ. Health, 1935, 25, 345—346).—The use of 1% Na_2CO_3 solution followed by culture on blood-agar plates is recommended. W. O. K.

Oxidation of acetoacetic acid produced by *B. coli*. F. P. MAZZA and R. ZANFAGNA (Boll. Soc. ital. Biol. sperim., 1934, 9, 1251—1252).—Palmitic, but not margaric, acid is oxidised to CH_3Ac-CO_2H (I) by *B. coli*, which then in aerobic conditions oxidises (I) to CO_2 and H_2O . $COMe_2$ is not produced, nor does decarboxylation take place. In anaerobic conditions *B. coli* hydrolyses (I) quantitatively to AcOH, which in aerobic conditions is then probably oxidised according to Thunberg's scheme; succinic and oxaloacetic acid are among the oxidation products. R. N. C.

Oxidation of pyruvic acid produced by *B. coli*. F. P. MAZZA and A. CIMMINO (Boll. Soc. ital. Biol. sperim., 1934, 9, 1252—1253).—*B. coli* has no carboxylase action on $AcCO_2H$ (I) either in aerobic or anaerobic conditions. $MeCHO$ is oxidised slowly

with a R.Q. of approx. 0.7. Dimedon inhibits oxidation of (I) to about 50%. In anaerobic conditions methylene-blue is not decolorised by *B. coli* in presence of (I), so that HCO_2H is not formed by hydrolysis. $H_2C_2O_4$ and CH_3Ac-CO_2H are not produced during oxidation of (I); the Meyer and Gorr oxidation schemes are therefore not possible. The R.Q. is initially about 0.75, rising to unity. Oxidation is initially a dehydrogenation, followed by almost complete oxidation to CO_2 and H_2O , and probably proceeds by way of $\alpha\delta$ -diketoadipic and succinic acids. R. N. C.

Carotenoids of two acid-fast bacteria. E. CHARGAFF and E. LEDERER (Ann. Inst. Pasteur, 1935, 54, 383—388).—*B. lombardo pellegrini* contains β - and γ -carotene (I) together with an unidentified xanthophyll (II) having absorption bands at 491 and 458 m μ . The Grassberger bacillus contains β - and γ -(I) and lycopene, together with a (II) similar to the above but having bands at 506 and 477 m μ . H. G. R.

Indole formation by *Bacterium coli*. I. Breakdown of tryptophan by washed suspensions of *B. coli*. II. Action of washed suspensions of *B. coli* on indole derivatives. D. D. WOODS (Biochem. J., 1935, 29, 640—648, 649—655).—I. *l*-Tryptophan (I) (0.02%) in phosphate buffer at p_H 7.2 is quantitatively converted by thick suspensions of washed *B. coli* at 37° under aerobic conditions into indole (II). The O_2 consumption corresponds with 5 O per mol. of (I): $C_{11}H_{12}O_2N_2 + 5O = C_8H_7N + 3CO_2 + NH_3 + H_2O$. *d*-Tryptophan is converted very slowly, if at all, into (II). Under anaerobic conditions (I) is converted almost quantitatively into 3-indolylpropionic acid (III), only about 5% of (II) being formed.

II. Under similar conditions no (II) formation either aerobically or anaerobically was observed when (I) was replaced by indole-carboxylic acid or -3-aldehyde, 3-indolylacetic acid, (III), and 3-indolylacrylic acid, but in presence of a source of N [e.g., tryptophan or $(NH_4)_2SO_4$] a small yield of (II) was obtained from 3-indolylpyruvic acid (IV). It is therefore probable that (IV) does not yield (II) directly, but may first be converted into (I). W. O. K.

Lactoflavin in micro-organisms. L. B. PETT (Biochem. J., 1935, 29, 937—944).—Bottom yeast produces lactoflavin (I) in amounts up to 0.004% of the dry wt. when grown in a medium containing glucose, $(NH_4)_2SO_4$, various inorg. salts, and 0.01% marmite. (I) production is depressed by conditions favourable for growth, e.g., aeration, but is promoted by substances which, by poisoning the Fe-containing catalysts, depress respiration without affecting fermentation, e.g., by KCN, cysteine, or C_5H_5N . PO_4''' is necessary for normal (I) production. Continued subculture of yeast in media containing KCN results in the production of a blue-fluorescing substance which partly or wholly replaces (I). Moulds and many bacterial species appear not to contain (I). A. E. O.

Sterol content of bacteria. *B. coli*. E. HECHT (Z. physiol. Chem., 1935, 231, 279—280).—By extraction with hot light petroleum, *B. coli* grown on Lockemann solution yields sterols (cf. this vol., 407). J. H. B.

Diastase-forming bacteria. A. DULL (Z. Spiritus-ind., 1935, 58, 17—18).—Many lactic organisms produced diastase (I), this production increasing when the amount of available sugar was small. Starch-dissolving bacteria of the human intestine were investigated on potato debris and starch granules from the faeces. Numerous (named) organisms were detected. I treatment of granules attacked by bacterial (I) gave a colourless rim and centre, with a violet intermediate zone. The (I)-producing intestinal flora of domestic and farm animals were also examined, after feeding the animals on starch and potato. I. A. P.

Anaerobic decomposition of plant materials. II. Factors influencing the anaerobic decomposition of rice-straw (*Oryza sativa*). C. N. ACHARYA (Biochem. J., 1935, 29, 953—960).—The optimum conditions for the anaerobic digestion of rice-straw by mesophilic organisms include the following: temp. 30—35°; p_H 7.5—8 (for gas formation); ratio of straw to H_2O 1:10. The necessary phosphate and the organisms required for the fermentation are present in the straw itself. The acids formed should be neutralised by $NH_4HCO_3 + KHCO_3$. A. E. O.

Metabolism of strict anaerobes (genus *Clostridium*). III. Oxidation of alanine by *Cl. sporogenes*. IV. Reduction of glycine by *Cl. sporogenes*. L. H. STICKLAND (Biochem. J., 1935, 29, 889—898).—The end-products of the oxidation of alanine in presence of the enzymes of *Cl. sporogenes*, Bellette (I), and proline or glycine are NH_3 , AcOH, and CO_2 . No direct evidence that $AcCO_2H$ occurs as an intermediate stage could be obtained, but indirect evidence favours this view. Washed suspensions of (I) reduce glycine to AcOH and NH_3 at the expense of the oxidation of alanine. P. W. C.

Occurrence and activity of urea-splitting bacteria in the sea. C. E. ZOBELL and C. B. FELTHAM (Science, 1935, 81, 234—236).—Physiologically-active urea-splitting bacteria (I) (1—10 per c.c.) occur throughout the 50 m. zone of the Pacific Ocean investigated. In general, few (I) are found at depths > 100 m. Surface mud from depths 160—1300 m. contains 10 to 10^3 (I) per g. (I) are also associated with the integumental slime and intestinal contents of several marine fish. Three different types have been isolated from the sea, (i) those which grow well in media containing no source of N except urea (II) and liberate no excess of NH_4 , (ii) those which multiply freely in (II) media and produce excess of NH_4 , and (iii) those which start to multiply in (II) media only when NH_4 -, NH_2 -acid, or peptone-N is added, after which (II) is decomposed with formation of NH_4 . No marine bacteria which require (II) for their growth have been observed. L. S. T.

Action of the *B. pullorum* and *B. gallinarum* group on milk-media and on neutral-red. G. PACHECO and C. RODRIGUES (Compt. rend. Soc. Biol., 1935, 118, 1019—1022).—Production of acidity and/or alkalinity in media prepared from milk is not a trustworthy criterion for bacteriological classification of these bacteria (I). Those types of (I) which produce gas in a medium containing sugar (not necessarily

glucose) or peptone cause fluorescence (II) when neutral-red is added whilst (I) which produce no gas cause no (II). Production of (II) is favoured by anaerobiosis. W. McC.

Acidophile pyorrhoea: acid-forming bacteria. M. WAKUI (J. Nippon Dental Assoc., 1934, 27, 754—781).—*L. acidophilus* isolated from tissues grew satisfactorily at p_H 6.0—7.2, produced gas from carbohydrates (I), and was unaffected by increasing concns. of (I) up to 5%. CH. ABS. (p)

Fibrinolytic activity of haemolytic streptococci in relation to the source of strains and to cultural reactions. W. S. TILLET (J. Bact., 1935, 29, 111—130).—The infectivity of β -haemolytic streptococci for man is related to the fibrinolytic power of the cultures. The latter is of val. in separating pathogenic from harmless organisms. A. G. P.

Precipitation of bacterial polysaccharides with calcium phosphate. *Pneumococcus*. L. D. FELTON, G. KAUFFMANN, and H. J. STAHL (J. Bact., 1935, 29, 149—161).—The separation of the sol. sp. substance of *Pneumococci* from broth cultures by means of Ca phosphate is described. A. G. P.

Effect of hydrogen-ion concentration on the lysis [by nucleic acids] of tubercle bacilli. R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 118, 983—986).—Nucleic acids have no sp. lytic action (I) on the bacilli (II). (I) sometimes observed is due to the acidity. (II) are destroyed at $p_H < 2$, the rate of destruction depending on the degree of acidity (5 min. with conc. HCl, HNO_3 , H_2SO_4). W. McC.

Fractions of *Brucella abortus*. I. Preparation, toxicity, and nature of alcoholic precipitate. II. Complement fixation and intradermal tests. III. Immunity experiments. R. GWATKIN (Canad. J. Res., 1935, 12, 115—124, 125—132, 133—145).—I. Pptn. of a filtered aq. digest of *B. abortus* with 95% EtOH (5 vols.) yields a practically pure carbohydrate (I), 0.03 g. of which is the min. lethal dose (intraperitoneally) for guinea-pigs. The toxicity and temp.-lowering effect of (I) are not affected by dialysis or filtration through a candle.

II. In the complement-fixation test in guinea-pigs, (I) exhibits marked antigenic properties. In infected, but not in normal, animals (I) produces dermal reactions. The substance is stable to CH_2O .

III. *Brucella* anti-serum (II), inhibits the action of intraperitoneally injected (I) in guinea-pigs, whilst adsorption by the bacteria removes the protective substance from (II). (I) removes antibodies *in vitro* as efficiently as whole cultures do. In small animals (I) enhances agglutinin production and phagocytosis but does not protect guinea-pigs against infection by eye with *B. abortus* nor prevent abortions in infected animals. F. O. H.

Activation *in vitro* of the specific agglutination of *Brucella* antibody by non-specific sera. C. NINNI, W. SARNOWIEC, and F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, 118, 1056—1058).—The addition of 2% of fresh untreated serum (man or animal, especially horse) increases the sp. agglutination titre by anti-*Brucella* sera; the agglutination is also accelerated and modified in character. Heating

the sera at 56° for 30 min. markedly reduces this property. Non-sp. human serum increases, and guinea-pig's diminishes, the zone of agglutination.

F. O. H.

Soluble toxin from bacillus of pneumonia. M. LEVY-BRUHL and Y. CADO (Compt. rend. Soc. Biol., 1935, 118, 954—955).—Friedlander's bacillus grown in a synthetic medium at p_H 7.8 produces a sol. substance (I), possibly a non-protein (biuret test negative), toxic to rabbits, guinea-pigs, and mice. (I) is not affected by heating at 60° for 45 min. W. McC.

Specific substances in *B. ærtrycke* and *B. gaertner*. (A) "Complete" antigen and "residual" antigen. (B) "Complete" antigen (the acid-soluble constituent of the endotoxin of the *S* forms). A. BOIVIN and L. MESROBEANU (Compt. rend. Soc. Biol., 1935, 118, 612—614, 614—616; cf. A., 1934, 1406).—(A) The sp. complex polysaccharide extracted from the *S* forms of *B. ærtrycke* and *B. gaertner* with cold $CCl_3 \cdot CO_2H$ [the "complete" antigen (I)] is toxic, antigenic, non-dialysable, and contains fatty acids. By treatment with hot aq. $AcOH$, (I) is converted into a "residual" antigen (II), which is dialysable, non-toxic, and non-antigenic, and has no fatty acids. (II) is obtainable from the bacilli by heating with aq. $AcOH$. The *R* forms of the bacilli do not yield (I) and (II).

(B) (I) is thermostable and acid-sol. Both forms of the bacilli contain a toxic thermostable substance which is not acid-sol.

A. L.

Chemical composition of the *S* and *R* forms of *B. ærtrycke* and *B. gaertner*. A. BOIVIN and L. MESROBEANU (Compt. rend. Soc. Biol., 1935, 118, 727—729).—Only the *R* form contains the "complete" antigen.

A. L.

Recovery of agglutinins according to the proportion of antibodies fixed on bacteria. P. SEDALIAN and J. CLAVEL (Compt. rend. Soc. Biol., 1935, 118, 887—888).—Recovery is max. at the concn. at which complete saturation of the bacteria occurs. Dissociation of the bacterial complex occurs when neither antigen nor antibody is in excess.

R. N. C.

Production of staphylococcus toxin. H. BONNET and S. THIEFFRY (Compt. rend. Soc. Biol., 1935, 118, 1062—1063).—The prep. of highly active toxin by culture at p_H 7.8 for 7 days in a medium containing 0.15% of glucose, over which air+20% CO_2 continuously passes, is described.

F. O. H.

Diversity of toxins produced by hæmolytic streptococci from scarlatinal and non-scarlatinal sources. F. H. FRASER (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 81—90).—Toxins (I) similar to those produced by scarlatinal (II) strains of hæmolytic streptococci (III) are produced by (III) in diseases other than scarlet fever. (II) cannot be distinguished from non-(II) strains on the basis of strength of (I) produced. There are qual. differences between the (I) from (II) and non-(II) and between (I) from different (II) strains. Streptococcal anti-toxin against a single strain of (I) neutralises most (II) and non-(II) strains.

W. McC.

Mechanism of the action of some organic compounds on bacterial toxins. S. SCHMIDT (Ann. Inst. Pasteur, 1935, 54, 325—331).—The effects of various types of org. compounds on diphtheria toxin are recorded. Aldehydes cause a considerable loss of antigenic power together with toxicity.

H. G. R.

Is bacteriophage a living organism? F. WYSS-CHODAT (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 134—137).—Bacteriophage is a substance of simple mol. constitution.

P. W. C.

Metabolism and enzymic character of bacteriophage. H. SCHULER (Biochem. Z., 1935, 276, 254—261).—The metabolism of the purified bacteriophage (I) of Schlesinger (A., 1933, 1084) in absence of *B. coli* is γQ_0 0.28, 0.05. In presence of *B. coli* the val. is < 40 . (I) is resistant to trypsin, papain, lipase, amylase, catalase, arginase, and urease. The amount of (I) and the phosphatase activity run parallel, 1 mg. causing the separation in 1 hr. at 38° from a 1% hexose diphosphate solution in 0.1M-glycine at p_H 8.6 of 0.5—1.0 mg. of P_2O_5 . A lytic action of kidney- and bone-phosphatase on *B. coli* could not be detected.

P. W. C.

Action of sodium ricinoleate on various micro-organisms. H. VIOLE (Compt. rend., 1935, 200, 1152—1154).—Tubercle, paratubercle, and syphilis bacilli are killed by Na ricinoleate; spirochætes and viruses are also sensitive, but not enzymes.

R. N. C.

Toxicity of brilliant-green for certain bacteria. E. K. KLINE (Amer. J. Publ. Health, 1935, 25, 314—318).—Various certified commercial samples of brilliant-green were not all equally bacteriostatic.

W. O. K.

Effect of adrenaline on the blood-sugar of phloridzinised animals. P. HOUSSA (Compt. rend. Soc. Biol., 1935, 118, 1214—1216).—Intravenous injection of adrenaline in phloridzinised animals has no hyperglycæmic effect, and can even provoke a fall in blood-sugar, which appears to be due to increased insulin production.

R. N. C.

Effects of adrenaline hydrochloride on the blood-sugar of hepatectomised dogs. J. LA BARRE and P. HOUSSA (Compt. rend. Soc. Biol., 1935, 118, 1217—1218).—The fall of blood-sugar following hepatectomy is not arrested by injection of adrenaline, the normal action of which is principally on hepatic glycogenolysis.

R. N. C.

Action of adrenal cortex extract. S. FIANDACA and I. CAPIZZI (Endokrinol., 1934, 14, 316—327; Chem. Zentr., 1934, ii, 3135).—The Schmitz-Kühnau extract *A* in rabbits increases blood-phosphatide (I), -cholesterol (II), and -inorg. P (III); total N (IV) is depressed. Extract *B* lowers (II), (IV), and Ca, whilst (III) and K are increased. Extract *C* lowers (I) and K, and increases Mg, P, and Ca; it has the weakest effect of the three.

R. N. C.

Adrenal cortex hormone influencing carbohydrate metabolism. "Cortormone," glucose, and lactic acid in the blood of rabbits. J. A. COLLAZO, J. PUYAL, and I. TORRES (Arch. Med. Cirurg. esp., 1933, 36, No. 39).—The adrenaline-free

extract causes slow hyperglycaemia and lactic acid vals. are modified accordingly. CH. ABS. (p)

Adrenal. VII. Relation of the adrenal cortical hormone to the vitamins. A. GROLLMANN and W. M. FIROR (J. Nutrition, 1934, 8, 569—582).—Adrenal cortical hormone (I) has no replacement activity in experimental avitaminosis- B_1 or - B_2 . Reported replaceability of vitamin-C by (I) is due to presence of ascorbic acid (II) in preps. of (I). (II) does not prolong life in adrenalectomised animals. A. G. P.

Inactivation of adrenaline by aldehydes. J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 118, 1118—1121).—The pressor action of *l*-adrenaline is partly or wholly destroyed by incubation with AcCHO, glyceraldehyde, or CH_2O at 35° for 1.5 hr. F. O. H.

Water and solid content of the brains of albino rats treated with the growth hormone. H. S. RUBINSTEIN and L. M. FOX (J. Comp. Neurol., 1934, 60, 349—353).—The growth hormone did not affect the relative size of the brain nor the H_2O or solid contents. Meat extract caused the two latter vals. to decrease slightly. CH. ABS. (p)

Purification of insulin. A. M. FISHER and D. A. SCOTT (Trans. Roy. Soc. Canada, 1934, [iii], 28, V, 75—80).—Attempts to increase the activity of insulin (I) by the method of Dingemanse (Arch. néerl. Physiol., 1927—1928, 12, 259) using (I) and C supplied by her were unsuccessful. W. MCC.

Precipitation of insulin. Rapid assay of commercial insulin preparations. I. I. NITZESCU and S. SECAREANU (Bull. Soc. Chim. biol., 1935, 17, 118—127).—Insulin (I) is pptd. quantitatively by 0.2% aq. $\text{K}_4\text{Fe}(\text{CN})_6$. Commercial preps. (II) treated in this way left a solution which had no (I) activity, but gave a ppt. with picric acid. The reaction is applied to determine the purity of (II). A. L.

Hypoglycaemic action of insulin on the same dogs before and after depancreatisation. E. AUBERTIN and R. CASTAGNON (Compt. rend. Soc. Biol., 1935, 118, 697—700).—The effect of insulin (I) injected subcutaneously on depancreatised dogs (II) is retarded but > when (I) is given intravenously. The effect of (I) on (II) is considerably > on normal dogs. A. L.

Assay of insulin preparations. O. KAUSCH (Pharm. Ztg., 1935, 80, 246—247).—A description of biological methods and a "chemical" method depending on the increase in CuO-reducing power of the urine is given. F. O. H.

Pancreas as a blood regulator. H. HALPRIN (J. Med. Soc. New Jersey, 1934, 31, 28—30).—Excessive pancreatic activity (I) causes hypotension and hypoglycaemia. A high-carbohydrate diet is beneficial. Decreased (I) leads to hypertension and is benefited by a low-salt, high-carbohydrate diet supplemented with pancreatic extract. CH. ABS. (p)

Corpus luteum hormone. D. VAN STOLK and H. PENAU (J. Pharm. Chim., 1935, [viii], 21, 193—210).—A lecture. A. E. O.

Role of the corpus luteum in the uterine activity of the rabbit. E. TÓTH (Arch. Gynakol., 1934, 158, 151—163; Chem. Zentr., 1934, ii, 3134).—Folliculin (I) restores the spontaneous contractions (II) of the uterus and its sensitivity (III) to pituitrin, that have been destroyed by castration. Corpus luteum hormone destroys (II) and (III) in normal animals, and hence must antagonise (I) production in the ovary. R. N. C.

Œstrogenic, luteal, and gonadotropic hormones in hæmophilia. W. B. CHEW, R. P. STETSON, G. VAN S. SMITH, and O. W. SMITH (Arch. Int. Med., 1935, 55, 431—444).—Œstrogenic (I), corpus luteum, and gonad-stimulating hormones have no effect on the coagulation time of the blood. The urine from cases of hæmophilia contains more (I) than that of normal males. H. G. R.

Refractoriness to ovarian stimulation in the Rhesus monkey. R. K. MEYER and E. L. GUSTUS (Science, 1935, 81, 209—210).—The ovaries of immature monkeys are at first markedly stimulated by the gonadotropic hormone (I) of the serum of pregnant mares, but later and during the chronic administration of (I) they regress to a relatively infantile condition. This apparent refractoriness seems to be related to the presence in the monkey serum of a substance which develops as administration of (I) is continued and inhibits its action. L. S. T.

Stability of international standard of œstrus-producing hormone in alcoholic solution. I. W. ROWLANDS and R. K. CALLOW (Biochem. J., 1935, 29, 837—841).—EtOH solutions of œstrone stored in sterile sealed ampoules at -2°, room temp., or at 37° for 12 months showed no decline in activity and only a small increase in ultra-violet absorption when kept at 37°. H. D.

Chemistry of folliculin. C. A. DARRUTY (Rev. med. Lat.-Amer., 1932, No. 200, 1168—1172).—Folliculin ($\text{C}_{18}\text{H}_{24}\text{O}_3$) has two forms, (i) active, ketonic, activity 8×10^6 units per g., (ii) a more sol. poly-alcohol, a precursor or excretory form, activity > 200,000 units per g. CH. ABS. (p)

Determination of folliculin. Physiological and international units. B. FRATTINI (Arch. Ist. Biochim. Ital., 1935, 7, 1—18).—The methods of determining folliculin are examined and each physiological unit (I) is compared with the international standard. (I) is influenced considerably by the technique and solvent employed. Aq. solutions of folliculin are more effective in small repeated doses, whilst oil solutions are effective only in large doses. R. N. C.

Comparison between the effects of ovarian transplants and of folliculin benzoate on the comb and spur of the capon. F. CARIDROIT (Compt. rend. Soc. Biol., 1935, 118, 627—629).—Injections of 1 mg. daily of folliculin (I) benzoate are without action on the growth of the comb and the spur of the capon. It would appear therefore that (I) is only part of the ovarian secretion. A. L.

Action of gonadotropic hormones on women with spontaneous cycle-insufficiency. H. E. VOSS (Endokrinol., 1934, 14, 301—309; Chem. Zentr., 1934, ii, 3134).—The gonadotropic hormone of preg-

nancy urine in large quantities produces a lapse of a single cycle in insufficient mice. The urines of some insufficient women contain the oestrogenic (I) but not the luteinising hormone (II). Other urines contain both, (I) being effective when small quantities are injected, and (II) with larger quantities; (II) is so potent as to decrease folliculin production.

R. N. C.

Follicular hormone and blood-cholesterol. C. ARTOM, L. CIOGLIA, and D. TORE (Boll. Soc. ital. Biol. sperim., 1934, 9, 1247—1249).—Injections in rabbits of solutions of folliculin (I) in oil have effects similar to those of aq. solutions on blood-cholesterol, but a larger quantity of (I) is necessary to produce the same effect, which persists longer. The "sensitisation" of the animal by repeated injections of (I) is more effective if small doses are used. R. N. C.

State of combination of the gonadotropic hormone in blood-serum. C. GUTMAN and J. DALSACE (Compt. rend. Soc. Biol., 1935, 118, 973—974).—In serum the hormone (I) is firmly bound to the proteins and cannot be separated by dialysis at pH 3.5 or 8.0. (I) is not bound to the lipins. W. McC.

Sex hormones: preparation from the urine of pregnancy. S. VACH (Časopis českoslov. Lek., 1934, 14, 65—72, 98—103; Chem. Zentr., 1934, ii, 2697).—Mainly a confirmation of the results of other workers. Progesterin could not be detected in the urine of pregnant women; among the hormones of the anterior lobe of the pituitary prolan-A and -B were isolated. H. N. R.

Sex hormones and chlorine economy. G. TOROK and L. NEUFELD (Klin. Woch., 1934, 13, 1251—1252; Chem. Zentr., 1934, ii, 2699).—Injection of female, male, and gonadotropic hormones causes an increased retention of Cl in children of both sexes, followed by increased elimination of Cl on cessation of the treatment. Corpus luteum extract does not show this effect. H. N. R.

Effect of menformone on eye-pressure. K. T. A. HALBERTSMA (Nederl. Tijdschr. Geneesk., 1934, 28, 4186—4192; Chem. Zentr., 1934, ii, 2699).—Eye-pressure in women is lowered by injection of 100 mouse units of menformone, and in men by 1000 mouse units. R. N. C.

Effects produced on rats by synthetic androsterone (male sex hormone). V. KORENCEVSKY (Nature, 1935, 135, 434).—Androsterone increases the wt. of the atrophied prostate, seminal vesicles, etc. of castrated male rats. In these and in ovariectomised female rats, it produces a return towards the normal in many other organs. It has no rejuvenating effect on old males and does not produce oestrus in ovariectomised females. L. S. T.

Folliculin and the masculinisation factor. A. MOSZKOWSKA (Compt. rend. Soc. Biol., 1935, 118, 625—626).—Whilst pituitary extract (I) is effective in producing the sexual characteristics in castrated male guinea-pigs only when used shortly after castration, (I) combined with folliculin is still effective after > 3 months. A. L.

Y Y

Anterior pituitary and human sex glands. H. O. NEUMANN (Med. Klinik, 1934, 30, 702—704; Chem. Zentr., 1934, ii, 2699).—Injection into rats of Promonta's "pre-hormone-B" (I) causes inhibition of body-growth, growth of the seminal vesicles, and increase of the interstitial cells of the testes. Adult male rats injected for 5 days with 100 rat units of prolan or 300 units of (I) lose their reproductive power for 7 weeks, the testes showing no damage. R. N. C.

Virilism, ovarian function disturbance, and anterior pituitary hormone excretion. H. O. NEUMANN (Klin. Woch., 1934, 13, 1278—1281; Chem. Zentr., 1934, ii, 2699).—In a few cases of virile hair growth in women the anterior pituitary hormone reactions in the urine were positive. R. N. C.

Masculinising action of anterior pituitary extracts on recently castrated male guinea-pigs. A. MOSZKOWSKA (Compt. rend. Soc. Biol., 1935, 118, 516—518).—In the male guinea-pig subcutaneous injection of anterior pituitary extract is only able to induce secondary sexual characteristics when the injections are given shortly after the castration. A. L.

Anterior pituitary gonadotropic hormones and blood-cholesterol. L. CIOGLIA and D. TORE (Boll. Soc. ital. Biol. sperim., 1934, 9, 1249—1251).—Injection of prolan (I) in normal or ovariectomised rabbits produces a rise in blood-cholesterol \propto the amount of (I) injected. R. N. C.

Corticotrophic hormone of the anterior pituitary. K. J. ANSELMINO, F. HOFFMANN, and L. HEROLD (Arch. Gynakol., 1934, 157, 86—102; Chem. Zentr., 1934, ii, 2851; cf. A., 1934, 1410).—The collodion ultrafiltrate is freed from pancreatic hormone by heating the neutral solution to 100° and pptn. with EtOH. The mouse unit is defined. R. N. C.

Pituitary hormones. A. JORES (Klin. Woch., 1934, 13, 1269—1270; Chem. Zentr., 1934, ii, 2699).—The melanophore hormone is formed from an inactive precursor by alkali, the activation occurring in the pituitary, and by the stimulating action of light on the opticus. R. N. C.

Action of anterior pituitary on the adrenals. B. A. HOUSSAY, A. BIASOTTI, P. MAZZOCCO, and R. SAMMARTINO (Rev. Soc. Argentina Biol., 1933, 9, 262—268).—The adrenaline content declined after injections. CH. ABS. (p)

Hypophysin and gastric acidity. E. N. VASQUEZ (Arch. Argentin. enferm., 1933, 8, No. 4).—Injection of anterior pituitary caused a reduction of the total and, notably, of free gastric acid. The effect was more intense in hyperacidity. CH. ABS. (p)

Thyrotropic effect of anterior pituitary preparations. J. G. HEYL (Acta Brev. Neerl. Physiol., 1933, 3, 111—112; Chem. Zentr., 1934, ii, 2700).—The action of the thyrotropic hormone on the thyroid is apparent in the size and form of the epithelial cells and the vacuolisation in the colloid. R. N. C.

Hyperglycæmic constituent of posterior lobe pituitary extract. D. V. HOLMAN and H. C. ELLSWORTH (J. Pharm. Exp. Ther., 1935, 53, 377—384).—

The hyperglycæmic activity of the pressor substance is 1/20 of that of the oxytocic substance (I) of the posterior lobe pituitary extract. The effect of one unit of pituitrin is about the same as that of one unit of (I).

H. D.

Effect of extracts of the posterior lobe of the pituitary on water exchange in the frog. P. REY (Compt. rend. Soc. Biol., 1935, 118, 949—951).—In *Rana temporaria* (fasting) injection of the extracts causes decrease in urinary excretion, retention of H_2O in the tissues, and increased absorption of H_2O through the skin.

W. McC.

Action of hormones on the growth of cell cultures. E. M. VERMEL and M. S. MITZKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 245—248).—Cultures of connective tissue cells of the chicken (fibrocytes of the skin and the heart, macrophages of the spleen) are inhibited by thyroid hormone only at high concns., whilst lower concns. have a slight stimulating effect. The growth-promoting hormone of the anterior lobe of the pituitary does not affect the growth of the interstitial cells of the chicken (heart fibrocytes).

W. O. K.

Action of thyroxine on the fowl embryo. GMELIN-SCHEDRINA (Ann. Physiol. Physicochim. biol., 1934, 10, 453—461; Chem. Zentr., 1934, ii, 2998).—Thyroxine produces hyperthyroidism in both the embryo (I) and the chick, the effect increasing with the age of (I).

R. N. C.

Effect of thyroxine on the growth of the roots of *Allium cepa*. P. FLORENTIN and M. EHRENFELD (Compt. rend. Soc. Biol., 1935, 118, 1003—1005).—Thyroxine (I) in H_2O (1:100,000) causes earlier appearance of the roots, slight restriction of their growth for 2 weeks, and then increased longitudinal growth. At first (I) produces an increase in the no., but later only in the size, of the cells at the extremity of the meristem.

W. McC.

Trephones and hormones of embryonic tissues. P. MENDELEEFF (Compt. rend. Soc. Biol., 1935, 118, 1219—1222).—The hormones of the embryonic guinea-pig thymus suppress fibroblast formation (I) and stimulate that of epithelial tissues in the isolated skin *in vitro*; the thymus juice also accelerates coagulation of plasma. The juice of the remainder of the embryo is rich in trephones and nucleophosphates, and stimulates (I), but does not accelerate coagulation.

R. N. C.

Relations between the action of extract of human tonsils and those of poisons for vegetative nerves or hormones. K. TOMINAGA (Biochem. Z., 1935, 276, 352—358).—Administration of the extract (I) causes great reduction (II) in the glycogen production (from glucose) of the rabbit liver. (II) is considerably restricted by simultaneous administration of cholic acid. (I) intensifies (II) produced by insulin, novocaine, or atropine but restricts (II) produced by adrenaline.

W. McC.

Vitamin-A in the nutrition of dairy cattle. E. B. MEIGS and H. T. CONVERSE (Rep. Proc. XXVI Ann. Mtg. Amer. Soc. Animal Prod., 1933, 58—61).—Vitamin-A contents of hay and pasture are recorded.

Ch. Abs.

Lipin increase after large doses of vitamin-A. H. FASOLD (Z. ges. exp. Med., 1934, 94, 35—37; Chem. Zentr., 1934, ii, 2705).—Neither hypervitaminotic rats nor those given large doses of vitamin-A and cholesterol (I) daily show any increase of total (I).

R. N. C.

Failure of crystalline carotene to produce hypervitaminosis-A. J. T. LEWIS and L. RETI (Compt. rend. Soc. Biol., 1935, 118, 577—580).—Whilst a quantity of the unsaponifiable portion of carrot oil containing 0.04 g. of carotene (I) administered daily *per os* was toxic for the white rat, the same amount of pure (I) was without effect.

A. L.

Presence of vitamin-A and substance A' in hepatic tissue. A. CHEVALLIER and Y. CHORON (Compt. rend. Soc. Biol., 1935, 118, 159—162).—The absorption curves of the liver contents of the rat at various stages of digestion show that vitamin-A (I) is converted into substance A' (II) (cf. A., 1934, 931) in 36 hr., when (II) can be extracted with EtOH. In the liver of the guinea-pig, neither (I) nor (II) is present at any stage in more than traces.

R. N. C.

Detection of vitamin-A in the blood. A. CHEVALLIER and Y. CHORON (Compt. rend. Soc. Biol., 1935, 118, 889—891).—EtOH extracts of blood dried with Na_2SO_4 , examined spectroscopically, give similar extinction vals. for all species.

R. N. C.

Keratinisation of the epithelial mucous membranes on vitamin-A and carotene deficiency. **Anti-infective action.** H. VON EULER and M. MALMBERG (Z. physiol. Chem., 1935, 232, 1—5).—Mice deprived of vitamin-A (I) and carotene (II) showed no colpokeratosis or xerophthalmia. The anti-infective action of (I) and (II) and the action on the mucous membranes may be an effect of the accumulation of purines, which would favour cell-nucleus formation.

J. H. B.

Crystalline vitamin-B₁. II. Elementary composition and ultra-violet absorption. O. WINTERSTEINER, R. R. WILLIAMS, and A. E. RUEHLE. **III. Cleavage of [the] vitamin with sulphite.** R. R. WILLIAMS, R. E. WATERMAN, J. C. KERESZTESY, and E. R. BUCHMAN (J. Amer. Chem. Soc., 1935, 57, 517—520, 536—537; cf. A., 1934, 817).—II. Vitamin-B₁ hydrochloride (dried over $CaCl_2$ at 55°/vac.), m.p. 250°, is $C_{12}H_{16}ON_4S_2HCl$; an indefinite amount of H_2O is retained or adsorbed from air at room temp. Absorption max. in H_2O or EtOH are observed at 267, 235, and 208 $m\mu$.

II. Vitamin-B₁ with aq. $Na_2SO_3-SO_2$ at p_H 4.8—5.0 at room temp. gives in several days a 97% yield of an acidic substance, $C_6H_9O_3N_3S$, cryst., and a basic substance, C_6H_9ONS (hydrochloride, cryst.).

R. S. C.

Action of crystalline vitamin-B₁ on tissue oxidation of chronic avitaminous pigeon's brain. H. RYDÉN (Biochem. J., 1935, 29, 860—865).—The increased O_2 uptake on addition of vitamin-B₁ (I) to excised brains from (I)-deficient pigeons, showing leg weakness without head retraction, occurs markedly only in the cerebrum.

H. D.

Potentiometric titration of solutions of vitamin-B₁. R. C. G. MOGGIDGE and A. G. OGSTON (Biochem. J., 1935, 29, 866—870).—Using the H_2

electrode (I) the electrometric titration of vitamin- B_1 (II) shows two basic groups, p_K 2.5 and 4.7, and one pseudo-acid group, p_K 8.3. After titrating with alkali the curve shows a shift to the alkaline side on titrating back with alkali. With the glass electrode (II) more reproducible titration curves were obtained and the basic groups had p_K 3.4 and 4.8 and the acid p_K 9.1; no alkaline shift was observed. The loss in (II) activity produced by titration with (III) is < with (I). H. D.

Blood-pyruvate in vitamin- B_1 deficiency. R. H. S. THOMPSON and R. E. JOHNSON (Biochem. J., 1935, 29, 694—700; cf. A., 1934, 932).—The HSO_3' -combining power of $\text{CCl}_3\cdot\text{CO}_2\text{H}$ filtrates of pigeon blood is greater in the case of B_1 -avitaminous than of normal or of cured birds. The increase is probably due to AcCO_2H or to some labile compound readily yielding the latter. Confirmatory observations have been made on the HSO_3' -binding capacity of rats' blood. W. O. K.

Relation of the vitamin-B complex (particularly vitamin- B_1) to carbohydrate retention. E. ABDERHALDEN and E. WERTHEIMER (Pflüger's Archiv, 1934, 235, 53—59).—Addition of glucose, lactose, or sucrose to a normal diet of wheat and barley meal produces the appearance of avitaminosis- B_1 in pigeons; galactose and fructose have no effect. The effective sugars accelerate the appearance of convulsions in birds fed on polished rice (I), and the min. curative dose of yeast is increased. Lactoflavin favours growth in birds fed with (I) for the first few days, after which body-wt. falls. R. N. C.

Vitamin- B_2 . Non-identity of vitamin- B_2 and flavins. C. A. ELVEHJEM and C. J. KOEHN, jun. (J. Biol. Chem., 1935, 108, 709—728).—The vitamin- B_2 (I) [anti-pellagra (II) factor] content of liver extracts is determined using chicks as the experimental animals. After fractionation and removal of flavins with fuller's earth, a colourless concentrate with high (II) activity is obtained. (II) activity is not destroyed by sunlight and (I) cannot be identical with hepatoflavin. M. S.

Flavin content of liver and muscle of healthy and B_2 -avitaminotic rats. R. KUHN, H. KALTSCHMITT, and T. WAGNER-JAUREGG (Z. physiol. Chem., 1935, 232, 36—40).—The flavin (I) content of rat's liver tends to a const. level (15—17 mg. per kg. of fresh liver) and is not unduly depressed or elevated by deprivation or excess of (I) in the diet. J. H. B.

Stability of vitamin- B_1 , - B_2 , and - B_4 . J. A. KEENAN, O. L. KLINE, C. A. ELVEHJEM, and E. B. HART (J. Nutrition, 1935, 9, 63—74).—Vitamin- B_1 in yeast (I), liver (II), and in a normal grain ration was destroyed by autoclaving, and, in (I) and (II), largely inactivated by heating at 100° for 24 hr. Inactivation of - B_2 in foodstuffs results from dry heating at 120° for 24 hr. Under these conditions - B_1 and - B_4 are relatively more stable. A. G. P.

Action of ascorbic acid in different stages of experimental scurvy. G. MOURIQUAND, V. EDEL, A. COEUR, and J. JOLY (Compt. rend. Soc. Biol., 1935, 118, 886—887).—Ascorbic acid cures scorbutic

dystrophy at all stages, but extreme cases are fatal owing to general nutritive disequilibrium.

R. N. C.

Behaviour of oxidised ascorbic acid added to minced tissues of normal and scorbutic animals. E. MARTINI and F. PINOTTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1243—1245).—The amount of dehydroascorbic acid reduced by the tissues decreases as avitaminosis proceeds. R. N. C.

Behaviour of the reduced and oxidised ascorbic acid of the tissues following scorbutogenic feeding. The scorbutic index. E. MARTINI and A. BONSIGNORE (Boll. Soc. ital. Biol. sperim., 1934, 9, 1240—1242).—Ascorbic acid (I) in the adrenals and liver falls immediately on the first administration of the scorbutogenic diet. Dehydroascorbic acid (II) remains high until (I) has completely disappeared, afterwards falling; in the adrenals it rises as (I) falls. The (II):(I) ratio ("scorbutic index") increases continuously. R. N. C.

Physiological action of ascorbic acid oxidised photodynamically. E. MARTINI and A. BONSIGNORE (Boll. Soc. ital. Biol. sperim., 1934, 9, 1238—1240).—The antiscorbutic action of ascorbic acid is decreased by photodynamic oxidation to vals. corresponding with those of dehydroascorbic acid. R. N. C.

Vitamin-C in pigment metabolism. W. VON DRIGALSKI (Klin. Woch., 1934, 84, 1354—1355; Chem. Zentr., 1934, ii, 2856).—Ultra-violet irradiation of persons on diets of varying vitamin-C content does not show any differences in the duration of the tans produced. R. N. C.

Effect of ascorbic acid on experimental goitre. A. W. SPENCE and E. F. SCOWEN (Biochem. J., 1935, 29, 562—566).—Ascorbic acid is not an antigoitrogenic substance. H. G. M.

The intestine as a storage dépôt for ascorbic acid. E. JACOBSEN (Compt. rend. Soc. Biol., 1935, 118, 924—926).—The small intestine (I) of the normal guinea-pig contains a store of ascorbic acid (II) about 1/3 of that of the adrenals (III), and equal to that of the liver (IV). The rate of exhaustion on the basal diet is similar for the three tissues. (II) ingested by animals the reserves of which have been exhausted is taken up primarily in (I), and later distributed among (I), (III), and (IV) in the normal ratio, an equilibrium between the reserves being established. R. N. C.

Blood- and urine-vitamin-C after injection of large amounts of vitamin-C. P. ROHMER, N. BEZSSONOFF, E. STOERR, and J. PÉRIER (Compt. rend. Soc. Biol., 1935, 118, 1090—1092).—Injection of 0.2 g. of ascorbic acid per kg. body-wt. produces no pathological changes in infants (I), guinea-pigs (II), or rabbits, the blood level attaining 0.025% within 1 hr. and falling to approx. zero within 15—25 hr. The urinary excretion with (I) increases after 15 hr.; with (II) it is not significant. F. O. H.

Antiscorbutic properties of the aqueous humour and crystalline lens. G. BIETTI and A. CARTENI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1245—1247).—The aq. humour and cryst. lens show antiscorbutic

properties < those of orange-juice containing equiv. quantities of ascorbic acid. R. N. C.

Variation of the vitamin-C content of the tissue. A. GIROUD and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 118, 1179—1182).—Ascorbic acid falls rapidly in all tissues of the guinea-pig on a vitamin-C-deficient diet, reaching a steady min. at the 10th day. R. N. C.

Errors in determining vitamin-C by Bezsonoff's reagent. N. BEZSSONOFF (Compt. rend. Soc. Biol., 1935, 118, 1088—1089).—Interference with the molybdophosphotungstate urine test for scurvy (A., 1926, 722) due to presence of polyphenolic substances (e.g., tannin) does not occur when excess of reagent is avoided. F. O. H.

Vitamin-C and the carotenoids. Maturation of fruits. A. GIROUD, R. RATSIMAMANGA, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 118, 874—876).—The ascorbic acid content of ripe fruits is high only in those species in which the colour is due to carotenoids. R. N. C.

Antiscorbutic value of lucerne. L. F. LEVY and F. W. FOX (Biochem. J., 1935, 29, 884—888).—Lucerne contains about 4 times as much vitamin-C as does citrus juice. The activity is rapidly lost on damaging the cells, but much of the vitamin remains after cooking. P. W. C.

Symbiotic production of vitamin-C by acetic bacteria and yeast. S. HERMANN and N. FODOR (Biochem. Z., 1935, 276, 323—325; cf. A., 1934, 118).—The bacteria (*B. xylinum*, *B. xylinoides*, *B. gluconicum*) and yeasts of kombucha acting together produce ascorbic acid from sugar. W. McC.

Influencing of the dopa-reaction by vitamin-C. T. GRUNBERG and H. SCHADE (Klin. Woch., 1934, 84, 1353—1354; Chem. Zentr., 1934, ii, 2856).—Vitamin-C inhibits the dopa-reaction in frozen sections of guinea-pigs' ears *in vitro*. The reaction is positive if the vitamin-C is washed out; hence its action is on the 3 : 4-(OH)₂C₆H₃·CH₂·CH(NH₂)·CO₂H. R. N. C.

Parallelism between ascorbic acid and chlorophyll. A. GIROUD, A. R. RATSIMAMANGA, and C. P. LEBLOND (Bull. Soc. Chim. biol., 1935, 17, 232—251).—A detailed account of work already noted (this vol., 131). P. W. C.

Vitamin-C. Synthesis of β-keto-ε-methylarabohexonolactone (l-rhamnoascorbic acid).—See this vol., 608.

Photodynamic action of flavins on ascorbic acid. E. MARTINI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1235—1237).—Illumination of mixtures of ascorbic acid with flavins causes an immediate fall of E_h. R. N. C.

Provitamin-D potencies, absorption spectra, and chemical properties of heat-treated cholesterol. M. L. HATHAWAY and F. C. KOCH (J. Biol. Chem., 1935, 108, 773—782).—Heat-treatment (max. temp. 200°) of cholesterol followed by extraction with EtOH yielded fractions with increased provitamin-D activity but containing no ergosterol. M. S.

Efficacy of vitamin-D administration in aqueous preparations. Y. VENAR and T. W. TODD (J. Nutrition, 1934, 8, 553—568).—Aq. preps. restore normal conditions in the growth area (I) of bones. This may occur at the expense of mineral from the bone shaft if the mineral ration is inadequate. Maintenance of normal morphology in (I) and the replenishment of skeletal deposits are separate phenomena. A. G. P.

Effect of phosphates on the bones of rachitic rats. C. A. LILLY, C. B. PEIRCE, and D. R. L. GRANT (J. Nutrition, 1935, 9, 25—35).—The correction of rickets, induced in rats by a high-Ca, low-P diet, by means of dietary PO₄ was similar to that resulting from administration of irradiated ergosterol. A. G. P.

Production and prevention of dental caries. M. C. AGNEW, R. G. AGNEW, and F. F. TISDALL (J. Amer. Dent. Assoc., 1933, 20, 193—212).—Dietary deficiency of P and vitamin-D (I) favours dental caries in rats. Administration of (I) to children is preventive and curative. CH. ABS.

Sequence and extent of tissue changes resulting from moderate doses of viosterol and parathyroid extract. A. F. MORGAN and Z. SAMSCH (J. Biol. Chem., 1935, 108, 741—752).—Growth of rats on normal diet was > that of rats receiving moderately excessive doses of vitamin-D (I), or receiving parathyroid (II) extract. The action of (I) and (II) hormone is not identical. M. S.

Effect of significant variations of calcium content of the A.O.A.C. basal rachitic ration on the percentage of bone-ash in chick tibiae. W. C. SUPPLEE (J. Assoc. Off. Agric. Chem., 1935, 18, 146—149).—No significant change in % of bone-ash is produced unless Ca is < 0.8 or > 1.0%. E. C. S.

Vitamin-E. L. SCHIOPPA (Arch. Ist. Biochim. Ital., 1935, 7, 123—150).—The usual method of evaluation of vitamin-E is untrustworthy, either through the absence of vitamin-C from the diet, or through the uncertainty of the wts. of the rats used. Wheat-germ and rice-spermoderm oils are both able to check sexual degeneration from deficiency, and also possess eutrophic characteristics. R. N. C.

Influence of the concentration of respiratory materials on the respiration rates of plants. M. GEIGER-HUBER (Jahrb. wiss. Bot., 1934, 81, 1—34).—The respiration rate (*R*) of beer yeast ∝ the concn. of glucose (I) in the medium within the range 0.0001—0.002*M*, increasing relatively more slowly up to 0.01*M*, and being practically unaffected by higher concns. of (I). Yeasts may be differentiated by the rate of increase of *R* with (I) or by the concn. of (I) necessary to produce 50% of the max. *R*. In the light of these results the possibility is examined of the regulation of plant respiration by means of the sugar starch equilibrium of the tissues. A. G. P.

Dynamic factor in the theory of the mineral nutrition of plants. A. QUARTAROLI (Annali Chim. Appl., 1935, 25, 53—80).—Catalytic elements (Fe, Cu, Mn, Zn, etc.) in plants are regarded as regulators of the velocity of the reactions accompanying veget-

active processes in accordance with climatic conditions. Certain accessory components (e.g., alkaloids, essential oils, active principles) require for their formation an increased supply of thermal or radiant energy, but this need is lowered by the ability of plants to accumulate large stores of catalytic elements. The parallelism between the contents of catalytic elements (especially Cu) and of certain vitamins in plants, and the analogies in the behaviour of co-activating pairs of elements, e.g., Fe+Cu, and Mg+Zn, in plants and animals, are discussed. T. H. P.

Infra-red radiation emitted by fluorescent leaves under the action of light. C. DHÉRE and A. RAFFY (Compt. rend., 1935, 200, 1146—1148).—The fluorescence spectrum of *Pelargonium zonale* leaves show a band in the infra-red with its apex at 738 mμ. R. N. C.

Plant leaves and their functions. J. RICHTER (Pharm. Zentr., 1935, 76, 145—150, 159—163).—A morphological and histological account. E. H. S.

Oil vesicles in the corky tissue of *Plectranthus fruticosus*; a case of high membrane elasticity. H. WENZL (Protoplasma, 1934, 22, 362—366).—The extensibility of the membrane is shown by immersion in CHCl_3 and in EtOH. The membrane also exhibits marked selective permeability. A. G. P.

Physiology of leaf cells of *Elodea canadensis*. K. GAHLEN (Protoplasma, 1934, 22, 337—361).—The course of plasmolysis and deplasmolysis in sugar and NaCl solutions is examined in relation to starch-sugar equilibria in leaves of different age and under different climatic conditions. A. G. P.

Biology of halophytes. II. Water economy. E. SCHRATZ (Jahrb. wiss. Bot., 1934, 81, 59—93; cf. this vol., 266).—An increase in concn. of the nutrient solution reduces the transpiration of H_2O by glycophytes. The action of NaCl in this respect is > that anticipated from the higher concn. produced. Similar effects occur with halophytes although < 0.5% of NaCl tends to improve growth. The total H_2O consumption (I) of plants is smaller from more conc. nutrients. NaCl has a sp. action in this respect also. Increased shoot growth resulting from additions of appropriate amounts of NaCl is followed by little or no change in (I). Within the genus *Plantago*, surface transpiration of halophytes is > that of glycophytes. A. G. P.

Suction tension and permeability to water of living and dead [plant] tissues. L. BRAUNER (Protoplasma, 1935, 22, 538—552).—The permeability of various tissues is examined by use of varying concns. of sugar solutions and by variation of the external pressure. A. G. P.

How do electrolytes enter the cell? W. J. V. OSTERHOUT (Proc. Nat. Acad. Sci., 1935, 21, 125—132).—The concn. changes occurring with large multinucleate cells of *Valonia* indicate that NH_3 does not penetrate as NH_4^+ nor by ionic exchange, but by combination with a constituent, HX, of the protoplasm. F. O. H.

Plasmolysis and deplasmolysis. W. J. P. VAN REINE (Proc. K. Akad. Wetensch. Amsterdam,

1935, 38, 199—209).—At 5°, 15°, 25°, and 35° and with concns. of sucrose (I) of < 0.48, 0.68, 0.71, and 0.67M, respectively, the areas of plasmolysis (II) of epidermal cells of onion bulbs assume curved surfaces, whilst the time before the onset of (II) decreases with increase in [(I)]; with concns. of > 0.78, 0.93, 0.95, and 0.88M, respectively, the surfaces are angular, whilst the time for this and the intermediary stage varies only slightly with [(I)]. No correlation appears to exist between (II) and deplasmolysis (III) alone or corr. for cellular osmotic pressures. Hence (III) is not the reversed process of (II). F. O. H.

Cell physiology of sea algæ. I. Suction force of *Elachistea*. II. Permeability changes in plasmolysis. III. Stimulated plasmolysis and plasmasystrophe. E. BUNNING (Protoplasma, 1934, 22, 444—456).—The effects of changes in concn. and osmotic pressure of external solutions on plasmolysis and permeability of the cells are examined. A. G. P.

Ecology of salt marshes in north-east U.S.A. Osmotic ratios of soils as a factor in plant distribution. Ecology of osmotic values and chemistry of cell sap in halophytes. M. STEINER (Jahrb. wiss. Bot., 1934, 81, 94—202).—Relationships are examined between the distribution of plant associations and the osmotic pressure (P) of the soil solution. Surface and subsoil layers are concerned. The P of plant saps is regulated (i) by active elimination of excessive NaCl or (ii) by increased H_2O intake. In *Juncus gerardi* there is no regulation of P of the sap, which varies simultaneously with the NaCl content of the soil. A. G. P.

Regulation of the media by plant tissues. V. KILLIAN and S. ANTONICKÝ (Protoplasma, 1935, 22, 581—592).—Reaction changes resulting from the introduction of H_2O and of slightly acid or alkaline solutions into stems of *Impatiens roylei*, Walp., are examined. The effect of the age of the tissue and of day or night conditions are recorded. A. G. P.

Hard seeds and broken seedlings in red clover (*Trifolium pratense*). IV. Early stages of germination (physical). A. NELSON and J. C. MACSWEEEN (Trans. Proc. Bot. Soc. Edinburgh, 1933, 31, 247—255).—The lining (I) of the testa of the broad bean contains osmotically active material and the free liquid within the testa of the swollen bean reduces Fehling's solution. During swelling the p_{H} of tissue beneath the testa decreases. The second stage of H_2O intake in swelling seeds is osmotic in character, due to the semipermeability of the coat and the formation of active substances by hydrolysis of carbohydrates in (I). CH. ABS. (p)

Action of vegetable juices on morphine. A. LEULIER and S. ADAM (Compt. rend. Soc. Biol., 1935, 118, 882—883).— H_2O_2 was necessary for the oxidation of morphine by a no. of vegetable juices containing oxidative enzymes. R. N. C.

Differentiation of strains of clovers and soya beans by the luminescence of germinated seeds. E. CHMELÁŘ and K. MOSTVOJ (Vestník čechoslov. Akad. Zemed., 1934, 10, 289—295).—Diagnosis of

various strains depends on coloured luminescence of seedling roots. A. G. P.

Growth-promoting substance in soil. E. G. PRINGSHEIM (Naturwiss., 1935, 23, 197—198).—The growth-promoting factor (I) from soil has a H_2O -solubility and heat-stability common to this class of substances. (I) is differentiated, however, by being insol. in EtOH and Et_2O , stable towards acids and alkalis, and destroyed by H_2O_2 ; it is associated with the humus substances. F. O. H.

(A) Polarity and growth-promoting substance. (B) Root growth, growth-promoting substance, and the theory of its action. A. T. CZAJA (Ber. deut. bot. Ges., 1935, 53, 197—220, 221—245).—(A) Highly conc. preps. of growth-promoting substance (I) applied in a manner to act transversely to the axis of the plant cause a restriction in the growth of stems together with a localised thickening of the tissue or a positive curvature. In roots growth inhibition and thickening occur. The effect is due to widening and, in some cases, simultaneous shortening of affected cells. Axial and transverse effects of (I) may be superimposed, the final action depending on the relative concns. of (I) applied simultaneously in the two directions. (I) effects an electrical and a morphological polarisation of the cells.

(B) Root growth and geotropic response are examined in relation to the streaming of (I) with special reference to the antagonistic effects of the axial stream in main roots and that arising in laterals. A. G. P.

Tryptophan reaction and detection of hetero-auxin.—See this vol., 639.

Effect of zinc on the growth of *Vitis*. J. DUFRENOY (Compt. rend. Soc. Biol., 1935, 118, 156—158).—The vegetative growth is influenced by $ZnSO_4$, which simultaneously permits the formation of clusters, the cytological symptoms (formation of endocellular cords) persisting. R. N. C.

Formation and organisation of plant-cell membranes. M. LUDTKE (Protoplasma, 1934, 22, 457—488).—A review. A. G. P.

Thiol postulate for cell proliferation. F. S. HAMMETT (Protoplasma, 1934, 22, 489—491).—A discussion of recent work. A. G. P.

Physiological salt solutions and the growth of tissues. E. HECHT (Protoplasma, 1935, 22, 553—560).—Comparisons of the effects of buffered and unbuffered solutions are recorded. A. G. P.

Non-protein-nitrogen of pulses. K. BHAGVAT and M. SREENIVASAYA (Biochem. J., 1935, 29, 909—913).—Five methods have been used for the determination of non-protein-N in different Indian pulses. The non-protein fraction varies according to the plants examined and the methods used. It is shown to contain the simpler peptides. H. T.

Variations in the sum, $N + P_2O_5 + K_2O$ per cent. of the dry matter of leaves in cultivated plants. H. LAGATU and L. MAUME (Compt. rend. Acad. Agric. France, 1935, 21, 85—92).—The summation val. of potato leaves was increased by surface irrigation (I) and further increased by subsoil (I). The mechanism of this effect is examined. A. G. P.

Constituents of *Ginkgo biloba*, L., fruit.—See this vol., 615.

Paraffin hydrocarbon in oil of birch buds. F. PETRU and J. HADACEK (Coll. Czech. Chem. Comm., 1935, 7, 90—92).—The paraffin isolated by Soden and Elze (A., 1905, i, 451) is $C_{25}H_{52}$, m.p. 53—54°, which has been extracted from birch bark by Ruzicka *et al.* (A., 1934, 529). F. R. G.

Highly unsaturated acids from oiticica oil.—See this vol., 607.

Phytochemistry. CXII. *Corydalis aurea*. H. ERPSON (J. Amer. Pharm. Assoc., 1935, 24, 113—115).—Light petroleum fractionation, etc. of the EtOH extract of air-dried *C. aurea* yields dimyristylcarbinol and the alkaloids, C_{11} , m.p. 138—140°, $[\alpha]_D^{25}$ —271° in $CHCl_3$ or abs. EtOH, 32.7—33.5% OMe, demethylated to a substance, m.p. 278—280° (decomp.); C_9 , m.p. 148—149°, probably identical with that isolated by Heyl (A., 1910, ii, 441) from *C. aurea* and by Chou (A., 1928, 927) from *C. ambigua*; D_2 , m.p. 200—202° (H oxalate, m.p. 242—243°), $[\alpha]_D^{25}$ 0°, free from OMe, and similar to corydalis-C of Chou (*ibid.*). F. O. H.

Perfumes of the violet. VI. Non-aldehydic components of violet leaf-oil. L. RUZICKA and H. SCHINZ (Helv. Chim. Acta, 1935, 18, 381—401; cf. this vol., 66).—The non-aldehydic portion of commercial violet leaf-oil contains a *salicylate*, $EtCO_2H$, *n*-heptoic, an octoic, b.p. 90—96°/0.2 mm. (*chloride*, b.p. 80—90°/12 mm.; β -*naphthylamide*, m.p. 82—83°, α_D 0), an octenoic, b.p. 105—118°/12 mm. (*chloride*, b.p. 80—90°/30 mm.; β -*naphthylamide*, m.p. > 95—96°, α_D 0), and palmitic acid, a mixture of active primary alcohols, b.p. 62—73°/12 mm., $C_6H_{12}O$, $C_7H_{14}O$, and $C_8H_{16}O$ (probably Δ^8 -*n*-octen- α -ol), a similar mixture (I), b.p. 96—98°/12 mm. [containing Δ^8 -nonadien- α -ol (*semicarbazone of pyruvate*, m.p. 114—115°), oxidised to $EtCHO$ and $(\cdot CH_2 \cdot CO_2H)_2$, and reduced to $n\text{-}C_8H_{19}OH$], and a mixture of *tert*-alcohols, probably $C_8H_{14}O$ and $C_8H_{16}O$. A second sample of oil gave similar products, but (I) contained also probably CH_2PhOH . The odour is due mainly to the aldehyde, but is enhanced by the primary alcohols. R. S. C.

Poisonous *Anacardiaceae*. A. GOUDSWAARD (Pharm. Tijdschr. Nederl.-Indie, 1934, 11, 209—217; Chem. Zentr., 1934, ii, 3143—3144).—A no. of skin-irritant saps of *Anacardiaceae* are described. A substance similar to cardol has been isolated from leaves and twigs of *Gluta rhengas*, and from twigs of a species of *Mangifera*. R. N. C.

Sugars of assimilating leaves. V. L. KRETOVITSCH (Z. physiol. Chem., 1935, 231, 265—276).—The leaves (*Betula alba*, *Tilia europaea*, *Populus* sp., *Convallaria majalis*, *Aspidium filix mas*, *Dahlia variabilis*) were collected on sunny days at 10 a.m. Reducing sugars were present in greater amount than *cryst. polysaccharides*, and fructose usually exceeded glucose. Small amounts of sugars and carbohydrates hydrolysed with difficulty, not pptd. by $Pb(OAc)_2$, insol. in 82% EtOH but sol. in H_2O , were found. J. H. B.

Fructose and fructosides in plant metabolism.

A. KIZEL and V. L. KRETOVITSCH (Sci. Inst. Cereal Res. Moscow, 1934, 13, 56—59).—Fructofuranose is the principal monosaccharide formed during photosynthesis. Fructose and fructosides act as precursors of starch. A trifructosan is obtained from rye, m.p. 185—200° (Ac derivative, $[\alpha]_D^{20} + 207^\circ$ in CHCl_3). CH. ABS. (p)

Carbohydrates in the bulbs of *Allium*. III. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1934, 10, 417—423).—Bulbs of *A. bakeri*, *A. ledefourianum* (I), and *A. fistulosum*, L., var. *cæspitosum*, Makino (II), contain, respectively: H_2O 70.43, 60.0, 75.87; N 1.65, 1.11, 1.76; crude protein 10.31, 6.83, 10.99; sol. carbohydrate 61.00, 64.40, 51.42; pentose 2.20, 1.55, 5.30; ash 2.20, 1.88, 3.75; Et_2O extract 0.40, 0.50, 1.61; crude fibre 2.45, 1.87, 7.12% of dry matter. The carbohydrate distribution is recorded. Fructan is present. (I) contains mannan, and (II) araban. Starch, dextrin, and inulin were not found. CH. ABS.

Sago palm. I. Changes in composition during ripening of the seed. K. NISHIDA (J. Agric. Chem. Soc. Japan, 1934, 10, 374—378).—The starch is max. (38%) in November. The ash, protein, dextrin, and starch increase, whilst the non-protein-N and crude fibre decrease, with maturation. CH. ABS.

Determination of biologically important carbohydrates in plant material. K. GEFFKEN (Bot. Archiv, 1934, 36, 345—376).—Plant samples for analysis are best killed by hot-air treatment. Alternatively, material should be extracted immediately with boiling H_2O . Treatment with CHCl_3 vapour does not satisfactorily arrest hydrolysis of sucrose and starch (I) may also be affected. Willstätter's hypiodite titration gives satisfactory results for sugars. The presence of fructose in *Ilex* (II) is indicated. The takadiastase method for determining (I) gives irregular results unless strictly standardised conditions are adopted. Seasonal variations in sugar contents of *Hedera* and (I) are recorded. Both show a "frost max." in winter. A. G. P.

Presence of sterols in algæ. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 194—195).—The presence of sterols in three types of algæ is demonstrated. J. W. B.

Hemicelluloses. I. Alcoholic sodium hydroxide as a pretreatment to extraction. A. G. NORMAN (Biochem. J., 1935, 29, 945—952).—Delignification by pretreatment by boiling with 1% NaOH in 50% EtOH prior to preparing hemicellulose (I) is inadmissible in quant. work, since the yield of (I) may be lowered by 50%. The (I) removed by this treatment does not represent a special group of the polyuronides. A. E. O.

Detection of lignin in cell walls. G. FRIESEN (Ber. deut. bot. Ges., 1935, 53, 186—196).—Customary methods are criticised. The phloroglucinol colour may be obtained with certain sugars. A modified HgS staining method is described. A. G. P.

Crystalline tea-tannin from green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res.

Tokyo, 1935, 26, 186—191).—Extraction with $\text{EtOAc} + 10\% \text{H}_2\text{O}$, concn., pptn. with Pb acetate, re-extraction with EtOAc , and treatment with CHCl_3 , Et_2O , and EtOH yielded 0.325% of cryst. tannin, $\text{C}_{22}\text{H}_{18}\text{O}_{10}$, $[\alpha]_D^{25} - 177.5^\circ$ in 95% EtOH (Ac₇ derivative, m.p. 123°) (cf. A., 1929, 627; 1930, 1295). F. O. H.

Determination of tannin in plant materials. I. *Cassia auriculata*. N. SRINIVASAN (J. Indian Inst. Sci., 1934, 17, A, 165—173).—Bark, ground to pass a 25—30-mesh sieve, is repeatedly extracted with boiling H_2O . Tannin in the extract is determined by the difference in refractometer reading before and after pptn. with fat-free caseinogen. A. G. P.

Constituents of the rhizome of *Cimicifuga racemosa*. F. MERCIER and J. BALANSARD (Compt. rend. Soc. Biol., 1935, 118, 166—168).—The rhizome contains four glucosides, viz.: (a) a glucosidic tannin, sol. in H_2O , sparingly sol. in org. solvents, hydrolysing to glucose and a phlobaphen; (b) an acid saponin, sol. in H_2O , the solution frothing on agitation and emulsifying Hg, pptd. by $\text{Pb}(\text{OAc})_2$ and $(\text{NH}_4)_2\text{SO}_4$, but not by $\text{Ba}(\text{OH})_2$, and hydrolysing to glucose and a brown resinous product; (c) a non-reducing fraction, very sol. in H_2O , EtOH, MeOH, and MeOAc, which reduces Fehling's solution after hydrolysis with HCl; (d) a fraction insol. in H_2O and sol. in org. solvents except Et_2O , light petroleum, and C_6H_6 , reducing Cu^{++} after hydrolysis, and, alone of the four, possessing a marked cardio-toxic action. R. N. C.

Apigenin from marguerites (*Chrysanthemum leucanthemum*). G. JACINI (Helv. Chim. Acta, 1935, 18, 276—278).—The petals of this flower contain glucosides (probably including or only a methylpentoside) of apigenin. R. S. C.

Saponins and sapogenins. III. Sapogenins from *Chlorogalum pomeridianum*. P. LIANG and C. R. NOLLER (J. Amer. Chem. Soc., 1935, 57, 525—527; cf. A., 1934, 1007).—The inner portion of the bulbs yields to MeOH tigogenin and chlorogenin, $\text{C}_{26}\text{H}_{42}\text{O}_4$, m.p. 273—276°, $[\alpha]_D^{24} - 52^\circ$ in CHCl_3 or Pr^nOH (dibenzoate, m.p. 200.5—204.5°, $[\alpha]_{5460}^{20} + 9.5^\circ$ in CHCl_3 ; di-o-bromobenzoate, m.p. 205—207°, $[\alpha]_{5460}^{20} - 9.5^\circ$ in CHCl_3 ; 2 O are probably oxidic). R. S. C.

Constituents of the Japanese domestic mushroom. II. Organic bases of *Hydnum aspratium*, Berk. S. INAGAKI (J. Pharm. Soc. Japan, 1934, 54, 824—828).—The aq. extract contained histidine, guanidine, choline, and NMe_3 . CH. ABS. (p)

Pharmacology and chemistry of coffee. A. HOLSTE and S. S. MIHOLIC (Arch. Hyg., 1934, 113, 108—111).—The caffeine (I) content of normal coffee-beans is 1.24—1.32%. In the prep. of coffee from normal or treated [containing 0.18—1.27% of (I)] beans, the German method extracts 80.9—98.5 and the Turkish 39.2—59.0% of (I). F. O. H.

Digitoxin content of *Digitalis purpurea*. E. BERTONASCO (Boll. Chim. farm., 1935, 74, 114).—Leaves of the plant in their second year of vegetation contain 0.22% of digitoxin. E. W. W.

Alkaloids of pomegranate (*Punica granatum*). J. CHAZE (Compt. rend. Soc. Biol., 1935, 118, 1065—

1068).—The distribution of alkaloids in the stem, roots, and leaves (indicated by KI_3 , $KBiI_4$, etc.) is described and a conception of their origin and migration advanced. F. O. H.

Brazilian *Simaruba* bark and its constituent drugs. F. W. FREISE (Apoth.-Ztg., 1934, 49, 1114—1116; Chem. Zentr., 1934, ii, 3144).—The constituents of the true bark vary considerably with the time of extraction, age of preservation, and manner of prep. The original species of *Simaruba* contains an alkaloid, $C_{24}H_{21}O_5N$, m.p. 215—220°; a bitter glucoside, hydrolysed by acids to *d*-glucose, *d*-rhamnose, *d*-fructose, and quercetin; a yellow essential oil, *d* 0.8945; a yellow, intensely bitter soft resin; tannin (if stored for > 1.5 years), and salts comprising chiefly $K_2C_2O_4$ and CaC_2O_4 . R. N. C.

Alkaloid of *Cereus coryne*, Solm. L. RETI, R. I. ARNOLD, and F. P. LUDUENA (Compt. rend. Soc. Biol., 1935, 118, 591—593).—The pharmacological action of the active base and its chemical behaviour suggest that it is a quaternary NH_4 derivative of hydroxytyramine (hydroxycaudicine). A. L.

Colouring matter of shiso. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1935, 11, 28—31).—Treatment of the leaves of shiso (*Perilla ocimoides*, L., var. *crispa*, Benth.) with $MeOH-HCl$, Pb acetate, etc. yields a colouring matter which on hydrolysis with alkali affords *p*-coumaric acid and cyanin (A., 1932, 1140). F. O. H.

Pigment of red cabbage. II. H. WILLSTAEDT (Biochem. Z., 1935, 276, 262—264).—The prep. of a pigment, $C_{28}H_{33}O_{16}Cl$, is described. P. W. C.

Extraction of sap from plant tissues. S. RAJAGOPAL and A. V. V. IYENGAR (J. Indian Inst. Sci., 1935, 18, A, 7—10).—In the expression of juice from sandal leaves, cytolysis is better effected by freezing in liquid air than by chemical cytolysing agents. Of the latter the best are $PhMe$ and $CHCl_3$ followed by freezing overnight at -16° . W. O. K.

Composition of the terminal shoots and fruits of two varieties of apple in relation to rootstock effects. L. G. G. WARNE and T. WALLACE (J. Pomology, 1935, 13, 1—31).—Correlation is established between the distribution of Ca , K , N , and Mg in the wood, bark, and leaves of terminal shoots and between the $P_2O_5:N$ ratio and growth rates. The influence of different stocks is shown on the contents of N and of certain mineral constituents of shoots and on the sugars and acidity of fruits. A. G. P.

Invertase in the latex of *Euphorbia cyparissias*, L. L. IURACEC (Compt. rend. Soc. Biol., 1935, 118, 611—612).—Reducing sugar is formed when the latex is allowed to react with sucrose. A. L.

Growth-inhibiting substance in lettuce seeds. A. L. SHUCK (Science, 1935, 81, 236).—Lettuce seeds form a substance of unknown nature which diffuses from the seed, and if present in sufficient amount prevents germination. L. S. T.

Toxic action [on plants]. IX. Toxicity of organic acids of the formic acid series. W. STILES and W. J. REES (Protoplasma, 1935, 22, 518—538; cf. A., 1933, 106).—As measured by the exudation of electrolytes from discs of potato tuber, the toxicity of the acids (I) declines from HCO_2H to $EtCO_2H$ and subsequently increases as the series is ascended. (I) is controlled jointly by dissociated H^+ and by undissociated acid mols. The HCO_2H mol. is approx. 0.003—0.01, and the nonoic acid mol. 0.65, times as toxic as H^+ . A. G. P.

Physiology and pathology of "leaf yellows" of sugar beet. E. W. SCHMIDT (Z. Wirts. Zuckerind., 1935, 85, 200—214).—Yellowed leaves have smaller chloroplasts and lowered contents of starch, protein, chlorophyll-*a* and -*b*, alkali-chlorophyllin, xanthophyll, and carotene. The proteolytic activity and the proportion and distribution of CaC_2O_4 are unchanged. Characteristic changes in chemical composition of leaves discoloured by insect and fungus attack, by unbalanced nutrition, etc. are examined. A. G. P.

Morphological reactions in saline and protein solutions. T. KOFMAN (Bull. Soc. Chim. biol., 1935, 17, 106—117).—The shape of terminal efflorescence on the osmotic growth formed by a crystal of $NiCl_2$ placed in aq. K_2SiO_3 (I) varies according to the nature of the supernatant liquid (II) and is often characteristic of (II). The method is suggested for the identification of mineral and biological liquids. A. L.

Osmometer from living *Valonia* cells and their application in permeability determinations. P. KORNMAN (Protoplasma, 1934, 21, 340—350; Chem. Zentr., 1934, ii, 3148).—The method and its application with various alcohols are described. H. J. E.

Rapid test for chlorate ion [in plant extracts].— See this vol., 594.

Micro-determination of biological carbon, especially of residual carbon in blood. V. RUPPERT (Z. physiol. Chem., 1935, 231, 213—225).—The method of Osuka (A., 1932, 550) is modified by a change in the form of apparatus, so that drying and combustion of liquids are performed in the same vessel, by introduction of a prepared oxidation mixture, and by use of a simpler method of titration. The error is $> 3\%$. The residual C in defibrinated human blood obtained by phosphotungstic acid pptn. is 132 mg. per 100 c.c. (mean val.). If protein is removed by $EtOH$ -light petroleum the val. is about 6 times as great. By extraction of this filtrate with light petroleum the fats and lipins in the residual C may be determined separately. J. H. B.

Micro-determination of fructose by Yamada's method. Determination of true glucose. H. OKAMURA (Japan. J. Med. Sci., 1935, II, 3, 9—14; cf. Yamada, A., 1933, 737; see also A., 1934, 1122).—Improved results are obtained if $CdCl_2$ is used for deproteinisation and $NaCl$ with Fe salt are added before colours are compared. Total true sugar (I) is determined by the method of Fujita *et al.* (A., 1932, 75). True glucose is (I)—fructose. W. McC.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1935.

General, Physical, and Inorganic Chemistry.

Structure of the hydrogen lines. K. BECHERT and J. MEIXNER (Ann. Physik, 1935, [v], 22, 525—536).—Theoretical. The difference between the observed splitting of the lines of the Balmer series for H and that given by Sommerfeld's theory is discussed. No difference between the lines for H and D can be found experimentally (cf. this vol., 271). The mass correction of Darwin can be derived by wave mechanics. The distance between the intensity max. of the fine structure is not changed by the hyperfine structure. A. J. M.

Extension of ultra-violet wave-length limit. H. ALFVÉN and V. H. SANNER (Nature, 1935, 135, 580—581).—The short-wave limit of the ultra-violet has been extended to 21 Å. by means of a spark discharge between C and C+LiNO₃ electrodes. L. S. T.

Calculation of band constants for the second positive nitrogen group. A. GUNTSCHE (Ann. Physik, 1935, [v], 22, 657—661).—Calculation of the band const. (*B* and *D*) for the second positive N group gives vals. disagreeing with those of Büttenbender and Herzberg (this vol., 271). It is emphasised that the form of the function is not known. A. J. M.

[Calculation of band constants for the second positive nitrogen group.] G. HERZBERG (Ann. Physik, 1935, [v], 22, 662).—The introduction of $(J+\frac{1}{2})$ in the expression for $\phi(J)$ gives results in agreement with experiment. A. J. M.

Stark effect in molecular spectra of nitrogen, carbon dioxide, and hydrogen. W. RAVE (Z. Physik, 1935, 94, 72—84). A. B. D. C.

Forbidden O I lines in the spectrum of *Nova Herculis* 1934. W. GROTRIAN and W. RAMBAUSKE (Naturwiss., 1935, 23, 248).—The spectrum has a strong emission line at 6300 and two weaker ones at 6362.2 and 5576.5 Å., which are the forbidden lines of the O I spectrum, $2p^1D_2-2p^1S_0$, $2p^3P_2-2p^1D_2$, and $2p^3P_1-2p^1D_2$. All these increased considerably in intensity during the early months of 1935. A. J. M.

Wave-length table for the vacuum spark spectrum of fluorine. B. EDLEN (Z. Physik, 1935, 94, 47—57). A. B. D. C.

Electronic excitation function of the metastable s_5 level of neon. J. M. W. MILATZ and L. S. URNSTEIN (Physica, 1935, 2, 355—362).—The excitation function (*I*) of the metastable s_5 level of Ne

was determined by measuring the absorption (1.5%) of light of λ 6402. The methods by which metastable atoms could be produced are considered, and it is shown that collisions of the second kind, bringing atoms from the s_4 to the s -level, and excitation by way of the p_9 level could not account for the no. of metastable atoms produced. It is concluded that the optical (*I*) measured is also the electrical (*I*) for the s_5 level. A. J. M.

Transition probabilities for the *D* lines of sodium from absolute intensity measurements, the dissociation of sodium salts, and the half width of the *D* lines in the luminous gas-air flame. R. MINKOWSKI, H. G. MÜLLER, and M. WEBER-SCHAFER (Z. Physik, 1935, 94, 145—171).—Na salts are only 30—80% dissociated in the ordinary gas flame, and deviations from thermal equilibrium are pronounced. A. B. D. C.

Transition probability for $2P-1S$ of sodium from absolute intensity measurements of flames. R. MINKOWSKI and M. WEBER-SCHAFER (Z. Physik, 1935, 94, 172—175).—The results of Held and Ornstein (A., 1932, 979) are discussed. A. B. D. C.

Mechanical moment of the cobalt nucleus. H. KOPFERMANN and E. RASMUSSEN (Z. Physik, 1935, 94, 58—67).—This moment is $7/2$. A. B. D. C.

Deep configurations of cobalt. H. H. MARVIN (Physical Rev., 1935, [ii], 47, 521—526).—Term vals. for Co I and *g*-factors for the Zeeman effect in intermediate coupling are calc. N. M. B.

Zeeman effect in the arc spectrum of cobalt. F. L. ROTH and P. F. BARTUNEK (Physical Rev., 1935, [ii], 47, 526—531).—Zeeman patterns for 151 lines in the range λ 3200—6500 are tabulated. Calc. and experimental *g*-factors for 100 terms are compared for *LS* and intermediate coupling. N. M. B.

Spectrum of selenium. V. Structure of Se II. S. G. KRISHNAMURTY and K. R. RAO (Proc. Roy. Soc., 1935, A, 149, 56—70; cf. A., 1934, 935).—About 200 lines between 8000 and 450 Å. ascribed to Se II have been classified as belonging to the quadruplet and doublet systems. The largest term, $4p^4S_{11}=174,994$ cm.⁻¹, gives for ionisation potential 21.6 volts. L. L. B.

Effect of magnetic field on the fluorescence of diatomic molecules of selenium. J. GENARD

(Physica, 1935, 2, 328—334).—The effect of a strong magnetic field on the resonance radiation of Se_2 vapour was determined. The effect varies from term to term.
A. J. M.

Intensity measurements with a reflexion echelon. J. H. GISOLF and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 225—229).—The relative intensities of the hyperfine structure components of the Cd line 4678 Å., 3P_0 — 3S_1 , have been measured.
R. S. B.

Hyperfine structures in La III. Nuclear magnetic moment of lanthanum. M. F. CRAWFORD and N. S. GRACE (Physical Rev., 1935, [ii], 47, 536—538).—Hyperfine structure separations and intensities in the resonance lines 3517 and 3172 Å. of La III were measured. The calc. moment is 2.8 nuclear magnetons.
N. M. B.

Zeeman effect in the tungsten spectrum. M. A. CATALAN and F. POGGIO (Anal. Fis. Quim., 1934, 32, 255—270).—After applying corrections to Beining's results (A., 1927, 491), vals. are obtained in accordance with Jack's data (A., 1909, ii, 280).
D. R. D.

Electrical and photo-technical properties of high-pressure mercury-vapour discharges. B. N. KLJARFELD and E. S. PLOKHOTSKI (J. Tech. Phys. U.S.S.R., 1934, 5, 796—803).—The dependence of spectral distribution and intensity on discharge characteristics was measured.
CH. ABS. (e)

Characteristics of Pb I, II, III, IV lines revealed in instantaneous spectrograms. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1935, 11, 43—46).—A qual. discussion of the principal features of the lines.
N. M. B.

Lines or bands in the spectrum of the night sky. J. V. KARANDIKAR (Indian J. Physics, 1935, 9, 245—250).—Data and those obtained by other investigators are tabulated. $\lambda\lambda$ 5577, 6300, and 6360 are attributed to at. O; the others are not identified.
N. M. B.

Classification of stellar spectra. H. N. RUSSELL, C. H. P. GAPOCHKIN, and D. H. MENZEL (Astrophys. J., 1935, 81, 107—118).
L. S. T.

Photochemical processes in comets. K. WURM (Chem.-Ztg., 1935, 59, 345—347).—The origin of the mols. present in the atm. of various parts of a comet, as indicated by a study of its spectrum, is discussed.
A. J. M.

Distribution of nuclear mechanical moments. S. TOLANSKY (Nature, 1935, 135, 620—621).—The difference in the distributions of nuclear mechanical moments of odd at. no. atoms (*A*) and of even at. no. atoms (*B*) is marked. Although class *B* is only one third as numerous as class *A*, yet more spins of $\frac{1}{2}$ occur in *B* than in *A*. High vals. for nuclear moments are improbable in class *B*, whilst class *A* tends to show that $3/2$ and $5/2$ are very stable vals. when there is an odd nuclear proton.
L. S. T.

Ion distribution during the initial stages of spark discharge in non-uniform fields. C. D. BRADLEY and L. B. SNODDY (Physical Rev., 1935, [ii], 47, 541—545).—A Wilson cloud-chamber method is

described for a direct study of ion distribution in the gap space, before visual or photographic luminosity has developed, with potential impulse $< 10^{-7}$ sec. duration.
N. M. B.

Optical terms calculated with Fermi's statistical potential. E. HELLMIG (Z. Physik, 1935, 94, 361—368).
A. B. D. C.

Isotope effect in band spectra of hydrides and deuterides. L. HULTHEN (Nature, 1935, 135, 543).—Theoretical.
L. S. T.

[Wave-mechanical theory of the Stark effect and atomic interactions.] C. W. OSEEN (Ark. Mat. Astr. Fys., 1934, A, 25, No. 2, 14 pp.; Chem. Zentr., 1934, ii, 3221).—The use of certain conceptions of classical physics in wave mechanics is criticised.
H. J. E.

Geiger counter applied to light measurements. B. STURM (Z. Physik, 1935, 94, 85—103).
A. B. D. C.

Electric arc. H. PLESSE (Ann. Physik, 1935, [v], 22, 473—499).—The conditions obtaining in the electric arc struck between various elements were investigated.
A. J. M.

Distribution of chief colours in the spectrum. H. P. J. VERBEEK and M. L. BAZEN (Physica, 1935, 2, 380—382).—The names given by 100 persons to light of 21 different λ are recorded.
A. J. M.

Precision measurements of the $K\alpha_{1,2}$ doublets of some of the lighter elements. P. HAGLUND (Z. Physik, 1935, 94, 369—376).—Results are given for Al, Si, and S.
A. B. D. C.

Intensity ratios of the fluorescent X-ray emission lines in the *L* region and their dependence on the voltage. H. HIRST and E. ALEXANDER (Phil. Mag., 1935, [vii], 19, 918—927).—Intensity ratios (*I*) of *L* emission lines of W, Tl, and U excited by X-rays and by cathode rays have been determined. (*I*) of lines originating from the same electron level are independent of voltage. (*I*) of other lines increase to a max. at 3—4 times the excitation voltage.
R. S.

***L* spectrum of mercury.** (M.L.E.) Y. CAUCHOIS (Compt. rend., 1935, 200, 1194—1196).—The $\lambda\lambda$ of the *L*-series X-ray lines of Hg have been redetermined and the results compared with previous data.
J. W. S.

Efficiency coefficients, intensity ratios, and absorption probabilities in the *L* series of the heavy elements. H. KUSTNER and E. ARENDS (Ann. Physik, 1935, [v], 22, 443—472).—The characteristic *L*-radiation for monochromatic X-rays of Ta, W, Ir, Pt, Au, Pb, and Bi was investigated. The efficiency coeffs., u_1 , u_2 , and u_3 , were determined for the three *L*-levels. and u_3 increase with increasing at. no., but u_2 decreases. The intensity ratios of the line groups at the various *L*-band edges were determined. With increasing at. no. there is an increase in the ratio $E_3 : E_2$, but a decrease in $(E_2 + E_3) : E_1$. The absorption probabilities (*I*) were also determined. The ratio of (*I*) in the $L_2 + L_3$ levels to that in L_1 increases with the distance from the edge, reaches a max., and then rapidly decreases, disagreeing with Schur's theory (A., 1930, 391).
A. J. M.

M series of element 91, protoactinium. W. C. PIERCE and A. V. GROSSE (Physical Rev., 1935, [ii], 47, 532—533).—Data and identifications for 14 lines are tabulated. Measurements for the corresponding *M* lines of U are given. N. M. B.

Disintegration of a monatomic thorium film on a tungsten cathode in a discharge in mercury vapour. N. MORGULIS and M. BERNADINER (Physikal. Z. Sovietunion, 1934, 6, 309—311).—The min. crit. potential of the ion to cause disintegration is calc. CH. ABS. (e)

Temperature ionisation of a gas. II. General theory and relation between temperature and pressure ionisation. M. SUGITA (Proc. Phys.-Math. Soc. Japan, 1934, 16, 401—413).—Theoretical. CH. ABS. (e)

Behaviour of electrons in chlorine. V. A. BAILEY and R. H. HEALEY (Phil. Mag., 1935, [vii], 19, 725—746; cf. A., 1934, 825).—A new method of investigation is described, in which the motion of electrons (I) in Cl₂ is studied by observations on mixtures of Cl, with He or CO₂. The probability of (I) becoming attached to a mol. with which it collides, and the mean free path of (I), are max. when the mean electronic velocity (*u*) is about 7.7×10^7 cm. per sec. The mean proportion of its own energy lost by (I) on collision with a mol. also varies with *u*, and shows parallelism with the optical absorption. The views of Franck and others are criticised. F. L. U.

Scattering absorption of electron rays. A. RECKNAGEL (Z. Physik, 1935, 94, 356—360).—Theoretical. A. B. D. C.

Production of [electron] pairs by collisions of particles. L. NORDHEIM (J. Phys. Radium, 1935, [vii], 6, 135—136).—Mathematical. N. M. B.

Production of electrons and positrons by collision of two particles. L. LANDAU and E. LIFSCHITZ (Physikal. Z. Sovietunion, 1934, 6, 244—257).—Theoretical. CH. ABS. (e)

Production of protons by bombardment of palladium with electrons. R. KOLLATH (Z. Physik, 1935, 94, 397—407).—A study of the production of protons from H₂ absorbed in Pd shows that it does not correspond with ejection from a solid surface but with electron collision in a H₂ atm. A. B. D. C.

Negative ions of iodine. I. Probe measurements. J. L. SPENCER-SMITH (Phil. Mag., 1935, [vii], 19, 806—823).—Measurements by means of a Langmuir probe show that the concn. of negative ions approx. = that of the positive ions and that the free electrons, when the pressure of I₂ vapour is between 0.1 and 0.5 mm. The effect of I₂ on the glow discharge in He has also been studied. F. L. U.

Negative ions of iodine. II. Ion beams. J. L. SPENCER-SMITH (Phil. Mag., 1935, [vii], 19, 1016—cf. preceding abstract).—A beam containing ions I', I₂', and I₃' obtained from the glow discharge in I₂ has been subjected to magnetic analysis. The presence of I'', I', I₂', and I₃' in a similar beam of positive ions has been established, and the distribution of both types of ions in the discharge determined.

Probability data are given for the collision of electrons and negative ions with neutral I₂ mols. R. S.

Production of ion currents in high vacuum with the aid of a magnetic field. A. A. SLUTZKIN, S. I. BRAUDE, and I. M. VIGDORCHIK (Physikal. Z. Sovietunion, 1934, 6, 268—279). CH. ABS. (e)

New ion sources for mass spectroscopy. A. J. DEMPSTER (Nature, 1935, 135, 542).—Positively-charged atoms are formed by sparks between solid electrodes in a high vac. The spark is coupled inductively to a high-frequency oscillating spark circuit. Abundant ions, many multiply-charged, are obtained from Pt, Au, W, Sn, Cu, Ni, Fe, Al, C, Be, and Li. L. S. T.

Masses of some light atoms determined by a new method. F. W. ASTON (Nature, 1935, 135, 541).—Mass differences of some of the lighter atoms have been determined by resolving and measuring in mass spectra naturally-occurring doublets which represent small residual differences between the atoms and mols. concerned. Provisional vals. for the masses relative to O¹⁶ obtained from the doublets D₂H₂, He₂D₂, C⁺⁺, D₃, and O₂CH₄ are H 1.0081, D 2.0148, He 4.0041, and C 12.0048. They are in better accord with the masses deduced from energy changes during artificial disintegrations. L. S. T.

Comparison of X-ray and γ-ray dosage. L. S. TAYLOR and F. L. MOHLER (Science, 1935, 81, 318—319).—Abs. measurements of the ionisation produced in CS₂ by γ-rays are recorded. L. S. T.

Radioactivity of potassium and rubidium. F. H. NEWMAN and H. J. WALKE (Phil. Mag., 1935, [vii], 19, 767—773; cf. this vol., 275).—Arguments in favour of the long-life activity of K being due to ¹⁹K⁴⁰, formed by bombardment of ¹⁹K³⁹ with neutrons of low energy, are given. Similar arguments indicate ³⁷Rb⁸⁶ as the active Rb isotope. F. L. U.

Radioactivity of rubidium. F. H. NEWMAN and H. J. WALKE (Nature, 1935, 135, 508).—The effects observed when Rb, Yt, and Sr are bombarded with neutrons support Klemperer's view that ³⁷Rb⁸⁶ is the source of the natural β-radioactivity of Rb. L. S. T.

Radioactivity of the rare earths. H. J. WALKE (Phil. Mag., 1935, [vii], 19, 878—886).—The results of Aston (A., 1934, 1150) are considered in relation to the author's theory of isotope synthesis (this vol., 427). R. S.

Expression for Bragg curves for α-particles from radioactive substances. M. FRANCIS (J. Phys. Radium, 1935, [vii], 6, 108—113).—Ionisation curves which, for certain α-rays, cannot be determined experimentally can be deduced from known curves for other substances. The method is illustrated for the U curve from that for Po. N. M. B.

Differential ionisation of single polonium α-rays in air and scattering of their range. H. SCHULZE (Z. Physik, 1935, 94, 104—133). A. B. D. C.

β- and γ-Rays of radium-D. J. A. GRAY (Canad. J. Res., 1935, 12, 408).—There is evidence that every atom of Ra-D emits a γ-ray on disintegration. The

total no. of β -rays emitted in 100 disintegrations should be 100 primary, 96 secondary, and about 100 tertiary. J. W. S.

Photo-electric absorption of γ -rays in heavy elements. H. R. HULME, J. McDUGALL, R. A. BUCKINGHAM, and R. H. FOWLER (Proc. Roy. Soc., 1935, A, 149, 131—151).—Results obtained by various authors for the photo-electric effect in H-like atoms are co-ordinated, and a method is developed for finding σ_K , the photo-electric absorption coeff. for the K shell, which is valid for all vals. of the at. no. and where $\sim mc^2$. Graphs are constructed giving the photo-electric absorption per atom for various elements in the range $h\nu_0 > 0.7mc^2$. L. L. B.

Interaction of hard γ -rays with atomic nuclei. C. Y. CHAO and T. T. KUNG (Chinese J. Physics, 1934, 1, 56—65).—The no. of counts with a Geiger-Müller counter using Th-C'' γ -rays has been compared for Pb and Al walls, with evidence for the interaction of the γ -rays with Pb nuclei, producing positive and negative electrons. R. S. B.

Artificial excitation of nuclear γ -radiation. E. KARA-MICHAILOVA (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 1—9; Chem. Zentr., 1934, ii, 3588).—Intense bombardment with α -particles from Po produced penetrating nuclear γ -radiation from Be, B, N, Al, Na, and Mg, but not from C, O, Si, P, S, Cl, and K. H. J. E.

Scattering of neutrons by protons. H. A. BETHE and R. PEIERLS (Proc. Roy. Soc., 1935, A, 149, 176—183).—Theoretical. The cross-section and angular distribution are calc. for the scattering of neutrons by protons. The result depends only on the known binding energy of the dipton, and is independent of the law of force assumed between neutron and proton. The scattering is almost isotropic for neutron energies up to 4×10^4 kv. L. L. B.

Transmutation of heavy hydrogen investigated by the cloud-track method. P. I. DEE and C. W. GILBERT (Proc. Roy. Soc., 1935, A, 149, 200—209).—By passing a beam of artificially accelerated ${}_1D$ ions into a gas mixture containing D_2 , the ${}_2He^3$ nuclei produced in the reaction ${}_1D + {}_1D \rightarrow {}_2He^3 + {}_0n^1$ have been detected in the expansion chamber. The range of the ${}_2He^3$ nucleus for zero bombarding energy is 4.3 ± 0.2 mm. The energy of the neutrons $= 1.8 \pm 0.2 \times 10^6$ e.v. The results are in agreement with the application of the conservation of momentum to the process assumed, and a val. of 1.008 ± 0.0004 is deduced for the mass of the neutron. L. L. B.

Loss of velocity of neutrons in heavy water. H. HERSZFINKIEL, J. ROTBLAT, and M. ŻYW (Nature, 1935, 135, 653—654).—The radioactivity induced in Ag by neutrons (I) from a Rn+Be source is increased by passing (I) through 98% D_2O , but to a smaller extent than by passage through H_2O . A small increase in the layer of D_2O leads proportionately to an activity $>$ is the case with H_2O , since in the collision of neutrons with diptons the effective scattering probably occurs mainly in a backward direction, whilst with protons it is always in the forward direction. L. S. T.

Disintegration of boron by slow neutrons. B. KURTSCHATOV, I. KURTSCHATOV, and G. LATICHEV (Compt. rend., 1935, 200, 1199—1201).—B is more readily disintegrated by collision with slow neutrons than with fast neutrons. Such collision leads to the production of two heavy particles, and not three as stated by Chadwick and Goldhaber (this vol., 277), the primary reaction being ${}_5B^{10} + {}_0n^1 \rightarrow {}_3Li^7 + {}_2He^4$. J. W. S.

Case of artificial radioactivity produced by bombardment with neutrons without capture of the neutron. B. KURTSCHATOV, I. KURTSCHATOV, L. MISSOVSKI, and L. ROUSSINOV (Compt. rend., 1935, 200, 1201—1203).—Irradiation of MeBr with neutrons yields γ -ray sources of half-life 18 min., 4—5 hr., and 36 hr. The last product also emits β -rays of about 6×10^5 e.v. It is shown to be an isotope of Br, and it is concluded that it is Br^{78} and that the action of the neutron causes emission of another neutron without fixation of the first. J. W. S.

Radiopotassium and other artificial radioelements. G. VON HEVESY and H. LEVI (Nature, 1935, 135, 580).— K^{42} has been obtained by bombarding $CaCO_3$ by neutrons from a Be+Rn source: ${}_{20}Ca^{42} + {}_0n^1 = {}_{19}K^{42} + {}_1H^1$. Owing to the low Ca^{42} content of $CaCO_3$ the yield of K^{42} is small. ${}_{19}K^{42}$ has thus been prepared from ${}_{19}K^{41}$, ${}_{20}Ca^{42}$, and ${}_{21}Sc^{45}$ by bombardment with ${}_0n^1$. Neutrons retarded by reflexion by H nuclei yield an active Ca isotope, which decays with a 4-hr. period, due to the reaction ${}_{20}Ca^{40} + {}_0n^1 = {}_{20}Ca^{41}$ or, probably, ${}_{20}Ca^{44} + {}_0n^1 = {}_{20}Ca^{45}$. Retarded neutrons and Zr give an active Zr decaying with a period of 40 hr., and β -rays. Active Hf, similarly produced, has a half-life period of several months. The reactions are presumably ${}_{40}Zr^{96} + {}_0n^1 = {}_{40}Zr^{97}$, and ${}_{72}Hf^{180} + {}_0n^1 = {}_{72}Hf^{181}$ and ${}_{72}Hf^{181} = {}_{73}Ta^{181} + \beta$. L. S. T.

Radio-caesium activated by neutrons. W. M. LATIMER, D. E. HULL, and W. F. LIBBY (J. Amer. Chem. Soc., 1935, 57, 781—782).—Radio-Cs emits a β -particle. The decay has a half-life period of 80—100 min. E. S. H.

Production of radioactivity by neutrons. J. C. McLENNAN, L. G. GRIMMETT, and J. READ (Nature, 1935, 135, 505).—The radioactivities produced by slow neutrons (cf. this vol., 276) in Zn, $CsNO_3$, $TlOAc$, and $Bi_2(CO_3)_3$ have half-lives of 100, 75, 97, and 0 min., respectively. The 6-min. half-life for Zn, reported by Fermi, was also obtained. The integral curve method used for calculating these vals. is superior to the differential curve method usually employed. L. S. T.

Artificial radioactivity of iridium. L. SOSNOWSKI (Compt. rend., 1935, 200, 922—924).—After irradiation with neutrons from Be excited by Ra γ -radiation, Ir shows radioactivity, one product emitting β -rays, half-life 3 days, and the other emitting both β and γ -rays, half-life 50 min. These results are not in accord with those of Fermi *et al.* (A., 1934, 1284). J. W. S.

Artificial transmutation of uranium by neutrons. II. O. HAHN and L. MEITNER (Naturwiss., 1935, 23, 230—231; cf. this vol., 278).—The substances of half-life 13 and 90 min., respectively, formed by the bombardment of U by neutrons, are not

isotopes, but can be separated by chemical methods. The 90-min. substance is a mixture of two elements of half-life 50—70 min. and 2—3 days, respectively, which may be isotopic. All these elements probably have at. no. > 92 . A. J. M.

Theory of β -rays and magnetic moment of the proton. G. C. WICK (*Atti R. Accad. Lincei*, 1935, [vi], 21, 170—173).—Theoretical. O. J. W.

Position of protons and neutrons in the natural system of elements. C. G. BEDREAG (*Compt. rend.*, 1935, 200, 1197—1199).—A scheme for various nuclei. J. W. S.

Influence of filtration on the properties of the [cosmic] radiation which produces showers [of secondary particles]. B. ROSSI and G. ALOCCO (*Atti R. Accad. Lincei*, 1935, [vi], 21, 167—170).—If the cosmic radiation is passed through sufficiently thick layers of matter the frequency of the showers produced is independent of the at. no. of the absorbing element (cf. A., 1933, 996). O. J. W.

Secondary and tertiary particles produced by cosmic rays. J. H. SAWYER, jun. (*Physical Rev.*, 1935, [ii], 47, 515—521; cf. A., 1933, 996).—The secondaries from Pb have little power to produce detectable tertiaries or showers from Pb or Al. The secondaries from Al produce more showers in Pb than the secondaries from air. A component of the cosmic rays softer than the corpuscular component is probably the chief source of the secondaries producing the showers. N. M. B.

Secondary effect of cosmic rays. M. ACKEMANN (*Z. Physik*, 1935, 94, 303—316).—New max. in secondary ray absorption measurements have been observed. A. B. D. C.

Annihilation of high-energy positive electrons in passing through matter. J. SOLOMON (*J. Phys. Radium*, 1935, [vii], 6, 114—116).—Mathematical. N. M. B.

Theory of the photon. K. V. NIKOLSKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 1, 372—377).—Mathematical. W. R. A.

Thermal equilibrium of elementary corpuscles. G. WATAGHIN (*Compt. rend.*, 1935, 200, 909—912; cf. A., 1934, 712).—Mathematical. J. W. S.

Synthesis of X-ray filtration curves from Kramers' emission law. L. SILBERSTEIN (*Phil. Mag.*, 1935, [vii], 19, 1042—1054; cf. A., 1933, 332).—Theoretical. R. S.

Thomas-Fermi method for metals. J. C. SLATER and H. M. KRUTTER (*Physical Rev.*, 1935, [ii], 47, 559—568).—Mathematical. N. M. B.

Electromagnetic field of Dirac's electron. K. NIKOLSKI (*Compt. rend.*, 1935, 200, 1086—1088).—Dirac's theory is employed to deduce Born and Infeld's system of electro-dynamic non-linear equations (*Proc. Roy. Soc.*, 1934, A, 144, 425). M. S. B.

Electromagnetic mass of the Dirac electron. N. KEMMER (*Ann. Physik*, 1935, [v], 22, 674—712).—Theoretical. The usual conception of the electromagnetic mass (I) as the coeff. of the term in the expression for the characteristic force, which \propto

acceleration, is not simply related to that derived from considerations of the self-energy of the electron (A., 1934, 711, 1150). More satisfactory results are obtained from consideration of the theory of "holes." (I) is shown to be $\propto \log$ (electron radius). A. J. M.

Calculation of atom form factors. B. V. S. NAGY (*Z. Physik*, 1935, 94, 229—230).—Correction and extension of previous vals. (A., 1934, 1285).

A. B. D. C.
Temperature and entropy of light quanta. R. VON HIRSCH (*Ann. Physik*, 1935, [v], 22, 609—628).—Theoretical. The thermodynamic theory of radiation is extended. The thermodynamics (I) of the Compton and photo-effects is discussed. The application of (I) to anomalous dispersion gives results in agreement with experiment. The natural width of spectral lines is calc. A. J. M.

Ideal gases. W. GLASER (*Z. Physik*, 1935, 94, 317—328).—Wien's displacement law is applied to particle waves and gives the energy distribution function for a relativistic corpuscular gas. A. B. D. C.

Determination of magnetic moments of molecules by the molecular-ray method. R. SCHNURMANN (*J. Phys. Radium*, 1935, [vii], 6, 99—107).—The Stern-Gerlach method gives satisfactory results for O, and NO. N. M. B.

Physical methods in chemistry. II. Absorption spectrum. L. J. N. VAN DER HULST and P. C. HENRIQUEZ (*Chem. Weekblad*, 1935, 32, 210—215).—A summary. D. R. D.

Zeeman effect and position of perturbation in the $A^1\Pi$ state of CO. R. SCHMID and L. GERO (*Z. Physik*, 1935, 94, 386—396). A. B. D. C.

Band system of neutral OH. III. Identification of the (2'2''), (3'0''), (3'3''), (4'1''), (4'2''), (4'3''), and (4'4'') bands. Formulation of the wave-numbers of the null lines. T. TANAKA and J. KOANA (*Proc. Phys.-Math. Soc. Japan*, 1934, 16, 365—400).—The spectrum of the O₂-H₂ flame was re-examined. CH. ABS. (e)

New band system of NH. R. W. LUNT, R. W. B. PEARSE, and E. C. W. SMITH (*Nature*, 1935, 135, 508).—A new band has been observed in the spectrum of a hollow cathode discharge through streaming NH₃. The upper level of the band is identical with that of the 3240 Å. band of the $^1\Pi \rightarrow$ system of NH, and the final level is identified with the lower $^1\Sigma^+$ level predicted for NH. L. S. T.

Spectroscopic constants of the di-atom PN. C. H. D. CLARK (*Nature*, 1935, 135, 544).—Experimental work (A., 1934, 7) confirms the author's predictions (this vol., 432). L. S. T.

Line absorption spectra of some salts of the transition elements, especially of cobalt and manganese. J. GIELESSEN (*Ann. Physik*, 1935, [v], 22, 537—560).—For Mn salts the absorption spectrum (I) consists of a strong line spectrum (II) and weak, general absorption, generally on the short-wave side of (II). There is a displacement towards the shorter waves, and a contraction of (I) through the series MnBr₂·4H₂O, MnCl₂·4H₂O, MnSO₄·H₂O. (I) of the hydrates of MnSO₄ are displaced towards the longer

waves as the no. of mols. of H_2O decreases. The chief absorption range is the same for all Mn salts investigated, both solid and in solution. For $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ at -189° there are two strong absorption bands, between which there are alternate strong and weak bands. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and various salts of Mo and W showed no selective absorption. (I) was investigated for many Co salts, and mixtures of Co halides with alkali halides and ZnCl_2 . (I) of these salts shows a line absorption, a weak general absorption, and for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ a strong continuous absorption, which for thin crystals may be split into a doublet. The effect on (I) of dehydration is the same as for Mn salts. Mixing CoCl_2 with the isomorphous ZnCl_2 produces displacement, as well as a new (I). Mixtures of CoCl_2 and alkali halides have entirely new (I).

A. J. M.

Absorption spectra of chlorides and oxychlorides of sulphur in the vapour state. R. K. ASUNDI and R. SAMUEL (Current Sci., 1935, 3, 417—418).—In the vapour state SCl_2 , S_2Cl_2 , and SOCl_2 show a strong absorption band in the region 2400—2900 Å., having its origin in $p-p$ linking between S and Cl. The absorption spectrum of SCl_2 is analogous to that of OCl_2 .

W. R. A.

Critical investigation of the absorption spectrum of potassium nitrate in the ultra-violet by the spectrographic and photo-electric method. J. ECKHOUDT (Natuurwetensch. Tijds., 1935, 17, 72—80).—A simple photo-electric method for measuring absorption in the ultra-violet is described, and applied to solutions of KNO_3 , which shows max. absorption from λ 2970 to 3050. The error is reduced to 2%.

S. C.

Absorption spectra of substances containing alkyl radicals. H. W. THOMPSON and J. J. FREWING (Nature, 1935, 135, 507—508).—Results obtained with the ultra-violet absorption spectra of HgEt_2 , GeMe_4 , NEt_3 , Me_2O , Et_2O , PEt_3 , and Et_2S are outlined.

L. S. T.

Absorption spectra of polycyclic hydrocarbons. I. Alkyl-substituted phenanthrenes. II. Partly reduced derivatives of phenanthrene etc. F. A. ASKEW (J.C.S., 1935, 509—512, 512—516).—I. Ultra-violet absorption spectra of 18 alkyl-substituted phenanthrenes are described, and their relationships to the *cyclo*-compounds are discussed.

II. Relationships between the spectra of 9:10-dihydro-, tetrahydro-, and two isomeric octahydro-phenanthrenes, *cis*- and *trans*-hexahydrochrysene, 7:8-dihydrophenalyl-7-*spirocyclopentane*, and fluorene, and those described above are discussed. It is shown that previous results for fluorene have been obtained with impure material.

F. L. U.

Ultra-violet absorption spectra of derivatives of diphenylene sulphide and of diphenylene sulphone. M. CHAIX (Compt. rend., 1935, 200, 1208—1210; cf. A., 1933, 1227).—Data have been obtained for 2:7- and 3:6-dichloro- and -dibromodiphenylene sulphone and for 2- and 3-chlorodiphenylene sulphone, in EtOH solution. 3- or 3:6-substituents decrease the sharpness of the diphenylene sulphone bands at 3250, 2900, and 2820 Å.,

whilst the 2430 Å. band remains sharp, but is shifted to longer λ . The absorption bands of 2- and 2:7-compounds are all sharp, but are shifted 50—100 Å. towards longer λ . 2:7-Compounds are more highly coloured than 3:6-compounds. Br exerts more bathochromic effect than Cl.

J. W. S.

Relations between the optical properties of the medium and the photochemical constants of tetraphenylrubene. Absorption spectrum. C. DUFRAISSE and M. BADOCHÉ (Compt. rend., 1935, 200, 929—931).—Solutions of 1:1':3:3'-tetraphenylrubene (I) in C_6H_6 obey Beer's law. The absorption max. of solutions of (I) in 16 different org. solvents are not identical, but the absorption curve is of const. form. With one exception the order of the displacement follows Kundt's rule. The displacements are not due to mol. association with the solvent.

J. W. S.

Continuous absorption spectra of polyatomic molecules. V. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1935, 23, 846—851; cf. A., 1933, 661).—Absorption-limit data are tabulated for 18 alcohols, $\text{MeOH} \cdot \text{C}_{12}\text{H}_{25} \cdot \text{OH}$. Dissociation energies of linkings are given and are discussed in relation to mol. structure.

N. M. B.

Influence of temperature on the absorption of some organic liquids in the near infra-red. B. BLOCH and M. ERRERA (J. Phys. Radium, 1935, [vii], 6, 154—158).—A detailed account of work already noted (A., 1934, 1288).

Infra-red spectrum, normal frequencies, and intramolecular forces in selenium and tellurium hexafluorides. H. SACHSSE and E. BARTHOLOME (Z. physikal. Chem., 1935, B, 28, 257—266).—From measurements of the infra-red spectra at 3—25 μ and the sp. heats, the normal frequencies have been determined, and from them by means of the general force law the seven general force consts. calc. As for SF_6 (A., 1934, 1055) the principal consts. can be represented by a system of Coulomb forces, but others, especially those involved in the interaction of neighbouring atoms, are considerably affected by angular forces.

R. C.

Intermolecular isomerism of α -picoline studied in the far infra-red. C. H. CARTWRIGHT and J. ERRERA (Compt. rend., 1935, 200, 914—916).—Measurements of the refractive index of α - (I) and β -picoline between 52 and 152 μ indicate that the at. polarisation is about 0.1 cm^3 in each case, and not 23.2 cm^3 as found by Rau *et al.* (A., 1934, 943) for (I). The existence of a tautomeric form of (I) is therefore not confirmed by the results.

J. W. S.

Intensity of Raman lines as a function of the frequency of the incident rays. L. S. ORNSTEIN and J. J. WENT (Physica, 1935, 2, 391—398).—The relationship between the intensity of Raman radiation and the frequency of the incident light was determined for crystals of calcite (I) and quartz (II). For (II) the ratio of intensities of Raman to incident radiation is equal to $(\nu - \nu_r)^4$, where ν , ν_r are the frequencies of the incident and Raman light, respectively. For (I) this does not hold owing to ultra-violet absorption. The reason for this is discussed.

A. J. M.

Raman spectrum of deuterium. T. F. ANDERSON and D. M. YOST (*J. Chem. Physics*, 1935, 3, 242—243).—Raman spectra of gaseous D_2 (99.5% purity) have been obtained at a pressure of 2.5 atm. The frequencies are in agreement with those calc. from Urey and Teal's equation (*Rev. Mod. Physics*, 1935, 7, 34). The result is important in connexion with the use of D to establish the structure of mols. containing H, since it indicates that the D—D distance is the same as the H—H distance, and, therefore, the M—D and M—H distances, where M is any atom, may be assumed equal. The force const. for D is also the same as for H. M. S. B.

Raman spectra of fused salts. E. J. SALSTROM and L. HARRIS (*J. Chem. Physics*, 1935, 3, 241—242).—Raman spectra have been observed for fused $ZnCl_2$ and $ZnBr_2$. The fact that these persist at about 100° above the m.p. indicates that the frequencies are not due to vibrations in the crystal lattice, but probably to oscillations in the Zn halide grouping. The mol. is not linear. No Raman lines have been observed for fused $LiBr$, $PbCl_2$, $PbBr_2$, and $CdCl_2$, but the experimental conditions were less satisfactory for these than for the Zn salts. M. S. B.

Magnetic and Raman spectra evidence on the structure of complex cyanides. D. M. BOSE (*Indian J. Physics*, 1935, 9, 277—286).—The Raman spectra of the double K cyanides of Ag, Ni, Zn, Cd, Cu, Co, Rh, Cr, Fe, and Ru can be interpreted on the assumption that the CN groups are present as double mols. $(CN)_2$, linked to the central paramagnetic atom by single or double linkings as indicated by magnetic properties. N. M. B.

Raman effects of organic molecules. (Vibration structure of acetylenes.) B. TIMM and R. MECKE (*Z. Physik*, 1935, 94, 1—10).—Vibrational frequencies are given for $(C\equiv CH)_2$ and $CH_3\cdot CH\cdot C\equiv CH$, and are assigned to the different groups. A. B. D. C.

Raman effect. XLI. Transition from vibrational spectra of XY_4 to those of XZ_4 . K. W. F. KOHLRAUSCH (*Z. physikal. Chem.*, 1935, B, 28, 340—350).—The transition of vibrational forms in $XY_4 \rightarrow ZXY_3 \rightarrow Z_2XY_2 \rightarrow Z_3XY \rightarrow Z_4X$ is worked out theoretically and the results are applied to the data for $CCl_4 \rightarrow CMe_4$, $CCl_4 \rightarrow CH_4$, and $CBr_4 \rightarrow CH_4$. R. C.

Raman spectra of methyldiethylcarbinol, benzyldimethylcarbinol, and the corresponding ethylenic hydrocarbons. J. SAVARD (*Bull. Soc. chim.*, 1935, [v], 2, 633—640).—The data are compared with those for $CMe_2Et\cdot OH$ (Nevgi *et al.*, A., 1934, 1056). D. R. D.

Rotational Raman scattering in benzene vapour. S. C. SIRKAR (*Indian J. Physics*, 1935, 9, 295—298).—A detailed account of results previously reported (cf. this vol., 146). N. M. B.

Raman spectra of dimethyl and diethyl trisulphides. N. G. PAI (*Indian J. Physics*, 1935, 9, 231—238).—Raman data are tabulated, and show that the compounds are not solutions of S in the corresponding disulphides, and that they do not contain a double linking. The probable structure is $S(SR)_2$. N. M. B.

Raman spectra of organo-metallic compounds. N. G. PAI (*Proc. Roy. Soc.*, 1935, A, 149, 29—35).—The Raman spectra of $ZnMe_2$, $ZnEt_2$, $HgMe_2$, $HgEt_2$, $BiMe_3$, $SnMe_4$, and $PbEt_4$ have been studied. Some of the lines show exceptionally large intensities. The dialkyls may be treated as symmetrical non-linear triatomic mols. of the type XY_2 , in which X has a large valency angle. $BiMe_3$ conforms to a pyramidal model, whilst the tetra-alkyls have a regular tetrahedral structure. L. L. B.

Absorption and fluorescence of the vapours of cuprous halides. J. TERRIEN (*Compt. rend.*, 1935, 200, 1096—1098).—Ultra-violet radiations of $\lambda < 2400 \text{ \AA}$. excite a bluish-green to blue fluorescence in Cu_2Cl_2 or Cu_2Br_2 vapour as the pressure rises. The intensity of emission \propto the first power of the exciting intensity, indicating the absorption of a single quantum of short λ . The energy thus acquired by 1 mol. of Cu_2Cl_2 is not sufficient to dissociate it into $2CuCl$ and excite one of the mols. M. S. B.

Quenching of fluorescence of liquids by halogen ions. E. SCHNEIDER (*Z. physikal. Chem.*, 1935, B, 28, 311—322).—The quenching of fluorescence is related to the photo-oxidation of iodide solutions sensitised by fluorescent substances. In the latter the quantum yield of I formation, referred to the no. of quanta absorbed by the fluorescent substance, ~ 1 . Extinction probably depends on $I'H_2O + Q = HI + OH'$, where Q is the amount of energy which would appear as the quantum of fluorescence radiation in absence of a collision of the second kind. It seems that in the photo-oxidation each HI mol. reacts with O before ionisation, an I_2 mol. being formed from each two HI mols. R. C.

Fluorescence spectrum of apatite in ultra-violet light. E. IWASE (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, 27, 1—9).—Fluorescent apatites (I) from Japan, Canada, Germany, and Norway have been examined. (I) occurring in ore veins in tabular crystals give two broad bands in the orange-yellow and blue-violet regions, whilst in the case of prismatic (I) in basic igneous rocks, the bands are less intense. The difference in crystal habit and fluorescence spectrum is attributed to the presence of impurities. R. S.

Thermal rotations of fluorescent molecules and duration of luminescence. A. JABŁOŃSKI and W. SZYMANOWSKI (*Nature*, 1935, 135, 582).—Contrary to theoretical expectations, the duration of luminescence of fluorescein in H_2O or $EtOH$ is $>$ in glycerol. The effect of thermal rotations of the dye mols. can account for this anomalous behaviour. L. S. T.

Mechanism of activation of oxygen by fluorescent dyes. J. FRANCK and H. LEVI (*Naturwiss.*, 1935, 23, 229—230).—The photo-sensitised oxidation of isoamylamine in the presence of chlorophyll (I) is considered. The theory of Krautsky (this vol., 311), postulating the existence of metastable conditions of excitation, is criticised. If the O_2 derives all its energy from the metastable condition, in order that the quantum efficiency may approach unity (Gaffron, A., 1933, 1214), the fluorescence should be extinguished by O_2 .

at relatively small concns.; this does not occur. It is suggested that the observed phosphorescence of (I) is a chemiluminescence. The absorption of light by (I) results in the removal of loosely-bound H atoms from (I) and formation of a radical in solution. The recombination energy may re-excite (I) giving rise to chemiluminescence. If O_2 is present, it combines with the liberated H, and after a period of exposure all the available H of (I) is used up, the acceptor then using the energy of (I), being thus rendered capable of reacting with O_2 .
A. J. M.

Photoluminescence of dye phosphors. A. JABŁOŃSKI (Z. Physik, 1935, 94, 38—46).—Mols. capable of phosphorescence have at least one metastable level: the case of one level is investigated and accounts for temp. variation of phosphorescence.
A. B. D. C.

Internal recombination during photo-dissociation of polyatomic molecules. A. TERENIN (Nature, 1935, 135, 543—544).—The photo-decomp. of SnI_4 vapour by light of 2500—2150 Å. is accompanied by a bright visible emission of the spectrum of I_2 with an abnormal distribution of intensity in the bands. The I_2 mol. is detached from the SnI_4 mol. in one primary process. The whole process is equiv. to a recombination of atoms in the act of photo-dissociation, or to a redistribution of valency linkings. A marked temp. coeff. indicates the necessity for an energy of activation for this type of photo-dissociation. The mechanism of the yellow fluorescence in BiI_3 vapour is similarly explained; under the action of suitable quanta and with some thermal activation an I mol. is detached from BiI_3 .
L. S. T.

Ionisation in gases by X-rays. L. H. MARTIN, J. C. BOWER, and T. H. LABY (J. Cancer Res. Comm. Sydney, 1935, 6, 131—143).—Cloud expansion chamber experiments are described and their bearing on the measurement of X-ray intensities by ionisation methods is discussed.
E. A. H. R.

Photo-dissociation of single crystals of potassium and sodium nitrates under polarised light. K. S. KRISHNAN and L. K. NARAYANASWAMY (Current Sci., 1935, 3, 417).—Nitrates of NH_4 , Na, K, Sr, Ba, Cd, Al, and Pb are dissociated to nitrites by light of $\lambda < 250 m\mu$. The dissociation appears to be confined to a surface layer 20 μ thick. Under linearly polarised light single crystals of NH_4NO_3 , $NaNO_3$, and KNO_3 show greater dissociation when the electric vector of the exciting light is in the plane of the NO_3' ions than when it is along the normal to the NO_3' ion plane. $KClO_3$ crystals show similar anisotropic photo-dissociation.
W. R. A.

Photo-electric study of monocrystalline sulphur. A. A. VOROBIEV (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 368—383).—On illumination (even with infra-red rays) S crystals become semiconductors. The effect persists for several min. after removing the light source.
CH. ABS. (e)

Rectification of alternating current by crystals. S. R. KHASTGIR and A. K. D. GUPTA (Indian J. Physics, 1935, 9, 255—276).—Two types of rectification were established; one type, in symmetrical crystals (galena, Fe pyrites, magnetite, molybdenite,

pyrolusite, cassiterite, and bornite), is associated with point contacts; the other type, a vol. rectification due to asymmetric conductance, is found for crystals having no centres of symmetry (carborundum, zincite, and Si).
N. M. B.

Red threshold of inner photo-effect and emission work for semi-conductors. J. H. DE BOER and W. C. VAN GEEL (Physica, 1935, 2, 286—298).—The thermal emission work, U , obtained from the effect of temp. on the conduction of a semi-conductor (I), is not equal to the energy val. $h\nu_r$ of the red threshold of the photo-electric conduction of (I). The Wilson theory of (I) (Proc. Roy. Soc., 1931, A, 133, 458) gives $2U = h\nu_r$, which also does not hold. The theory is criticised. A theory of (I) is put forward, supposing that semi-conduction consists of an ionisation of internally adsorbed atoms, which involves alterations in the binding energies. Potential curves are drawn for the various possible cases, and it is shown that $h\nu_r = U$.
A. J. M.

Asymmetric conductivity of an electrode system: metal-salt-adsorbed alkali metal. J. H. DE BOER and W. C. VAN GEEL (Physica, 1935, 2, 309—320).—A cell with a thin electrode ($> 2 \mu$) composed of Ag- CaF_2 -Cs shows asymmetric conductivity. This effect must be ascribed to differences in surface structure of the two metal electrodes. The Cs electrode (I), being adsorbed in holes in the salt layer, behaves like a set of points, thus producing an intense field, making the electron emission of (I) $>$ that of the Ag.
A. J. M.

Asymmetric conductivity of the combination: metal-insulating layer-salt layer-adsorbed alkali metal. W. C. VAN GEEL and J. H. DE BOER (Physica, 1935, 2, 321—327).—A cell of the type Ag-shellac layer- CaF_2 -K shows asymmetric conductivity. With alkali metal (I) positive, the relationship between current (i) and potential (V) is $i = Ae^{-hV}$; with (I) negative, $i = CV^{3/2}$. The phenomenon depends on electron emission in the cold. The insulating layer prevents conducting bridges through the salt layer.
A. J. M.

Photo-electric fatigue and oxidation. J. S. HUNTER (Phil. Mag., 1935, [vii], 19, 958—964; cf. A., 1934, 1149).—Photo-electric spectral distribution curves have been determined for Ag_2O , Bi_2O_3 , and Ni_2O_3 . Comparison of photo-electric thresholds indicates that an oxide film is not immediately formed when a clean metal surface is exposed to the air, but that adsorption occurs.
R. S.

Action of gases (H_2 , N_2 , O_2) on dye photo-cells. (MLLE.) C. STORA (Compt. rend., 1935, 200, 1191—1194; cf. A., 1934, 717; this vol., 586).—The negative photo-potential observed with certain dyes on metal electrodes in aq. K_2SO_4 in presence of O_2 is reversed in N_2 and may become strongly positive on passing H_2 through the solution. The negative photo-potential is attributed to the buffering effect of the atm. O_2 , eliminating any effect of the O_2 produced by photolysis of the H_2O , this being eliminated on passage of H_2 .
J. W. S.

Ionic rays. A. MENTRUP (Physikal. Z., 1935, 36, 335—340).—The conditions for producing ionic rays

strong enough for investigation in the mass spectrograph were studied with CdI_2 , PbCl_2 , TiCl_3 , AgBr , and LiCl . By increasing the surface bearing the salt, it is easy to obtain a current of 10^{-7} amp. at comparatively low temp. No saturation was obtained up to a potential of 90 volts, except in the case of LiCl (30 volts). A. J. M.

Electrical conductivity of compressed graphite powder. Z. SPECHT (Z. Elektrochem., 1935, 41, 204—206; cf. A., 1933, 114).—A reply to criticisms by Brunner and Hammerschmid (A., 1934, 367). F. L. U.

[Electrical conductivity of compressed graphite powder.] J. BRUNNER and H. HAMMERSCHMID (Z. Elektrochem., 1935, 41, 206—207).—A rejoinder to Specht (preceding abstract). F. L. U.

Determination of the resistance of carborundum by the eddy-current effect. L. I. RUSINOV (J. Tech. Phys. U.S.S.R., 1934, 4, 319—327).—The sp. resistance was 0.5. There was no indication of highly conducting particles between the SiC grains. CH. ABS. (e)

Insulating powers of amber, quartz glass, and sulphur in dry and moist air. W. GNANN (Physikal. Z., 1935, 36, 222—230).—The resistance and polarisation currents were determined. A. J. M.

Electrical conductivity of homopolar compounds. A. M. ZOLOTAREVA (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 384—387).—For C_{10}H_8 monocrystals the initial sp. conductivity (I) at 18° is $< 3 \times 10^{-11}$, and the residual (I) at 52° $< 10^{-18}$ mho. CH. ABS. (e)

Influence of photo-electric current on the breakdown voltage. B. M. VUL and I. M. GOLDMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 363—365).—The breakdown voltage of 20 coloured NaCl crystals has been examined under the influence of d.c., a.c., and suddenly impressed voltage. One half of the crystal was illuminated, the other half darkened. With suddenly impressed voltages no differences were observed between the two halves of the crystal. W. R. A.

Breakdown and conductivity in thin layers of liquids. T. MEYER (J. Chim. phys., 1935, 32, 199—209).—Conductivity and temp. coeffs. are given for 18 org. liquids under standard conditions $<$ breakdown (applied p.d.=350 volts across 20 μ). In poorly conducting media, current after breakdown \propto voltage, but the effective resistance is independent of the thickness of the film. D. R. D.

Rotations of molecules in solids and of the dielectric constant of solids and liquids. R. H. FOWLER (Proc. Roy. Soc., 1935, A, 149, 1—28).—Mathematical. Calculations are made of the changes of sp. heat and energy content in a transition region of a solid, and of the dielectric const. of a polar liquid and of Na K tartrate, which are in fair agreement with the experimental data. L. L. B.

Dielectric constant of liquids under high pressure. Z. T. CHANG (Chinese J. Physics, 1934, 1—55).— ϵ for PhMe , CS_2 , $n\text{-C}_5\text{H}_{12}$, $n\text{-C}_6\text{H}_{14}$, and Et_2O has been determined at 30° and 75° , and for $^{130}\text{-C}_5\text{H}_{11}\text{OH}$ at 22.4° , at pressures 1—12,000 kg.

per sq. cm., and at frequencies 600, 1000, and 2000 cycles per sec. ϵ is almost independent of frequency except for Et_2O and $\text{C}_5\text{H}_{11}\text{OH}$. $(\epsilon-1)/\{(\epsilon+2)d\}$ decreases with increasing pressure, the decrease increasing with the electric moment. R. S. B.

Measurement of absorption of short electric waves in dipole liquids. J. MALSCH and E. KEUTNER (Physikal. Z., 1935, 36, 288—292).—The method of Haase and Krause (A., 1934, 240, 1057) was used with $\text{C}_5\text{H}_{11}\text{OH}$, BuOH , PrOH , and EtOH . The absorbed energy is independent of λ , in agreement with dipole theory, but contrary to the results of Haase and Krause. The method is suitable for determining the const. y , governing the relaxation time in Debye's equation. The vals. of y for the above alcohols and hexyl alcohol are given. A. J. M.

Dielectric properties of acetylenic compounds. V. Acetylenic halides and alcohols. J. A. TOUSSAINT and H. H. WENZKE (J. Amer. Chem. Soc., 1935, 57, 668—670; cf. A., 1934, 1292).—The moments of the acetylenic halides are influenced by the position of the triple linking, greatest with I - and least with Cl -compounds. The moments of the acetylenic alcohols are $>$ those of the n -aliphatic alcohols. The moments of α -hydroxy- Δ^2 - and Δ^3 -octinene, Δ^3 -noninene, Δ^2 -heptinene, α -chloro-, α -bromo-, and α -iodo- Δ^2 -heptinene and -octinene, and α -hydroxy- n -heptane have been determined. E. J. S.

Effect of the hydrogen linking on the dielectric constants and b.p. of organic liquids. W. D. KUMLER (J. Amer. Chem. Soc., 1935, 57, 600—605).—By eliminating or making const. the effects of temp., electronic polarisation, at. polarisation, and no. of mols. per c.c., the relation between interaction of the mols. and dielectric const., ϵ , has been studied. Liquids that do not form H linkings have normal ϵ and *vice versa*. The conditions for the formation of H linkings are formulated. The structures of the association complexes in the liquid state of the carboxylic acids, HF , and HCN are discussed. H linkings raise the b.p. of the liquids considered by an average of 76° . The mol. wts. of NH_2Ac , NHETAc , and NET_2Ac in C_6H_6 have been determined. The connexion between H linking formation and resonance in amides is discussed. E. S. H.

Electric moments of dialkoxyalkanes. M. M. OTTO (J. Amer. Chem. Soc., 1935, 57, 693—695).—The electric moments of $\beta\beta$ -dimethoxy-, -diethoxy-, and -dipropoxy-heptane, $\text{CH}_2(\text{OEt})_2$, and $\text{CH}_2(\text{O-CH}_2\text{Bu}^\nu)_2$ have been determined. Evidence for the constancy of the valency angle $>\text{C}<_{\text{O}}$, where the two other attached groups are two H and that containing an amyl and a Me, is adduced. E. S. H.

Dipole moments of associated liquids. F. R. GOSS (J.C.S., 1935, 502—506; cf. A., 1934, 717).—Differences between the dielectric polarisation of liquids and gases are attributed mainly to decreases due to anisotropy and association of the solvent, and to an increase due to association of the solute. A formula for the polarisation of liquids is deduced

and exemplified by reference to PhNO_2 in various solvents. F. L. U.

Dipole moments of *p*-cymene, 2- and 3-halo-*geno-p*-cymenes, carvacrol, thymol, *p*-ethyltoluene, *p*-*tert*-butyltoluene, 1:3-dimethyl-5-*tert*-butylbenzene, *tert*-butylbenzene and its *p*-nitro-derivative. C. G. LE FÈVRE, R. J. W. LE FÈVRE, and (in part) K. W. ROBERTSON (J.C.S., 1935, 480—488; cf. A., 1933, 1153).—Dipole moments of the substances named have been determined, and are discussed with reference to the influence of the various substituents. F. L. U.

Electric moments of monohydric normal, secondary, and *iso*-alcohols. P. C. MAHANTI (Z. Physik, 1935, 94, 220—223).—Dipole moments of monohydric *sec*- and *iso*-alcohols of the aliphatic series are of the same order as those of primary alcohols, indicating that the moments are independent of the position of the OH, and of the branching of C chains. A. B. D. C.

Electric moment of some derivatives of the heterocyclic ring $\text{C}_2\text{N}_2\text{O}$. M. MILONE (Gazzetta, 1935, 65, 152—158).—The dipole moments of certain furazans, azoximes, and oxidiazoles have been measured. The vals. of for the three classes of compound are 4.0—4.7, 1.4—1.65, and $3.3\text{--}3.9 \times 10^{-18}$ e.s.u., respectively. The val. of can be used for identifying the isomeric derivatives of the three $\text{C}_2\text{N}_2\text{O}$ ring structures. O. J. W.

Dioximes. CVII. M. MILONE (Gazzetta, 1935, 65, 94—102).—The magnetic moments of glyoxime, and its Me, Me₂, Me Et, Me Prⁿ, Me C₆H₁₇, Ph (α and β), *p*-C₆H₄Me (α and β), Ph Me (α and β), and Ph₂ (α , β , and γ) derivatives, in dioxan solution are respectively 1.22, 0.882, 1.38, 1.106, 1.25, 1.485, 1.396, 1.702, 1.089, 1.66, 0.782, 1.161, 1.492, 2.12, and 1.55, each $\times 10^{-18}$. The β -forms, having the greater moment, presumably have the *amphi*-configuration (cf. A., 1931, 1156). E. W. W.

Directive influence of the electric moment on substitution in the benzene ring. W. J. SVIRBELY and J. C. WARNER (J. Amer. Chem. Soc., 1935, 57, 655—657).—If a mono-substituted C₆H₆ derivative possesses an electric moment $> 2.07D$, a second group will be directed to the *m*-position; if the moment is $< 2.07D$, the second group will be directed to the *o*- and *p*-positions. The principle of former polarity rules is not violated. E. S. H.

Detection of molecular interactions by the time of relaxation of polar molecules. P. GIRARD and P. ABADIE (Compt. rend., 1935, 200, 1187—1189).—The dispersions of pure alcohols and their mixtures with C₆H₆ have been studied and the times of relaxation (τ) of the mols. under various conditions deduced. τ increases initially on dilution, and reaches a max. in about 40—50% solutions, after which it diminishes. It is concluded that two types of mol. interaction can occur concurrently, and that these increase and diminish the time of relaxation, respectively. J. W. S.

Molecular volume of carbamide in complex ions. H. NAKAGAWA (Bull. Chem. Soc. Japan, 1935, 10, 130—134).—The mol. vol. of $\text{CO}(\text{NH}_2)_2$ (R) has

been determined in the following complex salts: $[\text{CaR}_6]\text{Br}_2$, $[\text{CaR}_6]\text{I}_2$, $[\text{CrR}_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{FeR}_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{AlR}_6]\text{I}_3$, $[\text{AlR}_6](\text{ClO}_4)_3$. The average val. approximates closely to the theoretical. Where H₂O of crystallisation was present its calc. mol. vol. was normal. M. S. B.

Refraction and dispersion of crystals. XI. Rotating prism method of determining dispersion photographically. P. WULFF and T. F. ANDERSON (Z. Physik, 1935, 94, 28—37; cf. A., 1934, 718).—A prism rotated continuously gives an edge on a photographic plate corresponding with min. deviation, and so gives the dispersion of the medium. Refractive indices for CsCl between 2000 and 7000 Å. are given to the fourth place. A. B. D. C.

(A) Anomalous dispersion in potassium vapour at high temperatures. V. K. PROKOFIEV. (B) Anomalous dispersion near the first two doublets of the principal series of rubidium and caesium. V. K. PROKOFIEV and G. SHTANDEL (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 347—358, 359—367).—(A) Vals. of $n-1$ at 4000 Å. for KI and KBr vapours are 10^{-4} and 5×10^{-5} , respectively.

(B) Measurements with Rb and Cs vapours are recorded. CH. ABS. (e)

Optical constants of the alkali metals. M. I. SERGEEV and M. G. CHERNIKHOVSKI (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 235—241).—Formulae are given for the absorption and dispersion of light by alkali metals and compared with data for K and Na. CH. ABS. (e)

Optical properties of salts in the system $(\text{NH}_4)_2\text{SO}_4\text{--CaSO}_4\text{--H}_2\text{O}$. A. GABRIEL (J. Amer. Chem. Soc., 1935, 57, 686—688).—The following vals. are recorded: $(\text{NH}_4)_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$, n_a 1.567, n_b 1.580, n_g 1.595; $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, n 1.532; $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$, n_a 1.521, n_b 1.529, n_g 1.531. E. S. H.

Pasteur's principle of molecular dissymmetry: *dextro*- and *laevo*-camphoric acids. B. K. SINGH (Current Sci., 1935, 3, 420—421).—Campbell's measurements (A., 1931, 848) on the rotatory power of *d*- and *l*-camphoric acids are repeated. Results are given for 10 λ between 4358 and 6709 Å. Contrary to Campbell no difference is found in $[\alpha]$ for the two enantiomorphs in EtOH. W. R. A.

Optical rotatory dispersion of α - and β -pinenes in the ultra-violet. R. PADMANABHAN and S. K. K. JATKAR (Current Sci., 1935, 3, 419—420).— β -Pinene gives no max. on the positive side of its rotatory dispersion curve. Neither α - nor β -pinene in EtOH gives max. at 2800 Å. as reported by Servant (A., 1932, 215). W. R. A.

Anomalous magnetic rotation of uranyl nitrate. P. L. KAPUR and M. R. VERMA (Current Sci., 1935, 3, 419).—The mol. magnetic rotation, 5.2, is const. over a wide range of concn. Unlike that of most diamagnetic substances, the Faraday effect is negative. W. R. A.

Planar configuration for quadricovalent nickel, palladium, and platinum. E. G. COX, F. W. PINKARD, W. WARDLAW, and K. C. WEBSTER (J.C.S.,

1935, 459—462).—Salicylaldoxime reacts with aq. K_2PtCl_4 to give a mixture of *disalicylaldoximino-platinous chloride* and *disalicylaldoximeplatinum* (I). (I) occurs in two modifications, neither of which is isomorphous with the corresponding Pd (II) or Ni (III) compound. X-Ray examination has shown (II) and (III) and one of the modifications of (I) to have a planar *trans*-configuration. (III) is diamagnetic. Pauling's theoretical conclusions (cf. A., 1931, 670) are thus substantiated. F. L. U.

Valency defined. E. A. FLOOD (J. Chem. Educ., 1935, 12, 132—134).—A discussion. L. S. T.

Inner-complex salts. S. A. VOSNESSENSKI (Uspekhi Khim. U.S.S.R., 1934, 4, 531—562).—A review. CH. ABS. (r)

New models of old molecules. T. H. HAZLEHURST, jun., and H. A. NEVILLE (J. Chem. Educ., 1935, 12, 128—132).—The construction and uses of mol. models which illustrate recent knowledge of at. structure are described. L. S. T.

Normal vibration frequencies of NH_3 , PH_3 , and AsH_3 . J. B. HOWARD (J. Chem. Physics, 1935, 3, 207—211).—Assuming the existence of valency forces in NH_3 , PH_3 , and AsH_3 , it can be shown that the high-frequency degenerate normal vibration, although theoretically active, does not appear as a fundamental in the infra-red spectra. The remaining three observed fundamentals can be accounted for satisfactorily. Fundamental frequencies have also been calc. for the isotopic mols. NH_2D , NHD_2 , and ND_3 , and provide a test for the val. predicted for the fourth fundamental in NH_3 . M. S. B.

Calculation of the fundamental frequencies of a molecule of the type X_6 with plane hexagonal symmetry. M. C. MANNEBACK (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 5—15; cf. this vol., 150).—The potential energy function and the frequencies of the fundamental modes of vibration are considered. R. S.

Rotating axes and polyatomic molecules. C. ECKART (Physical Rev., 1935, [ii], 47, 552—558; cf. A., 1934, 1164).—Mathematical. N. M. B.

Dipole rotation in solid non-crystalline materials. A. GEMANT (Phil. Mag., 1935, [vii], 19, 746—758).—Theoretical. The application of Debye's theory of dipole rotation to amorphous solids such as paraffin, glass, etc. is justified. F. L. U.

Interrelation of equilibrium nuclear distance with other molecular constants for diatomic molecules. R. A. NEWING (Phil. Mag., 1935, [vii], 19, 759—767).—A preliminary theoretical investigation of the general properties of potential curves for diat. mols. F. L. U.

Electrostatic energies of ionic lattices. F. HUND (Z. Physik, 1935, 94, 11—21).—Energies are calc. for lattices of the types AB and AB_2 ; apart from the no. and charges of the ions, the co-ordination nos. determine the energies of the lattice. A. B. D. C.

Resolution of bond eigenfunctions in terms of a linearly independent set. H. EYRING and H. GERSHINOWITZ (J. Chem. Physics, 1935, 3, 224—229). A method for obtaining coeffs. in the expansion of a bond eigenfunction in terms of a linearly independent

set has been devised. Coeffs. of eigenfunctions, expanded in terms of the Rumer set, may be determined for 6 linkings. M. S. B.

Quantum-mechanical treatment of molecules by the method of spin valency. G. WHELAND (J. Chem. Physics, 1935, 3, 230—240).—Mathematical. A consideration of the Slater method compared with that of Born, Heitler, Reimer, and Weyl. M. S. B.

General relation between vibration frequencies of isotopic molecules. Calculation of harmonic force constants. O. REDLICH (Z. physikal. Chem., 1935, B, 28, 371—382).—Theoretical. The frequencies of a particular type of vibration in two isotopic mols. are connected by an equation which involves only at. masses and moments of inertia, and not force consts. Comparison of the results deduced from this equation with experimental data for $CDCl_3$ (this vol., 146) shows slight discrepancies probably due to anharmonicity of the vibrations. R. C.

Internuclear distance and vibration frequency in diatomic molecules. H. S. ALLEN and A. K. LONGAIR (Phil. Mag., 1935, [vii], 19, 1032—1041).—Formulae connecting internuclear distance r_e and vibration frequency ω_e of diat. mols. are discussed and a new relation $\omega_e r_e^3 \sqrt{\mu} = \text{const.}$, where μ is the reduced mass in g., is proposed. The val. of the const. \propto the no. of completed electronic shells in the mol. R. S.

Ratio of the temperature coefficients of surface tension and density. L. SIBAIYA (Current Sci., 1935, 3, 418—419).—Theoretical. The experimental law that temp. coeff. (of surface tension)/coeff. of expansion has vals. between 2 and 3 is derived from Laplace's theory of capillarity. W. R. A.

Directional distribution of characteristic X-rays emitted within crystals. W. KOSSEL, V. LOECK, and H. VOGES (Z. Physik, 1935, 94, 139—144).—Characteristic radiation of at. groups within a crystal is excited when the crystal forms an antiscathode; its directional distribution due to Bragg reflexions has been studied for a single Cu crystal. A. B. D. C.

Precision measurements by the Debye-Scherrer method. M. STRAUMANIS and O. MELLIS (Z. Physik, 1935, 94, 184—191). A. B. D. C.

X-Rays from a Lenard tube with a platinum attachment. F. SCHMIDT (Physikal. Z., 1935, 36, 283—288).—A review of the history of the discovery of X-rays shows that Rontgen used a Lenard tube, and not a Hittorf or Crookes tube. Experiments with a replica of his apparatus show that the X-rays from it are strong, and easily detected by means of a Ba platinocyanide screen as used by Rontgen. The rays were not discovered by Lenard, although working with a similar tube, owing to his lack of detecting apparatus. A. J. M.

Scattering of X-rays at small angles. J. A. GRAY (Canad. J. Res., 1935, 12, 408—409; cf. A., 1930, 833).—Powders show either intense scattering at small angles, similar to that of gases (shown by artificial graphite, charcoal, and Si), or scattering due to refraction in or reflexion at the surfaces of the particles. The total intensity of radiation scattered by charcoal \propto the square of the λ of the primary rays. J. W. S.

X-Ray reflectivity and resolving power of the (10 0) planes of etched quartz crystals. L. G. PARRATT (Rev. Sci. Instr., 1935, [iii], 6, 113—115; cf. this vol., 57).—The widths of the (1, -1) rocking curves at half max. intensity, % reflexion, and coeff. of reflexion are tabulated and plotted for λ 0.56—7.11 Å., including at 6.7 Å. the absorption limit of Si. The main advantage of crystals cut parallel to the (10 0) planes lies in the relatively large grating-space, suiting the crystals to the range 5—8 Å. N. M. B.

Dynamics of molecular crystal lattices. I. Neon. V. DEITZ (J. Franklin Inst., 1935, 219, 459—469).—The lattice energy of a mol. crystal is considered, and the potential constns. in the equation for the complete lattice energy are evaluated. The method of Morgenau (Physical Rev., 1931, 37, 1425) is applied for calculating the attraction const. from spectroscopic data. The dynamics of the small vibrations of a face-centred cubic lattice are investigated by Born and Karman's method. A. J. M.

Significance of the persistence of the crystalline state above the m.p. R. E. BURK (Science, 1935, 81, 344—345).—Theoretical. L. S. T.

Scattering of X-rays by polyatomic gases. S. S. LU (Chinese J. Physics, 1933, 1, 51—73).—Abs. vals. of the intensity of total scattering, by comparison with that in O₂, are given for Cl₂, CO₂, N₂O, H₂S, CCl₄, and CHCl₃ for a range of scattering angles 15—130°, using Mo K α rays separated by balanced ZrO₂ and SrO filters. Results are in agreement with Woo's theory (cf. A., 1932, 892). N. M. B.

Dispersion of X-rays by nickel. I. Atomic-factor curve for nickel. I. UMANSKI and V. VEKSLER (Physikal. Z. Sovietunion, 1934, 6, 258—267).—Experimental and calc. vals. are compared. CH. ABS. (e)

X-Ray diffraction patterns of ice. E. F. BURTON and W. F. OLIVER (Nature, 1935, 135, 505—506).—X-Ray diffraction patterns of ice formed by condensation of H₂O vapour on Cu at (a) -85° and (b) at -155° show in case (a) lines characteristic of the close-packed hexagonal structure of ice, and in case (b) a diffuse line indicating the amorphous character of the condensate. The existence is indicated of a crit. temp., approx. -110°, below which the condensate is vitreous and above which crystals are formed. L. S. T.

Formation of ice crystals. O. BALLY (Helv. Chim. Acta, 1935, 18, 475—476).—The crystallisation of long needles of ice above the surface of H₂O, under special conditions of temp., wind, etc., is described. E. S. H.

C-Modification of neodymium and lanthanum sesquioxides. K. LÖHBERG (Z. physikal. Chem., 1935, B, 28, 402—407).—Cubic Nd₂O₃ (a 11.05 Å.) and La₂O₃ (a \approx 11.4 Å.) are C modifications. R. C.

Crystal structure of lead chromate produced in the intermicellar space of cellulose. U. YOSHIDA and N. MATSUMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 113B).—The PbCrO₄ exists as a crystal powder belonging to the tetragonal system, instead of the usual monoclinic system. A. G.

Crystal structure of caesium enneachlorodithallite, Cs₃Tl₂Cl₉. J. L. HOARD and L. GOLDSTEIN (J. Chem. Physics, 1935, 3, 199—202).—Cs₃Tl₂Cl₉ may form uniaxial hexagonal plates or prisms depending on the consns. of CsCl and TlCl₃ in the solution from which it crystallises. It is rhombohedral with a_0 9.58 Å. and α 83° 48', containing 2 mols. Extensive and perfect 60° twinning on the basal plane is shown. The X-ray data indicate approx. closest packing. Tl₂Cl₉''' is regarded as a covalent complex. The structure is compared with that of Cs₃As₂Cl₉ and KMgF₃. M. S. B.

Structure of methylammonium alum, NH₃MeAl(SO₄)₂.12H₂O. H. LIPSON (Phil. Mag., 1935, [vii], 19, 887—901).—X-Ray data and an electron density map of the salt are given and the interat. distances and dispositions deduced. The NH₃Me appears to be spherically symmetrical. The structure differs from that of K alum, but is apparently similar to that of Cs alum, and the possibility of distinguishing between the external forms of the two structures is suggested. R. S.

Classification of silicates. W. F. DE JONG (Natuurwetensch. Tijds., 1935, 17, 31—43).—The mineral silicates are classified according to their tetrahedral [SiO₄]₄ and [AlO₄]₅ structures. S. C.

Crystal structure of common zoisite. L. WALDBAUER and D. C. McCANN (Amer. Min., 1935, 20, 106—111; cf. A., 1931, 415).—X-Ray analysis of common translucent zoisite, from Praegratten, Austria, shows that it is made up of a mosaic of submicroscopic multiple twins of clinozoisite (I). (I) has $a:b:c=8.92:5.60:10.21$; space-group C_2^2 with 2 mols. per unit cell. L. S. T.

Crystal structure of diaspore. F. J. EWING (J. Chem. Physics, 1935, 3, 203—207).—The unit cell of diaspore has a 4.40, b 9.39, and c 2.84 Å., and contains 4AlHO₂. The structure is discussed on the basis of the co-ordination theory. The position of the H linkings has been determined. The formula may be written as (AlHO₂)_n or (HALO₂)_n to admit the known co-ordination no. of 6 for Al. Formulæ suggesting the existence of H₂O or OH' in the mol. are wrong. M. S. B.

Crystal structure of pyrophyllite, Al₂(OH)₂Si₄O₁₀. J. PALACIOS and J. A. BARASOAIN (Anal. Fis. Quim., 1934, 32, 271—274).—Pyrophyllite is monoclinic (pseudo-hexagonal) with a 5.20, b 9.06, c 18.29 Å., α 95° 41', 4 mols. per unit cell, d 2.77, space-group C_{2h}^3 (possibly C_2^3 or C_2^2). D. R. D.

Crystal structure of chromium, molybdenum, and tungsten hexacarbonyls. W. RUDORFF and U. HOFMANN (Z. physikal. Chem., 1935, B, 28, 351—370).—These crystallise in the rhombic system, space-group C_2^2 , and the unit cell contains four M(CO)₆ mols. The dimensions of the unit cell, a , b , and c , are: Cr(CO)₆, 11.7, 6.27, 10.8₉; Mo(CO)₆, 12.0₂, 6.4₈, 11.2₃; W(CO)₆, 11.9₀, 6.4₂, 11.2₁ Å. In Cr(CO)₆ and Mo(CO)₆ the distance C—O is 1.15, and the distances Cr—C and Mo—C are 1.80 and 2.13 Å., respectively. The results confirm the assumption that the CO groups surround the metal atom in the form of a regular octahedron, and support Langmuir and

Pauling's views on the co-ordinative atom linking in the carbonyls (A., 1931, 670). R. C.

Cyanuric triazide. (Miss) I. E. KNAGGS (J. Chem. Physics, 1935, 3, 241).—A comparison of the author's data with those of Hughes (this vol., 286). It has been shown that the electron densities at the centres of the atoms rise to > 8 and 10 electrons per sq. Å. for C and N, respectively. M. S. B.

Symmetry and structure of the crystals of the hydrochlorides of triaminotriethylamine. F. M. JAEGER and J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 243—248).— $N(C_2H_4 \cdot NH_2Cl)_3$ (cubic) is formed on slow evaporation of a solution of $N(C_2H_4 \cdot NH_2)_3$ in very slight excess of HCl; with a larger excess of HCl $N(C_2H_4 \cdot NH_2Cl)_3 \cdot HCl \cdot H_2O$ (hexagonal) is formed. The X-ray spectra of the crystals have been studied. R. S. B.

X-Ray investigation of the crystals of anthranilic acid. M. PRASAD and M. R. KAPADIA (Indian J. Physics, 1935, 9, 239—243).—Two types of crystals deposit on slow evaporation of solutions in EtOH. (I) has a 16.16, b 11.77, c 7.17 Å., d 1.355, space-group Q_h^1 . (II) has a 12.77, b 10.8, c 9.403 Å., d 1.422, space-group Q_h^2 . Each has 8 mols. per unit cell. N. M. B.

Space-group and atomic arrangements in anthraquinone crystals. I. K. BANERJEE and B. C. GUHA (Indian J. Physics, 1935, 9, 287—294).—Oscillation-photograph data for rotation about the b and c axes are tabulated. The space-group is V_h^2 . N. M. B.

X-Ray diffraction from hæmoglobin and other crystalline proteins. R. W. G. WYCKOFF and R. B. COREY (Science, 1935, 81, 365—366).—X-Ray photographs of edestin, excelsin, and hæmoglobin show that these proteins crystallise with H_2O of crystallisation which is readily lost. When this decomp. is prevented, typical powder patterns rich in sharp lines are obtained. Some of the spacings are much $>$ those found with insol. protein structures such as silk, hair, and tendon. L. S. T.

X-Ray single-crystal photographs of insulin. D. CROWFOOT (Nature, 1935, 135, 591—592).—The crystals form flat rhombohedra stable in air. They are simple rhombohedral cells with a 44.3 Å. and α 115°; d 1.306 ± 0.003 , calc. cell mol. wt. $39,300 \pm 800$. The wt. of insulin in the cell (cell mol. wt.— H_2O of crystallisation) is 37,200. The crystal unit cell appears to contain only 1 mol. of insulin. Each mol. is surrounded by 8 others, 2 at 30 Å. above and below along the trigonal axis and 6 at 44 Å. along the edges of the primitive rhombohedron. The shape of the mol. is approx. an oblate spheroid of diameters 44 and 30 Å. The crystal structure of insulin is compared with that of pepsin. L. S. T.

X-Ray rotation crystal and fibrous structure diagrams. IV. White and monochromatic X-rays. V. X-Ray diagrams of the cellulose micelle. M. ISHIHARA (J. Soc. Chem. Ind. Japan, 1935, 38, 105—107B, 107—110B).—IV. Mathematical. Data and photographs are given for hemp cellulose. A. G.

Penetration of pyridine and methyl alcohol into the lattice of cellulose. K. HUTINO and I. SAKURADA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 300—302).—The replacement of H_2O in the H_2O -cellulose lattice by C_5H_5N and MeOH has been established by X-ray examination. R. S.

Electron diffraction as a method of research. G. P. THOMSON (Nature, 1935, 135, 492—495).—A summary of recent results. L. S. T.

Diffraction of electrons in the determination of the lattice structure of organic compounds. G. NATTA, M. BACCAREDDA, and R. RIGAMONTI (Gazzetta, 1935, 65, 182—198).—Electron diffraction measurements have been made with a large no. of highly polymerised org. substances (celluloses, collodions, etc.) and compared with previously recorded data and with the results of X-ray measurements. Many of the photograms attributed by previous observers to collodion, celluloid, and other cellulose derivatives are due to very thin films (probably bimol.) of fatty impurities adsorbed on the surface, which can be avoided only by taking very great precautions. O. J. W.

Determination of the structure of simple molecules by electron interference. H. BOERSCH (Monatsh., 1935, 65, 311—337).—The results support a linear structure for the mols. of C_3O_2 and COS. CF_4 has a tetrahedral structure. The angle O—F—O in the OF_2 mol. is $100 \pm 3^\circ$. $(NMe)_2$ has a *trans* configuration. CH_2N_2 has a ring structure. Distances between the atoms in these compounds are deduced. E. S. H.

Influence of temperature on the diffraction of slow electrons by a graphite crystal. V. E. LASCHKAREV and G. A. KUZMIN (Physikal. Z. Sovietunion, 1934, 6, 211—223).—The temp. dependence is the same for X-rays and electrons. The inner potential of graphite is 18—20 volts.

CH. ABS. (e)
Absorption factor in electron diffraction. V. E. LASCHKAREV and A. S. CHABAN (Physikal. Z. Sovietunion, 1934, 6, 205—210).—Relative intensities of Debye lines were measured as a function of the angle of inclination of the oxidised cleavage plane of Mg. The absorption factor is of the same form for electrons and for X-rays. CH. ABS. (e)

Magnetic investigations of electromagnet cores of a new type. J. L. SNOEK (Physica, 1935, 2, 403—412).—A Ni-Fe alloy with 30—100% Ni was made anisotropic by first rolling down $> 99\%$ and recrystallising. The strip thus obtained behaves as if it were a single crystal with one axis parallel to the strip and one cube face in the surface. This is then rolled down to 30%, when it has a very high magnetic anisotropy in the plane of the strip. Determination of the magnetisation curves in a direction perpendicular to the plane of the strip and observations of the resistance change in a magnetic field indicate that the elementary magnets have min. energy in a direction in the plane of the strip. The permeability in a direction perpendicular to this is very low (35). A. J. M.

Influence of grain size on magnetic properties. W. E. RUDER (Trans. Amer. Soc. Metals, 1934, 22,

1120—1131).—Although there appears to be a slight relationship between grain size and hysteresis loss, other factors such as strain and purity of the alloys have a much greater influence. Orientation of the crystals is important, and single crystals may give vals. in one direction 100% > in other directions.

W. P. R.

Piezometric researches. I. Influence of high pressures on the temperature of fusion and temperature of transformation of organic substances. L. DEFFET (Bull. Soc. chim. Belg., 1935, 44, 41—80, 99—139).—The investigation was carried out at const. vol. in a special apparatus. The sources of error are discussed and fusion pressures (I) up to 1000 kg. per sq. cm., corresponding with a series of temp., are given for CCl_4 , MeNO_2 , C_2HCl_5 , $\text{C}_6\text{H}_4\text{Br}_2$, $\text{Bu}^\text{t}\text{OH}$, *tert.*- $\text{C}_5\text{H}_9\text{OH}$, HCO_2H , AcOH , EtCO_2H , $\text{Pr}^\text{c}\text{CO}_2\text{H}$, $\text{Bu}^\text{c}\text{CO}_2\text{H}$, *n*-hexoic, *n*-heptoic, and *n*-octoic acids, $\text{HCO}\cdot\text{NH}_2$, cyclohexane, C_6H_6 , PhNO_2 , *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, *o*- and *p*-xylene, PhOH , *m*-cresol, COPh , MeOBz , PhCN , NH_2Ph , NPhMe , *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and piperidine. The transition pressures and (I) of a no. of enantiomorphs have been studied over the same range: *n*-cetyl alcohol, transition point at atm. pressure (t.p.) 43.6—44.1°; *n*-dotriacontane, t.p. 64.3°; methylcyclopentanol, t.p. 29.15°, triple point at 2000 kg. per sq. cm. and 72°; MeOBz , t.p. 16.8°. The m.p. and (I) data are recorded for the monotropes: *n*-cetyl iodide, *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, Ph salicylate (II), CH_2I_2 , including a new form of (II). Vals. of $\delta=1+\Delta V/L$, where L is the latent heat of fusion and ΔV the difference between the sp. vol. of solid and liquid, have been calc. for a large no. of substances and good agreement was obtained with experiment. The relation between δ and various properties is discussed.

R. S.

Relation between fusion and strength. H. JEFFREYS (Phil. Mag., 1935, [vii], 19, 840—846).—The strength of materials forming the earth's crust is discussed from the point of view of the pressure required to lower the m.p. to the ordinary temp. For substances for which the necessary data are available the actual crushing strength is < that calc., although the order (of increasing or decreasing strength) is correctly given.

F. L. U.

Energy and elastic constants of some heteropolar crystals. V. ŽDANOV, A. ERSOHOV, and G. GALACHOV (Z. Physik, 1935, 94, 241—249).—Wave-mechanics calculations are given for alkali halide crystals.

A. B. D. C.

Hume-Rothery rule for intermetallic compounds. U. DEHLINGER (Z. Physik, 1935, 94, 231—240).—Bloch's theory of metals leads to the Hume-Rothery rule.

A. B. D. C.

Rotational and translational degrees of freedom in the solid state. New conceptions concerning the structure of solids. II. J. A. A. KETELAAR (Chem. Weekblad, 1935, 32, 262—270).—A review.

D. R. D.

Influence of mechanical deformation on the transformation velocity of polymorphic metals. E. COHEN, W. A. T. COHEN-DE MEESTER, and A. K. W. A. VAN LIESHOUT (Proc. K. Akad. Wetensch.

Amsterdam, 1935, 38, 377—387).—The velocity of transformation, v , of white to grey Sn at -50° is greatly increased by rolling, drawing, or cracking the white Sn, v increasing with the degree of deformation. Deformation at -80° gives a higher v at -50° than deformation at room temp. Tempering at 150° after deforming greatly reduces v . R. S. B.

Rate of polymorphic transformations. I. Tin plague. II. E. COHEN and A. K. W. A. VAN LIESHOUT (Z. physikal. Chem., 1935, 173, 1—31, 67—70).—I. The rate of transformation of grey into white Sn under xylene at 25.6° passes through a max. with increase in the no. of times which the specimen has been converted previously from one form into the other, and is especially affected by the temp. at which the preceding transformation into white Sn occurred. The rate is a max. when $\sim 30\%$ of white Sn has been formed. At 25.6° the rate of conversion of grey Sn which has previously been repeatedly converted in air is negligible. Such inactive Sn may, however, be rendered active again, and then undergoes reversible undelayed transformation at a measurable rate even near the transition point. Shaking during transformation of grey into white Sn causes great acceleration. The rate also depends on the previous thermal and mechanical treatment of the Sn. The results in conjunction with van Arkel and Koets' observations (A., 1927, 401) afford a general explanation of the delay and other phenomena associated with the transformation of Sn.

II. The "region of indifference" reported for various polymorphic transformations (Bridgman, Proc. Amer. Acad. Sci., 1916, 52, 57) is a purely accidental effect, depending on the previous treatment of the substance examined, and by appropriate variation of that treatment may be eliminated. Its elimination has been achieved for Sn and NH_4NO_3 .

R. C.

Physico-chemical studies on tin. X. Transition temperature grey tin white tin. E. COHEN and A. K. W. A. VAN LIESHOUT (Z. physikal. Chem., 1935, 173, 32—34).—By experiments with Sn activated so as to undergo reversible undelayed transformation in the immediate vicinity of the transition point (cf. preceding abstract) the latter has been found to be $13.2 \pm 0.1^\circ$.

R. C.

Transition of potassium superoxide. E. W. NEUMAN (J. Chem. Physics, 1935, 3, 243).—Heating and cooling curves for KO_2 show a break at $-75.5 \pm 0.5^\circ$. A colour change from deep orange to light cream occurs on cooling at approx. the same temp. It is not possible, by the method employed, to distinguish between a true polymorphic transition and a gradual one.

M. S. B.

Mol. wts. of cellulose and cellulose derivatives. E. O. KRAEMER and W. D. LANSING (J. Physical Chem., 1935, 39, 153—168).—Different methods for determining the mol. wt. of cellulose and its derivatives, and the relation between mol. wt. and viscosity, η , are discussed. There is a definite parallelism between degree of polymerisation of linear mols., such as cellulose, and the quantity $[\eta] = \lim_{c \rightarrow 0} (r_r - 1)/c$, where r_r is the ratio of η_{solution} to η_{solvent} at concn. c g. per 100 c.c. of solution. The ultra-centrifuge

method of mol. wt. determination gives more detailed information as to distribution of mol. wts. etc. than any other method.

M. S. B.

Mol. wts. of the phthalocyanines. J. M. ROBERTSON, R. P. LINSTEAD, and C. E. DENT (*Nature*, 1935, 135, 506—507).—Ni, Cu, and Pt phthalocyanines have α 19.9, 19.6, 23.9 Å., b 4.71, 4.79, 3.81 Å., c 14.9, 14.6, 16.9 Å., β 121.9°, 120.6°, 129.6°, respectively, 2 mols. per unit cell, space-group C_{2h}^2 ($P2_1/a$) and max. mol. wts. 586, 583, and 712, respectively. The min. mol. wts. from elementary analyses coincide with these vals. and hence the formula is $C_{32}H_{16}N_4M$, where M is the metal atom which must reside at the centre of symmetry, and the mol. wts. calc. from the formulæ are 571, 576, and 707, respectively. The cell dimensions show that the large flat mols. must be well spread out in the ac plane. The vals. of d , determined by flotation methods, are 1.63, 1.63, and 1.98, respectively, and the mol. vols. are practically const.

L. S. T.

Magnetic susceptibility of lithium hydride. **Diamagnetism of ionic crystals.** S. FREED and H. G. THODE (*J. Chem. Physics*, 1935, 3, 212—215).—The mol. magnetic susceptibility of LiH at 300° and 78° abs. is -4.60×10^{-6} with practically no temp. coeff. Deviations from theoretical vals. are ascribed to a paramagnetism present in all crystals, not included in the calculation.

M. S. B.

Magnetic susceptibility of cadmium compounds. W. R. A. HOLLENS and J. F. SPENCER (*J.C.S.*, 1935, 495—496).—Mass susceptibilities of 30 Cd compounds are recorded. Cd has at. susceptibility -24.85×10^{-6} . Cd borofluoride is described.

F. L. U.

Magneto-chemical investigations of organic compounds. I. Existence of diradicals. E. MULLER and I. MULLER-RODLOFF (*Annalen*, 1935, 517, 134—151).—Magnetic examination of 4:4'-(Tschitschibabin, A., 1907, i, 503) and 3:3'-diphenylene-bisdiphenylmethyl (I) (Schlenk *et al.*, A., 1915, i, 519), 2:3:6:7-dibenzanthracene, tetraphenylrubene, diphenyldiazomethane, and 4:4'-bisbenzhydryl- $\alpha\beta$ -diphenylethane shows that the existence of a C diradical can be detected only in the case of (I). Formation of a quinonoid system occurs whenever possible and diradicals can be detected only where such valency tautomerism is impossible. True diradicals can be expected only when there is no possibility of intermol. stabilisation (*ortho* compounds) or when the transition to a valency tautomeric, quinonoid system is excluded. Although magneto-chemical examination disproves the presence of considerable amounts of diradicals in the compounds mentioned above, it does not preclude the existence of amounts < 1 —2% in equilibrium with the less reactive form; it is not expedient, however, to ascribe to these compounds a radical structure, since the bulk of the material exists in a normal quinonoid state.

H. W.

Magnetic susceptibility of tetraphenylrubene and of its dissociable oxide. L. ENDERLIN (*Compt. rend.*, 1935, 200, 912—914).—The mol. susceptibilities tetraphenylrubene (I) and of its oxide (II) are -3440 and $-3525 (\times 10^{-7})$, respectively, whereas the calc. on the basis of the generally accepted

formula for (I) and Dufraisse's formula for (II) (A., 1933, 1284) are -3500 and $-3662 (\times 10^{-7})$. The results indicate that the O are attached to the nucleus by normal linkings.

J. W. S.

Diamagnetic susceptibility of water poly-merides. L. SIBAIYA (*Current Sci.*, 1935, 3, 421—422).—Vals. for χ_{20° are calc. for H_2O , $(H_2O)_2$, and $(H_2O)_3$ assuming the relative abundance given by Rao (cf. A., 1934, 942) from Raman spectra. The calc. vals. are compared with experimental data and discussed from the point of view of the additivity law and O valency.

W. R. A.

Adiabatic demagnetisation of some paramagnetic salts. W. J. DE HAAS and E. C. WIERSMA (*Physica*, 1935, 2, 335—340).—The effect of the magnetic field strength on the temp. reached by adiabatic demagnetisation was investigated for Fe NH_4 alum, $Ce(EtSO_4)_3 \cdot 9H_2O$, and K Cr alum mixed with 14.4 mols. of K Al alum. Fe NH_4 alum is a very suitable substance for reaching very low temp. $Ce(EtSO_4)_3$ is not so suitable. There is a considerable increase in the sp. heat of this substance in the neighbourhood of 0.1° abs. There is no effect of alteration of field strength. The dil. K Cr alum gave a temp. of 0.0044° abs., the lowest yet recorded.

A. J. M.

Thermo-electric effect with palladium-silver alloys charged with hydrogen. J. SCHNIEDER-MANN (*Ann. Physik*, 1935, [v], 22, 425—442).—The thermo-electric effect (I) (electron emission) of all Pd-Ag alloys is increased when they are charged with H_2 . The 60% Pd-40% Ag alloy shows min. (I) both when uncharged and when charged with H_2 ; it also shows the min. Hall effect and electrical conductivity. The increase in (I) on absorption of H_2 is due both to an increase in the no. of free electrons and to a decrease in the emission work, as is shown by the deviations of these alloys from the Richardson law. A summary of the physical properties of Pd-Ag alloys, both with and without adsorption of H_2 , is given.

A. J. M.

Thermo-electric power and resistance. L. NORDHEIM and C. J. GORTER (*Physica*, 1935, 2, 383—390).—The general theory of thermo-electric power (I) is discussed with reference to the parallelism between (I) and resistance. The effect of impurities (solid solutions) is considered. The disturbance in a ferromagnetic material may be regarded as a mixture effect.

A. J. M.

Superconductivity and diamagnetism. F. LONDON and H. LONDON (*Physica*, 1935, 2, 341—354).—Theoretical. The super-current is regarded as a kind of diamagnetic vol. current, maintained by a magnetic field, which may be produced by the current itself.

A. J. M.

Magnetic properties and critical currents of superconducting alloys. J. N. RABININ and L. W. SHUBNIKOW (*Nature*, 1935, 135, 581—582).—The relation between field strength and the magnetic induction at 2.11° abs. for a Pb-Tl alloy corresponding in composition with $PbTl_2$, and a Pb-Bi alloy (65% Pb) is described. Superconductivity is lost above a certain crit. field strength.

L. S. T.

Electromagnetic equations of the super-conductor. F. LONDON and H. LONDON (*Proc.*

Roy. Soc., 1935, **A**, 149, 71—88).—Mathematical. A new formulation of the dependence of current on field in superconductors is established. L. L. B.

Optical measurements of ultrasonic wave velocities in liquids. C. BACHEM and E. HIEDEMANN (Z. Physik, 1935, **94**, 68—71).—Measurements are given for PhMe, C_6H_6 , CCl_4 , and *m*-xylene. A. B. D. C.

Influence of ultrasonic waves on some physico-chemical properties. L. HAUSS (Bull. Soc. chim. Belg., 1935, **44**, 154—166; cf. this vol., 573).—Effects produced are discussed. The velocity of deposition of a suspensoid is diminished by ultrasonic waves. R. S.

Velocity of elastic waves in the mercury crystal and the characteristic temperature calculated therefrom. E. GRUNEISEN and H. HOYER (Ann. Physik, 1935, [v], **22**, 663—673).—The theory of the velocity of elastic waves (I) in trigonal crystals is given. (I) in the Hg crystal was determined by calculating the velocities of sound for a no. of directions in the crystal. The wave surface in Hg is similar to that in quartz. The Debye characteristic temp. ($\theta_{elast.}$) in the range over which the T^3 law holds is 68.6° . Comparison with shows greater agreement than is the case for Zn or Cd. At higher temp. $\theta_{elast.} < \theta_D$ for Hg, but the reverse is the case for Zn and Cd. A. J. M.

Theory of specific heat. III. Existence of pseudo- T^3 regions in the specific heat curve of a crystal. IV. Calculation of the specific heat of crystals from elastic data. M. BLACKMAN (Proc. Roy. Soc., 1935, **A**, 149, 117—125, 126—130; cf. this vol., 573).—III. The possibility of pseudo- T^3 regions in the sp. heat curve is deduced from the general form of the vibrational spectrum of a cubical lattice. The theory explains the discrepancies hitherto found between the θ_D vals. derived from thermal and from elastic data at low temp.

IV. A new method, based on considerations of lattice theory and on the geometrical form of the wave surfaces, is deduced, by which θ_D vals. can be calc. from elastic data. L. L. D.

Heat content of water and water vapour. W. KOCH (Z. Ver. deuts. Ing., 1934, **78**, 1160; Chem. Zentr., 1934, ii, 3602).—Data are tabulated. H. J. E.

Heat capacity curves of the simpler gases. VII. High-temperature heat capacities of oxygen and influence of the $^1\Delta$ level on the thermodynamic properties of the gas. H. L. JOHNSTON and M. K. WALKER (J. Amer. Chem. Soc., 1935, **57**, 682—684; cf. A., 1934, 1300).—Vals. of heat capacity, entropy, free energy, and dissociation of O_2 , based on spectroscopic data, are revised in accordance with the existence of the $^1\Delta$ electronic state. The influence of the $^1\Delta$ term is insignificant below 3000° abs. for the dissociation, and contributes < 0.002 g.-cal. to the mol. free energy function below 1750° ; to the mol. entropy below 1250° ; and to the mol. heat capacity below 1000° . The $^1\Delta$ contribution to the heat capacity attains a max. of nearly 0.6 g.-cal. at about 4500° abs. E. S. H.

Critique of the electrical differential method for the measurement of C_v for gases. VI. Specific heats of argon and air. M. TRAUTZ and A. REICHLE (Ann. Physik, 1935, [v], **22**, 513—524).—Improvements in the method previously used (A., 1927, 817) are described. C_v for air is 4.951 g.-cal./ 16° per degree, referred to zero pressure. A. J. M.

Specific heat of iron-carbon systems at high temperatures, and the heat changes accompanying those of phase. S. UMINO (Sci. Rep. Tôhoku, 1935, **23**, 665—793).—The heat content and mean and true sp. heat of 19 Fe-C alloys (0.07—5.07% C) were found by the method of mixtures at various temp. up to $> m.p.$ The heat content and sp. heat of cementite at high temp. were found by extrapolation. Data and curves are given for heats of dissolution of one form in another, heats of transition, and latent heats of fusion. N. M. B.

True specific heat of some metals and alloys. K. HONDA and M. TOKUNAGA (Sci. Rep. Tôhoku, 1935, **23**, 816—834).—Using an improved Nernst-Lindemann electrical method sp. heats were measured for Cu, Al, Fe, Mg, Cu-Ni, Mg-Zn, Mg-Al, Al-Cu, duralumin, brass, and bronze. The additive law was not obeyed by the alloys except in the case of bronze and brass (70% Cu). Brass (60% Cu) does not obey the law. N. M. B.

Specific heat of certain minerals and salts of the rare-earth elements. W. SWIENTOSŁAWSKI, J. SALCEWICZ, J. USAKIEWICZ, A. ZMACZYŃSKI, and J. ŻŁOTOWSKI (Rocz. Chem., 1935, **15**, 12—14).—The vals., determined in an ice calorimeter, are: Ag, c_p 0.05532, Sb, c_p 0.04745, johannite, $c_{7.5}$ 0.1290, thorite, c_p 0.1320, samarskite, c_8 0.1078, monazite, $c_{18.9}$ 0.1024, $ScF_3 \cdot 3NH_4F$, $c_{7.7}$ 0.4223, $Y(NO_3)_3$, $c_{7.8}$ 0.2752, $La(NO_3)_3 \cdot 6H_2O$, $c_{7.8}$ 0.2713, $Y_2(C_2O_4)_3 \cdot 12H_2O$, $c_{8.4}$ 0.4640, $La_2(C_2O_4)_3 \cdot 10.5H_2O$, $c_{8.3}$ 0.2647, sucrose, $c_{7.5}$ 0.2774. R. T.

Molecular latent heats. J. D. HUFFINGTON (Phil. Mag., 1935, [vii], **19**, 836—840).—Putting the const. of Trouton's rule = $CR \log (v_1/v_2)$, where v_1 and v_2 are vols. of saturated vapour and of liquid, it is shown that C is a definite function of L/T (L —mol. heat of vaporisation, T —abs. temp.). A table of vals. for 21 substances is given. F. L. U.

Heats of fusion and transformation of 1:4-dioxan. W. A. ROTH and I. MEYER (Z. Elektrochem., 1935, **41**, 229—231; cf. A., 1933, 217).—Heats of fusion and transformation of dioxan are, respectively, 34.25 and 6.32 g.-cal. per g. Dioxan undergoes a slow spontaneous change and is not suitable for use as a cryoscopic solvent. F. L. U.

Accommodation coefficient and the evaporation coefficient of water. T. ALTY and C. A. MACKAY (Proc. Roy. Soc., 1935, **A**, 149, 104—116).—Experiments are described in which H_2O vapour mols. are incident on a liquid surface of which the temp. is $<$ that of the vapour, and the energy transferred to the surface by the vapour mols. is measured. For H_2O at 10° , the evaporation coeff. is 0.036, the accommodation coeff. 1.0, indicating that, while only a small fraction of the vapour mols. enters the

liquid, all of them reach temp. equilibrium with the surface before re-evaporating into the vapour.

L. L. B.

Theory and laws of vaporisation. A. MISSENARD (Chaleur et Ind., 1934, 15, 129—141; Chem. Zentr., 1934, ii, 3601).—A discussion of the relation between vaporisation and convection.

H. J. E.

Density of water from various sources and isotopic ratio in hydrogen. J. N. RAKSHIT (J. Physical Chem., 1935, 39, 303).—It is suggested that the possible influence of the polymerisation of H_2O should be considered in the determination of the isotopic ratio of H_2 from very accurate d measurements of H_2O .

M. S. B.

Vapour pressure of neon at liquid hydrogen temperatures. W. H. KEESOM and J. HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 376).—The v.p. of Ne at 15—20.4° abs. is given by $\log_{10} p(\text{cm.}) = -111.76/T + 6.0424$, and agrees with vals. calc. by the theory for a monat. substance, with a heat of vaporisation at 0° abs. of 445.9 g.-cal. per mol.

R. S. B.

Vapour-pressure curve of formaldehyde, and related data. R. SPENCE and W. WILD (J.C.S., 1935, 506—509; cf. this vol., 608).—The v.-p. curve for CH_2O has been traced from the m.p. (−118°) to the b.p. (−19.2°). The heat of vaporisation = $6545 + 3.480T - 0.02885T^2$. Trouton's const. = 21.9 entropy units. CH_2O is a normal liquid. Polymerisation occurs only at a solid surface, and the polymeride is so insol. in the liquid that the v.p. of the latter is unaffected.

F. L. U.

Elementary derivation of the statistical fundamental formulæ of chemical thermodynamics. G. SCHUBIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 301—304).—Theoretical. Statistical-mechanical distribution formulæ have been derived for classical, Bose-Einstein, and Fermi-Dirac statistics.

R. S. B.

Boyle's law in the new theory of the equation of state. V. JACYNA, S. DEREVIJANKIN, A. OBNORSKI, and T. PARFENTJEV (Z. Physik, 1935, 94, 224—228).

A. B. D. C.

Foundation of thermodynamics. F. VON KRBEK (Z. Physik, 1935, 94, 204—210).—Theoretical. The equation of state for ideal gases is considered.

A. B. D. C.

Equation of state of real gases. W. FRITZ (Physikal. Z., 1935, 36, 217—220).—The thermodynamic bases of the Honigmann equation of state (A., 1931, 31), and of the adiabatic equations, $pv^n = \text{const.}$ and $Tp^{-(n-1)/n} = \text{const.}$, are examined, and it is shown that these equations contradict certain important thermodynamic requirements.

A. J. M.

Definition of the Gibbs potential. J. N. BRONSTED (J. Chem. Physics, 1935, 3, 223).—Explanation of an earlier reference to Gillespie and Coe's work on the physical interpretation of the chemical potential (cf. A., 1933, 217).

M. S. B.

Nernst's heat theorem. V. NJEGOVAN (Z. Physik, 1935, 94, 377—385).—Inadequacies of the third heat theorem can be overcome by choosing consts. suited to the phenomena involved.

A. B. D. C.

Calculation of physical properties of the rare gases from the Clausius virial. E. BRANDER (Soc. Sci. fenn., Comment. phys.-math., 1934, 7, No. 14, 9 pp.; Chem. Zentr., 1934, ii, 3601—3602).—Calc. vals. for b (in c.c.) are Ne 0.000930, A 0.00253, Kr 0.00341, Xe 0.00486. The at. radii are 1.25—1.27, 1.63—1.77, 1.86—1.96, and 2.13—2.20 ($\times 10^{-8}$ cm., respectively).

H. J. E.

Critical temperature of heavy water. E. H. RIESENFELD and T. L. CHANG (Z. physikal. Chem., 1935, B, 28, 408—409).—The crit. temp. of D_2O is 371.5°.

R. C.

Effect of temperature on the thermal conductivity and the accommodation coefficient of hydrogen. H. S. GREGORY (Proc. Roy. Soc., 1935, A, 149, 35—56).—Using a modification of the hot-wire method, in which the influence of convection and the temp. fall effect are eliminated in one operation, vals. have been obtained of the thermal conductivity K of H_2 , varying from 459×10^6 to 708×10^6 g.-cal. $\text{cm.}^{-1} \text{sec.}^{-1} \text{deg.}^{-1}$ at 295.1° and 593.4° abs., respectively, and of the accommodation coeff. f for the H_2 -Pt phase. The variation of K with temp. is given by $K_T = AT^n$. f has a min. val. of 0.21 at 520° abs. and is independent of pressure over the range considered.

L. L. B.

Thermal conductivity of deuterium. A. B. VAN CLEAVE and O. MAASS (Canad. J. Res., 1935, 12, 372—376).—The relative thermal conductivities of D_2 and of D_2 - H_2 mixtures, as measured by the hot-wire method, agree with the conclusion that D_2 has the same mol. diameter as H_2 (cf. this vol., 432). It follows that the mol. heats are the same.

J. W. S.

Thermal conductivity of polyatomic gases. A. R. UBBELOHDE (J. Chem. Physics, 1935, 3, 219—223).—It is shown that the thermal conductivity of polyat. gases may vary with pressure. A comparison between experimental and calc. data relating to heat transport suggests that a portion of the sp. heat at 0° has, probably, a relaxation const. considerably $< 10^6$ if discrepancies are due to restrictions on the energy exchange between mols. For such cases measurements of heat conductivity between parallel plates are probably preferable to the use of a vertical wire.

M. S. B.

Thermal conductivity and accommodation coefficient of carbon dioxide. C. T. ARCHER (Phil. Mag., 1935, [vii], 19, 901—918).—Contrary to Ibbs and Wakeman (A., 1932, 216), the thermal conductivity of CO_2 increases continuously from 3.47×10^{-5} g.-cal. at 0° to 8.94×10^{-5} at 318.8° according to $K_T = CT^{1.216}$. Vals. of the accommodation coeff. from 0.51 at 24.2° to 0.28 at 331.8° are given.

R. S.

Change of thermal conductivity of non-polar gases, of liquids, and solids owing to an electric field. G. GROETZINGER and R. FREY (Physikal. Z., 1935, 36, 292—297).—The hot-wire method of Schleiermacher was used to find the thermal conductivity (I) of air in an electric field. There was no effect up to a field strength of 120,000 volts per cm., but above this there was a rapid cooling of the wire due to ionisation. This is contrary to the results of

Senftleben (A., 1932, 328; see following abstract). The addition of small quantities of polar gases causes variation of (I) with weak fields. Liquids such as paraffin and petroleum, which do not show electrolytic conduction (II), give a considerable increase in (I) on application of a field. For solids not showing (II) (BzOH, paraffin wax, S, and colophony) the application of a field does not affect (I), but for solids showing (II), *e.g.*, $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, there is a fall in the temp. of the wire even with weak fields. A. J. M.

Change of thermal conductivity of non-polar gases, of liquids and solids owing to an electric field. H. SENFTLEBEN (Physikal. Z., 1935, 36, 297—298).—As the apparatus in earlier experiments (A., 1932, 328) was arranged differently from that of Grotzinger and Frey (preceding abstract), it is considered that the results are not at variance. A. J. M.

Heat-conductivity of simple cubical crystals. M. BLACKMAN (Phil. Mag., 1935, [vii], 19, 989—998).—The theory of Peierls (A., 1930, 282) is discussed. R. S.

Effect of cold-working on thermal conductivity. G. TANMANN and W. BOEHME (Ann. Physik, 1935, [v], 22, 500—506).—The % decrease of thermal conductivity (I) produced by cold-working of Fe, Ni, Cu, and Ag is equal to the % decrease of electrical conductivity due to the same cause. Both properties recover from the cold-working effect in the same temp. range. For the alloys 77% Ag—23% Zn and 72% Cu—28% Zn (II), the curve shows two recovery intervals, that at higher temp. being due to Ag or Cu, and at lower temp. to Zn. Plates were heated electrically at a point, and the diameters of the rings produced were measured. These diameters, measured parallel and perpendicular to the direction of rolling, were identical within the limits of experimental error. For (II) there were, however, differences in (I) of about 5%. A. J. M.

Comparison of viscosity data. F. T. MILES (J. Amer. Chem. Soc., 1935, 57, 698—699).—The correlation of the ratio η at m.p. to η at b.p. with mol. symmetry (cf. A., 1934, 1165) is due largely to the dependence of m.p. on mol. symmetry. E. S. H.

Theory of structure viscosity. I. W. PHILIPPOFF (Kolloid-Z., 1935, 71, 1—16).—The relation $\eta' = \eta_\infty + \eta_0 - \eta_\infty / (1 + P^2/\gamma^2)$ is confirmed, mainly by the analysis of published work. Methods of determining the consts. have been worked out. E. S. H.

Diffusion of gases. W. ROTH (Arch. Eisenhüttenw., 1934—1935, 8, 401—403).—Mathematical. Equations are given for calculating the diffusion of various common gases into one another and the effect thereon of temp., pressure, d , and mol. wt. Various diffusion coeff. are tabulated and some practical examples of their use are given. A. R. P.

Mutual diffusion of gases at high pressures. B. KRIES and N. SELJAKOV (Z. Physik, 1935, 94, 134—138).—Theoretical. Numerical examples are given for CO_2 and air. A. B. D. C.

Diffusion of hydrogen in palladium. B. DUHM (Z. Physik, 1935, 94, 434—456).—Diffusion measure-

ments afford evidence of true dissolution under certain conditions, and vals. for the diffusion coeff. and mobility are recorded. The ratio of these gives the effective proton charge in Pd as a fraction of the elementary charge. A. B. D. C.

Diffusion of hydrogen through aluminium. C. J. SMITHELLS and C. E. RANSLEY (Nature, 1935, 135, 548).—H₂ diffuses through Al at a rate which is easily measurable above 400°. The rate is given by $D = k\sqrt{P} \cdot e^{-b/T}$, where b is approx. 14,000. At 400—600°, the rate of diffusion is of the same order as that of H₂ through Cu, but the temp. coeff. is greater. L. S. T.

Diffusion of non-metallic elements in iron and steel. I. Diffusion of sulphur in iron and steel. II. Diffusion of oxygen in iron. A. BRAMLEY and F. W. HAYWOOD. III. Diffusion of phosphorus in iron and steel. A. BRAMLEY and A. T. COOPER. IV. Nitriding of iron and steel. A. BRAMLEY and J. T. WATTS (Trans. Faraday Soc., 1935, 31, 707—713, 713—717, 717—726, 726—734; cf. B., 1932, 386).—I. The rate of diffusion (D) of S in Fe is in accordance with Fick's law. In steel, the D of S and C are lowered by the presence of the other element.

II. The D of O in Fe is approx. 0.005 of that of C at the same temp. The presence of dissolved FeO lowers the D of C, but to a smaller extent than does S.

III. The abnormal shape of the [P]—depth curve obtained when P diffuses into Fe and steel may be due to an allotropic change in the metal. This explanation is supported by Haughton's Fe—P equilibrium diagram. The D of P in Fe < 0.01 of that of C, and is lowered further by addition of C. High P content has little influence on the D of C.

IV. Fe and steel are nitrided by heating at 850—1100° in N₂ containing NH₃ to an extent depending on the amount of O₂ in the gas or dissolved oxide in the metal. The max. effect is obtained when the nitriding atm. contains 2% of O₂. The presence on the surface of the slightest trace of crystals of Fe oxide completely inhibits nitriding in an atm. of NH₃. The D of the N increases with [dissolved oxide]. F. L. U.

Mixed crystal formation and lattice constants for silver-copper alloys. P. WIEST (Z. Physik, 1935, 94, 176—183).—The solubility of Ag at 600° is 0.6% greater for single than for mixed crystals; the difference increases with fall of temp. A. B. D. C.

Metals and alloys. XIII. Constitution of lithium-cadmium alloys. E. ZINTL and A. SCHNEIDER. XIV. Constitution of lithium-bismuth alloys. E. ZINTL and G. BRAUER (Z. Elektrochem., 1935, 41, 294—297, 297—303).—XIII. X-Ray analysis indicates the existence of four different crystal types in the system Li—Cd. This confirms the observations of Grube *et al.* (A., 1933, 18) by other methods. The β -phase is stable at higher temp. only, and probably has a cubic symmetry. It is formed from the β' -phase, which has a homogeneity region close to LiCd₃ and hexagonal structure, a 3.083 Å., c 4.889 Å., with 2 atoms per cell and statistical at. distribution.

The mixture phase between β and α , or Cd saturated with Li, shows two types of hexagonal packing with axial ratios, one > 1.8 and the other approx. 1.63, which is the ideal val. for closest packing. The γ -phase, LiCd , has a space-centred structure of the NaTi type, a 6.687 Å., and the γ' -phase, Li_3Cd , has a face-centred cubic lattice, a 4.250 Å., and statistical at. distribution.

XIV. X-Ray analysis gives results in agreement with those of Grube *et al.* (A., 1934, 724). Two stable forms are observed at room temp., α - LiBi , tetragonal space-centred, a 3.361, c 4.247 Å., and Li_3Bi , cubic, a 6.708 Å., 16 atoms in the cell. M. S. B.

Hardness study of transformations in gold-copper alloys. H. H. ASHER (J. Dental Res., 1934, 14, 349—358).—The Cu-Au system is an unbroken series of solid solutions with 1 major and 2 minor lattice changes, which are affected by heat-treatment.

CH. ABS. (e)

Widmannstätten structure. VII. Copper-silver system. C. S. BARRETT, H. F. KAISER, and R. F. MEHL (Amer. Inst. Min. Met. Eng., Inst. Metals Div., 1935, Tech. Pub. 595, 19 pp.).—A Widmannstätten figure (I) may be formed in Cu-rich Cu-Ag alloys (II) by extremely slow cooling. The Ag-rich ppt. occurs as plates parallel to $\{100\}$ planes of the Cu-rich matrix. The ppt. in Ag-rich (II) is usually a pearlite-like arrangement of irregular plates. By extremely slow cooling a (I) may be developed in which the Cu-rich ppt. forms plates parallel to the $\{111\}$ planes of the matrix. The mechanism of formation of (I) is discussed.

CH. ABS. (e)

Texture of rolled α -brass. V. I. IVERONOVA and G. S. ZHDANOV (Tech. Physics U.S.S.R., 1934, 1, 64—79; J. Tech. Phys. U.S.S.R., 1934, 5, 911—924).—The X-ray structure of brass is a function of the Zn content, the stable configuration starting at 10% Zn. The Zn changes the orientations of the (111) and (100) axes, but not the (112) axis.

CH. ABS. (e)

X-Ray investigations on α -tin bronzes. T. ISAWA and I. OBINATA (Mem. Ryojun Coll. Eng., Inouye Com. Vol., 1934, 235—242).—The solubility of Sn in Cu increases from 13.9% at $< 400^\circ$ to a max. of 15.9% at the eutectoid temp. (T) (530°) and then decreases to 14.45% at 750° . Tempering of the saturated solid solution quenched from T results in a slow separation of the excess of Sn accompanied by lattice distortion.

A. R. P.

Transformations in iron-aluminium alloys. C. SYKES and H. EVANS (Iron and Steel Inst., May, 1935. Advance copy, 23 pp.).—When alloys of Al and Fe near to Fe_3Al are slowly cooled, the lattice structure changes from a disordered to an ordered type with the evolution of heat beginning at 560° and extending over a wide temp. range, probably down to -200 — 250° ; the crit. temp. determined by the thermal method has been confirmed by resistivity measurements on samples quenched from various temp. Magnetic curves for Fe_3Al slowly cooled from 600° show a sharp max. at about 540° , but this is absent from heating curves. The magnetic transformation curve for ordered alloys with 13—17% Al is below that for disordered alloys, the transformation of the 14% Al

alloy occurring at 560° in the disordered and at 490° in the ordered state.

A. R. P.

Eutectoid transformation of the aluminium-zinc system. H. IMAI and M. HAGIYA (Mem. Ryojun Coll. Eng., Inouye Comm. Vol., 1934, 83—105).—The $\beta \rightarrow \alpha + \gamma$ transformation in the 21% Al alloy takes place at 270° ; after quenching from higher temp. a spontaneous heat evolution occurs, the temp. rising by 50° in 3.5 min., accompanied by a contraction which is very rapid during the first min. The resistance (R) rises rapidly for 2.5 min. after quenching, then slowly for another min., and finally decreases slowly. Max. hardness (H) is reached 13 min. after quenching, and after 15 min. a second evolution of heat occurs with a slight contraction in vol., a slight increase in R , and an abrupt decrease of H . Min. H is obtained in 1 hr. at 100° and normal R by storage for 1 month at room temp. or by slowly heating to 150° . These results indicate that the decomp. of β proceeds in 3 stages, $\beta \rightarrow \beta'$ occurring rapidly and $\beta' \rightarrow \alpha + \gamma$ slowly at room temp., whilst $\beta'' \rightarrow \alpha + \gamma$ occurs only on tempering at just below the eutectoid temp.

A. R. P.

Hall effect and other physical constants of alloys. IV. Bismuth-cadmium series. S. GABE and E. J. EVANS (Phil. Mag., 1935, [vii], 19, 773—787; cf. A., 1934, 137).—Property-composition diagrams are given for sp. resistance, temp. coeff. of resistance, thermoelectric power, Hall coeff., density, and sp. heat. The curves for the two last are linear, and all are continuous. Properties involving the passage of electric current show rapid variations at the Bi end, but there is no definite evidence of the existence in this region of a solid solution.

F. L. U.

Solidification diagrams of alloys formed by two alkali metals: potassium-rubidium alloys. E. RINCK (Compt. rend., 1935, 200, 1205—1206; cf. A., 1933, 771; this vol., 22).—K and Rb form a complete range of mixed crystals. The liquidus and solidus curves are very close and show a min. at $\text{K} + 2\text{Rb}$.

J. W. S.

Solid solubility of silicon in aluminium. S. KISHINO (J. Chem. Soc. Japan., 1934, 55, 1134—1139; cf. B., 1934, 1106).—Structural changes in Al-Si alloys quenched at various temp. have been studied by measurements of electrical resistance. Al dissolves 0.70% of Si at 502° and 1.19% at 545° to form a solid solution.

CH. ABS. (e)

Eutectoid iron-cementite diagram. J. SEIGLE (Bull. Assoc. tech. Fond., 1934, 8, 289—296; Chem. Zentr., 1934, ii, 3668).—Modifications of the equilibrium diagram are suggested. Progressive dissolution of Fe_3C occurs with rising temp.

H. J. E.

Diagrams for physico-chemical analysis of binary liquid systems. M. USANOVITSCH (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 378—385).—Mathematical.

W. R. A.

Viscosity of aqueous solutions. II. Mixed solutions of carbamide and urethane. A. BANCHETTI (Gazzetta, 1935, 65, 159—167; cf. A., 1934, 723).—Vals. of d and n are recorded for aq. solutions of carbamide, urethane, and their mixtures (I). Vals. for (I) follow the mixture rule.

O. J. W.

Viscosity and density of pure alkaline solutions and their mixtures. L. B. HITCHCOCK and J. S. McILHENNY (Ind. Eng. Chem., 1935, 27, 461—466).— η and d for solutions of NaOH, Na₂CO₃, KOH, K₂CO₃, and of mixtures of the first and last two have been determined at 20°, 30°, and 40° for concns. up to 8*N*, the Ostwald-Fenske viscosimeter being used. For the mixtures η shows a deviation of -10% from that given by the additive rule. C. I.

Vapour pressure of phosphoric acid solutions. I. A. KABLUKOV and K. I. ZAGVOZDKIN (Trans. Sci. Inst. Fertilisers U.S.S.R., 1933, No. 110, 4—11).—Data for aq. H₃PO₄ (5.67—87.11%) at 25°, 40°, 60°, and 80° are recorded. CH. ABS. (e)

Vapour pressures of aqueous solutions. L. FRANK (Z. Physik, 1935, 94, 408—410).—Duhring's rule is used to calculate the v.p. of conc. solutions of NaCl, KCl, CaCl₂, KBr, MgSO₄, CuSO₄, KI, ZnSO₄, LiCl, and sucrose. A. B. D. C.

Mixtures of deuterium and protium oxides as ideal solutions. W. F. K. WYNNE-JONES (J. Chem. Physics, 1935, 3, 197).—Determination of the composition of the vapour for mixtures of H₂O and D₂O of known composition shows that such mixtures can be regarded as ideal solutions. N. M. B.

Association and molecular polarisation. C. HENNINGS (Z. physikal. Chem., 1935, B, 28, 267—289).—The orientation polarisation curves of several aliphatic alcohols in C₆H₆ and C₆H₁₄ solutions of molar fractions 0.01—1 have been determined at 7° and 30°. With increasing concn. each curve in general passes through a min., then through a max. The effect of rise of temp. on the form of the curves is due principally to de-association; the decrease in orientation due to increasing vigour of the mol. motions plays only a subsidiary part. C₆H₆ has a more powerful de-associating action than C₆H₁₄, but this action is less pronounced towards complexes with a finite dipole moment than towards those with zero moment. With increasing chain length the alkyl group in the single mol. becomes more and more mobile, and is thus able to protect the OH group against association. Steric hindrance also opposes association. The rise in d of the solute with increasing concn. is most rapid when association to dipole-free double mols. is occurring, but continues during association to larger complexes. F.-p. measurements show rapid increase in mol. wt. with concn. The dipole moments of Pr^sOH and BuⁿOH are 1.63±0.02 and 1.55±0.02×10⁻¹⁸ e.s.u., respectively. R. C.

Optical investigation of system aldehyde-alcohol in indifferent solvents. O. GRABOWSKY and W. HEROLD (Z. physikal. Chem., 1935, B, 28, 290—302; cf. A., 1933, 1036).—Absorption measurements have been made. The reaction of EtOH with CCl₃CHO is the slower the more polar and polarisable is the solvent. With straight-chain alcohols the change from a non-polar to a polar solvent increases the shielding and saturation of the OH groups < for branched-chain alcohols. At 0° an association product of alcohol and semi-acetal in equimol. proportions seems to exist. This must lower the equilibrium aldehyde concn., but is unstable at higher

temp. For reaction of EtCHO in Et₂O solution the shielding of the OH of the alcohol influences both the reactivity and the shift of the absorption max. of the EtCHO caused by the alcohol similarly, whereas in C₆H₁₄ solution it affects the reactivity > the absorption shift. R. C.

Molar polarisations in extremely dilute solutions. Dipole moments of *d*-limonene, *d*-pinene, methyl benzoate, and ethyl benzoate. W. J. SVIRBELEY, J. E. ABLARD, and J. C. WARNER (J. Amer. Chem. Soc., 1935, 57, 652—655).—Dielectric consts. and d of C₆H₆ solutions of the above substances have been determined. E. S. H.

Multivalent amino-acids and peptides. III. Dielectric constants and electrostriction of the solvent in solutions of tetrapoles. J. P. GREENSTEIN, J. WYMAN, jun., and E. J. CORN (J. Amer. Chem. Soc., 1935, 57, 637—642; cf. A., 1934, 475).—Mols. having two NH₃⁺ and two CO₂⁻ groups in the isoelectric condition have been studied. Diaminodithiodihexanoic acid is composed of two mols. of ϵ -amino-hexanoic acid combined at the α -C atoms by S. Electrostatic attraction causes the chains to twist, and results in a relatively small effect on the dielectric consts. of solutions and on electrostriction of the solvent. Lysylglutamic acid is composed of a small dipole, glycylglycine, and a longer one between the ϵ -NH₂ of lysine and the γ -CO₂H of glutamic acid. Electrostatic repulsion results in a rod-shaped mol. in which the charged groups are widely separated, and the influences on increase of the dielectric const. of the solution and on the electrostriction of the solvent are maximal. E. S. H.

Relation between the structure of hydrocarbons and their miscibility with selective solvents. S. P. MULLIKEN and R. L. WAKEMAN (Rec. trav. chim., 1935, 54, 366—372).—Miscibility of hydrocarbons has been studied with nitromethane (a) and less fully with Et₂SO₄ and NH₂Ph (b) and CH₃Ph-OH (c). (a) For liquid hydrocarbons with an equal no. of C atoms the more saturated is the less miscible. Alkanes, cycloalkanes, dicycloalkanes, alkenes, cycloalkenes, and alkadienes with > 8 C are miscible at 20°. Alkines with C:C near the end of the chain are more sol. than alkadienes of the same mol. wt., and the temp. (*T*), at which demixing first appears on cooling a homogeneous mixture, rises as C:C moves to the centre of the mol. Aromatic hydrocarbons are more sol. than other types of the same mol. wt.; all are sol. below 55° and the lower ones below 20°. With solids, aromatic are more sol. than non-aromatic hydrocarbons of the same mol. wt. (b) Miscibility increases with unsaturation. $T_b < T_a$ and *T* for alkadienes and alkines is < for alkenes of the same mol. wt. (c) Alkanes are immiscible at temp. at which cycloalkanes of the same mol. wt. are miscible. An unknown non-acetylenic hydrocarbon can be tested for aromatic character by its miscibility (a) at 20° for b.p. 110—220°, and at 55° for b.p. 220—300°, aromatic compounds being miscible. With an unsaturated non-aromatic acyclic hydrocarbon the presence of C:C or of a higher degree of unsaturation can be shown by the miscibility with NH₂Ph, the temp. depending on the b.p. Whether a

saturated non-aromatic hydrocarbon is cyclic or acyclic can be tested with $\text{CH}_2\text{Ph}\cdot\text{OH}$ at 50° , cyclic compounds being miscible. R. S. B.

Diffusion of volatile materials into an inert gas stream. E. PRESTON (Trans. Faraday Soc., 1935, 31, 776—785; cf. A., 1933, 1242).—Further evidence is advanced for the view that evaporation proceeds from a "super surface" layer in equilibrium with the liquid phase in accordance with the Herz-Knudsen equation, and that its removal is governed by gaseous diffusion into the surrounding atm.

F. L. U.

Equilibrium for gaseous and liquid phases of oxygen-nitrogen mixtures. O. N. TRAPEZNIKOVA and L. V. SHUBNIKOV (J. Tech. Phys. U.S.S.R., 1934, 5, 949—953).—Data in presence and absence of a magnetic field are recorded. CH. ABS. (e)

Vapour pressure of the binary systems acetaldehyde-water and -acetic acid. N. M. MOROZOV, M. J. KAGAN, and E. S. GROSELT (J. Gen. Chem. Russ., 1934, 4, 1322—1326).—The v.p.-composition curves at 10° and 20° have been determined. R. T.

Ethyl alcohol-halogen compound azeotropic couples under normal pressure. M. LECAT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 43—47).—The formula for the azeotropic lowering (cf. A., 1927, 405) is shown to be in agreement with further experimental results. R. S.

Heterogeneous binary systems. Physical properties of systems of two liquid phases. III. H. SCHLEGEL (J. Chim. phys., 1935, 32, 215—234).—V.p., b.p., condensation, sp. heat, mutual solubility, electrical conductivity, and heat of mixing data have been obtained for the system $\text{NH}_3\text{Ph-cyclohexane}$. D. R. D.

Complex compounds of silver halides with halides and silver salts. S. V. GORBATSCHEV (J. Gen. Chem. Russ., 1934, 4, 1327—1337).—The solubility of AgX in aq. NaX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) and aq. AgNO_3 has been determined; the differences between the vals. found and those calc. suggest formation of complex salts, the nature of which is discussed. R. T.

Molecular solubility of one-third basic aluminium acetate. C. ROHMANN (Pharm. Ztg., 1935, 80, 493—495).—A review of published data supports the author's views (A., 1933, 569) rather than the theory that so-called basic Al acetate solutions are sols of $\text{Al}(\text{OH})_3$ peptised by AcOH . D. R. D.

Solubilities of some strychnine benzoates. C. F. POE, J. F. SUCHY, and G. L. BAKER (J. Physical Chem., 1935, 39, 239—241).—The solubilities of 27 salts of BzOH and substituted BzOH have been determined at 20 — 95° . M. S. B.

Solubilities of certain amino-acids and related compounds in water, densities of their solutions at 25° , and calculated heats of solution and partial molar volumes. II. J. B. DALTON and C. L. A. SCHMIDT (J. Biol. Chem., 1935, 109, 241—248).—Solubility data are recorded for *L*-asparagine, *L*-cystine, *a*-isoleucine, *dl*-methionine, *L*-phenylalanine, *dl*-serine, taurine, and *L*-tryptophan. Heats of dissolution and

mol. vols. are calc. and it is suggested that *dl*-isoleucine and *dl*-phenylalanine are *r*-compounds. H. T.

Effect of polarity on the solubilities of some organic acids. P. G. DESAI and A. M. PATEL (J. Indian Chem. Soc., 1935, 12, 131—136).—The solubilities of BzOH (I), $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (II), $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (III), $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (IV), and $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (V), which stand in increasing order of polarity, have been determined in 14 solvents of varying polarity. In slightly polar solvents the solubilities decrease with increasing polarity of the solute, the solubilities of (IV) and (V) being negligible. Solubility increases with polarity in the aromatic hydrocarbons, C_6H_{12} , and CCl_4 , but the order is not well defined for more polar substances. CHCl_3 behaves abnormally with all solutes, and COMe , and Bu^nOH are abnormal in some cases. (I), (II), and (III) probably form easily dissociable solvates with alcohols, whilst (IV) and (V) form hydrates with H_2O . M. S. B.

Physical chemistry of amino-acids, peptides, and related substances. III. Solubility of derivatives of the amino-acids in alcohol-water mixtures. T. L. McMEEKIN, E. J. COHN, and J. H. WEARE (J. Amer. Chem. Soc., 1935, 57, 626—633; cf. this vol., 26).—A study of certain derivatives of NH_2 -acids which are not zwitterions shows that the m.p. are $<$, and the apparent mol. vols. $>$, those of the NH_2 -acids. The ratio of the solubility in EtOH to that in H_2O is increased approx. 3-fold for each terminal CH_2 in the mol. A CH_2 placed between strongly polar groups does not appreciably affect the solubility ratio. The solubility of NH_2 -acids in $\text{EtOH-H}_2\text{O}$ mixtures varies in the same way as salts, whereas the solubility of the derivatives varies as other uncharged org. mols. E. S. H.

Distribution of saturated monobasic aliphatic acids between water and *o*-nitrotoluene. N. A. DE KOLOSOVSKI and F. S. KULIKOV (J. Gen. Chem. Russ., 1934, 4, 1370—1377).—Data are given for HCO_2H , AcOH , EtCO_2H , PrCO_2H , $\text{Bu}^n\text{CO}_2\text{H}$, $\text{CH}_3\text{Cl}\cdot\text{CO}_2\text{H}$, $\text{CHCl}_2\cdot\text{CO}_2\text{H}$, and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ at 25° . R. T.

Partition of tri- and tetra-methylglucoses between chloroform and water. J. Y. MACDONALD (J. Amer. Chem. Soc., 1935, 57, 771—772).—Partition coeffs. between H_2O and CHCl_3 are recorded for di- (I) and tri-methylmethylglucosides (II), tri- and tetra-methylglucose. Results obtained for the separation of (I) and (II) by partition confirm Irvine's conclusions relative to the methylation of sucrose. R. S. C.

Partition coefficient of acetone between neutral glycerides or their fatty acids and water. Influence of the alcoholic function of ricinoleic acid. A. LINDENBERG (Compt. rend. Soc. Biol., 1935, 118, 1086—1087).—The partition coeffs. are all approx. = 0.2 except for castor oil, triricinolein, and ricinoleic acid, when the vals. are 0.25—0.30, 0.35—0.40, and 0.35—0.38, respectively. In this respect COMe , resembles EtOH and MeOH . F. O. H.

Partition coefficient between oil and water of substances completely miscible in the two solvents. I. Methyl alcohol and acetic acid in

the system castor oil-water. II. Methyl alcohol, ethyl alcohol, and acetic acid in the system triricinolein-water. A. LINDENBERG (Compt. rend. Soc. Biol., 1935, 118, 441—444, 444—445).—I. Although MeOH and AcOH are miscible in all proportions with castor oil (I) and H_2O , their partition coeffs. in a (I)— H_2O system are different, being 0.12 and 0.2—0.24.

II. The partition coeffs. of MeOH, EtOH, and AcOH for the system triricinolein— H_2O are the same, viz., 0.23 at 20°.

A. L.

Physical chemistry of amino-acids, peptides, and related substances. IV. Distribution coefficients of amino-acids between water and butyl alcohol. A. ENGLAND, jun., and E. J. COHN (J. Amer. Chem. Soc., 1935, 57, 634—637; cf. this vol., 695).—Distribution coeffs. have been determined at 25°. As the length of the hydrocarbon chain increases the concn. in the aq. phase is less and that in the BuOH phase greater. NH_2 -acids with branched chains behave like smaller mols. BuOH and NH_2 -acids reciprocally diminish the solubility of the other in H_2O .

E. S. H.

Gas adsorption and Nernst's heat law. M. TEMKIN (Acta Physicochim. U.R.S.S., 1934, 1, 36—52).—On the basis of Langmuir's conception of adsorption, the adsorption equation is deduced thermodynamically. The adsorption equilibrium is determined by the vals. of the heat of reaction, the mol. heat, and the chemical const. The application of Nernst's approximation formula to the determination of the velocity of evaporation of O atoms from a W surface, the oxidation velocity of W, the velocity of evaporation of Th from a W surface, the time required for the adsorption of A on glass, and the evaluation of the heat of adsorption, gives vals. in good agreement with the results of experiment. The possibility of determining the true heat of activation in heterogeneous catalysis, and hence the equilibrium requirements and the mechanism of reaction, is discussed.

M. S. B.

Heterogeneous catalysis. I. Activated adsorption of hydrogen on carbon. E. STORFER (Z. Elektrochem., 1935, 41, 198—204).—The adsorption of H_2 on active C containing 1% of Ni has been measured at 155° and 206° and at pressures < 8 mm. Hg. Energies of activation are calc.

F. L. U.

State of the sorbed phase. I. Sorption velocity measurements with methane, ethane, and propane on activated carbon. E. BERL and E. WEINGAERTNER (Z. physikal. Chem., 1935, 173, 35—57).—Measurements have been made at 0—261° and 10^{-4} —1 cm. Above the crit. temp., T_c , in the linear region of the sorption Langmuir's velocity equation (I) is valid. Below T_c for C_2H_6 and C_3H_8 the velocity curves show that equilibrium is attained by at least two consecutive processes, for each of which (I) holds. These are taken to be sorption of the gas and two-dimensional condensation to liquid of the sorbed phase. The rate of establishment of equilibrium is a min. at T_c . Above T_c the variation of sorption velocity with temp. may be represented by an Arrhenius function, the energy of activation deduced from which, E , must be regarded as the energy barrier

between the sorption space and the extended phase when a mol. approaches the surface. For a given C, E is the same for all three gases, showing that sorption must occur at the Me group, i.e., the sorbed C_2H_6 and C_3H_8 mols. must have their axes perpendicular to the surface.

R. C.

Heats of adsorption of certain organic vapours on activated charcoal at 25° and 50°. J. N. PEARCE and G. H. REED (J. Physical Chem., 1935, 39, 293—301).—Heats of adsorption (I) of MeCl, Pr^iCl , BuⁿCl, Bu^sCl, and Bu^tCl on C have been measured at 25° and 50°, and of EtCl and Pr^iCl at 50°. The temp. coeff. is practically negligible. (I) increase with length of chain and for straight-chain compounds are > for branched. Total (I) for any vapour increase rectilinearly with the total amount adsorbed.

M. S. B.

Sorption of halogens by silica gel and charcoal. L. H. REYERSON and A. E. CAMERON (J. Physical Chem., 1935, 39, 181—190; cf. following abstract).—On coconut C the rate of sorption of Br and I is < on SiO_2 gel and it is impossible to remove all the Br by desorption. The type of isotherm obtained is quite different from those for SiO_2 ; it indicates the formation of a unimol. layer of adsorbed mols. followed at higher pressures by diffusion into the C.

M. S. B.

Sorption of bromine and iodine by silica gel. A. E. CAMERON and L. H. REYERSON (J. Physical Chem., 1935, 39, 169—179).—The sorption of Br by SiO_2 gel at 58°, 79°, 117.5°, and 137.7°, and that of I at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5° has been determined using a McBain and Bakr sorption balance with a quartz spiral manometer. Adsorption and desorption are completely reversible. The curves for Br at higher temp. are practically linear; the rest are convex towards the pressure axis, indicating weak binding forces and physical adsorption. The adsorption of Br is much > that of I. The data do not fit the classical adsorption isotherm.

M. S. B.

Adsorption from solution. III. Adsorption of picric acid by silica gel. L. S. TS'AI and T. S. LO (J. Chinese Chem. Soc., 1935, 3, 16—21).—The adsorption of picric acid from aq. solution by SiO_2 gel at 25° follows the Langmuir equation and is mainly a continuous process. The results may be explained by the presence of a H_2O envelope on the surface of the SiO_2 .

J. W. S.

Density and adsorption studies in the region of the critical temperature: system dimethyl ether-alumina. J. EDWARDS and O. MAASS (Canad. J. Res., 1935, 12, 357—371; cf. A., 1933, 1241).—A method is described for the simultaneous measurement of d and the adsorption of liquids, vapours, and gases near the crit. temp. (T_c). The adsorption of liquid Me_2O on Al_2O_3 begins only at 124°, but increases with temp. to a max., beyond which it follows the form of a normal isobar. The discontinuities observed in the adsorption cannot be attributed to changes in the d of the adsorbed phase or to persistence of liquid in the pores of the Al_2O_3 above T_c , and there is no evidence for the existence of a lag in T_c . As a d hysteresis is found up to 14° above T_c , the effects

are ascribed to the persistence of liquid-like structure in the gas. Irregularities in d are also observed below T_c . J. W. S.

Adsorption and hydrolysis of adsorbed glycogen. S. SIMONOVITS (Biochem. Z., 1935, 277, 72—76).—In their experiments with glycogen (I)—animal charcoal (II)—HCl and (I)—(II)—amylase, Bancroft and Fry (A., 1933, 457) overlook the fact that the product of hydrolysis of (I), viz., glucose (III), is itself adsorbed by (II). Adsorption of (I) by (II) is irreversible (difference from mechanical adsorption), and leads to no true equilibrium, and the adsorbed (I) is not eluted by AcOH, HCl, or (III). Hydrolysis of (I) at the (II) surface is complete. P. W. C.

Adsorption and ion exchange. A. H. W. ATEN, jun. (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 441—449).—Theoretical. Langmuir's formula is modified to allow for the influence of adsorbed mols. on the adsorption heat (E), which is given by $E = E_0 + ga$, where g is a const. and a is the amount adsorbed. The formula $a/p = k_1 a_{\max} e^{-a/a_{\max} + ga/RT}$ (I) is deduced (p =gas pressure, k_1 =const.) and is analogous to the formulæ of Schmidt, Williams, and Henry. (I) is applied to the exchange of ions in permutite, giving $\log x_A c_B / x_B c_A = k_2 x_A + k_3$ (II), where x_A and x_B are the amounts of exchangeable ions on the surface, and c_A and c_B are their aq. concns., k_2 and k_3 being const. The results of Rothmund and Kornfeld (A., 1918, ii, 315) agree with (II). R. S. B.

Sorption of basic dyes on Cellophane. N. ANDO (J. Chem. Soc. Japan, 1934, 55, 959—967).—The adsorption of methylene-blue by Cellophane follows Freundlich's equation. CH. ABS. (e)

Adsorption of optical sensitizers for silver salts. A. I. RABINOVITSCH, J. I. BOKINNIK, and T. B. RIDIGER (Kino-Photo Inst. Moscow, 1934, 2, 161—165).—A method is given for measuring the partition coeff. of the dyes between solution and AgBr. The adsorption is lowered by Br⁻. CH. ABS. (e)

Adsorption at crystal-solution interfaces. VII. Effect of stirring and growth rates on the habit and dye adsorption of alum crystals. Influence of acid and alkali media on the habit of alum crystals. (MISS) P. A. PAINE and W. G. FRANCE (J. Physical Chem., 1935, 39, 425—429).—Stirring causes a decrease in the size of the cube faces of K alum crystals grown from pure solutions or aq. Diamine Sky Blue of varying concn. From the same concn. of dye less colour is adsorbed by crystals from stirred than from unstirred solutions, or when prepared rapid cooling than by slow evaporation at room temp. An explanation based on rate of diffusion of ions is discussed. No appreciable change of habit occurs when alum crystals are grown from acid solutions or from solutions containing Na₂CO₃ from which Al(OH)₃ is not pptd. M. S. B.

Copper sulphide-water contact angles. C. C. WITT (J. Amer. Chem. Soc., 1935, 57, 775—776).—Contact angle is due to the presence of an adsorbed air film. E. S. H.

Surface friction and adsorption on metals. P. ERBINDER, N. KALINOVSKAJA, and H. MICHALLOVA

(Acta Physicochim. U.R.S.S., 1934, 1, 22—26).—Measurements have been made of the "lubricability," or diminution in the coeff. of friction, of Cu, alloys of Cu and Al, Al, Mg, and Sn by the pure media H₂O and vaseline oil, and by solutions in these of surface active materials such as p -C₆H₄Me·NH₂ (I) and NH₂Ph. (I) increases the coeff. of friction on Al and decreases it on Cu; it must therefore be oppositely oriented on the two surfaces. M. S. B.

Surface tension of homologous series. J. H. C. MERCKEL (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 387—393).—For solutions of straight-chain acids, esters, and alcohols σ varies linearly with c (mol. per litre) up to a definite concn., and in this range $\log \tan \theta$, where θ is the angle made by the σ - c line with the c axis, varies linearly with the no. (n) of C atoms in the series (n , 1—6). The plots of $\log \tan \theta$ against n are parallel for different types, and isomerides give identical points. At higher concns. for solutions of fixed concn. $\sigma = al^2 + bl + c$, where a , b , and c are const., and l =length of C chain. With Na salts of the fatty acids ($n=2$ —14), $\log \tan \theta$ is a quadratic function of n . Szyskowski's representation of capillary phenomena is criticised. R. S. B.

Investigation of adsorbed films by means of a photo-electric counter. C. OUELLET and E. K. RIDEAL (J. Chem. Physics, 1935, 3, 150—158).—A high-sensitivity tube counter of special design has been used to measure the changes in the work function ϕ of Au due to adsorbed layers. Accurate determinations of thresholds (T) can be made with continuous ultra-violet light of moderate intensity, and the quant. variation of ϕ with the amount of adsorbed material can be followed continuously. ϕ for strongly oxidised and strongly reduced Au differs by 1.58 volts; the oxidation shows two definite stages with respective increases in ϕ of 0.35 and 0.70 volt. The adsorption of I vapour is reversible and the resulting increase in ϕ varies with the I pressure according to a Langmuir isotherm, $\Delta\phi$ at saturation being +0.21 volt. The adsorption of EtOH on Au is reversible and gives rise to a double T consisting of the original Au T and a new T corresponding with a decrease of 0.49 volt in ϕ , this val. being independent of the EtOH pressure. The intensity of emission at the new T increases with the pressure, indicating that the EtOH is condensed as a two-dimensional liquid covering an area which increases with pressure. N. M. B.

Formation of multimolecular layers at the surface of separation between mercury and solution. A. FRUMKIN, A. GORODETZKAJA, and P. TSCHUGUNOV (Acta Physicochim. U.R.S.S., 1934, 1, 12—21).—Using the capillary electrometer it is shown that hexoic acid and PhOH are adsorbed as a multimol. layer at the surface of separation between Hg and aq. solution, contrary to the behaviour at a solution-air surface of separation. Since the thickening takes place without any abrupt change of potential, it is suggested that the hexoic acid layer must be ≤ 3 mols. thick, additions to the unimol. layer being made by double mols. in which the dipoles of the separate mols. counteract each other. M. S. B.

Surface pressures and potentials of unimolecular films of long molecules: polymerides of ω -hydroxydecoic acid. W. D. HARKINS, H. E. RIES, jun., and E. F. CARMAN (J. Amer. Chem. Soc., 1935, 57, 776—777).—The data show that the mols. lie flat on the surface, anchored by the polar groups at the ends and at every tenth C; they may have as many as 149 regions of attachment. E. S. H.

Surface potentials of aqueous solutions of octyl alcohol and octoic acid. I. SAWAI (Trans. Faraday Soc., 1935, 31, 765—769).—The surface potentials for both substances, measured by means of an air electrode coated with Po, increase with concn., and with decreasing p_H . The results are discussed. F. L. U.

Surface potentials of alkaloid solutions. B. KAMIENSKI (Bull. Acad. Polonaise, 1934, A, 391—393).—Aq. solution-air potentials ranging from 0 to 442 mv. have been observed with solutions of quinine, cinchonidine, cinchonine, strychnine, brucine, pilocarpine, atropine, amarine, morphine, codeine, veratrine, caffeine, and theobromine and their salts. J. G. A. G.

Electrokinetic properties of proteins. III. Role of electrical forces in the adsorption of gliadin at a glass-liquid interface. W. McK. MARTIN (J. Physical Chem., 1935, 39, 249—263).—A study of streaming potentials at a glass surface, in solutions of gliadin (I) of varying p_H , indicates that (I) is adsorbed from solutions in which it is positively charged, glass being always negative, but reversal of the charge of (I) to negative does not result in complete desorption. A highly purified solution of (I) is not chemically homogeneous, but contains within the isoelectric range both positively and negatively charged fractions. When (I) is adsorbed on glass free $\cdot\text{NH}_2$ and $\cdot\text{CO}_2\text{H}$ are turned towards the liquid phase; these react with acids and alkalis, respectively, within the p_H range 4.88—8.83. The true isoelectric range of a protein is probably identical with the " p_H stability region." M. S. B.

Linear phenomena. III. Linear adsorption and gelatinisation of lyophilic systems. D. TALMUD (Acta Physicochim. U.R.S.S., 1934, 1, 145—159).—The spontaneous formation of colloidal skins at the surface of solutions of half-colloids may be observed ultramicroscopically. It is suggested that this may be due to linear adsorption at the junction of the two phases of the solution with a third phase such as a gas at the surface or the wall of the containing vessel. The colloidal skin may be obtained artificially by the addition of insol. linear active materials, e.g., cetyl alcohol to saponin solutions. By repeatedly removing the skin, which may be regarded as due to two-dimensional gelatinisation, the whole solution may ultimately be gelatinised. A no. of phenomena, hitherto inexplicable, are probably due to linear adsorption. The connexion between linear adsorption and emulsification in the absence of emulsifiers, especially in solutions containing gases, is discussed. The application of linear adsorption to the stabilisation of foams has been demonstrated experimentally. M. S. B.

Theory of electrocapillarity. III. S. R. CRAXFORD, O. GATTY, and J. ST. L. PHILPOT (Phil. Mag., 1935, [vii], 19, 965—989; cf. A., 1934, 140).—The theory of electrocapillarity is considered in relation to a generalised mechanism in which only external work terms are involved, and a general equation derived which includes those of Lippmann and Gibbs as special cases. R. S.

New electrocapillary effect. N. BACH (Acta Physicochim. U.R.S.S., 1934, 1, 27—35).—When drops of Hg fall through a solution of a Hg^{I} salt and an indifferent electrolyte, such as KNO_3 , a current of electricity flows through the solution in the same direction as the current produced by electrokinetic effects and $>$ the latter. It is caused by the deformation of the Hg drops by the action of the induced surface charges. For a given concn. of Hg^{I} salt the current intensity increases with increasing total concn. of electrolyte; the electrokinetic current shows the contrary behaviour. By reducing the diameter of the Hg drops the electrocapillary effect is decreased, but it is improbable that the electrokinetic effect ever preponderates. M. S. B.

Role of evaporation in the phenomenon of imbibition by porous bodies. (Mlle.) P. BERTHIER (Compt. rend., 1935, 200, 1105—1107).—In an atm. saturated with H_2O vapour pure H_2O rises more rapidly than a solution in a strip of porous paper, the rate being least in the more viscous solutions, but in an atm. dried with CaCl_2 or other drying agent the rate of rise increases with concn. This behaviour is due to the greater rate of evaporation from the dil. solution in the porous support than from the conc. in a dry atm. M. S. B.

Electrokinetic potentials. I. Measurements at the interfaces between fibres and water. N. ANDÔ and A. ANDÔ (J. Chem. Soc. Japan, 1934, 55, 968—978).—Electrokinetic potentials of cotton, silk, and wool have been measured by the streaming-potential method. They are negative. CH. ABS. (e)

Factors influencing the cataphoresis of small particles in water. C. L. S. GILFORD (Phil. Mag., 1935, [vii], 19, 853—878).—The dependence of cataphoretic velocity (I) on the form of apparatus, temp., and the diameter, conductivity, and shape of particle has been examined. (I) vals. are given for graphite, sugar C, Sb, Sb_2S_3 , and MnO_2 in H_2O of different conductivities. The results are discussed in relation to current theories. R. S.

Electrophoresis of artificial calcium-carbamic acid complexes. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1329—1330).—Ca transport is cathodic in complexes derived from glycine, carbamide, or NH_3 , which are therefore not responsible for the anodic Ca transport in the electrophoresis of serum. R. N. C.

Electrodialysis of artificial systems of calcium chloride and alkali citrates. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1331—1333).—Addition of citrate to CaCl_2 solutions renders Ca transport anodic with small currents and cathodic with large

currents; Ca thus associates with citrates in such a system in a non-ionisable form. R. N. C.

Concentration changes at membranes and the electro-osmotic membrane potentials. J. J. BIKERMAN (J. Physical Chem., 1935, 39, 243—247).—From the theory of the diffuse double layer the concn. changes and potential differences at diaphragms through which an electro-osmotic current is driven have been derived and compared with experimental results. M. S. B.

"Diffusion effect" on ionic distribution. I. Theoretical considerations. T. TEORELL (Proc. Nat. Acad. Sci., 1935, 21, 152—161).—In an aq. system of strong electrolytes, characterised by a steady diffusion across an ion-permeable boundary (membrane), theoretical considerations predict (a) the possibility of development of concn. differences of "passive" ions ("diffusion effect" on ionic distribution), and (b) an approach to a steady state of the system as a whole, where the "passive" ions are in a true state of equilibrium. The "diffusion effect" appears when a concn. gradient is present and is due to differences in ionic mobility (relative impermeability), whereas the "Donnan effect" is caused by abs. impermeability of one or several ion species. Diffusion effects of the type discussed may be of biological importance. O. J. W.

Influence of the presence of a solute on the rate of osmosis. R. N. TRAXLER and H. N. HUNTZICKER (J. Physical Chem., 1935, 39, 431—435).—In the osmotic system C_5H_5N -rubber- H_2O , examined at 35°, the rate of osmosis of C_5H_5N into H_2O is retarded by solutes in either liquid, as shown by the effect of dissolving anthracene or $AgNO_3$ in C_5H_5N and sucrose or KCl in H_2O . Dissolved or dispersed rubber in C_5H_5N has also a marked retarding effect. M. S. B.

tert.-Butyl alcohol as a solvent for cryoscopic mol.-wt. determinations. G. S. PARKS, G. E. WARREN, and E. S. GREENE (J. Amer. Chem. Soc., 1935, 57, 616—619).—Determinations of the mol. wt. of 28 org. compounds show that Bu^oOH is a suitable solvent for most org. compounds, including primary alcohols and all classes of hydrocarbons. It is unsuitable for certain closely related *sec.*- and *tert.*-alcohols, owing to the formation of mixed crystals on freezing. The cryoscopic const. is 8.25.

E. S. H.

Osmotic behaviour of solutes as a function of the specific interaction between solvent and solute. K. FREDENHAGEN (Physikal. Z., 1935, 36, 321—335).—The lowering of v.p. is a consequence of the sp. interaction between solute and solvent in accordance with stoichiometric relations or those described by the term solvation. Only the former type is compatible with Raoult's law. The behaviour of polar solvents and solutes with respect to association (I) is discussed. When the mols. of the solvent possess a single polar group (II), the solute occurs in single mols. except where it is associated in the vapour phase. When the mols. of the solvent have more than one (II), the formation of solvates is possible. Introduction of (II) into the solvent mol. opposes (I) of the solute, but in the solute it aids (I).

A. J. M.

Dielectric constant of electrolytes. R. W. MCKAY (Canad. J. Res., 1935, 12, 377—397).—Bridge and voltage-resonance methods of measurement are described and discussed. Aq. solutions of NaCl, HCl, K_2SO_4 , $MgSO_4$, $CuSO_4$, and $K_4Fe(CN)_6$ at 23° and at 2×10^6 cycles show an increase in ϵ with concn. > that predicted by Debye and Falkenhagen (A., 1928, 957). The results are in approx. accord with those of Lattey and Davies (A., 1932, 120, 224). J. W. S.

Saturation effect of dielectric constants of solutions of electrolytes. W. HACKEL (Physikal. Z., 1935, 36, 220—222).—The saturation effect for $1-2 \times 10^{-3}$ molar solutions of LiF and KCl is < 0.1%. The difference between the effect for LiF and KCl is < 0.05%. A. J. M.

Electrical excitation in electrolytes. M. PLANCK (Z. Physik, 1935, 94, 469—472).—When ionic concns. can be assumed const., space-charge effects do not give appreciable differences in the over-all concns. of oppositely-charged ions. A. B. D. C.

Dielectric constants of solutions of amphoteric electrolytes. II. O. BLUH and J. KROCZEK (Z. physikal. Chem., 1935, B, 28, 410; cf. this vol., 166).—A correction. R. C.

Observation of the Brownian movement with the unaided eye. J. OBRIST (Physikal. Z., 1935, 36, 343—344).—Observations similar to those of Andreev (A., 1934, 361) were made in 1907 by Molisch, with the sap of spurge. Andreev's conclusions are criticised, and those of Lau and Johannesson (this vol., 162) confirmed. Conditions are described for observation of the Brownian movement in mastic sols with the unaided eye. A. J. M.

Observation of the Brownian movement with the unaided eye. J. SCHINTLMEISTER (Physikal. Z., 1935, 36, 345).—Attention is directed to the work of Molisch (see preceding abstract). A. J. M.

Sedimentation velocity and sediment volumes of native potato starch with variation of hydrogen-ion concentration. E. WIEGEL [with H. SCHULER] (Kolloid-Z., 1935, 71, 65—73).—Sedimentation velocity (I) increases rapidly with increasing $[H^+]$ of the suspension. In general, the sediment vol. increases with decreasing (I), but passes through a max. when a certain val. is reached. The sorption of HCl by starch has been studied and is discussed in relation to the above phenomena. E. S. H.

Velocity of vaporisation of small drops in a gas. N. FUKS (Physikal. Z. Sovietunion, 1934, 6, 224—243).—The Maxwell diffusion laws are extended to the evaporation of small drops. CH. ABS. (e)

Colloidal gases. III. Colloidal air and colloidal oxygen with a bubble size of 5 μ or 3 μ diameter. A. KRAUSE and K. KAPITAŃCZYK (Kolloid-Z., 1935, 71, 55—60; cf. A., 1934, 487).—The sols are prepared by dilution of distilled H_2O (containing dissolved air or O_2) with a large vol. of 18.55—19.60N-NaOH. E. S. H.

Aggregation of aerosols by sound waves. O. BRANDT and H. FREUND (Z. Physik, 1935, 94, 348—355).—Micro-cinematographic records of the stages of aggregation are reproduced. A. B. D. C.

Theory of coagulation of colloids and of smokes. W. R. HARPER (Trans. Faraday Soc., 1935, 31, 774—775).—Errors in a previous paper (A., 1934, 960) are corr. F. L. U.

Significance of gas phases in the mechanical synthesis of disperse mercury systems. (Agitation synthesis and ultrasonic-wave synthesis.) N. SATA (Kolloid-Z., 1935, 71, 48—55).—When shaken by hand, Hg disperses to a sol in 0.001M-K citrate in presence of air, but not in presence of H_2 , N_2 , or in vac. Under the influence of ultrasonic waves, dispersion takes place in presence of any of the above gases, or in vac., but unstable emulsions are formed, containing no colloidal particles. The order of rate of sedimentation after removal of the ultrasonic wave source is vac. $> H_2 = N_2 > \text{air}$. E. S. H.

Behaviour of high-molecular compounds in solution. R. SIGNER (Helv. Chim. Acta, 1935, 18, 701—703).—A discussion of the discrepancy between mol. wt. determined by the ultracentrifugal and osmotic methods. E. S. H.

Behaviour of complex and very complex molecules in solution. R. SIGNER (Helv. Chim. Acta, 1935, 18, 701—703).—Comparison of ultracentrifugal and v.-p. measurements shows that the osmotic behaviour of very long and short thread mols. is analogous. H. W.

Specific inductive capacity of colloidal solutions. J. J. BIKERMAN (J. Chim. phys., 1935, 32, 285—292; cf. A., 1934, 162).—The high dielectric const. of sols is explained by the existence of a conducting layer between the particle and the solvent, and an equation is derived which is in accord with the experimental data. R. S.

Colloidal sulphur. Dehydration of sulphur hydrosols. I. MARKEWITSCH (Rev. Chim. ind. Quesneville, 1934, 43, 175—178; Chem. Zentr., 1934, ii, 3736—3737).—Three types of crystal were isolated by the action of EtOH or EtOH-Et₂O on colloidal S: small rhombic crystals; long prismatic needles; and hexagonal lamellæ (m.p. 108.2°). H. J. E.

Viscosimetric investigations of structure formation in vanadium pentoxide sols. II. Influence of heating. A. RABINERSON and G. SCHUMANN (Kolloid-Z., 1935, 71, 87—94; cf. A., 1934, 1068).—When conc. V_2O_5 sols (1—1.5%) are heated for a short time at 50—80° the viscosity (η) decreases at first and then increases to above the initial val. Prolonged boiling gives unstable η vals. and ultimately a decrease in η . The behaviour is ascribed to (a) dissolution of colloid particles, (b) destruction of the oriented structures, (c) acceleration of the lengthwise growth of the particles, (d) acceleration of unoriented coagulation. E. S. H.

Viscosimetric investigations of structure formation in $Fe(OH)_3$ sols. I. Sols containing electrolyte. A. RABINERSON (Acta Physicochim. U.R.S.S., 1934, 1, 168—176; cf. A., 1934, 142).—The gradual peptisation of an aged $Fe(OH)_3$ gel on dilution is indicated by a decrease in viscosity with time. Discontinuities in the viscosity-time curves, in presence of K_2SO_4 , indicate changes of structure through the action of the electrolyte. The thixotropic behaviour

of $Fe(OH)_3$ gels has also been studied. The property may be retained by these gels for a considerable length of time. M. S. B.

Chromium hydroxide hydrosols and the Burton-Bishop rule. E. FISHER and C. H. SORUM (J. Physical Chem., 1935, 39, 283—287).—Purified $Cr(OH)_3$ sols follow the Burton-Bishop rule (I) for all ions. After the addition of sufficient $CrCl_3$ (I) for univalent ions breaks down. On dilution with EtOH the very highly purified sols do not follow (I) for univalent ions, but (I) holds for less highly purified sols. This is probably due to the greater influence of hydration on the stability of the highly purified sols. M. S. B.

Electrochemistry of colloids. II. Electrochemical properties of TiO_2 sols. V. KARGIN (Acta Physicochim. U.R.S.S., 1934, 1, 64—73).—Positive TiO_2 sols are prepared by pouring aq. $TiCl_4$ into H_2O and dialysing. With ice-cold H_2O a transparent hydrophilic sol is obtained. In hot H_2O the sol is milky and more hydrophobic. The former gelatinises on long dialysis. By peptising the gel with tartaric acid and dialysing a negative sol is obtained. A negative sol is also obtained by treatment of the positive sol with alkali. Potentiometric titration with salt solutions indicates that there is strong exchange adsorption of anions, but not of cations, whilst the reverse is the case with negative sols, where there is marked exchange displacement of cations including H^+ . By dilution of the positive sol there is no dissociation of TiO_2 into H^+ and the corresponding anion, as might be expected for an amphoteric compound, and the charge remains positive. M. S. B.

Red limit of the photo-electric effect in potassium-ether sols. V. KARGIN and E. FODIMAN (Acta Physicochim. U.R.S.S., 1934, 1, 74—78).—The external photo-electric effect of red monochromatic light on K-Et₂O sol, with and without adsorbed KI, has been studied. The adsorbed negative ions cause an increase in the photo-electric current and shift the limit of the effect towards the red end of the spectrum. After drying the sol the photo-electric current is still further increased, but the red limit is not altered, showing that the phenomena take place at the metal-solution and not at the solution-vapour interface. Hydrosols of Ag, Cu, and Bi show similar behaviour. M. S. B.

Heterogeneous chemical reactions under the silent electric discharge. XII. Preparation of colloidal solutions. II. S. MIYAMOTO (J. Chem. Soc. Japan, 1934, 55, 1273—1276; cf. this vol., 46).—As hydrosols are formed when dil. As_2O_3 solutions are subjected to a silent electric discharge in a current of H_2 . A mixture of AsH_3 and H_2 gives similar results. Alcohol sols are obtained by replacing H_2O by EtOH, Bu^iOH , or $C_5H_{11}OH$. Sb sols are formed from dil. aq. K Sb tartrate or $SbH_3 + H_2$ under similar conditions. Similar sols of HgCl are formed from $HgCl_2$ under the discharge. CH. ABS. (e)

Effect of temperature on the stability of a hydrosol of iron hydroxide in an alcohol-ether mixture. A. V. DUMANSKI and I. T. MARKEVITSCH (J. Phys. Chem. U.S.S.R., 1933, 4, 914—917).—Data

are given for temp. from -15° to 130° . The influence of temp. is discussed. CH. ABS. (e)

Depth effect of orienting forces and the stability of foams and emulsions. S. E. BRESLER and D. L. TALMUD (J. Phys. Chem. U.S.S.R., 1933, 4, 796—801).—Data are recorded for the effect of 3—25% aq. KCl, KBr, KI, K_2SO_4 , $K_3Fe(CN)_6$, KCNS, and $BaCl_2$ on C_6H_6 emulsions. Quasi-crystal complexes are oriented by the effect of the boundary layer, and in such cases the hydration of polar groups must exert an additional depth effect in some sizes of complexes. CH. ABS. (e)

Measure for the separation of emulsions (demulsification). E. L. LEDERER (Kolloid-Z., 1935, 71, 61—64).—The rate of separation of a phase is expressed by $dV/dt = k(1-V)V^2$, where V is the vol. of the liquid phases separating in the time t . E. S. H.

Viscosity and plasticity of disperse systems. III. Plastic properties of resin soaps. M. P. VOLAROVITSCH (Kolloid-Z., 1935, 71, 22—28; cf. this vol., 444).—Two methods of determining the flow velocity (θ) of resin soaps are described. Results show that θ is a physical const., which is independent of the dimensions of the apparatus. The dependence of θ on temp. and H_2O content has been investigated. E. S. H.

Quicksand as a thixotropic system. H. FREUNDLICH and F. JULIUSBURGER (Trans. Faraday Soc., 1935, 31, 769—774).—Samples of quicksand from the Lancashire coast have been shown to contain more fine clay than ordinary sand from the same localities. One such sample, containing 2.1% of clay, was thixotropic when mixed with sea- H_2O . The thixotropy vanished when the clay was removed by centrifuging. In all the samples examined thixotropy was associated with loose packing. F. L. U.

Dielectric investigations on dissolution, swelling, and thixotropy of cellulose triacetate in chloroform and chloroform-benzene. I. SAKURADA and S. LEE (Kolloid-Z., 1935, 71, 94—100).—Dielectric consts. have been determined in solutions of glucose penta-acetate (I) in C_6H_6 and of (I), cellobiose octa-acetate (II), cellulose-dextrin acetate (III), and cellulose triacetate (IV) in $CHCl_3$. 1 g. of (I) binds 0.14 g. of $CHCl_3$. The polarisations of (II), (III), and (IV) are practically equal. (IV) has a dipole moment of about 2×10^{-18} e.s.u., independently of the viscosity. Either the (IV) mol. is dissolved in a low-mol. form and the mol. is free to orient itself in the electric field, or the dipole groups in the (IV) mol. are free to rotate. In the thixotropic sol-gel transformation of (III) and (IV) in $C_6H_6-CHCl_3$ the dielectric const. and polarisation remain unaltered. (III) which has swelled in $C_6H_6-CHCl_3$ also possesses orientation polarisation, out to a smaller extent than in the dissolved state. E. S. H.

Coacervate sols and their relation to the theory of lyophilic colloidal stability. H. G. B. DE JONG and P. v. D. LINDE (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 419—426).—The effect of varying the ratio $EtOH/H_2O$ has been studied with glycogen sols. At 0—37 vol.-% of $EtOH$ the mixtures are clear, at 3—47% strong turbidity slowly develops, at 47—80% there is opalescence increasing to turbidity with

increasing concn. of $EtOH$, and at $> 80\%$ flocculation occurs. The opalescent mixtures (coacervate sols) behave as hydrophobic sols with a small negative charge which is unevenly distributed over the surface of a colloidal particle. The tendency towards spontaneous coacervation decreases as the charge on the particle increases. R. S. B.

Oriented coacervates and their bearing on the formation of colloid-crystals. H. G. B. DE JONG (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 426—434).—On adding 3 vols. of $EtOH$ to 2 vols. of a 2% starch sol (Huron) and warming the resulting opalescent coacervate sol at 70° for 15 min. a platelet sol (I) is formed. Electrolytes and oleic acid impede the formation of (I). The particles of (I) carry a negative charge, have a diameter 5—6 μ , flocculate on shaking, and can also be obtained reversibly by cooling clear sol from 90° . With $MeOH$ and Pr^iOH the plates are smaller. Other preps. of amyllum show a more complex but similar behaviour, all sols containing a variety of colloid fractions, some of which give ordinary and others oriented coacervates. The bearing of oriented coacervation on the formation of protein crystals is discussed. R. S. B.

Action of strong and weak bases on cellulose nitrate. II. Solvation of the polymeric-homologous series of cellulose nitrates treated with ammonia. L. I. MIRLAS (J. Gen. Chem. Russ., 1934, 4, 1338—1346).—According to Mark and Fickentscher's formula the sp. η should be $\propto M$ (mol. wt.), whilst according to Staudinger's formula $\eta \propto M^{0.5}$. M of cellulose nitrates treated with various concns. of aq. NH_3 have been calc. from these formulæ, and the deviations compared. R. T.

(A) Effect of heat-treatment on viscosity of gluten dispersed in alkali, acid, and neutral solvents. (B) Hydrolysis of gluten induced by solvent. W. H. COOK and R. C. ROSE (Canad. J. Res., 1935, 12, 238—247, 248—252).—(A) The decrease in η of dispersions of gluten in $NaOH$ on heating is $>$ in $AcOH$. In aq. carbamide and Na salicylate (I) heating below 70° decreases η ; above 70° η passes through a max.

(B) The unimol. velocity coeff. and temp. coeff. of hydrolysis of gluten in dil. aq. $NaOH$ are $>$ in aq. $AcOH$. Gluten is not hydrolysed in aq. carbamide or (I). H. D.

Explanation of hysteresis in the hydration and dehydration of gels. J. W. MCBAIN (J. Amer. Chem. Soc., 1935, 57, 699—700).—Hysteresis is a consequence of the v.-p. relations in capillaries. E. S. H.

Lyophilic colloids. V. Dissolution of gelatin and stability of its sols. I. N. PUTILOVA. VI. Fractionation of gelatin and physico-chemical properties of the different fractions. S. M. LIEPATOV and I. N. PUTILOVA (Kolloid-Z., 1935, 71, 80—82, 83—87; cf. A., 1934, 1306).—V. By fractionation of gelatin by dissolution in H_2O , and studies of the influence of the fractions on the rate of gelation and the rate of coagulation by $EtOH$, it is shown that the solubility and stability of gelatin depend on the concn. of the fractions of low mol. wt.

VI. The mol. wt., solvation no., and length of principal valency chains have been determined for different fractions of gelatin obtained by selective dissolution in H_2O . There is no evidence of the existence of different chemical species in the fractions.

E. S. H.

Existence of different forms of gelatin. N. PESKOV and N. ZURUPA (Kolloid-Z., 1935, 71, 73—79).—Experiments on dissolution in H_2O , adsorption by kaolin, and salting-out by $(NH_4)_2SO_4$ show the existence of five forms of gelatin, three of which have peptising properties. The changes occurring on ageing are discussed.

E. S. H.

Reaction of silver ions with gelatin. P. WULFF and W. EHRENBURG (Phot. Korr., 1934, 70, 155; Chem. Zentr., 1934, ii, 3891).—From conductivity and transport measurements it is shown that Ag^+ forms a complex anion with gelatin of the type $\{[Ag^+(Gel^-)_2]^- \}_n$. The solubility of $AgCl$ may be increased to 100 times its normal val. in H_2O by the presence of gelatin.

H. J. E.

Reaction of silver ions with gelatin. P. WULFF (Z. wiss. Phot., 1935, 34, 59—62; see preceding abstract).—Conductivity measurements show that $[Cl^-]$ is reduced by gelatin; the increased solubility of $AgCl$ in gelatin is therefore not due to the Cl^- . It is probable that about half the Ag^+ is free and the rest bound. Conductivities of various $AgCl$, Ag_2O , and $NaCl$ solutions in gelatin have been determined.

J. L.

Diffusion coefficients of molecules and ions from measurements of undisturbed diffusion in a stationary medium. W. G. EVERSOLE and E. W. DOUGHTY (J. Physical Chem., 1935, 39, 289—292).—Expressions for the coeff. of diffusion of charged and uncharged particles in a motionless medium have been deduced. Preliminary results of colorimetric measurements of the penetration of $CuCl_2$ into gels indicate the utility of the equation.

M. S. B.

Colloidal properties of the pectins. J. BONNER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 346—354).—The prep. of Na pectate (I), pectic acid (II), a pectinic acid (III), and a Na pectinate (IV) is described. A slight discrepancy between the reciprocal hexol no. (V) of (II) and its equiv. wt. may be due to adsorption of OH^- as this discrepancy decreases with increasing acidity. Th^{4+} also reverses the charge of (II). $Luteo-Co^{3+}$ and Ca^{2+} reduce but do not reverse the charge. The equiv. wt. of (I) obtained by direct titration is $>$ that obtained by back titration with $NaOH$, and depends on the period of drying owing to anhydride formation. The vals. of (V) for (III) and (IV) are much larger and, in agreement with their smaller charge density, their sols are not so readily pptd. by electrolytes. (III) forms complex and auto-complex coacervates.

E. A. H. R.

Combining weight of collagen.—See this vol., 769.

Theory of Liesegang rings. E. B. HUGHES (Kolloid-Z., 1935, 71, 100—103).—Analyses carried out at different depths of penetration into the gel are in accordance with the diffusion law. Basing

the theory on this law, the distances between the bands are accounted for.

E. S. H.

Calculation of the gaseous equilibrium $\frac{1}{2}I_2 + \frac{1}{2}Br_2 = IBr$. H. ZEISE (Z. Elektrochem., 1935, 41, 267—270).—From the calc. val. of the moment of inertia of IBr , 493×10^{-40} g.-cm.², and the heat of formation, 1380 g.-cal., deduced from microscopic data, vals. of K_p for temp. 298—2000° abs. have been obtained in good agreement with experimental results.

M. S. B.

Heat capacities and dissociation equilibria of gases. B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1935, 57, 612—614).—Data representing the energy content are given for H_2 , O_2 , N_2 , CO , NO , OH , CO_2 , H_2O , O_3 , Br , and HBr from 200° to 3500° abs. and the consts. for equilibria involving these gases and also Cl_2 and HCl from 300° to 5000° abs.

E. S. H.

Extremely small concentrations and the law of mass action. Ionic theory. I. M. KOLTHOFF (Chem. Weekblad, 1935, 32, 246—249).—The actual physical significance of concns. of the order of 10^{-25} is discussed and the evidence for their real existence and for the general validity of the law of mass action as applied to electrolytes is reviewed.

D. R. D.

Acids, bases, and salts. M. KILPATRICK (J. Chem. Educ., 1935, 12, 109—111).—A discussion.

L. S. T.

Activity and osmotic coefficients of strong and weak electrolytes. P. VAN RYSELBERGHE (J. Physical Chem., 1935, 39, 403—414).—Thermodynamic relations between the activity coeffs. and the osmotic coeffs. for undissociated, completely dissociated, and incompletely dissociated solutes have been derived using Gibbs' method. Simple formulæ have been deduced which are applicable at very low concn. or to a very weak electrolyte. Comparison is made with Lewis and Randall's method.

M. S. B.

Dissociation of carbamide in dilute solution. P. CRISTOL, J. FOURCADE, and R. SEIGNEURIN (Compt. rend., 1935, 200, 1369—1370).—The lowering of f.p., conductivity, and p_H vals. of solutions of carbamide in H_2O and in 0.9% aq. $NaCl$ indicate an equilibrium represented by $NH_2C \begin{smallmatrix} \diagup NH_3 \\ \diagdown O \end{smallmatrix} \rightleftharpoons NH_2C(NH_2) \cdot OH \rightleftharpoons NH_2C(NH_2) \cdot O^- + H^+$.

F. R. G.

Transmission of polar effects through space. I. JONES and F. G. SOPER (Chem. and Ind., 1935, 342—343).—The polar effect on the primary ionisation const. for a no. of org. acids varies inversely as the cube of the distance between the polar groups, independently of the no. of intervening C atoms.

C. W. G.

Slow hydrolysis: constitution and progressive change of aqueous solutions of stannic chloride. J. GUERON (Ann. Chim., 1935, [xi], 3, 225—326).—Freshly formed aq. solutions of $SnCl_4$, and the changes they undergo with time, have been studied by centrifuging, ultrafiltration, measurements of p_H , coagulation by Na_2SO_4 and by a glass surface, photometric measurements, viscosity determinations, and by examination of Raman spectra. Fresh solutions of $SnCl_4$ contain very few mols. of the salt but large quantities

of the ions SnCl_6^{4-} (I). These gradually disappear by hydrolysis and, after a period of induction, coagulation of the products of hydrolysis takes place. The process is autocatalytic and the walls of the vessel have a catalytic effect. The initial period of stabilisation of the solutions is due to the appearance in the solution of Sn^{4+} , probably as a result of the decomp. of the complex (I). When these ions in turn are removed by hydrolysis, coagulation takes place. In the stage preceding pptn. the solutions become thixotropic. "Slow hydrolysis," considered as a reaction which is sp. for solutions in which the product of hydrolysis is colloidal, does not exist. Previous study of the phenomenon in the more complicated case of FeCl_3 exclusively, has prevented the recognition of the two separate stages. M. S. B.

Sodium aluminate. A. MAFFEI (Gazzetta, 1935, 65, 108—116; cf. A., 1934, 732).—The hydrolysis of Na aluminate in solutions obtained by dissolving Al in NaOH has been studied potentiometrically, and is shown to be more complicated than in ordinary solutions containing excess of NaOH. O. J. W.

Concentration of hydrogen ions in aqueous solutions of complex cobaltamines and their absorption spectra. II. T. UEMURA and H. SUGEDA (Bull. Chem. Soc. Japan, 1935, 10, 85—97).—The relation between the coeff. of extinction and λ , for solutions of the following complex salts, has been studied by the method previously described (this vol. 579): $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ (*cis* and *trans*) (I), $[\text{Co}_2(\text{NH}_3)_6(\text{OH})_3]\text{Cl}_3$ (II), $[\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3]\text{Cl}_6$ (III), $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$ (blue, grey, and black) (IV), $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2$ (V), $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{SO}_4$ (violet and blue-grey) (VI), $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{SO}_4\text{H}$ (VII). Practically no change takes place in these solutions and those previously studied (*loc. cit.*) at $p_{\text{H}} < 7$. Above $p_{\text{H}} 7$ the triamines, except *trans*-(I), seem to change into polynuclear complexes in which the central atoms are linked by OH. (IV) and (V) give similar extinction curves in solution, as also do (VI) and (VII). The curves for (II) and (III) show characteristics previously noted for polynuclear complexes. Their absorption is stronger than for ordinary complexes and there is practically no absorption in the ultra-violet. M. S. B.

Hydrolysis of inorganic salts and the chemistry of the high-molecular hydrolysis products (including iso- and heteropoly-compounds). II. G. JANDER and K. F. JAHR (Kolloid-Beih., 1935, 297—354; cf. this vol., 181).—A review of published works, particularly on the complex acids of Mo, W, and V. The co-ordination formulæ of the complexes are discussed. E. S. H.

Equilibria of basic amino-acids in the formol titration. M. LEVY (J. Biol. Chem., 1935, 109, 365—381; cf. A., 1933, 381; Birch *et al.*, A., 1930, 1458).—The procedure and theoretical considerations previously applied to other NH_2 -acids are extended to arginine, lysine, and histidine. W. McC.

Titration constants of glyoxaline derivatives. LEVY (J. Biol. Chem., 1935, 109, 361—363).—The consts. for 4-(or 5-)methylglyoxaline, imin-

azolyl-lactic acid, histamine, and histidine have been determined by electrometric titration. W. McC.

Ampholytic nature of phospholipins. H. FISCHGOLD and E. CHAIN (Proc. Roy. Soc., 1935, B, 117, 239—257).—By titration in C_6H_6 -EtOH solution both the acid- and base-binding properties of phospholipins (I) may be determined. The (I) examined react with 1 equiv. of H^+ , but only those with a primary NH_2 react with alkali. It is inferred that the (I) containing a quaternary NH_4^+ base can exist only as cations or zwitterions, whilst those containing primary NH_2 can exist as zwitterions, neutral mols., anions, or cations. F. A. A.

Binary system strontium nitrate-strontium hydroxide. G. WOLF (Compt. rend., 1935, 200, 1203—1205).—The fusion diagram of the system shows a max. at 30.5% $\text{Sr}(\text{NO}_3)_2$, corresponding with $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{Sr}(\text{OH})_2$. J. W. S.

Binary system lead iodide-lead oxide. H. S. VAN KLOOSTER and R. M. OWENS (J. Amer. Chem. Soc., 1935, 57, 670—671).— $\text{PbI}_2 \cdot \text{PbO}$ decomposes at 465° yielding $\text{PbI}_2 \cdot 2\text{PbO}$ (m.p. 620°). The existence of $\text{PbI}_2 \cdot 4\text{PbO}$ (m.p. 650°) is tentatively indicated. A eutectic occurs at 30 mol.-% PbO and 365° . E. S. H.

Fusion diagram of the system ZrO_2 - SiO_2 . N. SHIRNOVA (J. Gen. Chem. Russ., 1934, 4, 1464—1470).—The compound ZrSiO_4 , m.p. 2430° , is confirmed, and eutectics at 2220° and 1705° with 42 and 97 mol.-% SiO_2 are recorded. R. T.

Thermal decomposition of palladium chloride and chloro-salts. F. PUCHE (Compt. rend., 1935, 200, 1206—1208).—The dissociation of PdCl_2 begins at 600° and the dissociation pressure reaches atm. at 920° . The log p - $1/T$ curves show that the m.p. of PdCl_2 is 936° , the latent heat of fusion 9, and the heat of formation of solid PdCl_2 26.3 kg.-cal. per mol. The heats of formation of K_2PdCl_4 and K_2PdCl_6 are 52.67 and 79.06 kg.-cal. per mol., respectively. K_2PdCl_6 dissociates into K_2PdCl_4 above 175° . J. W. S.

Phase diagrams of certain organic binary systems. XXII. N. A. PUSHIN and L. SLADOVIĆ (Bull. Soc. Chim. Yougoslav., 1934, 5, 135—141).—The m.-p. diagrams do not indicate compound formation in the systems *p*-cresol-resorcinol, -phenanthrene (I), *o*-cresol-(I), borneol- C_{10}H_8 , - NHPh_2 , -urethane, BzOH - α - and β - $\text{C}_{10}\text{H}_7\text{NH}_2$. R. T.

Thermal analysis of the system antipyrine-trichlorobutyl alcohol. A. RYCHTERÓWNA (Wiad. farm., 1934, 61, 95—97; Chem. Zentr., 1934, ii, 3647—3648).—No mol. compounds are formed. Eutectic mixtures containing (i) 40 mol.-% antipyrine (I) and (ii) 2 parts of (I) and 3 parts of trichlorobutyl alcohol have been observed. A. G. P.

Equilibrium of sodium sulphate, sulphuric acid, and water, and the causticising of sodium sulphate. T. OKUNO (Mem. Fac. Eng. Kyushu, 1935, 7, 275—355).—The ternary system has been studied at 25° , and for the lower concns. at 5 — 25° . The decomp.-time curves of NaHSO_4 have been determined at 300 — 600° , $\text{Na}_2\text{S}_2\text{O}_7$ being formed at 300° and Na_2SO_4 at higher temp. X-Ray studies show that all

solid phases are converted into Na_2SO_4 after heating at 420 – 500° . The recovery of coagulation solutions (containing Na_2SO_4) used in the artificial silk industry is discussed. The dissociation pressure of the system $2\text{NaHSO}_4(s) \rightleftharpoons \text{Na}_2\text{S}_2\text{O}_7(s) + \text{H}_2\text{O}(g)$ at 135 – 196° is given by $\log p_{\text{mm}} = -4303.9/T + 10.7436$ in agreement with vals. calc. by the Nernst theorem. For $\text{Na}_2\text{S}_2\text{O}_7(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + \text{SO}_3(g)$ at 330 – 380° $\log p_{\text{mm}} = -7132.44/T + 12.125$, and for $\text{NaHSO}_4(s) + \text{NaCl}(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + \text{HCl}(g)$ at 130 – 255° $\log p_{\text{mm}} = -5391.84/T + 13.5313$. The reduction of Na_2SO_4 by CO and by C has been studied at 700 – 900° , the reactions $\text{Na}_2\text{SO}_4 + 4\text{CO} \rightarrow \text{Na}_2\text{S} + 4\text{CO}_2$ and $\text{Na}_2\text{SO}_4 + 4\text{C} \rightarrow \text{Na}_2\text{S} + 4\text{CO}$ being accompanied by $3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S} \rightarrow 4\text{Na}_2\text{O} + 4\text{SO}_2$, $4\text{Na}_2\text{O} + 4\text{CO}_2 \rightarrow 4\text{Na}_2\text{CO}_3$, $4\text{SO}_2 + 8\text{CO} \rightarrow 8\text{CO}_2 + 2\text{S}_2$, $2\text{CO} + \text{CO}_2 + \text{C}$. A max. yield of Na_2S is obtained with $3\text{Na}_2\text{SO}_4 : 1\text{C}$ at 850° for 40 min., the yield decreasing with time. Reduction of Na_2SO_4 by CO and C has also been studied. The const., $[\text{S}'']/[\text{OH}']^2$, for the reaction $\text{Na}_2\text{S} + \text{CuO} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CuS}$ in solution is approx. 8.5×10^{-31} . The influence of concn. is small, and the yield decreases slightly with rising temp. The oxidation of CuS by O_2 gives CuO at 800° , but at lower temp. CuSO_4 is formed; at $> 1100^\circ$ CuO decomposes into Cu_2O and O_2 . For the reduction of BaSO_4 by CO, $\log(p_{\text{co}}/p_{\text{co}}) = 1111/T + 5.125 - 1.76 \times \log T + 6.65 \times 10^{-4}T - 7.75 \times 10^{-8}T^2$, calc. by theory and in fair agreement with the author's experiments. In addition to the main reaction $\text{BaSO}_4 + 4\text{CO} \rightarrow \text{BaS} + 4\text{CO}_2$ side reactions occur. The yield is a max. at 850° and decreases with time. A good yield of BaS is possible with only 15% of CO. The reaction $\text{BaS} + \text{CuO} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CuS}$ has been studied, with results similar to those with $\text{Na}_2\text{S} + \text{CuO} + \text{H}_2\text{O}$. The const., $[\text{OH}]^2/[\text{SO}_4']$, for the reaction $\text{Ba}(\text{OH})_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{NaOH}$ in solution is approx. 1.2×10^8 . A good yield of NaOH is obtained.

R. S. B.

Ternary systems. XX. Calcium sulphate, ammonium sulphate, and water. A. E. HILL and N. S. YANICK (J. Amer. Chem. Soc., 1935, 57, 645–651).—Equilibrium data for 100° , 75° , 50° , and 25° are recorded. No new solid phases are reported.

E. S. H.

Liquid-solid equilibria in the system naphthalene- α -naphthol- β -naphthol. K. HRYNAKOWSKI and M. SZMYT (Z. physikal. Chem., 1935, 173, 58–66).—Data for the ternary equilibrium are recorded.

R. C.

Thermal equilibria in ternary systems. III. Phenacetin-antipyrine-urethane. K. HRYNAKOWSKI and F. ADAMANIS [with A. DENIZOT and B. MARCINKOWSKI (Rocz. Chem., 1935, 15, 44–51)].—Compound formation is not observed; the ternary eutectic mixture, m.p. 29° , contains phenacetin 8.5, antipyrine 36, and urethane 55.5%.

R. T.

Oxidation-reduction equilibrium of metallic chromium. S. AOYAMA and E. KANDA (J. Chem. Soc. Japan, 1934, 55, 1174–1184).—The equilibrium $2\text{Cr} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cr}_2\text{O}_3 + 3\text{H}_2$ has been studied at low temp.; the data lead to $\Delta F_{298} = -112,502$ g.-cal. and $\Delta H_{298} = -107,980$ g.-cal. Vals. for the v.p. of ice (166.5 – 264.5° abs.) are recorded. CH. ABS. (e)

Constitution of glasses. E. JENCKEL (Z. Elektrochem., 1935, 41, 211–215; cf. A., 1934, 965).—Property-composition curves for a series of glasses, viz., B_2O_3 - Na_2O , $2\text{B}_2\text{O}_3$, B_2O_3 - BaO , $2\text{B}_2\text{O}_3$, B_2O_3 - PbO , B_2O_3 - SiO_2 , SiO_2 - Na_2O , B_2O_3 , B_2O_3 - Na_2O , SiO_2 , and Na_2O , SiO_2 - SiO_2 , indicate the existence of definite compounds. The properties studied were the transformation temp., sp. vol., coeff. of expansion, and reciprocal refractive index. F. L. U.

Oxidising power of basic slags. I. Determination of the binary diagram CaO - Fe_2O_3 . II. Determination of the dissociation pressures of Fe_2O_3 , CaO , Fe_2O_3 , and 2CaO , Fe_2O_3 . J. WHITE, R. GRAHAM, and R. HAY (Iron and Steel Inst., May 1935, Advance copy, 21 pp.).—I. On prolonged heating of 1:1 mol. mixtures of CaO and Fe_2O_3 at 1000° a dark powder is formed which melts at 1250° and solidifies to hard black needles of CaO , Fe_2O_3 . Optical evidence of 2CaO , Fe_2O_3 , formed by a peritectic reaction at 1450° , has also been obtained. A eutectic occurs at 90% Fe_2O_3 , 1210° ; Fe_2O_3 melts at 1595° with decomp.

II. Fe_2O_3 dissociates appreciably at 1100° and at the m.p. the dissociation pressure is about 5×10^5 atm. Fe_2O_3 and Fe_3O_4 appear to be mutually sol.; the solubilities increase rapidly between 1050° and the liquidus line at about 1520° . The pressure of O_2 from the two Ca ferrites is negligible below the peritectic temp.; at higher temp. the amount of Fe_2O_3 liberated by the peritectic reaction determines the dissociation pressure. A. R. P.

Heat and free energy of formation of arsenic trifluoride. D. M. YOST and J. E. SHERBORNE (J. Amer. Chem. Soc., 1935, 57, 700–701).—For gaseous AsF_3 , $\Delta H = -191,300$ g.-cal.; $\Delta F_{298} = -188,000$ g.-cal. E. S. H.

Heat evolved in metallic transformations. II. Cobalt. H. VON STEINWEHR and A. SCHULZE (Physikal. Z., 1935, 36, 307–311; cf. A., 1934, 725; B., 1934, 764).—The heat evolved in the transition of α - into β -Co is 0.1 ± 0.03 g.-cal. per g., and in the transition from the ferromagnetic to the paramagnetic state, 1.2 ± 0.07 g.-cal. per g. The α - β transition takes place at 380 – 420° , and the magnetic transition at 1070 – 1125° . A. J. M.

Latent heat of fusion of equilibrium mixtures of light and heavy water. L. JACOBS (Trans. Faraday Soc., 1935, 31, 813–821).—Mol. heats of fusion (L) of mixtures containing up to 97.7 mol.-% of D_2O have been determined. The extrapolated val. of L for 100% D_2O is 1525 ± 2 g.-cal. F. L. U.

Specific heat of a liquid and its vapour and its application to the heat of reaction in liquid mixtures. D. B. MACLEOD (Trans. Faraday Soc., 1935, 31, 746–748).—There is a nearly const. difference of about 9 g.-cal. between the mol. heats of different liquids and their respective vapours at the ordinary temp. This difference, which cannot be accounted for by expansion against internal forces in the liquid, is due to extra degrees of freedom in the liquid state. The origin of these is discussed, and it is shown that they account for the approx. equality of

heats of reaction between the components of widely different liquid mixtures. F. L. U.

(A) Determination of the heat capacity of aqueous solutions and the heat of dissolution of salts. M. M. POPOV, K. G. KHOMJAKOV, N. N. FEODOSIEV, and P. K. SHIROKIKH. (B) Heat capacity of aqueous solutions of phosphoric acid. M. M. POPOV, N. N. FEODOSIEV, and S. M. SKURATOV (Trans. Sci. Inst. Fertilisers U.S.S.R., 1933, No. 110, 12—23, 23—34).—(A) A comparison of experimental methods.

(B) Data are recorded for aq. H_3PO_4 (0—89.72%). CH. ABS. (e)

Heats of dissolution and of dilution of potassium and ammonium phosphates. K. G. KHOMJAKOV, S. F. JAVOROVSKAJA, and P. K. SHIROKIKH (Trans. Sci. Inst. Fertilisers U.S.S.R., 1933, No. 110, 34—46).—In addition to the thermal data, the solubilities of K_3PO_4 , K_2HPO_4 , and $\text{NH}_4\text{H}_2\text{PO}_4$ are recorded. CH. ABS. (e)

Temperature variation in transference numbers of concentrated solutions of sulphuric acid as determined by the galvanic cell method. W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 662—667).—Transference nos. have been calc. from e.m.f. data for the cell $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{H}_2\text{SO}_4(m)|\text{H}_2\text{SO}_4(m')|\text{Hg}_2\text{SO}_4|\text{Hg}$ over the range 0.05—17.0*M* and at 0°, 10°, 15°, 25°, 35°, 45°, and 60°. Extrapolations of the H^+ transference nos. to zero concn. and the limiting law based on the Debye-Hückel-Onsager conductance equations are given at various temp. E. S. H.

Mechanism of conductance. H. S. LUKENS (Trans. Electrochem. Soc., 1935, 67, 317—324).—By plotting the equipotential lines between two electrodes placed in an electrolyte, it has been shown that their contour is the same as in solid conductors in similar circumstances. The mechanism of electrolytic conductance is discussed in the light of this result. E. S. H.

Properties of electrolytic solutions. XVI. Conductance of electrolytes in anisole, ethylene bromide, and ethylene chloride at 25°. N. L. COX, C. A. KRAUS, and R. M. FUOSS (Trans. Faraday Soc., 1935, 31, 749—761; cf. this vol., 302).—Conductivities of several tetra-alkylammonium salts have been measured at concns. ranging from 1.6×10^{-2} to $1.3 \times 10^{-6}N$. The results are in accord with the ion association theory developed by Fuoss and Kraus. Ion dimensions calc. from the consts. of the association equilibria agree with accepted at. dimensions. F. L. U.

Conductivity of methoxides and ethoxides. W. F. K. WYNNE-JONES (J.C.S., 1935, 540).—The results of Jones *et al.* (A., 1934, 1071) are in good agreement with those of the author (A., 1928, 22), but their statement as to the author's correction for solvent conductivity is not correct. There appears to be no experimental basis for their assumption as to the amount of NH_3 probably present as impurity in MeOH. M. S. B.

Surface conductivity at solid-liquid interfaces. URBAN, H. L. WHITE, and E. A. STRASSNER (J. Physical Chem., 1935, 39, 311—330).—The sp.

surface conductivity (I) of Pyrex glass particles in aq. KCl and NaCl, concn. 1.25×10^{-4} — $1 \times 10^{-2}M$, has been determined using 1000-cycle a.c. (I) represents the same fraction of total conductivity as in a glass capillary of about 10 μ diameter. An equation for calculating (I) on the basis of the Stirn double layer has been developed and the calc. vals. are in good agreement with experiment, but the vals. calc. according to Gouy's theory are not. The sedimentation vol. decreases with increase of concn., but in KCl there is a sharp rise in vol. between 3×10^{-3} and $1 \times 10^{-2}M$. It is shown that this is probably not due to a "Hafteffekt." The thickness of the double layer for various concns. of KCl has been calc. M. S. B.

Magnitude of surface conductivity. J. W. MCBAIN and J. E. FOSTER (J. Physical Chem., 1935, 39, 331—342).—A.c. measurements of the sp. surface conductivity (I) at 25°, of KCl of different concn., at a glass-solution interface, give vals. varying from 9.96×10^{-8} to 264×10^{-8} for concn. 0.001—0.1*N*, in confirmation of previous results (A., 1930, 37, 704). The high results are in part due to irregularities at the surface of the glass as compared with the optically polished glass previously used. (I) at an air- H_2O interface (an ideally plane surface) is 3.8×10^{-8} for a closely packed film of stearic acid, 4.0×10^{-8} for palmitic, and 8.4×10^{-8} for oleic. The vals. are far > those calc. on the basis of current theories of the mobility of the ions in the outer portions only of the diffuse double layer. New cell designs are described. M. S. B.

Nature of the residual current observed with Zlotowski's moving cathode. N. THON (J. Chim. phys., 1935, 32, 269—272).—Contrary to Zlotowski (this vol., 171) it is suggested that the residual current is partly non-faradic, and the formula of Z has been derived on this basis. R. S.

Transport of electricity through phase boundaries. System I: glass-gas or vapour. II. Electrolytic introduction of hydrogen, nitrogen, and potassium into a glass diaphragm, and electrolytic transport of sodium through a glass diaphragm. C. STUBER (Z. physikal. Chem., 1935, 172, 401—428; cf. A., 1932, 230).—Experiments have been made on the passage of a glow d.c. discharge through a gas between a metal anode and a glass diaphragm backed by a metal cathode, the positive electricity carriers produced in the discharge being thereby introduced into the glass and replacing the alkali ions. Faraday's law is valid for the discharge of Na^+ and K^+ at the cathode and for the migration of Na^+ , K^+ , and H^+ from the gas phase into the glass. N migrates into the glass, but He , O , CO_2 , and CCl_4 do not. When cations do not migrate into the glass in electrolysis, $\text{SiO}_3(\text{SiO}_2)_x$ radicals are formed at the anode side of the glass and at higher temp. give $\text{SiO}_2(\text{SiO}_2)_x + \text{O}$. The disappearance of gases in the electrolysis cannot be explained by occlusion, diffusion, or clean-up effects. By electrolysis of Na and K vapours photo-electric cells having characteristics similar to those recorded in the literature have been prepared. R. C.

Hydrogen electrodes. M. VOLMER and H. WICK (Z. physikal. Chem., 1935, 172, 429—447).—For

bright Pt, Ir, and Au electrodes in specially purified aq. H_2SO_4 the c.d.-potential curves (I) for the discharge and dissolution of H are linear in the immediate vicinity of the equilibrium potential, as Volmer's theory of overvoltage requires (cf. A., 1933, 1122). At higher c.d. the discharge curves assume a pure logarithmic form, but the dissolution curves diverge from this form, due probably to retardation of $\text{H}_2 \rightarrow 2\text{H}$. Investigation of poisoning by As_2O_3 has shown that the effect of poisons on the kinetics of H discharge and dissolution consists in a raising of the energy threshold together with displacement of the latter in the double layer. Retardation of $2\text{H} \rightarrow \text{H}_2$ is probable, but has not been proved. Under the conditions under which H overvoltage at solid electrodes is measured, the electrode surface is almost always partly covered with impurities from the electrolyte. R. C.

Adsorption electrodes. II. Mineral electrodes. H. J. C. TENDELOO (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 434—441; cf. A., 1934, 749).—A thin plate of mica immersed in 0.1*N*- H_2SO_4 for 2 days behaves as a H electrode, with $\log E \propto \{[\text{H}_2\text{SO}_4] + \text{const.}\}$. Similarly, after immersion in slightly alkaline CaCl_2 the mica functions as a Ca electrode. Heavy spar, CaF_2 , and wollastonite were also studied as electrodes. R. S. B.

Periodic changes of potential of iron in nitric acid. I. M. KARSCHULIN (Z. Elektrochem., 1935, 41, 224—229; cf. A., 1934, 1072).—Oscillations of potential occurring when Fe is immersed in aq. HNO_3 (36—56 wt.-%) are influenced by concn., temp., and by whether the Fe is partly or completely immersed. The Fe becomes covered with a brownish layer during periods of increasing positive potential, which reaches a max. when the layer is destroyed by a sudden evolution of gas. The cycle is then repeated. During the dissolution of Fe in 41.7% HNO_3 evolution of gas occurs alternately on sharply bounded adjacent areas of metal. The results are discussed. F. L. U.

Mechanism of appearance of potential [at metallic electrodes] in solutions containing foreign ions. O. ESSIN and T. BEKLEMISHEVA (J. Gen. Chem. Russ., 1934, 4, 1394—1399).—The e.m.f. of Ag electrodes in aq. CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ is given by $E_{\text{Ag}|\text{CuX}} = a + bE_{\text{Cu}|\text{CuX}}$, where X is one of the above anions; the results are in accordance with those recorded for Au electrodes (this vol., 449), and by Schmid for Cu electrodes in aq. K and Na halides (A., 1933, 28, 354, 677). R. T.

Sodium discharge potential at the mercury cathode. W. W. STENDER, M. M. STROGANOV, and P. B. ZIVOTNSKY (Trans. Electrochem. Soc., 1935, 68, 23—33).—In 4.28*N*-NaCl solutions at 15°, 50°, and 70° with c.d. 2.88—30 amp. per sq. dm. the Na discharge potential at an amalgam cathode (0.02—0.4% Na) ranges from 0.1 to 0.15 volt. Overvoltage is essential to amalgamation and explains the progressive departure of the cathode potential from the equilibrium val. with increase in c.d. J. W. C.

Relations between fundamental electrochemical quantities. I. UHARA (J. Chem. Soc. Japan,

1934, 55, 1207—1222).—Theoretical. An expression is obtained which relates the electrode potential of a metal with the heat of formation of a salt of the metal, and its solubility in the solvent. Examples are discussed. CH. ABS. (e)

Electrode potential of ascorbic acid. N. BEZSONOFF (J. Chim. phys., 1935, 32, 210—214).—The oxidation-reduction potential curve of ascorbic acid against log. concn. consists of two inclined straight lines. Results of previous workers fall on one or other of these. The effect is ascribed to the presence of two reducing groups in the mol. D. R. D.

Oxidation of solutions of quinol. II. Physico-chemical study of alkaline solutions of quinol. A. SAINT-MAXEN (J. Chim. phys., 1935, 32, 273—284; cf. A., 1934, 8).—Conductivity and spectrophotometric data are given for aq. mixtures of quinol and bases. Acid (I) and neutral salts of quinol are formed, (I) having max. oxidisability. An oxidation mechanism involving a quinonoid form is suggested. R. S.

Electrolytic reduction potentials of organic compounds. XX. Reduction potential of quinine. M. SHIKATA and E. TAGUCHI (J. Electrochem. Assoc. Japan, 1934, 2, 234—239; cf. this vol., 305).—Reduction of quinine (I) occurs in 3 stages, in the first of which 2 H are required to reduce 1 mol. of (I) at p_{H} 8.1—10.8; the reduction potentials obey the Nernst formula. CH. ABS. (e)

Oxidation and reduction with hydrogen peroxide. W. D. BANCROFT and N. F. MURPHY (J. Physical Chem., 1935, 39, 377—397).—It is shown that, when the true e.m.f. of any oxidising or reducing agent in any solution is > the true e.m.f. of H_2O_2 in the same solution, that substance will be reduced by H_2O_2 ; if the converse is the case then it will be oxidised. The true e.m.f., relatively to the H electrode, of H_2O_2 in *M*-HCl or *M*- H_2SO_4 is $+1.16 \pm 0.03$ volt and in *M*-KOH $+0.30 \pm 0.02$ volt, not correcting for the diffusion potential. The primary reaction in the O_2 - H_2 gas cell is the formation of H_2O_2 . H_2O_2 is considered as dissociating reversibly into $2\text{H} + \text{O} \cdot \text{O}$. The singly linked O_2 is in an activated state. 2H is the reducing and $\text{O} \cdot \text{O}$ the oxidising agent. Numerous chemical reactions in which H_2O_2 takes part are discussed. M. S. B.

Polarographic studies with the dropping mercury cathode. XLVI. Current-voltage curves using small anodes. V. MAJER (Coll. Czech. Chem. Comm., 1935, 7, 146—157).—As the size of the anode is diminished to that of the dropping cathode, the diffusion currents, *i*, are not altered, but the current increments corresponding with the deposition of various metals are displaced towards larger e.m.f. vals. as the result of increase of resistance, or concn. polarisation. Hg droplets falling on the anode change the potential owing to stirring and the negative charge carried by the droplets. With very small vols. of solution, *i* decreases with time. J. G. A. G.

Influence of depolarisers on the photovoltaic effect in cells containing Grignard reagent. J. HARTY (J. Physical Chem., 1935, 39, 355

369).—Electrodes of Cu, Zn, Al, Fe, Pb, and Pt have been used in combination with MgEtBr and MgPhBr as electrolytes and EtBr and EtI as depolarisers. Voltage, current, resistance, and capacitance response to light under different conditions have been studied. The results are in accordance with Hammond's assumption (A., 1930, 846) of the presence of a unimol. layer of electrolyte on the surface of the electrode. If light produces, in or near this layer, excited mols. with dipole moments different from those of normal mols., and capable of displacing the latter, a change in the potential of the electrode will result. If the life period is short the electrode will recover in the dark and return to normal potential. Change in a.c. resistance must be due to change in the electrolyte, which probably consists in a change in the solvation and hence in the mobility of the ion. The formation or alteration of a double layer in the light would explain negative capacitance response, and difference in orientation of the mols. would explain the existence of positive and negative voltage and current responses. M. S. B.

Hydrogen overvoltage. P. P. PORFIROV (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 386—392).—Observations on the electrolysis of H_2SO_4 between a platinised Pt anode and Hg cathode show the existence of a contact resistance; this, however, is only contributory to the H overvoltage and is due to a film of H_2 which begins to form at low cathode polarisation. It decreases with increase in the c.d. and its max. coincides with the beginning of the increase in the current strength on the potential-c.d. curve. W. R. A.

Delayed ionic discharge as cause of hydrogen overvoltage and of cathodic polarisation generally. A. SMITS (Z. physikal. Chem., 1935, 172, 470—472).—A claim for priority over Erdey-Grüz and Volmer (A., 1930, 1376). Smits' theory of electro-motive equilibria also explains the primary process of anodic polarisation. R. C.

Overvoltage. VIII. Overvoltage at bright platinum electrodes in $2\text{N-H}_2\text{SO}_4$ for low c.d. determined with an oscillograph. A. L. FERGUSON and G. M. CHEN (J. Physical Chem., 1935, 39, 191—198).—Charge and discharge curves showing the influence of time and c.d. are given. A comparison is made of the direct, commutator, and electro-magnetic interrupter methods of studying overvoltage. A distinction between discharge curves due to pure resistance, those due to true depolarisation, and those due to a combination of the two is attempted. It is concluded that there is no transfer resistance at the surface of smooth Pt electrodes. M. S. B.

Role of transitory resistance in the phenomenon of overvoltage of hydrogen. P. P. PORFIROV (J. Gen. Chem. Russ., 1934, 4, 1311—1321).—The transitory resistance (I) established at a Hg cathode as a result of the formation of a film (II) of H_2 is not the sole cause of H overvoltage. The commencement of (II) formation is associated with insignificant cathodic polarisation. For d.c. the val. of (I) diminishes with increase in the c.d. R. T.

Overvoltage of halogens. F. T. CHANG and H. WICK (Z. physikal. Chem., 1935, 172, 448—458).—Overvoltage has been observed for Cl on bright Pt, and Cl and Br on Ir. The anodic overvoltage curves have a logarithmic character, which for Pt, however, is obliterated at higher c.d. by passivity phenomena. The cathodic curves deviate from the logarithmic form in the same way as those for H overvoltage (cf. this vol., 705) and can be represented approx. by $\eta = a - b \log I - cI$, where η is the potential and I the current and a , b , and c are consts. Possibly the term cI is due to supplementary retardation of $\text{X}_2 \rightarrow 2\text{X}$. The results obtained cannot be covered either by Tafel's or Volmer's theory of overvoltage. R. C.

Effect of an electric current on a protein cylinder according to Bois-Reymond. W. HABENICHT (Protoplasma, 1934, 22, 321—336).—A study has been made of the changes involved in the anodic shrinkage and cathodic expansion of small cylinders of ovalbumin carrying an electric current. The migration of H_2O and the effect of products of hydrolysis are considered. A. G. P.

Electromotive force produced by the flow of water vapour. A. MILHOUD (Compt. rend., 1935, 200, 1091—1093).—The production of electrical effects by the turbulent escape of H_2O vapour, through a blow-pipe of constricted section, has been confirmed (cf. *ibid.*, 1934, 198, 1586). In the presence of droplets an e.m.f. is set up which depends on the electrical conductivity of the solution. The concn. of the solution must be $> 0.001\text{N}$. For any one solution $E/(P_c - p)$ is a const. where E = e.m.f., P_c = crit. pressure, and p = escaping pressure. The acidity of the solution affects the polarity. H_2O alone and acid solutions give a positive and basic solutions a negative jet. With such solutions 0.01 volt may be obtained. M. S. B.

Absolute rate of a chemical reaction. W. H. RODEBUSH (J. Chem. Physics, 1935, 3, 242).—The different methods of approach to the study of the factors determining the abs. rate of a chemical reaction are indicated. M. S. B.

Reaction mechanisms. C. C. STEFFENS (J. Chem. Educ., 1935, 12, 115—120).—A review of recent ideas on reaction rates and mechanisms, particularly with regard to homogeneous gas reactions. L. S. T.

Application of Bodenstein's method of stationary concentrations of intermediate products in reaction kinetics. J. A. CHRISTIANSEN (Z. physikal. Chem., 1935, B, 28, 303—310).—The concept of "reaction sequences" is discussed and illustrated. R. C.

Measurement of reaction kinetics by means of light absorption. S. BODFORSS (Svensk Kem. Tidskr., 1935, 47, 33—41).—A crit. survey of the methods available, especially those involving photo-electric cells. R. P. B.

Reaction cycles. A. SKRABAL (Monatsh., 1935, 65, 275—310).—Theoretical. A mathematical study of reactions the simplest of which is exemplified by the interconversion of three tautomers. E. S. H.

Mechanism of self-propagating chain reactions. K. K. ANDREEV and J. B. CHARITON (Trans. Faraday Soc., 1935, **31**, 797—804; cf. A., 1934, 602).—Theoretical. An attempt is made to estimate the size of the localisation of chain centres required to initiate the detonation of an explosive by a macro-chain mechanism. F. L. U.

Kinetics of heterogeneous ortho-para-hydrogen transformation on solid oxygen. E. CREMER (Z. physikal. Chem., 1935, **B**, **28**, 383—392; cf. this vol., 586).—The rate of transformation at H_2 pressures of 50—760 mm. over solid O_2 at 20° abs. as catalyst has been measured. The results indicate that reaction occurs in an adsorbed film saturated with $o\text{-}H_2$. There is very little adsorption of $p\text{-}H_2$ or adsorption displacement of $o\text{-}$ by $p\text{-}H_2$. The heat of adsorption of $o\text{-}H_2$ is 428 ± 10 and that of $p\text{-}H_2$ < 326 g.-cal. The velocity is 10^4 — 10^5 as great as would be deduced from the frequency of collisions with the catalyst surface, the reason being that in the adsorbed state as compared with the gaseous state the ratio of the duration of collision between H and O mols., τ , to the time between two collisions is shifted in favour of τ , because in the adsorbed film the H is always in the sphere of action of the O. R. C.

Effect of frequency of the electric field on the velocity of combustion of gases. A. E. MALINOVSKI, V. S. ROSSIKHIN, and V. P. TIMKOVSKI (Physikal. Z. Sovietunion, 1934, **5**, 902—905).—The burning of a 25% C_2H_2 —75% air mixture was studied in fields of frequency 10^5 — 0.8×10^7 Hertz units. The velocity was lowered 6.7% at 10^5 and 0.6% at 10^7 Hertz units. CH. ABS. (e)

Lower limit of ignition of hydrogen-oxygen mixtures. W. E. GARNER and H. J. WILLAVOYS (Trans. Faraday Soc., 1935, **31**, 805—811; cf. A., 1931, 688).—The lower limits for ignition of H_2 — O_2 mixtures in mol. ratios 3:1, 2:1, 1:1, and 1:2 in the temp. range 350 — 600° are lower than those found by previous workers. The activation energy decreases with rise of temp. from 15 to 7 kg.-cal. Vals. of the limits near the crit. ignition pressure are greatly influenced by the state of the SiO_2 surface. The lower limit depends more on the O_2 pressure than on any other single factor. F. L. U.

Ignition of gaseous mixtures by the corona discharge. R. W. SLOANE (Phil. Mag., 1935, [vii], **19**, 998—1011).—A coal gas-air mixture (I) could not be ignited by discharges between electrodes of cold glass, ebonite, or paraffin wax, but white fibre, glass at 100° , or slate was effective. The variation of the least igniting % of coal gas with electrode temp. and conductivity has been determined, and igniting energies calc. Igniting currents are given for the steady corona discharge between slate electrodes in the most easily ignited (I). R. S.

Highly-attenuated flames of potassium and iodine vapours. E. ROTH and G. SCHAY (Z. physikal. Chem., 1935, **B**, **28**, 323—331).—These are essentially similar to $K+Cl_2$ and $K+Br_2$ flames (cf. A., 1933, 206). One of the differences is that the energy of the secondary gas reaction, $K_2+I=KI+K$, is insufficient to excite the violet K doublet, and there-

fore both the first stage of the reaction, $K+I_2=KI+I$, and the second, $K+I=KI$, excite only the red doublet. From the distribution of the KI formed and the variation of light yield with pressure and temp. the velocity coeffs. of the various reactions have been calc. The heat of dissociation of K_2 is calc. to be 18.7 kg.-cal. The mechanism previously suggested for the continuous light emission must be rejected; it must be supposed instead that a highly excited K atom is formed from a K ion and an electron and remains for a relatively long time in excited states, the excess energy being radiated away in a continuous manner by interaction with a K atom. R. C.

Highly-attenuated flames of potassium and mercuric chloride vapours. I. BERGER and G. SCHAY (Z. physikal. Chem., 1935, **B**, **28**, 332—339).—The mechanism is completely analogous to that of $Na+HgCl_2$ flames: $K+HgCl_2=KCl+HgCl$, $K+HgCl=KCl+Hg$ (cf. A., 1928, 1339). The second stage is responsible for the emission of the red and violet K doublets, whilst the first causes no light emission. Both red and violet emission exhibit the characteristics of flame type II. The emission of the red doublet is by primary excitation of the 3^2D level, not direct. There is an intense bluish glow on the wall, due to reaction of $HgCl_2$ mols. with K vapour there. A second wall reaction occurs between $HgCl$ radicals and K vapour, and is responsible for the electrical conductivity of the flame and the continuous emission. R. C.

Thermal decomposition of acetaldehyde and propaldehyde. F. PATAT and H. SACHSSE (Naturwiss., 1935, **23**, 247—248).—The theory of Rice and Herzfeld (A., 1934, 369) that the thermal decomp. of $MeCHO$ involves the formation of free radicals, with a subsequent chain mechanism, is disproved by the fact that $[H]$ during the decomp. is $< 4 \times 10^{-13}$ g.-mol. per litre. To bring this result into agreement with a chain mechanism would require a heat of activation of 29,000 g.-cal. for the reaction $CH_3+H_2=CH_4+H$, which is too high. Similar results were obtained with $EtCHO$. A. J. M.

Thermal decomposition of acetaldehyde. M. W. TRAVERS (Nature, 1935, **135**, 511). L. S. T.

Critical phenomena in the oxidation and self-inflammation of hydrocarbons. M. NEUMANN and B. ARVAVOV (Nature, 1935, **135**, 655—656).—The velocity of oxidation of C_5H_{12} in $C_5H_{12}+8O_2$ mixtures has been studied in quartz vessels at various pressures below the ignition limit over a temp. range 300 — 500° . At low temp. there is a rapid reaction, accompanied by chemiluminescence, after a fairly long induction period. The rate of reaction increases rapidly with a rise in temp. up to a max. at approx. 340° . From 350° to 500° increase is slow and after 500° , rapid. With increasing pressure two regions of thermal ignition at low, approx. 300° , and at high, approx. 500° , temp. are thus to be expected. The results support the view that in addition to the direct oxidation there is a catalytic reaction involved. L. S. T.

Thermal decomposition of nitrosyl chloride. G. WADDINGTON and R. C. TOLMAN (J. Amer. Chem.

Soc., 1935, 57, 689—692).—The homogeneous reaction between 150.1° and 250.7° is a bimol. decomp. accompanied by a termol. reverse reaction. When the energy of activation is expressed in g.-cal., the sp. rate const. as a function of temp. for the decomp. reaction is given by $k=4.3 \times 10^{11} T^{1/2} e^{-24,000/R/T}$ c.c. mol.⁻¹ sec.⁻¹ E. S. H.

Dependence of methane-oxygen low-pressure explosion limit on nature of reaction vessel surface. H. H. STORCH (J. Amer. Chem. Soc., 1935, 57, 685—686).—The limiting pressures vary widely with the treatment of the quartz surface of the reaction vessel. E. S. H.

Chemical kinetics of the reaction of oxygen with hydrogen and with deuterium. L. S. KASSEL and H. H. STORCH (J. Amer. Chem. Soc., 1935, 57, 672—678).—Theoretical. The theory of chain reactions for which the chains are broken at the wall at only a fraction of the total no. of collisions is developed and shown to differ from the case where every collision leads to destruction. The possible chain mechanisms for the explosion limits of H₂-O₂ have been investigated. Published experiments involving D₂ are analysed. E. S. H.

Kinetics of the reaction between oxyhalogen and halogen acids. J. HIRADE (Bull. Chem. Soc. Japan, 1935, 10, 97—121).—The following reactions have been studied in the presence of neutral salts and also of other acids: HClO₃ with HCl and HBr, HBrO₃ with HCl, and HIO₃ with HCl and HBr. The reaction velocity is expressed by the formula $-d(XO_3)/dt = kF(XO_3)^x(Y)^y(H)^z$, where F is Bronsted's kinetic activity factor and x , y , and z are 1, 1, and 2 for reactions HClO₃-HY, HBrO₃-HBr, and HIO₃-HI, 1, 2, 2 for HBrO₃-HCl and HBrO₃-HI, 1, 4, 4 for HIO₃-HCl, and 1, 2, 3 for HIO₃-HBr. The velocity coeffs. for the reduction of any one HXO₃ are in the order HI>HBr>HCl, following the order of the reduction potentials, and for the oxidation of any one HY, HIO₃>HBrO₃>HClO₃, with the single exception of the reaction HIO₃-HCl which takes place with difficulty. The primary process of the HClO₃-HCl reaction is $ClO_3^- + Cl^- + 2H^+ = HClO_3 + HCl$ HClO₂+HClO. Several secondary reactions occur to a varying extent, depending on conditions. Reaction mechanisms are also suggested for the other pairs of reactants. M. S. B.

Velocity of saponification of some simple triglycerides by ethyl-alcoholic potash. P. E. VERRADE and A. H. A. DE WILLIGEN (Rec. trav. chim., 1935, 54, 353—357).—The velocity coeffs. of saponification by EtOH-KOH of trioctoin, triononoin, tridecain, triundecain, trilaurein, and tritridecain are the same at 37.5°. The triglycerides form Et esters of the glyceride acid with EtOH very rapidly in presence of KOH, and these esters are saponified at the same rate. R. S. B.

Neutral salt action of the reaction between acetylglucolate and hydroxyl ions in dilute solution. A. VON KISS (Rec. trav. chim., 1935, 54, 337—344).—In presence of Li⁺, Na⁺, and K⁺ (as hydroxides) at ionic strengths (μ) 0.0014—0.03 the

reaction between OAc-CH₂-CO₂' and OH' at 0.0007—0.02M at 25° follows the simple Bronsted-Debye-Hückel formula (a), but there is a sp. action for each alkali metal ion, even at $\mu=0.0014$. Ca⁺⁺, Sr⁺⁺, and Ba⁺⁺, $\mu=0.0021$ —0.045, disagree with (a) and with the formula corr. for ionic size (b). With $\mu > 0.03$ Li⁺, Na⁺, and K⁺ agree with (b). On account of the sp. action of ions mixtures of hydroxides and salts give reaction coeffs. which do not agree with (a) and (b). R. S. B.

Carbon dioxide cleavage from dibromomalononic acid. (Miss) J. MUUS (J. Physical Chem., 1935, 39, 343—353).—The velocity of the reaction $CBr_2(CO_2H)_2 \rightarrow CHBr_2 \cdot CO_2H + CO_2$ has been determined at 25° for different p_H and different salt concns. At const. p_H the reaction is unimol. Concn. dissociation consts. of CBr₂(CO₂H)₂, determined electrometrically for salt concns. 0.1, 0.2, and 1.0N, are K_1 1 and K_2 9.0×10^{-3} , 1.5×10^{-2} , and 1.70×10^{-2} , respectively. The results are in agreement with the assumption that the reaction is due to the spontaneous decomp. of CBr₂(CO₂H)·CO₂'. The temp. coeff. is 4.01, giving an energy of activation of 25,000 g.-cal. The following concn. dissociation consts. have also been determined at 25°: glycine in 0.2N-salt 4.68×10^{-3} , citric acid in N-salt K_1 1.71×10^{-3} , K_2 8.05×10^{-5} , AcOH in N-salt 2.95×10^{-5} . M. S. B.

Fission of carbon chains. Thermal decomposition of hydrocarbons.—See this vol., 727.

Relationships between affinity and velocity of reaction. J. R. VELASCO (Anal. Fis. Quim., 1935, 32, 345—369).—Measurements of the velocity of reaction between diphenylsemicarbazide and toluquinone, benzoquinone, 2:6-dichlorobenzoquinone, and tolylsulphoquinone in glacial AcOH at 20°, 30°, and 40° indicate that $\log k_2/k_1 = 16.14(E_2 - E_1)$, where k_1 and k_2 are the velocity coeffs. and E_1 and E_2 are the oxidation potentials for two different quinones. D. R. D.

Temperature increment of reaction velocity in reactions of type $A_{solid} = B_{solid} + C_{gas}$. J. ZAWADZKI and S. BRETSNAJDER (Z. Elektrochem., 1935, 41, 215—223; cf. A., 1933, 911).—The velocity of decomp. of CaCO₃ (calcite) has been measured over the range 690—840° both in a vac. and at const. pressure. The temp. increment of the velocity=heat of reaction. Attention is directed to the similarity of condensation and vaporisation processes to combination and decomp. in reactions of the above type, with respect to rate of formation of nuclei and to temp. relations. F. L. U.

Kinetics of the electrochemical chlorination of benzene. W. JEUNEHOMME (J. Chim. phys., 1935, 32, 173—198).—PhCl and H are the primary products of electrolysis of HCl in MeOH containing C₆H₆. The chlorination proceeds partly by the homogeneous reaction of free dissolved Cl₂ with C₆H₆ near the anode and partly by direct reaction of Cl and C₆H₆ on the anode surface. In the former reaction the disappearance of Cl₂ follows a simple unimol. law and is accelerated by HCl; at low [HCl] MeOH is attacked rather than C₆H₆. On the electrode surface (bright Pt) the proportion of Cl atoms reacting directly with

C_6H_6 mols. is equal to the proportion by vol. of C_6H_6 in the liquid and the rate is independent of $[HCl]$.

D. R. D.

Apparent rates of oxidation of massicot and litharge. K. C. CHANG and Y. F. SU (J. Chinese Chem. Soc., 1935, 3, 86—94).—Differential equations representing the course of the reaction and the reaction const. at various temp. between 350° and 500° have been determined for the oxidation of the two forms of PbO .

J. W. S.

Ageing of ferric orthohydroxide, and its conversion into α - $FeO.H$ as a phenomenon of discontinuous crystallisation or devitrification. A. KRAUSE [with W. ŚWIATKOWSKA, H. TORNO, and J. STOCKÓWNA] (Rocz. Chem., 1935, 15, 15—25).—Determinations of the velocity of transformation of α - $Fe(OH)_3$ (I) into goethite (II) indicate that the process depends on formation of nuclei of amorphous cyclic polyferrous acids, which then undergo crystallisation with the production of (II). (I) gels are the most stable at the isoelectric point.

R. T.

Hydrolysis of secondary and tertiary alkyl halides. E. D. HUGHES (J. Amer. Chem. Soc., 1935, 57, 708—709).—Hydrolysis of Me and Et halides by dil. aq. $EtOH-KOH$ is unimol., that of Pr^iBr , Bu^iBr , and CMe_2EtBr bimol. The theory of Ingold et al. (A., 1933, 701) is applied to these and other results.

R. S. C.

Reactivity and constitution of nitric and sulphuric acids. V. Sulphonating action of sulphuric acid in aqueous and acetic solutions. VI. Viscosity, electrical conductivity, and Raman spectrum of mixtures of sulphuric and acetic acids. E. BRINER, J. W. HOEKSTRA, and B. SUSZ (Helv. Chim. Acta, 1935, 18, 684—693, 693—700; cf. this vol., 564).—V. The velocity of sulphonation of $PhOH$ is greater in $AcOH$ than in H_2O ; the temp. coeff. is greater in H_2O . The influence of concn. has also been studied. The facts suggest that non-dissociated H_2SO_4 is the sulphonating agent.

VI. The variation of properties with composition indicates the existence of $H_2SO_4.AcOH$. E. S. H.

Hydrolysis of ethyl iodide. J. GREENSPAN, S. LIOTTA, and V. K. LA MER (Trans. Faraday Soc., 1935, 31, 824—825).—Hydrolysis of EtI by dil. aq. $NaOH$ proceeds normally and quantitatively. Results reported by Moelwyn-Hughes (A., 1934, 152) are incorrect.

F. L. U.

Catalytic effect of hydrogen on the carbon monoxide flame. B. W. BRADFORD (Chem. and Ind., 1935, 469; cf. A., 1934, 145).—A reply (cf. this vol., 588). The walls did not have an appreciable differential effect on the flame reactions. J. G. A. G.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. III. Effect of unipolar substituents on the critical energy and probability factors in the interaction of benzyl bromide with pyridine and α -picoline in various solvents. J. W. BAKER and W. S. NATHAN (J.C.S., 1935, 519—527; cf. A., 1934, 970).—The supposed catalysis by salts (*loc. cit.*)

is due to the equilibrium $ArBr + ArC_5H_5N^+NO_3^- \rightleftharpoons$

$ArO-NO_2 + ArC_5H_5N^+Br^-$; and benzylpyridinium bromide catalyses slightly the reaction between CH_2PhBr and C_5H_5N in dry $COMe_2$ (I). From velocity measurements at 0—40°, the energy of activation of the reaction of p - $R-C_6H_4-CH_2Br$ ($R=H, Me, NO_2$) with C_5H_5N (II) and α -picoline (III) is 11.9—12.48 kg.-cal. in (I), 13.68—13.84 in aq. 90% $COMe_2$ (IV), and 15.3—16.0 in aq. 90% $EtOH$ (V). The probability factors ($\times 10^6$) are 0.047—0.139 with (III) and 0.515—0.87 with (II) in (I), 11.7—23.17 with (II) in (IV), and 91.3—836.7 with (II) in (V). These results are discussed with reference to the mechanism in ionising and non-ionising media.

J. G. A. G.

Exchange between ammonia and deuterium on catalytic iron surfaces. H. S. TAYLOR and J. C. JUNGERS (J. Amer. Chem. Soc., 1935, 57, 660—661).—The exchange occurs at an $Fe-K_2O-Al_2O_3$ catalyst at room temp., but not at fused quartz surfaces even at 300°. The bearing on the problem of kinetics of NH_3 synthesis is discussed.

E. S. H.

Exchange reactions between heavy hydrogen and hydrogen adsorbed in solids. A. FARKAS and L. FARKAS (Trans. Faraday Soc., 1935, 31, 821—824).—At temp. $> 600^\circ$ D_2 can undergo an exchange reaction with H_2 sorbed in SiO_2 or Pt even when these materials have been thoroughly outgassed in a high vac. Attention is directed to possible consequences of this effect.

F. L. U.

Hydrogen catalysis on nickel. I. Comparison of rates of para-hydrogen transformation and $H_2 + D_2 = 2HD$ on nickel. II. Sintering experiments. E. FAJANS (Z. physikal. Chem., 1935, B, 28, 239—251, 252—256).—I. Change in gas temp. at const. catalyst temp. affects the rate of the p - H_2 transformation (I) on Ni only to the extent that it alters the collision no. Comparing the effect of temp. on (I) and $H_2 + D_2 = 2HD$ (II) shows the heat of activation of (II) to be the greater by ~ 1410 g.-cal. The apparent order of both reactions is approx. the same (~ 0.7) and at 14° the ratio of the velocity coeff. of (I) to that of (II) is approx. const. at ~ 3 for catalysts of widely varying activity. It is concluded that both reactions have the same mechanism, involving passage through the at. state (III). The transition into (III) possibly requires a heat of activation, which for D_2 is $>$ for H_2 owing to the smaller zero point energy.

II. The sintering of the catalyst for (I) begins at temp. which are the lower the higher is its activity, A. In sintering at a given temp. A reaches a const. val. after the first ten min., which is independent of the initial A, but varies with the temp., i.e., with every sintering temp. corresponds a definite state of surface activity. The catalyst is reversibly poisoned when heated in H_2 .

R. C.

Decomposition of deuterio-ammonia on tungsten filaments. J. C. JUNGERS and H. S. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 679—681).—The decomp. at about 950° abs. and 3.5—15 cm. is an approx. zero-order reaction, which is slower than that of NH_3 under the same conditions in the ratio 1 : 1.0. The decrease in rate of decomp. in mixed ammonias

\propto the D content. The temp. coeffs. of NH_3 and ND_3 are the same. E. S. H.

Polymerisation of formaldehyde. J. E. CARRUTHERS and R. G. W. NORRISH (*Nature*, 1935, 135, 582—583).—Small amounts of HCO_2H (I) and of AcOH accelerate the polymerisation of CH_2O . With (I) the reaction is approx. unimol. and the rate is practically unaffected by packing the vessel with quartz tubes. (I) is not appreciably consumed. The polymerisation thus induced by (I) is regarded as a chain mechanism in which the starting of reaction chains and also the branching are controlled kinetically by (I). With MeCHO vapour at room temp. a similar polymerisation is induced by (I).

L. S. T.

Application of catalytic reactions in qualitative and quantitative microanalysis. R. LUCAS and F. GRASSNER (*Mikrochem.*, 1935, 17, 237—261).—A review.

Adsorption and catalysis. M. POLANYI (J.S.C.I., 1935, 54, 123—124r).—The energy relationships necessary for surface catalysis are discussed, with special reference to $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$. The most active catalytic surfaces for the H interchange are those in which the H-metal linking is of the order of 50,000 g.-cal. Metals are therefore divided into two groups: those in which the surface valencies are respectively weaker than 50,000 g.-cal. (slow catalysts) and about 50,000 g.-cal. (good catalysts). The possibility of catalytic reactions occurring by a dissolution process of the H in the at. state in the surface layers of the metal is discussed. Contrary to the various theories on activated adsorption, catalytic activity should not be a strong, but an extremely weak, adsorption.

Surface reactions at very low pressures. I. Platinum-chlorine. A. Processes on the surface of the metal in the form of filament. C. NOGAREDA (*Anal. Fis. Quím.*, 1934, 32, 286—344).— Cl_2 at approx. 10^{-6} mm. pressure was brought in contact with a heated Pt filament in an ice-cooled vessel. Examination of the velocity of the reaction and nature of the products indicates that at 600—900° the simple second-order reaction $\text{Pt} + 2\text{Cl}_2 \rightarrow \text{PtCl}_4$ occurs and adsorption is absent. At 1200°, adsorption of at. Cl takes place, followed by the zero-order reaction $\text{Pt} + 2\text{Cl}$ (adsorbed) $\rightarrow \text{PtCl}_2$, the PtCl_2 being subsequently oxidised to PtCl_4 (first-order reaction). D. R. D.

Catalytic activities of nickel-copper catalysts. K. YOSHIKAWA (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 308—312).—Ni and Ni-Cu catalysts have been progressively poisoned by thiophen. The no. of highly reactive centres is diminished by the addition of Cu to Ni, whilst the no. of moderately active centres and the total surface available for reaction are increased. R. S.

Heterogeneous catalysis in gas reactions, reactions between gases and non-gaseous substances, and the poisoning of catalysts. M. POURBAIX (*Bull. Soc. Belge Ing. Ind.*, 1934, No. 1—8, 67 pp.; *Chem. Zentr.*, 1934, ii, 3586—3587).—A review and discussion. H. J. E.

Catalytic decomposition of acetaldehyde. M. S. EBERT (*J. Physical Chem.*, 1935, 39, 421—424).—Of many catalysts examined, Ni, obtained by pptg. aq. $\text{Ni}(\text{NO}_3)_2$ with NaOH and reducing at 400°, was found to be the most satisfactory for the reaction $\text{MeCHO} \rightarrow \text{CO} + \text{CH}_4$ at 175—225°. Equilibrium conditions appear to be obtained, but attempts to reach them by synthesis were unsuccessful.

M. S. B.

Activity of chromium catalysts.—See B., 1935, 403.

Hydrogenation catalysts—See B., 1935, 403.

Activity of mixed catalysts in the simultaneous dehydration of ethyl alcohol and ammonia.—See this vol., 742.

Causes of increase in activity of platinum gauze in the oxidation of ammonia.—See B., 1935, 402.

[Catalytic] hydrogenation of acetylene.—See B., 1935, 394.

[Catalytic] transformation of carbon monoxide and carbon dioxide into methane at high pressure.—See B., 1935, 390.

Catalytic oxidation of methyl alcohol to formaldehyde.—See B., 1935, 442.

Autoxidation of α -pinene.—See this vol., 754.

Concentration of tritium (H^3). P. W. SELWOOD, H. S. TAYLOR, W. W. LOZIER, and W. BLEAKNEY (*J. Amer. Chem. Soc.*, 1935, 57, 780).—The concn. of H^3 has been increased to 1 in 10^4 by electrolysing 75 metric tons of H_2O down to 0.5 c.c. The abundance of H^3 in H_2O is 7 in 10^{10} . E. S. H.

Electrolytic concentration of oxygen isotopes. P. W. SELWOOD, H. S. TAYLOR, J. A. HIPPLE, jun., and W. BLEAKNEY (*J. Amer. Chem. Soc.*, 1935, 57, 642—644).—The concn. of O^{18} was increased only 10% by electrolysing 117 litres of H_2O down to 1 c.c. The ratio of sp. rates of discharge of O^{16} and O^{18} is 1.01. E. S. H.

Electrodeposition of (A) niobium, (B) tantalum. N. A. ISGARISHEV (*J. Gen. Chem. Russ.*, 1934, 4, 1415—1421, 1422—1427).—(A) [with G. E. KAPLAN]. During electrolysis of solutions containing Nb and Ta, part of the Nb is deposited as a bright, adherent coating on the cathode, an equal amount undergoes pptn. from the electrolyte, whilst the greater part is converted into a non-electrolytic form, not pptd. by tannin. Ta is not deposited.

(B) [with A. F. PREDE]. Ta is electrodeposited on Cu cathodes from solutions at 70—80°, containing 50% of resorcinol (I); deposition commences 1 hr. after passage of current, and does not take place when the anolyte and catholyte are separated by a diaphragm, pointing to the existence of a preparatory process in the anolyte. Satisfactory deposition is not obtained when a no. of other substances are substituted for (I). R. T.

Metallic gadolinium. F. TROMBE (*Bull. Soc. chim.*, 1935, [v], 2, 660—664).—A button of pure Gd (Si 0.7, Fe 0.3%) was obtained by electrolysing a bath containing GdCl_3 45, KCl 44, and LiCl 12% at

625—675° in a C crucible (serving as anode), using molten Cd (in a CaF_2 cup) as cathode, and distilling off the Cd from the resultant alloy in vac. (< 0.001 mm.) at 450—1240°. D. R. D.

Electro-deposition of chromium from chromic acid solutions.—See B., 1935, 413.

Oxidation of sulphur dioxide in a high-voltage arc discharge. L. A. KOLODKINA and N. N. NECHAEVA (J. Phys. Chem. U.S.S.R., 1933, 4, 845—853).—For the same power output more SO_3 is obtained at higher c.d. Decreasing the gas velocity or $[\text{SO}_2]$ in the SO_2 -air mixture increases the yield to 95—98% at low velocities and $[\text{SO}_2]$. Voltages from 9.5 to 34 kv. were used. For practical purposes 65—70% oxidation is possible. CH. ABS. (e)

Oxidation of sulphur dioxide in a high-frequency discharge. N. ZALOGIN and N. NECHAEVA (J. Phys. Chem. U.S.S.R., 1933, 4, 832—844).—The total O_3 yield increased with the velocity of the air stream, but the % yield decreased linearly. The yield of SO_3 (I) from SO_2 decreased linearly with increasing $[\text{SO}_2]$ in the gas mixture, and velocity of gas stream. Increasing H_2O vapour concn. increased (I) as an S-curve function. Glycerol and EtOH were used to stabilise the standard aq. Na_2SO_3 used for O_3 analysis. CH. ABS. (e)

Relation between p_H and photographic sensitivity. A. STEIGMANN (Phot. Ind., 1934, 32, 93).—The increased sensitivity of emulsions with an alkaline reaction is attributed (1) to complexes from the natural sensitizers of the gelatin (I) and the Ag halides yielding Ag_2S only in an alkaline medium; (2) to the decrease in protective action of (I) at 7—8.9 compared with p_H 5—6.5, which facilitates ripening. CH. ABS. (e)

[Photographic] density surfaces by physical development. H. ARENS (Z. wiss. Phot., 1935, 33, 281—286).—Densities are shown as contour lines (by projection) on $\log I$ - $\log t$ graphs, for fine-grain slow emulsions with chemical and with physical development, and for a large-grain emulsion by physical development; the only differences are those of degree. For $\log I > 0$, solarisation is found when proceeding along the time axis, but not when proceeding along a light-intensity axis for a given $\log t$ val. J. L.

Photographic development. W. MEIDINGER (Physikal. Z., 1935, 36, 312—320).—The kinetics of development of a very slow AgBr-gelatin emulsion (without AgI) with a metol-quinol developer containing excess of KBr has been investigated. The mean time for reduction of a nucleus over the whole range of the blackening curve, including solarisation, is independent of the length of exposure. The process of development depends on (a) the probability of the commencement of development, and (b) the reduction time. (b) is independent of length of exposure if conditions of development are the same. The effect of solarisation (I) is due to a decrease in (a), and not an increase in (b). The decrease in (I) due to NO_2 is due to increase in (a). The method might be employed to determine the distribution of the Ag particles in their primary separation from the

nuclei, and the structure of the blackening curve for physical development. A. J. M.

Influence of cations on the sensitivity of photographic emulsions. A. CHARRIOU and (MLLE.) S. VALETTE (Compt. rend., 1935, 200, 1189—1191).—The sensitivity (I) of a photographic emulsion ($\text{AgI}:\text{AgBr}=0.0465$) is unaffected by Cd, Al, or Mg. Mg diminishes the rate of formation of chemical fog (II). (I) and (II) are decreased by Th, Fe^{+++} , Zr, As, Pb, Co, and Cu, in increasing order of efficiency; (I) is decreased and (II) increased by Tl, NO_2 , Au, Ni, Fe^{++} , and Hg^{++} . Hg^+ , very low concns. of Fe^{++} , and Ag increase (I). Ag also increases (II).

J. W. S.

Pressure effect on photographic sensitivity. N. T. ZHANG and T. L. CHAO (Chinese J. Physics, 1934, 1, 66—75).—Pressures (p) of 0—1250 kg. per sq. cm. reduce the photographic sensitivity in the region of normal and over-exposure, and of reversal. For $p > 200$ kg. per sq. cm. $E_p/E = a + \alpha p$, where E is the illumination required to produce the same optical density without pressure as that obtained when the illumination E_0 is used with pressure, and a and α are consts. The influence of p decreases with λ ; with the same λ a and α vary greatly with the type of film. Applications are discussed.

R. S. B.

Ascorbic acid (vitamin-C) and photographic developing action. C. E. BILLS (Science, 1935, 81, 257—258).—Ascorbic acid (I) in aq. Na_2SO_3 and aq. Na_2CO_3 is a rapid developer which produces a black image and considerable fog. The addition of 20 mg. of KBr per litre restrains fog, retards development, and changes the colour of the image from black to brown. The action on various photographic papers is described. The bearing of the developing action of (I) on the theory relating developing function to mol. configuration is discussed.

L. S. T.

Influence of alkali iodides on the properties of photographic emulsions. A. CHARRIOU and (MLLE.) S. VALETTE (Compt. rend., 1935, 200, 916—918; cf. B., 1933, 333).—With increasing $[\text{I}^-]$ the sensitivity of a photographic emulsion (I) first decreases, passes through a min., and then increases. The greater is $[\text{AgI}]$ in (I) the less is the initial fall with addition of I^- and the greater is the increase of sensitivity with increasing $[\text{I}^-]$ after the min. Increasing $[\text{I}^-]$ also causes increasing tendency for solarisation up to the concn. which yields min. sensitivity, further additions decreasing this tendency. The observations invalidate the theories which attribute the deactivating properties of halides to halogenation of particles of Ag liberated by reduction of AgBr during prep. of (I).

J. W. S.

Decomposition of silver-gelatin complex and its significance for the light-sensitivity [of photographic emulsions]. W. SCHLEUSSNER (Z. wiss. Phot., 1935, 34, 63—71).—Ag ions form a complex with gelatin (Ag gelatinate) which decomposes in the warm to form a stabler complex (I) ("primary Ag") which is not decomposed by KCN. The rate of formation of (I) (in presence of a very little AgBr in a AgNO_3 -gelatin emulsion, a max. is reached in 2 hr.) is similar to the growth of sensitivity to light

and of fog developable in metol. Quinol gives no fog, small nuclei only being developed. The action of light appears to be the formation of large nuclei from (I), by liberation and wandering of electrons.

J. L.

Artificial photographic light sources. O. REEB (Z. wiss. Phot., 1935, 34, 77—87).—Various kinds of continuous light and short-emission sources are discussed and compared with regard to colour temp. and energy distribution and actinic val.

J. L.

Ultra-violet photolysis of fructose in pure and aqueous glycerol. R. CANTIENI (Helv. Chim. Acta, 1935, 18, 473—475).—Fructose in glycerol solution is decomposed by ultra-violet light with evolution of gas. With increasing addition of H_2O the rate of decomp. increases.

E. S. H.

Effect of temperature on the photochemical decomposition of acetone. C. A. WINKLER (Trans. Faraday Soc., 1935, 31, 761—765).—The quantum efficiency in the decomp. of $COMe_2$ over the range 2200—3300 Å. is five times as great at 100° as it is at 60°, and maintains the higher val. up to 400°. The influence of temp. on the rate of decomp. is much greater for higher than for lower λ . It is suggested that the efficiency increases with rise of temp. more rapidly for quanta of small than of large energy content, owing to the greater importance of the thermal contribution in the former case.

F. L. U.

Internal light filters. Effect of azo-dyes on the photolysis of diazo-compounds. M. HORIO and S. YAMASHITA (Z. wiss. Phot., 1935, 33, 273—280).—The photolysis of *p*-diazodiphenylamine sulphate and of 1:2:4-diazonaphtholsulphonic acid in aq. solutions, in the presence of varying amounts of Crystal-scarlet 6 RA extra, and of Orange II, has been studied by measurement of the absorption and the extinction coeffs. The source of light was a filtered Hg-vapour lamp, giving the lines 4360 and 4050 Å. The velocities of decomp. found agree with those calc. from the Luther-Weigert-Langendijk formulæ.

J. L.

Primary photochemical reactions. VI. Photochemical decomposition of cyclic ketones. (Miss) O. D. SALTMARSH and R. G. W. NORRISH (J.C.S., 1935, 455—459).—*cyclo*-Heptanone (I), -hexanone (II) and -pentanone (III) absorb light of λ 3500—2000 Å., and in the full radiation of the Hg lamp the decomp. of the vapours are: (1) (I) \rightarrow *cyclo*hexane + CO (80—95%) accompanied by (I) \rightarrow $2C_3H_6 + CO$ (4%), (2) (II) \rightarrow *cyclopentane* + CO (92%) accompanied by (I) \rightarrow $C_2H_4 + C_3H_6 + CO$ (8%), and (3) (III) \rightarrow $2C_2H_4 + CO$ (50%) with (III) \rightarrow $C_4H_8 + CO$ (50%). The CO is eliminated by the almost simultaneous rupture of the two linkings uniting it to the ring and, since the changes are either exothermic or thermo-neutral, it is suggested that the vibrations of the resulting cyclic hydrocarbon lead to slight decomp. in cases (1) and (2) and complete decomp. or isomerisation in case (3).

J. G. A. G.

Relations between the optical properties of the medium and the photochemical constants of tetraphenylrubene. C. DUFRASSE and M. BADOCHÉ (Compt. rend., 1935, 200, 1103—1105).—The relative

rates of photochemical oxidation of tetraphenylrubene have been determined in different solvents and compared with the variations in the position of max. absorption (I). In general the oxidation is more rapid the nearer (I) approaches the red, but no definite relations can be deduced. The behaviour of mixtures of solvents has also been studied. The positive activity of CS_2 is strongly diminished by Et_2O , but the negative activity of $PhNO_2$ is not affected by dilution.

M. S. B.

Photosynthesis of formaldehyde in tropical sunlight. V. GORE (J. Physical Chem., 1935, 39, 399—402).—The photo-reduction of nascent CO_2 to form CH_2O requires the presence of nascent H. An apparatus for exposing CO_2 and H_2 to light is described; the use of corks, rubber tubing, and taps is avoided. The impurities usually present in CO_2 prepared from marble and HCl are probably H_2S and SO_2 .

M. S. B.

Photographic emulsions.—See B., 1935, 525.

Origin of the luminosity which accompanies the detonation of explosives. H. MURAUER and A. MICHEL-LEVY (Compt. rend., 1935, 200, 924—926).—It is suggested that on the passage of a sufficiently powerful detonation wave the gas surrounding the explosive is compressed adiabatically, and hence is heated to a high temp. and becomes luminous. The fact that the luminosity does not disappear immediately is attributed to the formation of active gas, of which the luminosity decreases progressively.

J. W. S.

Chemical decomposition of silver oxide by slow electrons. P. H. WEI, P. A. ANDERSON, and Y. M. HSIEH (J. Chinese Chem. Soc., 1935, 3, 6—15).—No increase in conductivity could be observed > the increase due to ageing in a vac., when a thin film of Ag_2O was bombarded with an intense beam of electrons of up to 108 e.v. Explanations are suggested for the apparent non-reduction of the Ag_2O .

J. W. S.

Applications of deuterium. F. G. BRICKWEDDE (J. Washington Acad. Sci., 1935, 25, 157—166).—A review of published work, mainly on the study of mechanism of reactions by exchange between D and H.

E. S. H.

Alleged isotopic interchange between water and acetylene. R. P. BELL (J. Amer. Chem. Soc., 1935, 57, 778—779).—Recent work (A., 1934, 853) has not been confirmed.

E. S. H.

Isotopic interchange between acetylene and heavy water. L. H. REYERSON (J. Amer. Chem. Soc., 1935, 57, 779—780).—A reply (cf. preceding abstract).

E. S. H.

Action of molten lithium salts on glass. O. J. STEWART and D. W. YOUNG (J. Amer. Chem. Soc., 1935, 57, 695—698).—When soda-glass is immersed in molten $LiNO_3$ exchange occurs between Na and Li.

E. S. H.

Hydrolysis of alkali hydrides and the nature of the chemical linking between hydrogen and strongly electropositive metals. J. HENRIOT (Bull. Soc. chim. Belg., 1935, 44, 210—213).—Consistent with the theory that H_2 mols. are the

initial product of the hydrolysis of alkali hydrides, carefully purified NaH, KH, and CaH₂ do not decolorise aq. safranin-T. J. G. A. G.

Pure cuprous oxide for deducing the law of multiple proportions. R. SCHARF (Z. physik. chem. Unterr., 1934, 47, 202—204; Chem. Zentr., 1934, ii, 3581).—Pure Cu₂O is prepared by heating equiv. quantities of Cu and CuO to a red heat in absence of air. H. J. E.

Copper tetramminesulphate. I. Preparation, analysis, and preservation. P. G. PATER-NOSTO and E. DEL CARLO (Rev. fac. cienc. quim., La Plata, 1934, 9, 7—14).—Cu(NH₃)₄SO₄·H₂O, prepared and dried by the methods described, is stable in closed vessels. When heated in air it loses NH₃ and H₂O, but its composition remains unaltered after heating in sealed vessels to 250°. Aq. solutions < 0.05*M* hydrolyse immediately, pptg. basic Cu salts. More conc. solutions, or solutions to which NH₄ salts have been added, hydrolyse more slowly. F. A. A.

Production of magnesium and potassium chlorates. F. BRIERS (School Sci. Rev., 1934, 16, 277).—MgO is treated with Cl₂ to give MgCl₂ and Mg(ClO₃)₂. The latter is metathesised with KCl. Anhyd. MgCl₂ is electrolysed with gas-C anodes and molten Pb cathode. Mg is recovered from the resulting Mg-Pb alloy by making the alloy the anode in a fused MgCl₂ electrolyte and adjusting the current so that no Cl₂ is liberated. CH. ABS. (e)

Synthetic spinels coloured with cobalt. H. W. TROMNAU (Jahrb. Min., 1934, A, 68, 349—376; Chem. Zentr., 1934, ii, 3740).—The probable composition is MgO, *x*Al₂O₃ and CoAl₂O₄, *d* increasing and hardness decreasing with increasing [Co]. The optical properties are described. H. J. E.

Reduction of alkaline-earth arsenates by carbon. Tristrontium and tricalcium arsenates. H. GUÉRIN (Compt. rend., 1935, 200, 1210—1212; cf. this vol., 313).—Ca₃(AsO₄)₂ and Sr₃(AsO₄)₂ are reduced by C, slowly at 800° and rapidly at 850°, yielding first the arsenites and finally As and SrO or CaO. Rapid heating to 1500—1600° yields Ca₃As₂ and Sr₃As₂. If the heating is slow loss of As occurs. J. W. S.

Exchange reactions between finely-divided crystalline phases and gases. E. HERTEL and H. VON HOLT (Z. physikal. Chem., 1935, B, 28, 393—401).—Basic Zn chromate decomposes above 400° into ZnCr₂O₄ (spinel lattice), ZnO (zincite lattice), and O₂. ZnCr₂O₄ reacts with dry H₂S at 450—500°, ZnCr₂O₄ + 4H₂S = ZnCr₂S₄ + 4H₂O, the spinel lattice being retained, but somewhat distended; similarly ZnO yields wurtzite (I). Steam at 480° largely reconverts ZnCr₂S₄ into ZnCrO₄, but a little Cr sulphide is formed, which gives Cr₂O₃ on heating in air. (I) cannot be reconverted into ZnO by steam at 500°; O₂ is required. Dry H₂S at 450—500° converts Cr₂O₃ into amorphous Cr₂S₃. R. C.

Complex salts of 2 : 2'-dipyridyl with zinc and cadmium. II. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 235—242; cf. this vol., 312).—The following salts

have been prepared from 2 : 2'-dipyridyl (dipy) : [Zn dipy(H₂O)₂](NO₃)₂·H₂O, [Zn (dipy)₃](NO₃)₂·6H₂O, [Cd dipy(H₂O)₂](NO₃)₂·2H₂O, [Cd (dipy)₃](NO₃)₂·3H₂O, [Cd dipyCl₂], and [Cd (dipy)₂Cl₂·H₂O]. Crystal data are recorded. R. S. B.

Action of hot solutions of alkaline bases on mercuric iodide. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 657—658).—Delwaulle's results (A., 1934, 265) are confirmed. D. R. D.

Behaviour of mercuriammonium compounds with potassium cyanide. S. AUGUSTI (Gazzetta, 1935, 65, 117—119).—Mercuriammonium salts react with aq. KCN solutions liberating quantitatively 4 g.-mols. of KOH for every Hg₂N⁺ radical, e.g., Hg₂NCl + 8KCN + 4H₂O → 2K₂[Hg(CN)₄] + 4KOH + NH₄Cl. Titration of the KOH permits a volumetric determination of Hg₂N⁺. O. J. W.

Preparation of permutite by the dry method. I, II. J. K. DELIMARSKI (J. Gen. Chem. Russ., 1934, 4, 1400—1404, 1405—1406).—I. Permutite (I) prepared by Gans' method (cf. B., 1907, 872) disintegrates to a powder when treated with hot H₂O, rendering it unsuitable for technical purposes.

II [with F. G. SHAROVSKI]. The activity of (I) heated at 100—800° falls with rise in temp.; air-dried (I) is the most active. R. T.

Rare earths. II. [Scandium, yttrium, and lanthanum.] J. S. ŠTERBA-BÖHM and M. MELICHAR (Coll. Czech. Chem. Comm., 1935, 7, 131—145; cf. this vol., 606).—The degree of hydrolysis of 0.1*N* aq. acetates of Sc^{III}, Y^{III}, and La^{III} is 11.4%, 0.71%, and 0.31%, respectively. The complex salt K₂[Sc(OH)₅H₂O]·3H₂O (I) crystallises from solutions of Sc(OAc)₃ in conc. aq. KOH. Under similar conditions, Y(OAc)₃ affords crystals of Y(OH)₃. (I) decomposes in moist air. The following substances have been prepared: (HCO₂)₃Sc, (HCO₂)₂ScOH, (HCO₂)₆Li₃Sc·3H₂O, (HCO₂)₆Na₃Sc, (HCO₂)₆K₃Sc, Sc(OH)(OAc)₂, and 2Sc(OH)₃·H₂O. J. G. A. G.

Indium salts of organic acids.—See this vol., 730.

Silicon oxyhalides. H. RHEINBOLDT and W. WISFELD (Annalen, 1935, 517, 197—211).—SiCl₄ and O₂ (slight excess), when led through a porcelain tube at 1000°, give glassy, highly polymerised products; at 800° reaction is very slow; at 900° mainly Si₂OCl₆, m.p. -33°, b.p. 137°, is obtained; at 950—970° octachlorotetrasiloxan (I), Si₄O₄Cl₈, m.p. 77°, b.p. 92°/15 mm. (decomposed by H₂O), is also formed. SiBr₄ and O₂ do not react at 650°, and inflame at 705°, forming SiO₂ and Br; at 670—695° there are formed hexabromodisiloxan, Si₂OBr₆, m.p. 28.5°, b.p. about 120°/15 mm., and octabromotetrasiloxan (II), m.p. 123.5°, b.p. 170°/15 mm., both very sensitive to H₂O. (I) and (II) may be X₃SiO·SiX<O>SiX·OSiX₃ or, more probably, SiX₂<O·SiX₂·O>SiX₂.

R. S. C.

Oxidation of graphite. III. V. SHIVONEN (Suomen Kem., 1935, 8, B, 21—24; cf. A., 1934, 742).—A further discussion of the author's theory. F. L. U.

Structural changes taking place during the ageing of freshly-formed precipitates. III. Mechanism of ageing of lead sulphate precipitated at room temperature. IV. Ageing of fresh lead sulphate at room temperature in the air-dried state, and of precipitates covered with an adsorbed layer of wool-violet. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1935, 57, 597—600, 607—611; cf. A., 1934, 1069).—III. Scarcely any ageing of PbSO_4 occurs in EtOH ; in MeOH or 70% EtOH ageing is much slower than in H_2O . The retardation of ageing is due to the decreased velocity of recrystallisation, caused by the decreased solubility of PbSO_4 .

IV. Air-dried PbSO_4 ppts. undergo scarcely any ageing when kept below R.H. 0.6, and do not absorb H_2O , but above R.H. 0.85 slow ageing occurs, which is ascribed to internal recrystallisation, whilst about 2% of H_2O is absorbed in the capillaries. When the ppt. is covered by an adsorbed layer of wool-violet the velocity of recrystallisation is greatly diminished and little ageing occurs. The external surface of fresh PbSO_4 can be determined by the radioactive method if the ppt. is covered with adsorbed wool-violet and then shaken with Th-B solution. E. S. H.

Reaction between nitrogen dioxide and water vapour. I. N. KUZMINUKH and V. S. UDINTZEVA (Khimstroi, 1934, 6, 523—526).—The reaction between NO_2 and H_2O at 70—100° does not take place in the gaseous phase (cf. Burdik and Freed, A., 1921, ii, 313). This explanation is therefore not applicable to the oxidation of SO_2 by N oxides. CH. ABS. (e)

Fluorination of nitric acid. Nitroxyfluoride, NO_3F . O. RUFF and W. KWASNIK (Angew. Chem., 1935, 48, 238—240; cf. this vol., 181).— NO_3F is formed quantitatively when F_2 is passed into 100% HNO_3 at room temp. in a quartz apparatus. Mol. wt., O, N, and F determinations give the theoretical vals. The v.p. is given by $\log p = -1044.9/T - 7.478$; m.p. -175° , b.p. -45.9° , heat of vaporisation 4726 g.-cal. per mol., Trouton's const. 20.8, $d_{\text{liq.}} = 2.2148 - 0.003114T$. Solid or liquid NO_3F is exploded by mechanical shock. It is stable in dry glass or quartz, but gives OF_2 and O_2 with H_2O , OF_2 with 2% NaOH , and O_2 with 20% NaOH , whence the formula $\text{O}_2\text{N}\cdot\text{O}\cdot\text{F}$ is proposed. Numerous chemical properties and the effect on the respiratory system are described.

R. S.

Reaction of fluorine with nitric acid and with solid potassium nitrate to form NO_3F . D. M. YOST and A. BEERBOWER (J. Amer. Chem. Soc., 1935, 57, 782).—The observations of Cady (this vol., 181) are confirmed and further reactions of NO_3F noted.

E. S. H.

Products of hydrolysis of P_2I_4 , and the preparation of hypophosphoric acid from it. J. H. KOLITOWSKA (Rocz. Chem., 1935, 15, 29—36).—The products of hydrolysis of P_2I_4 by H_2O at 0° are H_3PO_3 , H_3PO_4 , PH_3 , P_{12}H_6 , and HI . $\text{H}_4\text{P}_2\text{O}_6$ (I) is obtained in 24% yield when P_2I_4 is added to aq. NaOH and H_2O_2 , whilst when these are added to the above reaction mixture after 24 hr. of hydrolysis with $\text{H}_2\text{O} \geq 10\%$ of (I) is produced. The method gives higher yields than other methods. R. T.

Preparation of inorganic reagents. I. Arsenic chloride. C. L. TSENG, M. HU, and M. HSÜ. II. Phosphorus tribromide. C. L. TSENG and T. S. HO. III. Hydrobromic acid. C. L. TSENG, T. S. HO, and P. T. CHIA. IV. Mercuric bromide. V. Sulphuryl chloride. C. L. TSENG and C. H. SZE (Sci. Quart. Nation. Univ. Peking, 1935, 5, 317—323; 324—336, 337—341, 342—345, 346—349).—I. Dumas' method gave an optimum yield (85% of theory) when the reactants in the proportions As_2O_3 99 g., NaCl 261 g., and conc. H_2SO_4 213 c.c. were heated slowly (3—4 hr.) to 180°.

II. The yields of PBr_3 obtained by the different published methods were almost identical.

III. NaBr (103 g.), H_2O (80 c.c.), and conc. H_2SO_4 (35 c.c.) were mixed at 0° (approx.) and the distillate at $< 200^\circ$, after repeated refractionation, afforded 85% of the stoichiometric yield of const.-b.p. aq. HBr .

IV. An adaptation of the method of Baker and Watson, (J.C.S., 1914, 105, 2531) is described.

V. The yield of SO_2Cl_2 synthesised by published methods from SO_2 and Cl_2 in the presence of camphor was 46% of stoichiometric, based on the wt. of NaHSO_3 used. J. G. A. G.

Preparation of pure vanadium. A. MORETTE (Compt. rend., 1935, 200, 1110—1112).—V has been prepared as a grey powder of 99.3% purity by the reduction of VCl_4 vapour by Mg at 700°, and of 98.9—99.5% purity by heating Mg with VCl_2 in an atm. of A or pure H_2 at $\geq 700^\circ$ for 1—2.5 hr. The V powder burns in the Bunsen flame, reacts violently with conc. HNO_3 giving V_2O_5 , and is dissolved by HF but not by HCl . M. S. B.

Manufacture of pure hydrofluoric acid.—See B., 1935, 451.

Preparation and properties of fluorine compounds. W. LANGE (Chem.-Ztg., 1935, 59, 393—395).—A review.

Slow action of fuming nitric acid vapours on different elements. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 625—626).— Cl_2 is oxidised in the course of 1—2 months at room temp. (15—18°) to HClO_3 , no HClO_4 being formed. Br is oxidised under the same conditions to HBrO_3 , I to HIO_3 , Se to SeO_2 , and white P to H_3PO_4 and some H_3PO_3 (which is subsequently completely oxidised to H_3PO_4). As is oxidised superficially to As_2O_3 , and Sb is oxidised to an even smaller extent. S and Te are not attacked. D. R. D.

Action of perchloric acid. J. R. PARTINGTON (Chem. and Ind., 1935, 468—469).—Mixtures of aq. HClO_4 and org. substances are liable to explode violently, even in the cold. J. G. A. G.

Reaction between iodine and oxalic acid in ethylene glycol as a solvent. B. K. CHATTERJEE and B. L. VAISHYA (J. Indian Chem. Soc., 1935, 12, 137—138).—I and $\text{H}_2\text{C}_2\text{O}_4$ will not react in $(\text{CH}_2\cdot\text{OH})_2$ (I), either in light or in the dark, even if as much as 50% by vol. of H_2O is mixed with it. If, as suggested by Griffith *et al.* (A., 1932, 1210), the intermediate formation of IOH takes place, the reaction ought to be favoured by (I). Earlier

work has shown the reaction to be ionic. It is evidently not independent of the medium, which should be such as to favour ionisation. M. S. B.

Preparation of trisodium periodate and periodic acid. J. LANGE and R. PARIS (J. Pharm. Chim., 1935, [viii], 21, 403—405).— $\text{Na}_3\text{H}_2\text{IO}_6$ (yield 90—100%) is obtained by treating NaI (50 g.) in 10% NaOH (2000 g.) with Br (240 g.) at 80° . H_5IO_6 is prepared by treating Ag_2HIO_5 with Br . S. C.

Ter- and quadri-valent manganese [chlorides]. J. H. KREPELKA and J. KUBIS (Coll. Czech. Chem. Comm., 1935, 7, 105—124).—A green solution containing MnCl_4 is obtained by passing dry HCl through an ethereal suspension of MnO_2 at -63° . At -76° , a brown solution containing more MnCl_4 is obtained. CCl_4 and light petroleum ppt. from these solutions a black unstable substance which affords in Et_2O a violet solution containing MnCl_3 . By replacing MnO_2 with Mn_2O_3 , MnCl_3 is obtained, but MnCl_4 could not be isolated. Earlier work is criticised. J. G. A. G.

Decomposition of permanganic acid and manganese dioxide. P. DUBOIS (Compt. rend., 1935, 200, 1107—1110).—A conc. solution of HMnO_4 , approx. 2.6*M*, crystallises at -11° . The crystals consist of ice containing varying quantities of HMnO_4 . Exposure of the solutions to diffused daylight results in gradual elimination of O_3 and pptn. of impure MnO_2 . This can be purified by repeated treatment with boiling HNO_3 . Drying at 100° gives $\text{MnO}_2 \cdot 0.56\text{H}_2\text{O}$ (I). By treating HMnO_4 solution directly with boiling HNO_3 and drying the ppt. at room temp., pure $\text{MnO}_2 \cdot 1.66\text{H}_2\text{O}$ (II) is obtained. Both (I) and (II) begin to lose O_2 above 200° but retain some H_2O up to 500° . Before giving Mn_2O_3 at 600° they either undergo allotropic transformation or form an oxide approx. $\text{MnO}_{1.9}$. The anhyd. MnO_2 , previously obtained by heating $\text{Mn}(\text{NO}_3)_2$ (A., 1934, 617), decomposes at 600° to Mn_2O_3 . M. S. B.

Recent researches on certain of the rarer elements. G. T. MORGAN (J.C.S., 1935, 554—570).—A lecture. An exposition is given of the work published by the author and colleagues on the org. derivatives of Se and Te. The extraction of Ge and Ga from Northumberland coal ash is described: the ash is distilled with conc. HCl and GeCl_4 distils over whilst GaCl_3 remains in the still. Re has been isolated from Australian molybdenite. In the final separation, 2:2'-dipyridyl pptd. the Mo as dipyridyl molybdate, leaving the Re in solution. The following complex salts have been prepared: $\text{K}_2\text{Na}[\text{ReO}(\text{CN})_4]$, $\text{K}_3[\text{ReO}(\text{CN})_4]$, 2:2':2''-tripyridyl rhenichloride, 2:2'-dipyridyl rhenichloride, bis-2:2'-dipyridyl rhenichloride, 2:2':2''-tripyridyl perrhenate, and 2:2'-dipyridyl perrhenate. The following co-ordination compounds have been prepared (2:2'-dipyridyl = dipy), chiefly from $\text{K}_2[\text{RuNOCl}_5]$: *cis*- and *trans*-[dipy RuNOCl_3], [dipy RuNOBr_3], [dipy RuNOI_3], [(dipy) $_2$][RuNOCl_5], [dipy][RuOHCl_5], [2:2':2''-tripyridyl RuNOCl_2] $\cdot\text{Cl}_2\cdot x\text{H}_2\text{O}$, and [tripyridyl RuNOCl_2] $[\text{RuNOCl}_5]$. J. G. A. G.

Reduction of ferric oxide by hydrogen and oxidation of metallic iron reduced from ferric

oxide. Y. GOTOH (Ryojun Coll. Eng., Inouye Commem. Vol., 1934, 393—413).—Reduction of pure Fe_2O_3 to Fe by H_2 takes place in two stages, Fe_3O_4 being formed between 250° and 300° . As the temp. is raised the Fe produced goes into solid solution in the Fe_3O_4 until that contains 21% Fe , after which a vigorous reduction ensues and the whole is converted into Fe at 480° . On heating the reduced Fe in air the reverse process occurs, Fe_3O_4 being formed at 80 — 250° until the product contains 66%, after which no further reaction occurs below 360° ; above this temp. magnetic Fe_2O_3 is formed which at $>500^\circ$ is converted into the non-magnetic form and at $>850^\circ$ into the rhombohedral form. FeO cannot be detected at any stage of either the oxidation or the reduction process. The effect of gas velocity on the rate of reduction and oxidation is shown graphically. A. R. P.

Change undergone by aqueous solutions of crystallised ferrous sulphate. R. SAN MARTIN (Anal. Fis. Quím., 1935, 32, 370—373).—Aq. FeSO_4 oxidises on exposure to air, basic Fe^{III} sulphate being pptd. and H_2SO_4 formed in solution. The reaction ceases when $[\text{H}_2\text{SO}_4]$ reaches a limiting val. and can be prevented by adding H_2SO_4 . D. R. D.

Reactions in solid state at room temperature. A. SERRA (Period. Min., 1934, 5, 175—179; Chem. Zentr., 1934, ii, 3913).—Various sulphide minerals (pyrites, Pb glance etc.) react with Ag , Zn , Sn , Au , Pb , or Cu foil or wire at room temp., giving a perceptible stain within 24 hr. J. S. A.

Basic salts. X. Chemistry and morphology of basic salts of bivalent metals. III. Basic cobalt chlorides. W. FEITKNECHT and G. FISCHER (Helv. Chim. Acta, 1935, 18, 555—569; cf. this vol. 461).—By incomplete pptn. of aq. CoCl_2 with NaOH an unstable, green basic chloride (I), approx. $\text{CoCl}(\text{OH}) \cdot 4\text{Co}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is formed. The conditions affecting its stability have been studied, and its structure is discussed in the light of X-ray data. By ageing of (I) or by slow hydrolysis of aq. CoCl_2 a stable, rose-coloured basic chloride, $\text{CoCl}_2 \cdot 3\text{Co}(\text{OH})_2$, is formed. E. S. H.

Coloration of cobalt salts. C. DUVAL (Compt. rend., 1935, 200, 934—936).—Electrophoresis in EtOH solution shows that the blue colour formed by CoCl_2 and LiCl is due to $[\text{Li}(\text{CoCl}_3(\text{H}_2\text{O})_3)]$. The compound $\text{H}[\text{CoCl}_3(\text{H}_2\text{O})_3]$ (I) is obtained by passing dry HCl over a mixture of equiv. parts of CoCl_2 and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at -5° in the dark and in contact with dry Et_2O . It is also obtained, together with $\text{Co}(\text{OH})_2$ and HCl , by heating $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. It is decomposed by excess of H_2O . The hydrate $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (II) is actually $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{H}_2\text{O})_6]$, and appears violet owing to the coexistence of a rose cation and blue anion. Passage of dry HCl through an Et_2O suspension of Co_2O_3 yields the green $[\text{CoCl}_6]$, which in air passes into (II). (I) yields blue salts with metals of which the polarisation potential is $>$ that of Al . With other metals it forms complexes, e.g., $[\text{CdCl}_6][\text{Co}(\text{H}_2\text{O})_6][\text{Cd}(\text{H}_2\text{O})_6]$. The rose hydrate is $[\text{CoCl}_6][\text{Co}(\text{H}_2\text{O})_6]_2$. J. W. S.

Formation of basic sulphate and precipitation of nickel from solution by magnesium. G. GIRE

(Compt. rend., 1935, 200, 1213—1215; cf. A., 1934, 159).—The amount of Ni deposited as $\text{NiSO}_4 \cdot 4\text{NiO} \cdot n\text{H}_2\text{O}$ from aq. NiSO_4 after dissolution of Mg therein increases with time towards a definite limit, which increases with dilution and with rise of temp. Higher temp. favours the attainment of equilibrium. This is due to a secondary reaction between SO_4^{--} , Ni^{++} , and OH' ions. The action of Mg also causes direct deposition of Ni, especially above 30° . Freshly pptd. $\text{Ni}(\text{OH})_2$ does not react with NiSO_4 .

J. W. S.

Mixed nickel nitrites of univalent and bivalent metals. I. A. FERRARI and C. COLLA (Gazzetta, 1935, 65, 168—176).—The prep. of the compounds $\text{M}_2\text{Hg}[\text{Ni}(\text{NO}_2)_6]$ is described (M = NH_4 , K, and Tl). These are isomorphous with $\text{K}_2\text{Pb}[\text{Ni}(\text{NO}_2)_6]$ (I) and have a 10.46, 10.29, 10.42 Å., respectively. With Rb and Cs there is a tendency to form $2\text{Rb}_2\text{Hg}[\text{Ni}(\text{NO}_2)_6]$, $[\text{Rb}_2\text{Hg}[\text{Hg}(\text{NO}_2)_6]]$ and $\text{Cs}_2\text{Hg}[\text{Ni}(\text{NO}_2)_6]$, $[\text{Cs}_2\text{Hg}[\text{Hg}(\text{NO}_2)_6]]$, with a 10.50 and 11.04 Å., respectively. These are also isomorphous with (I), and probably consist of solid solutions between the two component complex nitrites. By increasing the Ni:Hg ratio to 2:1 in the prep. the compound $\text{Rb}_2\text{Hg}[\text{Ni}(\text{NO}_2)_6]$ can be obtained, but not the corresponding Cs compound.

O. J. W.

Addition of hydrazine to nickel pyrophosphate. W. DALLER (Oesterr. Chem.-Ztg., 1935, 38, 76—77).—On adding aq. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (I) to a stirred solution of NiCO_3 in $\text{H}_4\text{P}_2\text{O}_7$, filtering, and drying, a greenish-blue compound (II) is obtained. Aq. (I), $\text{H}_4\text{P}_2\text{O}_7$, and NiSO_4 give a greenish-blue ppt. changing to a blue compound (III) on further addition of (I). On digesting with (I) (II) gives a reddish-violet compound (IV). A solution of $\text{Ni}_2\text{P}_2\text{O}_7$ in $\text{Na}_4\text{P}_2\text{O}_7$ gives with (I), after leaving in presence of EtOH for 6 weeks, a blue compound (V). The ppts. are dried by means of EtOH. The atoms of P and mols. of N_2H_4 per atom of Ni are (II) 1.132, 1.251, (III) 0.7005, 1.888, (IV) 0.5410, 3.000, and (V) 1.125, 1.817.

R. S. B.

Complexes formed between benzidine and metallic salts.—See this vol., 613.

Colorimetric determination of p_H at higher temperatures. III. W. NEUMANN (Z. anal. Chem., 1935, 101, 89—101; cf. A., 1934, 500).— Na_2SO_4 shows a p_H displacement (I) on heating opposite in sign to that of KCl or NaCl. (I) is compounded of a change in the ionic product of H_2O , and of a change in the salt error (II) of the indicator. At 100° , (I) is practically the same for H_2O and for neutral salts, indicating that (II) tends towards zero. Comparative results are given for CaCl_2 , MgCl_2 , and MgSO_4 .

J. S. A.

Indicator properties of some dinitro-derivatives. J. VAN DEN HAUTE (Natuurwetensch. Tijds., 1935, 17, 64—71).—Absorption curves, λ for max. extinction coeff. (E), K , and the p_H at which a sharp colour change takes place (vals. given in parentheses) have been determined for 3:5- (λ 4200, E 73,500, 0.91×10^{-3} , p_H 1.3—2.5) and 4:6-dinitroguaiacol (λ 4050, E 23,660, K 6.04×10^{-7} , p_H 5—7.5), 2:4-dinitrothymol (λ 4040, E 73,460, K 1.72×10^{-4} , p_H 2—3.4), and 4:6-dinitro-*o*-cresol (λ 4100, E 68,930,

K 6.41×10^{-5} , p_H 2.4—3.8). These compounds are excellent indicators at concns. of 6×10^{-6} if a step photometer is used.

S. C.

Determination of hydrogen with silver permanganate solution. F. HEIN and W. DANIEL (Z. anal. Chem., 1935, 99, 385—390; cf. A., 1931, 1256).—The slow evolution of O_2 from the AgMnO_4 solution (I) sweeps out dissolved N_2 , reabsorption of which may cause apparently high results for H_2 absorption. (I) should be resaturated with N_2 before use, and N_2 added to gases rich in H_2 to avoid error.

J. S. A.

New methods of water analysis.—See B., 1935, 432.

Heavy water. W. DOMINIK (Polish Agr. Forestal Ann., 1934, 33, 359—370).—Possibilities of using D_2O for the determination of OH and enolisable CO are discussed.

CH. ABS. (e)

Determination of chlorine in water by the *o*-tolidine method.—See B., 1935, 480.

Determination of small quantities of iodides. Application to the determination of small quantities of different metals. M. L. JEAN (Bull. Soc. chim., 1935, [v], 2, 605—616).—To determine < 0.01 g. of I' in 20—30 c.c. of solution, the I' is oxidised to IO_3' by aq. Br in presence of NaHCO_3 , the excess of Br reduced by CH_3O in presence of NaOH at 0° , the solution acidified with AcOH, and the IO_3' determined iodometrically. CrO_4^{--} and $\text{Cr}_2\text{O}_7^{--}$ are determined by adding a known quantity of I' in acid solution, boiling off the I liberated, and determining the excess of I' by the above procedure. Cr^{+++} must first be oxidised to CrO_4^{--} (e.g., by aq. Br, as in the oxidation of I'). Cr and I' may also be oxidised to CrO_4^{--} and IO_3' , respectively, using KMnO_4 in boiling alkaline solution and destroying the excess by means of EtOH, but the Br method is more convenient. Ag' is determined by adding an excess of I', adding aq. $\text{Ba}(\text{NO}_3)_2$ and Na_2CO_3 to carry down the ppt., filtering, and determining the I' remaining in solution as already described.

D. R. D.

Iodometric studies. III. Significance of concentration of iodide in dilute iodine solutions. R. V. TEIS (J. Gen. Chem. Russ., 1934, 4, 1364—1369).—The sensitivity of the starch-I reaction is greatest when the $[\text{KI}]$ is $< 1\%$, for 0.001—0.002N-I.

R. T.

Detection of fluoride ions. L. KULBERG (J. Gen. Chem. Russ., 1934, 4, 1440—1443).—The blue colour of aq. $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$ is intensified by F'; this reaction serves for detection of $\approx 3.3 \times 10$ g. of F', in presence of all other anions.

R. T.

Measuring syringes and their application, especially to accurate determination of oxygen in water by Winkler's method. A. KROGH (Kem. Maanedst. nord. Handelsbl. kem. Ind., 1934, 15, 105—109; Chem. Zentr., 1934, ii, 4002).—The micro-application of Winkler's $\text{Mn}(\text{OH})_2$ method is described, using graduated hypodermic syringes for titration.

J. S. A.

Potentiometric determination of sulphite. G. SPACU and C. DRAGULESCU (Z. anal. Chem., 1935, 101, 113—116).— SO_3^{--} is titrated potentiometrically with HgCl_2 in aq. EtOH solution, the end-point

corresponding with formation of $\text{Na}_2[\text{Hg}(\text{SO}_3)_2]$. O_2 and light should be excluded. J. S. A.

[Detection of sulphurous acid and its salts and of tin.] H. FREYTAG (Ber., 1935, 68, [B], 585—586; cf. A., 1934, 1321).—A reply to Feigl *et al.* (this vol., 462). H. W.

Application of acetone solutions of sulphur dioxide to the gravimetric determination of selenium. V. HOVORKA (Chem. Listy, 1935, 19, 73—75).— H_2SeO_3 is rapidly and quantitatively reduced to Se by COMe_2 saturated with SO_2 ; the presence of HCl is indispensable, pointing to the probability that Se_2Cl_2 is an intermediate product. R. T.

Conductometric determination of selenocyanides in presence of cyanides. R. RIPAN-TILICI (Z. anal. Chem., 1935, 100, 405—408).—Two breaks are obtained in the conductivity-titration curve, corresponding with formation of $[\text{Ag}(\text{CN})_2]'$ and with complete pptn. of $\text{AgCN} + \text{AgCNSe}$, whence CNSe' may be calc. J. S. A.

Potentiometric determination of selenocyanide in presence of halides. P. SPACU (Z. anal. Chem., 1935, 100, 397—405).— SeCN' may be titrated potentiometrically in presence of $\text{I}' + \text{Cl}'$ or $\text{Br}' + \text{Cl}'$, but the SeCN' and Br' end-points cannot be separated in presence of I' . J. S. A.

Detection of tellurium. M. ISHIBASHI and S. MORI (J. Chem. Soc. Japan, 1934, 55, 1262—1272).—The mineral powder is dissolved in hot H_2SO_4 , diluted, and Cu is added. Red TeSO_3 is formed. CH. ABS. (e)

Determination of small quantities of tellurium in lead.—See B., 1935, 459.

Absorption of ammonia in boric acid. F. J. WATSON (J. Soc. Chem. Ind. Victoria, 1933, 33, 799—801).— NH_3 may be distilled into H_3BO_3 and titrated directly with HCl, absorption being complete when a large excess of cooled aq. H_3BO_3 is used. J. S. A.

Hydroxyapatite precipitation as basis for volumetric determination of phosphoric acid in solutions containing calcium. P. DAMSGAARD-SØRENSEN (Kem. Maanedbl. nord. Handelsbl. kem. Ind., 1934, 15, 73—79; Chem. Zentr., 1934, ii, 3992).— H_3PO_4 may be titrated with NaOH, using Me-red + phenolphthalein as indicator, and matching the primary (I) and secondary end-points against citrate-HCl and borate-HCl buffers, respectively. In presence of excess of Ca, titration with NaOH [or titration with aq. $\text{Ca}(\text{OH})_2$ if Ca is absent] to a permanent red colour ppts. hydroxyapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$, and requires exactly 3.5 times the NaOH to reach (I). PO_4''' in 0.01N solution may be so titrated. J. S. A.

Elimination of phosphate ion in systematic qualitative analysis. E. KAHANE (Ann. Chim. Analyt., 1935, [iii], 17, 119—121).— NH_4OAc and then an excess of FeCl_3 are added to the solution, which is made just alkaline with aq. NH_3 . On boiling the solution until free NH_3 is completely removed, PO_4''' is pptd. with the Fe, Al, and Cr without

carrying down traces of Zn, Ba, Sr, Co, or Mn as in the usual procedure. J. S. A.

Determination of small amounts of arsenic. J. GANGL (Oesterr. Chem.-Ztg., 1935, 38, 64—69).—As is rapidly and completely reduced to AsH_3 by Zn dust and H_2SO_4 in a modified Marsh apparatus. The As is quantitatively deposited as a mirror (I) by passing the gas through a narrow SiO_2 tube heated to 500° , the AsH_3 being completely expelled from solution by boiling in a stream of H_2 . Quantities of As $< 10^{-6}$ g. may be determined by matching (I) against a standard. With larger amounts ($1-100 \times 10^{-6}$ g.) (I) is dissolved in ICl , and the liberated I titrated in acid solution with KIO_3 in presence of KCN, using a drop of CCl_4 as indicator. Reduction to As with NaH_2PO_2 is applicable for very small quantities only in the absence of other reducible metals. J. S. A.

Determination of small quantities of arsenic. C. J. SNLIDERS, jun., and A. J. W. VAN DER DRIFT (Chem. Weekblad, 1935, 32, 275—280).—200 c.c. of the neutral solution containing ≈ 0.01 mg. of As are refluxed for 30 min. with 2—3 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 10—15 drops of 40% $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in conc. HCl, 50 c.c. of 1:1 HCl, and 12—15 g. of Zn previously activated by immersion in acidified SnCl_2 solution. The gas evolved (H_2 and AsH_3) is washed with 15% CuCl in 1:1 HCl, and passed through a filter-paper soaked in HgBr_2 solution. The stain is developed by immersion for 2 min. in 20% aq. CdI_2 , dried, and compared with a standard. An accuracy of 0.001 mg. may be obtained. D. R. D.

New indicators for bromometric titrations. T. SOTGIA-ROVELLI (Boll. Chim. farm., 1935, 74, 265—270, 273—276).—If in the reaction $3\text{H}_3\text{AsO}_3 + \text{KBrO}_3 = 3\text{H}_3\text{AsO}_4 + \text{KBr}$, Me-orange (I) is used as indicator, it is decolorised by Br liberated by excess of HBrO_3 ; (I), however, reacts slowly. More suitable are Ponceau-3R, methylene-blue, or Bordeaux-B (all for titration of 0.1 or 0.01N solutions), or safranin, Azure-II, chrysoidine, or saffron-yellow (for 0.1N solutions). Fuchsin and litmus are unsuitable. E. W. W.

Electrical conductivity method for determining carbon dioxide and other reactive gases. R. G. NEWTON (Ann. Bot., 1935, 49, 381—398).—Apparatus for micro-determinations is described. A. G. P.

Determination of small concentrations. VIII. Carbon monoxide. A. V. PAMFILOV and S. L. KAGAN (J. Gen. Chem. Russ., 1934, 4, 1390—1393).—The usual methods are untrustworthy when the $[\text{CO}]$ is < 1 mg. per litre. R. T.

Conductometric determination of cyanates in presence of cyanides. R. RIPAN-TILICI (Z. anal. Chem., 1935, 99, 415—418).— CNO' may be titrated conductometrically with AgNO_3 in presence of CN' . Breaks in the curve correspond with formation of $[\text{Ag}(\text{CN})_2]'$ and with complete pptn. of $\text{AgCN} + \text{AgCNO}$. J. S. A.

Silicic acid and silicates. IV. Determination of silicic acid in insoluble silicates. F. W.

MEIER and L. STUCKERT (Z. anal. Chem., 1935, 101, 81—84; cf., B, 1932, 549).—The silicate is fused with $\text{CaCO}_3 + \text{NH}_4\text{Cl}$ to avoid subsequent formation of KClO_4 . The melt is extracted with H_2O , and the insol. residue heated with HClO_4 . The insolubilised SiO_2 is then washed with 10% HCl and ignited.

J. S. A.

Quantitative spectrographic analysis of alkali metals. Application to caesium in mineral waters. R. BOSSUET (Compt. rend., 1935, 200, 1094—1096).—0.025 c.c. of conc. mineral H_2O , or of a solution of the alkali chlorides previously separated, is volatilised in the $\text{O}_2\text{—C}_2\text{H}_2$ flame and the emission spectrum photographed. By increasing the dilution the limit at which the ultimate ray of Cs, λ 4555.3 Å., disappears may be determined. The [CsCl] of a no. of mineral waters is given. The same method may be applied to the determination of traces of Rb.

M. S. B.

Quantitative spectral analysis. III. R. BRECKPOT and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 16—30; cf. A., 1934, 857).—Data are given for the spectral determination of Li, Na, K, Sr, Ba, Si, P, Te, and Tl using a CuO base.

R. S.

Argentometric determination of sodium hydroxide and sodium sulphide in sodium aluminate.—See B., 1935, 451.

Determination of sodium [in water] by means of zinc uranyl acetate.—See B., 1935, 432.

Determination of small quantities of silver in water. J. JUST and A. SZNIOLIS (Arch. Chem. Farm., 1935, 2, 170—175).—Two drops of 10% aq. KI and 5—10 drops of 50% HCl are added to 100 ml. of H_2O , the solution is filtered through a membrane (I) of porosity $1\ \mu$ and of diameter 2.5 cm., 2 ml. of aq. H_2S are then passed through the (I), and the density of coloration of the (I) is compared with that given by standard solutions containing 0, 0.05, 0.1, 0.15, and 0.2 p.p.m. of Ag. The method can be applied to determine 0.0025 p.p.m. of Ag by increasing the vol. of the sample, and diminishing the diameter of the (I).

R. T.

New indicators for argentometric titrations. E. CHIRNOAGA (Z. anal. Chem., 1935, 101, 31—38).—Diphenylcarbazone may be used as an adsorption indicator in neutral solution, starch being added to stabilise the Ag halides in the colloidal state. $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ containing an excess of $\text{Fe}(\text{CN})_6'''$ may also be used in presence of NaOAc , turning white or yellow at the end-point.

J. S. A.

Determination of small amounts of silver with dithizone. H. FISCHER, G. LEOPOLDI, and H. VON USLAR (Z. anal. Chem., 1935, 101, 1—23).—The Ag solution, containing about 12×10^{-6} g. of Ag per c.c., is acidified with HNO_3 and treated with successive measured small amounts of a standard solution (I) of dithizone (II) in CCl_4 [2—4 mg. of (II) per c.c.], until the green colour of (I) persists. Ag is determined from the vol. of (I) required, or colorimetrically in the united extracts. Pb, Zn, Cd, As, Sb, Bi, and Au do not interfere, Ag being extracted preferentially. In presence of Hg or $> 10\%$ of Cu, Ag+Hg or Cu is extracted with (II), and Ag extracted with KCNS.

The KCNS solution is evaporated with H_2SO_4 , the residue dissolved in 15% HNO_3 , and Ag titrated. $0.1\text{—}2 \times 10^{-6}$ g. of Ag may be determined colorimetrically by shaking with the violet solution of the Cu-(II) compound, and matching the mixed colour against a standard Ag solution.

J. S. A.

Detection of calcium, strontium, and barium in their mixtures. N. A. TANANAEV (Z. anal. Chem., 1935, 100, 391—394).—On extraction of the dry nitrates with glacial AcOH , Ca and Mg dissolve, and may be quantitatively separated from Ba and Sr. Traces of Ca in presence of much Sr and Ba, but in absence of Mg, give an opalescence on evaporating with saturated aq. $\text{K}_4\text{Fe}(\text{CN})_6$ and redissolution in H_2O .

J. S. A.

Argentometric determination of barium oxide and barium sulphide in barium aluminate.—See B., 1935, 451.

8-Hydroxyquinoline and its application to [the determination of] magnesium. D. C. VUCETIĆ (Rev. fac. cienc. quim., La Plata, 1934, 9, 81—91).—The complex salt is pptd. in presence of NH_3 , NH_4Cl , and COMe_2 , washed, redissolved in HCl , and determined with KBrO_3 . Advantages over other methods are claimed.

F. A. A.

Colorimetric determination of zinc with dithizone. W. DECKERT (Z. anal. Chem., 1935, 100, 385—390).—To 50 c.c. of H_2O +1 c.c. of a saturated solution of dithizone (I) in 0.01N- NaOH , a measured vol. of the Zn solution is added until $1\text{—}3 \times 10^{-6}$ g. of Zn (matched roughly against standards) is present. The solution is diluted to 100 c.c. and examined colorimetrically. Alkalinity and excess of (I) must be identical for sample and standard. Urine and faeces are first oxidised with $\text{H}_2\text{SO}_4 + \text{HNO}_3$, or ashed dry below 450° . Cu is removed by adding 2 drops of aq. CuSO_4 and pptg. with H_2S . The filtrate is exactly neutralised, and Zn determined as above.

J. S. A.

Reaction of aminobenzoic acids with cadmium and zinc salts. J. V. DUBSKY and J. TRTILEK (Chem. Listy, 1935, 19, 76—77).—Aq. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{K}$ and Cd salts yield a cryst. ppt., $(p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{Cd}\cdot 2\text{H}_2\text{O}$ (I); Zn salts are not pptd. under analogous conditions. Cd cannot be quantitatively separated from Zn by pptn. as (I), which is extremely sol. in dil. acids and fairly sol. in H_2O . The solubility of $(m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{Cd}$ is $>$ that of (I).

R. T.

Quantitative separation of metals by hydrogen sulphide. VII. Separation of zinc from chromium and a new method of separating chromium from nickel, cobalt, and iron. H. KATO (J. Chem. Soc. Japan, 1934, 55, 1152—1155).—At p_{H} 2.3—4.0 Zn is pptd. as ZnS by H_2S while Cr remains in solution. At p_{H} 5 (with AcOH and NaOAc buffer) Ni, Co, and Fe are pptd. as sulphides from a solution containing Ni, Co, Fe, and Cr. Cr remains in solution.

CH. ABS. (e)

Induced precipitation in analysis. I. H. KATO (J. Chem. Soc. Japan, 1934, 55, 1148—1151).—The induced pptn. of $\text{Zn}(\text{OH})_2$ by the presence of KMnO_4

is probably of chemical nature, but that of FeS by ZnS is due to adsorption. CH. ABS. (e)

Importance of p_H for determination and separation of metals by anthranilic acid. H. GOTÔ (J. Chem. Soc. Japan, 1934, 55, 1156—1163).—The min. p_H for complete pptn. and the max. at which no pptn. takes place by anthranilic acid were respectively for Zn 4.72, 3.76; Cd 5.23, 4.25; Ni 4.51, 3.64; Co 4.41, 3.36; Mn 5.15, 4.10; Cu 2.79, 1.40. Cu can be pptd. alone from a solution containing the above metals. CH. ABS. (e)

Electrolytic determination of very small amounts of lead. A. NECKE and H. MULLER (Angew. Chem., 1935, 48, 259—261; cf. A., 1929, 286).—Pb is anodically deposited as PbO₂ from HNO₃ solution. The deposited Pb is determined colorimetrically by treating the PbO₂ with a 1% solution of "tetramethyl base" in AcOH. The method is applicable to 0.02—0.1 mg. of Pb in presence of a large excess of Cu. J. S. A.

Examination by a radioactive method of the quantitative analysis of very small amounts of lead by the method of P. Schmidt and co-workers. W. MESSERSCHMIDT and G. TARTLER (Angew. Chem., 1935, 48, 261—263).—Th-B was added to solutions of Pb(NO₃)₂ and the Pb deposited anodically as PbO₂ (cf. preceding abstract). Comparison of the Th-B in the deposit with that originally added to the solution, as measured by the γ -ray activity of the equilibrium products, showed that anodic deposition of > 0.03 mg. of Pb was practically quant. Some Th-C (i.e., Bi), but no Th-B (Pb), was deposited on the cathode. J. S. A.

Reactions of potassium iodide and bases with salts of lead, bismuth, mercury, copper, cadmium, and antimony. I. M. KORENMAN (Z. anal. Chem., 1935, 99, 402—410).—Aq. KI + a variety of aromatic and cyclic bases give insol. products with Pb, Bi, Hg, Cu, Cd, and Hg salts which are in no case strictly sp. Sensitive tests are given by C₅H₅N for Pb, by 8-hydroxyquinoline for Bi, and by *p*-aminodimethylaniline for Cu. J. S. A.

Determination of metals with anthranilic acid. IV. **Determination of lead and mercury.** H. FUNK and F. ROMER (Z. anal. Chem., 1935, 101, 85—88; cf. A., 1934, 621).—Hg and Pb are pptd. as Hg[or Pb](C₇H₆O₂N)₂ by addition of anthranilic acid to the cold neutral solution. The ppts. may be dried at 105°; the Pb, but not the Hg, compound may be titrated with KBrO₃. Pptn. of Hg is not quant. in presence of alkali chlorides. J. S. A.

Determination of lead in drinking water.—See B., 1935, 432.

***p*-Homosalicylaldoxime as a reagent for copper.** C. H. KAO and K. H. CHEN (J. Chinese Chem. Soc., 1935, 3, 22—26).—*p*-OH·C₆H₄·CH·NOH is recommended for detection and determination of Cu in solution acidified with AcOH and of Ni in neutral or slightly alkaline solution. Details are given for the separation of these metals from other metals and from each other. J. W. S.

Potentiometric determinations in alkaline solution. **Determination of copper and silver.**

C. DEL FRESNO and E. MAIRLOT (Anal. Fis. Quím., 1934, 32, 280—285).—In the potentiometric titration of alkaline solutions containing Ag and Cu with VOSO₄, the successive breaks correspond with the completion of the reactions Ag⁺→Ag, Cu²⁺→Cu⁺, and Cu⁺→Cu. An accuracy of 1% may be obtained in the determination. D. R. D.

Analysis by means of organic compounds. I. **Separation and determination of copper and cadmium by salicylaldoxime and electrolysis.** II. **Separation and determination of copper and cadmium by salicylaldoxime and hydroxyquinoline.** III. **Separation and determination of copper and lead by salicylaldoxime.** M. ISHIBASHI and H. KISHI (J. Chem. Soc. Japan, 1934, 55, 1060—1064, 1065—1066, 1067—1069).—I. Cu can be pptd. by salicylaldoxime (I) from a slightly acid solution containing Cu and Cd. Cd is determined by electrolysis of the filtrate, (I) favouring the deposition of Cd.

II. Cu is pptd. as above, Cd being pptd. from the filtrate as Cd(C₉H₆ON)₂, which is dried at 130° and weighed.

III. Cu is pptd. from the slightly acid solution, as above, by (I). NH₃ is added to the filtrate until the is > 6.5, Pb being then pptd. by (I), collected, and dried at 105°. CH. ABS. (e)

Systematic potentiometric analysis. III. **Separation and determination of mercury.** W. HILTNER and W. GITTEL (Z. anal. Chem., 1935, 101, 28—31; cf. this vol., 185).—Hg, As, Sb, and Sn are separated as thio-salts by treatment with Na₂S. HgS alone is pptd. by addition of H₂O₂, and is titrated potentiometrically with KI after dissolution in HCl-HNO₃. J. S. A.

Ammonium molybdate as a microchemical reagent. C. VAN ZIJF (Pharm. Weekblad, 1935, 72, 414—418).—Characteristic cryst. compounds are obtained when NH₄ molybdate (I) is added to solutions containing Al, Mn²⁺, or Ce³⁺; less characteristic ppts. are obtained with Zn, Ni, Co, Cr, Fe³⁺, Cu, Hg, Tl, or Ag and no result is produced with UO₂, Pb, Cd, Bi, Li, Mg, Ca, Sr, Ba, and Fe²⁺. (I) can sometimes be replaced by the K, Cs, or Rb but not by the Na salt. S. C.

Analysis of felspar.—See B., 1935, 451.

Determination of metallic iron in presence of iron oxides. **Reduced iron.** F. HARTLEY, W. H. LINNELL, F. E. READ, and H. G. ROLFE (Quart. J. Pharm., 1935, 8, 100—112).—The B.P. (1932) method gives inaccurate and variable results. A modification of the method of Wilner (Merck, Z. anal. Chem., 1902, 41, 710) is satisfactory. F. O. H.

Determination of iron in presence of titanium; an aeration process. W. M. THORNTON, jun., and R. ROSEMAN (J. Amer. Chem. Soc., 1935, 57, 619—621).—The procedure of Gooch and Newton (A., 1907, ii, 507) has been modified by using air instead of Bi₂O₃ as the differential oxidising agent. E. S. H.

Ammonium salt of nitrosophenylhydroxylamine as a quantitative reagent. E. BENEDETTI (Rev. fac. cienc. quim., La Plata, 1934, 9, 59—68).—

The conditions under which this compound may be used to determine Fe^{III} , Fe^{II} , and Cu^{II} are described.

F. A. A.

Determination of cobalt by means of nitroso- β -naphthol. L. PHILIPPO (Bull. Soc. chim. Belg., 1935, 44, 140—153).—Co nitroso- β -naphthol obtained from 50 c.c. of M-CoSO_4 is dried and decomposed by fuming HNO_3 (10 c.c.). Br (one drop) and conc. H_2SO_4 (20 c.c.) are added to the solution, which is then evaporated to fuming. H_2O (30 c.c.) is added, the solution boiled, neutralised by aq. NH_3 (50—60 c.c.) after addition of a further 30 c.c. of H_2O , and electrolysed for 24 hr. The determination of Co in presence of Ni, Zn, and Fe is described. The time can be reduced if after addition of conc. H_2SO_4 the solution is diluted, neutralised with K_2CO_3 , and boiled. Br (3—4 drops) and 2N-KOH (20 c.c.) are added and the ppt. is dissolved in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$. The solution is made alkaline with NH_3 and electrolysed for 3.5 hr. The method gives good results when applied to the analysis of mineral sulphides.

R. S.

Hg(SCN) $_4$ as reagent for cobalt. Comparison of $\text{Na}_2\text{Hg(SCN)}_4$, $\text{K}_2\text{Hg(SCN)}_4$, and $(\text{NH}_4)_2\text{Hg(SCN)}_4$. B. V. J. CUVELIER (Z. anal. Chem., 1935, 101, 108—113).— $\text{Na}_2[\text{Hg(SCN)}_4]$ is the most sensitive reagent, $\text{Co}[\text{Hg(SCN)}_4]$ being less sol. in NaCl than in KCl or NH_4Cl solutions. J. S. A.

Organic [external] indicator for dichromate titrations. P. F. THOMPSON and E. C. ALABASTER (J. Soc. Chem. Ind. Victoria, 1933, 33, 810—811).—Diphenylcarbazine in presence of AcOH gives a pink colour with excess of CrO_4^{2-} . In presence of Cu or Sn, HCl is added.

J. S. A.

Reactions in the iodometric determination of chromates. F. L. HAHN (J. Amer. Chem. Soc., 1935, 57, 614—616).—The excess of $\text{Na}_2\text{S}_2\text{O}_3$ consumed in the reaction is ascribed to the formation of a complex chromic thiosulphate, which reacts slowly with I.

E. S. H.

Separation of molybdenum in alloy steels, especially from tungsten, and its potentiometric determination.—See B., 1935, 458.

Determination of titanium in ferrous alloys.—See B., 1935, 410.

Determination of zirconium with 8-hydroxyquinoline. G. BALANESCU (Z. anal. Chem., 1935, 101, 101—108).—In presence of ≤ 5 c.c. of HNO_3 per 10 mg. of Zr, 8-hydroxyquinoline ppts. Zr as $\text{Zr}(\text{C}_8\text{H}_5\text{ON})_4$. The ppt. may be dried at 140° and weighed directly, titrated with KBrO_3 , or ignited to ZrO_2 . Ppts. of indefinite composition are obtained in presence of Cl^- .

J. S. A.

Detection of bismuth with sulphur-containing organic reagents. IV. J. V. DUBSKY, A. OKAC, and J. TRIFLEK (Z. anal. Chem., 1935, 100, 408—419).—Compounds containing thio- and thiol-S in :3-positions (e.g., 3-thiol-5-thio-1 : 2 : 4-triazole and 4-phenyltriazole, persulphocyanic acid, and trithio-ophanic acid) give sensitive orange to brilliant red insol. Bi compounds of general type BiB_3 , BiB_2Cl , and BiBCl_2 . Compounds with similarly linked (thiol and thioether) S atoms in 1 : 3-positions give non-sp.

yellow colorations. Cu^{2+} , Ag, Pb, and Hg^{2+} tend to give non-sp. ppts. with both classes of compounds.

J. S. A.

Volumetric determination of niobium. J. A. TSCHERNICHOV and M. P. KARSSAJEVSKAJA (Z. anal. Chem., 1935, 99, 398—402).—Contrary to the findings of Schwarz (A., 1934, 632), Nb cannot be determined accurately by reduction with Zn amalgam and re-oxidation with standard FeCl_3 .

J. S. A.

Action of sulphuric acid on platinum-gold-silver alloys and its importance in docimacy. K. W. FROHLICH (Z. Elektrochem., 1935, 41, 207—211).—The usual method for determining Pt and Au is subject to errors due to dissolution of Pt and, to a smaller extent, of Au by H_2SO_4 . The potential-temp. curves of Pt and Au intersect at 270° , above which the former is less "noble." Introduction of 1% of As_2O_3 into the H_2SO_4 used reduces the loss of Au to $1/5$ — $1/6$, and of Pt to $1/10$ — $1/20$, of that occurring with the pure acid, whilst the dissolution of Ag remains unaffected.

F. L. U.

Thermoregulator, operating without a relay. M. CENTNERSZWER and J. SZPER (Rocz. Chem., 1935, 15, 26—28).—A PhMe thermoregulator is described.

R. T.

Photo-electric temperature regulator. B. LANGE and E. VOOS (Z. techn. Physik, 1934, 15, 323—326; Chem. Zentr., 1934, ii, 3794).—The regulator is operated by a mirror galvanometer, a Se cell, and a thyatron. A constancy of $\pm 0.17^\circ$ up to 1000° is claimed.

H. J. E.

Standard tables for chromel-alumel thermocouples. W. F. ROESER, A. I. DAHL, and G. J. GOWENS (J. Res. Nat. Bur. Stand., 1935, 14, 239—246).—The tables give the thermal e.m.f. of chromel P-alumel, chromel P-Pt, and alumel-Pt over the range -310° to 2500°F .

E. S. H.

Methods of testing thermocouples and thermocouple materials. W. F. ROESER and H. T. WENSEL (J. Res. Nat. Bur. Stand., 1935, 14, 247—282).—The methods developed and used at the National Bureau of Standards are described.

E. S. H.

Experiments at very low temperatures obtained by the magnetic method. I. Production of low temperatures. N. KURTI and F. SIMON (Proc. Roy. Soc., 1935, A, 149, 152—176).—The production of very low temp. by the magnetic method is discussed with reference to the influence of the initial conditions of field and temp. and the characteristic properties of the substance. With the apparatus used it is possible, with even small amounts of substance, to maintain the low temp. for a very long time so that measurements may be carried out. $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{KBr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ have been investigated as working substances. The first of these is the most satisfactory, and starting at 1.2° abs. and 14 kilogauss a temp. of 0.038° abs. is reached.

L. L. B.

Apparatus for m.-p. determinations and pressure, vapour pressure, and thermo-regulators. P. C. HENRIQUEZ (Chem. Weekblad, 1935, 32, 239—242).—For determining m.p., a closed tube is

fitted with a silvered vac. jacket containing windows for observing the substance in a capillary tube attached to the thermometer. The stirred liquid is heated electrically by an immersion element. A pressure regulator is operated electrically, and another by the inability of Hg to pass through a sintered glass plate; the amount of air passing through the apparatus is regulated by suction through a porous porcelain tube. A compact v.-p. regulator using very small quantities of liquid is described. A temp. accurate to 0.01° can be obtained with a Hg regulator having a bulb the size of a Beckmann thermometer, a capillary tube 0.05 mm. diameter, and a Pt contact 0.025 mm. thick. S. C.

Instruments for measuring spectral absorption. W. J. H. MOLL, H. C. BURGER, and W. J. REICHERT (*J. Sci. Instr.*, 1935, 12, 148—152).—The normal spectrograph slit is replaced by a device containing seven slits, two of which have identical widths and the remainder known fractional widths. Identical light beams are passed through cells containing solution and solvent and then through the special slits. The absorption coeffs. are found by a graphical method from the seven spectra, which are compared by means of a microphotometer. C. W. G.

Illumination of the spectrograph in quantitative spectral analysis. R. BRECKPOT and L. LIALINE (*Ann. Soc. Sci. Bruxelles*, 1935, 55, B, 30—42).—The influence on the image of different types of illumination and size of slit is discussed. The best results are obtained with a lens of focal length 16.8 cm. between the source and the collimator, and slits of 0.01—0.025 mm. R. S.

Infra-red photography of coal. J. J. WALKER and L. SLATER (*Nature*, 1935, 135, 623).—Advantages are discussed. L. S. T.

Sensitivity of photon counters. R. AUDUBERT (*Compt. rend.*, 1935, 200, 918—920).—The sensitivity of photon counters, measured by comparison with a Hg-vapour resonance lamp, can reach 5×10^{-11} erg per sec. per sq. cm. with an Al cathode or 1.0×10^{-9} erg per sec. per sq. cm. with a CuI cathode. In either case there is a wide variation between the sensitivities of individual cathodes. The sensitivity increases rapidly with increasing voltage, but is independent of the residual gas in the cell. The best results are obtained with a plate or disc cathode and a wire or ring anode. The emission from various reactions studied varies from 10^{-6} to 10^{-9} erg per sec. per sq. cm. J. W. S.

Christiansen light filter. E. D. MCALISTER (*Smithsonian Misc. Coll.*, 1935, 93, 1—12).—Construction, advantages, and limitations are described. N. M. B.

Allison magneto-optic (A) method of analysis. M. A. JEPPESEN and R. M. BELL. (B) **Apparatus.** T. R. BALL (*Physical Rev.*, 1935, [ii], 47, 546—548, 548—551).—(A) Readings taken by a no. of investigators indicate that the Allison minima are not a function of the chemical solutions used.

(B) A comprehensive statistical study, using the Allison apparatus, is described. Results are inconclusive. N. M. B.

Circular dichroism and some physico-chemical applications. J. P. MATHEU (*Ann. Physique*, 1935, [xi], 3, 371—460).—A visual method of measurement in the visible range, and a modified form of Brace's method (cf. *Physical Rev.*, 1904, 18, 70) for the ultra-violet, are described. $\text{Cr}(\text{OH})_3$ in tartaric acid first forms a Cr tartrate which passes spontaneously into a complex chromotartrate as shown by the absorption spectrum and by optical activity. Investigation of the circular dichroism appearing shows that the formation is a second-order reaction. In alkaline solution the complex acts as a weak acid. Neutralisation by an alkali shows a regular variation of ionic and optical properties and indicates the formation of an alkaline chromotartrate giving in presence of alkaline tartrate an alkaline chromotritartrate marked by optical activity; the structure and equilibrium of this compound are investigated. Analogous compounds are formed by Fe, Co, and Al. N. M. B.

Linear photo-electric densitometer. C. W. MILLER (*Rev. Sci. Instr.*, 1935, [ii], 6, 125—127).—A portable instrument using a.c. and giving readings very nearly \propto density is described. It can be adapted to measuring the blackness of opaque objects. N. M. B.

Photo-electric conductive substances. IV. Filters for the thallium cell. C. ASAI (*J. Chem. Soc. Japan*, 1934, 55, 1099—1101).—A glass plate painted with a 0.5% tartrazine solution absorbs $\lambda < 4900 \text{ \AA.}$, and is a suitable filter. CH. ABS. (e)

Apparatus for photo-electric extinction measurements. S. BODFORSS (*Svensk Kem. Tidskr.*, 1935, 47, 41—50).—The method uses a Hg lamp, optical filters, and two Se "sperrschicht" cells. Examples are given of its use in studying rapid reactions, phenolphthalein + NaOH, reduction of $\text{PhN}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2 \cdot \alpha$, Me-orange, and methylene-blue by SnCl_2 , and reduction of HAuCl by H_2O_2 . R. P. B.

Cæsium photo-elements sensitised by sulphur. V. ROSHDESTVENSKI (*J. Tech. Phys. U.S.S.R.*, 1934, 4, 669—670).—The Ag cathode is treated with S vapour instead of with O_2 . The cell is not sensitive in the infra-red and has one max. in the visible. CH. ABS. (e)

Photo-electric conductive substances. III. Spectroscopic studies on the photo-electric conductive thallium cell. C. ASAI (*J. Chem. Soc. Japan*, 1934, 55, 979—990).—The Tl cell is photosensitive from 5100 to 12,000 \AA. (max. at 6480, 9550 \AA.). CH. ABS. (e)

Circuit for the analysis of Geiger-counter pulses. W. E. RAMSEY and M. R. LIPMAN (*Rev. Sci. Instr.*, 1935, [ii], 6, 121—125).—A circuit for measuring the variation of the counting rate with the voltage on the counter, the sizes of the pulses, the time of recovery, and the form of the recovery curve is described. N. M. B.

Apparatus for unipolar micro-electrolysis. S. WEHRLI (*Helv. Chim. Acta*, 1935, 18, 546—548).—An apparatus for the micro-determination of Pb by anodic deposition as PbO_2 is described. The anode

is a Pt wire; the Pb solution is separated from the cathode by a "diaphragm" of NH_4NO_3 solution.

E. S. H.

Electron microscope using purely magnetic fields. R. WALLAUSCHEK and P. BERGMANN (Z. Physik, 1935, 94, 329—347).—The general theory of the microscope is given, and is applied to determine the optical constns. of instruments with magnetic lenses.

A. B. D. C.

Securing rigidity of electrodes in conductometric work. B. N. SASTRI and M. SREENIVASAYA (J. Sci. Instr., 1935, 12, 167).—The Pt electrode is sealed to a frame of Pyrex glass.

C. W. G.

Large cloud chamber. G. HERZOG (J. Sci. Instr., 1935, 12, 153—159).—Internal dimensions are 50×25 cm. Straight tracks 50 cm. long have been obtained.

C. W. G.

Electro-analysis with three electrodes. J. GUZMAN and A. SARABIA (Anal. Fis. Quím., 1934, 32, 275—279).—To obtain quant. adherent deposits of metal on the cathode, a third electrode is placed in the liquid, a const. p.d. being maintained between this electrode and the cathode. Experimental details for the determination of Cu are given.

D. R. D.

Electro-endosmosis. VI. The "bubble-tube" method of measurement. F. FAIRBROTHER and A. E. STUBBS (J.C.S., 1935, 527—529).—If the length of the bubble is $>$ approx. 1.5 times the diameter, D , of the tube, the difference between the apparent velocity, U , of the liquid, as indicated by the bubble, and the true velocity is independent of the length of the bubble. When the thickness, d , of the film of liquid adhering to the walls of the tube is small compared with D , the fractional error, W , is given by $W = 4d/D = \sqrt{(U\eta/\sigma)}$, approx., where η and σ are the viscosity and density, respectively, of the liquid.

J. G. A. G.

Application of the buoyancy method in measuring the dielectric constant of electrolyte solutions. P. MORTIER (Wis.-en natuurk. Tijds., 1934, 7, 36—43; Chem. Zentr., 1934, ii, 3650).—A modification of Preuner and Pungs' method (Physikal. Z., 1919, 20, 543) applicable to dil. aq. KCl solutions is described.

H. J. E.

Determination of conductivity of solutions of any salt content. F. TÖDT (Chem.-Ztg., 1935, 59, —Apparatus which is applicable over a wide range of conductivity is described.

E. S. H.

Large permanent magnet for the spectrographic study of β -rays. J. SURUGUE (J. Phys. Radium, 1935, [vii], 6, 94—98).

N. M. B.

Magnetic dilatometer. T. C. RICHARDS (Iron and Steel Ind., 1935, 8, 261—264).

W. P. R.

Student's gas-density balance. C. C. COFFIN (J. Chem. Educ., 1935, 12, 142—143).

L. S. T.

Ventilation of laboratory fume cupboards. A. BARBOT (Bull. Soc. chim., 1935, [v], 2, 666—668).—An electric fan is described.

D. R. D.

Conicylindrical viscosimeter. M. MOONEY and R. H. EWART (Physics, 1934, 5, 350—354).—A rotating cylinder viscosimeter is described.

CH. ABS. (e)

Support for crucibles. C. O. HARVEY (Chem. and Ind., 1935, 391).—A no. of units, each consisting of a large and a small triangle, and made from fused SiO_2 tubing and Ni-Cr wire, are mounted on a common frame.

A. L. R.

Physical methods in the chemical laboratory. XXIII. Physical methods of analysis. P. WULFF (Angew. Chem., 1935, 48, 233—238; cf. A., 1934, 1324).—The influence of external factors on various physical methods of analysis, and their specificity, exactness, etc., are discussed in a general way.

R. S.

Apparatus for the determination of minute quantities of radium, radon, and thoron in solids, liquids, and gases. R. D. EVANS (Rev. Sci. Instr., 1935, [ii], 6, 99—112).—A double ionisation chamber apparatus with photographic recording of ionisation current is described. Gaseous samples are examined directly; liquids are boiled in a flask fitted with a reflux condenser and Rn is swept out by a current of N_2 through the liquid; solids are first treated by a modified fusion furnace method.

N. M. B.

Opening stoppered bottles. H. SCHANZ (Chem.-Ztg., 1935, 59, 369).—A simple method of removing jammed stoppers is described.

J. S. A.

Clamping glass tubing. J. A. V. FAIRBROTHER (J. Sci. Instr., 1935, 12, 169).—The glass tubing is held in a V-shaped slot in the end of a length of brass tubing by a wire or strip which passes around it and can be tightened by a screw and wing nut.

C. W. G.

New alloy suitable for use in radium beam therapy. J. C. McLENNAN and C. J. SMITHELLS (J. Sci. Instr., 1935, 12, 159—160).—A W-Ni-Cu alloy of d 16.5 has a mean absorption coeff. of 0.83 cm.^{-1} for hard γ -rays.

C. W. G.

Gas washing device. R. SPENCE (J.S.C.I., 1935, 54, 158r).—The gas bubbles up a spiral and discharges the washing liquid through a U-tube. The discharged liquid may be discarded, re-circulated, or pass into another washer arranged on the counter-current principle.

R. S.

Low-pressure gas bubbler. E. W. BLANK (J. Chem. Educ., 1935, 12, 124).—A gas-absorption bubbler suitable for small vols. of gases at very low pressures is described.

L. S. T.

Use of vacuum tubes in measurements. J. W. HORTON (Electr. Eng., 1935, 54, 93—102).—A bibliography and review.

CH. ABS. (e)

Plant for production of heavy water. W. G. BROWN and A. F. DAGGETT (J. Chem. Physics, 1935, 3, 216—218).—A more efficient electrolytic method for the production of heavy H_2O than previously used is described. The average fractionating factor, uncorr. for evaporation, is 8.6. The apparatus is explosion-proof. An additional purification stage is used to exclude N oxides.

M. S. B.

Apparatus for filtering with avoidance of evaporation. H. DE V. ROBLES (Chem. Weekblad, 1935, 32, 255—256).—The liquid flows from a stoppered vessel, A, through a sintered glass filter into

another closed vessel, *B*. A by-pass carries the displaced air back from *B* into *A*. D. R. D.

Laboratory fractionating column. H. C. S. SNETHLAGE (Chem. Weekblad, 1934, 31, 748—749).—By the use of the simple apparatus described it is possible to separate 100% MeOH from mixtures containing up to 96% of H₂O, at the rate of 3 c.c. per min. H. F. G.

Quantitative extraction. A. G. KUHLMANN (Z. Unters. Lebensm., 1935, 69, 221—227; cf. A., 1927, 1049).—Several modifications of the Soxhlet apparatus are described. E. C. S.

Extractor using a solution of volatile and non-volatile phases. A. J. BAILEY (Science, 1935, 81, 317).

High rotational speeds in vacuo. E. G. PICKELS and J. W. BEAMS (Science, 1935, 81, 342—343).—The adaptation of the air-driven ultracentrifuge for the production of high rotational speeds in a vac. is described. L. S. T.

Development of an air-driven ultracentrifuge. J. W. McBAIN and C. M. O'SULLIVAN (J. Amer. Chem. Soc., 1935, 57, 780—781).—The air-driven spinning top has been developed into an ultracentrifuge for sedimentation analysis. E. S. H.

Vacuum evaporation and distillation. H. N. NAUMANN (Biochem. J., 1935, 29, 994—997).—Improvements in the evaporation apparatus previously described (A., 1931, 191), whereby 5—30 litres of H₂O per hr. may be distilled at 20°, are detailed. H. D.

Visual demonstration of the evaporation of mercury. W. G. LEIGHTON and P. A. LEIGHTON (J. Chem. Educ., 1935, 12, 139—142).—An open vessel containing Hg is placed between an A-Hg lamp and a screen coated with anthracene, uranyl sulphate, or willemite. Even at room temp. sufficient Hg vapour is swept out of the dish to cast shadows on the fluorescent background. This provides a sensitive method for detecting small amounts of Hg either metallic or combined rising from a heated sample. L. S. T.

Law of volatility. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 658—660).—Illustrations are given of the principle that, if two vapours are capable of reacting to produce a non-volatile substance, the reaction will be carried over in this direction. D. R. D.

Ramsay and helium. M. W. TRAVERS (Nature, 1935, 135, 619).—Historical. L. S. T.

Geochemistry.

Effect of wind on the concentration of carbon dioxide in the air. D. SZYMKIEWICZ (Polish Agr. Forestal Ann., 1934, 33, 13—22).—With increasing wind velocity from 0 to 0.8 and 1.2 m. per sec. the [CO₂] decreases from 1.22 to 0.67 and 0.54 mg. per litre, respectively. CH. ABS. (e)

Sea-water of the Puget Sound region. T. G. THOMPSON and R. J. ROBINSON (Proc. 5th Pacific Sci. Cong., 1933, 2101—2107).—Analytical data are recorded. CH. ABS. (e)

Free ammonia, albuminoid nitrogen, and organic nitrogen (A) in the waters of the Puget Sound area, during the summers of 1931 and 1932, (B) in the waters of the Pacific Ocean off the coasts of Washington and Vancouver Island. R. J. ROBINSON and H. E. WIRTH (J. cons. intern. expl. mer, 1934, 9, No. 1, 15—27; No. 2, 187—195).—Data are recorded. CH. ABS. (e)

Rare gases. III. Helium-neon content of the ocean waters. W. D. URRY (J. Amer. Chem. Soc., 1935, 57, 657—659; cf. A., 1933, 20, 1008).—The ratio to O₂ content and the variation with depth have been determined. E. S. H.

Ratio argon:nitrogen in natural gases. M. GESLIN (Compt. rend., 1935, 200, 1137—1139).—Natural gas from oil, petroleum, hot, or mineral springs is found to have a ratio A:N₂ < for air. A study of the effect of the presence of fish, aquatic plants, Ra, etc. on the gases obtained from aquarium H₂O shows that the total combustible gases produced have a composition similar to CH₄, and that there is an increase in N₂, more rapid in presence of Ra, which probably originates in the destruction of

animal and vegetable matter and hence there is a diminution in the ratio A:N₂. M. S. B.

Helium "beds." R. WAGER (Naturwiss., 1935, 23, 233—237).—The origin and location of sources of He are described. A. J. M.

Coal and natural oil in the Pittsburgh region. E. LINTON (Science, 1935, 81, 252).—The fact that oil and coal happen to occur in the latitude and longitude of the Pittsburgh region has no bearing on their origin (cf. this vol., 324). L. S. T.

Petroleum geology of Western Canada. A. J. GOODMAN (J. Inst. Petroleum Tech., 1935, 21, 221—258).—Following a survey of the geological features of W. Canada, it is concluded that the greater part of the oil and gas probably originated in the Palaeozoic limestones, although some source rocks may occur in the Mesozoics. C. C.

Effects of geophysical factors on the evolution of oil and coal. D. WHITE (J. Inst. Petroleum Tech., 1935, 21, 301—310).—Progressive carbonisation of coal and the evolution of petroleum (I) occur under geophysical influences (II) by processes equiv. to natural underground cracking, the pressure being of dominant importance. (I) is the product of sedimentary deposits of org. mother-substances of varying composition through biochemical and geochemical changes which take place underground in course of time under (II) and vary with the ratios of pressure, temp., and time. C. C.

X-Ray examination of the minerals of the earth's crust. J. M. BLIJVOET and W. NIEUWENKAMP (Chem. Weekblad, 1934, 31, 740—747).—A

detailed account is given of the insight which has been obtained into the structure of the naturally occurring complex silicates, and the conditions governing their deposition from the magma, by means of X-ray examination. H. F. G.

Optical study of emeralds and other minerals coloured by chromium. P. VOGEL (Jahrb. Min., 1934, A, 68, 401—438; Chem. Zentr., 1934, ii, 3369).—Emeralds from the chief sources may be differentiated by their absorption curves (I). Natural and artificial rubies have the same (I). Artificial rubies coloured with Cr have a different (I) from spinel coloured with Cr. Spinel with an excess of γ - Al_2O_3 , coloured artificially with Cr_2O_3 , has a different (I) from emerald. Synthetic corundum and spinel coloured green by V give similar (I), resembling that of spinel coloured with Cr_2O_3 . Changes on tempering are discussed. H. J. E.

Constitution of stilpnomelane and stilpnochlorane. J. HOLZNER (Zentr. Min., 1934, A, 299—305; Chem. Zentr., 1934, ii, 3370).—From their constitution these substances are intermediate between the micas and the chlorites. The Ca in stilpnochlorane can be replaced in an exchange reaction by 2Tl. H. J. E.

Stainierite. L. DE LEENHEER (Natuurwetensch. Tijds., 1935, 17, 44—48).—Macroscopic, optical, and X-ray examination shows that stainierite (Co_2O_3 72.19, Fe_2O_3 9.93, Al_2O_3 7.22, H_2O 10.66%; hardness 4.5, d 4.32) is heterogeneous and an impure form of $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The dehydration curve is similar to that of mindigite. S. C.

Genetic relations of silver deposits and Keweenawan diabases in Ontario. E. S. MOORE (Econ. Geol., 1934, 29, 725—756).—Co and Ni arsenides and sulphides and native Ag are the typical ore minerals closely associated with diabase intrusions in the form of sills. The parent magma (I) contained Ag. The (I) of the diabase was the source of the ore solutions. CH. ABS. (e)

Additional limonite types of galena and sphalerite derivation. R. BLANCHARD and P. F. BOSWELL (Econ. Geol., 1934, 29, 671—690).—Two new types are described: the diamond-mesh box-work, derived from steel galena, and the pyramidal, derived by pseudomorphic replacement of ordinary galena. CH. ABS. (e)

Beryl-molybdenite deposit of Chaffee County, Colorado. K. K. LANDES (Econ. Geol., 1934, 29, 697—702).—The presence of beryl with molybdenite in the quartz vein indicates a deposition by hydrothermal solutions escaping from a deeper solidifying pegmatite. CH. ABS. (e)

North Carolina talc deposits. J. L. STUCKEY (J. Elisha Mitchell Sci. Soc., 1934, 50, 41—42).—The talc deposits are associated with marble, and are probably formed by hot solutions from quartz-diorite dikes after metamorphism (I) of the sediments, and not by simple (I) of MgCO_3 in the original limestone. CH. ABS. (e)

Differentiation in basalt lava, Island Magee, Co. Antrim. S. I. TOMKEIEFF (Geol. Mag., 1934, 71, 501—512).—There is a rapid increase of MgO with

depth. There has been a gravitational sinking of Mg-rich olivine, with the development of a border of iddingsite and chlorophaite produced by contact with a hydrous Fe-enriched residual magma.

CH. ABS. (e)

Contaminated tonalites of Loch Awe, Argyll. S. R. NOCKOLDS (Quart. J. Geol. Soc., 1934, 90, 302—321).—The normal tonalite is contaminated by argillaceous, argillo-lalcaeous, and calcareous xenoliths. The reaction process is discussed.

CH. ABS. (e)

Granite-schist contact in Stewart Island, New Zealand. G. J. WILLIAMS (Quart. J. Geol. Soc., 1934, 90, 322—353).—The development of the minerals is described and discussed.

CH. ABS. (e)

Ultrabasic epidiorite from St. Catherine's, Loch Fyne. J. D. H. WISEMAN (Geol. Mag., 1934, 71, 425—427).—The rock is characterised by the absence of feldspar, epidote, and sphene, and the present of penninite, and by the high MgO and Al_2O_3 and low alkali content.

CH. ABS. (e)

Secondary selenite crystals in tertiary strata in Texas. M. N. BROUGHTON (Amer. Min., 1934, 19, 466—473).—The occurrence is described. Its origin is discussed.

CH. ABS. (e)

Monticellite from Crestmore, California. R. S. MOEHLMAN and F. A. GONYER (Amer. Min., 1934, 19, 474—476).—The composition is SiO_2 37.46, FeO 3.98, MnO 0.52, MgO 22.78, CaO 35.20, H_2O 0.15%. Physical data are recorded. The mineral is associated with garnet, and with diopside as an interstitial material.

CH. ABS. (e)

Petrology of the kaolin deposits near Anna, Illinois. R. E. GRIM (Econ. Geol., 1934, 29, 659—670).—The chief mineral is kaolinite. SiO_2 , Fe oxide, and small amounts of kyanite, zircon, staurolite, tourmaline, ilmenite, leucocene, rutile, sillimanite, epidote, anatase, and chloritic material are present.

CH. ABS. (e)

Kaolinite in Illinois coal. C. G. BALL (Econ. Geol., 1934, 29, 767—776).—Chemical, optical, X-ray, and dehydration data are recorded for kaolinite found in desiccation cracks.

CH. ABS. (e)

Structures and textures of synthetic replacements in "open space." C. SCHOUTEN (Econ. Geol., 1934, 29, 611—658).—Experiments are described on synthetic replacements in polished specimens of pure crystals, and mineral and crystal aggregates. The synthetic products resembled various types of natural ingrowth.

CH. ABS. (e)

Petrology of the Pennsylvanian shales and non-calcareous underclays associated with Illinois coals. II, III. R. E. GRIM [with P. F. KERR and O. W. REES] (Bull. Amer. Ceram. Soc., 1935, 14, 129—134, 170—176; cf. this vol., 603).—The results of petrographic, chemical, and X-ray examinations are recorded.

J. A. S.

Mineral facies in metamorphic rocks. F. J. TURNER (Amer. J. Sci., 1935, [v], 29, 409—421).—The various assemblages of minerals that are stable under different conditions of temp. and pressure are considered. The presence of H_2O also has an im-

portant influence, and different cases are given by rising and falling temp. Green-schists, consisting of chlorite, epidote, and albite, are specially considered.

L. J. S.

Layered peridotitic laccoliths in Newfoundland. E. INGERSON (Amer. J. Sci., 1935, [v], 29, 422—440).—Large laccoliths in the Trout River area show at the base a thick zone of dunite and bronzite-peridotite, then a "critical zone" consisting of alternating layers of felspar-rich and olivine-rich rocks, and at the top a thinner zone of dunite and peridotite. Density determinations are given of the different types of rocks, and an explanation of the structure of the intrusion is offered.

L. J. S.

Radium content of lavas, California. R. D. EVANS and H. WILLIAMS (Amer. J. Sci., 1935, [v], 29, 441—452).—The Ra content was determined for different types of rocks, basalt to dacite (SiO_2 51.13—66.65%) from the same area (Lassen volcanic, National Park). They gave Ra 0.33—0.80 $\times 10^{-12}$ g. per g. The residual glass of the rock is richest in Ra, whilst felspar and biotite contain much less. There seems to be no connexion between the amount of Ra and the relative age of the lava flows.

L. J. S.

Volume variation and modification of the lattice of sepiolites as a function of temperature. G. MIGEON (Compt. rend., 1935, 200, 946—949; cf. A., 1933, 369; this vol., 323, 468).—X-Ray spectral analysis shows that all sepiolites have a common characteristic initial lattice, but certain spacings vary from sample to sample. At 300°, dehydration occurs, followed by contraction, but no great change occurs in the crystal structure. At 460—750° slow and continuous loss of H_2O occurs, lattice changes setting in at 600°. At 750—820° H_2O is lost rapidly, considerable contraction occurs, and enstatite is formed. At 900—1000° dehydration is completed, contraction is very rapid, and the SiO_2 produced is in the form of cristobalite.

J. W. S.

Sepiolite from Ampandrandava (Madagascar). H. LONGCHAMON (Compt. rend., 1935, 200, 949—951; cf. preceding abstract).—The fibrous structure of this sepiolite (sepiolite I) is attributed to chains of 4 Si and 11 O, to which Mg and OH ions are linked laterally. It loses 10.5% H_2O at 110° without change in crystal lattice. Change in the latter sets in at 300°, becomes rapid at 330—350°, and is complete at 500°. After heating at 500° the spacing along the fibre is unchanged but lateral spacings are reduced. This form (sepiolite II) is stable to 750° but above this temp. yields diffuse X-ray patterns with scarcely detectable periodicity along the fibre. At 780°, however, it yields the enstatite structure with the same longitudinal spacing as before. This passes into cristobalite at temp. varying from 850° to 1000°. Dilatometric and thermal analysis and study of the dehydration show that sepiolite I is a true Mg zeolite, whereas II has no zeolitic properties. Most of the H_2O is zeolitic, but part is necessary to the lattice structure.

J. W. S.

Jarosite in tuff from Potosi, Bolivia. C. MILTON (Amer. Min., 1935, 20, 176—178).—A fine-grained siliceous tuff, containing 16% of jarosite, is described.

L. S. T.

Lindgrenite, a new mineral. C. PALACHE (Amer. Min., 1935, 20, 187).—Lindgrenite, $\text{Cu}_2\text{MoO}_4 \cdot \text{Cu}(\text{OH})_2$, has $a : b : c = 0.5941 : 1 : 0.5124$, $\beta 92^\circ 12'$, and occurs as green crystals in veinlets in limonitic quartz in the Cu mine at Chuquicamata, Chile.

L. S. T.

Age and distribution of pegmatites. K. L. LANDES (Amer. Min., 1935, 20, 81—105, 153—175).—Most of the known pegmatites are pre-Cambrian in age. A compilation of pegmatite occurrences throughout the world and maps are given.

L. S. T.

Austinite, a new arsenate mineral, from Gold Hill, Utah. L. W. STAPLES (Amer. Min., 1935, 20, 112—119).—Austinite, $\text{CaZn}(\text{OH})\text{AsO}_4$, occurs as colourless orthorhombic crystals of prismatic habit and closely associated with adamite. The analysis is CaO 19.2, ZnO 32.5, As_2O_5 42.7, P_2O_5 0.1, H_2O 3.6, V_2O_5 0.0, residue 2.4, total 100.5%; $a : b : c = 0.657 : 1 : 0.832$, n_a 1.759 \pm 0.003, 1.763 \pm 0.003, n_y 1.783 \pm 0.003, d 4.12 approx.

L. S. T.

Contact metamorphic zone from the Little Belt Mountains, Montana. J. H. TAYLOR (Amer. Min., 1935, 20, 120—128).—The petrography and paragenesis of the two silicate zones surrounding the igneous rock are described. The abundance of prehnite is a characteristic feature of the zone of dark silicates. Scawtite occurs in the zone of light silicates.

L. S. T.

Anorthite from California. F. S. MILLER (Amer. Min., 1935, 20, 139—146).—The olivine-bearing phases of the San Marcos gabbro, San Luis Rey quadrangle, California, are composed predominantly of a plagioclase felspar which falls within the composition range of anorthite (94% An). Chemical analyses and the optical properties of this anorthite are given.

L. S. T.

Celestite from Chittenango Fall, New York. N. W. THIBAUT (Amer. Min., 1935, 20, 147—152).—The celestite, associated with much calcite, and smaller amounts of quartz and chalcedony, occurs as well-developed crystals lining irregular geodic cavities, and as massive and fibrous veins connecting the geodes. n_a 1.622, n_b 1.624, n_y 1.632; d 3.939—3.968. A little Ca, but no Ba, isomorphously replaces the Sr.

L. S. T.

Micro-diaclases in splinters of flint. Their importance in artificial coloration of microfossils and in particular of foraminifera. G. DEFLANDRE (Compt. rend., 1935, 200, 953—955).—When a polished splinter of flint is immersed for 2—4 hr. in a $\text{EtOH}-\text{H}_2\text{O}$ solution of Dahlia-violet, washed, and examined microscopically, micro-diaclases appear. It is uncertain whether these are due to shock in obtaining the splinter or in polishing the sample or whether they exist in the body of the flint. Their importance in respect of the coloration of micro-fossils is pointed out.

J. W. S.

Minerals from Csódi Mt., Hungary. R. REICHERT and J. ERDELYI (Tsch. Min. Petr. Mitt., 1935, 46, 237—255).—Descriptions with chemical analyses are given of zeolites (chabazite, analcime, and stilbite)

from cavities in andesite. The accompanying calcite is of various crystal habits. L. J. S.

Dissociation vapour pressure of sulphides and their order of deposition in magmatic ore deposits. E. KORDES (Tsch. Min. Petr. Mitt., 1935, 46, 256—288).—V.-p. curves (compiled from the lit.) for Zn, Cu, Fe, Ag, Pb, Bi, Sb, As, and Hg sulphides are in much the same order as that in which the corresponding sulphide minerals are deposited in hydrothermal veins, i.e., the least volatile are deposited earlier. L. J. S.

Presence of rare alkaline metals in amazonites. J. M. TOLMATSCHEV and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 321—323).—Amazonites from various localities have been analysed spectrographically for their content of Li, Rb, Cs, Ga, and Be. Ilmenski Mountain amazonite (I) contains the largest % of Rb, 1—2%, with Rb:Cs approx. 20:1. The composition of amazonites corresponds with $(K,Rb,Na)_2Al_2Si_6O_{18}$. (I) contains 0.0015—0.002% of Sr, which is much > the amount producible by radioactive disintegration of Rb. It is suggested that the Sr is present to the extent of 30% as Sr^{87} . In (I) Sr:Ca=approx. 1:100, and Y and Cu are $\times 0.001\%$, so that the blue colour cannot be due to the latter. Traces of Pb are present in all amazonites. R. S. B.

Linnæite group of cobalt-nickel-iron-copper sulphides. W. A. TARR (Amer. Min., 1935, 20, 69—80).—Available analyses are discussed for linnæite, carrollite, synchymite, siegenite, violarite, and polydymite. They should be represented by the general formula $R''R'''S_4$ where R'' is Co^{++} , Ni^{++} , Cu^{++} , and Fe^{++} and R''' Co^{+++} , Ni^{+++} , and Fe^{+++} . The Co, Ni, Fe, and Cu are isomorphous. The name "carrollite," $CuCo_2S_4$, is preferred for those minerals rich in Cu, whilst that of "synchymite" should be discarded. X-Ray investigations of all these members, except violarite, show that they possess the spinel structure type. L. S. T.

Magnetite cementing certain ore conglomerates of the Mesabi range. J. W. GRUNER (Econ. Geol., 1934, 29, 757—760).—The magnetite (FeO 30.94, Fe_2O_3 69.05%, MnO trace) was apparently of hydrothermal origin. CH. ABS. (e)

Recent vulcanism and the formation of iron ores. F. BEHREND (Z. deut. geol. Ges., 1934, 86, 360—367; Chem. Zentr., 1934, ii, 3370).—A description and discussion of Fe deposits in Santorin. H. J. E.

Organic minerals. IV. Chlorophyll and hæmin derivatives in rocks, petroleum, coals, and phosphorites. A. TREIBS (Annalen, 1935, 517, 172—196; cf. A., 1934, 387, 629).—In 22 of 27 specimens of petroleum examined, porphyrins (I) were immediately detected spectroscopically. In all cases deoxophylloerythroætioporphyrin predominated, other (I) being similar to and in similar amount to those already recorded (*loc. cit.*). In an individual oil-shale the proportion of complex was sufficient to permit its isolation and identification synthetically. It was thus shown to be a V compound, but the prep. by use of VCl_4 and NaOAc probably involves reduction of V^{IV} . The composition of the complex is not fully established, the analytical vals. lying between those of a VO [or $V(OH)_2$] and VO_2 derivative. The salts are stable towards conc. HCl and are only slowly decomposed by conc. H_2SO_4 . They can be reduced to complex leuco-compounds which are stable to acid but readily oxidised by air to the initial substances. The presence in petroleum and bituminous extracts of a Fe^{II} complex, apparently derived from mesoætioporphyrin and characterised by complete stability to air, is also established. All (I) previously detected in minerals could be observed in coals whilst in 3 samples a material closely resembling deuterioætioporphyrin and the corresponding acid porphyrin were observed. Phosphorites contain the same (I) as petroleum and oil-shales but the amounts of acidic (I) exceed those of ætioporphyrins. In an individual case a material with the properties of mesoporphyrin was detected. Coproporphyrin and a spectroscopic analogue of hæmatoporphyrin were present in guano and (I) in asphalt. It is considered that petroleum, bitumens, coals, and phosphorites cannot have been subjected to a temp. above 200° . The formation of phosphorites from guano is highly improbable and the participation of green plants in their production is suggested. The occurrence of (I) in complex union with V or Fe^{II} is a secondary phenomenon. Less firmly bound elements are displaced, thus accounting for the remarkable accumulation of V in the ashes of petroleum and asphalt. H. W.

Organic Chemistry.

Principles of the co-ordination theory and some applications to organic chemistry. G. URBAIN (Bull. Soc. chim., 1935, [v], 2, 555—569).—A lecture.

General mechanism of fission of carbon chains. R. CRIGGEE (Ber., 1935, 68, [B], 665—668).—The general hypothesis is that if 2 atoms or groups in the $\alpha\delta$ -position in a mol. are removed, the remainder undergoes fission between the β and γ atoms. Examples cited in favour of this view are (1) the formation of ethylenes by the cautious removal of metals from $\alpha\omega$ -dialkali-substituted butanes; (2) the production of C_2H_4 from $(\cdot CH_2 \cdot CH_2 \cdot I)_2$, (3) the fission of glycols by

$Pb(OAc)_4$, (4) Tiffeneau's interpretation of the pinacolin transformation through $\alpha\gamma$ -diradicals, (5) the conversion of β -OH-acids in which α -H atoms are replaced by alkyl into CO_2 and alkynes, $OH \cdot CHMe \cdot CMe_2 \cdot CO_2H \rightarrow \cdot CHMe \cdot CMe_2 \cdot CO \cdot O \rightarrow CHMe : CMe_2 + CO_2$, (6) the cracking of saturated hydrocarbons. H. W.

Thermal decomposition of hydrocarbons. P. P. BORISOV, E. M. SCHACHNAZAROVA, and E. I. MARGOLIS (J. Gen. Chem. Russ., 1934, 4, 1385—1389).—Hexane, cyclo-pentane, -hexane, and -hexene, decahydronaphthalene, and C_6H_6 give rise to H_2 and

saturated hydrocarbons when heated at 1200°; except in the case of C_6H_6 the content of unsaturated hydrocarbons rises with fall in temp. R. T.

Relation between the structure of hydrocarbons and their miscibility with selective solvents.—See this vol., 694.

Wurtz synthesis. W. HUCKEL, A. KRAEMER, and F. THIELE (J. pr. Chem., 1935, [ii], 142, 207—217).—The following are typical % yields (of the theoretical) of products obtained in Wurtz syntheses using Na or Na-K in xylene as a solvent (H_2 atm.). Saturated hydrocarbons were determined by isolation and/or explosion with O_2 , and unsaturated by catalytic reduction and by absorption in $Br-H_2O$: EtCl gives C_2H_4 5.5, C_2H_6 32, C_4H_{10} 12, EtBr giving 3, 33.5, and 27%, respectively. Pr^iCl affords C_3H_8 21.5, C_3H_6 10.5, C_6H_{14} 23, Pr^iBr giving 8, 6, and 65%, respectively; Pr^sCl , C_3H_8 40, C_3H_6 18.5, Pr^sBr giving 45 and 10%, respectively; MeBr gives C_2H_6 12.5%. MeBr+EtBr afford C_2H_6 7, C_2H_4 9.5, C_3H_8 15%, C_4H_{10} 28%; MeBr+ Pr^iBr give C_3H_8 3, C_3H_6 9.4, C_4H_{10} 7.5, C_6H_{14} 44%; MeBr+ Pr^sBr , C_2H_6 15, C_3H_6 15, and $CHMe_3$ 43%. Bromides react more readily than chlorides, but the results are not always reproducible.

J. W. B.

Highly-polymerised compounds. CXI. **Measurements of viscosity of paraffins.** H. STAUDINGER and F. STAIGER (Ber., 1925, 68, [B], 707—726).—For substances with spherical mols. the vals. of η_{sp}/c are const. over a very wide range of concn., whereas in the case of thread mols. this is the case only in dil. sol solution. In a paraffin such as ethylhentriacontane a 20% solution is intermediate between sol and gel; the vals. of η_{sp}/c are const. up to 5%, whereas in 8.4% solution discrepancies become obvious. With *n*- and *iso*-paraffins η (sp. viscosity of a chain link) = 1.5×10^{-3} in CCl_4 and 1.3×10^{-3} in C_6H_6 . With rising temp. η_{sp} diminishes regularly, and at 60° is 6—15% < at 20°. Similar relationships between η_{sp} and chain length are found with *n*-hexacontane as with simpler members of the series. With myristone and stearone (I) the vals. of η are approx. identical with those found with hydrocarbons. Measurements of the viscosity of paraffins in various solvents and mixtures of solvents are recorded, and the question of solvation is discussed. Comparative determinations of the mol. wt. of fractions of a hard paraffin by measurement of η_{sp} in PhCl and cryoscopically in $C_{10}H_8$ and camphor show that the correct relationships between η_{sp} and chain length are shown only when such mixtures are as homogeneous as possible. σ -Ethylidenepentatriacontane, m.p. 21.5° [ozonised to AcOH and (I)], is obtained by the action of a large excess of $MgEtI$ on (I) and distillation of the product in vac.; it is converted by H_2 at 150°/80 atm. in presence of cyclohexane and Ni into σ -ethylpentatriacontane, m.p. 39°.

H. W.

Titrimetric determination of iodine values [of unsaturated hydrocarbons] with bromine vapour. E. ROSSMANN (Angew. Chem., 1935, 48, 223—226).—A weighed quantity of Br sealed in a thin glass bulb is introduced into a round-bottomed flask fitted with a funnel having a stopcock and containing the substance (I) to be tested. The flask is

evacuated and (I) distributed around the flask wall, the Br bulb broken, and the whole placed in the dark. For substances containing one double linking a 200% excess of Br allows interaction to be complete in 10 min. If 3 double linkings are present 400—500% excess allows completion in the same time. Excess of Br is titrated with As_2O_3 after KBr solution, with CCl_4 if necessary, has been added or KI may be added and the I titrated. Excess of Br has no influence on results, blank tests are unnecessary, and no substitution reactions can occur. The method appears universally applicable.

C. I.

Reaction between oxygen and Δ^8 -butene. H. J. LUCAS, A. N. PRATER, and R. E. MORRIS (J. Amer. Chem. Soc., 1935, 57, 723—727).— Δ^8 -Butene and O_2 at 375—490° give much $MeCHO$, some butadiene, and (at 490°) CH_4 , with a little glyoxal (or $CHO \cdot CH_2 \cdot OH$), an olefine oxide, and acid (or acids), and peroxide. Absence of Ac_2 , $CHMeAc \cdot OH$, and $COMeEt$ shows that oxidation does not proceed by hydroxylation. A possible reaction mechanism, involving formation of $\beta\gamma$ -dioxidobutane, is proposed.

R. S. C.

Hydrocarbons C_8H_{14} formed by the interaction of crotonyl bromide and its magnesium derivative. R. LESPIEAU and P. HEITZMANN (Compt. rend., 1935, 200, 1077—1080; cf. Braun *et al.*, A., 1923, i, 286).—Crotonyl bromide and Mg yield a mixture of hydrocarbons from which $(-CH_2 \cdot CH \cdot CHMe)_2$ (I), b.p. 122—125° (tetrabromide, m.p. 184—184.5°), $CHMe \cdot CH \cdot CH_2 \cdot CHMe \cdot CH \cdot CH_2$ (II), b.p. 110—111° (di-iodide, m.p. 155—156°), and a trace of $(-CHMe \cdot CH \cdot CH_2)_2$ (III), b.p. 100° (tetraiodide, decomp. 100°), have been separated. Hydrogenation of (I) gives octane and of (II) gives methylheptane. Raman spectra indicate that (I) is a mixture of *cis*- and *trans*-forms.

F. N. W.

Synthesis of tetratriacontadiene. Its properties with special reference to oiliness. M. V. DOVER and C. J. HELMERS (Ind. Eng. Chem., 1935, 27, 455—458).—Electrolysis (conditions described) of oleic acid in $EtOH-H_2O$ containing K_2CO_3 at 50—60° affords tetratriacontadiene (I), m.p. 20.5—21° (purification described), which distils at 120—170°/1—1.5 mm. to give a liquid (II) and a viscous residue (III). (I) can be reduced (H_2 - PtO_2 - $FeSO_4$) and absorbs I nearly quantitatively. (II) probably contains decomp. products, and (III) polymerides, of (I).

J. L. D.

Iodo-silver benzoate complex [as] iodinating agent; probable structure of the complex. C. PREVOST (Compt. rend., 1935, 200, 942—944).—With $CPh \cdot CH$, the complex $AgI(OBz)_2$ (A., 1933, 711) yields $CPh \cdot CH$, $AgOBz$, and $BzOH$; with C_2H_2 , it gives $CH \cdot Cl$ and $[Cl]_2$. The structure $[Ag(OBz)_2]^{-}I^{+}$ is proposed.

E. W. W.

Isomerisation of hydrocarbons. I. Chlorination of hexane and octane isomerides with antimony pentachloride as a method for their determination. B. L. MOLDAVSKI and S. E. LIVSCHITZ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 507—513).—The amount of chlorination of *iso*- C_6H_{14} and *iso*- C_8H_{18} (I) by $SbCl_5$ (12 mols.) (cf. Schaarschmidt, B., 1932, 493) in CCl_4 or $CHCl_3$ depends on the $[SbCl_5]$, but, within the limits of experimental error, not on the

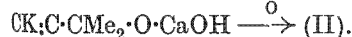
structure of (I). Traces of H_2O greatly inhibit the reaction, but in dry solution chlorination of (I) is readily effected (C_6H_{14} faster than C_8H_{18}) with 0.1*N*- SbCl_5 in CCl_4 at room temp., conditions under which the corresponding *n*-hydrocarbons (II) are unaffected: $\text{CR}'\text{R}''\text{MeCl}-\text{HCl} \rightarrow \text{CR}'\text{R}''\text{CH}_2+\text{SbCl}_5 \rightarrow \text{CR}'\text{R}''\text{CH}\cdot\text{CH}_2\text{Cl}$. A trustworthy method for the determination of (I) in presence of (II) is described. After interaction with a known vol. of standard $\text{SbCl}_5\text{-CHCl}_3$ for 2—6 hr., dil. HCl is added, and the excess of SbCl_5 is determined by titration with 0.1*N*- KBrO_3 (Me-orange). Comparison of the titre with that of a control experiment using a solution of (I) in (II) of known concn. enables the proportion of (II) to be determined. The results (examples given) are satisfactory even if the [(I)] is only 10%.

J. W. B.

Widmark's alcohol determination. C. A. MEIER and O. WYLER (*Arbeitsphysiol.*, 1934, 7, 528—535; *Chem. Zentr.*, 1934, ii, 3997).—Details of procedure are discussed.

J. S. A.

New methods of application of calcium carbide. L. KAZARJAN (*J. Gen. Chem. Russ.*, 1934, 4, 1347—1352).— COMe_2 (I) (1 mol.) is added to an Et_2O suspension of a 1:1-mol. mixture of KOH and CaC_2 (24 hr.; 0°), H_2O at 0° is added, the aq. layer is saturated with NaCl and Et_2O -extracted, and the combined Et_2O extracts are distilled, when $\text{CH}_3\text{C}\cdot\text{CMe}_2\cdot\text{OH}$ (II) is obtained in 70% yield. $(\text{OH}\cdot\text{CMe}_2\cdot\text{C})_2$ is obtained similarly (74% yield) when 2 mols. of (I) are taken. The reactions involved are $\text{CaC}_2+\text{KOH} \rightarrow \text{CK}\cdot\text{C}\cdot\text{CaOH}$ (III); $(\text{III})+(\text{I}) \rightarrow \text{OK}\cdot\text{CMe}_2\cdot\text{C}\cdot\text{C}\cdot\text{CaOH} \rightarrow$



R. T.

Compounds of oxyhalides with unsaturated substances. II. Reaction of nitrogen iodide with acids and alcohols in presence of olefines. A. A. PETROV (*J. Gen. Chem. Russ.*, 1934, 4, 1458—1463).—The following esters of β -iodo- γ -hydroxybutane (I) have been prepared by adding NI_3 to a mixture of $\text{CHMe}\cdot\text{CHMe}$ (II) and the appropriate acid at -10° : *formate*, b.p. $72.5^\circ/11$ mm., *propionate*, b.p. $97-98.5^\circ/15$ mm., *isobutyrate*, b.p. $101-109^\circ/15$ mm., *isovalerate*, b.p. $101-104^\circ/10$ mm. The ethers of (I) formerly described (this vol., 605) can also be obtained by conducting the above reaction in presence of the appropriate alcohol: $3\text{R}\cdot\text{CO}_2\text{H}+\text{NI}_3 \rightarrow \text{NH}_3+3\text{R}\cdot\text{CO}_2\text{I}$; $\text{R}\cdot\text{CO}_2\text{I}+\text{R}'\text{OH} \rightarrow \text{R}\cdot\text{CO}_2\text{H}+\text{R}'\text{OI}$; $\text{R}'\text{OI}+(\text{II}) \rightarrow \text{OR}'\cdot\text{CHMe}\cdot\text{CHMeI}$.

R. T.

Symmetrical amyl, hexyl, heptyl, and butyl sulphates. M. LEVAILLANT (*Compt. rend.*, 1935, 200, 940—942; cf. A., 1933, 1274).—Amyl chlorosulphonate and sulphite react (+ ZnCl_2 at 85°) to form *amyl sulphate*, m.p. $13-13.5^\circ$, b.p. $128-130^\circ/3$ mm. $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$ with SO_2Cl_2 and SOCl_2 respectively yields *hexyl chlorosulphonate*, b.p. $81^\circ/2.5$ mm., and *sulphite*, b.p. $156^\circ/11$ mm., which react to form *hexyl sulphate*. *n*-Heptyl chlorosulphonate, b.p. $90-92^\circ/3$ mm., and *sulphite* give *heptyl sulphate*, m.p. 13° . The last, and Bu_2SO_4 , are also prepared from the alcohols and SO_2Cl_2 , with the sulphites, without isolating the chlorosulphonates.

E. W. W.

Esters of thiosulphurous acid, $\text{H}_2\text{S}_2\text{O}_3$. H. STAMM (*Ber.*, 1935, 68, [B], 673—676).—The greenish-yellow $\text{Me}_2\text{S}_2\text{O}_3$ obtained according to Meuwesen (this vol., 326) contains about 2.5% of S_2Cl_2 . Mixtures of colourless $\text{Me}_2\text{S}_2\text{O}_3$ with 2.5% of S_2Cl_2 have the same colour and give all the chemical reactions, which are similarly exhibited by a solution of pure S_2Cl_2 in anhyd. Et_2O . $\text{Et}_2\text{S}_2\text{O}_3$ and S_2Cl_2 are not completely separable from one another by distillation under diminished pressure.

H. W.

Catalytic preparation of butyl acetate and butyl butyrate.—See B., 1935, 395.

Addition of hydrogen sulphide and mercaptans to alkylene oxides. C. D. NENITZESCU and N. SCARLĂTESCU (*Ber.*, 1935, 68, [B], 587—591).—When passed through a flask fitted with a Raschig column H_2S and $(\text{CH}_2)_2\text{O}$ give a 90.3% yield of $\text{S}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ if the rings have been moistened with the product; otherwise reaction does not appear to occur. $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SEt}$ is obtained similarly from $(\text{CH}_2)_2\text{O}$ and EtSH . PhSH and $(\text{CH}_2)_2\text{O}$ in presence of active C at room temp. afford *Ph β -hydroxyethyl sulphide*, whilst at 90° cyclohexene oxide (I) and PrSH yield *Pr α -2-hydroxy-1-cyclohexyl sulphide*, b.p. $96-97^\circ/3$ mm. (I) is transformed by PhSH and active C at $130-135^\circ$ into *Ph 2-hydroxy-1-cyclohexyl sulphide*, b.p. $148-149^\circ/4$ mm., oxidised by H_2O_2 in AcOH to *Ph 2-hydroxy-1-cyclohexyl sulphone*, m.p. 109° . CH_2Ph 2-hydroxy-1-cyclohexyl sulphide has b.p. $158-160^\circ/3$ mm. Epichlorohydrin (II) affords *Et* (III), b.p. $114-115^\circ/16$ mm., *Pr*, b.p. $95^\circ/4$ mm., *Ph*, b.p. $141^\circ/4$ mm. (corresponding *sulphone*, m.p. 72°), and CH_2Ph , b.p. $154-156^\circ/4$ mm., γ -chloro- β -hydroxypropyl sulphide. Addition of (III) to 40% aq. KOH yields *Et β - γ -oxido-*n*-propyl sulphide* (IV), b.p. $67^\circ/15$ mm., also obtained by addition of (II) to EtSH in KOH . When heated with NH_4Et at 140° (IV) yields *Et γ -diethylamino- β -hydroxy-*n*-propyl sulphide*, b.p. $131^\circ/17$ mm.; *Et γ -1-piperidino- β -hydroxy-*n*-propyl sulphide*, b.p. $130-131^\circ/4$ mm., is prepared similarly. (IV) and MeI in EtOH at room temp. yield *methylethyl- β - γ -oxido-*n*-propylsulphonium iodide*. H_2S and (II) afford non-distillable $\gamma\gamma$ -dichloro- $\beta\beta$ -dihydroxydipropyl sulphide.

H. W.

Mechanism of condensation of carbonyl compounds by means of alkali metals. G. V. TSCHELINCEV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 1, 393—397).—The following scheme is proposed for ester condensations: $\text{EtOAc}+\text{CH}_2\text{Na}\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{ONa}\cdot\text{CMe}(\text{OEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{COMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}+\text{NaOEt} \rightleftharpoons \text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}+\text{EtOH}$ (cf. A., 1934, 868). This correlates this condensation with the synthesis of carbonyl compounds by means of organometallic compounds of Zn, Mg, and Na (*i.e.*, $\text{R}\cdot\text{CO}_2\text{Et}+\text{MgR}'\text{I} \rightleftharpoons \text{MgI}\cdot\text{O}\cdot\text{CRR}'\cdot\text{OEt}$). The scheme also explains the condensation of aldehydes and esters with α -Cl-substituted esters, ketones, etc.

(*i.e.*, the formation of $\text{CHR} \rightarrow \text{CH}\cdot\text{CO}_2\text{Et}$ from $\text{R}\cdot\text{CHO}$ and $\text{CHClNa}\cdot\text{CO}_2\text{Et}$). The scheme is applied to the explanation of many condensations previously unexplained or explained with difficulty, and to the determination of the factors which control the direc-

tion of the reaction between two different reactants which can also condense with themselves.

H. G. M.

Rare earths.—See this vol., 714.

Indium salts of organic acids. J. B. EKELEY and W. W. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 773—774).—Basic salts, $\text{InX}_2\cdot\text{OH}$, are prepared, in which X is EtCO_2 , PrCO_2 , $\text{CCl}_3\cdot\text{CO}_2$, BzO , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2$.

R. S. C.

Constitution of formic acid and formates. T. R. SESHADRI (Current Sci., 1935, 3, 353—354).—The evidence in favour of the idea that the exceptional behaviour of HCO_2H , as compared with that of its homologues, is due to the presence of CHO is discussed.

F. N. W.

Action of nitric acid on dipropionyl peroxide. F. FICHTER and H. BUSS (Helv. Chim. Acta, 1935, 18, 549—555; cf. this vol., 472).—The nitrogenous esters obtained during electrolysis (I) of mixtures (II) of nitrate and propionate (III) are exclusively nitrates; nitrites or nitrite-nitrates are not present. The action of anhyd. fuming HNO_3 on dipropionyl peroxide yields EtNO_3 and EtCO_2Et , also obtained by (I); in addition EtNO_2 is produced. C_2H_4 is formed during electrolysis of (II) or (III). Hypotheses concerning the formation of butane derivatives during electrolysis are not supported experimentally.

Highly-polymerised compounds. CXII. Determination of molecular form by viscosity measurements. H. STAUDINGER and H. SCHWALENSTOCKER (Ber., 1935, 68, [B], 727—749).—Examination is made of the possibility of determining the mol. form of a large series of aliphatic compounds by measurement of the viscosity of their solutions and of correlating the results with other physical properties of the substances. In CCl_4 and C_6H_6 the vals. adopted for γ are 1.5×10^{-3} and 1.3×10^{-3} , respectively. The sp. viscosity of lauric, myristic, and palmitic acids ($c=1.4$) is the same as that of their respective anhydrides, which agrees with the view that the anhydride mols. are extended and the acids are bimol. and finds confirmation in the respective m.p. With methylene myristate, from the anhydride and $(\text{CH}_2\text{O})_n$ in presence of a little ZnCl_2 at 100° , the calc. and observed vals. of η_{sp} agree within experimental error. Tetramethylene dilaurate, m.p. 45.5° , dimyristate, m.p. 55.0° , and dipalmitate, m.p. 63.0° , have the straight chain $\text{Me}[\text{CH}_2]_x\text{CO}\cdot\text{O}[\text{CH}_2]_4\cdot\text{O}\cdot\text{CO}[\text{CH}_2]_x\text{Me}$. In CCl_4 and C_6H_6 the vals. of η_{sp} of ethylene laurate, m.p. 52.0° , myristate, m.p. 63.0° , and palmitate, m.p. 70.5° , are about $4.0 \times 10^{-3} < \text{calc.}$ for a straight chain and structures are discussed wherein the chain length is shortened by about 2 links. A similar anomaly is observed with $\alpha\beta$ -propylene dilaurate, m.p. 35.0° , dimyristate, m.p. 41.5° , and dipalmitate, m.p. 52.5 — 54.5° , and with $\alpha\gamma$ -butylene dilaurate, m.p. about 16.5° , dimyristate, m.p. 29.5 — 31.0° , and dipalmitate, m.p. 39.0 — 40° , and to a smaller extent with β -n-butoxyethyl laurate, m.p. about -4° to -3° , myristate, m.p. about 7° , and palmitate, m.p. 18.5° . Nonyl, m.p. 25.5° , and cetyl, m.p. 56 — 57° , oxalate, nonyl, b.p. $176^\circ/0.14$ mm., m.p.

21 — 21.5° , and cetyl, m.p. 55.5 — 56° , succinate, and nonyl, m.p. 17 — 18.5° , and cetyl adipate, m.p. 53° , have extended mols., whereas possible shortening of the chain occurs with nonyl, b.p. $167^\circ/0.18$ mm., m.p. about 0.5 — 1.5° , and cetyl malonate, m.p. 50.5° . Trilaurin, trimyristin, and tripalmitin appear to have extended mols. and the viscosity seems to be influenced by the large side-chain.

H. W.

Action of atomic hydrogen on oleic acid and paraffin oil. H. KROEPELIN and E. VOGEL [with H. PREIFFER] (Ber., 1935, 68, [B], 684—688).—Exposure of thin films of oleic acid (I) to at. H leads to the formation of stearic acid, a thin skin on the surface of the product which is not observed if O is completely absent, and a brown sticky polymerisate (II). The mean mol. wt. of (II) in boiling C_6H_6 is 1000—2000, depending greatly on the concn. 54% of the original double linkings are hydrogenated. CO_2H is partly reduced. (II) appears to contain an unassigned excess of O, but its formation is observed even when O is completely absent. It is considered that polymerisation is preceded by radical formation, $\text{C}_n\text{H}_{2n+2} + \text{H} = \text{C}_n\text{H}_{2n+1} + \text{H}_2$, and that the double linking of (I) is not fundamental for its polymerisation. In confirmation, paraffin oil when treated with at. H in complete absence of O shows increase of mean mol. wt. from 380 to 535; since the I val. increases from 0.2 to 14.0, double linkings are developed. In presence of a trace of O thin skins are formed (C 74.93, H 10.26, O 14.8%). Reduction of (I) by at. H occurs to only a moderate extent, whilst Et oleate does not appear to be reduced.

H. W.

Velocity of saponification of some simple triglycerides by ethyl-alcoholic potash.—See this vol., 709.

Synthesis of "alkeines" derived from α -alkoxypropionic acid. Z. RODEWALD and E. PEÁZEK (Rocz. Chem., 1935, 15, 81—87).— $\text{CHMeBr}\cdot\text{CO}_2\text{Me}$ and NaOMe in MeOH are boiled for 3 hr., NaOH is added, the solution is heated for a further 30 min., and $\text{OMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (I) is extracted from the product. The corresponding Et (II), b.p. $99^\circ/16$ mm. (chloride, b.p. 54 — $58^\circ/60$ mm.), and Pr (III) ether, b.p. $105^\circ/17$ mm. (chloride, b.p. $68^\circ/45$ mm.), are prepared analogously. The tropyl ester of (I), b.p. $160^\circ/24$ mm. (picrate, m.p. 187° ; picrolonate, m.p. 237°), of (II), b.p. 98 — $100^\circ/0.2$ — 0.3 mm. [picrate, m.p. 182 — 183° ; picrolonate, m.p. 193° ; methiodide, m.p. 255° (decomp.)], and of (III), b.p. $115^\circ/0.3$ mm. (picrate, m.p. 158° ; picrolonate, m.p. 175°), are obtained by passing dry HCl through a fused mixture of tropine and the appropriate acid at 110 (3 hr.). The chloride, b.p. $40^\circ/60$ mm., of (I) and $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ in Et_2O afford β -dimethylaminoethyl α -methoxypropionate, b.p. 86 — $88^\circ/16$ mm. (picrate of methiodide, m.p. 64°); the corresponding esters of (II), b.p. 95 — $96^\circ/16$ mm., and of (III), b.p. 112 — $115^\circ/17$ mm., are prepared similarly. R. T.

Ether-like compounds. XV. Ether-lactones with five-membered ring. M. H. PALOMAA, E. J. SALMI, and L. WALLIN [with T. A. SIITONEN] (Ber., 1935, 68, [B], 609—618).—The following esters are obtained by heating the requisite α -OH-acid with the

aldehyde or ketone in presence of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ as catalyst and, if necessary, Na_2SO_4 as absorbent of H_2O . Methylene lactate (I), b.p. $152\text{--}153^\circ/758$ mm., methylene α -hydroxyisobutyrate (II), b.p. $149.5\text{--}150^\circ/755$ mm., methylene α -hydroxy- α -methyl- n -butyrate (III), b.p. $165.5\text{--}166.5^\circ/762$ mm., and methylene α -hydroxy- α -ethyl- n -butyrate (IV), b.p. $68\text{--}69.5^\circ/8\text{--}9$ mm. Hydrolysis of (I), (II), (III), and (IV) by acid is an ester hydrolysis; the temp. coeffs. are similar to those of ester hydrolysis and increasing alkylation depresses the reactivity. Ethylidene lactate (V), b.p. $154\text{--}155^\circ/769$ mm., α -hydroxyisobutyrate (VI), b.p. $151\text{--}152^\circ/758$ mm., α -hydroxy- α -methyl- n -butyrate, (VII), b.p. $169\text{--}170^\circ/763$ mm., and α -hydroxy- α -ethyl- n -butyrate (VIII), b.p. $69.5\text{--}72^\circ/8\text{--}10$ mm., are described. In $0.1N\text{-HCl}$ hydrolysis of (V) is mainly due to H_2O , to which about half the total change is ascribed in the cases of (VI), (VII), and (VIII). Acid hydrolysis of (I)–(VIII) is greatly diminished by increased alkylation of the acidic component and this is even more the case with aq. hydrolysis. The temp. coeffs. of acid hydrolysis of (V)–(VIII) approximate to the vals. of acetal hydrolysis as the reactivity of the acidic component is depressed by alkylation. Propylidene, b.p. $68\text{--}69^\circ/19\text{--}20$ mm., and isobutylidene lactate, b.p. $68\text{--}69.5^\circ/14$ mm., have been obtained. H. W.

Phospho- l -lactic acid. T. WAGNER-JAUREGG (Ber., 1935, 68, [B], 670–673).— $l(+)$ -Lactic acid (I) in $\text{C}_6\text{H}_5\text{N}$ is converted by POCl_3 into phospho- l -lactic acid (II) isolated as the salt $\text{C}_6\text{H}_5\text{O}_{12}\text{P}_2\text{Ba}_3\cdot 4\text{H}_2\text{O}$, less sol. in hot than in cold H_2O . (II), as Na_3 or K_3 salt, has $[\alpha]_D -9.74^\circ$ in H_2O . (II) is about as readily hydrolysed as phosphoglyceric acid by HCl at 122° but is much more resistant to de-phosphorylating enzymes. Methylene-blue in presence of lactic dehydrase from *B. coli* in vac. is decolorised by (I) but not by (II); (II) is therefore not an intermediate product of the dehydrogenation of (I). H. W.

Synthesis of enol-phosphopyruvic acid. W. KIESSLING (Ber., 1935, 68, [B], 597–601).—Condensation of AcCO_2H with POCl_3 in quinoline at $40\text{--}60^\circ$ affords (10% yield) enol-phosphopyruvic acid (I), $\text{CH}_2\text{C}(\text{O}\cdot\text{PO}_3\text{H}_2)\cdot\text{CO}_2\text{H}$, with large amounts of complex by-products, usually free from P. (I) yields a $\text{Ag}\text{--}\text{Ba}$ salt (II), does not give a ppt. with $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$, yields CHI_3 with IO° with loss of H_3PO_4 , and is immediately decomposed by Hg salts into AcCO_2H and H_3PO_4 . (II) is catalytically hydrogenated (Pd) to phospholactic acid. (I) is therefore identical with the natural acid (Lohmann *et al.*, A., 1934, 1261). H. W.

Oxidation of ethyl hydrogen malonate by potassium persulphate. F. FICHTER and J. HEER (Helv. Chim. Acta, 1935, 18, 704–709).—Oxidation of $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ (I) with $\text{K}_2\text{S}_2\text{O}_8$ gives $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ (II), showing that the production of (II) from (I) by electrolysis is due to electrochemical oxidation and not to simple discharge. The reaction also affords AcOH and EtOAc but, under the experimental conditions, $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ cannot be formed from AcOH . The Crum Brown-Walker

and Kolbe syntheses of hydrocarbons are due to electrochemical oxidation. H. W.

Preparation of organic compounds containing deuterium. Dideuteromalononic deuteracid and trideuteracetic deuteracid. C. L. WILSON (J.C.S., 1935, 492–494).— C_3O_2 and D_2O in dry C_6H_6 give dideuteromalononic deuteracid, $\text{CD}_2(\text{CO}_2\text{D})_2$, m.p. $128\text{--}130^\circ$ (decomp.), no interchange of H and D in the C_6H_6 occurring. Decomp. at $140\text{--}150^\circ$ gives tri-deuteracetic deuteracid (I), $\text{CD}_3\cdot\text{CO}_2\text{D}$, m.p. 15.75° , for which v.p. are recorded between 20.0° (12.4 mm.) and 100.0° (437.9 mm.). (I) is more volatile than “light” AcOH , in agreement with Lewis’ views on the co-ordination of H and D. R. S. C.

Autoxidation of methyl sorbate. P. HEINANEN (Suomen Kem., 1935, 8, B, 5–6).—The product of autoxidation of Me sorbate is the $\gamma\delta$ -peroxide, which decomposes into MeCHO and Me fumaraldehyde, m.p. $35\text{--}36^\circ$ (2 : 4-dinitrophenylhydrazones, m.p. 194°), yielding AcOH and $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$. E. S. H.

Oxidation of phenols by peracetic acid. Passage from the aromatic to the aliphatic series. J. BOESEKEN and C. F. METZ (Rec. trav. chim., 1935, 54, 345–352).— $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$ with AcO_2H after 2 months gives β -bromomuconic acid (I), m.p. 213° , and β -bromo- $\gamma\delta$ -dihydroxy- $\gamma\delta$ -dihydromuconolactone, m.p. $167\text{--}168^\circ$. $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$ also gives (I), but 2 : 4- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{OH}$ and 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$ are not oxidised. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ similarly gives β -chloromuconic acid, m.p. 223° , and β -chloro- $\gamma\delta$ -dihydroxy- $\gamma\delta$ -dihydromuconolactone, m.p. 177° . $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ gives α -chloromuconic acid, m.p. 190° , and δ -chloro- $\Delta^{\alpha\gamma}$ -hexadienaldehydic acid, m.p. 145° . p -Cresol gives β -methylmuconic acid, m.p. 188.5° , and a lactonic acid, $\text{C}_7\text{H}_8\text{O}_4$, m.p. 124° ; the mother-liquors with HCl in MeOH yield a Me ester, $\text{C}_8\text{H}_{10}\text{O}_4$, b.p. 135° (high vac.). The configuration of the products is discussed. F. R. G.

Carbon dioxide cleavage from dibromomalonic acid.—See this vol., 709.

Transposition of insoluble tartrates by means of sodium carbonate solution. D. H. HART and D. PAPA (Rec. trav. chim., 1935, 54, 358–360).—1 g. of the common insol. tartrates after boiling with 50 c.c. of $1.5M\text{-Na}_2\text{CO}_3$ for 3 min. is 70–100% decomposed to Na tartrate. Special procedures have been devised for determining tartrate in Bi, Sn^{II} , Fe^{II} , and Ag salts. R. S. B.

Activation of r -tartaric acid by optically active malic acid. A. MCKENZIE and E. W. CHRISTIE (Biochem. Z., 1935, 277, 122–128).—K d - and l -tartrate have the same solubility in aq. solution of d - or l -malic acid, and the optical activation obtained in crystals separating on adding d - or l -malic acid to neutralised solution of r -tartaric acid is not due to such differences in solubility. P. W. C.

Conversion of the salts of isopropylidene sugar acids into methyl esters. T. REICHSTEIN, A. PEDOLIN, and A. GRUSSNER (Helv. Chim. Acta, 1935, 18, 598–601).—The salt is suspended or dissolved in MeOH and treated at a very low temp. with excess of $\text{HCl}\text{--}\text{MeOH}$ followed immediately by CH_2N_2 . The

duration of dangerous acidity is thus reduced to a tolerable min. *K* dl-isopropylideneglycerate (I), obtained by oxidising isopropylideneglycerol with KMnO_4 -KOH, thus yields *Me* dl-isopropylideneglycerate, b.p. $80^\circ/11$ mm., and *K* d-isopropylidenexyluronate gives the corresponding *Me* ester, b.p. $182^\circ/13$ mm., m.p. 103 — 104° (corr.), $[\alpha]_D^{25} -32.8^\circ \pm 0.5^\circ$ in MeOH. (I) and SOCl_2 in Et_2O yield dl-isopropylideneglyceryl chloride, b.p. about $58^\circ/12$ mm. H. W.

Optical rotations and other properties of the lead and calcium aldones. H. S. ISBELL (J. Res. Nat. Bur. Stand., 1935, 14, 305—315).—The prep. of the following substances is described: Pb gluconate, $[\alpha]_D^{20} -5.2^\circ$; Pb xylonate, $[\alpha]_D^{20} -6.8^\circ$; Pb galactonate, $[\alpha]_D^{20} -12.9^\circ$; Pb arabonate, $[\alpha]_D^{20} -6.70^\circ$; Pb mannonate, $[\alpha]_D^{20} -5.50^\circ$; Ca xylonate, $[\alpha]_D^{20} +13.5^\circ -0.53 c$ (where *c* is the no. of g. of salt in 100 ml.); Ca α -glucoheptonate, $[\alpha]_D^{20} +5.95^\circ$ in H_2O . Addition of Pb salts to the Ca salts of the α -OH-acids causes large changes in $[\alpha]$, which follow the configuration of the α -C atom in the aldonic acid. The Pb aldones are acids, which can be titrated with alkali and hydrolyse in solution giving small quantities of free aldonic acids which undergo lactone formation, causing small changes in rotation. E. S. H.

Electrolytic oxidation of xylose in presence of alkaline-earth bromides and carbonates. H. S. ISBELL and H. L. FRUSH (J. Res. Nat. Bur. Stand., 1935, 14, 359—362).—Using graphite electrodes the reaction yields Ca, Mg, $[\alpha]_D^{20} +14.70^\circ$ in H_2O , or Sr xylonate. E. S. H.

Errors in determination of vitamin-C.—See this vol., 670.

Degradation of l-isopropylideneascorbic acid. T. REICHSTEIN, A. GRUSSNER, and W. BOSSHARD (Helv. Chim. Acta, 1935, 18, 602—608).—l-isoPropylideneascorbic acid is oxidised by KMnO_4 -KOH to *K* l-isopropylidenethreonate, m.p. 158° (corr.), $[\alpha]_D^{22} +24.8^\circ$ in H_2O , converted by HCl-MeOH immediately followed by CH_2N_2 into *Me* l-isopropylidenethreonate (I), b.p. $65^\circ/0.1$ mm., $125^\circ/12$ mm., $[\alpha]_D^{21} +21.3^\circ$ in COMe_2 (corresponding amide, m.p. 89 — 90° , $[\alpha]_D +42.9^\circ \pm 3^\circ$ in COMe_2). (I) is hydrolysed by hot H_2O to l-threonic acid, $[\alpha]_D^{19} +9.54^\circ$ in H_2O [corresponding quinine salt, m.p. 163 — 165° (corr.)]. Treatment of (I) with Ag_2O and MeI in Et_2O yields *Me* l-methylisopropylidenethreonate (II), b.p. $110^\circ/12$ mm., $[\alpha]_D^{22} +49.7^\circ$ in MeOH, $[\alpha]_D^{21} +49.0^\circ$ in anhyd. COMe_2 (corresponding amide, m.p. 96.5 — 97.5° (corr.), $[\alpha]_D^{22} +43.7^\circ$ in COMe_2). Treatment of (II) with hot H_2O leads to l-methylthreonolactone, b.p. about 120 — $125^\circ/0.3$ mm. l-Methylthreonamide, m.p. 105 — 106° , $[\alpha]_D^{22} +96.4^\circ$ in MeOH, brucine l-methylthreonate ($+5\text{H}_2\text{O}$), m.p. 151 — 153° (corr.), and quinine l-methylthreonate ($+1.5\text{H}_2\text{O}$), m.p. 179° (corr.), are described.

H. W.

Detection and determination of gluconic acid. W. DIEMAIR, B. BLEYER, and L. SCHNEIDER (Z. Unters. Lebensm., 1935, 69, 212—220).— < 12 mg. of α -gluconic acid (I) may be detected in presence of glycerol, sorbitol, tannin, and malic and citric acids by pptn. as the phenylhydrazide (II), but the determination of (I) is inaccurate owing to adsorption of (II) by

C used for purifying the aq. solution. Detection of (I) in presence of d-glucose (III) is difficult owing to co-pptn. of the osazone (IV) of (III), but (II) may be separated from (IV) by reason of its greater solubility in hot H_2O . (I) could not be detected in pure apple-juice or cider.

E. C. S.

Preparation of 5-ketogluconic acid by bromine oxidation. E. W. COOK and R. T. MAJOR (J. Amer. Chem. Soc., 1935, 57, 773).—The reducing substance which remains after protracted oxidation of glucose to gluconic acid by electrolytic Br is identified as δ -ketogluconic acid.

R. S. C.

Preparation of d-mannuronic acid and its derivatives. R. G. AULT, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1935, 517—518).— α -Methylmannoside and dry 1% HCl-COMe₂ give the 2:3-isopropylidene (I), m.p. 105° , b.p. $145^\circ/0.02$ mm., $[\alpha]_D^{20} +28.3^\circ$ in MeOH, $+24.3^\circ$ in H_2O , and 2:3:4:6-diisopropylidene, m.p. 76° , derivatives. The structure of (I) is proved by quant. hydrolysis by 0.01N-HCl at 15° to α -methylmannopyranoside. (I) and KMnO_4 -KOH at 15 — 20° give *K* 2:3-isopropylidenemannuronide, amorphous, hygroscopic, $[\alpha]_D^{17.80} -4.5^\circ$ in H_2O , hydrolysed by 0.02N-HCl at 50° (1 hr.) to *K* α -methyl- α -mannuronide (II), $+0.5\text{EtOH}$, decomp. about 230° , $[\alpha]_D^{17.80} +48^\circ$ in H_2O , and amorphous, which with HClO_4 gives α -methylmannuronide hydrate (H_2O lost slowly at 80 — $90^\circ/\text{vac.}$), m.p. 108° , $[\alpha]_D^{19.80} +65.6^\circ$ in H_2O . This with 2.5% HCl at 100° yields (9 hr.) d-mannuronolactone, m.p. 143 — 144° , $[\alpha]_D^{19} +95^\circ$ (const.) in H_2O . (II) with Me_2SO_4 -KOH, followed by MeI- Ag_2O , affords the *Me* ester, b.p. $118^\circ/0.02$ mm., $[\alpha]_D^{20.780} +74^\circ$ in MeOH, $+61.4^\circ$ in CHCl_3 , of 2:3:4-trimethyl- α -mannuronide (III), hydrolysed by boiling N-NaOH to (III), b.p. 156 — $158^\circ/0.02$ mm., $[\alpha]_D^{20.780} +73^\circ$ in MeOH (salts and derivatives, oils).

R. S. C.

Methyl d-galacturonate and ascorbic acid. T. REICHSTEIN and A. GRUSSNER (Helv. Chim. Acta, 1935, 18, 608—610).— β -d-Galacturonic acid (I) is converted by CH_2N_2 in MeOH into *Me* α -d-galacturonate (II), m.p. 134 — 135.5° (corr.; microscope), $[\alpha]_D^{18} +75.8^\circ$ to 44° in H_2O , $[\alpha]_D^{18} +39^\circ$ (equilibrium val.) in MeOH. Treatment of (I) with alkali or of (II) with $\text{Al}(\text{OPr}^i)_3$ affords only min. amounts of reducing substances, thus indicating the non-production of ascorbic acid.

H. W.

Methylglucosides of naturally occurring hexuronic acids. IV. Polygalacturonic acid methylglucosides derived from Ehrlich's "Pektolsaure" and "Pektolactonsaure." L. BAUR and K. P. LINK (J. Biol. Chem., 1935, 109, 293—299).—The view of Ehrlich (A., 1929, 1273; 1930, 1163; 1932, 1063) that pectins contain basic units, each composed of 4 galacturonic acid mols., in ring ["pektolsaure" (I)] and open-chain ["pektolactonsaure" (II)] structures, is disproved. By treating citrus and apple pectins with HCl, acids are obtained with $[\alpha]$ etc. agreeing with Ehrlich's vals., but treatment with HCl-MeOH (cf. A., 1933, 595) dissolves only 30% of (I) and 90% of (II), and analysis of the methylglucosides of the residual *Me* polygalacturonate, and of the free acid and its Na and Ba salts,

shows that the residue contains approx. 10 galacturonic acid units in the mol. (cf. A., 1934, 633).

E. W. W.

Synthesis of polyketocarboxylic acids of the fatty acid series. I. E. LEHMANN and W. GRABOW (Ber., 1935, 68, [B], 703—707).—Addition of COMe_2 and $\text{Et}_2\text{C}_2\text{O}_4$ to Na wire under Et_2O and decomp. of the product with a large excess of acid gives *Et* $\alpha\gamma\epsilon\zeta\theta$ -pentaketodecoate (I), m.p. 144° (also $+1\text{H}_2\text{O}$, m.p. 119°), which gives a blackish-brown colour with FeCl_3 and is readily decomposed by alkali or alkali carbonates. When heated with ZnCl_2 at 145° (I) passes into *Et* *H* chelidonate, m.p. 227° (whence chelidonic acid, m.p. 262°), and *Et* 6- $\alpha\gamma$ -diketobutyl-4-pyrone-2-carboxylate (II), pale yellow needles or cubes, m.p. 99° , hydrolysed by NaOH to $\text{H}_2\text{C}_2\text{O}_4$ and small amounts of an isomeric ester, m.p. 57° . Very cautious treatment of (II) with Na_2CO_3 leads to 6- $\alpha\gamma$ -diketobutyl-4-pyrone-2-carboxylic acid (III), m.p. 213° (Me ester, needles or granules, m.p. 124°). With Br in CHCl_3 (II) affords *Et* 6- β -bromo- $\alpha\gamma$ -diketobutyl-4-pyrone-2-carboxylate, m.p. 140° . Treatment of (III) with boiling 20% HCl gives $\alpha\gamma\epsilon\zeta\theta$ -pentaketodecoic acid, m.p. 204° (decomp.), re-converted by MeOH-HCl into (III), and $\alpha\gamma\epsilon\zeta$ -tetraketo-octoic acid, m.p. 210° (decomp.).
H. W.

Action of methyl chlorosulphonate on methyl acetate; action of methyl sulphate on acetyl chloride. R. LEVAILLANT (Compt. rend., 1935, 200, 1053—1055).— ClSO_3Me (1 mol.) containing ZnCl_2 at 140 — 160° with MeOAc (>1 mol.) gives *Me* α -methylsulphoacetate, b.p. $157^\circ/21$ — 22 mm., also formed from AcCl with Me_2SO_4 containing ZnCl_2 at 140 — 150° .
J. L. D.

Photosynthesis of formaldehyde in tropical sunlight.—See this vol., 713.

Catalytic decomposition of acetaldehyde.—See this vol., 711.

Thermal decomposition of acetaldehyde and propaldehyde.—See this vol., 708.

Catalytic action of monoses on the formaldehyde condensation. A. KUSIN (Ber., 1935, 68, [B], 619—624).—Complete condensation of 4% CH_2O at 35 — 40° is caused by Ca fructosate (I) in 1—3 hr., whereas under the same conditions an equiv. amount of Ca(OH)_2 has no appreciable effect in 5 hr. An analogous acceleration is caused by fructose (II) and Ca(OH)_2 or Pb(OH)_2 . Since glycerol and mannitol are inactive the effect cannot be due to the polyhydroxy-groups. The absence of acceleration by sucrose (III) and the catalytic activity of glycollaldehyde (IV) exclude the possibility that cyclic forms (amylene- or butylene-oxide) or a semi-acetal OH participate in the change. The approx. equal catalytic activity of (II), glucose, maltose, and (III) does not justify the assumption that activity is due to free CO or CHO, but strongly suggests that the enol grouping with 2OH is responsible for the change. Catalytic activity is not observed when the formation of an enol [fructose penta-acetate or (III)] is rendered difficult. Condensation of CH_2O in presence of (II) does not take place at $p_H < 12$. Change occurs slowly at $p_H 12$; at $p_H 12.6$ acceleration is similar to that

observed with Pb(OH)_2 and at $p_H 14.9$ analogous to that produced by Ca(OH)_2 . The enhancement of the solubility of (I) in 50% MeOH at 0° by CH_2O indicates the production of unstable, intermediate products apparently derived mainly from unimol. CH_2O ; this view is supported by observations of the f.p. of solutions of (I) and CH_2O , separately and when mixed. It is suggested that a monose in active enol form accelerates the conversion of CH_2O into sugars in the green parts of plants.
H. W.

Highly sensitive reaction for the characterisation and determination of citral. J. BOUGAULT and E. CATTELAINE (J. Pharm. Chim., 1935, [viii], 21, 437—449).—The colour of methylene-blue in NaOH-MeOH slowly changes from blue to pink. The change is faster at 23° than at 0° , and in 0.1*N*- than in 0.01*N*- NaOH . It is greatly catalysed by citral (0.02 mg. in 5 c.c.), which may be determined colorimetrically by this effect. Many other substances have a similar action, but only in much larger quantities (74—867 mg.).
R. S. C.

Glyoxal. II. Glyoxal semiacetal. H. O. L. FISCHER and E. BAER (Helv. Chim. Acta, 1935, 18, 514—521; cf. A., 1926, 599).—Attempts to obtain glyoxal *Et*₂ acetal (I) by treatment of $\text{CH}_2\text{CH(OEt)}_2$ with dil. O_3 in EtOAc at low temp. and reduction of the ozonide (Pd-BaCO_3) were unsuccessful. Inter-action of glyceraldehyde *Et*₂ acetal (improved prep.) with Pb(OAc)_4 in C_6H_6 affords (I), b.p. 42 — $43^\circ/12$ — 13 mm., in 53.7% yield. (I) slowly polymerises when preserved, but the product becomes spontaneously depolymerised in solution or when distilled in vac. (I) is transformed by NHPh-NH_2 in dil. AcOH at 100° into glyoxaldiphenylhydrazone, m.p. 171 — 172° , and by CH(OEt)_3 and NH_4Cl in EtOH into glyoxal *Et*₄ acetal, b.p. 81 — $83^\circ/10$ mm. (I) is slowly converted by cold *N*- KOH into glycollaldehyde *Et*₂ acetal and $\text{CH(OEt)}_2\text{CO}_2\text{H}$.

[With H. NIDDECKER.] The action of MgMeI in Et_2O on (I) gives lactaldehyde *Et*₂ acetal (II), b.p. 63 — $64^\circ/12$ mm., hydrolysed to lactaldehyde (III), m.p. 105 — 106° . Treatment of (II) with $p\text{-NO}_2\text{C}_6\text{H}_4\text{NH-NH}_2$ in the requisite proportion gives the *p*-nitrophenylhydrazone, m.p. 127 — 128° , and *p*-nitrophenylosazone, decomp. 306 — 309° , of (III).
H. W.

Fluorination of organic compounds. I. P. C. RAY, H. C. GOSWAMI, and A. C. RAY (J. Indian Chem. Soc., 1935, 12, 93—95).—When heated with anhyd. TlF at 85 — 95° , CH_2AcBr , CH_2BzBr , and $\text{CH}_2\text{Br-CH(OEt)}_2$ afford, respectively, fluoroacetone, b.p. 72.5° [semicarbazone, m.p. 131.5° (decomp.)], ω -fluoroacetophenone, b.p. $98^\circ/18$ mm. (pyridinium, m.p. 161° and quinolinium, darkens 231° , salts), and fluoroacetal, b.p. $60^\circ/25$ mm.
J. W. B.

Hydroxymethylene ketones and their reaction products. V. Hydrolytic fission of double linkings conjugated with the carbonyl group. VI. Proof of $\alpha\delta$ -addition of Grignard salts to the conjugated double linkings of hydroxymethylene ketones. R. E. MEYER (Helv. Chim. Acta, 1935, 18, 461—466; 467—470; cf. this vol., 609).—V. β -Methyl- $\Delta^{\beta\gamma}$ -nonadien- ζ -one is converted by prolonged boiling with aq. K_2CO_3 into methylheptenone

and MeCHO. Similar results are recorded with β -methyl- Δ^7 -nonen- ζ -one and $\theta\mu$ -dimethyl- $\Delta^{8,9}$ -tridacatrien- δ -one. These observations and evidence from the lit. lead to the rule that double linkings conjugated with CO can be hydrolysed by alkali; H is added to the fragment carrying CO, whilst the original β -C forms a new CO.

VI. The action of MgEtI on the Mg salt of hydroxymethylenemethylheptanone gives OH-CO-compounds which on subsequent fission afford only methylheptanone and no trace of a higher ketone. Products, OH·CRET·CH₂·CHO, are therefore not formed. Addition of MgMeI or MgEtI to OH·CH compounds of Me ketones occurs exclusively in the $\alpha\delta$ -position and CO is not attacked. The synthesis of $\alpha\beta$ -unsaturated aldehydes cannot therefore be effected along these lines, but a method is afforded of introducing the group :CHR into ketones even when the latter do not condense with aldehydes. β -Methyl- Δ^7 -decen- ζ -one, b.p. 104—105°/12 mm., is described.

H. W.

"Ketol," OH·CHAc·CH₂Ac. M. HENZE (Z. physiol. Chem., 1935, 232, 123—124).—The liquid ketol (I), b.p. 113.5/12 mm., on keeping gives a cryst. modification (II), m.p. in glass 95°, in Jena glass 124—128°, in quartz 130—132°. (II) is a dimeric form; the *Me ether* of (I), m.p. 162°, is also dimeric.

J. H. B.

Rapid method for determination of reducing sugars. G. A. BRAVO (Boll. Uff. Staz. Sperim. Ind. Pelli, 1935, 13, 81—91).—The solution containing the sugar (in small quantity) is treated with a given quantity (excess) of Fehling's solution, accurately prepared, and the filtrate examined colorimetrically. From the colorimeter reading, the sugar content is read off on an empirical scale.

E. W. W.

Preparation of *l*-xylose. H. APPEL (J.C.S., 1935, 425—426; cf. Vargha, this vol., 325).—Triethylenesorbitol (cf. Helferich and Appel, A., 1931, 1038) heated with 50% aq. AcOH gives 1 : 2 : 3 : 4-diethylenesorbitol, m.p. 212—214°, $[\alpha]_D^{17}$ -11.1° in H₂O, which with Pb(OAc)₄ in C₆H₆ and AcOH and subsequent hydrolysis with 2N-H₂SO₄ gives *l*-xylose.

F. R. G.

d-Talose, diacetone(diisopropylidene-*d*-talose, and diacetone(diisopropylidene-*d*-talonolactone. W. BOSSHARD (Helv. Chim. Acta, 1935, 18, 482—490).—*d*-Galactonolactone is partly epimerised by C₅H₅N-H₂O at 130—135° and, after removal of *d*-galactonic acid as the Cd salt, *d*-talononic acid is isolated as the *K* salt, m.p. 171—172°, $[\alpha]_D^{19}$ +2.97° in H₂O. Reduction of *d*-talonolactone (I) by Na-Hg in H₂O leads to *d*-talose (II), m.p. 128—130° (Reichert microscope), $[\alpha]_D^{21}$ about +30° to $[\alpha]_D^{21}$ +20.6° in H₂O. Isolation of (II) from the crude syrup can also be effected through its *o*-nitrophenylhydrazone, m.p. 148.5—149°, $[\alpha]_D^{18}$ +88.3° in MeOH; indications of the formation of β -talose, m.p. 123—127°, are obtained. Treatment of (I) with COMe₂ containing CuSO₄ and a little conc. H₂SO₄ leads to a non-cryst. mixture (III) consisting mainly of 1 : 2 : 5 : 6-diisopropylidenetalofuranose, b.p. 110—120°/0.5 mm., $[\alpha]_D^{20}$ -25.2° in COMe₂, which does not reduce I solution. Oxidation of (III) with KMnO₄ gives very small

amounts of $\alpha\beta\delta\epsilon$ -diisopropylidenetalonic acid, isolated as the corresponding lactone, m.p. 129—130°, $[\alpha]_D$ +17°±2° in COMe₂ [also obtained from (I) and COMe₂-CuSO₄-H₂SO₄]. (III) therefore contains 2 : 3 : 5 : 6-diisopropylidenetalofuranose. H. W.

d-Gulomethylose (6-deoxy-*d*-gulose) and its relation to a reported inversion of *l*-rhamnose. P. A. LEVENE and J. COMPTON (J. Amer. Chem. Soc., 1935, 57, 777—778).—By the cyanohydrin reaction, followed by reduction with Na-Hg, 5-deoxy-*d*-xylose affords *d*-gulomethylosic (6-deoxy-*d*-gulonic) acid, $[\alpha]_D$ -5.0° in H₂O (*Na* salt, $[\alpha]_D$ +11.03° in H₂O), and lactone, m.p. 180—181°, $[\alpha]_D$ -68° in H₂O (*p*-bromophenylhydrazide, m.p. 132—133°, $[\alpha]_D$ +8.83° in H₂O), and *d*-gulomethylose (6-deoxy-*d*-gulose), amorphous, $[\alpha]_D$ -35.7° (const.) in H₂O [*p*-bromophenyl-hydrazone, m.p. 135°, $[\alpha]_D$ -16.1° \rightarrow +9.2° in EtOH, and -osazone, m.p. 195—196°, $[\alpha]_D$ 0° \rightarrow 15.3° in C₅H₅N-EtOH (3 : 2)], thus disproving the inversion postulated by Muskat (this vol., 199), which is also not in line with hydrolysis of diisopropylideneglucose and 5-methylisopropylidenexylose 3-*p*-toluenesulphonates.

R. S. C.

6-Deoxy-*d*-gulose. I. E. MUSKAT (J. Amer. Chem. Soc., 1935, 57, 778).—The substances of Levene *et al.* (preceding abstract) may not have the structures claimed.

R. S. C.

Action of phosphate on hexoses. I. Formation of acetol from glucose in acid solutions of potassium phosphate. R. NODZU (Bull. Chem. Soc. Japan, 1935, 10, 122—130).—Glucose (I) on prolonged boiling with 40% KH₂PO₄-K₂HPO₄ at *p*_H 4.8—7.1 affords a distillate which contains AcCHO (II), Ac₂, and CH₂Ac·OH (III) (cf. A., 1905, i, 3) isolated as their semicarbazones. 4—5% of (I) is converted into (III), which is determined in the distillate by Fischler's method (A., 1928, 870). The initial *p*_H influences only the rate of formation (max. at *p*_H 7.0—7.1) of (III). (I) as above with 5% of the phosphate mixture gives a low yield of (III) and a slower rate of formation.

J. L. D.

Composition of altered glucose solutions. N. MAYER (Compt. rend., 1935, 200, 1116—1118).—Glucose (2%) in 0.1N-NaOH after 30 min. at 100° in vac. loses its rotatory power and the solution contains HCO₂H, AcOH, and lactic acid in addition to substances capable of reducing methylene-blue. Traces of redoxin (?) and AcCHO have been found.

F. N. W.

Partition of tri- and tetra-methylglucoses between chloroform and water.—See this vol., 695.

Tritylation of sugar mercaptals. M. L. WOLFRAM, J. L. QUINN, and C. C. CHRISTMAN (J. Amer. Chem. Soc., 1935, 57, 713—717).—Glucose Et mercaptal, when treated with CPh₃Cl in C₅H₅N and then with BzCl, gives *d*-glucose Et mercaptal 2 : 3 : 4 : 5-tetrabenzoate 6-CPh₃ ether, m.p. 161—162°, $[\alpha]_D$ +49° in CHCl₃, which with dry HBr-CHCl₃ gives *d*-glucose Et mercaptal 2 : 3 : 4 : 5-tetrabenzoate 6-bromide, m.p. 169—170°, $[\alpha]_D^{24}$ +39° in CHCl₃. This with NaI-COMe₂ at 115° gives the 6-iodide, m.p. 165—166°, $[\alpha]_D$ +39°, hydrolysed by AgNO₃ in hot COMe₂, followed by CaCO₃ and HgCl₂, to *d*-glucose 2 : 3 : 4 : 5-

tetrabenzoate, m.p. 118—119°, $[\alpha]_D^{25} +69^\circ$ in EtOH. Galactose affords similarly *d*-galactose *Et* mercaptal 2:3:4:5-tetrabenzoate 6-*CPh*₃ ether, m.p. 138—139°, $[\alpha]_D -22.5^\circ$ in CHCl_3 , or by AcCl the corresponding *tetra*-acetate (I), m.p. 123—124°, $[\alpha]_D^{25} -22.5^\circ$ in CHCl_3 . Arabinose and xylose give *l*-arabinose, m.p. 101—102°, $[\alpha]_D^{27} -24^\circ$ in CHCl_3 , and *d*-xylose *Et* mercaptal 2:3:4:5-tetra-acetate 6-*CPh*₃ ether, m.p. 149—150°, $[\alpha]_D^{25} -20.5^\circ$ in CHCl_3 . (I) and $\text{HBr} \cdot \text{AcOH}$ gives *d*-galactose *Et* mercaptal 2:3:4:5-tetra-acetate (II), m.p. 96—97°, $[\alpha]_D -6.8^\circ$ in CHCl_3 , or occasionally its 6-bromide, m.p. 110—111°. Hydrolysis ($\text{CdCO}_3 \cdot \text{HgCl}_2$) of (II) gives *d*-galactose 2:3:4:5-tetra-acetate hydrate, m.p. 162°, $[\alpha]_D^{25} +10^\circ \rightarrow -38^\circ$ in $\text{C}_5\text{H}_5\text{N}$, whereas (I) gives similarly the *semi*acetate, m.p. 153°, $[\alpha]_D^{25} -28^\circ$ (stable) in CHCl_3 , $-29.5^\circ \rightarrow -16.5^\circ$ in MeOH, of aldehyde-*d*-galactose 2:3:4:5-tetra-acetate 6-*CPh*₃ ether (*semi*-carbazone, m.p. variable, $[\alpha]_D^{27} +200^\circ$ in CHCl_3).

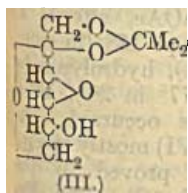
R. S. C.

Ketone sugar series. IV. Preparation of methyl- and ethyl-fructoside acetates. E. PACSU (J. Amer. Chem. Soc., 1935, 57, 745—747; cf. A., 1933, 937).— β -Acetochlorofructopyranose (I) and AgNO_3 in MeOH (a) with or (b) without $\text{C}_5\text{H}_5\text{N}$ give β -fructose tetra-acetate (II) (2%), Schlubach's (α -methylfructoside tetra-acetate [(a) 18, (b) 34%] (A., 1928, 873), and β -methylfructose <2:6> *tetra*-(ortho)-acetate, a glass, $[\alpha]_D^{20} -13.6^\circ$ in CHCl_3 [(a) 80, (b) 64%], which with alkali gives β -methylfructoside 3-(ortho)-acetate, cryst., $[\alpha]_D^{20} -12.4^\circ$ in H_2O , and with dil. acid, aq. MeOH, or hot H_2O gives (II). (I) and Ag_2O in EtOH give (II), a β -ethylfructoside tetra-acetate, m.p. 103—104°, $[\alpha]_D^{20} +51.6^\circ$ in CHCl_3 , and β -ethylfructoside *tetra*-(ortho)-acetate.

R. S. C.

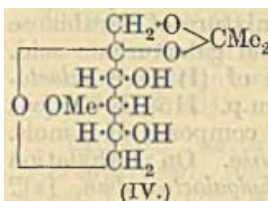
Acetone [isopropylidene] compounds of sugars and their derivatives. XIX. Transition, *d*-fructose — *d*-psicose (ψ -fructose) \rightarrow *d*-sorbse. H. OHLE and F. JUST (Ber., 1935, 68, [B], 601—609; cf. A., 1933, 492).—Hydrolysis of α -diisopropylidene-fructose *p*-toluenesulphonate (I) with 80% AcOH at 60° leads to 1:2-isopropylidene- α -fructose 3-*p*-toluenesulphonate (II), m.p. 124.5° (subsequent decomp.), $[\alpha]_D^{20} -113.0^\circ$ in CHCl_3 , which regenerates (I) with COMe , and CuSO_4 . (II) or isopropylidene- α -fructose and $p\text{-C}_6\text{H}_4\text{MeSO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ at 40° give isopropylidene- α -fructose tri-*p*-toluenesulphonate, m.p. $[\alpha]_D^{20} -121.4^\circ$ in CHCl_3 . isoPropylidene- α -fructose 4:5-diacetate 3-*p*-toluenesulphonate, m.p. 97°, $[\alpha]_D^{20} -133.0^\circ$ in CHCl_3 [from (II) and Ac_2O in $\text{C}_5\text{H}_5\text{N}$], and isopropylidene- α -fructose 4:5-dibenzoate 3-*p*-toluenesulphonate, m.p. 144°, $[\alpha]_D^{20} -316.2^\circ$ in CHCl_3 , are described.

Treatment of (II) with *N*-NaOH EtOH at 100° leads to 1:2-isopropylidene-3:4-anhydro-*d*-psicose (III) (psicose = ψ -fructose), m.p. 80°, $[\alpha]_D^{20} -47.6^\circ$ in CHCl_3 , which reduces boiling Fehling's solution,



but is indifferent towards cold OI . The ethylene-ring is sufficiently stable to allow (III) to be transformed by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 20° or by a large excess of boiling Ac_2O into 1:2-isopropylidene-3:4-anhydro-*d*-psicose 5-acetate, m.p. 81°, $[\alpha]_D^{20} +5.9^\circ$ in

CHCl_3 , by BzCl in $\text{C}_5\text{H}_5\text{N}$ at 40° into the corresponding 5-benzoate, m.p. 111.5°, $[\alpha]_D^{20} +24^\circ$ in CHCl_3 , and into the 5-*p*-toluenesulphonate, m.p. 95°, $[\alpha]_D^{20} +4.7^\circ$ in CHCl_3 . Ag_2O and boiling MeI transform (III) into 5-methyl-1:2-isopropylidene-3:4-anhydro-*d*-psicose, b.p. 90—92°/0.01 mm., $[\alpha]_D^{28} -2.8^\circ$ in CHCl_3 . Treatment of (III) with 2*N*-NaOH at 38° gives a dark oil from which, after acetylation, isopropylidene- α -fructose triacetate, m.p. 97°, is isolated in small amount; the main products of fission by alkali are not derived from *d*-fructose. Addition of NaOMe in



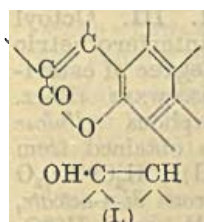
boiling MeOH to (III) leads to 4-methyl-1:2-isopropylidene-*d*-sorbse (IV), m.p. 112—113°, $[\alpha]_D^{25} -81.6^\circ$ in CHCl_3 (3:5-diacetate, m.p. 75°, $[\alpha]_D -92.8^\circ$ in CHCl_3), hydrolysed by 0.2*N*- H_2SO_4 at 100° to 4-methyl-*d*-sorbse, m.p. 126—127°, $[\alpha]_D^{20}$

$+33.2^\circ$ to $+27.5^\circ$ in EtOH (*phenylosazone*, m.p. 131—132°). Complete methylation of (IV) could not be effected by Ag_2O and MeI , whereas the action of MeI on the Na compound leads to 3:4:5-trimethyl-1:2-isopropylidene-*d*-sorbse (V), b.p. 105—106°/0.25 mm., $[\alpha]_D^{20} -59.6^\circ$ in H_2O (3:4:5-trimethyl-1:3-isopropylidene- α -fructose, b.p. 110—111°/0.08 mm., $[\alpha]_D^{20} -158.7^\circ$ in H_2O , is analogously obtained). Hydrolysis of (V) followed by oxidation with HNO_3 and treatment of the product with CH_2N_2 leads to $\text{Me}_2\text{C}_2\text{O}_4$, Me_2 -*l*-dimethoxysuccinate (*l*-dimethoxysuccindimethylamide, m.p. 202—203°, $[\alpha]_D^{20} -128.9^\circ$ in H_2O), and Me_2 -xylotrimethoxyglutarate (xylotrimethoxyglutardimethylamide, m.p. 164.5—165°, $[\alpha]_D^{20} \pm 0^\circ$). H. W.

Action of air on solutions of pure sucrose. M. GARINO, M. PARODI, and V. VIGNOLO (Gazzetta, 1935, 65, 132—143).—A 20% aq. solution of sucrose is oxidised by air very slowly at 20°, more rapidly at 100°, with evolution of CO_2 . At 100—130° the solution becomes brown, and glucosone and pentoses are formed. In presence of $\text{Ca}(\text{OH})_2$, oxidation is more rapid; CO is formed, with Ca salts and volatile aldehydes.

E. W. W.

Scilla and digitalis glucosides. A. STOLL (Pharm. Acta Helv., 1934, 9, 145—168; Chem. Zentr., 1934, ii, 3625).—Partly a summary of work already reported (cf. A., 1934, 1206). The ultra-violet



$\text{C}_{14}\text{H}_{30}$
(tricyclic)

absorption spectra of scillaridin-A (I) and scillarin-A show similar maxima to that of octatrienoic acid; partly on this basis the partial formula (I) is proposed. Irradiation of *Scilla* products gives rise to

no vitamin-D activity. Purpureagluconide-A and deacetyldigilamide-A are identical. The enzymes of *Digitalis* leaves are discussed.

H. N. R.

Thevetin, the crystalline glucoside of *Thevetia Nerifolia*. N. GHATAK (Proc. Acad. Sci., U.P., India, 1934, 4, 173—174).—A criticism of Chen *et al.* (A., 1934, 820). Thevetin is $\text{C}_{20}\text{H}_{30}\text{O}_6$ and is hydrolysed to glucose and thevetigenin, $\text{C}_{14}\text{H}_{20}\text{O}$, a OH-compound which gives an Ac derivative. H. G. M.

Solanine. A. HEIDUSCHKA and F. PHILIPPI (Ber., 1935, 68, [B], 669).—Acetylation of solanine according to Zemplén *et al.* (A., 1929, 51) affords *solanine hendeca-acetate*, $C_{74}H_{113}O_{25}N$, m.p. 200° after darkening at 182° and softening at 192° , hydrolysed by boiling 12% HCl to solanidine hydrochloride. H. W.

Galactoaraban prepared from the seeds of the peanut. R. MIYAMA (J. Dept. Agric. Kyushu, 1935, 4, 195—236).—The *galactoaraban* (I), insol. in H_2O , was extracted from the peanuts with 0.2% alkali, pptd. with EtOH, and purified as Cu salt. Hydrolysis of (I) with 3% H_2SO_4 gave a mixture of *l*-arabinose (2 mols.), galactose (1 mol.), and galacturonic acid. Acetolysis of the hepta-acetate of (I) gave *galactoarabotriose* (II) *nona-acetate*, m.p. 115 – 118° , $[\alpha]_D^{25} +95.4^\circ$, the trisaccharide being composed of 2 mols. of arabinose and 1 mol. of galactose. On methylation (Me_2SO_4) (I) formed *heptamethylgalactoaraban*, $[\alpha]_D^{25} +579.9^\circ$, hydrolysed by 1% MeOH-HCl at 100° to a mixture from which 2:3:4-trimethylgalactose and 2:3-dimethyl-*l*-arabinose were isolated. (I) is considered to be composed of polymerised (II), the individual sugar units being linked together through the 1 and 4 positions. M. S.

Xanthate formation of some polymeric carbohydrates. T. LIESER and A. HACKL (Technol. u. Chem. Papier- u. Zellstoff-Fabr., 1934, 31, 69—73; Chem. Zentr., 1934, ii, 3926).—Optimal conditions have been determined for xanthate formation from starch, glycogen (I), lichenin, mannan, inulin, and xylan. The [NaOH] necessary is < with cellulose. Xanthate formation rises with increasing [NaOH] to an optimum and then decreases [with the exception of (I)]. With the exception of (I) the optimum ratio of reactants is $2C_6H_{10}O_5 : CS_2$. It is concluded that, except for (I), the same no. of sugar-anhydride chains lie in the surface as in the interior of the micelles.

H. N. R.

Concentration and ionising tendency of carboxylic acid groups in cellulose and other natural products. S. M. NEALE (Nature, 1935, 135, 583).—The addition of NaCl to oxycellulose (I) liberates its acidic H ion. With excess of NaCl (I) can be titrated directly with NaOH using an indicator turning slightly on the acid side of the neutral point. L. S. T.

Compounds of high mol. wt. III. Octoyl esters of cellulose, and the interferometric method of determination of the degree of esterification of cellulose. A. NOWAKOWSKI (Rocz. Chem., 1935, 15, 69—80).—Amorphous *cellulose tri-n-octoate* (I), m.p. 167 – 170° , is obtained from ramie cellulose (II), $n-C_7H_{15}\cdot CO_2H$ (III), $(CH_2Cl\cdot CO)_2O$ (IV), and H_2SO_4 (0.1%) at 40° , fibrous *di-n-octoate*, m.p. 216 – 219° , from (II), (III), (IV), and $HClO_4$ (0.06%) in Et_2O at 60° , and fibrous (I), m.p. 182 – 186° , by soaking (II) in C_5H_5N for 5 days, adding $n-C_7H_{15}\cdot COCl$ and C_6H_6 , and boiling for 42 hr. X-Ray examination shows that the products containing > 60% of (III) retain the structure of (II), that of (I) being found when 60—80% of (III) is present.

R. T.

Bouveault's method for the preparation of aldehydes from organo-magnesium compounds

and *N*-disubstituted formamides. N. MAXIM and R. MAVRODINEANU (Bull. Soc. chim., 1935, [v], 2, 591—600).—With 1 mol. of $MgR'X$, $HCO\cdot NR_2$ affords mainly the aldehyde $R'\cdot CHO$ (Bouveault, A., 1904, i, 13), especially with formamides, and when R' contains a large no. of C atoms. With 3 mols. of $MgR'X$ the main product is the *tert.*-amine: $HCO\cdot NR_2 + 2MgR'X \longrightarrow NR_2\cdot CHR + MgO + MgX_2$, especially when $R_2 = Et_2$ or piperidyl, and thus are obtained: δ -diethylamino-*n*-heptane, b.p. $86^\circ/20$ mm. (picrate, m.p. 85°); hydroferrocyanide); γ -ethylamino-, b.p. $125^\circ/15$ mm. (picrate, m.p. 82°); hydroferrocyanide), and γ -methylamino-*n*-pentane, b.p. $128^\circ/12$ mm. (hydroferrocyanide); δ -ethylamino-, b.p. $142^\circ/18$ mm. (hydroferrocyanide), δ -methylamino-, b.p. $152^\circ/18$ mm. (hydroferrocyanide), and δ -diphenylamino- β -dimethyl-*n*-heptane, b.p. $185^\circ/7$ mm.; and γ -piperidino-*n*-heptane, b.p. 185° (picrate, m.p. 107°). J. W. B.

Stereochemical relationships of some optically active amines and amino-acids. I. Configuration of valine. F. BARROW and G. W. FERGUSON (J.C.S., 1935, 410—418).—If *Cabcy* and *Cabzy* have the same stereochemical configuration, replacement of *c* by *y* and *x*, respectively, gives compounds, *Cabzy*, of opposite configurations, provided that the possibility of Walden inversion is avoided by making the changes such that the C-c linking is not affected. By this method naturally occurring valine (I) is shown to have the same configuration as *L*(+)-alanine (II), in agreement with the less trustworthy methods of optical displacement. (I) is termed *L*(+)-valine. Et α -acetamidoisovalerate (modified prep.), b.p. 157 – $158^\circ/21$ mm., with Na-BuOH gives *dl*-valinol (III) [hydrochloride, m.p. 118 – 119° (lit. 114°); *N*-Bz, m.p. 81 – 82° , *ON*-Bz₂, m.p. 114° , and Bz₃, m.p. 135° , derivatives], also obtained (90% yield) from $NO_2\cdot CHPr^s\cdot CH_2\cdot OH$ and Fe-HCl-EtOH. (II) and HBr-AcOH at 130 – 140° give α -bromomethylisobutylamine hydrobromide, m.p. 211 – 212° (decomp. 203°), which is hydrogenated (Pd-C) in dil. AcOH to α -methylisobutylamine (IV) (hydrochloride, m.p. 203° ; *p*- $NO_2\cdot C_6H_4\cdot CO$ derivative, m.p. 115°), also obtained from $CMePr^s\cdot NOH$, b.p. 158 – 160° , by Na and $C_5H_{11}\cdot OH$. (I) and *d*-tartaric acid in EtOH give *D*(-)- (V) and *L*(+)-valinol (VI) [*H*(+)-tartrate of (V), H_2O , m.p. 116° , $[\alpha]_{5461}^{20} +102^\circ$ in H_2O ; hydrochlorides, m.p. 113° and 112 – 114° , $[\alpha]_{5461}^{20} -16.5$, $+16.4^\circ$ in H_2O , respectively; Bz₂, m.p. 117° , $[\alpha]_{5461}^{20} +20.2^\circ$, -20.1° , and Bz₃ derivatives, m.p. 119 , $[\alpha]_{5461}^{20} -133.8^\circ$, $+133.1^\circ$, in C_5H_5N , respectively]. *L*(-)-Formylvaline, $[\alpha]_{5461}^{20} -19.9^\circ$ in H_2O , with HCl-EtOH, followed by Ac_2O -NaOAc, affords *Et* *L*(-)- α -acetamidoisovalerate (VII), b.p. $158^\circ/21$ mm., cryst., $[\alpha]_{5461}^{20} -20.1^\circ$ (homogeneous), hydrolysed by hot 12% HBr to (I), $[\alpha]_{5461}^{20} +32.77^\circ$ in 20% HCl; only slight racemisation had thus occurred. Reduction (Na-EtOH) of (VII) gives (VI) mostly racemised, the identity of which was proved by the characteristic inversion of α of the Bz₂ and Bz₃ derivatives and by isolation of a little nearly pure (VI). (V) and (VI) afford the (-)- and (+)-isomerides (VIII) of (IV) (hydrochloride, m.p. 205° after sintering at 192° , $[\alpha]_{5461}^{20} -3.4^\circ$, $+3.5^\circ$ in H_2O , respectively, *p*- $NO_2\cdot C_6H_4\cdot CO$ derivatives, m.p. 112.5 , $[\alpha]_{5461}^{20}$

$\pm 55.8^\circ$ in C_5H_5N). The Et ester hydrochloride of (II), $[\alpha]_{D}^{20} +11.1^\circ$ in H_2O , with $MgMeI$ in Et_2O gives (+)- β -hydroxy- α -methylisobutylamine (IX) (hydrochloride, m.p. 136° , $[\alpha]_{D}^{20} +5.6^\circ$ in H_2O ; N-Bz derivative, m.p. 116° , $[\alpha]_{D}^{20} -17.2^\circ$ in C_5H_5N , $+8.1^\circ$ in $EtOH$). dl-(II) affords the dl-isomeride (X) of (IX) [hydrochloride, $+H_2O$, m.p. (anhyd.) 117° ; N-Bz derivative (XI), m.p. 96°], which is decomposed by HBr , but with PCl_5-CHCl_3 gives the chloride, hydrogenated (Pd-C) in $MeOH$ to (IV). (X) affords (IX) and its (-)-isomeride [(+)-tartrate, $+H_2O$, m.p. (anhyd.) $166-167^\circ$ (sinters at 161°) and (nearly pure) 122° (decomp.), $[\alpha]_{D}^{18,10} +22.2^\circ$, $+15.6^\circ$ in H_2O , respectively; hydrochloride, m.p. 140° , $+6.1$, -5.5° in H_2O ; Bz derivative, m.p. 116.5° , $[\alpha]_{D}^{20} -16.8^\circ$, $+17.7^\circ$ in C_5H_5N , $[\alpha]_{D}^{21,10} +8.3^\circ$, -8.0° in $EtOH$, respectively], which yield by PCl_5 a mixture of $NH_2 \cdot CHMe \cdot CMe_2Cl$ and $NH_2 \cdot CHMe \cdot CMe_2CH_2$, hydrogenated to (VIII) (hydrochloride, $[\alpha]_{D}^{20} -2.1^\circ$, $+2.4^\circ$ in H_2O ; p - $NO_2 \cdot C_6H_4 \cdot CO$ derivative, $[\alpha]_{D}^{21} +53.8^\circ$, -43.5° in C_5H_5N). dl-Benzoylalanine Me ester hydrochloride (modified prep.), m.p. 81° , with $MgMeI$ gives an 80% yield of (XI), which could not be converted into the N-benzoyl- α -methylisobutylamine and was largely decomposed by hot $KOH-EtOH$.
R. S. C.

Complex salts of amino-acids and peptides.
I. Metal complex salts of glycine and their specificity. M. BERGMANN and S. W. FOX (J. Biol. Chem., 1935, 109, 317-324).—The trioxalato-complex appears to be a sp. reagent for glycine (I), the nature of the central metal atom being of secondary importance. The presence of another cation (K, possibly NH_4 but not Na) is necessary for formation of a ppt. A method of separating (I) from gelatin hydrolysates is thus afforded. The following salts are described:

$[R = (I)]: [Cr(C_2O_4)_3]_4K_2, 2HCl, 22H_2O$;
 $[Cr(C_2O_4)_3]_3K_8R_9, HCl$; $[Cr(C_2O_4)_3]_6K_{18}R_5, 2H_2O$ (also $3H_2O$); $[Co(C_2O_4)_3]_9K_{18}R, HCl(?)$;
 $[Co(C_2O_4)_3]_2K_4R_2, HCl(?)$; $[Co(C_2O_4)_3]_4K_{11}R, 14H_2O$;
 $[Fe(C_2O_4)_3]_6K_{12}R_6, HCl, H_2O(?)$;
 $[Fe(C_2O_4)_3]_6K_{13}R_5, HCl, 4H_2O$;
 $[Fe(C_2O_4)_3]_2K_4R_2, HCl$.
H. T.

Action of iodoethyl alcohol on thiol compounds and proteins. D. R. GODDARD and M. P. SCHUBERT (Biochem. J., 1935, 29, 1009-1011).— $CH_2I \cdot CH_2OH$ (I) with cysteine gives S-(β -hydroxyethyl)cysteine. The reaction of (I) with glutathione and reduced wool protein (A., 1934, 1238) at pH 7.5 as followed by reduction in the I titre is similar to that of $CH_2I \cdot CO_2H$, but slower.
H. D.

Preparation of the optically active isomerides of homocystine and demonstration of their configurative relationship to naturally occurring methionine. V. DU VIGNEAUD and W. I. PATTERSON (J. Biol. Chem., 1935, 109, 97-103).—Homocystine (A., 1933, 151) is reduced by Na in liquid NH_3 , and treated with CH_2PhCl , and the resulting *ai*-S-benzylhomocystine [new m.p. $240-250^\circ$ (corr.)] converted by HCO_2H in Ac_2O into *-formyl*-dl-S-benzylhomocystine, m.p. $85-86^\circ$ (corr.). This yields the brucine salt, m.p. $125-128^\circ$, $[\alpha]_D^{20} -17^\circ$, of *-formyl*-d-S-benzylhomocystine, m.p. $247-252^\circ$, $[\alpha]_D^{20} +25$ in $N-HCl$, which when treated with Na in NH_3

and with air in presence of $FeCl_3$ gives d-homocystine (I), m.p. $281-284^\circ$ (corr.), $[\alpha]_D^{20} -77^\circ$ in $N-HCl$, $[\alpha]_D +16^\circ$ in H_2O . The mother-liquors similarly treated yield l-homocystine (II), $[\alpha]_D +77^\circ$ in $N-HCl$, $[\alpha]_D^{20} -16^\circ$ in H_2O . (II) is converted (cf. A., 1933, 1074) into l-methionine, identical with the natural substance; (I) yields d-methionine, $[\alpha]_D^{20} +8^\circ$ in H_2O , $[\alpha]_D -22^\circ$ in 0.2N-HCl.
E. W. W.

Iodometric determination of cysteine. T. F. LAVINE (J. Biol. Chem., 1935, 109, 141-145).—Cystine (I) is stable to I when in a solution of $N-HCl$ and $N-KI$. The indirect iodometric determination of cysteine at room temp. is accurate to $\pm 0.5\%$, and is consistent with its oxidation to (I) (cf. A., 1933, 266; 1934, 434).
E. W. W.

Mineral salts of carbamide. L. PALFRAY (Compt. rend., 1935, 200, 1051-1053).— $CO(NH_2)_2$ (2 mols.) with conc. H_2SO_4 (1 mol.) at room temp. gives $2CO(NH_2)_2 \cdot H_2SO_4$, and with excess of HBr below 75° it gives the salt $2CO(NH_2)_2 \cdot HBr$; equimol. amounts in Et_2O at room temp. give $CO(NH_2)_2 \cdot HBr$. $CO(NH_2)_2 \cdot HI$ is also described. These salts are very deliquescent, and at 80° decompose to give NH_4 salts. J. L. D.

Dissociation of carbamide in dilute solution.—See this vol., 702.

Electrolytic reduction of α' -dicyano- β -dimethylglutarimide. G. G. GRATTON and G. R. RAMAGE (J.C.S., 1935, 539).—This gives a poor yield of the lactam, m.p. 194° , of δ -amino- α - γ -dicyano- β -dimethylvaleric acid, which with conc. HCl at $130-140^\circ$ gives (?) 6-hydroxy-3(or 5)-carbamiyl-2:4-dimethylpyridine-5(or 3)-carboxylic acid, decomp. $> 360^\circ$.
R. S. C.

Silver derivatives of thiosemicarbazide and of thiosemicarbazones. V. HARLAY (Compt. rend., 1935, 200, 1220-1221).— $NH_2 \cdot CS \cdot NH \cdot NH_2$ (I) with $AgNO_3$ in equimol. amounts gives a *cryst. compound*, $[AgS \cdot C(NH_2) \cdot N \cdot NH_2]HNO_3$ (cf. A., 1902, i, 572), converted by $NaCl$ into the *chloride*. (I) (3 mols.) with $AgNO_3$ (2 mols.) affords another Ag derivative. These are stable to light. Acetonethiosemicarbazone (II) with excess of $AgNO_3$ gives an amorphous product, unstable to light. (II) (2 mols.) with $AgNO_3$ (1 mol.), and (II) (3 mols.) with $AgNO_3$ (2 mols.), give *cryst. and stable products*. Benzaldehydethiosemicarbazone affords analogous products, which combine with one another to form a stable substance. J. L. D.

Maleo- and fumaro-nitriles. J. DE WOLF and L. VAN DE STRAETE (Bull. Acad. roy. Belge, 1935, [v], 21, 216-225).— Me_2 maleate with saturated NH_3-H_2O at 10° in the dark gives malediamide (I) (cf. A., 1927, 652) and some fumaramide. (I) with P_2O_5 gives maleonitrile, m.p. $92.6-93^\circ$ (A., 1913, i, 253), and a substance, m.p. $48-54^\circ$.
J. L. D.

Citracono- and mesacono-nitriles. L. VAN DE STRAETE (Bull. Acad. roy. Belge, 1935, [v], 21, 226-235).—Citracon- and mesacon-amide (A., 1882, 1281) when heated with P_2O_5 give citracono-, m.p. $106.3-106.5^\circ$, and mesacono-nitrile, b.p. $66^\circ/10$ mm., respectively, the latter of which with conc. H_2SO_4 at room temp., or with H_2O_2 , gives a *product*, m.p. $147-148^\circ$.
J. L. D.

Properties and structure of maleo- and citracono-nitriles. P. BRUYLANTS (Bull. Acad. roy. Belg., 1935, [v], 21, 138—146).—From a discussion of differences in the *d*, *n*, and mol. refractions of maleo- and fumaro- and of citracono- and mesacono-nitriles, and a comparison with the small differences in the corresponding vals. for the respective Me esters, it is suggested that an "internal dinitrile" is formed by the elimination of 2H₂O from two amido-groups.

N. M. B.

Determination of selenocyanides.—See this vol., 718.

Hydrides of boron. IV. Methyl derivatives of diborane. H. I. SCHLESINGER and A. O. WALKER (J. Amer. Chem. Soc., 1935, 57, 621—625; cf. A., 1933, 1257).—The prep. of the following compounds is described: B₂H₅Me (I), B₂H₄Me₂ (II) (m.p. —150·2°), B₂H₃Me₃ (III) (m.p. —122·9°), B₂H₂Me₄ (IV) (m.p. —72·5°), BMe₃·OH (V). The v.d. and v.p. have been measured. The reactions with H₂O indicate that (IV) has a symmetrical structure, that in (II) both Me are attached to the same B, and that in (III) two Me groups are attached to one B and one Me to the other B. (V) is formed by reaction of (I), (III), and (IV) with H₂O. No indication of the formation of B₂HMe₅ or B₂Me₆ was observed.

E. S. H.

Formation of organo-metalloidal compounds by micro-organisms. III. Methylated alkyl- and dialkyl-arsines. F. CHALLENGER and L. ELLIS (J.C.S., 1935, 396—400; cf. A., 1934, 278).—Strain A (I) (cf. A., 1933, 266) growing on sterile bread crumbs containing diethylarsinic acid (II) evolves a gas which with Biginelli's solution (III) affords *AsMeEt₂·2HgCl₂*, m.p. 196—198°, decomp. 201°, and with HNO₃ and then Na picrate (IV) in H₂O, *OH·AsMeEt₂·O·C₆H₅(NO₂)₃*, m.p. 134—135°. Similarly the mould gas from *n*-propylarsinic acid with (III) affords *AsMe₂Pr·2HgCl₂*, m.p. 195°, decomp. 200°, and with CH₂PhCl and (IV) affords *benzyl-dimethyl-*n*-propylarsonium picrate*, m.p. 113—114°, and with HNO₃ and (IV) and H₂O, *hydroxydimethyl-*n*-propylarsonium picrate*, m.p. 143—144°, whilst that from allylarsinic acid with (III) affords *AsMe₂·C₃H₅·2HgCl₂*, m.p. 208—209° (decomp.) (m.p. depends on rate of heating), and with CH₂PhCl and (IV), *benzyl-dimethylallylarsonium picrate*, m.p. 96—97°. The mould does not reduce the double linking of the allyl group. The products from the mould gases were also obtained from synthetic arsines. The following substances are described: *AsMe₂Pr·HgCl₂*, m.p. 126—128°; *AsMeEt₃*, b.p. 112—114° (no b.p. in lit.) (*monomercurichloride*, m.p. 153—154°); *benzyl-methyl-dimethylarsonium picrate*, m.p. 85—86°, and *stypnate*, m.p. 89—90°; *AsEt₃·HgCl₂*, m.p. 161—162° (lit. 163—164°); *benzyl-trimethylstibonium picrate*, m.p. 183—185°; *AsMe₂·C₃H₅* (V), b.p. 108—109° (lit., b.p. about 160°) (*monomercurichloride*, m.p. 120—121°); *trimethylallylarsonium iodide*, m.p. 184—186°. (V) with limited access of air gave a product from which cacodylic acid (VI) and *hydroxydimethylallylarsonium picrate*, m.p. 159—160°, were isolated. Similarly *AsMe₃* (improved prep.) gives (VI) and *hydroxytrimethylarsonium picrate*, whilst *AsEt₃* gives (II) (A., 1930, 330). Growth of (I) on bread and on

aq. media containing K Sb tartrate gives no odour of alkylstibine.

H. G. M.

Synthesis of halides of tin alkyls. K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1934, 4, 1359—1363).—SnCl₄ and MgEtBr in Et₂O affords a mixture of SnEt₂Cl (I), SnEt₂Cl₂ (II), and SnEt₄ (III). (III) and SnCl₄ (2 hr.; 200°) yield (II), which with (III) gives (I); the corresponding bromides are prepared analogously.

R. T.

Processes of dehydrogenation. II. Action of selenium or palladised charcoal on cyclopentane derivatives at elevated temperature. L. RUZICKA and E. PEYER (Helv. Chim. Acta, 1935, 18, 676—684).—Chrysene does not appear to be formed when 3-methylcyclopentenophenanthrene is heated with Se or Pd-C at 450°, but the results are not regarded as final, on account of the small amount of available material. The fundamental possibility of the enlargement of a 5-C to a 6-C ring is established by the ready conversion of 1- or 2-methylhydrindene into C₁₀H₈ by Se or Pd-C at 450°, whereas at 350° or 400° the hydrocarbons remain unchanged. Similarly C₁₀H₈ is produced from 1- and 2-ethylhydrindene, 1-isooctylhydrindene (I), b.p. 100—102°/0·2 mm., 153°/12 mm., and methylisopropylhexahydrofluorene (II), b.p. 105°/0·6 mm., about 150°/10 mm., or from 1:2-diethyl-Δ¹-cyclohexene, b.p. 54—55°/10 mm., and Se at 420°. The yields of C₁₀H₈ vary from 5% to 50%, and are generally twice as great with Se as with Pd-C; they are maximal with Me derivatives, and diminish with the complexity of the hydrocarbon. If secondary reactions are to be avoided, the temp. of dehydrogenation must not therefore exceed 350°. The formation of aromatic from 5-membered rings above 400° does not invariably occur in an obvious manner, since elimination of groups occurs to a marked extent under these conditions. Indene derivatives in presence of Se or Pd-C at about 350° pass smoothly into almost homogeneous hydrindene derivatives, a part of the initial hydrocarbon being lost. The hydrogenation of the unsaturated 5-membered ring under conditions of dehydrogenation renders improbable the formation of methylcyclopentadienophenanthrene from sterol or bile acid derivatives. Treatment of Me isohexyl ketone with indene and KOH in boiling MeOH gives methylisohexylbenzofulvene, b.p. about 120°/0·2 mm., hydrogenated to (I), also obtained from methylisohexenylbenzofulvene (III), b.p. about 130°/0·2 mm. (III) is converted by 100% HCO₂H at 140° into methylisopropylfluorene, b.p. 105°/0·3 mm., hydrogenated (PtO₂ in MeOH) to (III).

H. W.

Purification of the common carotenoids and the quantitative measurement of their absorption spectra. E. S. MILLER (Bot. Gaz., 1935, 96, 447—467).—Improved methods are described and spectrographic data are given for α- and β-carotene, xanthophyll, and lycopene. The customary spectroscopic tests of purity are only approx. Detailed examination of absorption spectra affords the most trustworthy test. A quant. spectral method of analysis of binary mixtures of carotenoids is described.

Directive influence of electric moment on substitution in the benzene ring.—See this vol., 684.

Kinetics of the electrochemical chlorination of benzene.—See this vol., 709.

Preparation of hexaiodobenzene. J. F. DURAND and (MLLE.) M. MANCET (Bull. Soc. chim., 1935, [v], 2, 665—666).—Conditions for the prep. of C_6I_6 in 81% yield from C_6H_6 —61.5% oleum-I at 170—180° are given. The yield is largely dependent on the oleum concn. J. W. B.

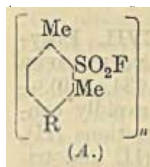
Condensation of isopropyl alcohol with toluene and its nitro-derivatives. G. DESSEIGNE (Bull. Soc. chim., 1935, [v], 2, 617—623).—Addition of Pr^iOH to $PhMe$ —78% H_2SO_4 at 70—100° and isolation of the product by steam distillation at 160° affords an 82% yield of *p*-cymene (I), together with small amounts of 2:4-di- (II), b.p. 225°/770 mm. (14%), and 2:4:6-tri-isopropyltoluene, b.p. 252—253°/757 mm. The proportion of (I) is decreased to 38% and that of (II) is increased to 47% when 95% H_2SO_4 is used. Similar condensation of Pr^iOH and *o*- $C_6H_4Me \cdot NO_2$ with 92—93% H_2SO_4 at 35—40° affords 2-nitro-*p*-cymene (reduced to the 2- NH_2 -derivative), identical with the nitration product from (I), and 2-nitro-4:6-diisopropyltoluene, b.p. 158°/15 mm., reduced (Clemmensen) to the 2- NH_2 -derivative, b.p. 141°/11 mm. (Ac derivative, m.p. 118°; hydrochloride, m.p. 226—228°). Similarly p - $C_6H_4Me \cdot NO_2$ at 70—80° affords 4-nitro-*o*-cymene, b.p. 144—145°/15 mm. [reduced to the 4- NH_2 -compound, b.p. 123°/15 mm. (Ac derivative, m.p. 103°; hydrochloride, m.p. 233°)], and 4-nitro-2:6-diisopropyltoluene, b.p. 168°/11 mm., m.p. 61°, reduced to the 4- NH_2 -compound, b.p. 146°/11 mm. (Ac derivative, m.p. 162°; hydrochloride, m.p. 245—247°). J. W. B.

Organic magnesium compounds. I. Reaction between phenyl *p*-toluenesulphonate and magnesium phenyl bromide in various solvents. K. MINE (J. Chem. Soc. Japan, 1934, 55, 905—909).— Et_2O , isoamyl ether, C_6H_6 , $PhMe$, and xylene are used as solvents. CH. ABS. (r)

Chlorinated derivatives of *p*-xylene. H. WAHL (Compt. rend., 1935, 200, 936—938).—From chloro-*p*-xylidines by the Sandmeyer reaction, 2:3-dichloro- (I), m.p. -2°, b.p. 230°, and 2:6-dichloro- (III), m.p. 15°, b.p. 222°/770 mm., -*p*-xylene, and 2:5-dichloro-*p*-xylene (III) are prepared. (I) and (II) are readily sulphonated by H_2SO_4 , and from (I) a sulphonyl chloride (IV), m.p. 62°, sulphonamide (V), m.p. 201°, and sulphonanilide (VI), m.p. 157°, and from (II) a sulphonyl chloride, m.p. 81°, sulphonamide, m.p. 150°, and sulphonanilide, m.p. 175°, are prepared. (III) is sulphonated only by oleum (decomp.), yielding a *K* sulphonate, from which a sulphonyl chloride, m.p. 71°, sulphonamide, m.p. 165°, and sulphonanilide, m.p. 171°, are obtained. When the fraction of b.p. 220—230° from the chlorination (VII) of *p*-xylene is treated with H_2SO_4 , it yields a *Ca* sulphonate from which (IV), (V), and (VI) are prepared, and, by hydrolysis (I). (I) is therefore obtained, as well as (III), during (VII). E. W. W.

Action of Grignard reagents on aromatic sulphonyl fluorides. D. T. GIBSON (J. pr. Chem., 1935, [u], 142, 218—222).—A criticism of Steinkopf

et al. (A., 1934, 1341). The calc. composition for the compounds $C_{17}H_{13}O_6S_4F_2$, m.p. 135° and m.p. 272° (from *m*-xylene-2:4-disulphonyl fluoride and $MgMeI$), is incorrect. The analytical data agree better with $C_9H_{11}O_4FS_2$ (A, R= SO_2Me ; $n=1$), m.p. 135°, and $C_{17}H_{13}O_6S_4F$ (A, R= SO_2 ; $n=2$), m.p. 272°. Only sulphonyl fluorides (I) give bis-sulphonylmethane derivatives (II) with Grignard reagents. $PhSO_2Me$ and $MgMeI$ in boiling xylene give $PhSH$; $PhSO_2F$ and $MgEtI$ give bisphenylsulphonylthane. Addition of $PhSO_2 \cdot CH_2Cl$ to the product ($PhSO_2 \cdot MgI$) of interaction of $PhSO_2F$ and $MgEtI$ affords a Cl-containing compound, m.p. 138°, readily converted by Na_2SO_3 into bisphenylsulphonylmethane (III). Hence the initial product of interaction between (I) and $MgRX$ is probably $PhSO_2 \cdot CH_2F$. *p*- $C_6H_4Me \cdot SO_2F$ and $MgMeI$ give bis-*p*-tolylsulphonylmethane, but with $MgPr^iI$, di-*p*-tolyl-disulphone results. Hence it is suggested that the formation of (II) is due to the intermediate compound ($PhSO_2F \rightarrow H$), $CH \cdot MgI$ resulting from the sp. co-ordinating power of F. The yield of (III) from $PhSO_2F$ and $MgMeI$ decreases greatly if excess of the Grignard reagent is used. J. W. B.



Action of Grignard reagents on aromatic sulphonyl fluorides. W. STEINKOPF (J. pr. Chem., 1935, [ii], 142, 223—224).—A reply to Gibson (preceding abstract). The formula given for the compound, m.p. 272°, from *m*-xylene-2:4-disulphonyl fluoride (A., 1934, 1341) was an error for $C_{17}H_{20}O_7S_4F_2$, with which the analytical data agree. J. W. B.

2:4-Dinitrodiphenylsulphones. J. D. LOUDON (J.C.S., 1935, 537—539).—2:4- $C_6H_3Cl(NO_2)_2$ or 2:4- $(NO_2)_2C_6H_3 \cdot SO_2C_6H_4Me \cdot p$ with the appropriate Na sulphinate in hot aq. $EtOH$ give 2:4:3'-trinitro-, m.p. 196—197°, and 2':5'-dichloro-2:4-dinitrodiphenylsulphone, m.p. 178°, and seven known 2:4-dinitrodiphenylsulphones. 4'-Chloro- (I) and -bromo-2:4-dinitrodiphenylsulphone with KNO_3 — H_2SO_4 give the 2:4:3'-(NO_2)₃-derivatives, m.p. 203° (II) and 210° (III), respectively. The sulphones are cleaved by piperidine (IV) to yield 2:4-dinitropiperidinobenzene. (II) or (III) with (IV) in dioxan gives 2:4:3'-trinitro-4'-piperidinodiphenylsulphone; the Cl is thus reactive, but *p*- $C_6H_4Cl \cdot SO_2Na$ and (II) give (I), apparently by exchange of aryl groups. A similar exchange is effected when most of the above sulphones are heated with an excess of a Na sulphinate in dioxan, the NO_2 -free nucleus being exchanged. Similarly 2:4-dinitrodiphenylsulphone with *p*-tolyl or *Me p*-toluenethiolsulphonate and a little Na_2CO_3 in dioxan give 2:4-dinitrophenyl-*p*-tolylsulphone. R. S. C.

Polymerisation of styrene, citral, and heptaldehyde. H. E. THOMPSON and R. E. BURK (J. Amer. Chem. Soc., 1935, 57, 711—713).—Highly purified citral and heptaldehyde are stable in absence of O_2 ; polymerisation normally occurs with absorption of 1 and 2 O, respectively. The rate of polymerisation of styrene (I) is very greatly reduced by careful purification and absence of O_2 , but is still governed by the presence of catalysts (already present or added);

normal polymerisation of (I) involves absorption of about 0.33 O, but no increase in mol. wt., and only a trace of non-volatile solid is observed. R. S. C.

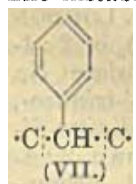
Highly-polymerised compounds. CVII. Polystyrenes. H. STAUDINGER and A. STEINHOFFER (Annalen, 1935, 517, 35—53; cf. A., 1934, 879).—At 400—500°/1 atm. polystyrene (I) is rapidly converted into $\text{CHPh}\cdot\text{CH}_2$ and distyrene fractions (II), whilst at 310—350° larger amounts of (II) and tri-styrene fractions (III) slowly result. If reaction is conducted in high vac., tetrastylene fractions (IV) are also isolated. (II), (III), and (IV) contain much unsaturated (V) and little saturated (VI) hydrocarbons. (V) cannot be obtained homogeneous and are identified by their derivatives. (VI) are isolated by further polymerisation of (V) and subsequent distillation. (II) contains $\alpha\gamma$ -diphenylpropane, b.p. 155—157°/12 mm., and $\alpha\gamma$ -diphenyl- Δ^2 -butene, oxidised to $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, m.p. 72—73°. (III) is composed of (?) $\alpha\gamma\epsilon$ -triphenylpentane, b.p. 170—172°/0.5 mm. [also obtained from $\text{CO}(\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$ and MgPhBr followed by dehydration of the carbinol $\text{OH}\cdot\text{CPh}(\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$ and hydrogenation (colloidal Pd) of the unsaturated hydrocarbon], and $\alpha\gamma\epsilon$ -triphenyl- Δ^4 -hexene, oxidised to *Ph* $\beta\delta$ -diphenyl-*n*-butyl ketone, m.p. 80—81° (oxime, m.p. 123—124°), also obtained by hydrogenation of β -phenyl- β -styrylpropionophenone. These results show that (I) is $\cdot\cdot[\cdot\text{CHPh}\cdot\text{CH}_2\cdot]_n\cdot\cdot$ and that cracking occurs according to the schemes, $\cdot\cdot[\cdot\text{CHPh}\cdot\text{CH}_2\cdot]_n\cdot\cdot \longrightarrow \text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CH}_2\cdot + \text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CH}_2\cdot$ and $\longrightarrow \text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}\cdot + \text{CH}_2\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CH}_2\cdot$.

The instability of (I) is ascribed to the presence of the allyl group [cf. (VII)]. It is proposed to designate the "double linking rule" of cracking the allyl grouping rule. The polymerisation of $\text{CHPh}\cdot\text{CH}_2$ is a chain process interrupted by a secondary change which occurs with increasing frequency as the rate of polymerisation increases. A condensation process is excluded (cf. Whitby *et al.*, A., 1928, 627), since the double linking of the higher polymerides is too sluggish and simpler products do not accompany the more complex in the final material. It appears probably that a double linking, due to wandering of H, is present in the terminal group of (I); its determination is not suitably effected by titration with Br, since substitution accompanies addition. The prep. of hemi-colloidal products by controlled cracking of complex (I) is described, a higher temp. being required for degradation as the process proceeds. The prep. of (I) with definite terminal groups has been attempted. (I) obtained in presence of conc. H_2SO_4 which gives relatively very simple products are entirely hydrocarbons. Similarly, cracking of (I), mean mol. wt. 125,000, in cyclohexane at 250° in presence of HI, AcOH, Ac_2O , CHCl_3 , or piperidine leads to products which do not contain halogen, Ac, or N. Hemi-colloidal products with foreign terminal groups are not formed when $\text{CHPh}\cdot\text{CH}_2$ is heated at 100° under N_2 with AcOH, Ac_2O , CHCl_3 , piperidine, MeOH, or $\text{MeOH}+5\%\text{HCl}$. Hydrocarbons are the sole products of the polymerisation of $\text{CHPh}\cdot\text{CH}_2$ at 250° in

cyclohexane containing HI, Ac_2O , AcOH, CHCl_3 , or piperidine. H. W.

Highly-polymerised compounds. CVIII. Viscosity of solutions of cyclic compounds. H. STAUDINGER and A. STEINHOFFER (Annalen, 1935, 517, 54—66).—Determination of η_{sp} (1.4%) of CH_2Ph_2 , $(\text{CH}_2\text{Ph})_2$, $\text{CH}_2(\text{CH}_2\text{Ph})_2$, $(\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$, $\text{CH}_2(\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$, $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph})_2$, and $\text{CH}_2[(\text{CH}_2)_4\text{Ph}]_2$ in C_6H_6 and CCl_4 , of hexa- and octadecylbenzene in C_6H_6 , of dicyclohexyl- $\alpha\delta$ -butane, - $\alpha\epsilon$ -pentane, and - $\alpha\zeta$ -hexane in C_6H_6 and CCl_4 and of Ph and cyclohexyl myristate, palmitate, and stearate in C_6H_6 and CCl_4 shows that the increment for the Ph or cyclohexyl group in C_6H_6 or CCl_4 is approx. 4.0×10^{-3} , being identical for each within the experimental limits. of substances with thread mols. depends mainly on the length of the mol. and the concn. of the solution, and is scarcely affected by differences in structure which cause profound differences in chemical and other physical properties. Thus dihexyl terephthalate, b.p. 235°/13 mm., m.p. 37°, and diheptylquinol, b.p. 286°/13 mm., m.p. 60—60.5°, have the same η_{sp} . The presence of a single Ph group in the side-chain of a compound causes an increase in viscosity of 4.5×10^{-3} in C_6H_6 and 7.0×10^{-3} in CCl_4 as shown by comparison of $\text{CH}_2[(\text{CH}_2)_4\text{Ph}]_2$ and $\text{CHPh}[(\text{CH}_2)_4\text{Ph}]_2$, $\text{CH}_2[(\text{CH}_2)_4\text{Ph}]_2$, and $\text{CHPh}[(\text{CH}_2)_4\text{Ph}]_2$, $\text{Ph}[(\text{CH}_2)_4\text{Bz}]$ and $\text{Ph}[(\text{CH}_2)_2\cdot\text{CHPh}\cdot\text{CH}_2\text{Bz}]$, $\text{Ph}[(\text{CH}_2)_7\text{Ph}]$ and $\text{CH}_2(\text{CHPh}\cdot\text{CH}_2)_2$. Comparison of $\text{CH}_2[(\text{CH}_2)_4\text{Ph}]_2$ with $\text{CO}[(\text{CH}_2)_4\text{Ph}]_2$, $\text{CH}_2[(\text{CH}_2)_2\text{Ph}]_2$ with $\text{CO}[(\text{CH}_2)_2\text{Ph}]_2$ and $\text{Ph}[(\text{CH}_2)_4\cdot\text{COPh}]$, and $\text{Ph}[(\text{CH}_2)_3\text{Ph}]$ with $\text{Ph}[(\text{CH}_2)_2\cdot\text{OPh}]$ shows that of ketones is identical with that of hydrocarbon in CCl_4 but somewhat greater in C_6H_6 . Saturated and unsaturated ketones have identical η_{sp} (examples $\text{Ph}[(\text{CH}_2)_2\cdot\text{CHPh}\cdot\text{CH}_2\text{Bz}]$ and $\text{CHPh}\cdot\text{CH}\cdot\text{CHPh}\cdot\text{CH}_2\text{Bz}$) but the increment for a conjugated double linking is 2.5×10^{-3} in C_6H_6 and 4×10^{-3} in CCl_4 [examples: $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Bz}$ and $\text{CHPh}\cdot\text{CHBz}$; $\text{CO}[(\text{CH}_2)_2\text{Ph}]_2$ and $\text{CO}(\text{CH}\cdot\text{CHPh})_2$; $\text{Ph}[(\text{CH}_2)_4\text{Bz}]$ and $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHBz}$; $\text{CO}[(\text{CH}_2)_2\text{Ph}]_2$ and $\text{CO}(\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh})_2$]. The observed and calc. vals. of a no. of simple polymeric styrenes are in harmony. Determinations of η_{sp} at 20°, 40°, and 60° of a series of the substances described above show that it diminishes with *t* rather less in C_6H_6 than in CCl_4 . $\alpha\epsilon\theta$ -Triphenylnonane, b.p. 216—218°/0.04 mm., and $\alpha\gamma\epsilon\eta$ -tetraphenylheptane, b.p. 260—262°/3 mm., are new. H. W.

Highly-polymerised compounds. CX. Constitution of polypropenylbenzene and its derivatives. H. STAUDINGER and E. DREHER (Annalen, 1935, 517, 73—104).—In contrast with styrene and *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}_2$, propenylbenzene derivatives (I) polymerise with difficulty, eu-colloidal products not being available since polymerisation does not occur in absence of catalysts. The introduction of a terminal Me diminishes the tendency of the etylenic linking towards polymerisation. Aromatic propenyl derivatives polymerise more readily than the corresponding allyl compounds, thus giving a possible method of separation. Polymerisation of (I) is a chain reaction occurring in the $\alpha\gamma$ -position (instead of



$\alpha\beta$ as with other ethylenic compounds) owing to the mobility of H in Me as a consequence of the allyl group. (I) is therefore $\cdots[\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2]_x$ but the nature of the terminal groups is undecided. Proof is furnished by the isolation of $\alpha\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m.p. 148°, and $\alpha\delta$ -*pp'*-dimethoxydiphenylbutadiene, m.p. 221—223°, from the products of the cracking of polypropenylbenzene (II) and polyanethole, respectively. (II) are hemi-colloidal, white products without distinctive m.p., sol. without swelling in various media to solutions of low viscosity which follow the Hagen-Poiseuille law. Cryoscopic determinations of the mol. wt. of (II) and their OEt-derivatives in C_6H_6 and cyclohexane give results in harmony with those obtained from measurements of $\eta_{\text{sp.}}$ but this is not the case with the OMe-compounds. In freezing C_{10}H_8 Δ is greater as the complexity of (II) (as measured in C_6H_6 or cyclohexane and by determination of viscosity) increases; in the case of the most complex fractions the mol. wt. 240 is indicated. The material recovered from such solutions is identical with the original, and the results are considered abnormal, since they do not harmonise with all other available chemical and physical evidence. Possibly the C_{10}H_8 mols. suffer reversible change due to the solute. Measurements of $\eta_{\text{sp.}}$ in C_6H_6 and C_{10}H_8 are recorded. $\eta_{\text{sp.}}$ of (II) and of polystyrenes is the same in C_6H_6 as in *m*-cresol, whereas for poly-*p*-methoxystyrenes, poly-*p*-methoxy- and -ethoxy-propenylbenzenes the vals. are higher in *m*-cresol than in C_6H_6 . This is attributed to the formation of oxonium salts, thus confirming the assumption made previously in the analogous case of the cellulose Me ethers (III) and cellulose acetates (IV). When due allowance is made for this complication, it is shown that the transformation of (IV) into (III) is accomplished without change in the degree of polymerisation, thus giving further important evidence of the macro-mol. structure of cellulose.

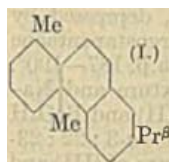
H. W.

Higher benzenoid hydrocarbons. Syntheses with the aid of metallo-derivatives. H. F. MILLER and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 766—771).—9-Chlorofluorene (I) reacts with Grignard reagents by double coupling to form bisdiphenylene-ethane (II) and dialkyl when the reagent exists mainly as MgR_2 , but gives 9-alkylfluorenes when much MgRX is present. Solvents which influence the equilibrium, $-\text{MgRX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2$, thus influence also the course of the reaction. Li 9-fluorenyl (III) is often more useful for syntheses than Mg 9-fluorenyl bromide (IV). Other Grignard reactions with fluorene (V), anthracene, and phenanthrene are reported. Mg 9-phenanthryl bromide (prep. from 9-bromophenanthrene in 92—93% yield) with the appropriate reagent in $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ gives 9-*n*-propyl- (47%), m.p. 74°, b.p. 265—270°/22 mm. (*picrate*, m.p. 134°), 9-*n*-butyl- (52%), m.p. 58°, b.p. 282—284°/20 mm. (*picrate*, m.p. 19.5°), and 9-acetyl-phenanthrene (27%), m.p. 73—74° (*picrate*, m.p. 107°; *oxime*, m.p. 154—155°), and with $\text{CH}(\text{OEt})_3$ phenanthrene-9-aldehyde (46% yield), m.p. 100—100° (*acetal*, m.p. 79—80°; *oxime*, m.p. 156—157°). (IV), prepared in 32% yield from (V) and MgEtBr in xylene and isolated by its insolubility in

Et_2O , does not react in xylene with Pr^nBr or Bu^nBr , but with $\text{CH}_2\text{Ph}\cdot\text{MgBr}$ gives $(\text{CH}_2\text{Ph})_2$ and (II), and with AcCl gives 9-acetylfluorene (58% yield), m.p. 107° (*oxime*, m.p. 167°), and with $\text{CH}(\text{OEt})_3$ an amorphous polymeride. (III), obtained in 80% yield from (V) and LiBu or LiMe, with Bu^nBr , AcCl , and $\text{CH}(\text{OEt})_3$ affords 9-*n*-butyl- (41%), m.p. 101°, b.p. 192—195°/33 mm., and 9-acetyl-fluorene (60%), m.p. 107°, and an amorphous polymeride, respectively. (I) with MgPhBr , $n\text{-C}_3\text{H}_{11}\cdot\text{MgBr}$, or MgBu^nBr in Et_2O or C_6H_6 gives 95% yields of (II); with Mg cyclohexyl bromide in Et_2O it gives 93% of (II), but in C_6H_6 70% of (II) and 20% of 9-cyclohexylfluorene, m.p. 102—103°; MgEtI in Et_2O gives 20% of (II) and 65% of 9-ethylfluorene, m.p. 106—107° (lit. an oil), b.p. 160—165°/10 mm. Grignard reagents could not be prepared from 9:10-dihydroanthracene (prep. in 76% yield by Na in liquid NH_3), 9-bromoanthracene, m.p. 100°, 2-bromo-fluorene, m.p. 110°, or 3-bromoacenaphthene (cf. lit.), m.p. 52°, b.p. 204—209°/30 mm., 327—332°/760 mm.

R. S. C.

Polyterpenes and polyterpenoids. XCVI. Constitution of fichtelite. L. RUZICKA and E. WALDMANN (Helv. Chim. Acta, 1935, 18, 611—612; cf. A., 1923, i, 819).—Dehydrogenation of fichtelite (I), m.p. 46° ($\text{Pd}-\text{C}$ at 330—370°), affords H_2 and CH_4 (8:1 by vol.). (I) is therefore a dimethylisopropylperhydrophenanthrene in which only the position of Me lost during hydrogenation is uncertain. (I) has probably the annexed constitution.



H. W.

1:2-Benzpyrene. L. F. FIESER and M. FIESER (J. Amer. Chem. Soc., 1935, 57, 782—783; cf. Cook *et al.*, A., 1933, 601).—The prep. of 1:2-benzpyrene (I), m.p. 176.5—177°, from pyrene is modified to give a 36% over-all yield. 1':2':3':4'-Tetrahydro-1:2-benzpyrene, m.p. 113° (*picrate*, m.p. 166°), is best (84%) prepared by hydrogenation (200°/3000 lb.); Cu chromite in EtOH of the tetrahydro-ketone (II) and is best removed from impure (I) by Se-dehydrogenation. (II) with MgMeI in C_6H_6 gives 4'-methyl-1':2'-dihydro-1:2-benzpyrene (73% yield), m.p. 155—156°, which with Se at 330° gives 4'-methyl-1:2-benzpyrene, m.p. 217.5—218° (*picrate*, m.p. 203—204°).

R. S. C.

Syntheses of polycyclic compounds related to sterols. III. 9-Methyl- and 3':9-dimethyl-cyclopentenophenanthrene. D. J. C. GAMBLE and G. A. R. KON (J.C.S., 1935, 443—445; cf. A., 1934, 288).—The Grignard reagent from 1:4- $\text{C}_{10}\text{H}_6\text{BrMe}$ with $(\text{CH}_2)_2\text{O}$ in Et_2O give α -(4-methyl-1-naphthyl)ethyl alcohol (I), b.p. 135°/0.5 mm., m.p. 60° (*picrate*, m.p. 107°), and with CO_2 1:4- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{CO}_2\text{H}$, oxidised to 1:4- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$. (I) with HBr at 100° affords the bromide, m.p. 45—46°, b.p. 142°/0.5 mm. (*picrate*, m.p. 72—73°; unstable), the Grignard reagent (II) of which with 2-methylcyclopentanone gives $\alpha\delta$ -di-(4-methyl-1-naphthyl)butane, m.p. 126—127°, b.p. about 230°/0.4 mm. (*dipicrate*, m.p. 174—175°; [$s\text{-C}_6\text{H}_3(\text{NO}_2)_3$]₂ compound, m.p. 192—193°), and a carbinol, dehydrated by P_2O_5 at 140° to 1:9-dimethyl-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene, b.p. 160°/0.5 mm., which affords (Se; 290—300°) 2:

cyclopentenophenanthrene (III), m.p. 109—110° [*picrate*, m.p. 153—154°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 170—171°, and $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ compound, m.p. 135—136°; *styphnate*, m.p. 190—191°]. 2:5-Dimethylcyclopentanone and (II) lead to 2:5-dimethyl-1- β -(4-methyl-1-naphthyl)ethylcyclopentan-1-ol, b.p. 185—190°/0.5 mm., 1:9:3'-trimethyl-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene, b.p. 170°/0.6 mm., and 9:3'-dimethyl-1:3-cyclopentenophenanthrene (IV), m.p. 80° [*picrate*, m.p. 134—135°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 149—150°, and $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ compound, m.p. 113—114°; *styphnate*, m.p. 159—160°]. The 3'-Me analogue (V) of (II) gives a *styphnate* (VI), m.p. 135—136°. The non-identity of (III) or (IV) with (V) confirms the now accepted structure of strophanthidin and uzarigenin. The impure *styphnate* of cyclopentenophenanthrene has m.p. 154°, but does not depress the m.p. of (VI).

R. S. C.

Hydrocarbons from neoergosterol. G. A. HASLEWOOD and (Miss) E. ROE (J.C.S., 1935, 465—467).—22-Dihydroneoergosterol (I), m.p. 141—143° (lit. 140°), from neoergosterol (II) in Et_2O or its acetate in COMe_2 and H_2 -Pd-black, and its 3:5-dinitrobenzoate, m.p. 216—218°, do not depress the m.p. of (II) and its ester, respectively. (I) with KHSO_4 gives *neorgostatetraene* (III), m.p. 63—64°, depressed by neorgostatatriene (IV) but not by neorgostapentaene (V), but with P_2O_5 a *dimeride*, $\text{C}_{54}\text{H}_{80}$, m.p. 187—190°. Dehydrogenation of (III) gives a mixture and $\text{Na-C}_5\text{H}_{11}\text{OH}$ does not effect reduction. (II) and BzO_2H give a product, hydrolysed to *neorgosta-3:22:23-triol*, m.p. 202—204°. Absorption spectra of (III) and (V) are very similar, but differ from that of (IV), indicating that the fifth ethylenic linking of (V) is in the side-chain and that the fourth of (III) and (V) is in ring I conjugated with an aromatic ring II, and thus supporting the allocation of the nuclear ethylenic linkings of ergosterol to ring II.

R. S. C.

Organic compounds of sulphur. XXV. Interaction between organic azides and aromatic thioketones and a new method of converting the azido-group into the amino-group. A. SCHONBERG and W. URBAN (J.C.S., 1935, 530—532).— RN_3 and $\text{CR}'_2\text{S}$ [$\text{R}=\text{Ph}$, $\alpha\text{-C}_6\text{H}_4$, CH_2Ph , SO_2Ph ; $\text{R}'_2=\text{Ph}_2$, $pp'\text{-(C}_6\text{H}_4\text{OMe)}_2$, $\text{C}_6\text{H}_4\text{OC}_6\text{H}_4$] heated together in N_2 give $\text{RN:CR}'_2$, whence the amine can be obtained. *Benzenesulphonimidoxanthen*, m.p. 165—166°, is described. PhN_3 does not react with CPh_2O .

F. R. G.

Activity of mixed catalysts in the simultaneous dehydration of (I) ethyl alcohol and ammonia, (II) ethyl alcohol and aniline. Catalytic preparation of ethylaniline. I. I. SCHUJKIN and A. A. BALANDIN (J. Gen. Chem. Russ., 1934, 4, 1444—1450, 1451—1457).—I. [With Z. I. Plotkin.] The yield of amines obtained by passing EtOH-NH_3 over various catalysts at 300—400° diminishes in the order $\text{Al}_2\text{O}_3=10:1$, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (I) $>$ $\text{Al}_2\text{O}_3\text{-ZnO}$ $>$ $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ $>$ $\text{Al}_2\text{O}_3\text{-SnO}$. Production of gaseous by-products is least with (I). The reactions involved are explained on the basis of the multiplet theory.

II. [With F. T. Dmov.] The yields of NHPhEt and NPhEt_2 are greater when Al_2O_3 alone is used as

catalyst (350°) than when it contains 5—20% of Fe_2O_3 , SnO , Cr_2O_3 , NiO , or ZnO .

R. T.

Electrolytic reduction of imido-ethers. H. WENKER (J. Amer. Chem. Soc., 1935, 57, 772).—By electrolytic reduction in $2N\text{-H}_2\text{SO}_4$ at 0° of the corresponding imido-ethers are prepared $\text{NH}_2\text{CH}_2\text{Ph}$ (76%), *m*- (76%) and *p*- $\text{C}_6\text{H}_4\text{Me-NHPh}$ (94%), NH_2Et (16%), $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (14%), and *p*-ethoxybenzylamine (66% yield) (*picrate*, m.p. 191°; *hydrochloride*, m.p. 234°).

R. S. C.

Preparation of *N*-substituted sulphon-*m*- and -*p*-toluidides. G. H. YOUNG (J. Amer. Chem. Soc., 1935, 57, 773; cf. this vol., 206).—*p*-Toluenesulphon-*N*-methyl-, m.p. 63°, -ethyl-, m.p. 60.5—61°, -*n*-propyl-, m.p. 51°, and -isoamyl-*m*-toluidide, m.p. 76.5° (80—98% yields), and *p*-toluenesulphon-*N*-isopropyl-, m.p. 107°, -isobutyl-, m.p. 73°, -*n*-amyl-, m.p. 59.5—60°, and -isoamyl-*p*-toluidide, m.p. 89.5—90° (60—91% yields), are prepared.

R. S. C.

General method of synthesis of the *N*-disubstituted aminoethylenes, CR:CR'NR''Ar . J. HOCH (Compt. rend., 1935, 200, 938—940).— CPhMe(OEt)_2 heated with NHPhMe forms $\alpha\text{-N-methylanilinostyrene}$, b.p. 161—162°/13 mm., which is reduced catalytically to CHPhMe:NPhMe , and hydrolysed (HCl) to COPhMe and NHPhMe . The following are similarly obtained: $\alpha\text{-N-ethylanilino-}$, b.p. 167°/12 mm., $\alpha\text{-N-methyl-p-toluidino-}$, b.p. 167°/10 mm., and $\alpha\text{-N-methyl-p-anisidino-}$, b.p. 185°/10 mm., -styrene; $\alpha\text{-N-methylanilino-}$, b.p. 170—171°/12 mm., $\alpha\text{-N-ethylanilino-}$, b.p. 175°/10 mm., $\alpha\text{-N-methyl-p-toluidino-}$, b.p. 181°/12 mm., and $\alpha\text{-N-methyl-p-anisidino-}$, b.p. 192—194°/9 mm., -*p*-methylstyrene; $\alpha\text{-N-methylanilino-p-methoxystyrene}$, m.p. 55°, b.p. 190—200°/12 mm. (decomp.), $\alpha\text{-N-methylanilino-}$, m.p. 82°, b.p. 230°/10 mm., and $\alpha\text{-N-methyl-p-toluidino-}$, m.p. 76°, b.p. 232°/10 mm., -stilbene; $\gamma\text{-N-methylanilino-}$, b.p. 129—131°/12 mm., and $\gamma\text{-N-methyl-p-anisidino-}$, b.p. 166—167°/17 mm., - Δ^7 -heptene; *N*-methylanilino-, b.p. 140/13 mm., *N*-ethylanilino-, b.p. 152—153°/15 mm., and *N*-methyl-*p*-toluidino-, b.p. 150°/10 mm., - Δ^1 -cyclohexene; and -methylanilino-, b.p. 205°/16 mm., and $\beta\text{-N-methyl-toluidino-}$, m.p. 69°, b.n. 207—208°/12 mm., -styrene.

E. W. W.

Tetrazotisation of aryl diamines with special reference to *o*-phenylenediamine. H. H. HODGSON and J. WALKER (J.C.S., 1935, 530; cf. Schoutissen, A., 1934, 67).—1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$, and *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in AcOH with $\text{NO}\cdot\text{SO}_3\text{H}$ (cf. *ibid.*, 181) give, without secondary reactions, tetrazo-solutions which with Cu_2Cl_2 (Sandmeyer) yield 70% of the theoretical amounts of the Cl_2 -derivatives.

F. R.

Stereochemistry of diphenyls. XXXIX. Synthesis of active 2:6-dibromo-3:3'-diamino-4:4'-ditolyl. W. I. PATTERSON and R. ADAMS (J. Amer. Chem. Soc., 1935, 57, 762—764; cf. A., 193, 1351).—A Ph_2 derivative, substituted in the 2:6- but not in the 2':6'-positions, is resolved. 2-Nitro-*p*-toluidine [prep. in 70% yield from 2:4- $\text{C}_6\text{H}_4\text{Me}(\text{NO}_2)_2$ and $\text{NH}_4\text{HS-EtOH}$] gives (diazo-reaction; 75% yield) 4-iodo-2-nitrotoluene, whic

with Cu in hot PhNO_2 gives 3:3'-dinitro-4:4'-ditolyl (39% yield), reduced by NaHS-EtOH to 3-nitro-4:4'-ditolyl (60% yield), m.p. 108–109° (*Ac* derivative, m.p. 193.5°). This with Br-AcOH affords 2:6-dibromo-3'-nitro-3-amino-4:4'-ditolyl, m.p. 139° (70% yield) (*Ac* derivative, m.p. 145.5–146°), oxidised by $\text{CrO}_3\text{-AcOH}$ to 2-nitro-*p*-toluic acid and reduced by Zn dust and AcOH to 2:6-dibromo-3:3'-diamino-4:4'-ditolyl, m.p. 174–175°, which is resolved by *d*-camphorsulphonic acid to the *d*-amine, m.p. 174–175° (probably racemisation occurs before melting), $[\alpha]_D^{25}$ about +0.78° in COMe_2 (slowly racemises in solution; half-life period, $P=70.2$ min.) (*d*-camphorsulphonate, m.p. 170–180°, $[\alpha]_D^{25}$ about +16° \rightarrow about +0.06° in EtOH ; $P=\text{about } 1230$ min.), and impure *l*-amine (impure *d*-camphorsulphonate, $[\alpha]_D^{20} -15.5^\circ \rightarrow [\alpha]_D^{25} -6.5^\circ$ in MeOH in 50 hr.). R. S. C.

Course of the reaction between magnesium organic compounds and hydroxyazo derivatives.

A. TAURINŠ (Acta Univ. Latviensis, Kim. Fak. Serija, 1934, 2, 321–338).—Mg alkyl halides afford cryst. ppts. with azophenols; the following such compounds are described: $\text{X, PhN:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot 2\text{Et}_2\text{O}$ (I) ($\text{X}=\text{CH}_2\text{Ph}\cdot\text{MgCl}$, MgEtBr , MgPhBr , MgMeI , MgPhI), $2\text{X, PhN:N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\alpha)\cdot n\text{Et}_2\text{O}$ (II), $\text{X, OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot n\text{Et}_2\text{O}$. (I) with H_2O regenerates the parent azo-compound; it is concluded that it is not an intermediate in the formation of the hydrazo-compound. Similar compounds, $\text{MgPh}_2\cdot 2\text{PhN:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot n\text{Et}_2\text{O}$ (III) and $\text{MgPh}_2\cdot \text{PhN:N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\alpha)\cdot n\text{Et}_2\text{O}$ (IV) are obtained with MgPh_2 , as also with Mg halides, which afford the compounds $2\text{MgBr}_2\cdot 3\text{PhN:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, $\text{MgI}_2\cdot 2\text{PhN:N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ and $2\text{MgBr}_2\cdot 3\text{PhN:N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\alpha)$. (I) may be obtained using instead of MgRHal a mixture of MgR_2 and MgHal_2 . (III) with MgHal_2 affords (I), and (IV) similarly yields (II). BeCl_2 can replace MgHal_2 in these reactions. CH. ABS. (r)

Preparation of hydrazobenzene. C. L. TSENG and F. M. FAN (Sci. Quart. Nat. Univ. Peking, 1935, 5, 350–357).—With Zn dust, < the stoichiometric proportion of NaOH is required to reduce PhNO_2 to $(\text{NHPh})_2$ (I). 80% of the theoretical yield of (I) was obtained by adding, with shaking, during 30 min., Zn dust (40 g.) to a mixture of NaOH (5.5 g.), H_2O (40 c.c.), PhNO_2 (20 g.), and 95% EtOH (80 c.c.) at 80–85° under a reflux. The reaction was completed at 87–90°, and 50% aq. EtOH (180 c.c.) was added before filtering at the b.p. J. G. A. G.

***m*-Nitrobenzohydrazides, 2:4-dinitrophenylhydrazones; separation of hydrazones by adsorption.** H. H. STRAIN (J. Amer. Chem. Soc., 1935, 57, 758–761).—Hydrazones may be purified and mixtures thereof often separated by adsorption on various neutral substances. The following are described: (a) *m*-nitrobenzohydrazides of COMe_2 , m.p. 147.5–149°, COMePh , m.p. 190–191°, CH_3Ac_2 , m.p. 119–121°, acetaldehyde, m.p. 169.5–171.5°, *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 194.5–196°, benzil, m.p. 232.5–235.5°, $\text{Pr}\cdot\text{CHO}$, m.p. 135.5–137°, carvone, m.p. 162–163°, $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, m.p. 206–207.5°, citral (commercial) (I), m.p. 100–101°, crotonalde-

hyde, m.p. 172.5–173.5°, β -cyclocitral (II), m.p. 184.5°, cyclohexanone, m.p. 140.5–141.5°, cyclopentanone (III), m.p. 148.5–149.5°, Ac_2 (dihydrazone) (IV), m.p. 320–321°, dicarvelone (mixture; dihydrazone), m.p. 95–100°, *p*-NMe $_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (V), +0.5 PhNO_2 , m.p. 219.5–221°, furfuraldehyde, m.p. 195–197°, glyoxal (dihydrazone) (VI), m.p. 339.5–340.5°, $\text{C}_6\text{H}_{13}\cdot\text{CHO}$, m.p. 108.5–110.5°, α - (VII), m.p. 149.5–150.5°, and β -ionone (VIII), m.p. 161–162.5°, $\text{Pr}^n\cdot\text{CHO}$, m.p. 141.5–142.5°, lævulic acid (IX), m.p. 181.5–182.5°, lævulaldehyde (dihydrazone) (X), m.p. 155.5–156°, menthone, m.p. 105–107°, mesityl oxide, m.p. 120–140°, 2-methylcyclohexanone (XI), m.p. 115.5–118°, methylheptenone, m.p. 99–100°, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$, m.p. 193–194°, *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 253–255°, nonaldehyde, m.p. 87°, piperonal, m.p. 229–230.5°, EtCHO , m.p. 156.5–158.5°, AcCO_2H (XII), m.p. 185.5–186.5°, AcCHO (dihydrazone) (XIII), m.p. 288.5°, thujone (XIV), m.p. 156–156.3°, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ (XV), m.p. 189–190.5°, 2:4:6-(NO_2) $_3\text{C}_6\text{H}_2\cdot\text{CHO}$, m.p. 238–239° (decomp.), vanillin, m.p. 213–215°, and veratraldehyde (XVI), m.p. 225.5–227.5°; (b) 2:4-dinitrophenylhydrazones of MeCHO , m.p. 163.5–164.5°, $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$, m.p. 96°, acetol, m.p. 127.5–129.5°, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_7\cdot\text{CHO}$, m.p. 114–115°, (I), m.p. 99–115°, (II), m.p. 171–172°, (III), m.p. 145.5–146.5°, (IV), m.p. 314–315°, (V), m.p. 324.5–326° (decomp.), geronic acid, m.p. 135.5–137°, (VI), m.p. 326–328°, (VII), m.p. 147.5–149.5°, (VIII), m.p. 128–129°, isogeronic acid, m.p. 140–141°, (IX), m.p. 206°, Et , m.p. 101–102°, Me , m.p. 141.5–142.5°, Pr^n , m.p. 67–68°, and Pr^n lævulate, m.p. 88–89°, (X), m.p. 235.5–236.5°, (XI), m.p. 135.5–137°, $\text{C}_8\text{H}_{17}\cdot\text{CHO}$, m.p. 100°, (XII), m.p. 218°, Et , m.p. 154.5–155°, Me , m.p. 186.5–187.5°, Pr^n , m.p. 119–120°, and Pr^n pyruvate, m.p. 160.5–161.5°, (XIII), m.p. 299–300°, (XIV), m.p. 106–107.5°, (XV), m.p. 232.5–234.5°, and (XVI), m.p. 261–263°. *m*-Nitrobenzohydrazide is stable in H_2O , but in acid slowly gives *NN'*-bis-*m*-nitrobenzohydrazide, m.p. 240–242°. 2:4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ is decomposed by alkalis, giving with hot Na_2CO_3 a substance, exploding at 190–192°, and with hot 6*N*- NaOH a substance, m.p. 145.5–147.5°; with a little AcOH in $\text{H}_2\text{SO}_4\text{-EtOH}$ it gives the *Ac* derivative, m.p. 201°. Pinacol gives the 2:4-dinitrophenylhydrazone of pinacolone. M.p. are corr. R. S. C.

Character of the diazonium group. Preparation of disazo-dyes from *m*-phenylenediamine.

H. A. J. SCHOUTISSEN (Rec. trav. chim., 1935, 54, 381–386).—Tetrazotised *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in conc. HCl couples with one mol. of a phenol, including β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ (I), PhOH , 2:6- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$, 1:8:3:6- $\text{NH}_2\cdot\text{C}_{10}\text{H}_4(\text{OH})(\text{SO}_3\text{H})_2$, α - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, and *o*-cresol, to give cryst. azo-diazo-compounds which couple with phenols in alkaline solution to give benzene-1:3-disazo- β -naphthol, m.p. 251°, -1:3-disazophenol, m.p. 216°, -1-azophenol-3-azo- β -naphthol, m.p. 230°, 1-azo- β -naphthol-3-azo- β -naphthol-6'-sulphonic acid (*Na* salt), and -1-azo- β -naphthol-3-azo-(1':8'-aminonaphthol-3':6'-disulphonic acid). Coupling with *p*-cresol or PhOMe does not give cryst. compounds. (I) with

KI in 2*N*-H₂SO₄ gives *m*-iodobenzenediazo- β -naphthol, m.p. 185—186°. The coupling in acid solution is attributed to the influence of the strongly negative character of a diazonium group on a diazo-group, the tetrazotised compound being given the structure N \equiv N(X)-C₆H₄-N \equiv NX in acid solution. F. R. G.

Thermal decomposition of γ -phenoxy- α -oxido- β -methylbutyric acid. B. ROTHSTEIN (Bull. Soc. chim., 1935, [v], 2, 653—656).—Condensation of CH₃Cl·CO₂Et with CH₃Ac·OPh in presence of NaOEt at < 0° affords a 73% yield of *Et* γ -phenoxy- α -oxido- β -methylbutyrate, b.p. 175—178°/15 mm., hydrolysed by KOH-EtOH to the corresponding acid (I), m.p. 73·5—74° (block) (*K* salt). Thermal decomp. of (I) at 160—180°/13 mm. occurs thus: (I) \rightarrow CO₂ + [OPh·CH₂·CHMe·CHO] \rightarrow PhOH + CH₂:CMe·CHO.

J. W. B.

Organic reactions with boron fluoride. IX. Alkylation of phenol with alcohols. F. J. SOWA, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 709—711; cf. this vol., 195).—PhOH·BF₃ (21%) with MeOH or EtOH at 170° (3 hr.) gives PhOMe (58%) or PhOEt (17%), respectively. PrⁿOH and PrⁱOH give 2 : 4-C₆H₃Prⁿ·OPrⁿ (11 and 13%), *o*- (28 and 32%) and *p*-C₆H₄Prⁿ·OH (20 and 16%, respectively). Reaction thus occurs by preliminary dehydration to C₃H₆ and not by direct condensation.

R. S. C.

Sulphonating action of sulphuric acid in aqueous and acetic solutions.—See this vol., 710.

Molecular compounds of phenols. G. T. MORGAN and A. E. J. PETTET (J.S.C.I., 1935, 54, 22—24r).—By f.p. determinations of mixtures of the two components, the following mol. compounds of phenol homologues were shown to be formed (molecular proportions and m.p. in parentheses): (a) with cineole: *m*-2- (1 : 1; m.p. 12·0°), *m*-4- (2 mols. xylenol, m.p. 37·9°), *m*-5- (1 : 1, m.p. -0·1), and *p*-xylenol (1 : 1, m.p. 26·8°); *o*- (1 : 1, m.p. 4·4°) and *p*-ethylphenol (1 : 1, m.p. -4·1°); 2-methyl-4- (2 mols. phenol, m.p. 4·1°) and 2-methyl-6-ethylphenol (1 : 1, m.p. -23·1°). (b) With *m*-5-xylylene: phenol (1 : 1, m.p. 9·2°); *o*- (1 : 1, m.p. 48·3°), *m*- (1 : 1, m.p. 4·9°); 2 mols. cresol, m.p. 10·1°, and *p*-cresol (2 mols. cresol, m.p. 20·2°); *m*-2- (1 : 1, m.p. 21·9°), *m*-4- (1 : 1, m.p. 36·3°), *m*-5- (1 : 1, m.p. 36·3°), and *p*-xylenol (1 : 1, m.p. 65·1°); *o*- (1 : 1, m.p. 30·0°) and *p*-ethylphenol (2 mols. phenol, m.p. 13·9°); 2- (1 : 1, m.p. 27·4°) and 3-methyl-4-ethylphenol (1 : 1, m.p. 23·5°); 2 mols. phenol m.p. 22·9°; 3-methyl-6- (1 : 1, m.p. 43·1°) and 4-methyl-2-ethylphenol (1 : 1, m.p. 33·0°). (c) With 3 : 5 : 3' : 5'-dixylylamine: *o*- (1 : 1, m.p. 16·1°), *m*- (2 mols. base, m.p. 31·5°), and *p*-cresol (1 : 1, m.p. 21·7°). Indications of metastable compounds were obtained between *o*-4-xylenol-cineole (2 : 1) and *o*-4-xylenol-*m*-5-xylylene (2 : 1). No combination could be detected between cineole and 3-methyl-4-, 3-methyl-6-, or 4-methyl-3-ethylphenol.

Synthesis of carvacrol. D. GARDNER, M. PROCOFFER, G. JUSOV, and M. L. CASELLI (Compt. rend., 1935, 200, 1114—1115).—Pure carvacrol, b.p. 236°, m.p. 0·5°, is obtained from *p*-cymene through the NO₂, NH₂, and diazo-compounds. It is also obtained by

the interaction of *o*-cresol and PrⁿOH in presence of P₂O₅. It can be converted into a carboxylic acid by CO₂ without pressure.

F. N. W.

4-Chloro-2-nitro- and -2-amino-phenol. M. MOTTIER (Arch. Sci. phys. nat., 1934, [v], 16, 301—303).—The prep. of these substances from *p*-C₆H₄Cl·OH is modified to give 65 and 53·6% yields, m.p. 86—87° and 137·5—138·5°, respectively.

R. S. C.

Methyl-*p*-aminophenol. N. I. KIRILLOV (Photo-Kino Ind., 1933, 70—80).—The prep. of *p*-methylaminophenol by condensation of *p*-aminophenol (I) and PhCHO and by methylation of (I) hydrochloride with MeOH is described, the first process being used technically.

CH. ABS. (r)

Preparation of phenacetin from phenol in laboratory practice. S. VLADUTA (Curierul Farm., 1934, 4, No. 5, 16—20; No. 6, 1—10; No. 7, 1—17; Chem. Zentr., 1934, ii, 3611).—The available methods are discussed. The best yield of *p*-nitrophenol (I) is obtained from PhOH and HNO₃ (*d* 1·09) at 15—25°. Reduction of (I) is best carried out with Zn dust or NaHSO₃.

H. N. R.

Preparation of 1-alkyl- β -naphthols. K. DZIEWOŃSKI and C. DRAGAN [with C. MARCHOVNA] (Bull. Acad. Polonaise, 1934, A, 398—401).— β -C₁₀H₇·OH, dry NPhMe, or NPhEt₂, and a trace of β -C₁₀H₇·ONa at 300° (autoclave) give 55—60% yields of 1-methyl-, m.p. 101° (*picrate*, m.p. 163—164°), and 1-ethyl- β -naphthol, m.p. 105° (*Bz* derivative, m.p. 75°), with a little alkali-insol. substance (not an *O*-alkyl compound).

R. S. C.

Action of hydroxylamine on certain naphthalene derivatives. S. V. BOGDANOV and I. I. LEVKOEY (J. Gen. Chem. Russ., 1934, 4, 1353—1358; cf. A., 1933, 389).—NH₂ 2-nitroso- α -naphthol-4-sulphonate is obtained from aq. NH₂OH, HCl and 1-amino- β -, 2-amino- α -, or 1-nitroso- β -naphthol-4-sulphonic acid; the corresponding 5-sulphonate is obtained analogously from 2-amino- α -naphthol- or 1-2-naphthylenediamine-5-sulphonic acid. The mechanism of the reactions involved is discussed.

R. T.

Substituted phenyldihydroresorcinols. L. E. HINKEL, E. E. AYLING, and J. F. J. DIPPY (J.C.S., 1935, 539—540).—*o*-Chlorobenzylideneacetone (modified prep.), m.p. 24·5° (lit., an oil), b.p. 160—163°/17 mm., CH₂(CO₂Et)₂, and NaOEt at 100° give 5-*o*-chlorophenyldihydroresorcinol, m.p. 149° (decomp.). The 5-*o*-, m.p. 145°, and -*p*-OMe-compounds, m.p. 175° (decomp.), are similarly prepared.

R. S. C.

Catalytic reduction of substituted ω -nitrostyrenes. B. REICHERT and W. KOCH (Arch. Pharm., 1935, 273, 265—274).—Good yields (90%) of CH₃·Ar·CH·NOH are obtained by reduction of CHAr·CH·NO₂ with Pd-C-H₂ in C₅H₅N, and thus are obtained β -*o*-, -*p*-, -2 : 4- (I), and -3 : 4-dimethoxy- and -3 : 4-methylenedioxy-phenylacetaldoxime. (I) is converted by Ac₂O into 2 : 4-dimethoxyphenylacetone nitrile, m.p. 75°, hydrolysed to the known acid. Reduction of (I) in H₂C₂O₄-EtOH with H₂-PtO₂ at room temp. affords the oxalate + 0·5H₂O (II), m.p. 155°, of β -2 : 4-dimethoxyphenylethylamine (*Bz* derivative, m.p. 115°), and the oxalate, m.p.

170°, of di-(β -2:4-dimethoxyphenylethyl)hydroxylamine, m.p. 128° (hydrochloride, m.p. 151°), reduced (Sn-HCl-aq. EtOH) to di-(β -2:4-dimethoxyphenylethyl)amine, isolated as its *H* oxalate, m.p. 203° [also by direct reduction of (I)]. With NaNO_2 (II) gives β -2:4-dimethoxyphenylethyl alcohol, m.p. 67°. By similar methods are obtained the *H* oxalate, m.p. 180°, of β -o-anisylethylamine, and the oxalate, m.p. 137°, of di-(β -o-anisylethyl)hydroxylamine.

J. W. B.

Highly-polymerised compounds. CIX. Viscosity of polyphenyl ethers. H. STAUDINGER and F. STAIGER (Annalen, 1935, 517, 67—72).—Determinations of the viscosity of polyphenyl ethers in CCl_4 and C_6H_6 at 20° and 60° and in CHCl_3 at 20°, 40°, and 60° show that η_{sp} varies with temp. in the manner observed with other compounds of low mol. wt. In C_6H_6 and CHCl_3 the increments for a Ph group are greater for the simple than for the more complex products, whereas in CCl_4 they remain const. In CCl_4 and in C_6H_6 for the substances rich in Ph the increment is 3.0×10^{-3} , which is approx. the val. found for simple aromatic compounds. The viscosity increases regularly with successive addition of OPh to the ether mol. The following compounds have been employed: Ph_2O ; quinol Ph_2 ether (I), m.p. 77°; *pp'*-diphenoxydiphenyl ether (II) m.p. 110°; quinol *pp'*-diphenoxydiphenyl ether, m.p. 151°, prep. by converting (I) into the corresponding Br_2 -compound, m.p. 131°, which is treated according to Allmann *et al.* (A., 1907, i, 35); *pp'*-diphenoxydiphenoxydiphenyl ether ($\text{OPh} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4)_2\text{O}$, m.p. 173°, obtained similarly from the Br_2 -compound, m.p. 162°, of (II). Quinol is quantitatively converted by H_2 at 200°/150 atm. in EtOH in presence of Ni into *cis*-quinol, m.p. 103—104°. The corresponding dibromide is transformed by NaOPh in PhOH containing Cu powder into *Ph* Δ^3 -cyclohexenyl ether (III) and by cyclohexanol into cyclohexyl Δ^3 -cyclohexenyl ether (IV). In 1.4% solution in CCl_4 , Ph_2O , CH_2Ph_2 , (III), and (IV) have the same η_{sp} within the limits of experimental error; measurements are recorded at 20°, 40°, and 60°.

H. W.

Configuration of alicyclic alcohols. II. Configuration and cryoscopic behaviour of alcohols. W. HUCKEL, K. KUMETAT, and W. PREUSS [with, in part, SEVERIN, J. YANTSCHULEVITSCH, B. SCHWERIN, MÜLLER-LOTZ, and (FRLN.) H. KASCZEMEK] (Annalen, 1935, 517, 229—244; cf. this vol., 340).—The *cis*-forms of alicyclic alcohols, *e.g.*, the 2-alkylcyclohexanols, have usually higher d and n_D , but lower $[M]_D$ and η , than the *trans*-forms. The former are also less associated (cryoscopic determination) in solvents, particularly in cyclohexane and C_6H_6 , and the apparent mol. wt. increases more slowly with increasing concn. This is probably due to steric "protection" of the OH, since α -decalols are less associated than their β -isomerides, but more than the 9-decalols. This explanation is in line with the lower rate of hydrolysis of esters of the *cis*- and α -isomerides. The 9-decalols, m.p. 54° and 65°, are thus shown to be the *trans*- and *cis*-forms, respectively. Other factors, at present not understood, are, however, also concerned; thus, *e.g.*, *trans*-2-cyclohexyl-

cyclohexanol shows a much more rapid increase in mol. wt. with concn. than the *cis*-isomeride (curves cross at 0.4 mol.-%) or than *tert*-1-cyclohexylcyclohexanol (curves cross at 0.8 mol.-%) in cyclohexanol. The following data appear to be new: *cis*- α -hydrindanol (prep. by Na-EtOH), an oil (H phthalate, m.p. 140°), and an isomeride [prep. by catalytic hydrogenation (A)], m.p. 18° (H phthalate, m.p. 127°): *cis*-4-hydroxyhydrindane [prep. by (A)], dimorphic (H phthalate, m.p. 134°); 1-ethylcyclopentan-1-ol (from cyclopentanone and MgEtBr), m.p. -8°, b.p. 155—157°/760 mm., 61°/17 mm.

R. S. C.

Products of the transformation of acetylenic carbinols. Constitution of the compounds derived from phenylethylmethylethinylcarbinol. H. RUPE and H. WERDENBERG (Helv. Chim. Acta, 1935, 18, 542—546).—The ketone, b.p. 140—140.5°/9 mm. (semicarbazone, m.p. 182°), obtained by Rupe *et al.* (A., 1931, 1050) by the action of HCO_2H on $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{C} \equiv \text{CH}$ is converted by O_3 in CCl_4 into $\text{CH}_2\text{Ph} \cdot \text{COMe}$, AcOH , and BzOH and is therefore α -phenyl- β -methyl- Δ^3 -penten-8-one. The aldehyde obtained simultaneously (*loc. cit.*) when ozonised gives $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{COMe}$ and HCO_2H and hence is 8-phenyl- β -methyl- Δ^3 -pentenal (I). (I) polymerises and resinifies very readily. It condenses with COMe_2 to a product (semicarbazone $\text{C}_{16}\text{H}_{21}\text{ON}$, m.p. 164°).

H. W.

[Law of periodicity and the conjugated system.] P. PETRENKO-KRITSCHENKO (Ber., 1935, 68, [B], 618; cf. A., 1934, 1000).—A reply to Hantzsch *et al.* (this vol., 487).

H. W.

Condensation of cholesteryl chloroformate with alcohols and phenols. E. SCHADENDORFF and A. VERDINO (Monatsh., 1934, 65, 338—347).—By condensation in Et_2O or C_6H_6 of cholesteryl chloroformate with the appropriate OH-compound in presence of $\text{C}_6\text{H}_5\text{N}$, NHPH_2 , or Na, dicholesteryl carbonate, m.p. 176°, and the following are obtained: *Et*, m.p. 83°, *Ph*, m.p. 123°, *m*-, m.p. 116°, and *p*-tolyl, m.p. 122°, sinters 115°, *m*-, m.p. 134°, and *p*-nitrophenyl, m.p. 162°, *o*-carbomethoxyphenyl, m.p. 130—131°, *o*-carbophenoxyphenyl, m.p. 150—151°, 2:4:6-tribromophenyl, m.p. 111°, *p*-aldehydophenyl, m.p. 129°, α -, m.p. 166°, and β -naphthyl, m.p. 173°, sinters 164°, 4-benzeneazophenyl, m.p. 166°, *p*-(cholesterylcarbonyl)phenyl, m.p. 215°, cholesteryl-carbonates; *o*-, m.p. 160—161°, *m*-, m.p. 216°, sinters 213°, and *p*-, m.p. 234°, sinters 215°, -phenylene dicholesteryl dicarbonate; pyrogallol, m.p. 213°, sinters 180°, and phloroglucinol, m.p. 143°, tricholesteryl tricarbonate. Many of the esters form liquid crystals.

F. R. G.

Condensation products from alcohols and phenols.—See B., 1935, 443.

cycloHexadienes. N. D. ZELINSKI, J. I. DENISENKO, and M. S. EVENTOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 313—320).—*cis*-cycloHexane-1:4-diol and freshly heated MgSO_4 on warming (4—5 hr.) afford $\Delta^{1:3}$ (I), b.p. 80.5—80.7°/752 mm. (cf. lit.), and $\Delta^{1:4}$ (II), b.p. 88.8—89.2°/758 mm. (cf. lit.), -cyclohexadiene in the proportion 8:1. CO_2 is passed through the mixture during the progress of the re-

action and removes the products, which are then condensed. When KHSO_4 is used (I) and (II) are formed in the proportion 1 : 2. (I) and (II) are separated by fractional distillation from BaO . With $\text{EtOH-H}_2\text{SO}_4$ (I) gives a dark blue-violet coloration, whilst (II) gives a pink and faintly blue-violet coloration. Oxidation of (I) with 1% aq. KMnO_4 below 0° gives 1 : 2 : 3 : 4-tetrahydroxycyclohexane, m.p. $153-154^\circ$, which has a sweet taste. Similarly (II) affords 1 : 2 : 4 : 5-tetrahydroxycyclohexane, m.p. $239-240^\circ$ (cf. A., 1931, 945).

H. G. M.

Constitution of Δ^3 -cyclohexene-1 : 2-diol; some $\alpha\beta$ -derivatives of adipic acid. P. BEDOS and A. RUYER (Compt. rend., 1935, 200, 944-946).—The Δ^3 -structure for this diol (cf. A., 1933, 500) is confirmed by oxidation (Thiele method) of its dibromide to $\alpha\beta$ -dibromoadipic acid, m.p. 143° , which is hydrolysed to the $(\text{OH})_2$ -acid (not isolated), and reduced to a Δ^1 -butylene- $\alpha\delta$ -dicarboxylic acid, (I), m.p. 210° , stereoisomeric with $\Delta^{\alpha\beta}$ -dihydromuconic acid. (I) is reduced quantitatively to adipic acid, and oxidised to oxalic and succinic acids.

E. W. W.

Condensation of 2 : 6-dimethylol-*p*-cresol with esters of higher fatty acids. T. P. HILDITCH and C. J. SMITH (J.S.C.I., 1935, 54, 111-115t).—When 2 : 6-dimethylol-*p*-cresol (I) and a simple (Me) ester of a saturated (palmitic) or monoethylenic (oleic) acid are heated together at 240° , a certain amount of displacement of the Me by the phenolic alcohol group takes place, but no other action of condensation between the phenolic alcohol and the aliphatic ester. With polyethenoid esters, condensation at the unsaturated centres proceeds to a considerable extent, especially in the case of elaeostearic esters. No condensation occurs when (I) and aliphatic paraffins are heated together at 240° . The interaction with linseed oil (II) or tung oil (III) is determined by the nature of the component fatty acids of these oils. In the case of (III) it proceeds far towards completion. Boiled (II) appears to interact more readily than raw (II). The mixed linoleo-linolenoglycerides of (II) enter most readily into condensation, and saturated or oleic radicals do not commence to pass into the petrol-insol. resin product until condensation has taken place to a marked extent.

Inositolphosphoric acid compounds. III. Compounds of ferric inositolphosphate with the sodium and potassium salts of certain hydroxyacids. S. OTOLSKI (Rocz. Chem., 1935, 15, 99-104).— Fe_3 inositolphosphate yields a 1 : 3-compound ($+15\text{H}_2\text{O}$) with $(\text{NH}_4)_3$ citrate, a 1 : 5-compound ($+10\text{H}_2\text{O}$) with K_3 citrate, a 1 : 6-compound ($+10\text{H}_2\text{O}$) with $(\text{NH}_4)_2$ malate, and a 1 : 8-compound ($+16\text{H}_2\text{O}$) with K_2 malate. The salts are readily sol. in H_2O .

R. T.

Bromination of substances containing two aromatic nuclei. I. Bromination of tolyl and nitrophenyl benzoates. G. V. JADHAV and Y. I. RANGWALA (J. Indian Chem. Soc., 1935, 12, 89-92).—With Br and HNO_3 (d 1.45) on a water-bath the Bz derivatives of *o*-, *m*-, and *p*-cresol afford, respectively, 4-bromo-*o*-, 4-bromo-*m*-, and 2-bromo-*p*-tolyl benzoate, m.p. $< 0^\circ$, identical with synthetic specimens. On similar treatment of *o*-, *m*-, and *p*-nitrophenyl benzo-

ate, Br enters the benzoic nucleus to give, respectively, *o*-, m.p. 105° , *m*-, m.p. 132° , and *p*-nitrophenyl *m*-bromobenzoate, m.p. 122° , converted by further bromination into *o*-, m.p. 132° , *m*-, m.p. 165° , and *p*-nitrophenyl 2 : 5-dibromobenzoate, m.p. $183-184^\circ$, respectively.

J. W. B.

5-Bromo-2 : 4-dimethylbenzoic acid. Nuclear halogenation with alkaline hypohalite solution. C. H. FISHER and M. GRANT (J. Amer. Chem. Soc., 1935, 57, 718-719).— NaOBr gives good yields of the derived benzoic acid from $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, benzoin, deoxybenzoin, CH_2PhCl , CH_2PhBr , *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Cl}$, *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Br}$, and *m*- $\text{C}_6\text{H}_4\text{Ac}\cdot\text{NO}_2$. Since the speed of conversion of the benzyl halides into benzoic acids is approx. \propto the rate of hydrolysis of the former, it is believed that hydrolysis of the halomethyl group precedes oxidation. Two Me groups, however, cause halogenation of the Ph nucleus. Thus, 5-bromo-2 : 4-dimethylbenzoic acid (I), m.p. $180-181^\circ$ (amide, m.p. $197.5-198.5^\circ$), also obtained from *o*-bromo-2 : 4-dimethylbenzonitrile, m.p. $88-89^\circ$, is formed from 2 : 4-dimethylacetophenone (II) (cf. Perkin *et al.*, A., 1926, 64), -phenacyl chloride, -benzoic or -mandelic acid, 5-bromo-*p*-cumene and HNO_3 give a different acid, m.p. $172-173^\circ$, previously considered to be (I). β -isodurylic acid gives (NaOBr) 3-bromo-2 : 4 : 6-trimethylbenzoic acid, and (II) and NaOCl give an acid, m.p. $164-165.6^\circ$, probably 5-chloro-2 : 4-dimethylbenzoic acid.

R. S. C.

Metabolism of norleucine, isoleucine, and valine. I. Synthesis of some phenyl derivatives. H. E. CARTER (J. Biol. Chem., 1935, 108, 619-632).—Series of phenylated NH_2 -acids and fatty acids were made for the purpose of studying their behaviour in animal metabolism. α -Amino- β -phenylhexoic and - β -methyl- γ -phenylbutyric acid, m.p. $235-245^\circ$, were synthesised by the method of Braun (A., 1912, i, 265) modified by replacing Br by NH_2 before decarboxylation. *Et* α -carbethoxy- γ -phenyl- β -ethylbutyrate, b.p. $145-147^\circ$ (4 mm.), - δ -phenyl- β -methylvalerate, b.p. $159-161^\circ$ (2 mm.), α -carboxy- γ -phenyl- β -methylbutyric, m.p. $143-145^\circ$, - γ -phenyl- β -ethylbutyric, m.p. $150-151^\circ$, - δ -phenyl- β -methylvaleric, m.p. $83-84^\circ$, α -bromo- α -carboxy- γ -phenyl- β -methylbutyric, m.p. $153-154^\circ$, - γ -phenyl- β -ethylbutyric, m.p. $152-153^\circ$, - δ -phenyl- β -methylvaleric, m.p. $118-119^\circ$, α -amino- α -carboxy- γ -phenyl- β -methylbutyric, m.p. $255-265^\circ$, - γ -phenyl- β -ethylbutyric, m.p. $240-245^\circ$, and - δ -phenyl- β -methylvaleric acid, m.p. $225-230^\circ$, are described. α -Amino- δ -phenyl- β -benzylvaleric acid, m.p. $240-250^\circ$ (I), is prepared by treatment of dimethylcinnamylidenemalonate with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ in Et_2O and hydrolysis, giving α -carboxy- γ -styryl- β -benzylbutyric acid, m.p. $177-179^\circ$ (II), which with PBr_3 gives α -bromo- α -carboxy- δ -phenyl- β -benzylvaleric acid, m.p. $150-152^\circ$; this with aq. NH_3 gives α -amino- α -carboxy- δ -phenyl- β -benzylvaleric acid, m.p. $245-255^\circ$; on decarboxylation (I) is obtained. From (II) γ -styryl- β -benzylbutyric, b.p. $215-217/1\text{ mm.}$, and δ -phenyl- β -benzylvaleric acid, b.p. $210-215/3\text{ mm.}$, are obtained. α -Amino- γ -phenyl- β -benzylbutyric acid, m.p. $260-270^\circ$ (III), is prepared from ethoxymethylenemalonate ester by treatment with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$, giving *Et* α -carbethoxy- γ -phenyl-

β -benzylbutyrate, b.p. 188—203°/3 mm., which on hydrolysis gives α -carboxy- γ -phenyl- β -benzylbutyric, m.p. 153—155° (IV), and γ -phenyl- β -benzylbutyric acid, b.p. 195—200°/2 mm. Treatment of (IV) with PBr_3 gives α -bromo- α -carboxy- γ -phenyl- β -benzylbutyric acid, m.p. 166—168°, which with aq. NH_3 gives α -amino- α -carboxy- γ -phenyl- β -benzylbutyric acid, m.p. 265—275°, which on decarboxylation gives (III). β -Bromo- α -phenylbutane, b.p. 98—99°/1 mm., is made by reduction of $\text{CH}_2\text{Ph}\cdot\text{COEt}$ to the carbinol and treatment with PBr_3 at -5° . H. D.

Reactions of aminobenzoic acids with cadmium and zinc salts.—See this vol., 719.

Syntheses of isomeric phenylbutadienecarboxylic acids. II. Synthesis of isochavivic acid. H. LOHAUS and H. GALL (Annalen, 1935, 517, 278—289; cf. A., 1934, 1348).—*iso*Chavivic acid (I) is synthesised in poor yield, thus completing the series of isomeric δ -phenylbutadiene- α -carboxylic acids. Here, as in the diphenylbutadiene and dibromomuconic ester series, the order of increasing stability, as judged by the m.p., is *trans-trans* > *cis-cis* > *cis-trans*. Therefore, (I), and not chavivic acid as assumed by Ott (A., 1922, i, 1026), occurs as piperide in pepper. Piperonal and MeCHO in $\text{NaOH}\cdot\text{EtOH}$ at 8—10° give a little piperinaldehyde, b.p. 185—195°/0.05 mm., m.p. 108° (lit. 89—90°) [phenylhydrazone, m.p. 158—159° (lit. 190—192°); stereoisomeric *oximes*, m.p. 171° and 195°], and piperonylacetaldehyde (II) (30% yield), b.p. 170—185°/0.05 mm.; (II) with cold $\text{Br}\cdot\text{AcOH}$ gives α -bromo-*cis*-piperonylacetaldehyde (III), m.p. 104° (*oxime*, m.p. 182°), and some $\alpha\beta$ -dibromo-compound, m.p. 131° (*oxime*, m.p. 205°; oxidised by KMnO_4 to 6-bromopiperonylic acid, m.p. 203°). (II), $\text{CH}_2(\text{CO}_2\text{Me})_2$, and a few drops of piperidine (IV) in MeOH give slowly *Me* 3:4-methylenedioxy- γ -*cis*-cinnamylidenemalonate, m.p. 111°, and (III) gives similarly the γ -Br-ester, m.p. 126°. (II), $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, and a little (IV) in MeOH give rapidly a little *Me* α -cyano-3:4-methylenedioxy-cinnamate, m.p. 169° [derived from residual piperonal in (II)], and *Me* 3:4-methylenedioxy-cinnamylidenemalonate (75% yield), m.p. 189° (*Et* ester, similarly obtained from $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 130°); (III) gives similarly a little piperidine hydrobromide by loss of HBr , but mostly *Me* γ -bromo- α -cyano-3:4-methylenedioxy- γ -*cis*-cinnamylidenemalonate, m.p. 167° (also obtained in very poor yield by adding Br to *Me* α -cyano-3:4-methylenedioxy- γ -*trans*-cinnamylidenemalonate and removing HBr by $\text{KOAc}\cdot\text{MeOH}$), which with Zn dust in 90% MeOH gives a bimol., amorphous substance, $\text{C}_{28}\text{H}_{20}\text{O}_8\text{N}_2$, m.p. 98—102° after sintering; the product previously obtained similarly from the corresponding CH_2O_2 -free ester is also bimol. (II) and NaOAc in hot Ac_2O give γ -bromoisochavivic acid (V), m.p. 216° (*Me* ester, m.p. 10—121°), also obtained in poor yield, with a substance, m.p. 152°, from (III) and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_2\text{H}_5\text{N}$ at about 140°. (V) and Zn dust in hot 90% MeOH or EtOH give much piperic acid (VI) (with or without its ester) and a little 3:4-methylenedioxy- α -rans- γ -*cis*- δ -phenylbutadiene- α -carboxylic acid (I), m.p. 135—139°, hydrogenated (Pd -black) in MeOH to $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$. The configuration of the γ -link-

ing of (I) follows from the non-identity of (I) with piperic or isopiperic acid, that of the α -linking from the fact that the *trans*-compound (VI) accompanied (I) and that inversion during hydrogenation is improbable. Other configurations cited above follow.

R. S. C.

Effect of substituents on formation of chloralides of salicylic acid and its derivatives. R. L. ALIMCHANDANI, N. M. SHAH, and S. G. DEO (Current Sci., 1935, 3, 354).—*o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{CCl}_3\cdot\text{CHO}$ give 2-methoxy-5- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzoic acid (A., 1934, 1216), but 3- and 5-nitro-6-hydroxybenzoic acid and the corresponding *Me* ethers fail to react with $\text{CCl}_3\cdot\text{CHO}$. F. N. W.

Action of thionyl chloride on phenylglycollic acid. P. CARRE and D. LIBERMANN (Compt. rend., 1935, 200, 1215—1217).— SOCl_2 with $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (I) gives $\text{CHPhCl}\cdot\text{CO}_2\text{H}$ (cf. A., 1934, 290; J.C.S., 1911, 99, 1910) and CHPhCl_2 which arises from PhCHO by the decomp. ($>30^\circ$) of an anhydro-sulphite (II) (cf. A., 1922, i, 715). In Et_2O at 0° (I) with SOCl_2 gives an oil, converted by EtOH into $\text{OH}\cdot\text{CHPh}\cdot(\text{O}_2\text{Et})_2$ which is formed from (II). $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ is converted into COPh_2 probably through an anhydro-sulphite (cf. A., 1902, i, 31), since *tert*-alcohols yield no chlorosulphites. J. L. D.

Preparation of δ -phenyl- β -methyl-*n*-valeraldehyde. H. RUPE, H. HIRSCHMANN, and H. WERDENBERG (Helv. Chim. Acta, 1935, 18, 535—542).—The action of Mg and HgCl_2 on $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in $\text{C}_6\text{H}_6\cdot\text{Et}_2\text{O}$ gives *Et* β -hydroxy- δ -phenyl- β -methyl-*n*-valerate, which loses H_2O when distilled in vac. with formation of a mixture (I) of the corresponding unsaturated esters. Hydrolysis of (I) gives a mixture of acids from which δ -phenyl- β -methyl- γ -valerolactone, b.p. 179—181°/11 mm. (*Ca* salt of corresponding OH -acid), is obtained by treatment with 50% H_2SO_4 , which does not affect the δ -phenyl- β -methyl- Δ^{α} -*n*-pentoic acid, b.p. 179°/10 mm. (*Ca* salt). Hydrogenation of (I) (Ni -dil. EtOH) affords *Et* δ -phenyl- β -methyl-*n*-valerate, b.p. 151—154°/12 mm., reduced by Na and EtOH in light petroleum to ϵ -phenyl- γ -methyl-*n*-amyl alcohol (II), b.p. 141—143°/11 mm. Catalytic oxidation of (II) (Ag -asbestos) gives δ -phenyl- β -methyl-*n*-valeraldehyde, b.p. 142—144°/11 mm. (semicarbazone, m.p. 130), which very rapidly polymerises. H. W.

6-Nitroveratraldehyde and hippuric acid. A. OLIVERIO (Gazzetta, 1935, 65, 143—152).—The condensation product of veratraldehyde and hippuric acid (I) is hydrolysed, through the cinnamic acid, to the acetic acid, which can be nitrated to 6-nitro-3:4-dimethoxyphenylacetic acid (II), m.p. 207—208°. The product from 6-nitroveratraldehyde and (I), 2-phenyl-4-(6'-nitro-3':4'-dimethoxybenzylidene)-1:3:5-oxazolone, m.p. 227—228°, is similarly hydrolysed to 6-nitro- α -benzamido-3:4-dimethoxycinnamic acid, m.p. 250—251°, which is, however, further hydrolysed, not to (II), but to 6-nitrohomoveratrole. More vigorous hydrolysis (aq. KOH) yields 6-nitrohomocatechol, but if $\text{KOH}\cdot\text{EtOH}$ is used, *Me* is replaced by *Et*, and 6-nitro-3:4-dithoxytoluene, m.p. 114°, is obtained.

E. W. W.

Decomposition of acetylphthalimide. C. D. HURD, M. F. DULL, and J. W. WILLIAMS (J. Amer. Chem. Soc., 1935, 57, 774—775).—Pyrolysis of o - $C_6H_4(CO)_2NAc$ gives $AcOH$, Ac_2O , $COMe$, and a little keten, but no keten dimeride (cf. A., 1932, 849).
R. S. C.

Mercuration and decarboxylation of polycarboxylic acids. K. DZIEWONSKI and W. KAHL [with W. DYMEK] (Bull. Acad. Polonaise, 1934, A, 394—397, and Roc. Chem., 1935, 15, 89—91).—Mercuration and decarboxylation of o - and *peri*-dicarboxylic acids is effected in good yield in 1—3 hr. at 160—180°/10—20 atm. in presence of a little H_2O . At higher temp. both CO_2H may be removed. The following are obtained: $BzOH$ from o - $C_6H_4(CO_2H)_2$; α - $C_{10}H_7\cdot CO_2H$ from 1:8- $C_{10}H_6(CO_2H)_2$; 3- (22·3%) and 6- $OMe\cdot C_{10}H_6\cdot CO_2H$ (27·6%) from 3-methoxynaphthalic anhydride; 3- (33%) and 6- $NO_2\cdot C_{10}H_6\cdot CO_2H$ (17%) and β - $C_{10}H_7\cdot NO_2$ (28%) from 3-nitronaphthalic anhydride.
R. S. C.

Derivatives of 1:4-di- α -naphthyl-naphthalene. R. WEISS and J. KOLTES (Monatsh., 1935, 65, 351—356).—1:2-Di- α -naphthylisobenzofuran (I) (improved prep.) with maleic anhydride in xylene at b.p. gives 1:4-di- α -naphthyl-1:4-oxido-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride, m.p. 243—245°, converted by cold HCl in $EtOH$ into Et_2 1:4-di-naphthyl-naphthalene-2:3-dicarboxylate, m.p. 218—220°, hydrolysed by KOH - $EtOH$ to 1:4-di- α -naphthyl-naphthalene-2:3-dicarboxylic anhydride (compound with xylene, m.p. 282—285°). The product from (I) and acraldehyde in $EtOH$ at b.p., when treated with dry HCl yields 1:4-di- α -naphthyl-2-naphthaldehyde, m.p. 268—270°, the oxime, m.p. 268—270°, of which with Ac_2O at b.p. gives the acetyloxime, m.p. 185—187°, which with NH_2Ph at b.p. under reduced pressure yields 1:4-di- α -naphthyl-2-naphthonitrile, m.p. 225—227°.
F. R. G.

Derivatives of 0:3:3-dicyclooctane. J. C. BARDHAN and S. K. BANERJI (J.C.S., 1935, 474—476).—Condensation of $Et \Delta^1$ -cyclopentenecarboxylate with $CN\cdot CHNa\cdot CO_2Et$ yields α -cyano-1-carbethoxycyclopentane-2-acetic acid (I) as well as the Et ester (II) (cf. Cook *et al.*, A., 1934, 1002). (I) on distillation under reduced pressure gives 1-carbethoxycyclopentane-2-acetonitrile, b.p. 128°/4 mm., 265°/757 mm., and with $EtOH$ in H_2SO_4 yields (II), the Na derivative of which with $CH_2Br\cdot CO_2Et$ in $EtOH$ yields $Et \alpha$ -cyano- α -2-carbethoxy-1-cyclopentylsuccinate, b.p. 207°/5 mm., hydrolysed with aq. H_2SO_4 to 2-carboxy-1-cyclopentylsuccinic acid, m.p. 202°, the Et ester, b.p. 172°/4 mm., of which, heated with pulverised Na in C_6H_6 for 3 hr., yields Et 0:3:3-dicyclooctan-1-one-2:3-dicarboxylate, b.p. 166°/6 mm., which with aq. $FeCl_3$ gives a reddish-violet colour and with aq. HCl yields the corresponding acid, a gum (semicarbazone, m.p. 210°).
F. R. G.

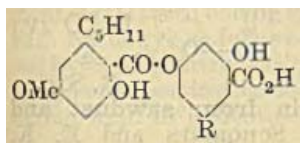
Constitution of diploschistessic acid. G. KOLLER and H. HAMBURG (Monatsh., 1935, 65, 367—374).—Diploschistessic acid (I) (cf. Zopf, A., 1906, i, 672) from *Diploschistes scruposus*, L., and *D. bryophilus*, Erh., is 3-hydroxy-5-(2':3':4'-trihydroxy-6'-methylbenzoyl)- o -toluic acid, possibly mixed with 3:4-dihydroxy-5-(2':4'-dihydroxy-6'-methylbenzoyl)- o -

toluic acid. (I) gives an Ac_4 derivative, m.p. 157° (decomp. in evacuated tube) (Me ester, m.p. 162°), and with hot $MeOH$ in a sealed tube yields orcinol and Me 3:4:5-trihydroxy- o -toluate, m.p. 155°, sublimes 140°/0·008 mm., which with conc. HCl yields an oil converted at 110—130°/0·008 mm. into 5-methylpyrogallol, also formed by reduction of gallaldehyde with Zn and conc. HCl .
F. R. G.

Synthesis of substances related to cochenillic and carminic acids. A. N. MELDRUM and K. S. VAIDYANATHAN (Proc. Indian Acad. Sci., 1935, 1, A, 510—527).— Me 5-methoxy- m -toluate with $CCl_3\cdot CHO\cdot H_2O$ in H_2SO_4 at 50° gives 5-methoxy-3-methyl- (I), m.p. 118°, and 3-methoxy-5-methyl-2-trichloromethylphthalide (II), m.p. 138° (cf. J.C.S., 1911, 99, 1712) (at 0° a product, [(I)+(II)], m.p. 116°, is obtained), hydrolysed to 5-methoxy-3-methyl- (III) and 3-methoxy-5-methyl-phthalide-2-carboxylic acid (IV). Similarly, 5-hydroxy- m -toluic acid affords 5-hydroxy-3-methyl- (V), m.p. 178° (Ac derivative, m.p. 128°), and 3-hydroxy-5-methyl-2-trichloromethylphthalide (VI), m.p. 184° (Ac derivative, m.p. 164°), which with $BzCl$ in C_5H_5N gives (VII) (below). (V) and (VI) with hot $NaOH$ give, respectively, 5-hydroxy-3-methyl-, m.p. 223° [methylated to (III)], and 3-hydroxy-5-methyl-phthalide-2-carboxylic acid, m.p. 214° [methylated to (IV)], which with $BzCl$ in C_5H_5N gives 2-benzoyl-6-carboxy-4-methylmandelic acid (VII), m.p. 45°. (V) and (VI) with Zn - $AcOH$ at room temp. give 5-hydroxy-2-, m.p. 229°, and 5-hydroxy-6- β -dichloroethyl- m -toluic acid, m.p. 179° (Ac derivative, m.p. 138°), respectively, converted by H_2SO_4 into 4-hydroxy-2-carboxy-6-methyl-, m.p. 210°, and 2-hydroxy-6-carboxy-4-methyl-phenylacetic acid, m.p. 254°, respectively, which with $NaOH$ - $KMnO_4$ give β - (A., 1897, i, 539) and γ -coccinic acid (VIII), (A., 1921, i, 111). (V) with Br in $AcOH$ at 100° gives 4:6-dibromo-5-hydroxy-3-methyl-2-trichloromethyl phthalide, m.p. 214°, which with warm $NaOH$ affords 4:6-dibromo-5-hydroxy-3-methylphthalide-2-carboxylic acid, m.p. 268°, oxidised ($KMnO_4$ - $NaOH$) to 4:6-dibromo-5-hydroxy-3-methylphthalic acid, m.p. 128° (anhydride, m.p. 197°). Similarly were obtained 4:6-dibromo-3-hydroxy-5-methyl-2-trichloromethylphthalide, m.p. 216°, 4:6-dibromo-3-hydroxy-5-methylphthalide-2-carboxylic acid, m.p. 230° (decomp.), and 4:6-dibromo-3-hydroxy-5-methylphthalic acid, m.p. 187° (decomp.) (anhydride, m.p. 272°). (II) with Zn - $AcOH$ at room temp. gives 5-methoxy-6- β -dichloroethyl- m -toluic acid, m.p. 174°, converted by conc. H_2SO_4 into 2-methoxy-6-carboxy-4-methylphenylacetic acid, m.p. 209° (anhydride, m.p. 160°) [oxidised to the Me ether of (VIII)], which with $CCl_3\cdot CHO$ in H_2SO_4 gives 5-methoxy-3-methyl-2-trichloromethyl-6-carboxymethylphthalide, m.p. 241°, reduced (Zn - $AcOH$) to 2-methoxy-6-carboxy-4-methyl-5- β -dichloroethylphenylacetic acid (IX), m.p. 145°. (XI) with hot conc. H_2SO_4 gives 3-methoxy-5-methyl-2:6- α -carboxymethylbenzoic acid (X), m.p. 254°. (I) similarly affords the analogous series of compounds: 5-methoxy-2- β -dichloroethyl- m -toluic acid, m.p. 143°, 4-methoxy-6-carboxy-2-methylphenylacetic acid, 180° (anhydride, m.p. 134°); 3-methoxy-5-methyl-2-trichloromethyl-6-carboxymethylphthalide, m.p. 241°, and 4-methoxy-2-methyl-5- β -dichloroethyl-6-carboxy-

phenylacetic acid, m.p. 136°, which is converted into (X). (X) with KOH-KMnO₄ at 50–60° gives some cochenillic acid, m.p. 225° (A., 1897, i, 539) [identical with the acid obtained from cochineal (cf. A., 1913, i, 977)], but mainly the Me ether, m.p. 200° (cf. A., 1910, i, 487). J. L. D.

Lichen substances. L. Components of *Parmelia perlata*, Ach. Y. ASAHINA and F. FUJIKAWA (Ber., 1935, 68, [B], 634–639).—Extraction of *P. perlata*, Ach., from Europe (probably *P. cetrarioides*, Del., var. *typica*, Du Rietz) with Et₂O yields a mixture (I) of atranorin and chloroatranorin and *perlatic acid* (diolivetolcarboxylic acid Me₁ ether) (II; R=C₅H₁₁), m.p. 108°, very similar except m.p. to Zopf's imbricatic acid (III). It is hydrolysed by alkali to olivetolcarboxylic acid Me₁ ether, m.p. 126°, olivetol



(IV), m.p. 41°, and CO₂. Cautious treatment with MeOH-KOH leads to Me olivetolcarboxylate *p*-Me ether (V) and olivetolcarboxylic acid. (II) is converted by CH₂N₂ and subsequent hydrolysis into olivetolcarboxylic acid Me₂ ether and olivetolcarboxylic acid *o*-Me ether. Extraction of a further sample of European *P. perlata*, Ach., scarcely differing externally from that used above, affords (I) and imbricatic acid (VI), m.p. 125–126°. (VI) is hydrolysed by KOH to (V), divarin, and CO₂ and with MeO-KOH affords (V) and divaric acid. (VI) is therefore (II) with R=Pr. Extraction of a Japanese lichen of very similar type gave (VI) and an acid, m.p. 112°, hydrolysis of which affords (IV) and (V). It is considered to be a mixture of (II) and (VI). (III) is regarded as a similar mixture from which (VI) would have been obtained if further purification had been possible, and the name "imbricatic acid" is hence assigned to (VI). H. W.

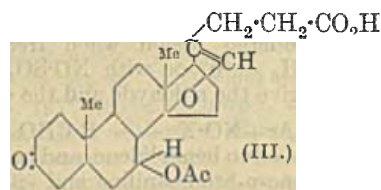
Isomerism of apocholic and dihydroxycholenic acids. K. YAMASAKI (Z. physiol. Chem., 1935, 233, 10–12).—HCl in AcOH or CHCl₃ converts dihydroxycholenic acid (I) into apocholic acid (II), with production of some isodihydroxycholenic acid (III), (cf. A., 1933, 1162). In the Hammarsten reaction of cholic acid (I) is probably first formed with elimination H₂O, (II) being then produced and transformed into (III). W. McC.

Fate of dehydrocholic acid and dehydrodeoxycholic acid in the toad. K. YAMASAKI and K. KYOGOKU (Z. physiol. Chem., 1935, 233, 29–35; cf. Shibuya, A., 1933, 974).—*iso*Reductodehydrocholic acid (acetate, m.p. 216–217°) on oxidation with CrO_3 yields dehydrocholic acid. The urine of toads to which Na dehydrodeoxycholate has been subcutaneously administered yields β -3-hydroxy-12-ketocholanic acid, m.p. 125°, $[\alpha]_D^{25} +99.89^\circ$ in EtOH (oxime of Me ester, m.p. 100°; acetate, m.p. 175–179°), an isomeric acid, m.p. 220° (Me ester, m.p. 115°; acetate, m.p. 195–205°), and deoxybilanic acid, m.p. 112–120° (Me ester, m.p. 144–145°), is obtained by hydrolysis of Me diacetyldeoxycholate (Wieland *et al.*, A., 1933,

158) to the corresponding *monoacetyl acid*, m.p. 163–167°, which is then oxidised with CrO₃ in AcOH to 12-acetoxy-3-ketocholanic acid, m.p. 95–96°.

W. McC.

Constitution of the poisons of the native toad. VIII. H. WIELAND and G. HESSE (Annalen, 1935, 517, 22–34).—New analyses of bufotalin (I), m.p. 223° (decomp.) after slight softening at 150°, bufotalone (II), m.p. 287° (improved prep.), and bufotalin, m.p. 224°, confirm the presence of 24C. The aldo-enolic nature of the lactone group of (I) is established by the isolation of HCO₂H from the products of ozonisation of (I). Fission of the ring occurs very readily and the liberated CHO group is readily identified by ammoniacal Ag solution or fuchsin-H₂SO₄. The course of the change appears to be $\text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \end{smallmatrix} \text{O} \rightarrow \text{C}(\text{CH} \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{CH}(\text{CHO}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. (I) and Ba(OH)₂ in MeOH give the (non-homogeneous) salt C₂₆H₃₆O₇·Ba, whereas under rather more drastic conditions Ac is simultaneously removed yielding the acid, C₂₄H₃₄O₅, m.p. 220° (decomp.) after softening (Me ester, m.p. 225–230° after softening at 185°). Treatment of (II) with Ba(OH)₂ in MeOH affords the (non-homogeneous) salt, C₂₆H₃₅O₇·Na (corresponding *bisdinitrophenylhydrazone*, decomp. >181°). (II) is converted by 0.05N-KOH in EtOH at 0°, by 0.1N-NaOH in



C₅H₅N, or by Ag₂O-EtOH into *anhydrobufotalonic acid* (? III), m.p. 232–233° (decomp.), in place of the expected dicarboxylic acid. The corresponding Ac-free acid is obtained from (I). Further evidence of the existence of the same tetracyclic ring system in (I), the bile acids, and sterols is obtained by the isolation of chrysene from the products of the dehydrogenation of (I) by Se. Bufotalidin (formerly designated bufotalone), m.p. 228°, is C₂₄H₃₂O₆. It contains an unsaturated lactone group and gives an Ac derivative, C₂₆H₃₄O₇, m.p. 244–245° after softening and becoming yellow at 235°. It contains 3 double linkings and is free from Ac. Bufotalinin, m.p. 233°, shows only a feeble Liebermann reaction and is very unstable; Ac is present. H. W.

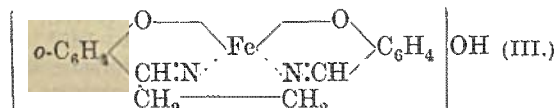
Polyterpenes and polyterpenoids. XCVII. Identity of the steric configuration of hydroxyl in position 3 in lithocholic acid and epicoprosterol. L. RUZICKA and M. W. GOLDBERG (Helv. Chem. Acta, 1935, 18, 668–675).—Lithocholic acid (I) obtained by a modification of the method of Wieland *et al.* (A., 1932, 1248) has m.p. 184–185° (corr.), $[\alpha]_D^{25} +35.5^\circ$ in abs. EtOH and m.p. 184–185°, $[\alpha]_D^{25} +33.8^\circ$ when prepared according to Borsche *et al.* (A., 1922, i, 1159). Since these data harmonise with those of natural (I) the steric identity of the samples may be regarded as established. Since the synthetic acids are obtained under conditions which cause about

80% isomerisation of coprosterol to *epicoprosterol* (II), the *epi*-position of the 3-OH in (I) is highly probable, but this cannot be assumed for deoxycholic or cholic acid. Proof of the steric configuration of the 3-OH is afforded by the oxidation of acetyl-lithocholic acid to 3-*epihydroxy*ætiocholan-17-one (III), m.p. 150–151°, $[\alpha]_D +104.7^\circ$ in abs. EtOH (semicarbazone, m.p. 253–254°), identical with that obtained from *epicoprosteryl* acetate (A., 1934, 1222). Further, reduction of Me lithocholate (IV) according to Bouveault leads to the diol $C_{24}H_{42}O_2$, m.p. 179–180°, $[\alpha]_D +35.2^\circ$ in MeOH, the diacetate of which is oxidised to (III). (III) is converted by MgMeI in Et₂O followed by Ac₂O into *dehydronorepicoprosteryl acetate*, m.p. 111.5–112.5°, reduced (PtO₂ in Et₂O) to *norepicoprosteryl acetate*, m.p. 93°, $[\alpha]_D +48.2^\circ$ in C₆H₆, which is hydrolysed to *norepicoprosterol* (V), m.p. 153–154°, $[\alpha]_D +29.2^\circ$ in C₆H₆. 3-Hydroxy-*allocholan*-17-one and 3-hydroxy*cholanone* are immediately pptd. by digitonin in slightly aq. EtOH, whereas ppts. are not given by (II) or (V). The precipitability of a sterol or bile acid derivative is not incontrovertible evidence of the steric arrangement of the 3-OH. Androsterone and (I) are the only naturally occurring compounds in which the *epi*-position of OH is beyond doubt. H. W.

Action of nitrosyl chloride and nitrosylsulphuric acid on aromatic Schiff's bases. J. TURCAN (Bull. Soc. chim., 1935, [v], 2, 627–632).—Schiff's bases undergo fission when treated with NOCl in dry C₆H₆ at 0° or with NO·SO₄H in dry Et₂O at –5°, to give the aldehyde and the diazonium salt: $CHR:NAr + NO \cdot X \longrightarrow R \cdot CHO + ArN_2X$. Such fission is applied to benzylidene- and heptylidene-aniline, benzylidene-*p*-bromoaniline and - α -naphthylamine. Mechanisms are suggested. J. W. B.

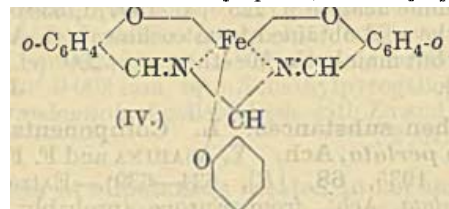
Dehydration of the hydrobenzoin of α -phenyl- β -vinylethylene glycol; formation of α -phenylcrotonaldehyde. M. Tiffeneau and P. Weill (Compt. rend., 1935, 200, 1217–1219).—Acraldehyde with PhCHO and Zn–Cu in EtOH–H₂O gives $\gamma\delta$ -*dihydroxy- δ -phenyl- Δ^2 -butylene* (I), m.p. 43°, together with some divinylethylene glycol and hydrobenzoin. (I) with boiling HCO₂H gives only α -*phenylcrotonaldehyde* (II), b.p. 117°/15 mm. (*semicarbazone*, m.p. 201°; *oxime*, m.p. 116°). The reaction mechanism is by way of α -phenylisocrotonaldehyde (involving migration either of Ph or CH₂:CH), which then isomerises to (II). J. L. D.

Cyclic iron compounds formed by auxiliary valencies. T. Tsumaki (Bull. Chem. Soc. Japan, 1935, 10, 74–81; cf. A., 1933, 824).—*o*-OH·C₆H₄·CHO (I), (·CH₂·NH₂)₂, and FeSO₄ (II) in aq. C₅H₅N in presence of air give the *hydroxide* (III), +0.25C₅H₅N (not lost at 130°) and +2H₂O (not lost at 140°), which in dil. H₂SO₄ gives the sulphate. (III) may also be

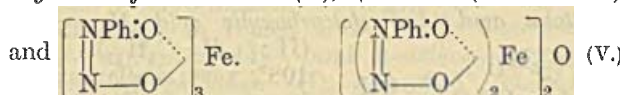


obtained by passing CO₂ into an aq. suspension of the corresponding oxide. (I), (II), and NH₃ in aq.

EtOH at 100° give the *substance* (IV), +PhNO₂ (lost at 150°), derived from OH·C₆H₄·CH(N:CH·C₆H₄·OH)



Cupferron and (II) in H₂O give "*phenylnitrosohydroxylamine ferric oxide*" (V), +2EtOH (lost at 110°)



R. S. C.

Preparation of vanillin from sawdust and sulphite liquor. P. P. SCHORIGIN and E. K. SMOLJANINOVA (J. Gen. Chem. Russ., 1934, 4, 1428–1433).—Kürschner's method (A., 1925, i, 1387) gives trustworthy results for determination of vanillin (I); the raw product should first be freed from volatile aldehydes by steam-distillation. Sulphite liquor gives higher yields of (I) than does sawdust, when treated by Kürschner's method. The yields are not increased when oxidising agents are present during hydrolysis, as would follow from Freudenberg's theory of the structure of lignin (A., 1933, 276).

R. T.

Planar configuration for quadrivalent nickel, palladium, and platinum.—See this vol., 684.

Fused carbon rings. IV. Further investigation of 0 : 3 : 3-dicyclooctanones in relation to the strain theory. J. W. BARRETT and R. P. LINSTEAD (J.C.S., 1935, 436–442).—Et cyclopentanone-2-acetate and CN·CH₂·CO₂Et with piperidine give an *ester* (I), m.p. 84°, as well as Et cyclopentylidenecyanoacetate-2-acetate, b.p. 172–174°/2 mm. (cf. A., 1934, 1002). (I) with conc. HCl gives, probably, the *lactone* of cyclopentanol-1 : 2-diacetic acid, m.p. 83°, reduced by Al–Hg to Et cyclopentane-1-cyanoacetate-2-acetate, and with conc. HCl gives a mixture of *cis*- and *trans*-cyclopentane-1 : 2-diacetic acids, which with BaO at 300° gives the pure *trans*-acid (I), m.p. 133 (cf. Hückel *et al.*, this vol., 211), together with *cis*- β -0 : 3 : 3-dicyclooctanone (II), m.p. –33° to –34°. (I) with BaO at 340° gives *trans*- β -0 : 3 : 3-dicyclooctanone (III), m.p. 13–14°, the structure of which is confirmed by oxidation with conc. HNO₃ or KMnO₄ to *trans*-cyclopentane-1-carboxy-2-acetic acid. The semicarbazone (IV) of (II) heated with KOH and a little MeOH gives *cis*-0 : 3 : 3-dicyclooctane (V), b.p. 136°. The (IV) of (III) heated with NaOEt gives *trans*-0 : 3 : 3-dicyclooctane (VI), b.p. 132°, m.p. –36°, and a *compound*, m.p. 188°. The lactone of cyclopentanol-2-acetic acid is shown to be the *cis*-isomeride. The b.p., d_4^{25} , n_D^{25} , exaltation, and heats of combustion are recorded for (II), (III), (V), and (VI).

F. R. G.

Synthesis of jasmone. W. TREFF and H. WERNER (Ber., 1935, 68, [B], 640–644; cf. A., 1933, 1296).— Δ^2 -Hexenol (from Japanese peppermint oil and containing 7% of *n*-hexyl alcohol) is transformed

into Δ^7 -hexenyl bromide, b.p. 46—47°/13 mm., converted by NaCN in EtOH-H₂O into Δ^7 -heptenonitrile, b.p. 49—50°/5 mm., whence Δ^7 -heptenoic acid (I), b.p. 98—100°/5 mm. [oxidised by KMnO₄ to (·CH₂·CO₂H)₂]. The chloride, b.p. 51—53°/5 mm., of (I) is transformed by Br at room temp. and subsequently at 70—100° followed by EtOH into *Et* $\alpha\delta$ -tribromo-*n*-heptate (II), b.p. 155—160°/5 mm. (II) is converted by Et laevulate and activated Zn filings in C₆H₆ into the substance (III),

$\text{CH}_2=\text{CH}_2 \rightarrow \text{CMe} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHEt}$, b.p. 163—164°/5 mm., and a product hydrolysed to (II). Treatment of (III) with boiling EtOH-HCl and of the product with Na in xylene followed by 20% H₂SO₄ leads to 3-methyl-2- Δ^6 -pentenyl- Δ^2 -cyclopentenone, b.p. 109—110°/5 mm. [semicarbazone, m.p. 204—206° (decomp.); oxime, m.p. 45°], identical with natural jasmone.

H. W.

Hydroxymethylene ketones and their reaction products. VII. Synthesis of an isomeride of irone. R. E. MEYER (Helv. Chim. Acta, 1935, 18, 470—473).—*cyclo*Geranyl Me ketone is transformed by NaOEt and HCO₂Et into the corresponding OH·CH ketone, the Mg salt of which is converted by MgMeI into a product (I) which loses H₂O with difficulty and does not give MeCHO when distilled in vac. Treatment of the acetate of (I) with Cu powder in petroleum at 150—160° yields α -2 : 6 : 6-trimethyl- Δ^1 (or 2)-*cyclo*hexenyl- Δ^7 -penten- β -one, b.p. 134—136°/10 mm.

H. W.

Haloform reaction. XV. Stepwise halogenation. B. A. BULL, W. E. ROSS, and R. C. FUSON (J. Amer. Chem. Soc., 1935, 57, 764—765; cf. A., 1934, 990).—Combination of steric hindrance and solubility in alkali stabilises ω -halogenoacetophenones to such an extent that every step in the successive ω -halogenation and subsequent hydrolysis of a COPhMe derivative by hypohalite can be separately realised. 2 : 4 : 6-Tribromo-3-acetylbenzonitrile (modified prep.; 35% yield) is hydrolysed [H₂SO₄-AcOH-H₂O 2 : 1 : 1 (vol.); NaNO₂] to 2 : 4 : 6-tribromo-3-acetylbenzoic acid (I), m.p. 192—193° (decomp.), converted by NaOBr at 0° into the (15 min.) ω -Br- (II), m.p. 178—179° (decomp.), (1 hr.) $\omega\omega$ -Br₂- (III), m.p. 187—188° (decomp.) [also obtained from (II) by NaOBr (1 hr.) and (24 hr.) $\omega\omega\omega$ -Br₃- (IV) compounds, m.p. 196° (decomp.) also obtained (24 hr.) from (II) and (III)]. (I) and NaOCl at 0° (5 min.) give the $\omega\omega$ -Cl₂- (V), m.p. 180—181° (decomp.), and (1 hr.) $\omega\omega\omega$ -Cl₃- compound (VI), m.p. 182—183° (decomp.). (IV) and (VI) are unchanged by cold aq. NaOH (5 min.), but, when warmed, give 2 : 4 : 6-tribromoisophthalic acid, m.p. 275—277°, also obtained from (II), (III), and (V) by warm hypohalites. The ω -Cl-compound could not be isolated.

R. S. C.

Acid degradation. M. S. NEWMAN (J. Amer. Chem. Soc., 1935, 57, 732—735).—Reaction of α -Br-acids with NaN₃ (modified prep.) in various solvents is described. Chlorides, CHRBr·COCl, react best in AcOH. C₅H₅N is better than C₆H₆, but removes HBr from chlorides, CH₂R·CR'Br·COCl, leading, however, eventually also to ketones. Hydrolysis of the azide is by way of the carbimide, since

CHPhBr·COCl and NaN₃ yield some CHPhBr·NCO, hydrolysed by acid to PhCHO and with EtOH giving CHPh(NH·CO₂Et)₂. α -Bromo-hexahydrobenzoyl and -cyclopentylacetyl chloride (I) give ketone and aldehyde, respectively, without ring change. *cyclo*Pentanaldehyde, from (I) or from the *glycide* ester, b.p. 90—93°/3—4 mm., from *cyclopentanone* and CH₂Cl·CO₂Et, has b.p. 135—136° (*dimedone* derivative, m.p. 162—163°).

R. S. C.

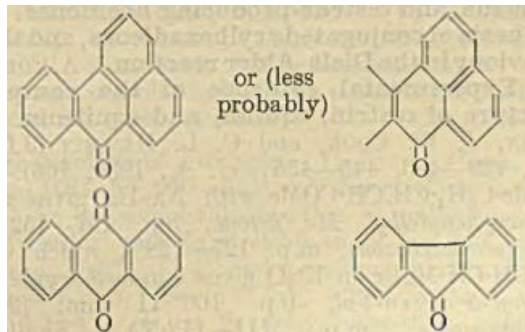
Cleavage of unsymmetrical ketones by potassium hydroxide. I. W. E. BACHMANN (J. Amer. Chem. Soc., 1935, 57, 737—738).—By determination of the amount of each acid formed from ketones, CORR', by hot, solid KOH the following relative tenacities are calc.: *p*-, 1.38, and *m*-C₆H₄Me, 1.08; *p*-C₆H₄Ph, 1.04; Ph, 1; 3-, 0.82, and 2-phenanthryl, 0.79; *o*-C₆H₄Me, 0.22; 9-, 0.05, and 1-phenanthryl, 0.04. The orientation as well as the substituent is thus of importance. The C₆H₄Me·COPh and C₆H₄Me·CO·C₆H₄Ph series give mutually consistent results.

R. S. C.

Synthesis of di-*p*-xenylketen. E. SCHILOV and S. BURMISTROV (Ber., 1935, 68, [B], 582—584).—Di-*p*-diphenyl ketone (I), m.p. 236°, from Ph₂, COCl₂, and AlCl₃, is converted by Na-Hg followed by CO₂ in Et₂O into di-*p*-diphenylglycollic acid (II), m.p. 182.4—184°, which with PCl₅ in CCl₄ affords (I), dichlorodi-*p*-diphenylmethane and chlorodi-*p*-diphenylacetyl chloride (III), m.p. 109.5° [chlorodi-*p*-diphenylacetanilide, m.p. 174° (slight decomp.)]. (III) and Zn-Hg in Et₂O yield di-*p*-diphenylketen (IV), m.p. 197° (slight decomp.), which gives an intense green colour with conc. H₂SO₄, loses CO at 250° with formation of a strongly fluorescent material, and is unusually stable towards O₂ in boiling C₆H₆. (II) is reduced by HI and red P in AcOH to di-*p*-diphenylacetic acid, m.p. 208°, whence the corresponding chloride, m.p. 110°, and anilide, m.p. 278°, also obtained from (IV) and NH₂Ph in Et₂O.

H. W.

Use of Grignard reagent for locating certain ethylenic linkings in polynuclear ring systems. I. Benzanthrone. C. F. H. ALLEN and S. C. OVERBAUGH (J. Amer. Chem. Soc., 1935, 57, 740—744).—Cases of 1 : 6-addition of Grignard reagents to benzanthrone (I) are disproved. 1 : 4-Addition is normal for (I), but 1 : 2-addition occurs with anthrone, anthraquinone, and fluorenone. The structures given below are thus indicated, at least in Et₂O. "Diene" syntheses are of diagnostic val. only when positive.



(I) (modified prep.) gives (Grignard; 3 mols. of reagent in Et₂O) 4-phenyl- (II) (42%), m.p. 186°, 4-

benzyl- (III) (22%), m.p. 135°, and 4-heptyl-benzanthrone (61% yield), m.p. 77—78°. Structures are proved as follows. (II) and KMnO_4 give 4-phenylanthraquinone-1-carboxylic acid, m.p. 288—290° (decomp.) [*Me* ester, m.p. 197—198° (IV)], decarboxylated by Cu at 140—160° to 1-phenylanthraquinone. *Me* cinnamylideneacetate and α -naphthaquinone give (IV) and *Me* 4-phenyl-1:2:3:4-tetrahydroanthraquinone-1-carboxylate, m.p. 164—165°. (II) and CrO_3 -AcOH give an acid, $\text{C}_{21}\text{H}_{12}\text{O}_4$, m.p. 286—288° (decomp.), probably not an anthraquinone derivative [*Me* ester, m.p. 216—217° (cf. lit.)]. (III) and CrO_3 give 4-benzoylanthraquinone-1-carboxylic acid (75% yield), m.p. 275—278° (decomp.) (*Me* ester, m.p. 184—185°), leading to 1-benzoyl- and 1:4-dibenzoyl-anthraquinone, m.p. 225—227°. The prep. of (II), (III), etc. leads to much tar, which may contain some 1:2-additive product and certainly contains some reduced compounds, since treatment with benzoquinone gives a vigorous reaction leading to more substituted benzanthrone. $\text{MgBr}\cdot\text{Cl}$ and (I) give by 1:2-addition 10-tert.-butylbenzanthren-10-ol (20%), m.p. 140° (*Et* ether, m.p. 159—160°), oxidised by CrO_3 to anthraquinone-1-carboxylic acid, m.p. 286—288° (decomp.) (*Me* ester, m.p. 188—190°). R. S. C.

Dioximes. CVI. E. DURIO (Gazzetta, 1935, 65, 89—94).—The dioximes of glyoxal and its *Me*, *Me*₂, and *Me* CH_2Ph homologues, with $\text{NHPh}\cdot\text{NH}_2$ at 150—170°, yield the corresponding osazones. At the same temp., aminoethyl- and α - and β -amino-phenylglyoximes fail to react. The α -form of γ -benzildioxime yields β -benzilozasone, but the β -form does not react. The α -form of phenylglyoxime yields phenylglyoxal- α -osazone, m.p. 156—157° (decomp.), and, with $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$, phenylglyoxal- α -*p*-bromosazone, m.p. 203° (decomp.); the β -form yields the osazone of m.p. 154°, now named phenylglyoxal- β -osazone (*Ac* derivative, m.p. 204—205°). The β -form of *p*-tolylglyoxime gives *p*-tolylglyoxal- β -osazone, m.p. 167—168° (decomp.); the α -form, a mixture of the latter with *p*-tolylglyoxal- α -osazone, m.p. 145°.

E. W. W.

Compounds of palladium with benzylmethylglyoxime. F. P. DWYER and D. P. MELLOR (J. Amer. Chem. Soc., 1935, 57, 605—607).—The prep. and properties of *cis*- and *trans*-isomerides of *Pd* bis-anti-benzylmethylglyoxime (m.p. 207—208° and 175°, respectively) are described. E. S. H.

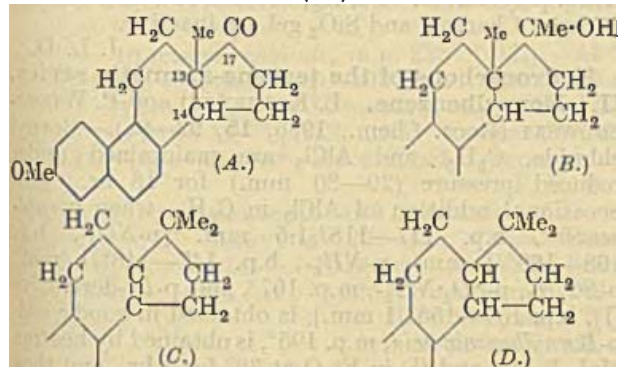
Synthesis of compounds related to the sterols, bile acids, and oestrus-producing hormones. V. **Synthesis of conjugated arylhexadienes, and their behaviour in the Diels Alder reaction.** A. COHEN. VI. Experimental evidence of the complete structure of oestrin, equilin, and equilenin. A. COHEN, J. W. COOK, and C. L. HEWETT (J.C.S., 1935, 429—436, 445—455; cf. A., 1934, 766).—V. *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ with Na-Hg gives β -methoxyphenylethyl *Me* ketone, b.p. 151—152°/10 mm. (semicarbazone, m.p. 127—128°), which with $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{MgBr}$ in Et_2O gives ζ -*m*-methoxyphenyl- δ -methyl- Δ^a -hexen- δ -ol, b.p. 166°/11 mm. (3:5-dinitrobenzoate, m.p. 111—112·5°). Similarly $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHO}$ and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COMe}$ yield, respectively, ζ -phenyl- Δ^a -hexen- δ -ol, b.p. 130°/11 mm. (3:5-

dinitrobenzoate, m.p. 82—83°), and ζ -phenyl- δ -methyl- Δ^a -hexen- δ -ol, b.p. 135°/13 mm. (3:5-dinitrobenzoate, m.p. 80—81°), converted by KHSO_4 at 140—145° (45 min.) into phenyl- δ -methyl- Δ^a -hexadiene, b.p. 116°/12 mm. *Me*, b.p. 148°/15 mm., and *Et* β -methoxyphenylpropionate, b.p. 156—157°/15 mm., with Na in EtOH give γ -*m*-methoxyphenyl-*n*-propyl alcohol (I), b.p. 155—157°/15 mm. (3:5-dinitrobenzoate, m.p. 69—70°), also obtained in poor yield from *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ with Na and EtOH . $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ and the *Mg* derivatives of the chloride, b.p. 137°/15 mm., from (I) and of γ -phenyl-*n*-propyl chloride in Et_2O give, respectively, ζ -*m*-methoxyphenyl- Δ^a -hexen- γ -ol, b.p. 177°/14 mm. (3:5-dinitrobenzoate, m.p. 106—107°), and ζ -phenyl- Δ^a -hexen- γ -ol, b.p. 135°/12 mm. (3:5-dinitrobenzoate, m.p. 113—114°), which with KHSO_4 give, respectively, ζ -*m*-methoxyphenyl-, b.p. 149/18 mm., and -phenyl- Δ^a -hexadiene, b.p. 99·5—100·5°/11 mm. This last, but not the other dienes, reacts with maleic anhydride in warm xylene to give 3- β -phenylethyl-1:2:3:6-tetrahydrophthalic anhydride, m.p. 123—125° [*K* *H* salt + $2\text{H}_2\text{O}$, cryst.; *Me* *H* ester (II), m.p. 137—138°; *Me*₂ ester, b.p. 155—160°/0·1 mm.], which with AcOH and H_2SO_4 at 100° gives an oil and this with *Se* yields 3- β -phenylethylphthalic anhydride, m.p. 153—154° (softens 148°), sublimes 170°/0·1 mm. [also obtained by dehydrogenation with Pt-black of the product from (II) and 85% H_2SO_4].

VI. β -6-Methoxy-1-naphthylethyl bromide (III), b.p. 155°/0·4 mm., m.p. 57—58° [from the alcohol (improved prep.) and PBr_3], heated (3—4 hr.) with *Et*-methylcyclopentanone-6-carboxylate (cf. Cornubert *et al.*, A., 1930, 776) and finely-divided *K* in C_6H_6 gives *Et* 2-(β -6'-methoxy-1'-naphthylethyl)-5-methylcyclopentanone-2-carboxylate, b.p. 212°/0·2 mm. (semicarbazone, m.p. 161—163°), which with 50% aq. H_2SO_4 yields 7-methoxy-1'-methyl-1:2-cyclopentenophenanthrene, m.p. 97·5—98° [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 129°]. Similarly *Et* 4-methylcyclopentanone-2-carboxylate (cf. Dieckmann, A., 1901, i, 539) gives *Et* 2-(β -6'-methoxy-1'-naphthylethyl)-4-methylcyclopentanone-2-carboxylate, b.p. about 205°/0·05—0·1 mm., and 7-methoxy-2'-methyl-1:2-cyclopentenophenanthrene, m.p. 136·5—137·5° [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 132—133°]. The *Mg* derivative of (III) with 2:5-dimethylcyclopentanone in dry Et_2O gives a carbinol, b.p. 160—200°/0·5 mm., converted by KHSO_4 at 160° (1 hr.) into 1-(β -6'-methoxy-1'-naphthylethyl)-2:5-dimethyl- Δ^1 -cyclopentene, b.p. 164—169°/0·4 mm. (*picrate*, m.p. 80—82°), which with AlCl_3 in CS_2 at 0° (5 hr.) yields 7-methoxy-1:3'-dimethyl-1:2:3:4-tetrahydro-1:2-cyclopentenophenanthrene, b.p. 175°/0·2 mm. [*picrate*, m.p. 87—88°; *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 98°], which is converted by *Se* at 300—310° (15 hr.) into 7-methoxy-3'-methyl-1:2-cyclopentenophenanthrene (IV), m.p. 146·5—148·5°, sublimes 150—160°/0·1 mm. [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 135·5—136·5°]. 2:2-Dimethylcyclopentanone and $\text{Et}_2\text{C}_2\text{O}_4$ with NaOEt in EtOH yields *Et* 2:2-dimethylcyclopentanone-5-glyoxylate (V), b.p. 141°/12 mm. (brownish-red colour with FeCl_3), hydrolysed to 2:2-dimethylcyclopentanone-5-glyoxylic acid, m.p. 75—76°. (V) boiled with *K* in C_6H_6 and *MeI* (5 hr.) gives *Et* 2:2:5-trimethylcyclopentanone-5-glyoxylate,

b.p. 135°/10 mm., hydrolysed by conc. HCl to 2 : 2 : 5-trimethylcyclopentanone, which with the Mg derivative of (III) in dry Et₂O gives 5-ethylnerolin, b.p. 120—130°/0.5 mm., 165°/10 mm., m.p. 54—55° (picrate, m.p. 83—84°), and a carbinol, b.p. > 190°/0.3 mm., converted by successive treatment with KHSO₄ at 160°, AlCl₃ in CS₂, and Se at 300—320° (13 hr.) into 7-methoxy-3 : 3'-dimethyl-1 : 2-cyclopentenophenanthrene (VI), m.p. 165—165.5° [*s*-C₆H₃(NO₂)₃ compound, m.p. 170—171.5°]. 7-Methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydro-1 : 2-cyclopentenophenanthrene with NaOEt in EtOH at 190—195° (20 hr.) yields 7-hydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydro-1 : 2-cyclopentenophenanthrene, m.p. 131.5—132° (benzoate, m.p. 141—141.5°, sublimes 170°).

The Me ether (A) of equilenin (VII) with MeMgI in Et₂O gives the methylcarbinol (B), m.p. 133—133.5°, dehydrated with KHSO₄ at 160—170° (1 hr.) to a compound C₂₀H₂₂O (C), m.p. 131—132°, hydrogenated (Pd-black, moist Et₂O) to a compound C₂₀H₂₄O (D), m.p. 131—132°, converted by Se at 300—310° for 17 hr. into (VI).



Similarly the Me ether, m.p. 160.5—161.5°, of equilin (VIII) gives a methylcarbinol, m.p. 133—134°, dehydrated to a compound C₂₀H₂₁O, m.p. 112—117°, converted by Se at 295—305° (7 hr.) into (VI); the Me ether (cf. Butenandt *et al.*, A., 1932, 781) of oestrone (IX) also yields a methylcarbinol, m.p. 95—100°, dehydrated to a compound C₂₀H₂₈O, m.p. 58—60°, possibly a mixture of isomerides, hydrogenated to a gum which with Se at 300—320° (21.5 hr.) yields (VI), showing that (VII), (VIII), and (IX) have a keto-group at C₁₇ and a quaternary Me at C₁₃ which migrates to C₁₇ during dehydration with KHSO₄. The Me ether of trihydroxyestratriene with ZnCl₂ at 170—180° (0.5 hr.) gave a product which with Se at 295—305° (8.5 hr.) yields (IV), the quaternary Me group migrating as above, proving its attachment at C₁₃ and not C₁₄.

F. R. G.

Isomerisation of hydroxyketones. "Phenylketol." COPh·CH(OH)·CH₂·COMe. M. HENZE (*Z. physiol. Chem.*, 1935, 232, 117—122).—NaOEt in EtOH converts "phenylketol" into the isomeride (I), OH·CHPh·CO·CH₂·COMe, m.p. 59—59.5°, and a compound, C₂₂H₂₀O₄, m.p. 248° (Cu salt, m.p. 147°). With NHPH₂NH₂, (I) gives the pyrazole, m.p. 115° (acetate, m.p. 93°). With aq. NaOH (I) affords BzOH, OH·CHPh·CO₂H, and CHPhAc·OH. The possible mechanism of the isomeric change is discussed. J. H. B.

Cyclic compounds from aromatic diamines and chloral. R. WEISS and L. CHLEDOWSKI (*Monatsh.*, 1935, 65, 357—366).—*oo'*-Diaminodiphenyl and CCl₃·CHO heated in C₆H₆ give a trichloroethylidene derivative, m.p. 111°, shown to be

CCl₃·CH<NH-C₆H₄-NH-C₆H₄ (I), by the formation of a (NO)₂-derivative, m.p. 133° (decomp.). *m*-C₆H₄(COCl)₂ and PhOMe with AlCl₃ in CS₂ yield a mixture of 4 : 4'-dimethoxy-*m*- (II), m.p. 146—149°, and 4 : 4'-dimethoxy-*p*-, m.p. 239°, -dibenzoylbenzene, the latter being also given by *p*-C₆H₄(COCl)₂. (II) with HBr in AcOH at b.p. gives 4 : 4'-dihydroxy-*m*-dibenzoylbenzene (III) (dihydrate, m.p. 215°) and with HNO₃ in AcOH gives as by-product 3'-nitro-4'-hydroxy-*m*-benzoylbenzoic acid, m.p. 231° (Et ester, m.p. 130°), and as main product, 3 : 3'-dinitro-4 : 4'-dimethoxy-*m*-dibenzoylbenzene (IV), m.p. 174—177°, which with HBr in AcOH yields 3 : 3'-dinitro-4 : 4'-dihydroxy-*m*-dibenzoylbenzene, m.p. 195°, also given by (III) and aq. HNO₃. (IV) is reduced by aq. (NH₄)₂S to 3 : 3'-diamino-4 : 4'-dimethoxy-*m*-dibenzoylbenzene, m.p. 189° (Ac₂ derivative, m.p. 201°). Ac₂ derivative, m.p. 185°, which heated with CCl₃·CHO in CHCl₃ gives *s*-trichloroethylidene-3 : 3'-diamino-4 : 4'-dimethoxy-*m*-dibenzoylbenzene, m.p. 200° (decomp.), which is considered to be a cyclic compound of the same type as (I). F. R. G.

Constitution and structure of chitin. K. H. MEYER and G. W. PANKOW (*Helv. Chim. Acta*, 1935, 18, 589—598).—Detailed roentgenographic measurements of chitin are recorded and an arrangement of the chitobiose residues in the elementary cell of chitin is suggested. H. W.

Decomposition products of substances containing uronic acid, by heating in autoclave. I. K. ASO (*J. Agric. Chem. Soc. Japan*, 1934, 10, 1189—1200).—Alginic acid heated for 3 hr. (autoclave) at 160° yields alginetin (I), C₁₀H₈O₄, m.p. 235° [diacetate, m.p. 125°; dibenzoate, m.p. 187°; Me derivative (II), m.p. 215°; monoacetylmonomethyl derivative, m.p. 171°]. Oxidation of (I) with H₂O₂ affords 2 : 3-dihydroxybenzoic acid (III), whilst alkali fusion yields pyrocatechol, AcOH, and (III). (II) with H₂O₂ yields 2-hydroxy-3-methoxybenzoic acid (IV). The Me₂ derivative (V) of (I) yields (IV) with H₂O₂ and with EtOH-KOH a phenolic substance (VI), m.p. 66°, AcOH, and (IV). (VI) (possibly 2-hydroxy-3 : ω-dimethoxyacetophenone) has two OMe groups and yields an oxime, m.p. 126°. (V) is obtained from (VI) by means of Ac₂O and NaOAc. (I) is possibly 2-methyl-3 : 8-dihydroxychromone. Reductive acid was obtained from a polyuronate by heating with dil. H₂SO₄ (autoclave). CH. ABS. (7)

Constitution of miliacin. H. ITO (*J. Chem. Soc. Japan*, 1934, 55, 910—913).—Miliacin (I) is isolated from the unsaponifiable fraction of millet-seed oil; when distilled with Zn, it yields an oil, b.p. 283—289°/0.76 mm., [α]_D²⁰ +11.4°, and a resinous mixture of two substances, m.p. 116—118°, [α]_D¹⁷ +26.8°, and m.p. 187°, [α]_D¹⁸ +18.4°. (I) on Se dehydrogenation affords a liquid, C₁₃H₁₄(?) (picrate, m.p. 131°), and a substance, m.p. 187—188°, [α]_D¹⁵ -21.4°. CH. ABS. (7)

Composition of *Salvia miltiorrhiza*. I. (Chinese drug, tan-shin.) M. NAKAO and T. FUKUSHIMA (J. Pharm. Soc. Japan, 1934, **54**, 844—858).—The three cryst. substances isolated from the EtOH extract of tan-shin are termed *tanshinones* and it is suggested that they are derived from an *o*-diketone; colour reactions are described. *Tanshinone* I (I), $C_{18}H_{12}O_3$, m.p. 231° (*quinoxaline*, m.p. 218—219°; *oxime*, m.p. 169—171°; *acetate*, m.p. 204—207°; *quinol*, m.p. 75—85°), affords an *acid*, $C_{18}H_{14}O_5$ (dibasic?), m.p. 265° (*anhydride*, m.p. 185°), which on oxidation yields a dibasic *acid* (II), $C_{18}H_{10}O_4$, m.p. 193°, and an *acid*, $C_{18}H_{12}O_5$ or 6 , m.p. 319°; yielding (II) and a neutral substance, m.p. 110—120°, with EtOH-KOH. *Tanshinone* II, $C_{18}H_{18}O_3$, m.p. 216° (*quinoxaline*, m.p. 206°; *oxime*, m.p. 198°), is more sol. than (I). *Tanshinone* III, $C_{19}H_{20}O_3$, m.p. 182° (*quinoxaline*, m.p. 149°; *oxime*, m.p. 170—172°), is even more sol.

CH. ABS. (r)

Cardiac glucosides. XI. Identity of α -scillanic acid with allocholanolic acid. A. STOLL, A. HOFMANN, and A. HELFENSTEIN (Helv. Chim. Acta, 1935, **18**, 644—659; see this vol., 609).—Scillaridin A is best converted by sublimation in vac. into anhydro-scillaridin A, which is hydrogenated (PtO₂ in AcOH) to scillanic acid (I) and decahydroanhydroscillaridin. Repeated crystallisation of (I) from AcOH raises the m.p. to 165—166°. Treatment of this acid with CH₂N₂ and purification of the product from MeOH affords *Me* α -scillanate (II), m.p. 94° (which does not depress the m.p. of *Me* allocholanate), and *Me* β -scillanate (III), m.p. 72—74°. *Pr*^a scillanate, m.p. 104°, does not depress the m.p. of *Pr*^a allocholanate. Hydrolysis of (II) yields α -scillanic acid, m.p. 172—173°, identical with allocholanolic acid. β -Scillanic acid, m.p. 143—145°, is derived from (III). The prep. of pure allocholanolic acid and its derivatives and of cholanolic acid is described. Sufficient evidence is not available to enable a decision to be made between the C₂₄ and C₂₅ formulation of (I).

H. W.

Saponins. O. DAFERT [with F. BAUER, M. BAUER, V. CAPESIUS, and S. GREIFINGER]. **Saponin and sapogenin of *Chenopodium ambrosioides*, L.** O. DAFERT [with V. CAPESIUS and S. GREIFINGER] (Sci. Pharm., 1934, **5**, 84—86; Chem. Zentr., 1934, ii, 3389; cf. this vol., 348).—All parts of *C. ambrosioides* contain a saponin (I), the distribution of which is discussed. (I) is isolated by extraction with EtOH and purified by extraction with Et₂O; it contains a free CO₂H. Hydrolysis of (I) (HCl) affords *chenopodiumsapogenin* (II), $C_{30}H_{48}O_4$, m.p. 271—272 (K salt; *Ac*₁ derivative, m.p. 180°; *Br*₂-compound, $C_{30}H_{46}O_4Br_2$, m.p. 210°). (II) gives the Liebermann reaction and contains one CO₂H and two OH; treatment with EtOH-HCl gives a substance, $C_{28}H_{44}O_4$, m.p. 376°, and another substance, m.p. 208°.

H. N. R.

[**Sulphite liquor lactone and tsugaresinol.**] K. H. SLOTTA (Helv. Chim. Acta, 1935, **18**, 701).—Comment on the publication of Emde *et al.* (this vol., 623).

H. W.

Constitution of lac. Pure lac resin.—See B., 1935, 465.

Transformation of rhodoxanthin into zeaxanthin. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1935, **18**, 477—480).—Reduction of dihydro-rhodoxanthin in C₆H₆ with Al(OPrⁱ)₃ in PrⁱOH gives zeaxanthin, m.p. 205° (*acetate*, m.p. 154—155°).

H. W.

Amber. III. L. SCHMID and H. KÖRPETH (Monatsh., 1935, **65**, 348—350; cf. A., 1933, 831).—The trimethylnaphthalene from the EtOH-insol. portion of amber with Se, is 1:2:5-C₁₀H₅Me₃ (cf. Ruzicka and Hosking, A., 1931, 231) oxidised with aq. KMnO₄ to 1:2:3-C₆H₃(CO₂H)₃ and 1:2:3:4-C₆H₂(CO₂H)₄.

F. R. G.

Autoxidation of α -pinene and catalysts related thereto. K. SUZUKI (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 179—191).—The oxidation of *d*- α -pinene is strongly catalysed by the oxides and many salts of Pb, Co, and Mn, to give, above 40°, verbenone (I) and a polymeride; below 20°, a gum containing mainly an unsaturated peroxide which decomposes at 140° to a mixture of verbenol, (I), and a polymeride. Pt, Ag, Cr, and Ti oxides are less active. Charcoal and SiO₂ gel are inactive.

J. L. D.

Hydrocarbons of the terpene-aromatic series. II. Bornylbenzene. L. KAMIENSKI and P. WIERZCHOWSKI (Rocz. Chem., 1935, **15**, 92—98).—Bornyl chloride, C₆H₆, and AlCl₃ are maintained under reduced pressure (20—30 mm.) for 18 hr., with occasional addition of AlCl₃ in C₆H₆, when *bornylbenzene*, b.p. 117—118°/1.5 mm. [p-NO₂-, b.p. 168—169°/1 mm., p-NH₂-, b.p. 147—148°/1 mm., p-SO₃H-, p-SO₂NH₂-, m.p. 167°, and p-Br-derivative (I), b.p. 154—155°/1 mm.], is obtained in good yield. *p*-Bornylbenzoic acid, m.p. 195°, is obtained by heating MeI, I, Mg, and (I) in Et₂O at 36° for 4 hr., and then passing CO₂ through the mixture at 0° for 3 hr.

R. T.

Pasteur's principle of molecular dissymmetry. Dextro- and lævo-camphoric acids.—See this vol., 684.

Reactions of the α -mononitrile of camphoric acid. F. SALMON-LEGAGNEUR (Compt. rend., 1935, **200**, 1222—1224).—The chloride of camphoro-nitrile (I) with AlCl₃ in CHCl₃ affords 3-cyano-1:1-trimethyl- Δ^2 -cyclopentene, b.p. 86—88°/11 mm. (hydrolysed to isolauronolamide), which is different from the product obtained in C₆H₆ solution (cf. A., 1927, 1081). (I) with CHNa(CO₂Et)₂ and ZnPhBr in C₆H₆ gives, respectively, *Et* 3-cyano-1:2:2-trimethylcyclopentanoylmalonate (II), m.p. 53°, and -cyclopentyl Ph ketone (III), m.p. 93—94°. (III) is easily hydrolysed to the *amide*, m.p. 150—170° (decomp.), further hydrolysed to the *acid* (IV) with difficulty. (II), (III), or (IV) does not give an oxime or semicarbazone. (I) with excess of MgPhBr (cf. A., 1926, 613) gives 3-cyano-, m.p. 161—162° [also obtained from MgPhBr and (III)], 3-benzoyl-1-hydroxybenzhydryl-1:2:2-trimethylcyclopentane, m.p. 141—142°, and a small amount of 1:3-dibenzoyl-1:2:2-trimethylcyclopentane, m.p. 118°.

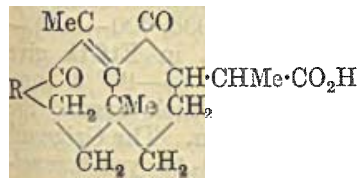
J. L. D.

New oxidation product of camphor. K. MIYAKE (Proc. Imp. Acad. Tokyo, 1935, **11**, 106—109). Camphor and CrO₃-AcOH-Ac₂O at 60—80 give

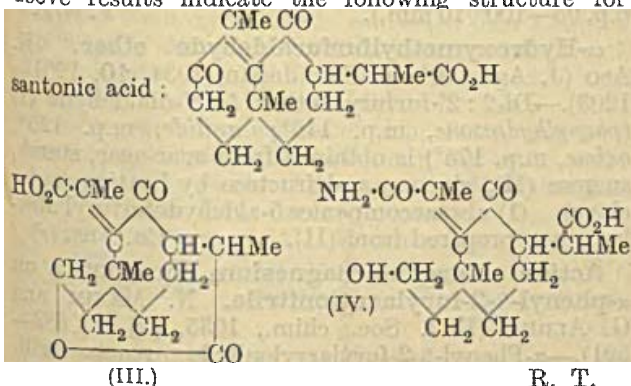
camphorquinone (traces), 5- (6%) and impure 6-*ketocamphor* (I) (18%), m.p. about 180° (*dioxime*, m.p. 241—242°, α 0°). (I) with 2% HCl or 5% Na_2CO_3 at 60° gives dl-4-*keto*-2:2:3-*trimethylcyclopentane-1-acetic acid*, m.p. 65—66° [*semicarbazone*, m.p. 240°; *oxime*, m.p. 185°; *Me* ester, b.p. 126°/1 mm., 223°/760 mm. (*semicarbazone*, m.p. 186°)], resolved by quinine to the *l*-form, an oil, $[\alpha]_D^{15}$ -77.5° (*semicarbazone*, m.p. 240°; *oxime*, m.p. 184°); the *d*-form, from campholenitrile, has $[\alpha]_D^{15}$ +79.17° and gives derivatives with identical m.p. R. S. C.

Mercury derivatives of camphor. II. J. D. LOUDON (J.C.S., 1935, 535—536).—3-*Chloro*- (I), m.p. 157° (decomp.), and 3-*bromo-camphor*-10-, m.p. 165° (decomp.), and 3-*chloro*- and 3-*bromo-camphor*- π -*sulphinic acid*, m.p. 149° (decomp.), are prepared from the corresponding acid chlorides and Na_2SO_3 . (I) and HgCl_2 in $\text{C}_5\text{H}_5\text{N}$ give 3-*chlorocamphor*-10-*mercuri-chloride*, m.p. 218—219°, $[\alpha]_{5461}^{16}$ +5.0° in CHCl_3 , which with Cu forms *bis*-3-*chlorocamphor*-10-*mercury*, m.p. 175°, $[\alpha]_{5461}^{16}$ -22.8° in $\text{C}_5\text{H}_5\text{N}$, with Br-KBr affords 3-*chloro*-10-*bromocamphor*, and with I yields 3-*chloro*-10-*iodocamphor*, m.p. 89°. 3-*Bromo-camphor*-10-*mercuri-chloride*, m.p. 232°, $[\alpha]_{5461}^{16}$ +44.8° in $\text{C}_5\text{H}_5\text{N}$, -*bromide*, m.p. 195°, and -*iodide*, m.p. 173°, *bis*-3-*bromocamphor*-10-*mercury*, m.p. 188—189°, $[\alpha]_{5461}^{16}$ +29.13° in $\text{C}_5\text{H}_5\text{N}$, and 3-*bromo*-10-*iodo-camphor*, m.p. 88—89°, are similarly prepared. F. R. S.

Structure of santonin and santonic acid. A. ABKIN and S. MEDVEDEV (J. Gen. Chem. Russ., 1934, 4, 1407—1414).—Santonin (I) and liquid NH_3 (3 days; room temp.) yield the *amide*, m.p. 162—163° (decomp.), $[\alpha]_D^{25}$ -15.33° in EtOH, of



santoninic acid. Santonic acid, prepared in 60% yield from (I) and aq. $\text{Ba}(\text{OH})_2$, when oxidised with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ yields a lactone (II), m.p. 233—234°, $[\alpha]_D^{24}$ -23.46° in EtOH, converted into the isomeric lactone (III), m.p. 142.5—143°, $[\alpha]_D^{25}$ +159.87° in EtOH, by heating with aq. NaOH. (II) and liquid NH_3 (30 min.; room temp.) yield the *amide* (IV), m.p. 194—195° (decomp.), $[\alpha]_D^{25}$ +62.55° in EtOH, which affords the lactam (V), m.p. 217—217.5°, $[\alpha]_D^{25}$ +133.2° in EtOH, when heated at 75—80° with 5% aq. NaOH. The above results indicate the following structure for



3 E

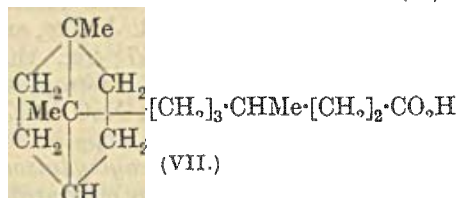
R. T.

Methylsantene compounds derived from fenchyl alcohol. N. J. TOIVONEN (Suomen Kem., 1935, 8, B, 10—12).—Isolation of mesantenol (I), b.p. 105°/25 mm., from mesantene (A., 1930, 348) is best effected by treatment with $\text{AcOH-H}_2\text{SO}_4$ until 30—35% esterification has occurred; the alcohol obtained by hydrolysis of the acetate is purified through its *H* phthalate, m.p. 105—106°. Oxidation of (I) with $\text{Na}_2\text{Cr}_2\text{O}_7$ -aq. H_2SO_4 affords mesantenone, b.p. 201°, α_D -0.12° (10 cm.), purified through its *semicarbazone*, m.p. 206—207°. J. W. B.

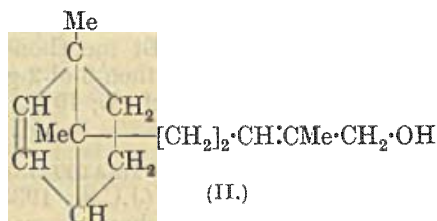
Syntheses in the sesquiterpene series. II. Condensation of ethyl oxalate and tetrahydrocarvone. A. E. BRADFIELD, E. R. JONES, and J. L. SIMONSEN (J.C.S., 1935, 315—317; cf. this vol., 88).—*l*-Tetrahydrocarvone (2:4-*dinitrophenylhydrazone*, m.p. 133°) and $\text{Et}_2\text{C}_2\text{O}_4$ and NaOEt-EtOH at 0° afford *Et* α -*keto*- γ -methyl- γ -isopropylsuberate (I), b.p. 148.5/1.4 mm. (2:4-*dinitrophenylhydrazone*, m.p. 50°; *Ac* derivative, b.p. 163°/2 mm.), separated from unchanged materials by hydrolysis (MeOH-KOH) to the acid (II) (*Ag* salt; *Me* ester, b.p. 153°/2.5 mm.) and subsequent esterification ($\text{EtOH-H}_2\text{SO}_4$). A cyclic β -ketonic ester (cf. A., 1913, i, 1066) is not formed owing to the fission even at 0° of the intermediate glyoxylic ester by NaOEt to (I). (I) is a mixture of the ketonic and enolic forms; its $[R_L]$ suggests that it is mainly enolic. Oxidation of (II) with H_2O_2 -NaOH affords *d*- α -methyl- δ -isopropylpimelic acid (cf. A., 1921, i, 37) (*diamide*, m.p. 181—182°; *di-p*-toluidide, m.p. 156—157°). (II) with H_2SO_4 at 80—85° gives the lactone of Δ^1 -menthen-2-ol-3-glyoxylic acid, m.p. 115° (2:4-*dinitrophenylhydrazone*, decomp. 95°). Under similar conditions *l*-menthone and $\text{Et}_2\text{C}_2\text{O}_4$ gave *Et* menthone-2-carboxylate and a little Δ^3 -menthen-3-ol-2-glyoxylo-lactone, m.p. 138° (lit. 142.5°) (cf. A., 1913, i, 1066). No ring fission occurred. H. G. M.

α - and β -Santalols. A. E. BRADFIELD, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1935, 309—315).— α - (I) and β -santalol (II) have been obtained pure by distilling Mysore *Santalum album* oil. (I) has b.p. 166—167°/14 mm., α_{5461}^{25} +10.3° (lit. α_D +1°) [allophanate, m.p. 162—163°; strychnine salt of the *H* phthalate, m.p. 144—145° (lit. 155°)]. (I) oxidised by O_3 gives $\text{CH}_3\text{Ac-OH}$, tricycloekasantalic acid (III), and tricycloekasantalal [*semicarbazone*, m.p. 163—164° (lit. about 156°)]. (I) with SOCl_2 and $\text{C}_5\text{H}_5\text{N}$ gives α -santalyl chloride (IV), b.p. 155—158°/14 mm., oxidised (KMnO_4) to (III) and a chloroketone, b.p. 150—160°/17 mm., and with O_3 gives CH_3O . (IV) and $\text{CHNa}(\text{CO}_2\text{Et})_2$ give *Et* α -santalylmalonate, b.p. 212—213°/13 mm., hydrolysed to the acid (V), m.p. 120—121° (*K* salt), which loses CO_2 at 160—180° to give α -santalylacetic acid (VI), b.p. 188°/2 mm. (V) is oxidised by KMnO_4 to β -*keto*- δ -teresantalylbutylmalonic acid (*semicarbazone*, decomp. 172—173°), and by O_3 to (III), no keto-acid being detected. (VI) is oxidised by KMnO_4 to γ -*keto*- ϵ -teresantalylhexoic acid, $\text{C}_{16}\text{H}_{24}\text{O}_3$ (*Me* ester, b.p. 211°/17 mm.; *semicarbazone*, m.p. 176—177°, and phenyl*semicarbazone*, m.p. 192—193°, of *Me* ester), which when distilled (13 mm.) gives H_2O and a neutral oil, b.p. 200—210°, is stable to NaOBr at 0°, but at 28° gives an oil

which is freed from Br by treatment with NaOH-H₂O-Zn at 100°, affording β -teresanalylpropionic acid, C₁₃H₂₀O₂ (Ag salt; Me ester, b.p. 140–145°/19 mm.). (V) is hydrogenated (Pd on norit) to the H₂-acid, which is converted at 160–180° into dihydro- α -santalylacetic acid, b.p. 208–210°/15 mm. [α -aminoanthraquinonyl derivative, m.p. 105–106° (sinters 94°)]. This with HBr-AcOH in a sealed tube at 100° affords bromotetrahydrosantalylacetic acid, which is reduced (Na-EtOH) to tetrahydrosantalylacetic acid (VII), b.p. 210–213°/16 mm. (p-bromophenacyl, m.p. 52–53°, and diphenacyl derivative, m.p. 61–62°), considered to be as shown. Pure (II) has b.p.



177–178°/17 mm., α_{D161} –87.1° (allophanate, m.p. 159–160°). The strychnine salt of the H phthalate forms mixed crystals with the corresponding salts of (I). (II) with O₃ gave CH₂O and CH₃Ac·OH. The following derivatives of (II) were prepared in a similar manner to those of (I): β -santalyl chloride, b.p. 161°/20 mm.; β -santalylmalonic acid, m.p. 99–101° (Et₂ ester, b.p. 219–220°/15 mm.) (with O₃ gave CH₂O). This acid was hydrogenated in EtOH solution at 50–60° and 3 atm, giving tetrahydro- β -santalylacetic acid identical with (VII). Therefore the constitution of (II) is as shown. Although (V) is an apparently



homogeneous cryst. solid, the products of oxidation by KMnO₄ and by O₃ show that the ethylenic linking in the side chain is mobile, either under the action of reagents or merely on dissolution. This is regarded as tautomerism (cf. A., 1932, 144, 1111).

H. G. M.

Terpene compounds. I. Synthetical investigations in the cadinene group. J. C. BARDHAN and S. K. BANERJI (J.C.S., 1935, 476–479).—Et Δ^3 -tetrahydro-*p*-toluate (I) (improved prep.), CN·CH₂·CO₂Et, and Na give Et 1-carbethoxy-4-methylcyclohexane-2- α -(α -cyanoglutarate), b.p. 198°/2 mm., hydrolysed to the - α -glutarate, b.p. 168°/2 mm. Cyclisation (Na-C₆H₆) and hydrolysis of this ester affords 1-keto-6-methyldecalin-4-carboxylic acid, m.p. 191° (semicarbazone, m.p. 216°), the Et ester, b.p. 142°/3 mm. (semicarbazone, m.p. 192°; oxime, m.p. 160°), of which with MgMeI gives a neutral product, dehydrogenated (Se) to cadalene, and an acidic product in small yield. (I) and CN·CHNa·CO₂Et form Et 1-carbethoxy-4-methylcyclohexane-2- α -cyanosuccinate (II), b.p. 215°/7 mm., hydrolysed to -2-succinate, b.p. 165–167°/2 mm., which is cyclised to Et 7-methyl-

[0 : 3 : 4-dicyclo]nonan-2-one-3 : 4-dicarboxylate, b.p. 186°/7 mm. [semicarbazone of acid, m.p. 221–222° (decomp.)], or followed by MeI to Et 3 : 7-dimethyl-[0 : 3 : 4-dicyclo]nonan-2-one-3 : 4-dicarboxylate, b.p. 175°/8 mm. (II) and CHMeBr·CO₂Et afford Et 1-carbethoxy-4-methylcyclohexane-2-(α -cyano- α' -methylsuccinate), b.p. 208°/8 mm., hydrolysed to -2- α' -methylsuccinate, b.p. 175°/7 mm.

F. R. S.

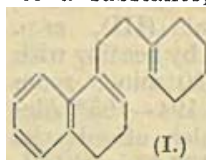
Caryophyllenes. II. G. R. RAMAGE and J. L. SIMONSEN (J.C.S., 1935, 532–535).—During the purification of dehydronorcaraphyllenic acid (I) an optically inactive acid, C₈H₁₂O₄, m.p. 148–149°, has been isolated. Oxidation of (I) with O₃ gives α' -keto- α -dimethylglutaric acid (2 : 4-dinitrophenylhydrazones A (+0.5EtOH), decomp. 243°, B (+0.5EtOH), decomp. 215–217°, and C (+4.5H₂O), m.p. 132°; p-nitrophenylhydrazone, decomp. 192°; phenylsemicarbazone, decomp. 165°, which is oxidised (H₂O₂) to as-dimethylsuccinic acid. (I) is probably

Bromocaryophyllenic acid is converted (Ag₂O) into the OH-acid, which is oxidised (PbO₂ followed by KMnO₄) to *d-cis*-norcaryophyllenic acid. Caryophyllenic acid is probably

Hippuric acid and Ac₂O-NaOAc give 2-phenyl-4-isopropylideneoxazolone, m.p. 99–100°, which with KOH followed by HCl forms α -benzamido- β - β -dimethylacrylic acid, decomp. 217°, and with HCl yields dimethylpyruvic acid (phenylsemicarbazone, m.p. 137°; p-nitrophenylhydrazone, m.p. 155°; 2 : 4-dinitrophenylhydrazone, m.p. 194–195°).

F. R. S.

Synthesis of polyterpenoid compounds. I. J. W. COOK and A. DANSI (J.C.S., 1935, 500–502).—Et Δ^1 -cyclohexenylacetate and Na in EtOH give β - Δ^1 -cyclohexenylethyl alcohol, b.p. 85–90°/8 mm. (3 : 5-dinitrobenzoate, m.p. 80°), which forms the corresponding bromide, b.p. 90°/7 mm. The Grignard compound with cyclohexanone gives β - Δ^1 -cyclohexenylethylcyclohexanol, b.p. 89–91°/0.3 mm., dehydrated to a substance, b.p. 97–98°/4–5 mm., and with



α -tetralone forms a carbinol, b.p. 140–175°/6 mm., dehydrated to a hydrocarbon (I), dehydrogenated (Se) to chrysene. Reduction (Na-Hg) of Et α -4-(methyl- Δ^1 -cyclohexenyl)propionate yields β -(4-methyl- Δ^1 -cyclohexenyl)-*n*-propyl alcohol, b.p. 105–109°/10 mm. (3 : 5-dinitrobenzoate, m.p. 71°; bromide, b.p. 95–100°/10 mm.).

F. R. S.

ω -Hydroxymethylfurfuraldehyde ether. K. ASO (J. Agric. Chem. Soc. Japan, 1934, 10, 1201–1203).—Di-2 : 2'-furfuryl ether 5 : 5'-dialdehyde (I) (phenylhydrazone, m.p. 145°; anilide, m.p. 125°; oxime, m.p. 175°) is obtained from agar-agar, starch, sucrose (II), glucose, and fructose by heating (autoclave). (I) also accompanies 5-aldehydfurfuryl alcohol when prepared from (II).

CH. ABS. (r)

Action of organo-magnesium compounds on α -phenyl- β -2-furylacrylonitrile. N. MAXIM and G. ALDEA (Bull. Soc. chim., 1935, [v], 2, 582–591).— α -Phenyl- β -2-furylacrylonitrile reacts with the appropriate MgRX to give saturated nitriles

$C_4H_3O \cdot CHR \cdot CHPh \cdot CN$, whence the corresponding acids are obtained. Thus are prepared: α -phenyl- β -2-furyl-valeronitrile, b.p. $181^\circ/18$ mm., and -valeric acid, m.p. 93° (chloride, b.p. $167^\circ/18$ mm.; amide, m.p. 136° ; Et ester, b.p. $180^\circ/22$ mm.), -n-hexonitrile, b.p. $191^\circ/23$ mm., and -n-hexoic acid, m.p. 124° (chloride, b.p. 174 — $175^\circ/18$ mm.; amide, m.p. 164° ; Et ester, b.p. $184^\circ/18$ mm.), -8-methyl-n-hexonitrile, b.p. $187^\circ/19$ mm., and -8-methyl-n-hexoic acid, m.p. 107° (chloride, b.p. $185^\circ/25$ mm.; amide, m.p. 132° ; Et ester, b.p. 184 — $185^\circ/18$ mm.), and $\alpha\beta$ -diphenyl- β -2-furyl-propionitrile, b.p. $225^\circ/15$ mm., and -propionic acid, m.p. 172° (chloride, b.p. $210^\circ/14$ mm.; amide, m.p. 179° ; Et ester, b.p. $213^\circ/10$ mm.). J. W. B.

α -Phenyl- β -2-furylacrylic acid and its derivatives. N. MAXIM and N. STANCOVICI (Bull. Soc. chim., 1935, [v], 2, 600—605).—The following derivatives of α -phenyl- β -2-furylacrylic acid (Rohmer, A., 1898, i, 300, modified) are prepared by usual methods: chloride, b.p. $183^\circ/15$ mm., m.p. 43° ; Me, m.p. 88° , Et, m.p. 54° , Pr, b.p. $187^\circ/17$ mm., Bu, b.p. $204^\circ/17$ mm., and n -C₅H₁₁, b.p. $210^\circ/17$ mm., esters; amide, m.p. 127° ; diethylamide, b.p. $211^\circ/17$ mm.; anilide, b.p. $255^\circ/11$ mm., m.p. 104° ; methyl-, b.p. $234^\circ/17$ mm., and ethyl-anilide, b.p. $236^\circ/18$ mm.; dimethyl-, b.p. $205^\circ/16$ mm., and diphenyl-amide, b.p. $272^\circ/12$ mm., m.p. 108° . J. W. B.

Geometrical inversion in the acids derived from coumarins. B. B. DEY, R. H. R. RAO, and T. S. SESHADRI (J. Indian Chem. Soc., 1935, 12, 140—141).—Corrections and further experimental details to previous work (this vol., 211) are given. J. W. B.

Dimethyldiphenylene oxide and its oxidation product. Y. SUGI and H. SHINDO (J. Pharm. Soc. Japan, 1934, 54, 829—844).—3-Iodo-2-methoxytoluene (I) heated with Cu yields 2:2'-dimethoxy-3:3'-dimethyldiphenyl, m.p. 61° ; this with HI affords 2:2'-dihydroxy-3:3'-dimethyldiphenyl, m.p. 89° (diacetate, an oil; dibenzoate, m.p. 147°), which with either ZnCl₂ or HBr gives 1:8-dimethyldiphenylene oxide, m.p. 89° . 2-Nitro-3-hydroxytoluene (acetate, m.p. 58°) is converted into 2-amino-3-methoxytoluene, b.p. $96^\circ/4$ mm. (benzoate, m.p. 136°), and then into 2-iodo-3-methoxytoluene, m.p. 49° , b.p. $99^\circ/1$ mm.; this, treated similarly to (I), yields 2:2'-dimethoxy-, m.p. 124° , and 2:2'-dihydroxy-6:6'-dimethyldiphenyl, m.p. 164° (diacetate, m.p. 87° ; dibenzoate, m.p. 136°), and 4:5-dimethyldiphenylene oxide, m.p. 62° . In a similar manner, 4-nitro-3-methoxytoluene is converted into 4-amino-, b.p. 93 — $94^\circ/3$ mm., and 4-iodo-3-methoxytoluene, b.p. $101^\circ/1.5$ mm.; 2:2'-dimethoxy-, m.p. 122° , and 2:2'-dihydroxy-4:4'-dimethyldiphenyl, m.p. 120° (diacetate, an oil; dibenzoate, m.p. 148°), and 2:7-dimethyldiphenylene oxide (II), m.p. 80 — 81° . Oxidation of (II) yields 7-carboxy-2-methyldiphenylene oxide, m.p. $> 280^\circ$, decarboxylated to 2-methyldiphenylene oxide, m.p. 65° . More drastic oxidation of (I) affords 2:7-dicarboxydiphenylene oxide (Me₂ ester, m.p. 245°), decarboxylated to diphenylene oxide. CH. ABS. (r)

Transformation of *d*-catechin into cyanidin chloride. H. APPEL and R. ROBINSON (J.C.S.,

1935, 426—429).—Br in technical (not pure) dioxan and *d*-catechin Me₄ or Me₅ ether give bromocyanidin Me₄ ether bromide, which with PhOH-I-P gives cyanidin iodide and thence the chloride. F. R. S.

Constitution of fustin. I. Constitution of the wood of *Rhus succedanea*, L. Non-glucoside nature of fustin. II, III. Constitution of hazeic acid. IV. Constitution of fustin and synthesis of methylfustin. T. OYAMADA (J. Chem. Soc. Japan, 1934, 55, 755—762, 763—774, 775—785, 785—790).—I. Extraction with EtOAc yields fisetin and fustin (I). (I) gives neither pentoses nor hexoses with H₂SO₄.

II, III. (I) with CH₂N₂ affords methylfustin (II), m.p. 142 — 143° , which with alkali gives 7:3':4'-trimethoxy-3-hydroxyflavone and trimethylhazeic acid (III), m.p. 138° . This latter with CH₂N₂ yields the Me ester (IV), m.p. 171 — 172° , of tetramethylhazeic acid (V), m.p. 188 — 190° . (IV) and (V) are also obtained directly from (I) with Me₂SO₄. (III) with acids affords anhydrotrimethylhazeolactone, C₁₈H₁₆O₅, m.p. 185° , which gives anhydrotrimethylhazeic acid (VI) on prolonged heating with alkali. (VI) with CH₂N₂ yields the Me ester, m.p. 116° , of anhydro-tetramethylhazeic acid, m.p. 166 — 168° [also by fusion of (V)]. (V) with KMnO₄ affords a ketone, m.p. 98.5 — 99.5° , the oxime (VII), m.p. 134 — 136° , of which is converted by PCl₅ into an amide, m.p. 120 — 122° , hydrolysed to a homoveratric acid, m.p. 96 — 98° , and (?) 2:4-dimethoxyaniline, m.p. 36 — 38° . Hazeic acid is therefore 2:4-dihydroxybenzyl-3:4-dihydroxyphenylglycollic acid.

IV. 2-Acetoxy-3':4:4'-trimethoxychalkone is converted into the dibromide, m.p. 122 — 124° , and thence into the diacetate, m.p. 133 — 134° ; this undergoes ring-closure with HCl, yielding (II), m.p. 142 — 143° . (I) is thus dihydrofisetin. CH. ABS. (r)

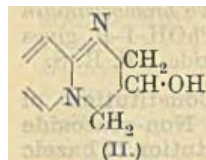
Action of sodium sulphide on polymethylene halides and the formation of "polythiophans." R. W. BOST and M. W. CONN (J. Elisha Mitchell Sci. Soc., 1934, 50, 182—188).—The formation and physical and chemical properties of polymerides of thiophan [tetrahydrothiophen] are described. The m.p. of (C₃H₆S)₆, (C₅H₁₀S)₅, (C₅H₁₀SO)₅, and (C₆H₁₂S)₄ are 51° , 66° , 220° (decomp.), and 68° , respectively. Vigorous reduction gives H₂S and a hydrocarbon, but no mercaptan. CH. ABS. (e)

Reduction of pyridine to piperidine in presence of nickel. M. I. USCHAKOV, S. S. LIFSCHITZ, and N. V. JDANOVA (Bull. Soc. chim., 1935, [v], 2, 573—576).—C₅H₅N is readily reduced to piperidine, without the formation of any by-products, by H₂ and a Ni-0.4%Pd-SiO₂ gel (or Ni-Co) catalyst (I) at 130 — 150° . When fatigued, (I) is reactivated by addition of H₂O at 150 — 450° , and subsequent reduction at 450° . J. W. B.

Effect of unipolar substituents on the critical energy and probability factors in the interaction of benzyl bromide with pyridine and α -picoline.—See this vol., 710.

Condensation of aliphatic oxides with 2-amino-pyridine. I. KNUNJANZ (Compt. rend. Acad. Sci.

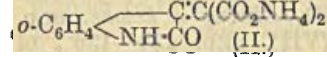
U.R.S.S., 1935, 1, 501—506).—2-Aminopyridine (I) condenses with dry $(\text{CH}_2)_2\text{O}$ in MeOH at room temp. to give 2-imino-1- β -hydroxyethyl-1:2-dihydropyridine, b.p. 184—185°/17 mm., m.p. 112—113°, hydrolysed to the corresponding 2-keto-compound, b.p. 185°/9 mm., m.p. 100°. (I), therefore, probably reacts as 2-imino-1:2-dihydropyridine. With epichlorohydrin (I) gives the hydrochloride, m.p. 190°, of substance (II) [platinichloride, m.p. 215° (decomp.); oily base]. J. W. B.



Manufacture of therapeutic agents.—See B., 1935, 430.

Condensation reactions of cyclic ketones. III. Oxindole-malonic acid derivatives. H. G. LINDWALL and A. J. HILL (J. Amer. Chem. Soc., 1935, 57, 735—737; cf. A., 1930, 480).—Isatin (I) and $\text{CH}_2(\text{CO}\cdot\text{NH}_2)_2$ or $\text{CH}_2(\text{CO}\cdot\text{NHPh})_2$ in 3% NH_3 -EtOH at 70° give 3-diformamido-, m.p. 245°, and 3-diformanilido-methyleneoxindole, m.p. 320°. $\text{CH}_2(\text{CO}_2\text{Et})_2$ and a little NH_4Et in EtOH at room temp. give *Et*₄oxindole-3:3-dimalonate, m.p. 152°. (I) and 10% NH_3 -EtOH at 60° give the salt (II), giving with HCl

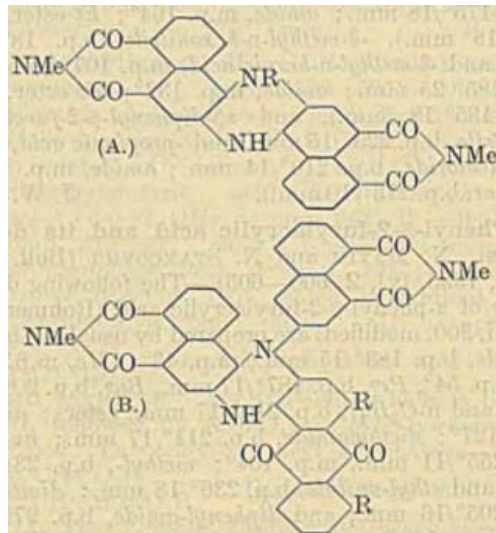
o- C_6H_4 — $\text{C}(\text{CO}_2\text{NH}_4)_2$ at room temp. 2-hydroxycinchoninic acid (III), with HCl-EtOH the Et ester of (III), with red P and HI at 140° 2-keto-1:2:3:4-tetrahydrocinchoninic acid; the Ag₂ salt with H_2SO_4 gives (III) and 1 mol. of CO_2 , but with H_2S at 40° a substance, m.p. about 122°, which with warm H_2O_2 yields (I). R. S. C.



[Preparation of] isatin derivatives.—See B., 1935, 444.

Derivatives of naphthalomethylimide. E. M. FRANCIS and J. L. SIMONSEN (J.C.S., 1935, 496—499).—Naphthalomethylimide (I) and HNO_3 in boiling AcOH give 3-nitronaphthalomethylimide. (II), m.p. 226—228°, also obtained from the imide, m.p. 308°, sinters 305°, of 3-nitronaphthalic anhydride with Me_2SO_4 and K_2CO_3 . (II) in boiling aq. EtOH with NaHSO_3 yields 3-aminonaphthalomethylimide (III), m.p. 278—280° (azo- β -naphthol, m.p. 315—317°, and Ac, m.p. 329—330°, derivative), the diazonium derivative of which with aq. H_2SO_4 and $(\text{CHCl}_2)_2$ yields 3-hydroxynaphthalomethylimide (IV), m.p. 272—273°, and 3-chloronaphthalomethylimide, m.p. 182—183°. 1-Chloroanthraquinone (V) and its 5- (VI) and 4- (VII) -benzamido-derivatives heated with (III), CuCl_2 , and NaOAc in amyl alcohol give respectively 3:1-anthraquinonylamino-naphthalomethylimide, m.p. 286—287°, and its 5-, m.p. 338—339°, and 4-, m.p. 330—331°, -benzamido-derivatives, but in PhNO_2 at 200—210° (7 hr.) (V) yield anthraquinone with a compound, $\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_4$, regarded as the dihydroazine (A; R=H), whilst (VI) and (VII) give respectively a red compound, $\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_4$ (VIII), m.p. 331—333°, and a purple compound, $\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_4$ (IX), m.p. 320—323°, together with 1-benzamidoanthraquinone. (VIII) and (IX) are regarded as either (A; R=4- or 5-benzamidoanthraquinonyl) or (B; R=H or NHBz). Nitration of (I) with HNO_3 in boiling Ac_2O gives 3:6-dinitronaphthalomethylimide, m.p. 280°, also obtained from 3:6-dinitronaphthalic anhydride and dil. aq. NH_2Me , and reduced by NaHSO_3 to 3:6-diaminonaphthalomethylimide, m.p. > 400° (Ac₂, decomp. 383—384°, and 4-benzamidoanthraquinonyl derivative, m.p. 295—297°, sinters 280°). 4-Benzoylnaphthalic anhydride with dil. aq. NH_2Me gives

4-benzoylnaphthalomethylimide, m.p. 190—191°. Fusion of (IV) with KOH at 230° (2 hr.) gives an insol. phenol which with Na_2CO_3 and Me_2SO_4 in PhNO_2 yields the α -di-imide of 1:7-(or 1:12)-dimethoxyperylene-3:4:9:10-tetracarboxylic acid, m.p. > 400°, a purple vat dye, which in conc. H_2SO_4 is oxidised with MnO_2 in presence of H_3BO_3 to a phenol, methylated as above to the isomeric β -di-imide, m.p. > 400°, a red vat dye. F. R. G.



Reactions of 4-hydroxy-2-methylquinoline. A. MEYER and (Mlle.) M. MAURIN (Compt. rend., 1935, 200, 931—933).—4-Hydroxy-2-methylquinoline (I) does not condense with aromatic aldehydes (II), but N^+V salts (III) of (I) heated with (II) in $\text{C}_5\text{H}_5\text{N}$ yield styrylquinolines; (III) also condense with *p*-nitrosoamines to form *p*-aminoanilquinolines (cf. A., 1926, 1153). When treated with alkalis, (III) yield isocyanines. E. W. W.


Synthesis of quinoline derivatives. A. GIACALONE (Gazzetta, 1935, 65, 124—128).—*p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ heated with AcCl , Ac_2O , and ZnCl_2 gives 2-(2'-amino-*m*-tolyl)-4:6-dimethylquinoline, m.p. 252—253° (hydrochloride, decomp. 290°; aurichloride; Ac derivative, m.p. 286°; β -naphtholazo-derivative, m.p. 202—203°). E. W. W.

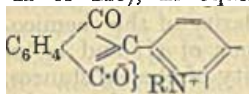
[Manufacture of] 6:7-diethoxy-1-(3':4':5'-triethoxybenzyl)isoquinoline.—See B., 1935, 382.

Production of 6:7-dialkoxy-1-3':4':5'-trialkyloxyphenylisoquinolines. [Spasmolytics.]—See B., 1935, 478.

Constitution of the phthalones. R. KUHN and F. BAR (Annalen, 1935, 516, 155—161).—The K derivative of quinophthalone (I) (Eibner *et al.*, A., 1902, i, 644) with Me_2SO_4 in xylene at 150° anorates its *N*-Me derivative (II), m.p. 249.5° (corr.), oxidised by dil. HNO_3 to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (III) and *N*-methyl-

α -quinolone. Similar methylation of pyrophthalone (IV) affords an *N-Me* derivative (V), $+2\text{H}_2\text{O}$ and anhyd., m.p. 165° (corr.) (perchlorate, m.p. 179°) [also obtained in 30% yield by the action of $\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$ on (IV)], similarly oxidised to (III) and *N*-methyl- α -pyridone. The similarity of the absorption spectra of (I) and (II) and of (IV) and (V) shows that all have

structures of the type $\text{C}_2\text{H}_4 \begin{matrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{matrix} \text{C} :$  ($\text{R} =$
H or Me), in equilibrium with the betaine forms



J. W. B.

Tautomerism of the products of condensation of aromatic aldehydes with barbituric acid. M. KRAKOWSKI (Arch. Chem. Farm., 1935, 2, 164—170).—The products of condensation of barbituric acid with *vanillin*, m.p. 263—270° (decomp.), and with *bourbonal*, m.p. 270° (decomp.), change colour when treated with aq. NaOH, owing to a quinonoid rearrangement; this is not possible in the cases of the compounds with *piperonal*, decomp. 200°, and with *veratraldehyde*, decomp. 270°.

R. T.

R. T.

4(5)- β -Alkylaminoethylglyoxalines. B. GARFORTH and F. L. PYMAN (J.C.S., 1935, 489—492).—*Et* α -amino- γ -phenoxybutyrate hydrochloride, m.p. 210°, is obtained from the corresponding Br-derivative (improved prep.). Reduction of α -aminobutyro lactone hydrobromide (Na-Hg) followed by NH_4CNS gives 4(5)- β -hydroxyethyl-2-thiolglyoxaline, m.p. 193°, oxidised (HNO_3) to 4(5)- β -hydroxyethylglyoxaline (I), m.p. 92° (picrate, m.p. 144°). Esterification and reduction of α -amino- γ -phenoxybutyric acid, followed by NH_4CNS , affords 4(5)- β -phenoxyethyl-2-thiolglyoxaline, m.p. 172°, oxidised (HNO_3) to 4(5)- β -phenoxyethylglyoxaline hydrochloride, m.p. 136—137°, which could not be satisfactorily dephenoxyated. (I) and SOCl_2 yield 4(5)-chloroethylglyoxaline hydrochloride, m.p. 126°, which with the appropriate amine affords 4(5)- β -methylaminoethylglyoxaline dipicrate (+ H_2O), m.p. 188°, dihydrochloride, m.p. 176—177°, and dihydrobromide, m.p. 167°; 4(5)- β -dimethylaminoethylglyoxaline dipicrate, m.p. 233°, and dihydrochloride, m.p. 188°; 4(5)- β -trimethylaminoethylglyoxaline dipicrate, m.p. 212°, and chloride hydrochloride, m.p. 229°; 4(5)- β -ethylaminoglyoxaline dipicrate (+ $2\text{H}_2\text{O}$), m.p. 186°, and dihydrochloride, m.p. 169°; and 4(5)- β -aminoethylglyoxaline (histamine). Fargher and Pyman (J.C.S., 1921, 119, 734) did not obtain 4(5)- β -methylaminoethylglyoxaline by decarboxylation of *dl*-methylhistidine. F. R. S.

F. R. S.

Products of oxidation of 5- α - β - γ -tetrahydroxybutyl-(*d*-arabino)glyoxaline with nitric acid. J. PARROD (Compt. rend., 1935, **200**, 1049—1051).—Glucose with HNO_3 (*d* 1.38) at 100° gives 5-glyoxalylglyoxylic acid (*K* salt; *nitrate*), a little *glyoxaline- α -carboxylic acid*, and the *nitrate* of the lactone of γ -5-glyoxaline- α - β - γ -trihydroxy-(*d*-arabino)butyric acid ($+ \text{H}_2\text{O}$, m.p. 104°). J. L. D.

J. L. D.

Synthesis of 2:2'-dipyridyl from pyridine and ferric chloride and dipyridyl complex salts.

F. HEIN and H. SCHWEDLER (Ber., 1935, **68**, [B], 681—684; cf. A., 1928, 1262).—The optimal conditions for the prep. of 2 : 2'-dipyridyl (I), m.p. 71—72°, consist in heating C_5H_5N and $FeCl_3$ (mol. ratio, 2.5 : 1) for 4 hr. at $330^\circ \pm 10^\circ$. (I) is determined by pptn. as the complex salt with $HgBr_2$. The *compounds* [$(C_5H_4N \cdot NC_5H_4)_2Ag$]NO₃ and [$(C_5H_4N \cdot NC_5H_4)_2Ag$]S₂O₈·H₂O, are described.

H. W.

Complex salts of 2 : 2'-dipyridyl with zinc and cadmium.—See this vol., 714.

Indoles and isatogens. XVII. Benzodipyrroles. II. Two oxindoles of the benzodipyrrole series. P. RUGELI, B. B. BUSSEMAKER, and W. MULLER (Helv. Chim. Acta, 1935, **18**, 613—623; cf. A., 1933, 285).— Et_2 *m*-phenylenediacetate (prep. from *m*-xylene described) is converted by conc. H_2SO_4 and HNO_3 (*d* 1.52) into Et_2 4:6-dinitrophenylene-1:3-diacetate, which is smoothly reduced (H_2 , Ni, EtOH) to Et_2 4:6-diaminophenylene-1:3-diacetate (I), m.p. 68° [picrate, m.p. 135° ; Ac_2 derivative, m.p. 187°]. (I) with boiling 10% HCl affords 2:6-diketotetrahydro-*lin-m*-benzodipyrrole (II) [2:6-dihydroxy α -benzbispyrrole of Davies *et al.* (J.C.S., 1922, **121**, 2652)], which darkens at 255° and becomes charred at 300° ; the Ac_2 derivative has m.p. about 295° (Berl). Et_2 *p*-phenylenediacetate, conc. H_2SO_4 and HNO_3 (*d* 1.52) afford Et_2 2-nitrophenylene-1:4-diacetate, m.p. 49.5° (96% yield), catalytically reduced to Et_2 2-aminophenylene-1:4-diacetate (III), m.p. 46.5° [picrate; Ac derivative (IV), m.p. 95.5°]. Oxindolyl-6-acetic acid, m.p. 250° , is obtained by the action of boiling 10% HCl on (III) or of boiling conc. HCl on (IV). Addition of (IV) to conc. HNO_3 at -5° yields Et_2 σ -nitro-2-acetamidophenylene-1:4-diacetate, m.p. 118° , reduced (Ni) to Et_2 σ -amino-2-acetamidophenylene-1:4-diacetate (V), m.p. 142° [Et_2 2:5-diacetamidophenylene-1:4-diacetate (V), m.p. 234°]. Treatment of (IV) or (V) with boiling conc. HCl yields 2:6-diketotetrahydro-*lin-p*-benzodipyrrole (VI), decomp. about 285 — 290° . H. W.

H. W.

Pyrimidines. CXLV. Alkamine ethers of the pyrimidine and quinoxaline series. J. L. DONLEAVY and M. A. KRIS (J. Amer. Chem. Soc., 1935 57, 753—754; cf. this vol., 358).—The prep. of 2 : 4-dihydroxy-6-methylpyrimidine, m.p. 270—280° (decomp.), is modified. The following *pyrimidine* derivatives are prepared from the Cl-compounds and Na aminoalkoxides : 2 : 4-di- β -diethylaminoethoxy- (I) m.p. 190—191°; 2 : 4-di- β -diethyl- (II) and -*dit*butylaminoethoxy-6-methyl-, m.p. 198—201° and 227—230°, respectively, 4- β -diethylaminoethoxy-6-methyl- (III) m.p. 146°, and 4- γ -diethylaminopropoxy-6-methyl- (IV), m.p. 125—127°. 2 : 4-Di-3-diethylaminoethoxyquinoxaline, m.p. 209—210°, is also prepared. (I)—(IV) have no local anæsthetic action and are irritant and somewhat toxic to mice when injected subcutaneously.

R. S. C.

Quinazolines. XXXIX. Synthesis of quinazoline derivatives structurally analogous to the angostura alkaloids, galiopine and galipine. (Miss) E. B. MARR and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 729—732).—Hydrogenation (PtO_2 ; 96% EtOH; 29 lb. per sq. in.; 26°) of pure quinazoline gives 3 : 4-dihydroquinazoline [hydrochloride, m.p. 231—234°; picrate, m.p. 219—220° (corr.) (lit. about 215°)]. 2- β -Phenylethyl-4-quinazoline, m.p. 209.5—210.5° (corr.), is prepared by hydrogenation (above conditions; poor yield) or Na-Hg reduction of 2-styryl-4-quinazoline and by treating N- β -phenylpropionylantranilic acid, m.p. 138.7—139.7° (corr.), first with Ac_2O and then with hot aq. NH_3 ; with PCl_3 and POCl_3 it gives 4-chloro-2-phenylethylquinazoline (50%), which with NaOMe affords 4-methoxy-2-phenylethylquinazoline, m.p. 58.5—59.5° (corr.). 2-3 : 4-Dimethoxystyryl-4-quinazoline, m.p. 268—269° (corr.) (prep. without solvent), is reduced (Na-Hg) to 2-homoveratryl-4-quinazoline, m.p. 209—210° (corr.), converted into 4-chloro-, m.p. 116—118°, and thence into 4-methoxy-2-homoveratrylquinazoline, m.p. 96.3—97.3° (corr.). R. S. C.

Pyridylnitropyrazole. II. Derivatives of 4-nitro-5-pyridylpyrazole. H. LUND (J.C.S., 1935, 418—420).—3-Nitro-5-pyridylpyrazole is nitrated to the 3 : 4-dinitro-compound (I) (hydrochloride), which is reduced (H_2S) to the 4-nitro-3-amino-derivative (hydrochloride). The amine forms the diazonium nitrate and perchlorate, and the chloride is deaminated to 4-nitro-5-pyridylpyrazole. (I) is reduced (SnCl_2) to 4-nitro-3-hydroxylamino-5-pyridylpyrazole, decomp. 177—178°, which with O_2 gives the 3-azoxy-compound, and with HCl-KBrO_3 followed by HClO_4 gives 4-nitro-3-nitroso-5-pyridylpyrazole perchlorate. (I) is reduced (NaHSO_3) to 3 : 4-diamino-5-pyridylpyrazole. F. R. S.

Eight-membered heterocyclic nuclei. A. GIACALONE (Gazzetta, 1935, 65, 120—123).—2-Amino-5-methylbenzophenone hydrochloride, m.p. 179—180°, when heated yields (I), m.p. 197—198°. The hydrochloride of anthranilic acid when heated yields $\text{NH}_2\text{Ph.HCl}$; that of the Me or Et ester dissociates, losing HCl .

[Di- and tri-pyridyl compounds of] rarer elements.—See this vol., 716.

Preparation of trimethylenetrinitroamine. G. SOLLAZZO (Boll. Chim. farm., 1935, 74, 221—224, 227—228).—An improved yield (cf. A., 1933, 150) is obtained by treating dry, finely-powdered $(\text{CH}_3)_3\text{N}$ with 99% HNO_3 (d 1.52), for 12 hr. at $< 10^\circ$. At -45° the yield is no greater, but the reaction is much smoother and safer. Results under other conditions are described. E. W. W.

Degradation of flavins by light. P. KARRER and H. F. MEERWEIN (Helv. Chim. Acta, 1935, 18, 480—482).— o - $\text{C}_6\text{H}_4\text{Cl.NO}_2$ and β -aminopropane- α -diol in boiling $\text{C}_5\text{H}_5\text{N}$ give o -nitro- α -dihydroxy- β -isopropylaniline, reduced (Pt-H_2 -EtOH) and then condensed with alloxan to 9- α -dihydroxy- β -isopropylisalloxazine (I), decomp. 261—263°. In neutral

aq. or aq.-MeOH solution (I) is very rapidly degraded by light with production of some alloxazine (II). In alkaline solution degradation occurs still more readily but the formation of (II) could not be established. H. W.

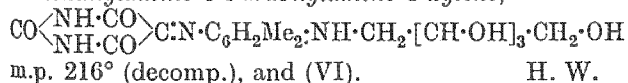
Synthesis of lactoflavin (vitamin- B_2) and other flavins. H. VON EULER, P. KARRER, M. MALMBERG, K. SCHOPP, F. BENZ, B. BECKER, and P. FREI (Helv. Chim. Acta, 1935, 18, 522—535).—Repeated crystallisation of 6 : 7-dimethyl-9-d-1'-ribitylisoalloxazine (I) has removed the discrepancy in m.p. observed previously. The complete similarity of the chemico-physical and biological behaviour of (I) and lactoflavin (II) establishes the identity of the substances. The antipellagra action of each requires further study. The products of lower biological activity observed in (II) are regarded as impurities. Other synthetic flavins are biologically inactive or have little effect. The B_2 action depends on the nature of the sugar side-chain.

Catalytic reduction (Pd) of d -ribose and 3-amino-4-carbethoxyamino- o -xylene gives 2-carbethoxyamino-4 : 5-dimethylphenyl- d -ribamine, m.p. 170°, $[\alpha]_D^{20}$ $-13.0^\circ \pm 2^\circ$ in H_2O , hydrolysed and condensed with alloxan in dil. HCl to (I), m.p. 282°, $[\alpha]_D^{20}$ $-92.6^\circ \pm 7^\circ$ in 0.05N-NaOH (tetra-acetate, m.p. 238—239°). The following compounds are obtained analogously: 6 : 7-dimethyl-9-d-1'-xylitylisoalloxazine, m.p. 278—280°, $[\alpha]_D^{20}$ $-82.2^\circ \pm 7^\circ$ in 0.05N-NaOH (tetra-acetate, m.p. 216°); 2-carbethoxyamino-4 : 5-dimethylphenyl-1-rhamnamine, m.p. 183°, 6 : 7-dimethyl-9-1'-rhamnitylisoalloxazine, m.p. 269—270°, $[\alpha]_D^{20}$ $-51.9^\circ \pm 6^\circ$ in 0.05N-NaOH (tetra-acetate, m.p. 224°), and (?) 2-hydroxy-5 : 6-dimethyl-1-1'-rhamnitylbenzimidazole, m.p. 219—220°; 6 : 7-dimethyl-9-1'-arabitylisoalloxazine tetra-acetate, m.p. 215°; 2-carbethoxyamino-5-methylphenyl- d -galactamine, m.p. 139°, and 7-methyl-9-d-1'-dulcetylisoalloxazine, m.p. 239°, $[\alpha]_{D_{44}}^{20}$ $-30.6^\circ \pm 6^\circ$ in 0.05N-NaOH (penta-acetate, m.p. 222° after softening at 150°); 2-carbethoxyamino-5-methylphenyl-1-arabamine, m.p. 170°, and 7-methyl-9-1'-arabitylisoalloxazine, m.p. 284°, $[\alpha]_{D_{44}}^{20}$ $-46.3^\circ \pm 6^\circ$ in 0.05N-NaOH; 2-carbethoxyamino-5-methylphenyl- d -glucamine, m.p. 137—138°, $[\alpha]_D^{20}$ $-12.2^\circ \pm 2^\circ$ in H_2O , and 7-methyl-9-d-1'-sorbitylisoalloxazine (penta-acetate); 2-carbethoxyamino-5-methylphenyl- d -mannamine, m.p. 168—169°, $[\alpha]_D^{20}$ $+26.7^\circ \pm 3^\circ$ in H_2O , and 7-methyl-9-d-1'-mannitylisoalloxazine, m.p. 272° (penta-acetate, m.p. 199°). H. W.

Sugar-like side-chain of lactoflavin. R. KUHN, H. RUDY, and F. WEYGAND (Ber., 1935, 68, [B], 625—634; cf. A., 1934, 1460).—The hypothesis that lactoflavin (I) contains a tetrahydroxy- n -butyl chain is strengthened by the isolation of a *disopropylidene* derivative (II), m.p. 293° (corr., decomp.), $[\alpha]_D^{20}$ $+117.5^\circ$ in $\text{CHCl}_3 + 10\%$ of EtOH. (II) like the corresponding tetra-acetate is freely sol. in CHCl_3 , from which it is not removed by H_2O . It is readily hydrolysed by dil. AcOH to (I). The absorption spectra of (I) and (II) are nearly identical. *isoPropylidenelactoflavin* has m.p. 277° (corr., decomp.). Treatment of (I) with $\text{Pb}(\text{OAc})_4$ yields 6 : 7-dimethylalloxazine, identified by transformation by CH_2N_2 into 1 : 3 : 6 : 7-tetramethylalloxazine, m.p. 250

(corr.); it is assumed that 6:7-dimethylflavin-9-acetaldehyde is intermediately produced and then undergoes alloxazine fission even more readily than the corresponding -9-acetic acid. Crystallisation of (I) from various media shows that the m.p. of the most sol. fraction (III) can be raised to 293°, but elementary composition and $[\alpha]_D$ remain unchanged from (III) to the most sparingly sol. portions (IV). (I) of m.p. 271° and 293°, respectively, yield the same Ac_4 derivative, m.p. 243°. Probably within these limits the temp. of decomp. is influenced by traces of impurity and the m.p. may possibly be raised further. The marked dependence of $[\alpha]_D$ on concn. in 0.05N- or 0.1N-NaOH is the same for all fractions and marked differences between $[\alpha]_D$ of (III) and (IV) are not observed in the strongly dextrorotatory solutions containing $Na_2B_4O_7$ in which $[\alpha]_D$ is nearly independent of concn. The fractionations do not entirely preclude the presence of other flavins but are not in harmony with the views of Karrer *et al.* (cf. this vol., 359).

4:5-Dinitro-o-xylene is condensed with *l*-arabamine in 80% EtOH at 135° to 4-nitro-5-l-arabitylamino-o-xylene (V), m.p. 216°, $[\alpha]_D -1^\circ \pm 1^\circ$ in C_6H_5N , the absorption spectrum of which very closely resembles that of 4-nitro-5-methylamino-o-xylene. (V) and alloxan in boiling dil. HCl give 6:7-dimethyl-9-l-araboflavin (VI), m.p. 294–295° (decomp.), $[\alpha]_D^{25} -80.4 \pm 10^\circ$ in 0.1N-NaOH, $[\alpha]_D^{25} +367^\circ \pm 10^\circ$ in presence of $Na_2B_4O_7$, $[\alpha]_{589}^{25} +220^\circ \pm 10^\circ$ in presence of $Na_2B_4O_7$. The m.p. is not influenced by the presence of (I) of differing origin. The half-periods of photolysis of (I) and (VI) are almost identical. Nevertheless, the identity of (I) and (VI) is not regarded as established since the m.p. of the Ac_4 derivative of (VI) could not be raised above 217° by repeated chromatographic analysis whereas the Ac_4 derivative of (I) has m.p. 243°, and the biological activity of (VI) is at least 3 times > that of (I). Reduction (H_2 -PtO₂) of (V) and treatment of the product with alloxan in boiling dil. AcOH leads to 4-alloxanylamino-5-l-arabitylamino-o-xylene,

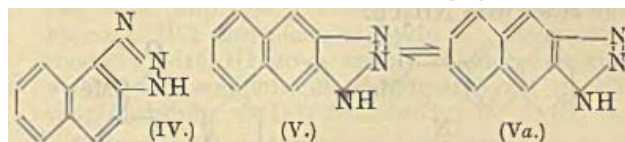


Tricyclic compounds in which naphthalene is allied to a heterocyclic component. K. FRIES, R. WALTER, and K. SCHILLING (Annalen, 1935, 516, 248–285).—Re-determinations show that the heat of combustion of anthracene (I) is 7 kg.-cal. > that of phenanthrene (II), in accordance with the view that the latter is the more stable compound. For (I) the

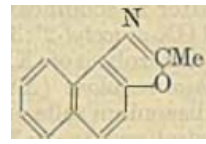
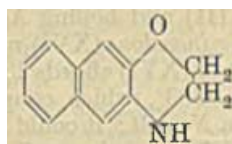


constitution 1a is preferred to 1b since 2:6-dihydroxyanthracene is converted by Br in dioxan into 1:5-dibromo-2:6-dihydroxyanthracene, decomp. 135°; the Me_2 ether, m.p. 280° (decomp.) after blackening at 275° (obtained with CH_2N_2), is oxidised by CrO_3 in AcOH to 1:5-dibromo-2:6-dimethoxyanthraquinone (III), decomp. 345°. (III) is synthesised by the action of P_2O_5 on 2-bromo-3-methoxybenzoic acid, m.p. 154° (*l*-amino-3-methoxybenzoic acid, m.p. 167°).

In *ang*-naphthatriazole (IV) in contrast with *lin*-naphthatriazole (V) no part of the ring system is in a



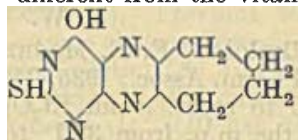
state of strain, in accordance with which it has the lower heat of combustion. (IV) is markedly less saturated than (V) as shown by the relative ease of hydrogenation and chemical behaviour which differ as do those of (I) and (II). Hydrogenation of (V) by Na-Hg in boiling EtOH leads to 8:9-dihydro-*lin*-naphthatriazole, m.p. 157° (1-Me, m.p. 147°, and 1-Ac, m.p. 173°, derivatives), oxidised by $Na_2Cr_2O_7$ and dil. H_2SO_4 to *lin*-naphthatriazole-8:9-quinone (VI), m.p. 241° (1-acetyl-, m.p. 149°, and 1-methyl-, m.p. 175°, *lin*-naphthatriazole are described). Catalytic hydrogenation of (V) (Pt-sponge in AcOH) of (V) gives 4:5:6:7-tetrahydro-*lin*-naphthatriazole (VII), m.p. 162° (1-Ac, m.p. 114°, and 1-Me, m.p. 99°, derivatives), oxidised to (VI). Partial hydrogenation of (V) gives a mixture of (V) and (VII). Under similar conditions hydrogenation of (IV) is scarcely appreciable. (VII), also obtained by oxidation of (V), is stable towards NH_2Ph in boiling EtOH. It gives a 1-Ac, m.p. 186°, and 1-Me, m.p. 237°, derivative. It is converted by Zn dust in boiling Ac_2O into the Ac_3 derivative, m.p. 165°, of 8:9-dihydroxy-*lin*-naphthatriazole. Chlorination of (V) in AcOH gives 8:9-dichloro-*lin*-naphthatriazole, m.p. 291° (decomp.), oxidised to (VI); attempts to obtain an additive product or to introduce ICl were unsuccessful. Br in AcOH at room temp. transforms (V), apparently through a very unstable dibromide, into 9-bromo-*lin*-naphthatriazole, m.p. 244° (decomp.), whereas a larger proportion of halogen gives 8:9-dibromo-*lin*-naphthatriazole, m.p. 278° (decomp.), oxidised to (VI). (V) and CH_2O in EtOH afford 1-hydroxymethyl-*lin*-naphthatriazole, m.p. 191° with loss of CH_2O . *lin*-Naphthatriazole-1-acetic acid, m.p. 229°, is derived from (V), NaOH, and $CH_2Cl \cdot CO_2Na$. 1-Chloroacetyl-*lin*-naphthatriazole, m.p. 179°, from (V) and $CH_2Cl \cdot COCl$ in boiling C_6H_6 ,



is transformed by $AlCl_3$ in $PhNO_2$ into *lin*-naphthamorpholone (VIII), m.p. 270°, also obtained from 2:3- $NH_2 \cdot C_{10}H_6 \cdot OH$ and $CH_2Cl \cdot CO_2H$.

2:3- $C_{10}H_6(NH_2)_2$ is transformed by boiling HCO_2H into *lin*-naphthiminazole, m.p. 221° (1-Ac derivative, m.p. 172°), which is not reduced by Na-Hg or catalytically. It is oxidised by $Na_2Cr_2O_7$ and boiling dil. H_2SO_4 to *lin*-naphthiminazole-8:9-quinone, m.p. > 400° after blackening at 320°, which does not react with NH_2Ph , gives a 1-Me derivative, m.p. 286°, with NaOH and Me_2SO_4 and is reduced by Zn dust and boiling Ac_2O to the Ac_3 derivative, m.p. 216°, of 8:9-dihydroxy-*lin*-naphthiminazole. 2-Methyl-*lin*-naphthiminazole, m.p. 286°, from 2:3- $C_{10}H_6(NH_2)_2$ and AcOH

3 : 4 : 5 : 6-tetrahydrobenzpyrimidine (II), and with alloxan yields *thioltrihydroxybispyrimidine*. On oxidation of (II) in aq. solution the appearance of fluorescence corresponds rather closely with the behaviour of vitamin- B_1 , but the substances are very different from the vitamin in other respects. (II) is



F. R. S.

Chlorophyll. LIV. Chlorophyll *b*. VII. Fine structure of chlorophyll *b*. H. FISCHER and J. GRASSL (Annalen, 1935, 517, 1—21).—Phæophorbide *b* (I) has the same isocyclic ring as phæophorbide *a* (II) and its abnormal reactions are attributed to the presence of CHO at 3. Treatment of phæophorbide *b* monoxime (CHO stabilised by conversion into CH:N.OH) with CH_2N_2 in MeOH gives the oxime of rhodin *g* Me₃ ester, m.p. 238°. Phæophorbide *b* dioxime is merely esterified by CH_2N_2 . Treatment of methylphæophorbide *b* monoxime (III) with anhyd. KOAc and boiling Ac_2O yields *pyrophæophorbide b nitrile*, m.p. 256°, which could not be hydrolysed to the corresponding acid. In contrast to dihydrophæophorbide *b*, methylphæophorbide *b* and $\text{CHN}_2\cdot\text{CO}_2\text{Me}$ give an additive product (IV), $\text{C}_{39}\text{H}_{40}\text{O}_8\text{N}_4$, m.p. 262°, in which the presence of CHO is shown by isolation of the *monoxime* (V), m.p. 264°, and of the isocyclic ring by that of the *dioxime*, m.p. 263°. Treatment of (III) with $\text{CHN}_2\cdot\text{CO}_2\text{Me}$ affords (V), hydrolysed by 20% HCl to (IV). Oxidation of (III) with $\text{CrO}_3\text{--H}_2\text{SO}_4$ gives ill-defined results, whereas treatment with HI (*d* 1.7) in AcOH yields a cryst. porphyrin converted by CH_2N_2 into phæoporphyrin *b*₆ Me ester (VI), m.p. 276° (monoxime). Oxidation of (VI) with $\text{CrO}_3\text{--H}_2\text{SO}_4$ gives a compound, m.p. 202°, identical with that obtained by oxidation of the adduct, m.p. 205°, of protoporphyrin and $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ and of (II) with $\text{CHN}_2\cdot\text{CO}_2\text{Et}$. The formulation of the unsaturated side-chain cannot be decided definitely, but it and CHO cannot be attached to the same pyrrole nucleus, and position 2 in nucleus I is the sole available position

difficulty starting with (V). Oxidation of (VII) with I in abs. EtOH yields 10-ethoxyphæoporphyrin *b*₆ (Me ester, m.p. 274°; *oxime*, m.p. 283°), converted by conc. HCl into phæoporphyrin *b*₆. Reduction of rhodin *g* with HI gives mainly rhodinoporphyrin *g*₆ with small amounts of rhodinoporphyrin *g*₅. The simplified prep. of (I) is described. H. W.

Chlorophyll and hæmin derivatives in rocks, petroleum, coals, and phosphorites.—See this vol., 727.

Composition and specificity of hæmoglobins. Spectral characters and specificity of hæmoglobins.—See this vol., 640.

Benzantrones with condensed heterocyclic rings, their derivatives, and dyestuffs derived from them. I. M. KITAJIMA (J. Chem. Soc. Japan, 1934, 55, 887—895).—The prep. and properties of a no. of benzantrone deoxy-compounds are described. CH. ABS. (r)

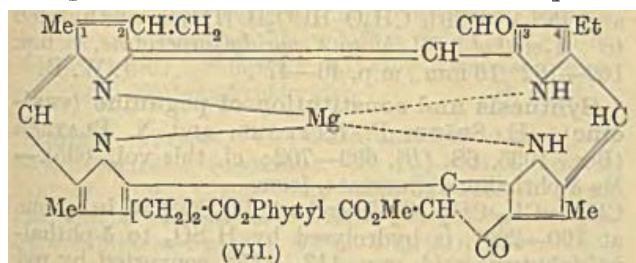
Pyrolysis of saccharinoxime. (SNA.) A. MANNESSIER-MAMELI (Gazzetta, 1935, 65, 77—84).—Decomp. of saccharinoxime (I) at 208° (cf. A., 1933, 288) gives oxides of N, saccharin (II), and *ψ*-saccharinamine (III), new m.p. 315° (Ac derivative, m.p. 256°). The action of HNO_2 on (I) also gives (II) and (III), with a substance, m.p. 190°. Treatment of (III) with NaOH gives NH_3 and (III). E. W. W.

Action of hydroxylamine hydrochloride on oximinotriphenylpyrrole. T. AJELLO (Gazzetta, 1935, 65, 176—182).—These react to give a substance, $\text{C}_{22}\text{H}_{16}\text{O}_6\text{N}_2$ (I), m.p. 170—171°, reduced to $\text{C}_{22}\text{H}_{18}\text{ON}_2$, m.p. 98°, and hydrolysed (KOH-EtOH) to a substance, $\text{C}_{15}\text{H}_{12}\text{ON}_2$ (II). The formulæ $\text{CPh}\cdot\text{CHPh}\cdot\text{CBz}$ $\text{N}\text{---}\text{O}\text{---}\text{N}$

and $\text{CPh}\cdot\text{CHPh}\cdot\text{CH}$ $\text{N}\text{---}\text{O}\text{---}\text{N}$ are suggested for (I) and (II), respectively. E. W. W.

Dioximes. CVIII. P. GRAMATIERI (Gazzetta, 1935, 65, 102—108).—When the phenylhydrazone of 3-benzoyl-5-phenyl-1 : 2 : 4-oxadiazole (I) is heated, the oxadiazole ring is opened, and a triazole ring closed, forming 5-benzamido-2 : 4-diphenyl-1 : 2 : 3-triazole, m.p. 190°. From this, the 5- NH_2 -compound, m.p. 83—84°, and its benzylidene derivative, m.p. 126—127°, are prepared. The *p*-bromophenylhydrazone, m.p. 146°, of (I) similarly gives 5-benzamido-4-phenyl-2-*p*-bromophenyl-1 : 2 : 3-triazole, m.p. 185°. The phenylhydrazone, m.p. 178° (softens at 110°), of 3-*p*-tolyl-5-phenyl-1 : 2 : 4-oxadiazole, m.p. 115° (decomp.), which is obtained (HCl) from its *oxime*, m.p. 174—175°, in turn obtained (NaOH) from the *Bz* derivative, m.p. 174°, of β -amino-*p*-tolylglyoxime, similarly isomerises to 5-benzamido-2-phenyl-4-*p*-tolyl-1 : 2 : 3-triazole, m.p. 177—178°. E. W. W.

Thionaphthenopyrazoles. W. J. BARRY and E. W. McCLELLAND (J.C.S., 1935, 471—474).—3-Hydroxy-2-acetyl-1-thionaphthen (I) with $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ yields 1-phenyl-3-methyl-4 : 5-thionaphthenopyrazole (II), m.p. 120°, oxidised to the *S*-dioxide, and with *p*- $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{NH}\cdot\text{NH}_2$ gives 1-*p*-bromophenyl-3-methyl-4 : 5-thionaphthenopyrazole, m.p. 159°, oxidised to the dioxide, m.p. 207°. 3-Hydroxy-2-acetyl-1-thionaphthen-*p*-bromophenylhydrazone, m.p.



since methylethylmaleinimide is not available from intact chlorophyll *b*, which is therefore probably formulated as shown.

Reduction of phæoporphyrin *b*₆ (VII) (*monoxime*, m.p. > 300°, *dioxime*) [$\text{H}_2\text{--Pd--HCO}_2\text{H}$] leads to phæoporphyrin *a*₅ and 9-hydroxydeoxyphæoporphyrin *a*₅, transformed by warm conc. H_2SO_4 into phyloerythrin, thus accomplishing the transition from the *b* to the *a* series in a porphyrin with isocyclic ring; a similar change is accomplished with greater

160—161°, and 1:3-diphenyl-4:5-thionaphthenopyrazole, m.p. 171°, are similarly oxidised to the dioxides. (I) and $N_2H_4 \cdot HCl$ give a bis-compound, m.p. 305°, and 3-methyl-4:5-thionaphthenopyrazole, m.p. 185°, oxidised to the dioxide, m.p. 244—246°. Reduction (Na) of (II) affords 1:5-diphenyl-3-methylpyrazoline and a product, m.p. 122—124° (NO-compound, m.p. 202—203°; Br-compound, m.p. 142—143°), which is probably a diphenylmethylpyrazole. F. R. S.

Manufacture of heterocyclic amino-compounds.—See B., 1934, 444.

Production of compounds of the cyanine type.—See B., 1935, 398.

Alkaloids of the Chinese drug "chin-shih-hu."

III. Dendrobine. H. SUZUKI, I. KEIMATSU, and K. ITO (J. Pharm. Soc. Japan, 1934, 54, 802—819, 820—823).—Dendrobine (I) is now regarded as $C_{16}H_{25}O_2N$. (I), with EtOH-KOH, yields *dendrobic acid* (II), $C_{16}H_{25}O_3N$, m.p. 227°, $[\alpha]_D^{25} -27.5^\circ$ in EtOH [aurichloride, decomp. 85°; methiodide (III), decomp. 211°; Me ester (IV), m.p. 94°, $[\alpha]_D^{25} -17.5^\circ$ in EtOH]. (IV) forms an aurichloride, m.p. 169°, and an Ac derivative, m.p. 76° [aurichloride, m.p. 93—103° (decomp.)]. (II) or (IV) with H_2O_2 affords *dendrobine N-oxide*, $C_{16}H_{25}O_3N \cdot H_2O_2$, decomp. 150°, $[\alpha]_D^{25} -37.76^\circ$ in EtOH (aurichloride, decomp. 184°). (III) with moist Ag_2O yields *dendrobine methoxyhydroxide*, decomp. 251° (aurichlorides, anhyd., decomp. 237—239°; + H_2O , decomp. 200°). (I) with CNBr yields *cyanonordendrobine*, m.p. 188°, which with dil. HCl gives *nordendrobinecarbamide* (V), $C_{15}H_{23}O_2N \cdot CO \cdot NH_2$, decomp. 240°, $[\alpha]_D^{25} -127.9^\circ$ in EtOH (aurichloride, decomp. 176°). (V) yields *nordendrobic acid* (aurichloride, decomp. 197°) when treated with EtOH-KOH. (V), with HNO_2 , affords a carbamic acid, $C_{16}H_{23}O_4N$, m.p. 134°, and *nordendrobine*, m.p. 117—118° [Ac derivative, m.p. 114.5°, $[\alpha]_D^{25} -149.5^\circ$ in EtOH; NO-derivative (VI), m.p. 172°]. (VI) is also formed from (V) with HNO_2 . The alkaloids present in *Dendro flaviflorum*, *D. linawianum*, and *D. longicalcaratum* have been examined. CH. ABS. (r)

Senecio alkaloids. I. Alkaloids of *S. platyphyllus*, D.C. A. OREKHOV [with W. TIEDEBEL] (Ber., 1935, 68, [B], 650—655).—The air-dried roots are moistened with 10% NH_3 and extracted with $C_2H_4Cl_2$. The extract is shaken with 3N-HCl, which is neutralised with 50% NaOH and treated with excess of 25% NH_3 , whereby *seneciphylline* (I), $C_{17}H_{23}O_5N$, m.p. 217—218° (decomp.), $[\alpha]_D -128.04^\circ$, is pptd. The mother-liquors from (I) are extracted with Et_2O , whereby *platyphylline* (II), $C_{17}H_{25}O_5N$, m.p. 124—125°, $[\alpha]_D -45.09^\circ$ in $CHCl_3$, is obtained. (II) is a moderately strong base which contains 1 OH but not OMe or NMe. N is *tert.* and probably bicyclic. It gives a perchlorate, m.p. 222—223° (decomp.) after becoming discoloured at 210°, *picrolonate*, m.p. 205—206° (decomp.), *aurichloride*, m.p. 200—201° (decomp.), and *methiodide*, m.p. 216—217°. It is hydrolysed by NaOH-EtOH to the monobasic *platyneic acid*, $C_{16}H_{14}O_4$, m.p. 154—155°, which contains 1 OH and *platyneine*, $C_7H_{11}O_3N$ [aurichloride, m.p. 209—210° (decomp.)]. (I) contains 1 OH, whereas OMe and NMe are absent. N is *tert.* It yields a perchlorate, darkens at about 220° and subsequently chars,

picrate, m.p. 182—183°, *aurichloride*, m.p. 162—163° (decomp.), *platinichloride*, darkens at 205° and subsequently chars, and *methiodide*, m.p. 231—232° (decomp.). (I) is hydrolysed to an acid (or mixture) and an NH_2 -alcohol (*aurichloride*, m.p. 163—164°). In view of the difficulties of combustion, the C_{17} formulæ are recorded with reserve.

H. W.

Crystalline ephedrine alkaloid. E. E. MOORE and D. L. TABERN (J. Amer. Pharm. Assoc., 1935, 24, 211—213).—Addition of H_2O to cryst. (from Et_2O) anhyd. ephedrine (I) lowers the m.p. from 38.1° to 32.1° when a eutectic mixture of (I)—(I) hydrate containing 1.5% of H_2O is present; with further addition the m.p. rises to a max. of 40° with 5% of H_2O , corresponding to a hemihydrate.

F. O. H.

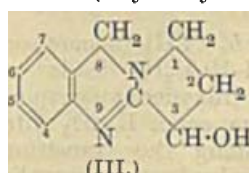
Ergot alkaloids. W. A. JACOBS and L. C. CRAIG (Science, 1935, 81, 256—257).—Lysergic acid (I), phenylalanine (II), and NH_3 have been obtained from ergotamine (III) and there is evidence that proline (IV) is also a constituent of (III). Neither isobutyrylformic acid (V) nor its reduction product could be detected in the cleavage products of (III), but $AcCO_2H$ (VI) has been detected after alkaline hydrolysis. Ergotamine and ergotoxine appear to be derivatives of (I), (II), (IV), and (V), but in (III) and in ergotamine (V) is replaced by (VI).

L. S. T.

Introduction of an amino-group into alkaloids by sodamide and potassamide. II. α -Aminoanabesine. M. I. KABATSCHEV and M. M. KATZNELSON (Bull. Soc. chim., 1935, [v], 2, 576—582).—Treatment of anabesine with $NaNH_2$ in $NPhMe_3$ at 135—145° affords a mixture of α - (I), m.p. 89.5—90°, and α' -aminoanabesine (II), m.p. 109° (main product), separated by fractional crystallisation from $PhMe$ and H_2O . (I) is 2-(2'-amino-3'-pyridyl)piperidine [platinichloride, darkens 260°, not melting at 300°; *picrate*, m.p. 244.5—245° (decomp.)], a constitution erroneously assigned by Menschikov *et al.* (A., 1934, 422) to (II), which is actually 2-(6'-amino-3'-pyridyl)piperidine. Thus with HNO_3 -HCl (I) and (II) give, respectively, α -, b.p. 126°/1.8 mm., m.p. 58.5—59.5°, and α' -chloroanabesine (III), m.p. 99.5—100°, oxidised by $KMnO_4$ to, respectively, 2- and 6-chloropyridine-3-carboxylic acid (also synthesised from the 6-OH-acid and PCl_5). With $CH_2O \cdot HCO_2H$ (III) is methylated to 1-methyl-2-(6'-chloro-3'-pyridyl)piperidine, b.p. 160—162°/16 mm., m.p. 46—47°.

J. W. B.

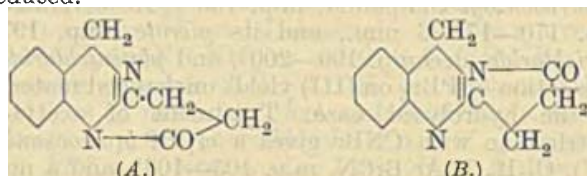
Synthesis and constitution of peganine (vasicine). E. SPATH and F. KUFFNER, and N. PLATZER (Ber., 1935, 68, [B], 699—702; cf. this vol., 635).—Me δ -phthalimidobutyrate, from $CH_2Br \cdot CH_2 \cdot CH_2 \cdot CO_2Me$ and o - $C_6H_4(CO_2)NK$ in xylene at 190—200°, is hydrolysed by H_2SO_4 to δ -phthalimidobutyric acid, m.p. 113—115°, converted by red P-Br followed by $BaCO_3$ -boiling H_2O into δ -phthalimido- β -hydroxybutyric acid (I), m.p. 147—148°.



(I) is hydrolysed (25% HCl at 100°), esterified (MeOH-HCl), and condensed with o - $NO_2 \cdot C_6H_4 \cdot CH_2Cl$ to 3-hydroxy-1-o-nitrobenzylpyrrolid-2-one (II), m.p. 150—151° (vac.), accompanied by 3-hydroxypyrrolidone, m.p. 84—85°. Reduction of (II)

by SnCl_2 and HCl in AcOH leads through the NH_2 -compound to 3-hydroxy- Δ^9 -pegene (III), m.p. 211–212° (vac.), identical with natural peganine. H. W.

Constitution of vasicine. J. N. RAY, K. S. NARANG, and H. R. JUNEJA (Current Sci., 1935, 3, 352–353).—Previous work on the constitution of vasicine (I) is reviewed. The picrolonates of reduced (electrolytic) (A) 4-hydroxy-2-propylquinazoline and 4-hydroxy-3-allylquinazoline differ from that of reduced (I). (B) has been synthesised but not yet reduced.



F. N. W.

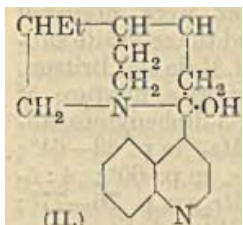
Harmine and harmaline series. II. Nitro- and amino-derivatives of harmine and harmaline.
O-Alkyl ethers of harmol and harmalol. R. KONOVALOVA and A. OREKHOV (Arch. Pharm., 1935, 273, 156–163; cf. A., 1934, 1236).—Harmaline (I) can be oxidised to harmine (II) by $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ (cf. A., 1927, 682; 1934, 1117). (I) and (II) can be demethylated to give harmalol (III) and harmol (IV), respectively, by means of syrupy H_3PO_4 (d 1.7) at 120°. The following were prepared from (IV), NaOR and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{R}$ (R =requisite alkyl): *harmalol O-Et*, m.p. 199–200°; *O-Pr*, m.p. 203–204°; *O-Bu*, m.p. 218–220°; and *O-isomyl*, m.p. 237–238°, *ethers* (cf. A., 1933, 839). The *O-Et*, m.p. 247–249°, and *O-Pr*, m.p. 195–197°, *ethers* of (III) were prepared similarly. Nitroharmaline (V), m.p. 132° (decomp.) (lit. m.p. 122°) (improved prep.), is oxidised (CrO_3) to nitroharmine (VI) (cf. A., 1912, i, 645), which with $\text{MeI-PhNO}_2\text{-PhMe}$ gives *Py-N-methylnitroharmine hydriodide*, and this with NaOH or aq. NH_3 affords the *base* (darkens at 250° and decomp. at 270°). *Py-N-Methylnitroharmaline*, m.p. 189–190° (*hydriodide*, m.p. 200–205°), is obtained in a similar manner. Reduction (Fe-HCl) of (V) gives *aminoharmaline*, m.p. 209–210° (+ H_2O , lost at 105°). The *hydrochloride* and unstable *dihydrochloride* are described. In solution the *base* is readily oxidised by air. Similarly (VI) affords *aminoharmine*, m.p. 231–232° (*hydrochloride*). H. G. M.

Indole series. V. Complete synthesis of physostigmine (eserine). P. L. JULIAN and J. PKL (J. Amer. Chem. Soc., 1935, 57, 755–757; cf. this vol., 635).—*dl*-Eserethole could not be resolved by *d*-camphorsulphonic (I) or *d*-tartaric acid. *dl*-5-Ethoxy-1:3-dimethyloxindolylethylmethylamine (II) (modified prep.) and (I) give usually the *d*-camphorsulphonate, m.p. 78°, of (II), or, best when appropriately seeded, the salt, m.p. 160°, of the *d*-amine (*picrate*, m.p. 175°), $[\alpha]^{25}_D + 30^\circ$ in EtOH ; the *base* from the mother-liquors affords the *d*-tartrate, m.p. 175–176°, of the *l*-amine, $[\alpha]^{25}_D - 30^\circ$ in EtOH (*picrate*, m.p. 175°; *dl*-*picrate*, m.p. 192°), which by reactions already described yields *l*-eserethole, *l*-eseroline, and *l*-physostigmine, identical with the natural product and its derivatives. R. S. C.

Optical crystallographic data for some salts of cinchonine. C. F. POE and C. A. SWISHER (J. Amer. Chem. Soc., 1935, 57, 748–749).—The optical properties of 13 salts of cinchonine are described. The following are new: *perchlorate*, + H_2O , *bromate*, + H_2O , *o-chlorobenzoate*, *chlorate*, + H_2O , *nitrate*, + H_2O , and *iodate*, + H_2O . R. S. C.

Stereochemical studies. III. Connexion between optical rotation and configuration of quinine alkaloids. R. LUDWICZAKÓWNA and J. SUSZKO (Rocz. Chem., 1935, 15, 57–67, and Bull. Acad. Polonaise, 1934, A, 402–412).—The $[M]_D$ - $[\text{HCl}]$ curves of cupreidine, cinchonine chloride, deoxycinchonine, α -isocinchonine, β -isoquinidine, *N*-benzylcinchotoxine, and cinchene in EtOH are of the same general type, showing that C atom (4), which is in cinchonine combined with a carbinol OH, does not, as stated by Emde (A., 1932, 759), determine the optical behaviour of the cinchona alkaloids; the validity of Emde's conclusions, based on optical methods, as to the configuration of these alkaloids is questioned. The above compounds exhibit max. rotation in presence of about 2 equivs. of HCl , that of cinchotoxine falls to a const. val. in presence of > 1 equiv. of HCl , whilst that of *N*-methyl- β -isoquinidine falls abruptly from 0 to 2 equivs., and then gradually with increasing $[\text{HCl}]$. R. T.

Rearrangement of hydrocinchonine by esterification in two stages. R. LUDWICZAKÓWNA and J. SUSZKO (Arch. Chem. Farm., 1935, 2, 196–202).—Hydrocinchonine in $\text{C}_6\text{H}_5\text{N}$ gives a *p*-toluenesulphonyl derivative, m.p. 166–167° (decomp.), $[\alpha]^{20}_D + 52.5^\circ$ in EtOH , converted by KOBz in EtOH (at the b.p.; 95 hr.) into the *Bz* derivative (I), m.p. 141–142°, $[\alpha]^{18}_D - 25.5^\circ$ in EtOH , of heterohydrocinchonine (II), m.p. 201–202°, $[\alpha]^{20}_D + 154.5^\circ$ in EtOH , prepared by hydrolysis of (I). The structure (II) is also assigned to the product obtained analogously from cinchonine, and erroneously termed *epicinchonine* (A., 1933, 288). R. T.



Spatial rearrangement of quinine alkaloids to epi-bases. J. FIENZIUSZKO and J. SUSZKO (Arch. Chem. Farm., 1935, 2, 139–148, and Bull. Acad. Polonaise, 1934, A, 415–420).—Hydrocinchonidine (I) is heated at 160° with 25% HCl for 50 hr., 10% aq. NaNO_2 is added to complete pptn. of *N*-nitrosohydrocinchotoxine (II), m.p. 99–100°, $[\alpha]^{20}_D - 21.0^\circ$ in EtOH (*hydrochloride*, m.p. 107–108°), the solution is made alkaline and extracted with Et_2O , (I) is eliminated from the extract as tartrate, and *epihydrocinchonidine* (III), m.p. 107–108°, $[\alpha]^{15}_D + 46.0^\circ$ in EtOH (*picrate*, an oil; *picrolonate*, m.p. 196–198°; *methiodide*, m.p. 237–238°, $[\alpha]^{15}_D + 38.0^\circ$ in H_2O ; *benzoate*, m.p. 137–138°, $[\alpha]^{15}_D - 71.0^\circ$ in EtOH), is isolated from the residual solution. *epiHydrocinchonine* (IV), m.p. 128–129°, $[\alpha]^{20}_D + 89.0^\circ$ in EtOH (*picrate*, m.p. 212–213°; *picrolonate*, an oil; *methiodide*, m.p. 231–232°, $[\alpha]^{20}_D + 54^\circ$ in H_2O ; *benzoate*, m.p. 156–157°, $[\alpha]^{15}_D + 157^\circ$ in EtOH), is prepared from hydrocinchonine hydrochloride and 25% HCl (50 hr. at 160°). Hydrocinchotoxine, obtained by

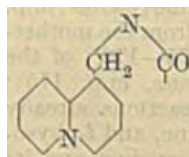
heating (III) or (IV) with 25% aq. AcOH at 100° (30 hr.), yields (II) when heated with HNO₂ (cf. A., 1932, 759). R. T.

Cinchona alkaloids in pneumonia. II. Ketone formation with sodamide. (MISS) A. G. RENFREW and L. H. CRETCHER (J. Amer. Chem. Soc., 1935, 57, 738—739; cf. this vol., 636).—Dihydroquinine and cinchonine with NaNH₂ in hot xylene give 40 and 21% yields, respectively, of the corresponding ketones (cf. Tschitschibabin, B., 1923, 1201). Na in xylene gives very poor yields. δ -Methylpentan- β -ol and benzhydryl do not give ketones with NaNH₂. R. S. C.

Constitution of apocinchene and synthesis of its methyl and ethyl ethers. J. KENNER and F. S. STATHAM (J.C.S., 1935, 299—303).—*m*-NO₂·C₆H₄·COMe is reduced [(NH₄)₂S] to the amine, which affords *m*-OH·C₆H₄·COMe, the semicarbazone, m.p. 194—196°, of which with KOH at 190° gives *m*-C₆H₄Et·OH (p-nitrobenzoate, m.p. 68°) (better yields than by Clemmensen's method). *m*-C₆H₄Et·OAc with AlCl₃ in PhNO₂ at 0° yields 4-hydroxy-2-ethylacetophenone (I), b.p. 150—152°/0.45 mm., m.p. 102° (semicarbazone, m.p. 172°; p-nitrobenzoate, m.p. 80°), converted by H₂O₂ into ethylquinol. (I) is reduced (Clemmensen) to 3:4-diethylphenol (II), b.p. 106°/0.5 mm. (p-nitrobenzoate, m.p. 81—82°; Me ether, b.p. 124—125°/23 mm.; Et ether, b.p. 120—125°/20 mm.). The acetate of (II), b.p. 113—115°/0.35 mm., with AlCl₃ at 140° gives 2-hydroxy-4:5-diethylacetophenone, b.p. 134—137°/0.75 mm. [semicarbazone, m.p. 240°; Me ether, m.p. 35—39° (semicarbazone, m.p. 128°)]. The following substituted β -chloropropiophenones were prepared from β -chloropropionyl chloride and the requisite substituted benzene and AlCl₃ in CS₂ [cf. Hale and Britton, A., 1919, i, 332, which method gives a mixture of β -chloropropiophenone (III) and 1:3-diphenylpropan-1-one in the prep. of (III)]: 4-OMe-, m.p. 63—64°; 4-Me, m.p. 80—81°; 2-OMe-5-Me, m.p. 60°; 4:5-Me₂, m.p. 71—72°; 2-OMe-4:5-Me₂, m.p. 76—77°; 2-OMe-4:5-Et₂, m.p. 41°; 2-OEt-4:5-Et₂, m.p. 81—82°. These ketones were converted into the corresponding substituted 4-phenylquinolines by Blaise and Maire's method (A., 1908, i, 566) for 4-alkylquinolines. The picrates of these substances have the following m.p.: 4-OMe, 232—234° (decomp.); 4-Me, 206° (decomp.); 2-OMe-5-Me, 213° (decomp.); 4:5-Me₂, 250—253°; 2-OMe-4:5-Me₂, 215° (decomp.); 2-OMe-4:5-Et₂ (IV), 200° (decomp.); 2-OEt-4:5-Et₂ (V), 180—181° (decomp.). (IV) and (V) are identical, respectively, with the picrates of the Me and Et ethers of apocinchene (VI) (cf. A., 1885, 1248), and the free base from (V) was identical with the Et ether of (VI). (VI) is therefore 4-(2'-hydroxy-4':5'-diethyl)quinoline. H. G. M.

Constitution of matrine. XV. Products of the distillation of potassium matrinate with soda-lime. H. KONDO, E. OCHIAI, K. TSUDA, and S. YOSHIDA. XVI. Dehydrogenation of matrine. H. KONDO and K. TSUDA (Ber., 1935, 68, [B], 570—581, 644—650).—XV. The basic portion of the products of the distillation of K matrinate with CaO-NaOH consists essentially of matrine (I), α - (II) and β -matrinidine. An unstable fraction, b.p. 55—90°/

14 mm., is also present which is catalytically hydrogenated to 1-butylpiperidine and norlupinane, thus confirming the identity of β -lupinane obtained by distillation of (I) with Zn dust. The *tert*-N of (I) therefore belongs to the lupinane ring as with other leguminosæ alkaloids. (II) contains a double linking and is readily hydrogenated (Pd-C in AcOH) to dihydro- α -matrinidine C₁₂H₂₂N₂, b.p. 122—123°/2 mm., m.p. 66° [hydrochloride, decomp. > 340°; methiodide, decomp. 246°; picrate, decomp. 251°; Bz derivative (III), m.p. 112°, and its platinichloride; p-nitrobenzoyl compound, m.p. 136°; Ac derivative, b.p. 170—173°/3 mm., and its picrate, m.p. 197°, aurichloride, decomp. 199—200°, and platinichloride]. The action of PBr₅ on (III) yields unchanged material or the hydrolysed base. Treatment of acetyl- α -matrinidine with CNBr gives a cryst. bromocyanide (IV), C₁₂H₂₁N₂Ac, BrCN, m.p. 105—106°, and a non-cryst., probably isomeric bromocyanide (V) which decomposes when heated in high vac. (IV) is dehalogenated (H₂-Pd-C) and hydrolysed by conc. HCl to the corresponding sec.-amines, C₁₂H₂₄N₂ (VI), b.p. 130°/6 mm., m.p. 42—45° (picrate, decomp. 163—164°; hydrobromide, decomp. > 320°; platinichloride; di-p-nitrobenzoate, m.p. 240—241°), and C₁₂H₂₃N₂Ac (VII), b.p. 160—162°/6 mm., m.p. 79—80° (platinichloride, decomp. 188—189°; benzoate, m.p. 135—136°; picrate, decomp. 163—164°). Stronger heating with conc. HCl converts (VII) into (VI). When similarly treated (V) affords two bases, C₁₂H₂₁N₂ (VIII), b.p. 126—127°/6 mm., and C₁₂H₂₄ON₂ (IX), b.p. 170—175°/6 mm., m.p. 128—129°. (VIII) gives a hydrobromide, C₁₂H₂₄N₂·2HBr, decomp. > 350°, di- α -naphthylcarbamate, decomp. 281°, and amorphous di-p-nitrobenzoate, decomp. 224—226°, whilst (IX) yields a hydrobromide, decomp. > 330°, and aurichloride, m.p. about 185° after softening at 96°. Dehydrogenation of (VI) and (VIII) is effected by 40% Pd-asbestos at 270—310° and the products are separated by KH₂PO₄ into a more strongly (X) and a more weakly (XI) basic portion. (XI) from each is C₁₂H₁₄N₂, b.p. 119—120°/2 mm. It gives the red Ehrlich reaction and the pine-shaving change only when impure. Although scarcely basic in character it gives a methiodide, m.p. 217—218° (decomp.), picrate, m.p. 187—188°, and styphnate, m.p. 178—179°. (X) from (VI) is C₁₂H₁₈N₂, m.p. 160—170°/4 mm., m.p. 111° (hydrochloride, m.p. 179°; aurichloride, m.p. 126°; picrate, m.p. 147°; methiodide, m.p. 166—167°). It is a sec.-*tert*-amine of which the *tert*-N is as weak as in the compound C₁₂H₁₄N₂. (X) from (VIII) is C₁₂H₁₈N₂, b.p. 148—150°/2 mm., m.p. 189—190° (methiodide, m.p. 205—206°; picrate, m.p. 192—194°), and is identical with the product of the distillation of α -matrinidine with Zn dust. Dehydro- α -matrinidine, b.p. 178°/3 mm. (picrate, m.p. 214—215°; styphnate, m.p. 189°; hydrochloride, decomp. 282°; aurichloride, m.p. 139°), is obtained as by-product. Oxidation of the base C₁₂H₁₄N₂ with KMnO₄ affords quinolinic acid with small amounts of a neutral cryst. substance. The annexed scheme shows the fundamental skeleton of (I).

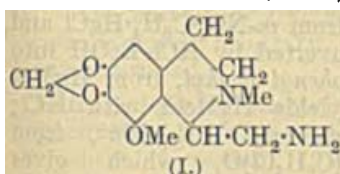


scheme shows the fundamental skeleton of (I).

XVI. (I) is not affected by CNBr in boiling C_6H_6 or PhMe and is unchanged by H_2 under pressure in presence of PtO_2 -AcOH. (I) is dehydrogenated by Pd-asbestos at 280–310° and the product is separated by KH_2PO_4 into octadehydromatrine (XII) $C_{15}H_{16}ON_2$, m.p. 175–177°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH, and the substance (XIII) $C_{14}H_{20}N_2$, b.p. 138°/0.001 mm. (XII) gives a violet pine-shaving reaction and reddish-violet Ehrlich test; it is indifferent towards CH_2N_2 , resembling 2-pyridone in these respects. It dissolves in dil. HCl. AuCl₃ and PtCl₄ are immediately reduced and $KMnO_4$ is slowly decolorised. A methiodide or acyl derivatives could not be obtained. It does not react with $NH_2 \cdot CO \cdot NH \cdot NH_2$ or $p\text{-NO}_2 \cdot C_6H_4 \cdot NH \cdot NH_2$. It is stable towards KOH-EtOH or molten KOH. (XIII) is a monacidic, *tert.*-amine, giving a hydrochloride, m.p. 208°, aurichloride, m.p. 118°, methiodide, m.p. 129°, and picrate, m.p. 142°. Since it does not yield NO- or Ac derivatives, the second N is probably *tert.* It probably contains 2 double linkings but is very resistant towards catalytic hydrogenation (PtO_2) under pressure. Under these conditions, (XII) is reduced to didehydromatrine (XIV), $C_{15}H_{12}ON_2$, m.p. 103°. (XIV) does not give a reaction with $FeCl_3$ or the Ehrlich test and is unaffected by KOH-EtOH. It forms a weakly basic NO-derivative. The hydrochloride, m.p. 171°, non-cryst. methiodide (identified as the aurichloride, m.p. 96°, of the corresponding methochloride), and picrate, m.p. 147°, are described. (XIV) in Et_2O is converted by $BzCl$ -NaOH into the *Bz* derivative, m.p. 70° (hydrochloride, m.p. 223°); the $p\text{-NO}_2 \cdot C_6H_4 \cdot CO$ compound has m.p. 98°.

H. W.

Derivatives of 1-methylanhydrocotarnine. O. J. MAGIDSON and I. E. GORBOVIZKI (Ber., 1935, 68, [B], 656–664).—Nitromethylanhydrocotarnine (Hope *et al.*, J.C.S., 1911, 99, 2114) is reduced by SnCl₂ and



HCl at 28–30° to 1-aminomethylanhydrocotarnine (I), m.p. 183° (decomp.) [picrate, m.p. 150–151° (decomp.); hydrochloride, m.p. 170° (decomp.)]; *Ac* deriv-

ative, m.p. 155–160°]. Condensation of (I) with the requisite aldehyde and hydrogenation (PtO_2) of the Schiff's bases leads to the following aminomethylanhydrocotarnines: benzylidene-, m.p. 150°; non-cryst. benzyl- (hygroscopic dihydrochloride, m.p. 172–173° or m.p. 181–183° in sealed capillary); veratrylidene-, m.p. 140–141°; 3':4'-dimethoxybenzyl- [dihydrochloride (+H₂O), m.p. 184°]; vanillylidene-, m.p. 192°; non-cryst. vanillyl- (dihydrochloride, m.p. 131° in sealed tube); piperonylidene-, m.p. 161–162°; non-cryst. piperonyl- (dihydrochloride, m.p. 178.5–180.5°); 3':4'-dihydroxybenzylidene-, m.p. 192°; 3':4'-dihydroxybenzyl- (dihydrochloride); furfurylidene, m.p. 154–155°; 4'-hydroxybenzylidene-, m.p. 180–181°; 4'-hydroxybenzyl- [dihydrochloride (+2H₂O), m.p. 91–93°]; 4'-methoxybenzylidene-, m.p. 153–154°; 4'-methoxybenzyl- (dihydrochloride, m.p. 196–197°); 2'-hydroxybenzylidene-, m.p. 145–146°; 2'-hydroxybenzyl- (dihydrochloride, m.p. 200°). $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ is converted by $NEt_3 \cdot CH_2 \cdot CH_2 \cdot Cl$, HCl at 100° into β -diethylaminoethyl-*p*-toluidine, b.p. 136–140°/6 mm.,

which with cotarnine and NaOEt in EtOH at 40–50° yields 4'- β -diethylaminoethylaminobenzylanhydrocotarnine (very hygroscopic trihydrochloride; platini-chloride, $C_{25}H_{35}O_3N_3 \cdot H_2PtCl_6$, m.p. 165°). Anhydrocotarnino-*p*-acetamidotoluene (cf. Ahluwalia *et al.*, A., 1932, 1047) has m.p. 121–125°. The physiological behaviour of the compounds is fully described.

H. W.

New synthesis of 3:11-dimethoxyoxyprotoberberine, and syntheses of 2:3-methylenedioxy-11:12-dimethoxyoxyprotoberberine and 2:3:11:12-tetramethoxyoxyprotoberberine. S. N. CHAKRAVARTI and M. SWAMINATHAN (J.C.S., 1935, 293–295).—5-Methoxyhomophthalic acid and β -methoxyphenylethylamine at 180° yield 5-methoxyhomophthalic- β -m-methoxyphenylethylimide, m.p. 133°, hydrolysed to 5-methoxyhomophthalic- β -m-methoxyphenylethylamic acid, m.p. 167°, the *Me* ester, m.p. 85°, of which with $POCl_3$ yields 3:11-dimethoxyoxyprotoberberine (A., 1927, 1096). Therefore, in the conversion (*loc. cit.*) of formyl-6-methoxy-1-(3'-methoxybenzyl)-1:2:3:4-tetrahydroisoquinoline into 3:11-dimethoxydihydroprotoberberine, ring-closure takes place *para* to the 3'-OMe; the constitution of dimethoxytetrahydroprotoberberine is not thereby fully determined. In a similar way, 5:6-dimethoxyhomophthalic acid (I) and β -piperonylethylamine at 180° give 5:6-dimethoxyhomophthalic- β -piperonylethylimide, m.p. 223°, hydrolysed to 5:6-dimethoxyhomophthalic- β -piperonylethylamic acid, m.p. 245°, the *Me* ester, m.p. 169–170°, of which with $POCl_3$ yields 11:12-dimethoxy-2:3-methylenedioxyoxyprotoberberine, m.p. and mixed m.p. 230–231° (A., 1934, 669). Also, (I) and β -veratrylethylamine at 180° give 5:6-dimethoxyhomophthalic- β -veratrylethylimide, m.p. 180°, hydrolysed to the amic acid, m.p. 165°, the *Me* ester, m.p. 123°, of which with $POCl_3$ yields 2:3:11:12-tetramethoxyoxyprotoberberine (II), m.p. 190–191°. 2:3:11:12-Tetramethoxytetrahydroprotoberberine is converted by I in EtOH + NaOAc into 2:3:11:12-tetramethoxyprotoberberinium iodide (III), m.p. 245° [chloride (IV), m.p. 225°, from (III) and AgCl]. (IV) and aq. KOH afford (II). H. G. M.

Tetraphenylarsonium halides. F. F. BLICKE and E. MONROE (J. Amer. Chem. Soc., 1935, 57, 720–722).—AsPh₃O with MgMeBr gives triphenylmethylarsonium bromide and with MgPhBr or MgPhI tetraphenylarsonium bromide (I), m.p. 273–275° (with 2Br gives a tribromide, m.p. 215–216°), and iodide (I), m.p. 312–313° (with 2I gives a tri-iodide, m.p. 228–230°). (I) and HCl give the chloride (III), m.p. 256–257° (compound with 1HCl, *cryst.*). (I) or (III) with HI or NaI give (II). MgPhBr with AsPh₃Cl₂ or AsPh₃Cl₂ gives AsPh₃ and Ph₂, but with AsPhO₂ affords some (I). (I) behaves as a strong electrolyte, but in an attempt to prepare AsPh₄ a little AsPh₄Cl₃ only was obtained. (III) has no trypanocidal action and no germicidal action against *S. haemolyticus*, but is germicidal against *S. aureus* at 1:600. R. S. C.

Phenyl- and diphenyl-arsines. F. F. BLICKE and J. F. ONETO (J. Amer. Chem. Soc., 1935, 57, 749–753; cf. A., 1933, 518).—The following reactions were effected in N₂. AsPhCl-OMe and AsH₂Ph in C_6H_6 give (AsPh)₂. AsH₂Ph and CPh₃Cl give

AsPh(CPh₃)₂ and HCl, which react further to give AsPhCl₂ and CHPh₃. AsHPh₂ (I) and CH₂Cl·CO₂H (II) at 160° give AcOH and AsPh₂Cl, which with more (I) gives (AsPh₂)₂ (III), m.p. 129—131°; this with more (II) yields AsPh₂Cl (modified prep. from AsHPh₂ and CH₂Cl·COCl; 65% yield). MgPhBr and (I) give AsPh₂·MgBr, which with HgCl₂ affords first (III) and then AsPh₂Cl, with AsCl₃, I, or AsPh₃I gives (III), with (m-NO₂·C₆H₄)₂AsI, m.p. 113—115° (lit. 112°), yields [(m-NO₂·C₆H₄)₂As]₂, with CHPh₂Br gives (CHPh₂)₂ and (III), with CPh₂Cl₂ gives (III) and (CPh₂)₂, with o-C₆H₄(CH₂Br)₂ gives ω-di(diphenylarsino)-o-xylene (IV), m.p. 104—105° (HgCl₂-compound, m.p. 220—221°), with COPh₂ gives (CPh₂·OH)₂, and with CPh₃Br gives a mixture containing CPh₃, which with HCl affords CHPh₃ and AsPh₂Cl. AsPh₂Cl is unaffected by HCl in presence of CPh₃, but (III) and CPh₃ with HCl give AsPh₂Cl and CHPh₃; it is believed that an equilibrium, (III)+2CPh₃ ⇌ 2AsPh₂·CPh₃, exists. AsPh₂·MgBr and CPh₃ with (not without) H₂O give (I), which then reacts with the CPh₃ to form (III) and CHPh₃. (IV) slowly absorbs O₂ in solution and with I gives AsPh₂I and o-C₆H₄(CH₂I)₂. The prep. of bromo-, iodo-, m.p. 94—95°, and hydroxy-, m.p. 156—157°, unimol. in (CH₂Br)₂, -diphenylarsine is described. R. S. C.

Conversion of 3-nitro-4-methylphenylarsinic acid into 3-amino-4-carboxyphenylarsinic acid by intramolecular dismutation, and the action of hydrobromic acid on m-arsanilic acid and 3-amino-4-carboxyphenylarsinic acid. A. H. C. P. GILLIESON, W. O. KERMAK, and W. T. SPRAGG (J.C.S., 1935, 470—471).—3-Nitro-4-methylphenylarsinic acid and 30% aq. NaOH give 3-amino-4-carboxyphenylarsinic acid, which with HBr gives p-C₆H₄Br·NH₂, identified as the Ac derivative. HBr and m-arsanilic acid form p-C₆H₄Br·NH₂. The mechanism of the reaction is discussed; HBr probably causes decarboxylation. F. R. S.

New derivatives of p-arsanilic acid. VI. p-Arsinopimelanilic and p-arsinosuberanilic acid and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1935, 290—293).—With SOCl₂ Me H pimelate yields its acid chloride, b.p. 135—136°/17 mm., which with atoxyl gives Me p-arsonopimelanilate (I) (Na salt). The Et compound (II) (Na salt) was similarly prepared. (I) and (II) are hydrolysed to the corresponding acid, which with aq. SO₂-HCl-I (trace) affords crude p-dichloroarsinopimelanilic acid, m.p. 114—116°, hydrolysed to p-oxyarsinopimelanilic acid. The following amides, p-AsO₃H₂·C₆H₄·CO·[CH₂]₅·CO·NRR', were prepared from (I) or (II) and the corresponding amine: R, R' = H, H [Na salt (+2H₂O)]; H, Me [NH₂Me salt, Na salt (+2H₂O)]; Me, Me [can be prepared from (I) but not (II)] [Na salt (+3H₂O)]; H, Et [Na salt (+2H₂O)]; H, Pr [Na salt (+H₂O)]. Pimetyl dichloride and atoxyl afford pimelanilido-pp'-diarsinic acid (Na₂ salt). With SOCl₂, Me H suberate yields its acid chloride, b.p. 163—165°/34 mm., which with atoxyl gives Me p-arsonosuberanilate [Na salt (+H₂O)]. The Et compound (Na and Na₂ salts) was similarly prepared. These esters are hydrolysed to the acid [Na salt (+H₂O)], which affords p-dichloroarsinosuberanilic acid, m.p. 152—156°, hydrolysed to p-oxy-

arsinosuberanilic acid. The following amides p-AsO₃H₂·C₆H₄·CO·[CH₂]₆·CO·NRR' are described: R, R' = H, H [Na salt (+2H₂O)], H, Me (Na salt); Me, Me [Na salt (+H₂O)]; H, Et [Na salt (+H₂O)]. Suberyl dichloride with atoxyl and NaOH affords suberanilido-pp'-diarsinic acid [Na₂ salt (+2H₂O)]. The Na salts of these compounds have a smaller trypanocidal power than the corresponding succinic and glutaric homologues, which are the most active members in this series (cf. A., 1931, 636; 1932, 290).

H. G. M.

Mesityldimethylphosphine. W. C. DAVIES (J.C.S., 1935, 462—464).—Mesityldichlorophosphine (I) and MgMeI give mesityldimethylphosphine, b.p. 133°/16 mm. (methiodide, m.p. 232°; ethiodide, m.p. 168°; additive compound, m.p. 58—59°, with CS₂). The rates of addition of (I) to alkyl iodides show it to be more reactive than the As analogue. F. R. S.

Synthesis of asymmetric organo-mercury compounds. R. C. FREIDLIN, A. N. NESMEJANOV, and K. A. KOZESCHKOV (Ber., 1935, 68, [B], 565—569).—Hot alcoholic solutions of the Hg aryl (alkyl) salt, the arylating agent (I), and aq. alkali are rapidly cooled. Apparently any organo-metallic or -metalloid compound which in the widest sense can be mercurated can function as (I). The individuality of liquid (aromatic-aliphatic) compounds which cannot be distilled without decomp. is regarded as established when they yield no distillate when heated at 100°/10—15 mm. The following changes are recorded: Hg phenyl ethyl, from HgEtBr, Sr Ph₂Cl₂, and NaOH, transformed by HCl into HgEtCl, m.p. 192°; Hg methyl α-naphthyl, m.p. 84—86°, from HgMeI and Sn(C₁₀H₇)₂, which gives C₁₀H₈ with HCl-EtOH; Hg phenyl p-nitrophenyl, m.p. 144—145° (decomp.), from p-NO₂·C₆H₄·HgCl and SnPh₃Cl₂, converted by HCl-EtOH into NO₂·C₆H₄·HgCl; Hg phenyl m-nitrophenyl, m.p. 113—115°, from m-NO₂·C₆H₄·HgCl and SnPh₃Cl₂ or SnPhCl₃, converted by HCl-EtOH into m-NO₂·C₆H₄·HgCl; Hg phenyl methyl, from HgMeI and BPh(OH)₂, which yields HgMeCl with HCl; Hg benzyl p-chlorophenyl, m.p. 104—108°, from CH₂Ph·HgCl and Sb(C₆H₄Cl)O, which gives CH₂Ph·HgCl with HCl-EtOH. H. W.

Mercuration of coumarins. D. CHAKRAVARTI (J. Indian Chem. Soc., 1935, 12, 139—140).—A criticism of Naik *et al.* (A., 1934, 1107). Sen *et al.* (A., 1930, 487) have shown that mercuration of coumarin gives 3:5-di(acetoxymercuri)-o-coumaric acid, not 6:8-bisacetoxymercuricoumarin; 6-nitro-coumarin gives 5-nitro-o-coumaric acid (cf. Dey *et al.*, this vol., 211), without removal of NO₂. J. W. B.

Trimethyltriallyltriamine and its mercury derivatives. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1935, 2, 160—164).—Allylamine and CH₂O in Et₂O at 0° yield the compound $\text{CH}_2 < \begin{smallmatrix} \text{NR} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{NR} \end{smallmatrix} \text{NR}$ (R=allyl), b.p. 138—141° (picrate, m.p. 139°), which with Hg(OAc)₂ in MeOH affords the acetoxymercuri-derivative [R=CH₂·CH(OMe)·CH₂·Hg·OAc], readily hydrolysed by aq. NaOH to the corresponding hydrazomercuri-compound. R.

Manufacture of benzanthranyl selenium compounds.—See B., 1935, 444.

Tin *m*-tolyl derivatives. K. A. KOTSCHESCHKOV and M. M. NAD (J. Gen. Chem. Russ., 1934, 4, 1434—1439).— RMgBr ($\text{R}=\text{m-C}_6\text{H}_4\text{Me}$) and SnCl_4 in Et_2O give SnR_4 , which with SnCl_4 affords R_2SnCl_2 (I), m.p. 39—40°, an EtOH solution of which gives R_2SnO on saturation with NH_3 , R_2SnS , m.p. 121.5—122°, with KHS , and RHgCl with HgCl_2 . (I) and SnCl_4 (2 hr. at 100°, then 5 hr. at 160—185°, and 2 hr. at 210—215°) yield R_2SnCl_3 , b.p. 150—151°/23 mm., which affords *m*-tolylstannic acid, decomp. 295°, when hydrolysed with aq. KOH . R. T.

Action of different radiations on gelatin. P. KRONENBERGER (Boll. Soc. ital. Biol. sperim., 1934, 9, 1336—1339). R. N. C.

Combining weight of collagen. J. BEEK, jun. (J. Res. Nat. Bur. Stand., 1935, 14, 217—225).—The adsorption of aq. HCl (0—1.7*M*) by collagen (I) in presence of saturated or nearly saturated aq. NaCl has been measured. The absorption is reversible. There is a series of < 3 N-containing groups in (I) which react with HCl , forming salts with varying hydrolysis consts. 3N in each unit of 38 are in groups which are much more basic than the remainder. The apparent equiv. of (I) in dil. acid solution is approx. 1000. H. J. E.

Fractionation of gelatin. Different forms of gelatin.—See this vol., 701, 702.

Fractionation of gluten dispersed in sodium salicylate solution. A. G. MCCALLA and R. C. ROSE (Canad. J. Res., 1935, 12, 346—356).—The pptn. of gluten (I) from solutions of Na salicylate by MgSO_4 yields fractions having progressively more amide-N and less arginine-N except for the final 10—15% which is probably a definite protein. The fractions all differ in composition from (I) but when united, dissolved, and reprecipitated, produce the original (I). The customary fractionation into glutenin and gliadin is purely arbitrary, only one protein complex being concerned. A. G. P.

Semi-micro-volumetric determination of organically combined halogen. W. KIMURA (Fettechem. Umschau, 1935, 42, 32—34, 41—46; cf. this vol., 183).—The original Stepanow-Bacon titrimetric method, whilst satisfactory for fatty-aromatic compounds containing halogen in the aliphatic chain, fails for compounds such as *p*-chloro- ω -elaiidylacetophenone, where the halogen is in the aromatic nucleus. E. L.

"Nitroguanylhya zones" of some common aldehydes and ketones. W. F. WHITMORE, A. J. REVUKAS, and G. B. L. SMITH (J. Amer. Chem. Soc., 1935, 57, 706—707).—CO-compounds (1—5 drops or 0.05 g. in 1 ml. of H_2O or pure MeOH), *N*-nitro-*N'*-aminoguanidine (5 ml. of aq. solution saturated at 70°), and AcOH (0.25 ml.) at room temp. or 0° give very rapidly *N*-nitroguanylimines (termed *nitroguanylhya zones*), $\text{NO}_2\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{N}:\text{CRR}'$, which slowly decompose in light and are hydrolysed by hot 10% HCl . They are suitable for identification purposes. Compounds from the following are described: *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 200°; PhCHO , m.p. 188°; $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, m.p. 186°; citral, m.p. 135—136.5°; CH_2O , m.p. 169°; piperonal, m.p. 220°;

vanillin, m.p. 186—187°; *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 213°; COMe_2 , m.p. 164—165°; COPhMe , m.p. 161—162°; $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, m.p. 130—131°; *cyclo*-hexanone, m.p. 161.5°, explodes at high temp.; COMeEt , m.p. 136.5°; COMePr , m.p. 109—110°; COMeBu , m.p. 109—110°; AcCO_2H , m.p. 181.5°. M.p. are corr. R. S. C.

Chloranil, a differentiating reagent for amines. J. SIRADJIAN (Bull. Soc. chim., 1935, [v], 2, 623—625).—The reaction (B., 1931, 696) whereby chloranil gives red, violet, and emerald-green colorations with, respectively, primary, *sec.*-, and *tert.*-amines affords a general test for these substances. Certain exceptions are noted. J. W. B.

Analysis of pentosans. Condensation reactions furfuraldehyde-phloroglucinol, methylfurfuraldehyde-phloroglucinol, and the separation of furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde by means of their phloroglucides. F. TROST (Boll. Soc. adriatica Sci. natur. Trieste, 1932, 31, 5—30; Chem. Zentr., 1934, ii, 3800).—The composition of the phloroglucides of furfuraldehyde (I) and methylfurfuraldehyde (II) depends on the proportions of reactants employed. If the proportion is 1:1, furfuraldehydephloroglucide (III) is $\text{C}_{11}\text{H}_{10}\text{O}_4$, and methylfurfuraldehydephloroglucide $\text{C}_{12}\text{H}_{10}\text{O}_4$. (I) and (II) are separated from hydroxymethylfurfuraldehyde by rapid steam-distillation, and (I) from (II) by boiling the phloroglucides with 0.05*N*- NaOH for 1 hr., (III) remaining undissolved. H. N. R.

Determination of indoxyl, indigotin, indirubin, and the indoxyl-thymol complex of Jolles. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1935, 17, 403—419).—A comparison is made of the colorimetric methods of determining indoxyl (I) by conversion into indigotin or indirubin and by the (best) method of Jolles (A., 1915, ii, 593), with which, under described conditions, 0.2 mg. of (I) per litre may be detected in 10 c.c. of serum. A. L.

Clinical porphyrin investigations, their quantitative and qualitative technique. R. FIKENTSCHER and K. FRANKE (Klin. Woch., 1934, 13, 285—289; Chem. Zentr., 1934, ii, 3801).—Known methods for the determination of porphyrins are discussed; a simple method for small quantities is described. H. N. R.

Morphine reaction with iodic acid in papaverine hydrochloride. J. ROZEBOOM (Pharm. Weekblad, 1935, 72, 498—500).—Since CHCl_3 dissolves papaverine hydrochloride (insol. in CCl_4 and CS_2) it cannot be used in the KIO_3 test. S. C.

Titration of alkaloid salts and the indicator Poirrier-blue. F. REIMERS (Arch. Pharm., 1935, 273, 140—155).—Alkaloid salts can be titrated with alkali to phenolphthalein in a H_2O - EtOH medium or one which contains CHCl_3 , or better in a H_2O - EtOH medium with Poirrier-blue (I) as indicator. The absorption curve of (I) in various H_2O - EtOH - HCl and H_2O - EtOH - NaOH mixtures, and the dissociation const. in H_2O and in 50% and 75% EtOH , have been determined. The rate of bleaching of (I) in alkaline solution has been examined. H. G. M.

Biochemistry.

Oxygen dissociation curves of the blood of birds. E. H. CHRISTENSEN and D. B. DILL (J. Biol. Chem., 1935, **109**, 443—448).—The blood (I) (muscovy duck, domestic fowl, ring-necked pheasant, pigeon, domestic duck, domestic goose) has an affinity for O_2 < that of human blood (II), but the O_2 dissociation curves of (I) and (II) are similar in form. Bird erythrocytes, hæmolysed with H_2O , yield a homogeneous solution (III) of hæmoglobin and a red jelly. The affinity for O_2 of (III) is much < that of whole blood. W. McC.

Determination of oxygen in blood in the presence of ether. J. L. SHAW and V. DOWNING (J. Biol. Chem., 1935, **109**, 405—417).—A modification of the procedure of Van Slyke *et al.* (A., 1924, ii, 872) is described. The error is < 1%. 1 c.c. of blood is used. W. McC.

Effect of oxygenation and reduction on the equilibrium of hæmocyanin with acids and bases. J. SHACK (J. Biol. Chem., 1935, **109**, 383—393).—The H^+ activity of the serum (I) of the dialysed hæmocyanin (II) of the horseshoe crab (*Limulus polyphemus*) is unchanged by oxygenation (III), but the serum (IV) of the lobster (*Homarus americanus*) is made more acidic by (III), the max. difference in base bound being 0.758 equiv. for each O. (III) decreases the dissociation const. of a diacid or dibasic group by about 0.8—0.9 p_H unit. Titration curves for the oxygenated and reduced forms of (I), (II), and (IV) are given. W. McC.

Absorption spectrum of the carbon monoxide-hæmochromogen. R. HOFFMANN and W. SCHWARZACHER (Z. physiol. Chem., 1935, **232**, 199—201).—Muscle kept at 60° in presence of CO forms the CO-hæmochromogen. The absorption max. were determined. J. H. B.

Direct determination of carbamino-compounds of carbon dioxide with hæmoglobin. J. K. W. FERGUSON and F. J. W. ROUGHTON (J. Physiol., 1934, **83**, 68—86).— HCO_3^- and dissolved CO_2 in hæmoglobin (I) solutions equilibrated with CO_2 -containing gas mixtures are pptd. by rapid mixing with 6% $BaCl_2$ in NaOH solution and $NaHCO_3$ solution of suitable concn., followed by immediate centrifuging at 1° to remove the $BaCO_3$. The carbamino-compounds (II) of CO_2 and (I) remain in solution, and the CO_2 is determined gasometrically. R. N. C.

Chemical relationships and physiological importance of carbamino-compounds of carbon dioxide with hæmoglobin. J. K. W. FERGUSON and F. J. W. ROUGHTON (J. Physiol., 1934, **83**, 87—102).— CO_2 forms carbamino-compounds (I) with hæmoglobin (II) at p_H 7; the amount of combination at a given CO_2 pressure increases with p_H , but is reduced by rise of temp. and oxygenation of (II), these effects being probably due to changes in the no. and character of the uncharged NH_2 groups in the (II) mol. Carbamino- CO_2 amounts to approx. 2% of the total CO_2 in oxyhæmoglobin, and approx. 10% in (II), at 37°, 7.0—7.4, and a CO_2 pressure of 30—60 mm. It is inferred that (I) play an important

part in CO_2 transport in the respiratory cycle. Evidence is given suggesting that another form of bound CO_2 ("y-bound") is present besides (I) in blood.

R. N. C.

Measurement of red-cell volume. V. Behaviour of cells from oxalated and from defibrinated blood in hypotonic plasma and saline. E. PONDER and E. J. ROBINSON (J. Physiol., 1934, **83**, 34—38).—The red cell behaves as a more "perfect" osmometer in hypotonic defibrinated serum (I) than in oxalated plasma (II), if the tonicity is < 0.6. It behaves as an "imperfect" osmometer in (I) and (II) if the tonicity is < 0.6, and also in hypotonic NaCl solution, losing osmotically-active substances into the surrounding medium if the latter differs considerably from normal. The H_2O content, "critical vol." (III), and "perfection" of the cell as an osmometer, which three factors control the critical tonicity of the cell, behave in accordance with the above view. (III) in serum or plasma is > in NaCl solution.

R. N. C.

Determination of fructose in blood. L. D. SCOTT (Biochem. J., 1935, **29**, 1012—1016).—Fructose is determined in the $ZnSO_4$ -NaOH filtrate of blood by addition of Na tauroglycocholate in EtOH (A., 1934, 1019), evaporation to dryness and addition of conc. HCl, and comparison of the purple colour developed with a standard. The fructose content of venous blood is < that of capillary blood. H. D.

Relationship of blood-sugar level to systemic blood-pressure. H. KOSTERLITZ (Proc. Roy. Soc., 1935, **B**, 117, 436—454).—When liver-glycogen (I) is min., a fall in blood-pressure (II) below a crit. val. (45 mm. of Hg for the rat) produces a decrease in blood-sugar, which is re-established on restoration of (II). With ample (I), a fall in (II) is accompanied by hyperglycæmia. H. G. R.

Origin of the hyperglycæmia caused by centripetal excitation of the dog's vagus nerve divided at the neck. J. MALMEJAC and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, **118**, 1343—1345).—The hyperglycæmia is not due to a depressor effect, and it is not related to the vasodilation. H. G. R.

State of combination of cholesterol in blood-serum. O. MELLANDER (Biochem. Z., 1935, **277**, 305—313; cf. Theorell, this vol., 188).—Examination of blood-serum by the cataphoretic method shows that partial separation of the albumin (I) from the globulin (II) is thus effected. At least part of the cholesterol (III) exists free or very loosely bound. After cataphoresis zones containing (I) and (III) but no (II), and those containing (II) free from (III) and (I) free from (III) are found, whilst the ratios (III) : (I) and (III) : (II) vary in different part of the tube. If (III) is united to protein at all, then it is to one of the fractions of (I) or (II), and not to them as wholes. W. McC.

Cholesterolaemia after infra-red irradiation of the castrated dog. S. MALCZYNSKI and J. LANKOSZ (Compt. rend. Soc. Biol., 1935, **118**, 1367

1369).—The cholesterolemia is independent of the reticulo-endothelial system and of the ovaries.

H. G. R.

Determination of free cholesterol by digitonin. R. GOFFINET (Compt. rend. Soc. Biol., 1935, 118, 1481—1483).—Proteins are pptd. from serum or plasma with COMe_2 , and the ppt. is extracted for 6 hr. with the filtrate. Cholesterol is pptd. from the solution with digitonin, washed, dried, and weighed.

R. N. C.

Physico-chemical studies of fish blood. Neutralisation and buffer-coefficient curves. A. A. DRILHON and G. FLORENCE (Compt. rend. Soc. Biol., 1935, 118, 1320—1323).—The curves for *Muroena* and fresh- and salt- H_2O eels show a qual, but not a quant. similarity.

H. G. R.

Supposed coagulation of oxalate plasma by trypsin. J. MELLANBY (Proc. Roy. Soc., 1935, B, 117, 352—357).—Coagulation of oxalate plasma (I) by trypsin (II) is due to the conversion of prothrombin into thrombin by Ca^{++} present in (II), the quantity of Ca required depending on the thrombokinase in (I).

H. G. R.

Blood-coagulation. I. Rôle of prothrombin and of platelets in the formation of thrombin. II. Formation of fibrin from thrombin and fibrinogen. H. EAGLE (J. Gen. Physiol., 1935, 18, 531—545, 547—555).—I. Solutions of prothrombin (I) liberate thrombin (II) on the addition of Ca^{++} , whether fibrinogen is present or not. The data indicate that thrombin is a cause, not a product, of coagulation of fibrinogen. Platelets or cephalin accelerate the formation of (II), but the amount formed is dependent only on the concn. of (I). Horse, human, rabbit, or dog platelets accelerate the conversion of (I) derived from any of these species.

II. Ca is necessary for the formation of thrombin (I), but may be pptd. as oxalate without affecting the activity of (I) in converting fibrinogen (II) into fibrin. It is calc. that fibrin cannot be a Ca compound unless (II) has mol. wt. $>10^6$. (I) may coagulate >200 times its own wt. of (II), and its action is probably enzymic.

F. A. A.

Hypercoagulability of the blood due to intramuscular injection of sodium citrate. D. DE SOUZA and F. D. M. HOOKING (J. Physiol., 1934, 83, 49—55).—The alkali reserve and coagulability of the blood are increased by intramuscular injections of Na citrate (I) and NaHCO_3 , and diminished by NH_4Cl . The increased coagulability from (I) is due partly to the increase in alkaline reserve and partly to (II) absorption into the blood-stream.

R. N. C.

Kinetics of hæmolysis in cell-taurocholate-serum systems. E. PONDER and A. S. GORDON (Proc. Roy. Soc., 1935, B, 117, 272—288).—The rate of hæmolysis of cells in contact with Na taurocholate (I) may be increased or decreased on the addition of serum (II), according to the conditions. This may be accounted for by assuming that (I) acts partly as a lysin, partly as a sensitiser for the subsequently added lysin (II).

F. A. A.

Stability of antivenoms. E. GRASSET and A. ZOUTENDYK (Compt. rend. Soc. Biol., 1935, 118, 1403—1406).—Cobra antivenoms (I) and that of *Bitis*

arietans (II) are stable over long periods in the cold. They are inactivated by heating above 60° ; (I) in broth solution at 60° form toxic substances with the solvent. (II) is not affected by changes of p_H , nor are (I) except at $p_H 2$, when they become toxic. Addition of lecithin has no effect on (I) or (II).

R. N. C.

Co-existence in the blood of an animal in a state of anaphylactic presensitisation of a sensitising and of a preserving substance. F. MAIGNON (Compt. rend. Soc. Biol., 1935, 118, 1295—1298).—The sensitising substance is adsorbed by the antigen, whilst the preserving substance, which inhibits the anaphylactic effect, is not.

H. G. R.

Precipitin reactions and viscosity. M. COPPO (Compt. rend. Soc. Biol., 1935, 118, 1307—1309).— η of the antigen-antibody mixture (I) rises to a max. at 20—40 min. and then falls to a const. val. The max. increase in η corresponds with a max. speed of flocculation and depends also on the vol. of (I) and temp.

H. G. R.

Osmotic relationships in the hen's egg as determined by relative vapour pressures. J. M. JOHLIN (J. Gen. Physiol., 1935, 18, 481—484).—The osmotic pressure of the yolk is $>$ that of the white (cf. A., 1932, 1153; 1933, 522).

F. A. A.

Electrical properties of isolated frog skin. R. J. PUMPHREY (J. Exp. Biol., 1934, 11, 423—432).—The difference of potential between the inner and outer surfaces of the skin acts as an electrode reversible for K^+ , but not for Ca^{++} or Na^+ . CH. ABS. (p)

Collagen. II. Carbohydrate content. W. GRASSMANN and H. SCHLEICH (Biochem. Z., 1935, 277, 320—328; cf. A., 1934, 671; Sørensen *et al.*, A., 1933, 731).—Collagen (I) from the dried hides of animals (cattle) contains about 1% of carbohydrate (II), which is an equimol. mixture or compound of glucose and galactose. If (II) is lactose and each mol. of (I) is combined with 1 mol. of (II), the mol. wt. of (I) is about 34,500.

W. McC.

Vitreous body. W. S. DUKE-ELDER and H. DAVSON (Biochem. J., 1935, 29, 1121—1129; cf. this vol., 232).—The possibilities of the vitreous body (I) swelling in glaucoma are studied. A gel at its swelling max. at a given p_H takes up further H_2O on changing the p_H suitably; the changes in the elastic properties of (I) on treatment with solutions of KCNS , K_2SO_4 , and dil. HCl are to be interpreted as changes in stability as opposed to reversible changes in hydration, and hence it is deduced that (I) originates *in vivo* as a sol-gel change. The muco-protein in (I) is probably an important factor in its stability. A possible mechanism whereby (I) may increase in vol. is shown.

H. D.

Fluorescence spectra of the flavins of some animal organs. H. BERRY and B. GOUZON (Compt. rend. Soc. Biol., 1935, 119, 101—103).—The flavins from egg-white, guinea-pig liver, and horse-adrenals show fluorescence spectra in the green and yellow, between 515 and 615 m μ .

R. N. C.

Asterubin, a sulphur-containing guanidine compound of living organisms. D. ACKERMANN (Z. physiol. Chem., 1935, 232, 206—212).—The aq.

extract of *Asterias rubens*, L. (I), and *A. glacialis*, L. (II), yields *asterubin* (III), m.p. 272—273° (decomp.). (III) gives no $\text{NH}_2\text{-N}$ with HNO_2 and contains 2 NMe groups. KMnO_4 oxidation affords guanidine. Hydrolysis with aq. Ba(OH)_2 gives NHMe_2 and carbamyltaurine. Hence (III) is $\text{NH}_2\text{C(NMe}_2\text{)-NH-CH}_2\text{-CH}_2\text{-SO}_3\text{H}$. (I) yields in the fraction not pptd. by phosphotungstic acid (IV), glycine and taurine, (II) gives in the (IV) ppt. adenine and *d*-arginine and in the filtrate, glycine, leucine, and tyrosine in addition to (III). J. H. B.

Boric acid reaction and the structure of the nucleic acids. K. MAKINO (Z. physiol. Chem., 1935, 233, 186—188; cf. Boesken, A., 1913, i, 1147).—Deoxyribonucleoside (I) obtained from extract of ox intestine by treatment with nucleotidase reacts positively to the H_3BO_3 test (II). Hence the nucleosides (III) have a pyran ring structure, and consequently the PO_4 of (I) is attached to the 3rd or 4th C of the ribose residue. The mixture obtained by digesting thymonucleic acid (IV) with pancreas-polynucleotidase (free from nucleophosphatase) reacts negatively to (II). Hence deoxyribonucleotides contain no OH corresponding with that of (III) which is phosphorylated. (II) is positive with adenosine, guanosine, inosine, and uridine, and negative with adenylic, guanylic, cytosylic, uracylic, and yeast nucleic acids, and (IV). W. McC.

Determination of reduced glutathione in tissues. A. FUJITA and D. IWATAKE (Biochem. Z., 1935, 277, 284—292).—The accuracy of the iodometric determination of reduced glutathione (I) in biological material (II) is increased by deproteinising with HPO_3 (which prevents interference by Fe^{+++}) and by freezing (II) immediately after the death of the animal from which (II) is taken (prevention of interference by cysteine). Interference by ascorbic acid (III) is avoided by colorimetric determination by the nitroprusside method after removal of protein with HPO_3 and addition of KCN and NH_3 in order to increase persistence of the colour. The (I) and (III) contents of animal organs are given. In addition to (I) and (III), kidney contains other substances which react with I. W. McC.

α - β transformation of muscle-protein *in situ*. W. T. ASTBURY and S. DICKINSON (Nature, 1935, 135, 765).—The predicted α - β transformation (this vol., 376) on stretching myosin has been accomplished by stretching the sartorius muscle of the frog and the retractor muscle of the foot of *Mytilus edulis*.

L. S. T.

Pantothenic acid content of animal tissues. E. ROHRMAN, G. E. BURGET, and R. J. WILLIAMS (Proc. Soc. Exp. Biol. Med., 1934, 32, 473—474).—Pantothenic acid is present in all tissues in measurable amounts. The liver shows the greatest content, but the val. is relatively low in the fresh liver, increasing through autolysis on keeping. R. N. C.

Thyroxine and di-iodotyrosine content of the foetus and the new-born. A. W. ELMER and M. SCHEPS (Compt. rend. Soc. Biol., 1935, 118, 1370—1372).—Thyroids of foetus and the new-born contain 1.3—12.3 and 10.6—11.3 total I, 0.6—3.2 and 5.2—

9.8 thyroxine-I, 0.7—9.1 and 5.4—6.0 ($\times 10^{-6}$ g.) di-iodotyrosine-I, respectively. H. G. R.

Distribution of iodine in adrenal cortex and medulla. A. W. ELMER and M. SCHEPS (Compt. rend. Soc. Biol., 1935, 118, 1374—1376).—Ox cortex contains 46 and medulla 18×10^{-6} g. per 100 g. of dry gland. The presence of thyroxine could not be demonstrated. H. G. R.

Spontaneous decomposition of lecithin. C. W. PRICE (Biochem. J., 1935, 29, 1021—1024).—Following keeping in absence of air, lecithin (I) changes in its electrophoretic behaviour and isoelectric point, the final material more closely resembling (I) *in situ* than that freshly extracted: this is due to removal from the latter of free fatty acids during purification (cf. A., 1933, 778, 1244; this vol., 194). F. O. H.

Fatty substances of shellfish. IV. M. TSUJIMOTO and H. KOYANAGI (J. Soc. Chem. Ind., Japan, 1935, 38, 118—120b).—The soft bodies of “Kumano-kogi” [*Tegula (chlorostoma) xanthostigma* (A. Adams)], after boiling in H_2O , gave on extraction with Et_2O 0.43% COMe_2 -insol. phosphatides; 0.56% fat which on saponification yielded acids, m.p. 32.5—33.5°, I val., 153.4, neutralisation val., 196.7, Et_2O -insol. bromides, 40.3%; and cholesterol (20% on fat). The bodies of three “Shako” [*Tridacna gigas* (Linné)] preserved in EtOH gave, on extraction with Et_2O , 0.04% COMe_2 -insol. matter, 0.9% fat, yielding acids, m.p. 42—43°, I val., 91.3, neutralisation val., 213.5, Et_2O -insol. bromides 16.3%, containing 69.95% Br. The unsaponifiable matter (12.2% on fat) consists of “shakosterol” $\text{C}_{29}\text{H}_{48}\text{O}_2$, m.p. 147° (acetate, m.p. 156—157°). G. H. C.

Biochemical aspects of fats. I. W. E. ANDERSON and H. H. WILLIAMS (Oil and Soap, 1935, 12, 65—68).—A discussion of the distribution and function of cholesterol in the organism. G. H. C.

Determination of chlorine in the nervous centres. L. LANGERON, M. PAGET, and J. LEDIEU (Compt. rend. Soc. Biol., 1935, 118, 1535—1536).—Cl is determined in brain-tissue by the method of Delaville and Broun after drying over H_2SO_4 . Cl and H_2O vals. are given for the brains of a no. of patients. R. N. C.

Sodium and chloride in frog muscle. W. O. FENN, D. M. COBB, and B. S. MARSH (Amer. J. Physiol., 1934, 110, 261—272).—The normal Na : Cl ratio (I) in frog plasma is 1.36, and in muscle 2.27. Cl fluctuates $>$ Na in plasma under varying conditions. In muscles soaked in Ringer's solution (I) falls to 1.06 in 5 hr. at 22°; [Na] increases from 24.5% to 33% of the outside concn., whilst [Cl] increases from 14.5% to 31%. In normal muscle *in vivo* 41% of the Na is in excess of the Cl, which diffuses more readily. R. N. C.

Marchi's staining method. III. Artefacts and effects of perfusion. R. L. SWANK and H. A. DAVENPORT (Stain Tech., 1935, 10, 45—52).—The artefacts (I) recognised and investigated in preps. made by Marchi's method are: intrinsic (I), traumatic (I), perfusion (I), and (I) produced by Et_2O anaesthesia. They consist of physically changed myelin.

H. W. D.

Poisons of the native toad.—See this vol., 749.

Polypeptides in human saliva. S. DELAUNAY and R. JAHIEL (Compt. rend. Soc. Biol., 1935, 118, 1418—1420).—Normal human saliva contains polypeptides. R. N. C.

Sodium content of normal cerebrospinal fluid. W. L. DULIERE and R. MINNE (Compt. rend. Soc. Biol., 1935, 118, 1645—1646).—The normal fluid contains 3.35—3.43 g. of Na per litre. R. N. C.

Lipin components of the lymph of the thoracic duct of the dog. S. H. BROCKETT, M. A. SPIERS, and H. E. HEMWICH (Amer. J. Physiol., 1934, 110, 342—347).—Serum-lipins and the free:total cholesterol ratio are const. in the post-absorptive state. The lipin content of thoracic lymph is \propto the total fatty acids (I) present. Feeding with fat increases (I), lipin-P, and total cholesterol. The portal vein does not carry (I) from the intestine to the liver during digestion. Injection of adrenaline does not affect (I), but increases glucose and lactic acid in the lymph. R. N. C.

Isolation of 3-hydroxy-6-ketoallocholanolic acid from pig's bile. E. FERNHOLZ (Z. physiol. Chem., 1935, 232, 202—205).—Pig's bile after hydrolysis (KOH) gave hyodeoxycholic acid. From the residues after esterification (MeOH- H_2SO_4) and acetylation in C_5H_5N , *Me* 3-acetoxy-6-ketoallocholanate, m.p. 185°, $[\alpha]_D -8^\circ$ in $CHCl_3$, was obtained, indicating the presence of the corresponding acid (*Me* ester, m.p. 135—137°) in the bile. The *allo*-configuration may result from the treatment with KOH. J. H. B.

Intragastric factors in the regulation of gastric acidity. C. M. WILHELMJ, L. C. HENRICH, and F. C. HILL (Amer. J. Physiol., 1934, 110, 251—260).—The secretion of the whole stomach is composed of an acid secretion (I) and a non-acid secretion (II), [Cl] in the two fractions being 578—604 and approx. 353 mg., respectively, per 100 c.c. (II) is somewhat limited in amount, this being independent of the amount of (I); its alkalinity is 0.04*N*. Total neutral Cl in the isolated stomach is somewhat small, and does not rise as (I) falls. The most important intragastric factor in the regulation of gastric secretion is the intensity of the stimulus for (II). R. N. C.

Isolation of mucoitinsulphuric acid from canine gastric juice. S. A. KOMAROV (J. Biol. Chem., 1935, 109, 177—187).—The conc. filtered canine gastric juice was hydrolysed at room temp. with NaOH and the product pptd. with EtOH. The ppt. was dissolved in H_2O and poured into AcOH. After washing the ppt. formed with EtOH and Et₂O and drying in vac. the material was extracted with H_2O and again pptd. with AcOH etc. The products were identified as mucoitinsulphuric acid (I), mucoitin, and the Na salt of (I). Mucoprotein (II) (A., 1932, 639) treated as above gave the Ba salt of (I) on treatment with $Ba(OH)_2$. All preps. gave negative biuret and P tests and positive naphthoresorcinol and org. SO_4 tests. The relative yields of (I) prepared from gastric juice directly and from (II) indicated that (I) was present only as an integral part of (II). H. D.

Influence of various anions of the lyotropic series on the sodium and chloride content of fluid in the intestine. H. S. BURNS and M. B. VISSCHER (Amer. J. Physiol., 1934, 110, 490—498).— H_2O or hypotonic NaCl or urea solutions introduced into the intestine become conc. to vals. $>$ their respective blood concns. (I). Cl accumulation (II) is restrained by Na_2SO_4 , NaH_2PO_4 , Na citrate, $NaNO_3$, and NaOAc, and disappears from the intestine against a diffusion gradient to reach a concn. $<$ (I); NaSCN, on the contrary, accelerates (II). The effects cannot be explained by simple diffusion or osmosis. R. N. C.

Ante-natal secretion of human mammary gland and comparison between this and that obtained directly after birth. S. T. WIDDOWS, M. F. LOWENFELD, M. BOND, C. SHISKIN, and E. I. TAYLOR (Biochem. J., 1935, 29, 1145—1166; cf. A., 1930, 805).—Three classes of ante-natal milk (I) differing in their viscosity are obtained independently of the absence or presence of previous lactation or the period of pregnancy. The protein, ash, Cl', and Ca:P ratio of (I) are $>$ in post-natal milk (II). The Ca, P, and sugar contents of (I) are $<$ in (II); Ca vals., however, showed considerable variations. The sugar content is related to the viscosity of the secretion. H. D.

Presence of an indophenol-oxidase in fresh raw milk. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, 118, 1637—1639).—The action of the indophenol-oxidase of fresh milk is inhibited by CH_2O and KCN, and favoured by urethane owing to the inhibitory effect of the latter on the dehydrogenases. R. N. C.

Oxygen consumption by fresh raw milk. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, 118, 1639—1642).—Fresh milk contains an oxidase capable of activating mol. O_2 , the action being inhibited by 0.01*N*-KCN; the oxidase is hence not one of the known dehydrogenases, the actions of which are not inhibited by this KCN concn. R. N. C.

Deproteinisation of biological liquids. Application to micro-determination of lactose in cows' milk. M. PAGET and Y. DUPONT (Compt. rend. Soc. Biol., 1935, 118, 1536—1538).— $K_4Fe(CN)_6$ and $Zn(OAc)_2$ solutions form a suitable deproteinising agent. Lactose in milk is determined micrometrically after deproteinisation by the mercurio-iodometric method. R. N. C.

Influence of fat in fodder on the fat content of cows' milk. Z. MOCZARSKI and J. BORMANN (Polish Agric. Forest Ann., 1934, 33, 201—208).—The fat content of rape cake did not cause diminution of milk yields if fed at rates $<$ 0.1% of the live wt.; milk-fat yields were, however, lowered. CH. ABS. (p)

Effect of ingested cod-liver oil, shark-liver oil, and salmon oil on the composition of the blood and milk of lactating cows. C. M. McCAY and L. A. MAYNARD (J. Biol. Chem., 1935, 109, 29—37).—Five cows were given cod-liver oil (I), shark-liver oil (II), and salmon oil (III) for periods of 2 weeks with periods between without oil. The

usual lowering of milk-fat after (I) was observed, but (II) and (III) did not appear to have the same effect. The non-saponifiable fraction of (I) has no effect on milk-fat, whilst the triglycerides appear to carry the injurious fraction. No relation was found between oil feeding and composition of blood other than the increase of I val. of plasma-lipins. The total lipins of mammary plasma were consistently lower than those from blood. Neither lipin-P nor inorg. P vals. of the plasma supported the view that phospholipins are the blood precursors of milk-fat. Feeding pasture grass to cows does not counter-effect the lowering of milk-fat after (I).

P. W. C.

Uric acid and urochrome in urine. M. RANGIER (Bull. Soc. Chim. biol., 1935, 17, 502—518; cf. A., 1933, 738).—By adsorption on C and elution with aq. NH_3 a solution of the uric acid-urochrome (I) complex present in urine is obtained. From this on treatment with aq. NH_3 , uric acid (II) is pptd., the urochrome (III) being obtained after concentrating and adding EtOH. At p_{H} 6.2, (II) and (III) unite to give (I).

A. L.

Urinary lyochromes. W. KOSCHARA (Z. physiol. Chem., 1935, 232, 101—116).—The purest preps. of uroflavin (I), although agreeing in most properties with lactoflavin, show a C content 1% less. (I) is probably a mixture of lyochromes (II). H_2S decomposes (II) slightly, and should be avoided in later stages of purification. Human urine contains, in addition to (I), aquoflavin, and two other (II), differentiated by chromatogram (III) and behaviour on alkaline photolysis. A method of determination of (II) uses (III) in conjunction with a KMnO_4 treatment. Human urine contains in winter $< 10^{-5}$ g., in summer $3\text{--}5.5 \times 10^{-5}$ g., of (II) per 100 c.c.

J. H. B.

Determination of nitrate-nitrite-nitrogen in urine. R. GOOTZ and H. TUNGER (Z. physiol. Chem., 1935, 233, 67—74).—0.5 g. of Na_2CO_3 is added to 20—50 c.c. of urine made alkaline with 2N-NaOH and the liquid is evaporated to dryness at low temp. ($> 60^\circ$) in a vac. The apparatus is filled with CO_2 , 50 c.c. of 80% aq. H_2SO_4 and 3—4 c.c. of Hg are added to the residue, and the whole is vigorously shaken for 15 min. Then a saturated solution of Na_2SO_4 in 80% aq. H_2SO_4 is added and the mixture of gases present is passed over CuO and Cu at low red-heat into a nitrometer. Only N united to O is determined. The error is 16%.

W. McC.

Urinary calcium debit and polyuria from ingestion of water. H. GOFFART and L. BRULL (Compt. rend. Soc. Biol., 1935, 118, 1630—1632).—Increase of polyuria from ingestion of H_2O is accompanied by a proportional increase of urinary Ca debit, which stabilises itself at a val. $>$ the initial val.

R. N. C.

Relationship of the urea clearance to the renal blood-flow. D. D. VAN SLYKE, C. P. RHOADS, A. HILLER, and A. ALVING (Amer. J. Physiol., 1934, 110, 387—391).—Urea clearance in dogs is \propto renal blood-flow.

R. N. C.

Crystalline stercobilin. C. J. WATSON (Z. physiol. Chem., 1935, 233, 39—58; cf. A., 1934, 98,

915).—More detailed chemical and crystallographic examination of the stercobilin (I), its salts (hydrochloride, hydrobromide), and the FeCl_3 compound and its ester indicates that the substance of Heilmayer *et al.* (A., 1934, 1386) is identical with (I). Possibly (I) and its salts form loose compounds with CHCl_3 and EtOH, which have absorption spectra different from that of (I). The formula for (I) is probably $\text{C}_{33}\text{H}_{46}\text{O}_7\text{N}_4$ or $\text{C}_{33}\text{H}_{46}\text{O}_6\text{N}_4$. Reduction of (I) does not give mesobilirubinogen (II). A cryst. substance produced by the action of air and light on (II) is not identical with (I).

W. McC.

Distribution of sterols in human faeces. Ileal contents. J. A. GARDNER, H. GAINSBOROUGH, and R. M. MURRAY (Biochem. J., 1935, 29, 1139—1144).—Ileostomy and caecostomy excreta contained only cholesterol and traces of β -cholestanol; hence coprosterol is formed in the colon.

H. D.

Diet and disease. S. J. COWELL (Nature, 1935, 135, 716—718).

L. S. T.

Carbon monoxide in the blood in illness. M. LOEPER, E. BIOY, J. TONNET, and A. VARAY (Compt. rend. Soc. Biol., 1935, 118, 1309—1310).—High vals. are observed in asthma, diabetes, and rheumatism.

H. G. R.

Spectrography of normal and pathological gastric juice, more particularly in pernicious anaemia. L. KARZAG (Compt. rend. Soc. Biol., 1935, 118, 1417—1418).—The substances responsible for the selective absorption shown by the gastric juice (I) are ultrafilterable, and similar to vitamin- B_1 and $-B_2$ in physico-chemical behaviour. The selectivity of the spectrum of (I) is increased by ingestion of EtOH. The extinction coeff. is increased in a no. of gastric affections, but diminished in pernicious anaemia. The active substances are present in a large no. of the tissues.

R. N. C.

Colloid-osmotic (oncotic) pressure. XXXII. Can the displacement of the colloid-osmotic pressure be responsible for the lowering of water excretion in pernicious anaemia? E. KYLIN (Acta med. scand., 1934, 82, 558—566; Chem. Zentr., 1934, iii, 3975).—Serum-albumin and the colloid-osmotic pressure (I) are $<$ normal in pernicious anaemia. H_2O excretion is considerably reduced, and shows no variations parallel with (I).

R. N. C.

Use of grain-fed pigeons in the biological assay of liver preparations. M. R. GURD (Quart. J. Pharm., 1935, 8, 39—53).—Modified methods of staining show all pigeon (I) erythrocytes to contain some reticulation. Enumeration of the more densely reticulated cells fails to indicate any response to administration of active liver extracts by grain-fed (I) (cf. A., 1933, 414).

F. O. H.

Production of cancer by pure hydrocarbons. III. G. BARRY, J. W. COOK, G. A. D. HASLEWOOD, C. L. HEWETT, I. HIEGER, and E. L. KENNAWAY (Proc. Roy. Soc., 1935, B, 117, 318—351).—140 compounds, mostly polycyclic aromatic hydrocarbons, have been tested for cancer-producing activity (I). Of 71 compounds not related in structure to 1:2-benzanthracene (II), only 6 give positive results, of these only 3:4-benzphenanthrene having consider-

able (I). 69 compounds related to (II) have been tested, 25 showing positive results. Most of these are derivatives of (II) having substituents in positions 5 or 6 or both, either alkyl groups or saturated or aromatic rings. Other active compounds are 1:2-benzpyrene, 1:2:7:8-dibenzanthracene, and 3:4:5:6-dibenzacridine. Additional rings or substitution in the *meso* positions tend to reduce (I). Methylcholanthrene is the most active compound so far tested. F. A. A.

Lactic gelling of serum not specific for cancer. R. GILLER (Compt. rend. Soc. Biol., 1935, 118, 1324—1325).—The gelling obtained with lactic acid is not sp. for cancer, being obtained with syphilis, tuberculosis, and leprosy. H. G. R.

Poisoning of glycolytic processes. F. EICH-HOLTZ and K. BAUMGART (Arch. exp. Path. Pharm., 1935, 178, 161—166).—The inhibition of glycolysis produced in tumour tissue (I) by substances (II) forming complexes with heavy metals (A., 1929, 594) is demonstrable in the intact animal to an extent comparable with that by $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ or insulin (III). (II) attack different phases of carbohydrate metabolism (IV), and hence produce varying symptoms of general toxicity. Following treatment with (III), but not with (II), the fall in lactic acid content of (I) is parallel to the increased sensitivity to X-irradiation, which, together with the decreased sensitivity due to adrenaline, is not related to the changes in (IV). F. O. H.

Intravenous injection in cancer of the products of the ferric chloride-ascorbic acid reaction. F. ARLONG, A. MOREL, and A. JOSSEAND (Compt. rend. Soc. Biol., 1935, 118, 1435—1437).—The violet FeCl_3 -ascorbic acid compound has a therapeutic effect in cancer. R. N. C.

Cystinuria. II. Metabolism of cystine, cysteine, methionine, and glutathione. E. BRAND, G. F. CAHILL, and M. M. HARRIS (J. Biol. Chem., 1935, 109, 69—83).—In a case of cystinuria (I), cystine (II) and glutathione (III) are almost completely oxidised, the latter giving a small amount of extra (II). Cysteine (IV) and methionine (V) are excreted largely as extra (II), only a small amount being oxidised to inorg. S. Only (III) and no (IV) was found in the urine. (II) can be catabolised without previous reduction and (III) without previous hydrolysis. The behaviour of an NH_2 -acid is very different, depending on whether it is catabolised as the free acid or as a peptide. (V) is at any rate in part converted into (IV). The (II) excretion in (I) is caused mainly by dietary (V), but the error of metabolism is concerned with the handling of (IV). (II) is not therefore an essential NH_2 -acid. P. W. C.

Iodometric determination of blood-sugar in diabetes. H. BIERRY, B. GOUZON, and C. MAGNAN (Compt. rend. Soc. Biol., 1935, 118, 1350—1352).—The iodometric and Cu-reduction methods give comparable results. H. G. R.

Dangers and injuries in insulin application. E. WIECHMANN (Fortschr. Ther., 1934, 10, 468—476; Chem. Zentr., 1934, ii, 3974—3975).—The

means of avoiding excessive insulin hypoglycæmia are described. R. N. C.

Acetonuria in infectious diseases in relation to glycogen insufficiency of the liver. A. SLATTINEANU, I. BALTEANU, M. SIBI, M. FRANKE, E. VEIT, and P. FILDEN (Compt. rend. Soc. Biol., 1935, 118, 1595—1598).—Acetonuria (I) in infectious diseases is associated with blood-sugar and fever, and occurs when the glycogen function of the liver is disturbed by febrile conditions. In the absence of glucose incomplete combustion of proteins gives rise to (I). R. N. C.

Specific chemotherapy of milk-fever by the parenteral administration of calcium borogluconate. H. DRYERRE and J. R. GREIG (Vet. Rec., 1935, 15, 456—459).—Ca borogluconate is formed when Ca gluconate (I) is dissolved in aq. H_3BO_3 and the solution evaporated; it differs from both the parent substances in cryst. properties, and does not give the H_3BO_3 flame reaction. It is more sol. in H_2O than (I), the solution showing a lower p_{H} . It exerts a therapeutic effect in milk-fever. R. N. C.

Iodine content of blood and urine and basal metabolism; their value in the diagnosis of thyroid function. A. W. ELMER and M. SCHEPS (Acta med. scand., 1934, 82, 126—136; Chem. Zentr., 1934, ii, 3974).—Blood-I (and in severe cases urinary I) rises simultaneously with basal metabolism in hyperthyroidism and falls similarly in hypothyroidism. R. N. C.

Hypothyroidism induced by complete removal of the normal thyroid gland in chronic heart disease. H. L. BLUMGART and D. DAVIS (Endocrinol., 1934, 18, 693—700).—Basal metabolism (I) begins to fall one week after thyroidectomy (II), and reaches its min. between the 3rd and 9th weeks. Hypothyroidism does not appear until (I) has remained low for some weeks. Serum-cholesterol increases gradually after (II), and continues to increase after (I) has reached its min. Myxœdema is controlled without raising (I) by daily small doses of thyroid. R. N. C.

Bound water in cardiac muscle in relation to ventricular fibrillation. N. D. KEHAR and E. V. MCCOLLUM (Amer. J. Physiol., 1934, 110, 485—487).—Ventricular fibrillation produces increase of free and decrease of bound H_2O . R. N. C.

Oxygen utilisation and lactic acid production in the extremities during rest and exercise in subjects with normal and in those with diseased cardio-vascular systems. S. WEISS and L. B. ELLIS (Arch. Int. Med., 1935, 55, 665—680).—In normal subjects O_2 utilisation of the arm and leg is approx. the same; after exercise (I) it is approx. doubled, and returns to normal within 10 min. Lactic acid also rises after (I) with a mixing effect of the circulation. In cases of heart disease a higher basal heart rate with a greater increase and a slower return to normal were observed. H. G. R.

Chemical composition of hydatid liquid. LEMAITRE and RIBERE (Compt. rend. Soc. Biol., 1935, 118, 1578—1579).—Mean vals. are given for the

fundamental analysis of hydatid liquid. Creatinine, NH_4 salts, and lecithin are normal constituents, but not necessarily cholesterol or inositol. It contains a proteolytic and a glycolytic enzyme, the former acting at pH 6.7. R. N. C.

Acute agranulocytosis of kala-azar: negative effect of urea-stibamine and neostibosan on blood of normal rabbits. L. S. ZIA and C. E. FORKNER (Proc. Soc. Exp. Biol. Med., 1934, **32**, 536—538). R. N. C.

Ketonic substances and hepatectomy in the dog. M. FRANKE and S. MALCZYNSKI (Compt. rend. Soc. Biol., 1935, **118**, 1604—1606).—Blood- COMe_2 and $-\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ rise slightly 1 hr. after hepatectomy (I), and then fall to zero or very small vals. β -Hydroxybutyric acid increases steadily after (I). R. N. C.

Lactacidæmia after extirpation of the liver. M. FRANKE and S. MALCZYNSKI (Compt. rend. Soc. Biol., 1935, **118**, 1607—1608).—Blood-lactic acid rises steadily in dogs after hepatectomy. R. N. C.

Ether-extractable indirect bilirubin in icteric sera. B. VARELA-FUENTES and C. VIANA (Compt. rend. Soc. Biol., 1935, **118**, 1518—1520).—A further fraction of indirect bilirubin was extracted by Et_2O from the sera of 10 cases of icterus after exhaustive extraction with CHCl_3 . R. N. C.

Nature of the ether-extractable indirect bilirubin of icteric sera. B. VARELA-FUENTES, M. C. RUBINO, and C. VIANA (Compt. rend. Soc. Biol., 1935, **118**, 1520—1524).— Et_2O -extractable indirect bilirubin (I) is not adsorbed on serum-globulins (II) when these are pptd., nor is it produced by addition of (II) from normal sera to common icteric sera that do not contain (I). (II) are increased and the albumin-(II) ratio is decreased in sera containing (II). R. N. C.

Phosphovanillic reaction of bile salts in tissue extracts of the icteric dog. E. CHABROL, R. CHARONNAT, and J. COTTET (Compt. rend. Soc. Biol., 1935, **118**, 1316—1317).—The reaction has been used to show the distribution of bile salts in the tissues of jaundiced dogs. H. G. R.

Changes in the serum during malaria therapy. E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, **118**, 1334—1336).—Henry's reaction depends on a rise in the ratio of flocculable albumin to protective colloids, which is brought about by either a rise in pseudoglobulin or a lowering in serum-albumin \times cholesterol. H. G. R.

Role of cholesterol in melano-flocculation (Henry reaction). E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, **118**, 1573—1575).—Addition of cholesterol (I) to serum does not increase the intensity of melano-flocculation (II). The increased opacity is due to the additive effects of (II) and pptn. of dissolved (I). Et_2O extraction does not remove any other substance that can increase (II); on the contrary, it increases the index of flocculability. R. N. C.

Relation between pseudoglobulins and "super-flocculation" of serum in distilled water. F.

TRENSZ (Compt. rend. Soc. Biol., 1935, **118**, 1332—1333).—Qual. differences were observed in the "super-flocculation" due to paludism and other pathological states. H. G. R.

Polypeptidorachia in general paralysis. Cytopolypeptidic dissociation. A. PRUNELL (Compt. rend. Soc. Biol., 1935, **118**, 1515—1517).—Polypeptides (I) showed increases in the cerebrospinal fluids in cases of general paralysis. R. N. C.

Change of equilibrium in the blood and oedema of the pregnant woman. E. LÉVY-SOLAL and M. LAUDAT (Compt. rend. Soc. Biol., 1935, **118**, 1325—1328).—Hypoproteinaemia, which occurs rarely in pregnancy, is not the cause of the oedema which occurs at about 7 months. H. G. R.

Variations of the phosphorus-nitrogen ratio of the bone in the course of experimental rickets in the rat. I. GARCIA (Compt. rend. Soc. Biol., 1935, **119**, 109—111).—Bone- H_2O increases with the seriousness of the rachitic lesions. N per g. dry wt. increases, P per g. wet or dry wt. decreases, and the P/N ratio falls below the min. normal val. R. N. C.

Spontaneous calcification of the bone in the course of experimental rickets in the rat: chemical and radiographic tests. I. GARCIA (Compt. rend. Soc. Biol., 1935, **119**, 111—114).—Bone-N rises in rickets (I), falling again to normal when calcification (II) begins. P falls in (I) and rises again during (II), but is always $<$ normal. The P/N ratio behaves similarly to P. R. N. C.

Production of methylglyoxal in rachitic tissues. G. POPOVICIU and N. MUNTEANU (Compt. rend. Soc. Biol., 1935, **118**, 1502—1503).— AcCHO increases in the liver and muscles of rachitic animals. R. N. C.

Relation between acetonuria and hepatic insufficiency in scarlatina. A. SLATINEANU, I. BALTEANU, M. SIBI, E. BUTESCU, and Z. PARASCHIVESCU (Compt. rend. Soc. Biol., 1935, **118**, 1592—1594).—Acetonuria is as common in patients with hepatic insufficiency as in those without it. R. N. C.

Effect of irradiated ergosterol and calcium lactate on calcification of trichina cysts. W. W. WANTLAND (Proc. Soc. Exp. Biol. Med., 1934, **32**, 438—444).—Irradiated ergosterol and Ca lactate administered to rabbits with trichiniasis cause marked calcification of the cysts, which is not shown by untreated animals. R. N. C.

Significance of Vernes' resorcinol reaction in tuberculosis. V. CHORINE and R. PRUDHOMME (Bull. Acad. Méd., 1934, **111**, [3], 98, 378—382; Chem. Zentr., 1934, ii, 3998).—The resorcinol pptn. depends on a diminution of albumin and a disproportionate increase in eu- and pseudo-globulins, and indicates a disturbance of protein equilibrium. J. S. A.

Uroporphyrin regularly produced in acute porphyrinuria. J. WALDENSTROM, H. FINK, and W. HOERBURGER (Z. physiol. Chem., 1935, **233**, 1—9).—The urine of persons suffering from the disease contains a uroporphyrin (m.p. of ester 238—258) sol. in AcOH and EtOAc . W. McC.

Basal metabolism in old age. J. R. MATSON and F. A. HITCHCOCK (Amer. J. Physiol., 1934, 110, 329—341).—Basal metabolism in old women is < the standards; results for men agree with the Harris-Benedict standard, but are < the other standards. The metabolic rate is not related to the degree of senility. The sex difference is of approx. the same magnitude as for middle-aged adults. R. N. C.

Respiratory metabolism of infra-human primates. J. M. BRUHN (Amer. J. Physiol., 1934, 110, 477—484).—Vals. are given for a no. of species of apes and monkeys. The metabolic rate is not altered by extirpation of the frontal cortex. R. N. C.

Chemical aspects of biological oxidations. N. R. DHAR (J. Indian Chem. Soc., 1935, 12, 96—130).—An address. J. W. B.

Phenosafranine as an anticatalyst of the Pasteur effect. F. DICKENS (Nature, 1935, 135, 762—763).—Phenosafranine (I) is the most vigorous sp. inhibitor of the Pasteur effect yet described. When slices of rat brain are suspended in Ringer's solution containing glucose and (I) in $10^{-5}M$ concn. is added, the carbohydrate respiration of the brain remains unimpaired, the R.Q. remains at the carbohydrate level, but the aerobic acid formation (lactic acid) increases to approx. that found under anaerobic conditions. (I) also inhibits the Pasteur mechanism in tumours. L. S. T.

Biochemical differences between cortex and medullary substance of the kidney. B. KISCH (Biochem. Z., 1935, 277, 210—222).—As regards the effect on its respiration of hypertonic solutions of salts (NaCl, KCl, NaNO₃, Na₂SO₄, K₂SO₄, NH₄Cl), [H⁺], org. nutrient substances (pyruvate, lactate, glucose), and NH₂-acids (alanine, serine) the cortex (I) of the kidney (II) differs, in some cases greatly, from the medullary substance. Deamination of added alanine occurs only or chiefly in (I). The function of (II) is determined not only by the nature of the blood which passes through it, but also, to an important extent, by that of the urine which it secretes. W. McC.

Mechanism of respiration. K. A. C. ELLIOT (Nature, 1935, 135, 762).—Two types of transplantable rat tumour, a sarcoma and a carcinoma, while respiring at a rate equal to that of many other tissues, are unable to oxidise succinic or malic acid. Szent-Gyorgyi's generalisation that respiration consists mainly of a reversible oxidation of these acids (this vol., 519) is criticised. L. S. T.

Metabolism of tissues excised from adrenalectomised rats. H. E. HIMWICH, J. F. FAZIKAS, S. B. BARKER, and M. H. HURLBURT (Amer. J. Physiol., 1934, 110, 348—351).—The respiratory metabolism of the liver, kidney, and diaphragm is unaltered by adrenalectomy; that of the testicle and brain shows a decreased O₂ consumption (I) in absence of glucose, and the R.Q. of the brain is decreased. (I) of the cerebral cortex in presence of glucose is decreased, but this is not due to the inability of the brain to oxidise carbohydrate. R. N. C.

Respiratory quotient of muscle of depancreatized dogs. H. E. HIMWICH, W. GOLDFARB, N. RAKEITEN, L. H. NAHUM, and D. DUBOIS (Amer. J. Physiol., 1934, 110, 352—356).—The R.Q. of the resting leg muscle of the depancreatized dog varies, generally being > 0.7, but occasionally less. Ketones are removed from the blood when the R.Q. is > 0.7, but liberated when it is < 0.7, suggesting that the low R.Q. is due to incomplete combustion of fatty acid. R. N. C.

Utilisation of the calorogenic action of di-iodothyronine and thyroxine in muscular exercise. A. CANZANELLI, M. SEGAL, and D. RAPPORT (Amer. J. Physiol., 1934, 110, 410—415).—The energy of the calorogenic actions of di-iodothyronine and thyroxine cannot be used for muscular work, and in addition the performance after these substances are given shows a relative "inefficiency" as compared with that under basal conditions, or after meat-protein or tyrosine. R. N. C.

Use of ethyl alcohol as a fuel in muscular exercise. A. CANZANELLI, R. GUILD, and D. RAPPORT (Amer. J. Physiol., 1934, 110, 416—421).—EtOH cannot be used as a source of oxidative energy for muscular exercise. R. N. C.

Pulmonary glycolysis in normal and depancreatized dogs. L. BINET and M. MARQUIS (Compt. rend. Soc. Biol., 1935, 118, 1394—1396).—The R.Q. of the air passing through the isolated lung of the normal dog remains steady at unity or oscillates around it, whilst the glucose of the perfusing blood falls. In depancreatized dogs the R.Q. falls after perfusion for 1 hr., whilst glucose increases; the R.Q. can be restored to its initial val. by addition of glucose or insulin to the perfusing blood as required. R. N. C.

Relationship between cell metabolism and growth. E. BUMM (Deut. med. Woch., 1934, 60, 1173—1176; Chem. Zentr., 1934, ii, 3965).—The significance of glycolysis in the growth, division, and energy supply of the cell is discussed. A. G. P.

Effect of low atmospheric pressure on the glycogen content of the rat. G. EVANS (Amer. J. Physiol., 1934, 110, 273—277).—Total carbohydrate of rats increases considerably when they are starved for 24 hr. at $\frac{1}{2}$ atm.; the greatest increase occurs in the liver, and cannot be accounted for by carbohydrate mobilisation, since no decrease occurs in any of the other carbohydrate stores of the body. It is concluded that the extra glycogen is derived from protein or fat by interconversion. Evidence is given that the process necessitates the presence of adrenal tissue. R. N. C.

Maximum rate of intravenous assimilation of glucose in the resting dog under application of isovolumetric water regulation. M. WIERZUCHOWSKI, A. GOSTYNSKA, and H. FISZEL (Compt. rend. Soc. Biol., 1935, 118, 1680—1682).—Continuous intravenous injection of glucose results in glycosuria if the rate of injection (I) is > 1 g. per kg. per hr.; at 9 g. per kg. per hr. 50% of the glucose is excreted. Blood-glucose remains normal until (I) reaches 6 g. per kg. per hr., when it begins to rise rapidly. R. N. C.

Behaviour of lactic acid in blood and urine during continuous intravenous injection of glucose over the whole scale of assimilation. M. WIERZUCHOWSKI and T. CHMIELEWSKI (Compt. rend. Soc. Biol., 1935, **118**, 1682—1684).—Blood-lactic acid in dogs increases steadily with the rate of continuous injection (I) of glucose. Lactic acid excretion remains low until (I) becomes > 4 g. per kg. per hr., when it increases with (I). R. N. C.

Methylglyoxal and other fission products of anaerobic carbohydrate metabolism. M. GOLDENBERG, F. GOTTDENKER, and C. J. ROTHBERGER (Arch. exp. Path. Pharm., 1935, **178**, 201—211).—Intermediate products of anaerobic carbohydrate metabolism other than AcCHO , viz., glyceraldehyde and lactic, pyruvic, glycerophosphoric, phosphoglyceric, hexose-mono- and -di-phosphoric acids, have no action on the heart and blood-vessels. Glyoxal itself is inactive. The role of AcCHO in the changes in heart-beat and circulation during exercise and other conditions producing certain types of carbohydrate degradation is discussed. F. O. H.

Heterogonic growth and chemical composition of the liver in pigeons. L. KAUFMANN and A. NOWOTNA (Pflüger's Archiv, 1934, **235**, 247—255).—The liver grows more rapidly than the remainder of the body during the first week of life, H_2O and protein (I) increasing during this time. After the first week growth slackens, and H_2O and (I) decrease. Glycogen (II) rises rapidly during the first 3 weeks, whilst fat falls. (I) increase is isogonic with the liver-wt. (III) during this period, afterwards becoming negatively heterogonic. (II) increase is positively, and fat increase negatively, heterogonic with (III) until the 6th week, after which (II) increase becomes negatively heterogonic and fat increase isogonic. R. N. C.

Ability of various carbohydrates to replace fats in diets containing dried milk. D. J. LEVINE (Z. Vitaminforsch., 1935, **4**, 92—105).—The subnormal liver-glycogenesis (I) in rats fed on fat-free dried milk is increased by addition to the diet of glucose or sucrose, to a smaller extent by maltose, and still less by lactose. Addition of bread products (I) $>$ that due to flours (barley $>$ wheat $>$ rice $>$ maize), which, however, are superior to pure sugars, probably owing to their protein and fat content. The glycogen content of the liver is dependent on diet and rate of growth; for a fixed diet it can be calc. from the latter. F. O. H.

Rôle of placenta in fat metabolism of rabbit foetus. E. M. BOYD (Biochem. J., 1935, **29**, 985—993).—The phospholipin (I), cholesteryl ester (II), neutral fat (III), and free cholesterol (IV) in the placenta (V) and foetus (VI) of rabbits were determined from the 14th to 32nd day of pregnancy. The concn. of (I) and (IV) in (VI) increases continuously during pregnancy, whilst in (V), (I) passes through a min. and (IV) increases slowly. (II) passes through a max. in (V) and is unchanged in (VI); (III) rises suddenly in (VI) at approx. the 23rd day, and again becomes const. at a high level, and in (V) it decreases slowly throughout the period studied. The opinion

that (V) actively transfers lipins as opposed to behaving as a passive membrane is expressed. H. D.

Fate of dehydrocholic and dehydrodeoxycholic acids in the toad.—See this vol., 749.

Nature of the amphibian organisation centre.
I. Chemical properties of the evocator. C. H. WADDINGTON, J. NEEDHAM, W. W. NOWINSKI, and R. LEMBERG. **II. Induction by synthetic polycyclic hydrocarbons.** C. H. WADDINGTON and D. M. NEEDHAM (Proc. Roy. Soc., 1935, **B**, **117**, 289—310, 310—317).—I. Details of experiments previously reported (A., 1934, 551, 1029) are given. The evocator substance (I) from newt bodies and mammalian liver extracts is unsaponifiable and is precipitable by digitonin. A similar active substance can be extracted from crude preps. of glycogen (II): this may account for the activity of (II) claimed by some workers.

II. Details are given of the experiments of which the (positive) results have already been reported (A., 1934, 1029). F. A. A.

Transformations of the nucleotides in heart muscle. **I.** D. FERDMANN and L. GALPERIN (Biochem. Z., 1935, **277**, 191—202).—The fraction of the extract of the heart muscle (I) of the dog which contains P compounds hydrolysed by $N\text{-HCl}$ in 30 min. at 100° consists of adenine dinucleotide (II) and at least one other P compound. About 40% of the pentoses (III) of (I) is in the form of (II). Short autolysis (IV) of (I) in H_2O causes increase (not due to decomp. of nucleoproteins), long (IV) decrease, in the (III) content. At p_{H} 9.4 presence of Mg restricts production of (III) during (IV). The (II) content of (I) decreases during (IV), but if Mg^{++} is added the degradation of (II) is retarded. W. McC.

Transformations of adenosinetriphosphoric acid in muscle. **I. Dephosphorylation during muscular activity.** D. FERDMANN, O. FEIN-SCHMIDT, and M. DMITRENKO (Biochem. Z., 1935, **277**, 203—209; cf. A., 1933, 736; Lohmann, A., 1934, 1020).—In the frog, muscular activity results in the breakdown of the adenosinetriphosphoric acid (I) of muscle (II), $\text{H}_4\text{P}_2\text{O}_7$ being liberated. Resynthesis of (I) occurs as (II) recovers from fatigue. W. McC.

Formation of adenosinetriphosphoric acid and the rôle of phosphagens. P. ÖSTERN, T. BARANOWSKI, and J. REIS (Compt. rend. Soc. Biol., 1935, **118**, 1414—1417).—Autolysed frog-muscle extract (I) slowly hydrolyses phosphoglyceric acid (II); addition of adenylic acid (III) produces slow formation of adenosinetriphosphoric acid (IV), all the P being converted into (IV) or phosphopyruvic acid (V). If creatine has been previously removed from (I) by dialysis, addition of (II) results in partial formation of (V) without liberation of PO_4''' ; (III) then causes a rapid formation of (IV), which contains 50% of the P of the (II) added. Hence the dephosphorylation of (II) takes place in two steps, creatine-phosphoric acid not being an obligatory intermediary.

Proteolysis in regenerating tissues. **III. Changes in the activity of tissue-protease during**

the regeneration of amphibian organs. V. N. ORECHOVITSCH, N. V. BROMLEY, and N. A. KUSMINA (Biochem. Z., 1935, 277, 186—190; cf. A., 1934, 1252).—In tadpoles, tissue (I) regenerating up to 3 days after amputation of the tail does not differ from ordinary tissue (II) as regards proteolytic activity (III), but from the 3rd until the 11th day (I) has (III) much > that of (II). After the 11th day (III) of (I) decreases, and reaches the normal val. on the 13th day. Tissue from the residual part of the amputated tail behaves like (I) as regards (III). W. McC.

Effect of intermittent and unequal supply of protein on the nutrition of rats. M. MATSUOKA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 15—16).—Groups of animals are fed a protein-free diet, the protein deficiency being supplied at different intervals, but on a single day. The controls (I), which receive protein every day, grow better than the experimental animals (II), although the food consumption of (I) is inferior to that of (II) on a protein-free diet. The total protein intake of (II) is < that of (I). J. D. L.

Metabolism of *l*- and *dl*-methionine in adult and growing dogs maintained on diets of various protein contents. J. A. STEKOL (J. Biol. Chem., 1935, 109, 147—157; cf. A., 1934, 1392).—Dogs were given a diet until the urinary constituents remained const., when methionine was administered, and the urine was analysed until the output or urinary products returned to normal. 63—71% of *l*- (I) and *dl*-methionine (II) fed to adult dogs on a protein-free diet was retained, and the remainder excreted as inorg. SO_4 . 74—100% of (II) in growing dogs maintained on Cowgill's diet was retained. 75—81% of (I) and (II) fed to growing dogs on a low-S diet was retained; N-retention occurred on the day of administration. H. D.

Metabolism of norleucine, isoleucine, and valine. Synthesis of phenyl derivatives.—See this vol., 746.

Urea formation in the animal body. H. A. KREBS (Ergebn. Enzymforsch., 1934, 3, 247—264; Chem. Zentr., 1934, ii, 3523).—Theoretical.

R. N. C.

Heat production of muscle and nerve. A. V. HILL (Nature, 1935, 135, 721—724). L. S. T.

Report of physiological chemist, 1932—1933. F. J. WARTH (Imp. Inst. Agric. Res. Pusa, Sci. Rept., 1934, 124—133).—Rations containing CaO 0.73, and P_2O_5 0.47% for young heifers were not improved by mineral supplements.

The composition of milk was not significantly affected by increasing the protein level (I) of the ration above normal requirement. High (I) tended slightly to prolong the lactation period.

Conversion of fresh sorghum (II) into hay increased the crude fibre (III) content and decreased that of sol. carbohydrate (IV). The digestibility of (III) and (IV) was lowered. Rice straw provided just sufficient P but insufficient Ca for mature bullocks. (II) hay contained adequate amounts of Ca and P.

Glycuronic acid is present in all urines from Indian

cattle and sheep in amounts which vary considerably with the ration, but are not much affected by high SO_4 feeding.

A negative SO_4 and S balance in cattle was changed to a positive one by feeding with Na_2SO_4 . CH. ABS. (p)

Influence of nutrition on metabolism. III. Effect of potassium on resting and working metabolism. F. BRUMAN (Deut. Arch. klin. Med., 1934, 176, 589—611; Chem. Zentr., 1934, ii, 3520—3521).—Administration to man of 5 g. of K daily (as various salts in weakly alkaline solution) resulted in increased Na elimination, increased Ca retention, markedly increased urinary NH_4 , and small increases in urea, total N, creatinine, and creatine. The K given was partly retained. Cl' excretion was unaffected. Basal metabolism was somewhat increased. During work and the subsequent recovery period O_2 consumption was considerably depressed as a result of the increased nutrient effect. A. G. P.

Theory of narcosis. K. H. MEYER and H. HEMMI (Arch. Sci. phys. nat., 1934, 16, Suppl., 204—207).—The partition coeffs. of a no. of narcotics between the gaseous phase and oleyl alcohol (I) and between H_2O and (I) were compared with their narcotic activity. It is concluded that all the substances examined are active when their concn. in the body-lipins is between 0.03 and 0.05 mol. per litre. H. D.

Effect of narcosis on water and mineral tolerance in fresh-water animals. E. HUF (Pflüger's Archiv, 1934, 235, 129—140).—Blood-Cl (I) in *Limnaea stagnalis* (II) is increased on immersion in dil. sea- H_2O (III), NaCl being absorbed through the intestine and skin. (I) falls during narcosis (IV) in (II) and in *Potamobius* (V); the fall is more marked in (II), the wt. of which increases through absorption of H_2O , whilst the wt. of (V) is unaltered. The changes in (II) are reversible if (IV) is of short duration; after more prolonged (IV), (I) remains low when the wt. has reached its initial val. In (V), low (I) after (IV) is restored to the normal by immersion in dil. (III). Blood-Na, -Ca, and -Mg in (II) fall with (I), whilst -K increases. R. N. C.

Action of chloroform on the lipin-phosphorus content of guinea-pig liver. E. BUDING (Compt. rend. Soc. Biol., 1935, 119, 51—53).— CHCl_3 poisoning produces an increase of total fat and a fall of lipin-P in the liver, both effects being > those produced in yellow fever. R. N. C.

Narcotic potency of some cyclic acetals. P. K. KNOEFL (J. Pharm. Exp. Ther., 1935, 53, 440—444).—The pharmacological action of the cyclic acetals approaches that of paraldehyde as the structure becomes more similar. H. G. R.

Acetanilide poisoning. S. PAYNE (J. Pharm. Exp. Ther., 1935, 53, 401—417).—Ingestion of acetanilide causes anaemia, methaemoglobinemia, and an increase in blood-PhOH, but no cardiac damage. Prolonged administration produces tolerance. H. G. R.

Distribution of phenol between olive oil and serum. A. HEEDE and S. STENSIG (Dansk Tidsskr. Farm., 1935, 9, 86—94).—The distribution coeff.

between olive oil and serum differs little from that between olive oil and H_2O (1 : 6). R. P. B.

Acetonitrile test for thyroid. F. WOKES (Quart. J. Pharm., 1935, 8, 54—60).—The susceptibility of mice to MeCN poisoning and the degree of protection (I) afforded by thyroid administration are dependent on temp. Thus at 38° the lethal dose is approx. one fifth of that at room temp., whilst (I) is very slight; at 7—18° (I) occurs, but the flatness of the dose-mortality curve indicates the unsuitability of the method. F. O. H.

Relation between chemical constitution and taste. A. GIACALONE [with G. COLLESANO] (Gazzetta, 1935, 65, 129—131).—The p_H in 1% solution, solubility, and taste of NH_2Ac and its Cl , Cl_2 , Cl_3 , Br , Br_2 , Br_3 , and I derivatives are compared. With increase of negative substituents, sweetness increases. E. W. W.

Refractive index of serum during the action of a depressor substance: acetylcholine. L. JUNG and M. PIERRE (Compt. rend. Soc. Biol., 1935, 118, 1451—1453).—The circulatory variations produced by acetylcholine have no effect on the refractive index of the serum. R. N. C.

Depressor substances in extracts of intestine. J. H. GADDUM and H. SCHILD (J. Physiol., 1934, 83, 1—14).—The depressor effect of intestinal extracts on atropinised cats is due almost entirely to histamine (I), and there is no evidence of any other acid-stable depressor substance. Substance P (II) is present in $CCl_3 \cdot CO_2H$ extracts of the intestine. The adenosine fraction (alkali-stable depressors) is partly destroyed by autolysis or HNO_2 and is pptd. by $COMe_2$; (II) is stable to these agents and is sol. in $COMe_2$. (I) is destroyed by HNO_2 under conditions where (II) is stable. (II) is carried towards the cathode by an electric current. R. N. C.

Response of the isolated uterus of the guinea-pig to histamine. H. J. PHELPS (Biochem. J., 1935, 29, 1043—1047).—Guinea-pig uterus shows an increased response to histamine (I) in alkaline solutions which might be expected if the activity of (I) is due to the apolar adsorption of non-ionised mols. by cell-surfaces. P. W. C.

Quinine action. W. WARAST (Arch. Schiffs- u. Tropen-Hyg., 1934, 38, 222—232; Chem. Zentr., 1934, ii, 3524).—Adsorption of quinine (I) by erythrocytes (II) \propto (I) concn. and the amount of (II). The adsorption coeff. is 14.7. CO_2 does not displace (I) from (II). In presence of As, (I) does not cause formation of methæmoglobin. R. N. C.

Distribution of quinine in the endocrine organs. M. T. REGNIER (Compt. rend. Soc. Biol., 1935, 118, 1290—1292).—The quinine, 24 hr. after ingestion, in the organs of a dog was comparable in amount to that found in a human foetus, the mother having absorbed 1.5 g. 12 hr. before parturition. H. G. R.

Morphine, codeine, and their derivatives. VIII. Monoacetyl- and diacetyl-morphine and their hydrogenated derivatives. N. B. EDDY and H. A. HOWES (J. Pharm. Exp. Ther., 1935, 53, 430—439).—Analgesic (I) and toxic (II) effects of morphine

and dihydromorphine are increased by acetylation. Whereas (I) and depressant action are decreased by hydrogenation of both mono- and diacetylmorphine, (II) is increased. H. G. R.

Effects of sympathetic stimulation and of adrenaline on muscle-glycogen. A. B. CORKILL, H. P. MARKS, and S. SOSKIN (J. Physiol., 1934, 83, 26—33).—Sympathetic stimulation (I) and adrenaline both produce a fall of muscle-glycogen (II). Ergotoxine abolishes the effect of (I) without having any sp. effect on (II). R. N. C.

Pharmacological and bactericidal properties of umbellulone. M. E. DRAKE and E. T. STUHR (J. Amer. Pharm. Assoc., 1935, 24, 196—207).—Umbellulone, a ketone from *Umbellularia californica*, produces methæmoglobin from blood *in vitro* and *in vivo* and hæmolysis in men, guinea-pigs, and horses. It has marked fungicidal and bactericidal actions in concns. \leq 2.0 and 0.2%, respectively, whilst the phenol coeff. is 6.25. The min. lethal dose in dogs is 0.178 c.c. per kg. body-wt. F. O. H.

Mechanism of cell-stimulation by substances foreign to the body. G. ORZECZOWSKI (Arch. exp. Path. Pharm., 1935, 178, 229—251).—No action on cell growth by substances such as strophanthin can be detected in cultures (pure or containing leucocytes) of fowl's-heart fibroblasts. Menthol has a typical action on the metabolism of yeasts. The sensitivity of cells in cultures appears to be $>$ that *in vivo*. F. O. H.

Bioassay of digitalis. II. New leg-vein and intramuscular guinea-pig methods. J. H. DEFANDORF (J. Amer. Pharm. Assoc., 1935, 24, 276—280). H. D.

Effect of caffeine and theobromine on digitalis toxicity. H. B. HAAG and J. D. WOODLEY (J. Pharm. Exp. Ther., 1935, 53, 465—473).—In normal doses caffeine or theobromine does not affect the toxicity (I) of ouabain, strophanthin, or digitalis. Larger doses increase (I) of all preps. H. G. R.

Active substance of grass-pollen. I. Activation of an active group of small mol. wt. by colloidal substances. C. E. BENJAMINS, H. A. E. VAN DISHOECK, and J. L. M. GERMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 308—319).—A pollen extract, after ultrafiltration or proteolytic digestion, gives a diminished but positive skin reaction with hay-fever patients. Activity is enhanced by protective colloids (especially proteins). The active principle is therefore of small mol. wt., but it needs a non-sp. colloidal carrier to exert its full activity. E. A. H. R.

Complexes formed by bromoacetic acid and organic bases and toxins. L. GENEVOIS and G. MANDELLON (Compt. rend. Soc. Biol., 1935, 118, 1353—1354).—Complexes are formed with org. bases, e.g., strychnine, NH_2 -acids, and toxins at a definite p_H between 6 and 9. H. G. R.

Effect of some substances on the mechanism of formation of β -hydroxybutyric and oxalic acids. P. H. FLEURET (Compt. rend. Soc. Biol., 1935, 118, 1569—1572).—Methylene-blue in small, slowly-increasing quantities diminishes urinary β -hydroxy-

butyric acid (I) and increases $\text{H}_2\text{C}_2\text{O}_4$ (II) in dogs on a carbohydrate diet; larger quantities diminish (I) considerably and increase (II) slightly at first, both increasing abruptly later. $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$ lowers (I) and (II) in small quantities, but increases (I) considerably in larger quantities. (I) is increased by oxidation inhibitors (III); (II) is lowered by quinine, but increased by other (III). KNO_3 lowers (I) and (II).

R. N. C.

Modifications of the metabolism of the thymus through injection of cyclopentylidinitrophenol in the guinea-pig. M. CHEVREMENT (Compt. rend. Soc. Biol., 1935, 118, 1473—1476).—Respiration and aerobic and anaerobic fermentation of the thymus rise to max. vals. 30 min. after injection of cyclopentylidinitrophenol, afterwards falling to normal.

R. N. C.

Modifications of the radio-sensitivity of the thymus after injection of cyclopentylidinitrophenol in the guinea-pig. M. CHEVREMENT (Compt. rend. Soc. Biol., 1935, 118, 1476—1479).—The metabolic acceleration provoked by cyclopentylidinitrophenol in the thymus increases its radio-sensitivity.

R. N. C.

Action of germanin on diuresis. E. ZUNZ and O. VESSELOVSKY (Compt. rend. Soc. Biol., 1935, 118, 1620—1622).—Intramuscular injection of germanin (Bayer 205) reduces the diuresis following ingestion of H_2O or NaCl or urea solutions.

R. N. C.

Salvarsan and galactose assimilation. O. SATKE and K. THUMS (Z. klin. Med., 1935, 121, 748—757; Chem. Zentr., 1934, ii, 3523).—Injection of neosalvarsan in persons with normal galactosuria (I) and normal or increased hyperglycaemic difference (II) produces no abnormal (I), but in cases of increased (I) and (II), (I) falls below the upper normal limit.

R. N. C.

Biochemistry of lead in blood. J. TEISINGER (Biochem. Z., 1935, 277, 178—185).—Examination by the method of Heyrovsky (A., 1932, 1101) of human blood-serum and erythrocytes (I) to which Pb^{++} has been added indicates that the Pb^{++} is adsorbed on the colloidal protein, especially that of (I), the resistance of which in hypotonic solutions is thereby increased. Appreciable combination of the Pb^{++} with PO_4^{+++} probably does not occur.

W. McC.

Action of simple and complex derivatives of manganese, cobalt, and nickel. F. HENDRYCH and J. ESCOBAR-BORDOY (Arch. exp. Path. Pharm., 1935, 178, 167—177).—All the compounds investigated produce paralysis of the central nervous system and heart and diminish the blood-pressure, whilst the simple salts are most, and the tervalent complex derivatives least, toxic on intravenous injection. Co^{II} and Ni^{II} salts accelerate the heart, whilst Mn^{II} and Co^{III} salts are inactive. The simple salts paralyse, and the complex augment, the movements of the isolated rabbit's intestine. Co salts and MnCl_2 citrate, whilst complex Mn and all Ni salts contract, blood-vessels (frog).

F. O. H.

Catalytic action of iron. III. Oral administration. F. EICHHOLTZ and H. UNRATH (Arch.

exp. Path. Pharm., 1935, 178, 154—160; cf. A., 1934, 1031).—Conversion of orally administered Fe^{II} into the catalytically active form in mice is approx. 25% of that of subcutaneously injected Fe^{II} . Fe^{III} citrate and, to a greater extent, ferrum reductum have an activity (I) < that of Fe^{II} , whilst saccharated ferric oxide is inactive. With Fe^{II} salts, (I) is independent of the anion. Max. (I) occurs approx. 8 min. after ingestion and then rapidly diminishes. Ascorbic acid, which stabilises Fe^{II} , neither influences (I) nor reduces Fe^{III} in tissue juices.

F. O. H.

Possibility of acute poisoning by iron. Comparison with that by manganese. F. HENDRYCH and K. KLIMESCH (Arch. exp. Path. Pharm., 1935, 178, 178—188).—Excessive administration of certain derivatives of Fe produces liver degeneration (I) in rabbits. Ingestion or subcutaneous injection of large amounts of FeCl_2 induces no morphological changes, even though by the latter route death occurs with comparative rapidity. Repeated administration of Na Fe^{III} citrate or FeCO_3 and also of Na Mn citrate or MnCl_2 produces (I). Impairment of kidney function occurs more frequently with Mn than with Fe salts.

F. O. H.

Experimental uranium nephritis: action of insulin on acidosis. L. BRULL and E. HAIRS (Compt. rend. Soc. Biol., 1935, 118, 1632—1634).—The acidosis provoked in dogs by $\text{UO}_2(\text{NO}_3)_2$ is due to org. acid accumulation, and is not reduced by insulin.

R. N. C.

Skin sensitivity to dichromate. C. E. HERCUS and H. D. PURVES (Lancet, 1935, 228, 985—987).—A definite skin reaction has been obtained in a human being with 3.3×10^{-6} g. of $\text{K}_2\text{Cr}_2\text{O}_7$, applied externally and with 3.3×10^{-9} g. on intradermal inoculation. Attempts at passive transfer failed.

L. S. T.

Hyperglycaemia produced by salts. H. JENTGENS (Biochem. Z., 1935, 277, 273—278).—In fasting rabbits, injection of 5 c.c. of M - or $2M$ - NaCl , $-\text{NaBr}$, or $-\text{NaI}$ results, within 1 hr., in a 1° rise of body-temp. The NaI and still more the NaBr cause increase in the blood-sugar level, but the NaCl does not affect it.

W. McC.

Comparison of the effects of potassium iodide and of di-iodotyrosine on basal metabolism. W. J. SIEBERT and C. S. LINTON (J. Pharm. Exp. Ther., 1935, 53, 418—429).—Di-iodotyrosine causes the same qual. effects as KI in doses which contain the same amount of I . In thyroidectomised guinea-pigs, the basal metabolic rate is lowered and the rise caused by thyroxine is prevented.

H. G. R.

Chemical basis of mud therapy. V. KILIAN (Arch. exp. Path. Pharm., 1935, 178, 197—200).—The application of medicinal mud (Pištany) to the shaved skin of rabbits is followed by an absorption of free and combined S resulting in the presence of H_2S in the blood. Inflammation especially associated with the lymph-glands occurs.

F. O. H.

Chronic toxicosis in dairy cows due to ingestion of fluorine. P. H. PHILLIPS, E. B. HART, and G. BONSTEDT (Wisconsin Agric. Exp. Sta. Res. Bull., 1934, No. 123, 30 pp.).—The crit. margin of tolerance of F for dairy cows is 2—3 mg. per kg. body-wt.

Higher proportions caused loss of wt. and reduction in milk yield, lowered food consumption, and inanition. Addition of 1.25–2.50% of raw rock phosphate to the ration caused F cachexia. No influence on the F content or nutritional val. of the milk was detected. Ingestion of F is followed by storage of F in inactive tissues (bones and teeth). More active organs (liver) have very low F contents.

A. G. P.

Absorbability of calcium compounds. A. R. BLISS, jun., and R. W. MORRISON (J. Amer. Pharm. Assoc., 1935, 24, 280–285; cf. A., 1934, 1133).—The absorption of Ca lactate (I), gluconate, chloride, inositolhexaphosphate, phosphate, and glycerophosphate is measured in mice by its antagonistic action to Mg narcosis. (I) is most rapidly absorbed.

H. D.

Injectable calcium salts. A. LUMIERE and H. BRUN (Compt. rend. Soc. Biol., 1935, 118, 1453–1455).—Org. Ca salts are only very feebly toxic when injected intravenously; when injected subcutaneously or intramuscularly only those of acids derived from sugars are absorbed.

R. N. C.

Cardio-stimulatory form of calcium. K. POHLE (Arch. exp. Path. Pharm., 1935, 178, 109–147).—The Ca of body-fluids occurs as Ca^{++} and as free or protein-bound complexes (I) (containing PO_4 and fatty acids), an equilibrium existing between Ca^{++} and (I). PO_4 and high fatty acids which ppt. Ca *in vitro* increase the action of Ca on the heart (II) even with Ca deficiency; hence the action of Ca on (II) depends not on Ca^{++} but on (I). Strophanthin causes a liberation of Ca by the perfused tortoise's (II), the alteration in the three Ca fractions being due not to ionisation of Ca, but to removal of (I) by adsorption. *Digitalis* preps., however, appear to enter into (I) to an extent modified by disease of (II).

F. O. H.

Analysis of fatigue in nerve-muscle preparations. I. WALIDOW (Pflüger's Archiv, 1934, 235, 147–155).—Perfusion of a previously fatigued nerve-muscle prep. with Ringer's solution containing 0.06–0.2% Ca produces augmentation of the muscular spasms. The effect is due to the action of Ca on the nerve-endings, the "local fatigue" of which is abolished. Ba has a feeble effect, whilst Mg and Sr are without effect.

R. N. C.

Effect of γ -irradiation on growth and nitrogenous metabolism of the protozoon *Bodo caudatus*. N. R. LAWRIE and M. ROBERTSON (Biochem. J., 1935, 29, 1017–1020).— γ -Irradiation from Ra produces first a decrease in NH_3 production (I) (this vol., 535) coinciding with only a slight response in size and rate of division (II) of the cells; this is followed by a depression of (II) and an increase in (I) and size of cells. The final stage (approx. 20 hr. from start) is characterised by a moderate stimulation of (I), maintenance of increased size, and absence of any marked effect on (II).

F. O. H.

Photolethal effects of quartz ultra-violet radiation on *Paramecium*. A. C. GIESE and P. A. LEIGHTON (J. Gen. Physiol., 1935, 18, 557–571).—The absorption by *Paramecia* of radiation of wave-lengths 2804, 2654, and 2537 Å. is about equal; it

is less for wave-lengths 3025 and 3130 Å. All these except 3130 are photolethal, from 8 to 10×10^{12} quanta per *Paramecium* being necessary to produce 50% vesiculation.

F. A. A.

Determination of the concentration of enzyme preparations. W. R. JOHNSTON and S. JOSZA (J. Amer. Chem. Soc., 1935, 57, 701–706).—Enzyme reactions are not strictly unimol. *K* thus does not accurately define the concn. of enzyme (I). This is best determined by the initial rate of reaction, to which it is often strictly proportional. A "liquefon" is defined as the amount of starch-liquefying (I) which will convert standard starch paste (II) at the rate of 25 mg. of dry starch per min. at zero time under the following conditions: 100 g. of (II), 10 c.c. of infusion containing 0.75–7 mg. of α -amylase (III), diluted to 10 litres, at 21°, viscosities being measured in a modified pipette at intervals during the first 10–20 min. (III) is activated by NaCl, 25 g. per litre giving the max. effect.

R. S. C.

Diffusion of the dehydrogenase of higher fatty acids in different organs. F. P. MAZZA and G. STOLFI (Boll. Soc. ital. Biol. sperim., 1933, 8, 1780–1781; Chem. Zentr., 1934, ii, 3966–3967).—The oxidising action occurs in liver and in fatty tissues examined by Quagliariello (A., 1933, 747), but not in fresh milk, pancreas, duodenal mucosa, muscle, or kidney extracts.

A. G. P.

Tissue metabolism. VI. Lactic dehydrogenase, xanthine-oxidase, and nucleosidase in tumour and muscle extracts. E. BOYLAND and M. E. BOYLAND (Biochem. J., 1935, 29, 1097–1101).—Lactic dehydrogenase (I) similar to that in heart-muscle is present in rat, mouse, and rabbit muscle, and in mouse and rat tumours. Rat and mouse muscle extracts contain xanthine-oxidase (II) and adenine-nucleosidase. Rat and mouse tumour extracts contain (II) and rapidly attack adenylypyrophosphate or (I) co-enzyme.

J. N. A.

Components of dehydrase systems. V. Actions of cozymase, Warburg's co-enzyme, and adenylypyrophosphate. H. VON EULER, E. ADLER, F. SCHLENK, and G. GUNTHER (Z. physiol. Chem., 1935, 233, 120–147; cf. A., 1934, 1257).—Cozymase (I), which is probably not a mixture, acts as co-enzyme in the hexose monophosphate (II) and EtOH-dehydrase (III) (from yeast) systems. (I) and the respiratory co-enzyme (IV) (Warburg) from horse blood-cells are interchangeable in (II), but (IV) cannot replace (I) in (III). (I) and (IV) are interchangeable in the glucose-dehydrase system from liver and probably also in the (III) system from liver. Adenylypyrophosphoric acid shows no co-enzyme action in (II) and (III) and cannot replace (I) alcoholic fermentation. In (II) purest (I) has about a seventieth of the effect of (IV). (IV) is much more thermolabile than is (I).

W. McC.

Cozymase. IV. K. MYRBACK and B. ÖRTENBLAD. **V.** K. MYRBACK. **VI.** Preparation and properties of highly active cozymase. K. MYRBACK and B. ÖRTENBLAD. **VII.** Cozymase from animal organs. K. MYRBACK (Z. physiol. Chem., 1935, 233, 87–94, 95–119, 148–153, 154–158,

cf. A., 1934, 1035).—IV. The purification of cozymase (I) (from yeast) is simplified if impurities (II) are removed by pptn. with $\text{Pb}(\text{OAc})_2$ instead of with Hg salts, but the yield (50%) is lowered. Subsequent treatment with picric acid may usually be omitted. Partly purified (I) is further purified by removing (II) with benzidine or by pptg. (I) with $\text{UO}_2(\text{OAc})_2$. A cryst. *strychnine* (III) salt is obtained which contains about 7 mols. of (III) for each P. After heating with dil. alkali (I) behaves as a dibasic acid. This fact and the N and P contents indicate that (I) is a mononucleotide in which one of the usually free OH groups of the H_3PO_4 residue is substituted with a radical of unknown composition.

V. Active (I) has a strong reducing power which is greatly diminished (to 40% of original val.) by heating at 100° in alkaline solution with proportionate decrease in the activity.

VI. Increased purity is achieved in the isolation of (I) by successive fractional pptn. of (I) with salts of heavy metals and removal of (II) by similar pptn. The purest samples contain 6.7% of P and 14.3% of N (10% of purine-N).

VII. (I) from the organs of the rabbit and dog is identical with that from yeast. W. MoC.

Schardinger's milk enzyme. L. REICHEL (Naturwiss., 1935, 23, 260—261).—Milk-aldehyde dismutase under aerobic and anaerobic conditions and contains no lactoflavin which is responsible for the dehydrogenation observed by Wieland (cf. A., 1930, 248; 1931, 389). J. L. D.

Action of the aldehyde-dehydrogenase of milk on cytochrome-C, isolated from yeast. E. J. BIGWOOD, J. THOMAS, and D. WOLFERS (Compt. rend. Soc. Biol., 1935, 118, 1488—1490).—Cytochrome (I) is reduced by aldehyde-dehydrogenase (milk) in anaerobic conditions. In aerobic conditions the reduction is scarcely observed, since the reduced (I) is immediately reoxidised by an oxidase, the action of which is inhibited by KCN. R. N. C.

Enzyme action in relation to the biological effects of radiation. G. HARKER (J. Cancer Res. Comm. Sydney, 1935, 6, 159—161).—The irradiation of indophenol-oxidase by a radon seed has but little effect on its activity, so that if the biological effects of radiation on cancer cells are due to modifications of the enzyme reactions, the dehydrogenases are probably affected. E. A. H. R.

Purification of the enzymes which oxidise certain amino-acids. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1935, 109, 131—140).—Celite is added to a suspension of macerated kidney (I) at p_H 6.9 and, after centrifuging, the celite is extracted with HPO_4 buffer and Na_2CO_3 , and the extract is dialysed. *dl*-Phenylalanine, -alanine, -proline, -leucine, -isoleucine, -valine, and *d*-phenylalanine are rapidly deaminated and oxidised by the extract, whereas the natural isomerides are attacked slowly or not at all. The oxidation of the *dl*-mixtures corresponds with the unnatural isomeride. Only proline is oxidised by a liver extract prepared similarly, whereas a suspension of liver cells (II) oxidises all slowly. The oxidations are not inhibited by KCN or

F'; methylene-blue is reduced by all the NH_2 -acids studied in the presence of the extract, but the rates are not \propto the rates of oxidation. (I) oxidises *dl*-phenylglycine, whilst (II) does not; glycine is not oxidised by either (I) or (II). H. D.

Destruction of histamine by the lung. L. BINET and M. MARQUIS (Compt. rend. Soc. Biol., 1935, 118, 1235—1236).—Lung tissue shows a histaminolytic effect. H. G. R.

Emulsin. XIX. Action of ozone on almond-emulsin. B. HELFERICH and S. R. PETERSEN (Z. physiol. Chem., 1935, 233, 75—80; cf. this vol., 250, 401).—In the ozonisation of org. compounds (I) the amount of O_3 consumed and hence the amount of (I) attacked is determined by adding bromide-bromate solution, conc. HCl, and KI to the solution containing unconsumed O_3 and titrating with $\text{Na}_2\text{S}_2\text{O}_3$. The amount (about 0.0031 g.) of O_3 required to destroy one unit of emulsin (II) is determined. The resistance of (II) to attack by O_3 is unaffected by addition of tyrosine, cystine, or maleic acid, but is slightly increased by that of histidine, phenylalanine, cysteine, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$, or α -glucosidase (III) from yeast (which consume the O_3), and considerably increased by that of tryptophan (IV), glycyl-tryptophan, or β -indolylacetic acid (which consume part of the O_3). Destruction of (IV) by O_3 is greatest at p_H 5.0—5.7, 1.5 mols. (3 mols. in absence of buffer) of O_3 being required. As regards attack by O_3 , β -*d*-galactosidase resembles (II), malt diastase is more sensitive, but otherwise resembles (II), and (III) requires much more O_3 for destruction because it contains a substance which consumes or catalytically decomposes O_3 . W. MoC.

Salivary, pancreatic, and "Aspergillus" amylase as mixtures of two enzymes. G. GIESBERGER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 344—345).—The evidence (A., 1934, 1136) afforded by diffusion experiments in gelatin for the dual nature of certain amylases (I) is unsound. On dilution, α -malt (I) gives the same concentric rings as a mixture of α - and β -(I). E. A. H. R.

Preparation of starch substrates for amylase determinations. W. R. THOMPSON (J. Biol. Chem., 1935, 109, 201—202).—The method of determination of amylase activity described previously (this vol., 402) is modified by storage of the solution of sol. starch in 0.3M-NaOAc at 25° followed by heating to 100° before proceeding. H. D.

Enzymic hydrolysis of sucrose in the presence of formaldehyde. A. CHAUDUN (Bull. Soc. Chim. biol., 1935, 17, 519—522).—The influence of CH_2O on the hydrolysis of sucrose (I) by invertase is like that of glycerol, EtOH, and MeOH, viz., the rate of hydrolysis is lowered and at the same time the wt. of (I) in solution when the hydrolysis ceases to be a linear function of time is greater. A. L.

Lactase activity of intestinal mucosa of dog and some characteristics of intestinal lactase. F. A. CAJORI (J. Biol. Chem., 1935, 109, 159—168; cf. A., 1934, 808).—Lactase (I) activity is uninfluenced by phosphates. The Michaelis const. of (I) is 0.006.

(I) is adsorbed readily, from slightly acid solution, by $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$. H. D.

Glyoxalase. III. Glyoxalase as a reagent for the micro-determination of glutathione. G. E. WOODWARD. **IV.** Antiglyoxalase action of kidney and pancreas preparations. G. E. WOODWARD, M. P. MUNRO, and E. F. SCHROEDER (J. Biol. Chem., 1935, **109**, 1—10, 11—27).—III. A manometric method is described for determination of reduced glutathione (I) which depends on the measurement of the activating effect of (I) on COMe_2 -yeast glyoxalase, the effect being sp. and cysteine, thioneine, ascorbic acid, or oxidised (I) does not produce any activity. (I) vals. for tissues are, but for blood are not, lower than by the iodometric method.

IV. Kidney tissue of rat, rabbit, pig, and horse contains a powerful inhibitor of glyoxalase, which increases with time. The inhibitor destroys the co-enzyme (I) without destroying its SH group. The antiglyoxalase effect of pancreas is due to 2 factors, one of which acts on the enzyme, the other resembling the kidney inhibitor. P. W. C.

[Esterase models.] W. LANGENBECK (Ber., 1935, **68**, [B], 776—777; cf. A., 1934, 509, 849).—On account of the widely differing experimental conditions, the criticisms of Olivier (this vol., 659) are regarded as unjustified. H. W.

Phosphatases. I. Kidney-phosphatase. **II.** Preparation of highly active phosphatase from animal material. H. ALBERS and E. ALBERS (Z. physiol. Chem., 1935, **232**, 165—188, 189—195).—I. A mixture of PhMe and EtOAc is the best autolysing agent for the prep. of phosphatase (I) from animal organs. (I) is purified by fractional pptn. with EtOH. The total (I) content of the fractions is $>$ that of the original solution owing to elimination of inhibitors. The purest preps. (150 units per mg.) still contain Mg salts and inorg. PO_4''' . The product contains no (I) with p_{H} optimum in the acid range. The mol. wt. of (I) by "free diffusion" is 6000—10,000. Dialysis produces rapid inactivation of (I).

II. The liberation of (I) by PhMe and EtOAc is conducted in presence of EtOH (25—30% actual concn.). This protects the (I) and prevents the dissolution of protein substances. The (I) is then pptd. by increasing the EtOH concn. to 65%. A prep. with an activity of 40—50 units per mg. is thus obtained. J. H. B.

Fermentation enzymes. II. Yeast-phosphatase. A. SCHAFFNER, E. BAUER, and H. BERL (Z. physiol. Chem., 1935, **232**, 213—228).—A redoxase extract of orange-pips can replace the redoxase of yeast in the phosphorylating system containing cozymase (I), hexosediphosphoric acid (II), and MeCHO (III). The intermediate enzyme (IV) of Warburg and Christian can be freed from phosphorylating action by $\text{Al}(\text{OH})_3$, C_v , and is then active only in presence of "yeast-phosphatase" (V), (II), and (III). (V) loses its activity as a component of the system after treatment with $\text{Al}(\text{OH})_3$, C_v ; it is now free from zymohexase (VI) and can be replaced by muscle-(VI). (V)-free (VI) and (V)-free (IV) can produce synthesis of hexose ester. (VI) can be omitted if dihydroxy-

acetonephosphoric acid (VII) replaces (II); thus in the system (VII), (III), (I), hexose, and H_3PO_4 , (III) alone is needed. J. H. B.

Degradation of nucleic acid with nuclease from ox-kidney. K. MAKINO (Z. physiol. Chem., 1935, **232**, 196—198).—From the products of fission were isolated guanylic acid, guanosine, uridine, guanine, hypoxanthine, and xanthine, but no adenosine, cytidine, adenine, cytosine, or uracyl, indicating that the 6- NH_2 is more readily deaminated than the 2- NH_2 in the purine nucleus. J. H. B.

Enzymic histochemistry. XV. Micro-determination of arginase. K. LINDERSTRÖM-LANG, L. WEIL, and H. HOLTER (Z. physiol. Chem., 1935, **233**, 174—180).—Improvements in a modification of the urease (I) method (cf. A., 1933, 1218) are described. Determinations are more rapidly and easily made by titrating liberated ornithine (II) in $\text{EtOH} + \text{COMe}_2$ (1 : 1) with 0.05*N*- $\text{NMe}_4\cdot\text{OH}$ in 90% EtOH (indicator: thymol-blue). CO_2 must be excluded. The second method, which determines about 95% of (II), is inapplicable if large amounts of (I) are present. W. McC.

Enzymic hydrolysis of raw and heat-treated egg-white. E. W. COHN and A. WHITE (J. Biol. Chem., 1935, **109**, 169—175).—The enzymic hydrolysis of egg-white (I) before and after heating is determined by formol titration. Trypsin has little effect on unheated (I) solutions unless previously treated with pepsin. The tryptic hydrolysis increases with the time of pre-heating at 100° of (I) up to 30 min. both with and without pre-treatment with pepsin. H. D.

Action of dyes and narcotics on proteolytic enzymes. Trypsin and papain. K. BASU and R. CHAKRAVARTI (J. Indian Chem. Soc., 1935, **12**, 82—88).—Inhibition ($> 36\%$) of the hydrolysis of peptone by trypsin (activated by cystine) at p_{H} 8.67, and by papain (activated by cysteine) at p_{H} 5.0, at 37° is effected by addition of 0.02% of acid dyes and by some basic dyes, the action being sp. The enzymes must therefore be amphoteric in character. Of various narcotics and other substances investigated only gallic acid, vanillin, and ethylurethane exhibit appreciable inhibiting action, which in all cases increases with time. J. W. B.

Detection of enzymes of the trypsin and papain types. J. B. SUMNER and S. F. HOWELL (J. Biol. Chem., 1935, **109**, 429—431).—The enzymes (I) [trypsin, fig-tree protease, taka-diastase, papain-cysteine, bromelin-cysteine, (I) of extract of green malt, invertase] are detected by allowing them to act, in buffered solution, on hide powder containing pptd. BaSO_4 which is liberated, causing turbidity. W. McC.

Influence of oxidising and reducing agents on the activity of papain. III. T. BERSIN and H. KOSTER (Z. physiol. Chem., 1935, **233**, 59—66; cf. A., 1934, 450).—At p_{H} 5 and 40° papain (I), after oxidation with H_2O_2 , is reactivated by the hydrochloride of 3-amino-4-hydroxy-, *p*-acetamido-, or the hydrochloride of *p*-amino-phenylarsine oxide, but is inactivated by *p*-acetamidophenylarsinic acid or its Na H salt. Reversibly oxidised (I) does no

coagulate milk. The action of (I) is explained by supposing that its NH_2 group, activated by dipole induction, reacts with a CO-NH (probably terminal) in the substrate, (I) being subsequently regenerated by hydrolysis. W. McC.

Crystalline chymotrypsin and chymotrypsinogen. I. Isolation, crystallisation, and properties of a new proteolytic enzyme and its precursor. M. KUNITZ and J. H. NORTHROP (J. Gen. Physiol., 1935, 18, 433—458; cf. A., 1934, 219).—The activation of cryst. chymotrypsinogen (I) by trypsin (II) follows a unimol. course and the rate is a max. at 7—8. The product, chymotrypsin (III), has the same mol. wt. as (I), but 6 more primary NH_2 -groups. (III) clots milk but not blood-plasma, and hydrolyses sturine, caseinogen, gelatin, and hæmoglobin more slowly than does (II). (III) attacks caseinogen at different linkings from those attacked by (II), and does not attack di- or poly-peptides. (III) may be inactivated by pepsin digestion, heat, or acid. F. A. A.

Determination of the rennet activity of chymotrypsin. M. KUNITZ (J. Gen. Physiol., 1935, 18, 459—466).—Milk powder solution + chymotrypsin flow through a graduated tube at a determined rate. The graduation reached when the milk clots gives the time taken. F. A. A.

Monolayers of proteolytic enzymes and proteins. III. Enzyme reactions and penetration of protein monolayers. J. H. SCHULMAN and A. H. HUGHES (Biochem. J., 1935, 29, 1236—1242).—A fatty acid-protein complex which can be extracted from pancreatin (I), but not from the sp. proteolytic enzymes, simulates the action of (I) on monolayers (II) of proteins and fats, and accounts for the reported activity of bulk-inactive preps. of (I) on such (II). The action of chymotrypsin, chymotrypsinogen, and cryst. pepsin on (II) of protein and tripalmitin is described. F. A. A.

Effect of halogen salts on the clotting of milk by trypsin. W. M. CLIFFORD (Biochem. J., 1935, 29, 1059—1063).—Milk gives a firm clot with trypsin if the halogen salts of Li, Na, K, NH_4 , Mg, Ca, or Ba are added, the coagulating action being least with the fluorides and the alkaline-earth metals being only slightly more efficient than the alkali metals. Mg salts are less powerful than those of Ca or Ba. At concns. above 0.25M the salts of Mg, Ca, Ba are less effective than at concns. between 0.125 and 0.015M. P. W. C.

Activation of cathepsin. E. WALDSCHMIDT-LEITZ and K. BARTUNEK (Z. physiol. Chem., 1935, 233, 36—38).—Since most of the activator (I) (e.g., in spleen) seems to be bound in the form of a symplex to insol. cell-substance of high mol. wt. and requires to be liberated and made sol. by treatment with glycerol, results derived from investigation of pulped or minced tissues or extracts of them are untrustworthy. Living material should be used. W. McC.

Physico-chemical factors in the interferometric technique of Hirsch. A. GRIGAUT and E. BETTEND (Bull. Soc. Chim. biol., 1935, 17, 420—431).—The fall (I) in the concn. of sera often shown in the application

of the interferometric method of Hirsch indicates that, apart from enzymic and H_2O -absorptive actions which take place, there are in addition phenomena of adsorption which cause (I) and depend on the physical nature of the different sera. A. L.

Saccharomyces and other fungi still alive in the pure cultures of Hansen and Klocken. O. WINGE and A. HJORT (Compt. rend. Trav. Lab. Carlsberg, 1935, 21, 51—58).—Several cultures kept in 10% sucrose or beer wort since 1886—1922 are still living. E. A. H. R.

Mechanism of fermentation of dihydroxyacetone. H. LEHMANN (Biochem. Z., 1935, 277, 261—267; cf. Iwasaki, A., 1929, 354).—Dihydroxyacetone (I) on fermentation with *Saccharomyces Ludwigii* is converted into hexosediphosphoric acid (II). (I)-phosphoric acid is a secondary product derived from (II). W. McC.

Effect of dyes on yeast fermentation as influenced by hydrogen-ion concentration. E. ADAMS and W. J. ROBBINS (J. Agric. Res., 1934, 49, 1025—1031).—The toxicity to yeast of rose-Bengal and eosin was greater in the more acid solutions, notably in those having $p_{\text{H}} < 6.0$ and < 5.0 , respectively. Safranin was more toxic in the less acid solutions, especially at $p_{\text{H}} > 6.0$. Toxicity of brilliant-green increased with falling p_{H} to approx. 5.5, when pptn. occurred. Dahlia was least toxic in acid solutions, but the influence of reaction was not great. A. G. P.

Action of 2:4-dinitrophenol on American baker's yeast (Fleischmann yeast). L. GENEVOIS and P. CREAC'H (Compt. rend. Soc. Biol., 1935, 118, 1357—1359; cf. A., 1934, 1262).—Respiration of Fleischmann's yeast is not increased by 2:4-dinitrophenol, but the latter is reduced. H. G. R.

Action of 2:4-dinitrophenol on French baker's yeast (Springer's yeast). L. GENEVOIS and R. SARIC (Compt. rend. Soc. Biol., 1935, 118, 1354—1356).—Previous conclusions (this vol., 253) are maintained, contrary to Plantefol (this vol., 405). H. G. R.

Action of 2:4-dinitrophenol on yeast respiration. L. PLANTEFOL (Compt. rend. Soc. Biol., 1935, 118, 1359—1360).—Polemical (cf. preceding abstract). H. G. R.

Action of Rontgen rays on yeast fermentation. V. GRONCHI (Strahlenther., 1934, 51, 319—338; Chem. Zentr., 1934, ii, 3971).—Production of CO_2 from glucose by yeast is stimulated by radiations of 0.37 and 0.16 Å. The effect for hard is $>$ for soft rays. A. G. P.

Nutrition of *Polytoma caudatum*, var. *astigmata* (colourless Chlamydomonadine), and synthesis of starch by leucophytes. A. LWOFF and L. PROVASOLI (Compt. rend. Soc. Biol., 1935, 119, 90—93).—Growth of *Polytoma caudatum astigmata* (I) is poor in media lacking AcOH , addition of which accelerates development. AcOH can be replaced by EtCO_2H , $\text{Pr}^{\text{c}}\text{CO}_2\text{H}$, AcCO_2H , or starch, but not by $\text{Pr}^{\text{b}}\text{CO}_2\text{H}$, n -valeric, hexoic, or lactic acid. (I) does not grow rapidly with asparagine or other single NH_2 -acid as the sole N source, even in presence of

NaOAc. (I) can synthesise starch through the action of a superficial reticulated leucoplast, similar to those found in chlorophyll-containing organisms. R. N. C.

Variability of monosporic cultures of *Coccomyces hiemalis*. R. O. MAGIE (Phytopath., 1935, 25, 26—27).—Variations in colour, growth, acid production, and spore formation were unrelated to the nature of N or C sources utilised. Growth was influenced by temp. and p_H . A. G. P.

Formation of organo-metalloidal compounds by micro-organisms.—See this vol., 738.

Beneficial fungi. C. M. HAENSELER (New Jersey Agric., 1934, 16, No. 2, 6).—*Rhizoctonia* (I) failed to grow in media previously carrying *Trichoderma* (II). Toxin produced by (II) was destroyed by heating to 80° for 10 min., by ageing for 10 days, or by exposure to O₂ for 5 min. Media so treated permitted growth of (I). CH. ABS. (p)

Effect of temperature, salt, and acidity on the growth of *Oospora lactis*. H. MACY and A. E. ANDERSON (Nat. Butter and Cheese J., 1934, 25, No. 22, 28—29).—Growth of the mould on whey-agar was affected by 1% and arrested by 10% salt. On buttermilk the corresponding vals. were 2.5 and 10%. Acidity had little influence on growth. Growth was retarded at 10° and 2° and ceased at -23°. Combined effects of high salt concn., low temp., and/or [H⁺] were observed. CH. ABS. (p)

Biochemistry of micro-organisms. XLIV. Fulvic acid, a new crystalline yellow pigment, a metabolic product of *Penicillium griseofulvum*, Dierckx, *P. flexuosum*, Dale, and *P. brefeldianum*, Dodge. A. E. OXFORD, H. RAISTRICK, and P. SIMONART (Biochem. J., 1935, 29, 1102—1115).—*P. griseofulvum* (I), *P. flexuosum* (II), and *P. brefeldianum* (III), when grown on a synthetic medium containing glucose, NH₄ tartrate, and mineral salts, give rise to a yellow pigment, fulvic acid, C₁₄H₁₂O₈, m.p. 246° (decomp.) [K salt, Et ester, m.p. 230—234° (decomp.), Me₃, m.p. 192°, Et₃, m.p. 172—174°, derivatives]. On acetylation the acid loses 1 mol. of H₂O forming the Ac₂ derivative, m.p. > 310°, of C₁₄H₁₀O₇. (I) and (II) also produce 6-methylsalicylic acid. The mycelium of (I) yields a cryst. N-containing compound, m.p. 165° (decomp.); and the mycelium of (III) a neutral compound C₄₀H₇₉O₅N, m.p. 132—135°. J. N. A.

Cultural factors necessary to determine the fertility of soil by means of *Aspergillus niger*, Cramer. A. SARTORY, R. SARTORY, J. MEYER, and F. AENOLD (Compt. rend., 1935, 200, 1692—1694).—The influence of K and P on the growth of *A. niger* (I) is determined in a culture medium of known composition. Low sugar (II) content and high p_H increase the sensitivity of moulds to P and K, whereas high (II) and N contents retard growth, the effect being greater for moulds other than (I). The medium must be dil. so that the constituents of the added soil other than K and P will not affect the yield of (I). J. L. D.

Serologically active (haptenic) carbohydrates of genotypes of *Neurospora tetrasperma* and *N.*

sitophila. H. W. WILCOX and G. K. K. LINK (Phytopath., 1935, 25, 39).—Polysaccharides isolated from strains of these organisms gave positive precipitin reactions with rabbit's antisera. A. G. P.

Action of urinary growth-factors. Action on a micro-organism. W. H. SCHOPFER (Arch. Sci. phys. nat., 1934, 16, Suppl., 200—203).—Extracts of dried human urine (I) by COMe₂, CHCl₃, abs. EtOH, 95% EtOH, H₂O, 50% COMe₂, and MeOH gave growths of *Phycomyces* increasing in order. (I) decolorised by C and pregnandiol were inactive. H. D.

Fermentation of rare sugars by members of the colon and aerogenes groups of bacteria. II. Cellobiose. C. F. POE and D. E. KLEMMER (J. Biol. Chem., 1935, 109, 43—46).—A table summarises the formation by *Escherichia coli*, *E. communior* and *politana*, *Aerobacter aerogenes*, and *A. cloacae*, when grown on a nutrient broth-cellobiose medium, of CO₂, H₂, volatile and non-volatile acids, EtOH etc. and curves show the changes of p_H . P. W. C.

Comparison of presumptive tests for the coli-aerogenes group of bacteria. I. V. SHUNK (J. Elisha Mitchell Sci. Soc., 1934, 50, 42—43).—*E. coli* and *A. aerogenes* produced gas in lactose-bile salt media containing brilliant-green, but not in those with crystal-violet or basic fuchsin. Gas production occurs with all 3 dyes if a certain fluorescent bacterium, capable of lowering the oxidation-reduction potential, is present. CH. ABS. (p)

Soft rot and colon-typhoid-dysentery groups of bacteria. II. Physiology. A. R. STANLEY (Phytopath., 1935, 25, 34—35).—The customary physiological tests (sugar fermentation, NO₃⁻ reduction, indole formation, etc.) are insufficient for sp. identification of these organisms. A. G. P.

Isolation of typhoid and paratyphoid bacilli from water. J. SZPER (Compt. rend. Soc. Biol., 1935, 118, 1675—1677).—The bacilli are isolated from large excesses of *B. coli* by growing in a medium containing conc. Na₂S₄O₆. R. N. C.

Action of sodium tetrathionate on the development of typhoid and paratyphoid bacilli. J. SZPER (Compt. rend. Soc. Biol., 1935, 118, 1677—1679).—Na₂S₄O₆ in high concn. inhibits growth of *B. coli*, but only retards that of typhoid bacilli as compared with their growth in bile medium. R. N. C.

Composition of a mineral medium particularly favourable for the growth of typhoid bacilli. Filtrates of typhoid bacilli cultivated on this medium; their mode of action; their utilisation in therapy. F. LE CHUITON, R. PIROT, C. BERGE, and J. PENNANEAC'H (Compt. rend. Soc. Biol., 1935, 119, 71—73).—The composition of a modified Uschinsky medium for the growth of typhoid bacilli is given. The filtrates from typhoid bacterial cultures apparently contain no anti-virus; they produce allergic shocks in guinea-pigs and rabbits, and improvement in serious typhoid cases. R. N. C.

Types of specific carbohydrates in the cholera and cholera-like vibrios. R. W. LINTON and B. N. MITRA (Proc. Soc. Exp. Biol. Med., 1934, 32, 464—

468).—The majority of the vibrios contain polysaccharides (I) formed from an aldobionic acid consisting of galactose and glycuronic acid; this is condensed with galactose in the (I) of the cholera vibrios, and with arabinose in that of the non-agglutinating *H₂O* vibrios. A few strains contain a third (I) formed from glucose only. R. N. C.

Proteins and carbohydrates of the cholera and cholera-like vibrios. R. W. LINTON and B. N. MITRA (Proc. Soc. Exp. Biol. Med., 1934, 32, 468—473).—Two types of pseudoglobulins occur in the cholera and *H₂O* vibrios, respectively. The vibrios can be classified in several groups from their sp. protein and carbohydrate contents. R. N. C.

Existence in the *S* and *R* forms of *B. aertrycke* and *B. gaertner* of an enzyme that cleaves the "complete" antigen with liberation of the "residual" antigen. A. BORVIN and L. MESROBEANU (Compt. rend. Soc. Biol., 1935, 118, 1671—1673).—The enzyme eliminates the fatty acids from the "complete" antigen of the *S* forms of both bacilli, liberating the non-toxic "residual" antigen. The enzyme is intimately associated with the bacteria, from which it cannot be separated by diffusion or autolysis; it attacks the antigen equally well whether the latter is enclosed in the bacteria or has been added to the medium, the optimum p_H being 7—8. It is not inhibited by NaF, but is destroyed by trypsin-kinase or by heating to 100° at p_H 7. (Cf. this vol., 665.) R. N. C.

Spectrum of diphtheria toxin. F. OTTENSOOSER, A. KRUPSKI, and F. ALMASY (Biochem. Z., 1935, 277, 314—319; cf. Coulter *et al.*, A., 1932, 969).—100 g. of the toxin (I) contain hæmochromogen (II) equiv. to 0.7 mg. of hæmatin. The spectrum of (II) (3400—6400 Å.) is very similar to that of *C₆H₅N* (II), and exhibits a band at 4080 Å. There is no relationship between the (II) content of (I) and its toxicity or time of flocculation. W. McC.

Stabilisation and recovery of diphtheria antitoxin flocculated by the toxin. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 118, 1401—1403).—The antitoxin (I) is recovered from the flocculate by addition of 0.5% of *CH₂O*, followed immediately by 2% of *NH₂·C₁₀H₄(SO₃Na)₃*, and adjusting to p_H 5 with 20% citric acid; (I) is pptd. with globulins, whilst the toxin remains in solution. The ppt. after washing is dissolved in aq. NaOH; the solution contains most of the (I) from the flocculate. (I) is stabilised by momentary contact with the *CH₂O*; prolonged contact or a more conc. *CH₂O* solution destroys it. R. N. C.

Fermentation-inhibiting substance produced by *B. coli*. N. WEINSTOCK (Proc. Soc. Exp. Biol. Med., 1934; 32, 556—559).—Fermentation of glucose, galactose, and dextrin by *C. diphtheriæ* is inhibited or retarded by broth in which *B. coli* has previously been cultivated. The inhibiting substance is relatively thermostable. R. N. C.

Comparative study of the content and composition of ash in a bacterial species and its virulence. C. BARBER (Compt. rend. Soc. Biol., 1935, 118, 1655—1657).—The ash content of pneu-

mococci and streptococci is lower in the strains that are more pathogenic to mice; ash-Ca increases with pathogenic power, whilst other metals decrease.

R. N. C.

Root nodule bacteria of leguminous plants. XVI. Effect of air content of the medium on the function of the nodule and on the excretion of nitrogen. XVII. Efficiency of different strains of clover nodule bacteria. A. I. VIRTANEN (J. Agric. Sci., 1935, 25, 278—289, 290—296).—XVI. The rate of excretion of N from nodules (I) in sand cultures or the supply of air to the roots. Submergence of roots in liquid media resulted in abundant growth of (I), but poor plant growth and small N excretion from (I). The plants had a low N content. (I) thus obtained were capable of fixing N when re-exposed to air. The N compounds excreted by (I) and also those assimilated by the plants are probably derived from the decomp. of proteins of (I).

XVII. Different strains of *Rh. trifolii* retained their characteristic sizes and N contents during a 3-year growth period. Inoculation of plants with a more efficient strain in the third year did not affect growth. A. G. P.

Hydroxylamine, hydrazine, and amide as intermediate products of nitrogen fixation by *Azotobacter*. D. BURK and C. K. HORNER (Naturwiss., 1935, 23, 259—260; cf. A., 1934, 1265).—< 3 mg. per litre of *NH₂OH* has no effect (higher concns. are toxic) on the respiratory exchanges during 38 hr. of *Azotobacter* in 21% *O₂*—79% *H₂*, although equiv. amounts of *NO₃'*-N or *N₂* result in a doubling of the colony in 3—4 hr., which indicates that *NH₂OH* is not utilised. 0.1 mg. of *NO₃'*- or *NH₃*-N per litre causes a max. growth, unaffected by concns. up to 5000 mg. of N per litre. *N₂H₄* cannot be utilised, but *HCN* (< 1 mg. per litre) can. J. L. D.

Formation of hyponitrous acid as an intermediate compound in the biological or photochemical oxidation of ammonia to nitrous acid. II. Microbiological oxidation. A. S. CORBET (Biochem. J., 1935, 29, 1086—1096).—Oxidation of (*NH₄*)₂SO₄ by soil micro-organisms can proceed thus: *NH₃* → *NH₂OH* → *H₂N₂O₂* → *HNO₂* → *HNO₃*. Frequently oxidation ceases after about 5% conversion of *NH₄* salt into *NO₂'*. *NH₂OH* has only a transitory existence at p_H 6 and above, but *CaN₂O₂* is an important intermediate. Oxidation of *NO₂'* to *NO₃'* may be due to autoxidation in acid media. J. N. A.

Anaerobic decomposition of plant materials. III. Comparison of the course of decomposition of rice straw under anaerobic, aerobic, and partly aerobic conditions. C. N. ACHARYA (Biochem. J., 1935, 29, 1116—1120).—Under aerobic (I), partly aerobic (II), and anaerobic (III) conditions, the relative rates of decomp., together with the amounts of protein formed, decrease in the order (I), (II), (III). Cellulose and lignin are more easily attacked under (II) than (III). In general, the results under (II) are intermediate between (I) and (III). Mild aeration under (III) gives an increase of *H₂* with *CH₄* and org. acids, whilst strong aeration increases the *CO₂*. J. N. A.

Action of bios on processes of putrefaction. K. SUCHORUKOV and T. EPEL-BOGOSLOVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 636—641).—Bios preps. from brewer's yeast stimulate multiplication of and proteolytic action by *B. subtilis* and *Proteus vulgaris*; no activation of proteases occurs.

F. O. H.

Reduction potentials of bacterial suspensions. J. YUDKIN (Biochem. J., 1935, 29, 1130—1138).—A modification of Green's apparatus (A., 1933, 785) is used to measure the redox potentials (I) of *B. coli*, *B. alkaligenes*, and *Cl. sporogenes*. (I) falls with time and is unaffected by succinate; glucose and formate induce more negative (I). Enclosing the Pt electrode in a collodion sac produces no change in (I). (I) determined colorimetrically have little relation to those determined electrometrically, whilst electrolytic determinations in the presence of indicators (II) gave the same vals. as (II) alone. There is no correlation between the mode of life of the cultures studied and their (I).

H. D.

Butyl alcohol-acetone fermentation in sugar media. H. REYNOLDS, H. D. COILE, and C. H. WERKMAN (Iowa State Coll. J. Sci., 1934, 8, 415—426).—Seven strains of *Clostridium acetobutylicum* showed similar courses of fermentation. Use of H₂O-insol. proteins (ovalbumin, casein, zein) as sole sources of N in glucose media proved successful. Reported differences in fermentation results are due to factors not now recognised as significant.

CH. ABS. (p)

Preparation of the specific soluble substance from vaccinia virus. W. K. CH'EN (Proc. Soc. Exp. Biol. Med., 1934, 32, 491—494).—The virus-infected tissue is suspended in 0.9% NaCl and autolysed under Et₂O for 7 days. The suspension is then centrifuged, filtered, and boiled for 5 min. at p_H 5.5; the ppt. is removed by centrifuge and the liquid boiled at p_H 8.0, filtered, and evaporated in vac. to 1/3 vol. The active material is pptd. with 1:1 EtOH-Et₂O, dried, dissolved in H₂O, dialysed, and finally purified by repeated pptn. with EtOH. The product has no antigenic properties. Similar products are prepared in small quantities from the normal tissue; they resemble the product from the virus culture chemically, but not serologically.

R. N. C.

Negative stains in the demonstration of bacteria. R. W. CUMLEY (Stain Tech., 1935, 10, 53—56).—Indian ink, nigrosine, induline, Congo-red, Poirier's blue, aniline-blue, China-blue, blue de Lyon, and night-blue are recommended. H. W. D.

Inhibition of growth of pollen and mould under X- and cathode-ray exposure. C. P. HASKINS and C. N. MOORE (Radiology, 1934, 23, 710—719).—The incident energy required to inhibit mycelial growth in moulds by hard X-rays is 2.1× that for soft X-rays. The corresponding ratio for pollen is 6.

CH. ABS. (p)

Action of cinnamic acid in chloroform, of mercuric chloride, and of tincture of iodine on hyphomycetes. W. ALDICK (Arch. Dermatol. Syphilis, 1934, 170, 410—424; Chem. Zentr., 1934, ii, 3969—

3970).—Comparative effects of these materials on the growth of *Trichophyton gypsum* are recorded.

Relation of action of chlorine to bacterial death. C. S. MUDGE and F. R. SMITH (Amer. J. Publ. Health, 1935, 25, 442—447).—When milk in which bacteria had grown was treated for 3—10 min. with NaOCl the plates in which the action was stopped with Na₂S₂O₃ when plating gave a higher count than those in which it was not, and a 1:10 dilution gave higher results than the usual direct plate. When a mixture of H₂O and bacteria was chlorinated and plated and also run in several dilutions, a reduction of 99% was recorded on the plate, but virtually none by the serial tubes.

C. J.

Effect of dilute solutions of certain antiseptics on the viability of tubercle bacilli. S. R. DOUGLAS and P. HARTLEY (Tubercle, 1934, 16, 97—99).—Data for PhOH and "merthiolate" are given. Results with CH₃O were inconclusive.

CH. ABS. (p)

Sterilisation by ultra-violet emissions from a high-tension lamp. E. GILLES (Compt. rend. Soc. Biol., 1935, 118, 1440—1442).—The radiations kill young cultures without affecting the media.

R. N. C.

Physiological production of sympathin in the liver. G. P. WHITELAW and J. C. SNYDER (Amer. J. Physiol., 1934, 110, 247—250).—Sympathin is liberated from the liver under such physiological conditions as those of the decorticate animal.

R. N. C.

Action of pepsin on the succagogic and hypoglycæmic activity of secretin. J. LA BARRE and J. LEDRUT (Bull. Soc. Chim. biol., 1935, 17, 459—471).—By the action of pepsin on secretin and pptn. with CCl₃·CO₂H a substance, "incrétin," is obtained having no succagogic, but considerable hypoglycæmic, activity when injected into normal rabbits and depancreatized dogs.

A. L.

Purification of callicrein. F. BISCHOFF and A. H. ELLIOT (J. Biol. Chem., 1935, 109, 419—427).—Purity 2—5 times that attained by Kraut *et al.* (A., 1932, 547) is reached by concn. of the urine in a vac., dialysis, pptn. with HCl, fractional pptn. with 75% EtOH saturated with NaCl, selective adsorption on Zn(OH)₂, elution with aq. NaHCO₃, and another fractional pptn. with EtOH, the p_H being maintained throughout within the limits of stability of the crude product. The purified material is unstable.

W. McC.

Crystalline insulin. D. A. SCOTT and A. M. FISHER (Biochem. J., 1935, 29, 1048—1054).—Ash determinations on different samples of insulin (I) (of original ash content of 0.02%) crystallised from NH₄OAc solutions with Zn, Co, or Cd showed const. vals. for the respective metals. The average ash content of each (I) salt was ∝ the at. wt. of the metal it contained, indicating that cryst. (I) contains the metals as chemically combined constituents.

P. W. C.

Zinc content of bovine pancreas. A. M. FISHER and D. A. SCOTT (Biochem. J., 1935, 29, 1055—1058).—Bovine pancreas (I) contained 20 mg. o

Zn per kg. of fresh tissue irrespective of the age of the animal from which the gland was obtained. The amount of Zn in (I) was thus many times that necessary to account for the available insulin (II) as the Zn salt, and the amount of (II) extractable did not bear any simple relationship to the Zn content of the (I). Co and Ni were not detected in (I). P. W. C.

Crystalline insulin. II. (Appendix.) E. BRUCH (Arch. exp. Path. Pharm., 1935, 178, 396; see A., 1934, 223).—The oxidation (I) of commercial insulin preps. by alkaline $K_3Fe(CN)_6$ (*loc. cit.*) is not related to their physiological activity, which, however, appears to be \propto the difference in the vals. of (I) before and after inactivation. F. O. H.

Insulin. XIII. The sulphur of insulin. K. FREUDENBERG and T. WEGMANN (Z. physiol. Chem., 1935, 233, 159—171; cf. A., 1933, 321).—The activity of insulin (I) is diminished and/or destroyed by Na_2CO_3 , cysteine (II), reduced glutathione, thioglycollic acid, thiolactic acid, leuco-methylene-blue, H_2S , H_2S_2 , Na_2SO_3 , HCN , CH_2CO , ascorbic acid, quinol, I, BzO_2H , $NaOH$, or irradiation (III). If inactivation is not carried too far, reactivation (*e.g.*, with H_2O_2) is attained in some cases [(II), (III)]. In most or all of these actions the S-S group of (I) is involved. Inactivation by $NaOH$ is accompanied by elimination of H_2S and a little NH_3 . At pH 7.4, CH_2I-CO_2H attacks (I) only slowly. The NH_2-N of (I) cannot be satisfactorily determined by Van Slyke's method because org. S compounds reduce HNO_2 to N_2 . The products of the action of H_2S_2 on (I) are very toxic. The mol. wt. of (I) is 9000—18,000. W. McC.

Time curve after insulin. M. C. HRUBETZ (Amer. J. Physiol., 1934, 110, 384—386).—Blood-sugar in rats reaches its min. 1 hr. after injection of insulin, and after 3 hr. has risen again to a level < the initial level, where it remains steady, and this is the same level reached by the blood-sugar of rats starved for 6 hr. without insulin. There is no indication of a late hyperglycaemia in the injected animals.

R. N. C.

Calcium in supersensitivity to insulin. H. HUNDSCHIEDT (Zentr. inn. Med., 1934, 55, 369—371; Chem. Zentr., 1934, ii, 3519).—In cases of supersensitivity administration of Ca preps. permits satisfactory insulin therapy. A. G. P.

Effect of insulin on the purine metabolism of the Dalmatian coach dog. I. L. CHAIKOFF and P. S. LARSON (J. Biol. Chem., 1935, 109, 85—95).—Insulin increased the output of uric acid, but did not affect the excretion of allantoin. 1 hr. after injection of insulin, the blood-uric acid (I) began to increase, the max. effect after 10 units of hormone being obtained after 3 hr. When hypoglycaemia was inhibited by ingestion of glucose just before administration of insulin, (I) did not increase. P. W. C.

Effect of "chronic" experimental liver damage on the blood-sugar response to insulin. R. G. SPRAGUE (Amer. J. Physiol., 1934, 110, 488—489).—Dogs with Eck fistulae are slightly more sensitive to insulin than normal dogs. R. N. C.

Modifications of gastric secretory activity under the influence of parathyroid extracts. J. LA

BARRE and P. DESTREE (Compt. rend. Soc. Biol., 1935, 118, 1624—1627).—Injection of parathyroid hormone in dogs causes an increase in free and total HCl and mucus in the gastric secretion that reaches its max. at the 3rd hr. A series of injections at 3—4 day intervals causes a steady increase of mucus secretion. R. N. C.

Action of parathyroid hormone in normal and hypophysectomised pigeons. O. RIDDLE and L. B. DOTTI (Proc. Soc. Exp. Biol. Med., 1934, 32, 507—509).—Parathormone increases serum-Ca in normal, hypophysectomised, and thyroidectomised pigeons. R. N. C.

Evaluation of parathyroid hormone by means of sodium fluoride. M. KOCHMANN (Deut. med. Woch., 1934, 60, 1062—1063; Chem. Zentr., 1934, ii, 3519).—The hormone counteracts the lethal dose of NaF or $H_2C_2O_4$ in mice. A. G. P.

Adrenal. VIII. Preparation of adrenal cortical hormone suitable for oral administration. A. GROLLMAN, W. M. FIROR, and E. GROLLMAN (J. Biol. Chem., 1935, 109, 189—200).—The aq. $COMe_2$ extract of pig cortical hormone (I) (A., 1933, 642) is chilled, lipins are removed, and the $COMe_2$ is distilled off. (I) is adsorbed on norit at pH 7.0 and the norit-hormone prep. is washed with dil. HCl and $NaOH$, and assayed by feeding to adrenalectomised rats (II) and dogs. The same equiv. of gland is required to keep (II) in perfect health in oral charcoal feeding or intraperitoneal injection. H. D.

Cortico-adrenal influence on blood-sugar mobilisation. R. L. ZWEMER and R. C. SULLIVAN (Endocrinol., 1934, 18, 730—738).—Removal of the adrenal cortex (I) in cats has a more marked effect on blood-sugar (II) than removal of the medulla. The fall of (II) \propto the time after removal of (I). Although (II) definitely decreases after complete adrenalectomy, it remains within the lower normal limit for some days. The low (II) is not due to depletion of reserves; it can be raised rapidly by excitement, adrenaline (III), cortin (IV), or (III) and (IV) mixed. The rate of rise and fall of (II) after injection of (IV) is < that after (III); the mixture produces a rapid rise and a slow fall. R. N. C.

Inter-relationship of the adrenal cortex and the anterior lobe of the pituitary. H. B. SHUMACKER, jun., and W. M. FIROR (Endocrinol., 1934, 18, 676—692).—Hypertrophy or atrophy of the pituitary (I) in the rat causes a similar change in the adrenal cortex (II). Removal of (I) destroys the capacity of (II) to undergo compensatory hypertrophy, whilst (II) insufficiency causes changes in (I). Removal of (I) and (II) lowers the rate of growth and body-temp., which in (I)-deficient animals cannot be restored by (II) hormone. Atrophy of the gonads after removal of (I) is not due to lack of (II) hormone, but that after removal of (II) is probably due to (I) degeneration. (I) transplants induce oestrus and premature maturity in adrenalectomised female rats. R. N. C.

Perfusion of adrenal gland with reference to mechanism of adrenaline stabilisation. R. D. H. HEARD and A. D. WELCH (Biochem. J., 1935, 29,

998—1008).—A Ringer-Locke perfusate (I) of the adrenal of the ox contains pressor activity (II). Acetylcholine added to (I) gave no increased (II), eserine gave a slight increase; the adrenaline (III) output was increased by 150% by both drugs. (I) on shaking at 38° maintained their (II) const. for 3—21 hr., when (II) decreased fairly rapidly; the ascorbic acid (IV) content decreased continuously under these conditions. (III) added to (I) is similarly stabilised. No correlation exists between the amounts of (III) and (IV) secreted on perfusion. SH groups were absent from (I) both before and after reduction with Sn and HCl. The curves of O₂ uptake of (IV)+(III) and glutathione+(III) with time are characteristic of redox systems, and are similar to that of (I)+(IV). The presence of an inhibitor to the oxidation of (IV) in (I) is postulated and shown to exist in cell-free extracts of liver. H. D.

Adsorption by erythrocytes of substances in the blood, especially adrenaline. W. BROSS and P. KUBIKOWSKI (Arch. exp. Path. Pharm., 1935, 178, 212—228).—Adrenaline (I) is less rapidly destroyed in blood (II) than was previously believed. Thus (I) added to whole (II) retains most of its pressor action after 7 days at 0° and a little after 7 days at 37° with hæmolyzed (II); with serum from bacterially decomposed (II) at 37°, no activity remains after 7 days. The methylene-blue technique (Euler, A., 1933, 986) gives acceleration with human serum and erythrocytes (III) at concns. of < 1:400 and 1:3200, respectively, indicating [(I)] in (II) of 3.233×10^{-11} g. per c.c. (cf. *ibid.*). The transport function of (III) for (I) and other hormones, toxins, etc. is discussed. F. O. H.

Effect of adrenaline on the purine metabolism of ordinary and Dalmatian dogs. I. L. CHAIKOFF, P. S. LARSON, and L. S. READ (J. Biol. Chem., 1935, 109, 395—404).—Subcutaneous injection of adrenaline (amounts insufficient to increase blood-pressure) into ordinary and Dalmatian (I) dogs causes increase in the urinary excretion of allantoin. In (I) urinary excretion of uric acid (II) also increases and the (II) content of the blood increases greatly. W. McC.

[Chemistry of] oxytocin. K. FREUDENBERG, E. WEISS, and H. BILLER (Z. physiol. Chem., 1935, 233, 172—173).—Acid hydrolysis of oxytocin (I) produces tyrosine, cystine, and small amounts of histidine, but these may be derived from impurities. (I) is destroyed by papain (II) (optimum at p_H 7) and by HCN-activated (II), which also destroys the SH groups. Trypsin and tyrosinase destroy (I) and BzO₂H, H₂O₂, alkali, and ultra-violet light (III) damage it, but it is only slowly attacked by cysteine (even at 8.6) and scarcely affected by Na amalgam in aq. NaHCO₃. In neutral or alkaline solution it is rapidly, in acid solution only slightly, attacked by I. Neutral or alkaline aq. Na₂SO₃ and H₂ in presence of Pd rapidly attack it, but some of the activity is restored on subsequent treatment with H₂O₂. (I) differs from insulin in having a lower mol. wt. and in being less sensitive to attack by BzO₂H, H₂O₂, alkali, or (III), but more sensitive to attack by CH₃CO. W. McC.

Action of posterior pituitary on blood-lactic acid. A. D. MARENZI (An. Farm. Biochim., 1934, 5, 18—24; Chem. Zentr., 1934, ii, 3518).—Prolonged intravenous injections of extracts of standard posterior pituitary powder into anaesthetised dogs increase blood-lactic acid if the dosage is > 1 mg. of powder per kg. per hr. A. G. P.

Comparative study of the effects of preparation of the posterior lobe of the pituitary gland on water interchange in frogs. F. R. STEGGERDA and H. E. ESSEX (Proc. Soc. Exp. Biol. Med., 1934, 32, 425—428).—Posterior pituitary preps. cause an increase in wt. of frogs due to increased H₂O absorption. The effect of pitocin is > that of pitressin. Pitocin increases the rate of loss of H₂O when the frogs are kept out of H₂O. R. N. C.

Kidney as a site of thyroid action. K. OBERDISSE and E. RODA (Arch. exp. Path. Pharm., 1935, 178, 252—259).—The average vals. of Q_{O_2} for rabbit's liver, brain, and kidney (I) are 12.3, 10.3, and 12.7 c.c. per hr. per mg. dry-wt., respectively. That of (I) is increased by approx. 54% by injection of thyroxine (II), whilst denervation of the one (I) does not influence either its normal val. or the increase due to hyperthyroidism when compared with the other (I). The data indicate that (II) does not act through the nervous system, but on the peripheral tissues (cf. A., 1931, 1337). F. O. H.

Influence of thyrotropic hormone on blood-and organ-fats and -lipins, blood-sugar, diuresis, and excretion of sodium chloride and urea in rabbits. F. ROTHSCHILD and H. STAUB (Arch. exp. Path. Pharm., 1935, 178, 189—196).—Single or, to a greater extent, continuous intravenous injection of thyrotropic hormone produces changes in the blood-levels of petrol-sol. substances (but not in the I val.), and free and esterified cholesterol. The I val. of the depot-fat is increased. Hyperglycæmia and loss in body-wt. occur after large doses. Small doses tend to increase and large doses to decrease the urinary excretion of H₂O, NaCl, and urea (cf. A., 1933, 1209; 1934, 701). F. O. H.

Action of the thyrotropic substance of anterior pituitary origin on the thyroxine content of the blood. E. ZUNZ and L. LA BARRE (Compt. rend. Soc. Biol., 1935, 118, 1622—1624).—Blood-thyroxine is increased by intravenous injection of thyrotropic hormone. R. N. C.

Carotenæmia in animals treated with thyroxine or thyrotropic hormone. Carotene in the adrenals after injection of thyroxine. C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1934, 118, 1659—1660).—Blood-carotene in the duck is decreased by injection of thyroxine or thyrotropic hormone. Thyroxine increases carotene in the adrenals. R. N. C.

Response of adult rat testes, sex accessories, and adrenals to injections of prolactin. O. RIDDLE, E. L. LAHR, R. W. BATES, and C. S. MORAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 509—512).—Daily injections of prolactin in adult rats do not affect the wt. of the testes, but decrease that of Cowper's glands and increase that of the adrenals.

Follicle-stimulating hormone and prolan do not increase the wt. of the testes, even in relatively high doses. R. N. C.

Stability of prolan; its enzymic nature. H. VON EULER and B. ZONDEK (Skand. Arch. Physiol., 1934, 68, 232—244; Chem. Zentr., 1934, ii, 3518).—Prolan (I) loses 50% activity on heating for 45 min. (with p_H 7—8) at the "crit. death temp." 62°. In this respect and in its inactivation by exposure to ultra-violet radiation (I) exhibits enzyme-like properties. A. G. P.

Human corpus luteum and progestin. J. P. PRATT (Endocrinol., 1934, 18, 667—675).—The progestin content of the human corpus luteum is < that of the sow. R. N. C.

Œstrin and progestin content of the corpus luteum of the sow. C. A. ELDEN (Proc. Soc. Exp. Biol. Med., 1934, 32, 515—516).—Progestin is max. in the early corpus luteum 6—7 days after rupture of the follicle, falling steadily after this period. Œstrin rises to a max. in the fully-formed corpus luteum. R. N. C.

Hormone of the corpus luteum. D. VAN STOLK and H. PÉNAU (Bull. Soc. Chim. biol., 1935, 17, 472—484).—A review. A. L.

Effect of gonadotropic hormones during gestation and lactation. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Proc. Soc. Exp. Biol. Med., 1934, 32, 530—534).—The ovarian response of the pregnant rat to the gonadotropic hormones from pregnancy urine (I) and from the anterior pituitary (II) is > that of the non-pregnant rat, the increase persisting after birth if nursing is not allowed. In hypophysectomised rats (I) preps. produce only thæcal luteinisation (III), which is also produced in lactation (IV) and pregnancy together with granulosa (III). (II) preps. do not produce thæcal (III) during (IV). Neither (I) nor (II) preps. produce the ordinary uterine reaction during (IV). R. N. C.

Production of ovulation by gonadotropic extracts. L. E. CASIDA (Endocrinol., 1934, 18, 714—720).—Folliculin does not produce ovulation (I) in rats or rabbits when injected alone, but it occurs after subsequent injection of luteinising hormone (II). Anterior pituitary extract produces (I) in some strains of rats when injected alone, and in all strains when combined with small quantities of (II); larger quantities of (II) inhibit (I) with formation of corpora lutea atretica. R. N. C.

Quantitative and qualitative response to distributed dosage with gonadotropic extracts. L. C. MAXWELL (Amer. J. Physiol., 1934, 110, 458—463).—The potency of gonadotropic pituitary extracts is increased 50 times by distributed dosage and addition of Zn salts. Zn salts also increase the augmenting effect of the pituitary synergist on pregnancy urine extracts. R. N. C.

Pregnancy urine given by mouth to gonadectomised rats: its effect on spontaneous activity and on the reproductive tract. C. P. RICHTER (Amer. J. Physiol., 1934, 110, 499—512). R. N. C.

Anti-gonadotropic substances. C. BACHMAN, J. B. COLLIP, and H. SELYE (Proc. Soc. Exp. Biol. Med., 1934, 32, 544—547).—Chronic administration of gonadotropic extracts (I) from pregnancy urine or the pituitary in rabbits results in the formation of substances inhibiting their action. Sera from animals so treated produce passive resistance to (I) when injected into other animals. R. N. C.

Effect of ovarian hormone on the pituitary, thyroid, and adrenal glands of spayed female rats. D. H. ANDERSEN (J. Physiol., 1934, 83, 15—25).—The atrophied endocrines are restored to the normal wts. at œstrus by amniotin; hypertrophy can be produced in the thyroid and adrenals. R. N. C.

Action of prolan and folliculin on the testicle. M. PEPE and C. VACCA (Boll. Soc. ital. Biol. sperim., 1934, 8, 1782—1784).—Prolan causes premature maturity and testicular hypertrophy in young male rats, whilst folliculin produces testicular atrophy. R. N. C.

Experimental hyperplasia of the prostate. A. S. PARKES and S. ZUCKERMAN (Lancet, 1935, 228, 925—928).—Injection of œstrone into immature rhesus monkeys results in (a) a diminution in the no. of true prostatic glands with a corresponding increase in the amount of fibromuscular stroma and (b) epithelial growth in the uterus masculinus. L. S. T.

Demonstration of œstrin in the blood of women. C. F. FLUHMANN (Endocrinol., 1934, 18, 705—713).—Serum containing œstrin, injected into spayed female mice, produces a mucification of the vaginal mucosa. During the menstrual cycle serum-œstrin shows a max. at the middle of the interval, a secondary max. during menstruation (I), and min. just before and after (II). R. N. C.

Comparison of theelin prepared from stallion urine, human urine, and from theelol; colorimetric determination of theelin and theelol. G. F. CARTLAND, R. K. MEYER, L. C. MILLER, and M. H. RUTZ (J. Biol. Chem., 1935, 109, 213—220).—Theelin (I) is obtained from stallion urine by extraction of the latter, acid to congo-red, with BuOH, washing the extract with aq. NaCl, concn. in a vac. to a brown oil, and thence by the method of Butenandt (A., 1930, 1480). (I) prepared thus is identical with that obtained from theelol and from human pregnancy urine. The Kober (A., 1931, 1195) colorimetric determination of (I) is modified slightly. H. D.

Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones.—See this vol., 752.

Masculinising action of urine. P. GLEY (Compt. rend. Soc. Biol., 1935, 119, 32—33).—Extracts of adult male urine provoke equally well comb-growth and the appearance of other secondary sex characteristics in capons. R. N. C.

Melanophore hormone in urine. S. KONSULOFF (Klin. Woch., 1934, 13, 490—491; Chem. Zentr., 1934, ii, 3974).—The melanophore hormone content of the urine is considerably increased in pregnancy. R. N. C.

Discovery and significance of vitamins. F. G. HOPKINS (Nature, 1935, 135, 708—712). L. S. T.

Structure and physiological activity. J. PRYDE (Nature, 1935, 135, 713—716).—The structures of vitamins, hormones, and carcinogenic compounds are discussed. L. S. T.

[Examination of] vitamins in Wood's light. A. KARSTEN (Z. Vitaminforsch., 1935, 4, 139—143).—The behaviour of vitamin-containing preps. in Wood's light is discussed and a suitable lamp described (cf. B., 1929, 291). F. O. H.

Spectrophotometry of vitamin-A colour test. E. ROSENTHAL and M. WELTNER (Biochem. J., 1935, 29, 1036—1038).—The purplish-red colour of the SbCl_3 -pyrocatechol test for vitamin-A (A., 1934, 225) shows max. at 545 and 475 $\text{m}\mu$ within 10 min. of testing; with the guaiacol modification, the colour remains unchanged for several hr. with max. at 545 and 478 $\text{m}\mu$. F. O. H.

Determination of vitamin-A in blood. E. ROSENTHAL and C. SZILARD (Biochem. J., 1935, 29, 1039—1042).—The light petroleum extract from 10—30 ml. of blood is dried in a vac. in presence of Na_2SO_4 and the residue is treated with CHCl_3 - SbCl_3 -guaiacol reagent (cf. preceding abstract). The resulting colour is compared with 0.001% aq. KMnO_4 or the "grey solution" of Leitz. F. O. H.

Determination of vitamin-A with the Hilger vitameter equipped with a device for photographic recording. O. NOTEVARP (Biochem. J., 1935, 29, 1227—1235).—Comparison is made between traces made by the light on photographic paper. Increased accuracy is obtained and satisfactory agreement found between the vitameter readings, spectrographic determinations of the absorption at 328 $\text{m}\mu$, and the blue vals. A differential method for determining vitamin-A (I) in oils is described, depending on the destruction of the (I) by irradiation. F. A. A.

Vitamin-A-active substances in egg-yolk. A. E. GILLAN and I. M. HEILBRON (Biochem. J., 1935, 29, 1064—1067).—Using chromatographic methods with spectroscopic control, the unsaponifiable fraction of egg-yolk, after a phase test separation of carotene from xanthophyll followed by adsorption of the latter on CaCO_3 , has been shown to contain vitamin-A both by the SbCl_3 blue test and by the characteristic adsorption band at 328 $\text{m}\mu$. The petroleum phasic carotenoids consist of kryptoxanthin (I) and β -carotene. By feeding fowls on a diet rich in maize, it has been possible to increase the (I) content of the resulting yolks, although the final val. was still small. P. W. C.

Antagonism between vitamin-A and thyroxine. I. ABELIN (Z. Vitaminforsch., 1935, 4, 120—128).—Administration of vitamin-A to rats diminishes the increase in basal metabolic rate due to thyroid preps. (I); the retardation in growth due to excess (I) is also largely counteracted. The antagonism depends on the opposing effects on cell-lipin metabolism and muscle-glycogenesis. F. O. H.

Relation of lipolysis in blood to the defence reaction of the animal organism under administration of different vitamins. K. HOLM (Z. Immunitäts., 1934, 82, 479—494).—Vitamin-D in small quantities increases lipolysis (I) and the bactericidal index, but lowers them in toxic overdoses. Vitamin-A increases (I) slightly. R. N. C.

Respiration of tissues containing varying amounts of vitamin-A. A. CHEVALLIER and H. ROUX (Compt. rend. Soc. Biol., 1935, 118, 1348—1349).—No correlation was observed between the vitamin-A content and respiration of rat or guinea-pig liver. H. G. R.

Effects of vitamin-A-deficient diets on reproduction of sows. E. H. HUGHES (J. Agric. Res., 1934, 49, 943—953).—Pigs were unable to reproduce when fed for considerable periods on a no. of barley-containing rations, unless a supplement of cod-liver oil was given. When fed as sole source of vitamin-A, barley supplied insufficient -A for reproduction. Additional protein feeding (caseinogen) together with -A enhanced the action of the vitamin. A. G. P.

Relation of vitamin-A and its precursor to liver disorder and to resistance to infection. E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1934, 13, 1497—1502; Chem. Zentr., 1934, ii, 3521).—During complete avitaminosis in rats and guinea-pigs vitamin-A can be utilised and stored, but its formation from the pro-vitamin ceases. In thyrogenic liver disorders, -A consumption increases and the reserve is lowered. In this condition the ability to utilise and store -A increased 8-fold. Metabolism of -A is related to glycogen metabolism in the liver. A. G. P.

Growth, productivity, life period, and progeny of guinea-pigs receiving high dosages of yeast (vitamin-B). P. MARANGONI (Boll. Soc. ital. Biol. sperim., 1933, 8, 1753—1756; Chem. Zentr., 1934, ii, 3977).—Dosages of 8—10 g. daily of beer yeast produced no ill effects, even in pregnant animals. The live-wt. increases of the young were > those of control animals. Puberty was reached in 4—5 months. The second generation was productive, but the progeny did not live. A. G. P.

Vitamin-B₁ content of glutinous rice. J. P. SFRUYT and W. F. DONATH (Geneesk. Tijds. Nederl.-Ind., 1935, 75, 502—514).—Black varieties of glutinous rice (ketan) have a larger -B₁ content than white varieties. Results obtained by the "haematocrit" method correspond well with those obtained from the bird (*Munia maja*) test. Vals. > 1.2 international units per g. have been found. The process of "puffing" (about 15 atm. pressure at 150—160°) entirely destroys the vitamin. P. G. M.

Antineuritic (B₁) vitamin content of "black" katjang idjoe (*Phaseolus radiatus*). J. P. SFRUYT and W. F. DONATH (Geneesk. Tijds. Nederl.-Ind., 1935, 7, 601—602).—Black katjang idjoe has the same vitamin-B₁ content as the green variety. S. C.

Degradation of flavins by light. Synthesis of lactoflavin (vitamin-B₂) and other flavins. Sugar-like side-chain of lactoflavin.—See this vol., 760.

Micro-determination of vitamin-C. D. GLICK (J. Biol. Chem., 1935, 109, 433—436).—The method is a refinement of that (I) of Birch *et al.* (A., 1933, 646). For extraction of the vitamin (II) and prep. and standardisation of the 2:6-dichlorophenol-indophenol solution (III) the procedure of Bessey *et al.* (A., 1934, 227) is adopted, 9% AcOH replacing $\text{CCl}_3\text{-CO}_2\text{H}$. (III) is placed in the burette. The amount of (II) determined is about one fiftieth of that determined by (I). W. McC.

Determination of vitamin-C with 2:6-dichlorophenol-indophenol. A. FUJITA and D. IWATAKE (Biochem. Z., 1935, 277, 293—295).— $\text{CCl}_3\text{-CO}_2\text{H}$ (I) oxidises vitamin-C and decolorises the indicator. The procedure of Harris *et al.* (A., 1933, 541) is more accurate than that of Tillmans (A., 1932, 310), but (I) should be replaced by 2% aq. HPO_3 . W. McC.

Colorimetric determination of vitamin-C. A. FUJITA, D. IWATAKE, and T. MIYATA (Biochem. Z., 1935, 277, 296—304).—Ascorbic acid (I) (4 c.c. of solution containing 0.5—10.0 mg. per 100 c.c.) in 2% aq. HPO_3 is accurately determined by adding first 1 c.c. of a solution of 2 g. of Na_2WO_4 in 10 c.c. of dil. H_2SO_4 , then 0.4 c.c. of 2N-NaOH, and comparing the blue colour produced with that of a standard. The reaction is sp. and not given by substances (e.g. in liver, lungs, kidney, adrenals, heart) [other than (I)] which reduce 2:6-dichlorophenol-indophenol. < 0.003 mg. of (I) can be detected. W. McC.

Determination of glutathione and ascorbic acid in animal tissues. K. WACHHOLDER, K. ANDERS, and K. UHLENBROOCK (Z. physiol. Chem., 1935, 233, 181—185; cf. this vol., 511).—The ascorbic acid (I) of the tissues (II) is iodometrically determined, after destroying the glutathione (III) with CH_2O and the (III) by subtracting the (I) val. from that obtained before addition of CH_2O , but since (I) is partly attacked by CH_2O , a correction must be applied. The CH_2O is added after deproteinisation and in concn. < that previously used. The (II) vals. agree with those of Binet *et al.* (A., 1934, 574). (II) contain also other material which consumes I. (III) interferes with determination of (I) by Tillmans' method. The (I) and (II) contents of the organs of the rabbit and dog are given. W. McC.

Antiscorbutic activity of ascorbic acid isolated from Japanese green tea. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 10—12; cf. A., 1934, 1416).—0.8 mg. per day of ascorbic acid derived from Japanese green tea, or 0.5 mg. from Natumikan (Japanese lemon) juice, cures scurvy in guinea-pigs. J. L. D.

Ascorbic acid in the pituitary gland. A. GIROUD, C. P. LEBLOND, and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1935, 118, 1311—1312).—The ascorbic acid contents of the anterior lobe, pars intermedia, and posterior lobe of ox pituitary are 1.65, 2.01, and 0.55 mg. per g. of tissue, respectively. H. G. R.

Vitamin-C content and reducing power of normal and pathological urine. W. VON DRIGALSKI (Z. Vitaminforsch., 1935, 4, 128—136).—The

daily urinary excretion of vitamin-C (I) by healthy adults was 36—79 mg., average 50 mg. Higher vals. were given only after ingestion of diets very rich in (I). With children the val. was 16—30 mg. according to age, whilst it fluctuated considerably with various diseases. Breast-fed children receive large amounts of (I) from the mother. The highest [(I)] in urine observed was 0.0104%.

F. O. H.

Catalytic oxidation of ascorbic acid. A. E. KELLIE and S. S. ZILVA (Biochem. J., 1935, 29, 1028—1035).—Normal distilled H_2O , but not H_2O repeatedly distilled in glass or SiO_2 apparatus, contains sufficient Cu and Fe to catalyse the irreversible oxidation (I) of aq. ascorbic acid. Dehydroascorbic acid (II) is an intermediary in (I). Saturation of H_2O with O_2 has no marked effect on (I). (I) is inhibited by aq. extracts of liver, kidney, muscle, spleen, intestine, and by plasma, intact or haemolysed erythrocytes (III), and 0.1N-NaCl, but not by leucocytes. With (III), there is an initial (I) which \propto the amount of (III) added and does not occur with CO-treated (III). (II) is probably reduced in the organism before acting as vitamin-C (A., 1934, 1271).

F. O. H.

Effect of vitamin-C on metabolism. F. STRIECK (Biochem. Z., 1935, 277, 279—283).—In dogs, oral, subcutaneous, or intravenous administration of ascorbic acid (I) results in increase, lasting about 3 hr., in the O_2 consumption, the magnitude of the effect being independent of the dose (0.05—1.0 g.). Prolonged treatment has no cumulative effect. In healthy persons doses of 0.4—1.0 g. in some cases produce increases of short duration (up to 37%) in the basal metabolism (II); in other cases they have no effect. In diseased persons having increased basal (II) no further increase follows administration of (I) nor is the R.Q. affected.

W. McC.

Effect of fluorine feeding on the storage of vitamin-C in the rat and guinea-pig. H. M. HAUCK (J. Agric. Res., 1934, 49, 1041—1045).—Addition of 0.15% of NaF to the diet over a period of 3—5 weeks did not prevent normal storage of vitamin-C in the adrenals and livers of guinea-pigs and rats.

A. G. P.

Spectroscopic analysis of vitamin-D in wool-fat. H. TOPELMANN and W. SCHUHKNECHT (Z. Vitaminforsch., 1935, 4, 111—120).—Vitamin-D is not detectable spectroscopically in ultra-violet-irradiated lanolin or other wool-fat preps.; hence, if present, the content is < 0.03%.

F. O. H.

Effect of viosterol on the calcium content of dog's bile. K. K. JONES and G. H. LAING (Amer. J. Physiol., 1934, 110, 471—476).—Viosterol raises bile-Ca and lowers bile-flow only when given in quantities large enough to increase definitely the blood-Ca. Bile-Ca is uniform when bile-flow and blood-Ca are normal. Total Ca excretion in bile under normal conditions is almost completely dependent on the vol. output.

R. N. C.

Thyrotropic action of vitamin-D. N. GOORMAGHTIGH and H. HANDOVSKY (Compt. rend. Soc. Biol., 1935, 118, 1616—1619).—Vitamin-D in dogs produces a hyperthyroidism which attains its max. at the 10th day, afterwards decreasing slowly until

at the 50th day it is < normal. The sensitivity of the blood-pressure to adrenaline increases and decreases with the thyroid function. R. N. C.

Vitamin-E and fertility of poultry. F. ENDER (Z. Vitaminforsch., 1935, 4, 106—111).—Administration of wheat-germ oil (0.17—0.18 g. per day) to fowls increases the yield of living chicks from the artificially incubated fertilised eggs. F. O. H.

Carbon dioxide assimilation [in plants]. J. FRANCK (Naturwiss., 1935, 23, 226—229).—The mechanism of the formation of dehydrochlorophylls is discussed, and the cycle of chemical and energy exchanges involved in the assimilation process and fluorescent phenomena of chlorophyll is examined. A. G. P.

Chlorophyll fluorescence and assimilation of carbonic acid. III. Effect of carbonic acid on fluorescence in living leaves. H. KAUTSKY and A. HIRSCH (Biochem. Z., 1935, 277, 250—260; cf. this vol., 263, 311).—When the assimilation (I) of CO_2 by green leaves (II) is restricted by reduction of temp. or addition of phenylurethane or HCN the fluorescence (III) on irradiation, which is otherwise of short duration, is prolonged and/or intensified, but, since increase (up to 1%) in the concn. of the CO_2 supplied to (II) has no appreciable effect on the duration or intensity of (III), no direct transfer of the light energy absorbed by the chlorophyll to free or bound CO_2 occurs. Very high (up to 50%) concns. of CO_2 unfavourably affect (I) and interfere with the usual course of (III). W. McC.

Kinetics of photosynthesis. E. C. C. BALY (Proc. Roy. Soc., 1935, B, 117, 218—239).—The following scheme is proposed for the cycle of reactions occurring in photosynthesis; (a) a chlorophyll- a - CO_2 - H_2O complex (I) under the influence of light gives chlorophyll- b (II) and CH_2O , which polymerises to hexoses; (b) in a dark reaction (II) is reduced (by carotene?) to chlorophyll- a (III); (c), (III) combines with CO_2 and H_2O to form (I). Kinetic formulae for the photostationary state thus set up account for the experimental results of various workers, on the effects of temp., CO_2 concn., total light intensity, relative intensities of red and blue light, irradiation with flashing light, and poisons, on photosynthesis by *Chlorella*. F. A. A.

Relation between chlorophyll content and rate of photosynthesis. W. E. FLEISCHER (J. Gen. Physiol., 1935, 18, 573—597).—The rate of photosynthesis by a strain of *Chlorella* is \propto the chlorophyll content when the latter is varied by varying the Fe or N supply. The behaviour when the Mg supply is varied is more complex. F. A. A.

Chlorophyll b.—See this vol., 763.

Effect of age on assimilation of leaves. B. N. SINGH and K. N. LAL (Ann. Bot., 1935, 49, 291—307).—Assimilation (I)—age curves of wheat, linseed, and sugar-cane under optimum conditions show low vals. in the early stages, reaching a max. at the period of max. growth and maturity, and declining towards the senescent stage. With reduced $[\text{CO}_2]$ equiv. to that of the atm. early vals. are maintained at a steady level throughout growth. The intensity of

(I) is controlled by the H_2O status, the chlorophyll content of leaves, and by catalytic substances, e.g. K and Ca. Different stages of development are marked by changes in rates of (I). The age and development of leaves is an important internal factor controlling the intensity of (I) and its mechanism. A. G. P.

Transpiration and pressure deficit. I. F. M. HAINES (Ann. Bot., 1935, 49, 213—238).—The absorption of H_2O by cut branches, the upper ends of which are sealed in a pressure vessel, is inversely related to the pressure applied. It is also influenced by the previous history of the branch. The effect is due to alteration of the vols. of the leaf cells and to modified transpiration rates. A. G. P.

Translocation and growth balance in woody plants. W. E. LOOMIS (Ann. Bot., 1935, 49, 247—272).—In 2-year apple and poplar trees movement of carbohydrates and org. N compounds, but not that of ash constituents, is temporarily checked by phloem ringing. In all trees examined N occurs in the tops only in the org. form. The carbohydrate level in sprouting segments is > in those bearing active leaves with cambial growth, although photosynthetic activity precedes normal cambial development. Primary growth is preceded by accumulation of simpler forms of org. N. The latter are probably condensed to form protoplasmic proteins in the apical meristems or in the leaves, but not in the cambium. The polarity of sprout growth and rooting is discussed together with the activity of hormones. A. G. P.

Respiration of the roots of plants. H. LUNDEGARDH and H. BURSTROM (Biochem. Z., 1935, 277, 223—249; cf. A., 1933, 874).—The basal respiration (I) of the roots (wheat seedlings) is independent of the respiration (II) due to the anions (III) (Cl^- , NO_3^-) in the nutrient medium. For (I) the presence of free O_2 is essential, whilst (III) control the uptake of residual O_2 . The formula for aerobic conditions holds also for anaerobic. Concns. of KCN which greatly restrict anaerobic (II) leave (I) unaffected. Other poisons (Co, Pb, Tl, Hg, Cu) exhibit sp. differences as regards their action on (I) and (II). Anaerobic uptake of (III) is accompanied by an oxido-reduction process in which C of the hexose mol. is converted completely into CO_2 without the intervention of free O_2 . W. McC.

Effect of halogenated aliphatic compounds on the respiration of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1935, 7, 1—17; cf. A., 1934, 1418).—The respiratory activity (I) of tubers was increased by exposure to the vapours of a no. of halogen derivatives of the aliphatic hydrocarbons. In all cases the CO_2 output was increased even when > lethal concns. were used. The following comparative effects are recorded for low concns.: alkyl iodides > bromides > chlorides, n -halides > sec.-halides, $\text{C}_2\text{H}_4\text{Br}_2$ > $\text{C}_2\text{H}_4\text{BrCl}$ > $\text{C}_2\text{H}_4\text{Cl}_2$, ethylene compounds > ethylidene compounds, propylene bromide < trimethylene bromide, α - > β - > *iso*-butylene bromide. Of the four simplest alkylene bromides $\text{C}_2\text{H}_4\text{Br}_2$ is the most effective. Increased (I) under these conditions is associated with increased p_{H} of the expressed juices. A. G. P.

Analysis of the effect of phosphorus supply on transpiration ratio in plants. R. F. WILLIAMS (Austral. J. Exp. Biol., 1935, 13, 49—66).—An increase in P supply from a low to a moderate amount reduced the transpiration ratio (I) (ratio of H_2O transpired to amount of dry matter formed) of Algerian oats (*Avena sativa*), but an additional supply had no further effect. Except for the earliest period, the reduction in the ratio is due to a decrease with treatment in the transpiration rate per unit wt. of plant dependent on (a) a decrease in the transpiration rate per unit wt. of leaf, and (b) a decrease in the leaf-wt. ratio during part of the life cycle. Increased P supply tends to raise (I) indirectly through an effect on growth, but this action is more than balanced by the previously mentioned effect on transpiration rate. A significant correlation was found between the relative transpiration rate per unit wt. of leaf and the N content of the leaves.

W. O. K.

Growth-promoting substance as a factor in the formation of plant organisms. V. M. KATUNSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 661—667).—Application of growth-promoting factor (I) by contact with coleoptiles of *Avena* and *Zea mays* inhibits the regenerative cell-division by cut surfaces of succulent leaves and the formation of adventitious rootlets by *Vicia faba* in which the growing points of the roots have been removed. The action of (I) is thus mainly one of cell-elongation and depression of development of plant organs.

F. O. H.

Indole-3-*n*-propionic acid as a growth hormone and the quantitative measurement of plant response. A. E. HITCHCOCK (Contr. Boyce Thompson Inst., 1935, 7, 87—95).—The acid possesses the same ability as hetero-auxin to produce bending, proliferation, and rooting responses in plants. The effects vary with the concn. of active material used, the method of application, and the species of plant. Quant. measurements are described. Positive effects are produced by a no. of other org. substances examined.

A. G. P.

Location of oxidase in the apricot. R. SAMISCH (Amer. J. Bot., 1935, 22, 291—293).—In ripe apricots oxidase (I) activity is highest in the epidermis especially in stomatal guard cells. It is also high in cells surrounding the fibro-vascular bundles, but is absent from the vessels. Within the cells (I) is located in vacuolar sap, but not in the protoplast.

A. G. P.

Nitrogen absorption [by plants] and aeration. J. W. SHIVE (New Jersey Agric., 1934, 16, No. 5, —3).—The total yield of tomato plants in H_2O cultures was increased by aerating the medium, absorption by the roots being much greater at p_H 7 than at p_H 4. Plants in aerated media removed up to 60% more N than those unaerated, the effect being more marked on NH_4 - than on NO_3 -N. Poorer growth in the absence of aeration results from O_2 deficiency and not from CO_2 accumulation.

CH. ABS. (p)

Oxyhydrogenating enzyme systems in germinating seeds. I. H. VON EULER and R. WEICHERT (physiol. Chem., 1935, 233, 81—86; cf. this vol.,

263).—Chlorophyll-defective (I) can be distinguished from normal (II) barley seedlings after 1 day's germination by means of the fluorescence microscope. As regards changes in dehydrase content, (I), (II), and (I) and (II) which have been exposed to X-rays behave similarly, all exhibiting great decreases in the first few days of germination [donators from the seedlings and Na malate (III), citrate, and succinate]. The decrease is especially pronounced with (III). The catalase content of (I) is < that of (II). W. McC.

Influence of heavy water on plants. A. J. EWART (Austral. J. Exp. Biol., 1935, 13, 9—15).—Dil. heavy water (1—1.3 per 1000) exerts a weak but usually inhibiting action on the growth of non-chlorophyllous plants and bacteria and on the germination of oat seeds. In the case of chlorophyllous plants slight acceleration of growth may be observed.

W. O. K.

Effects of radioactive mud on germination of seeds and growth of seedlings. L. HAVAS (J. Agric. Sci., 1935, 25, 197—216).—Stimulation of germination and growth resulted from exposure of seed to a Hungarian radioactive mud, the effect being produced by direct contact or by exposure at a short distance from a large amount of mud. Prolonged exposure had a deleterious effect. Wheat seeds treated with vital stains respond to irradiation in a manner which is influenced by the stain.

A. G. P.

Catabolism of fat and phosphatides in germinating soya beans. W. ZIMMERMANN and A. BAUMANN (Fettechem. Umschau, 1935, 42, 65—69).—Changes in content and character (acid and I vals.) of the total lipins and phosphatides during the germination of soya beans in sand, earth, or exposed to light, are described. Heavy soils delay growth (and may cause death) of the seedlings by restricting access of air.

E. L.

Effect of nitrate-nitrogen on the carbohydrate metabolism of inoculated soya beans. F. S. ORCUTT and P. W. WILSON (Soil Sci., 1935, 39, 289—296).—Low $[NO_3^-]$ in the nutrient reduced the level of sol. sugars in the plant sap, probably as a result of protein formation. Intermediate $[NO_3^-]$ stimulated photosynthesis and increased nodulation and N fixation. Higher $[NO_3^-]$ decreased the sugar level in the sap, since photosynthetic capacity, under these conditions, became the limiting factor in protein formation. Nodules were fewer and smaller.

A. G. P.

Dynamics of metabolism during the ripening process of the red currant. O. J. SOBOLEVSKAJA and R. C. TURETZKAJA (Bull. Acad. Sci. U.R.S.S., 1934, 1341—1365).—During the formation of the green berry there is a steady production of protein and carbohydrates [largely polysaccharides (I)]. In the softening stage prior to colouring invert-sugar (II) is translocated rapidly from the leaves. In the final colouring stage the increasing (II) content is still further supplemented by decomp. of (I). The accumulation of sucrose (III) in the final stages of ripening is brought about by the cessation of decomp. of (III), and not by increased synthesis from glucose and fructose.

A. G. P.

Formation of rubber and resin and their movement in plants. N. N. KISELEY, A. P. OSIPOV, and K. A. KUZMINA (Bull. Acad. Sci. U.R.S.S., 1934, 1367—1386).—Formation of rubber and resin (or at least their precursors) is photosynthetic. The subsequent transformation may continue in the dark. The flow of latex in darkness is $>$ in light. Rubber is not a by-product, but plays a definite part in the metabolism of the plant. The rubber content of plants shows daily variations with max. in the afternoon.

A. G. P.

Effect of long and short day and shading on nodule development and on composition of the soya bean. E. W. HOPKINS (Soil. Sci., 1935, 39, 297—321).—Plants exposed to short day periods had high starch (I) and N contents whether the NO_3^- supply was high or low. With advancing age, accumulation of (I) in low- NO_3^- plants increased and the N constituents contained a larger proportion of simpler compounds. Plants grown under long-day conditions had lower (I) and N contents, notably in stems. With a low NO_3^- supply such plants showed declining carbohydrate (II) and increasing N contents with advancing age. Shaded plants contained less (II) and more N than the unshaded. The wt. of nodules produced relative to the total wt. of plants was decreased by high NO_3^- supply, short days, and shading.

A. G. P.

Two varieties of chromatin in the nuclei of *Lilium Martagon*. M. LENOIR (Compt. rend. Soc. Biol., 1935, 118, 1554—1556).—The double coloration shown by every important nuclear chromatic body of *Lilium Martagon* at the points of contact with the karyoplasm and the cytoplasm indicates the presence of two physically or chemically different varieties of chromatin.

R. N. C.

Inorganic composition of wheat grown in Eastern Australia. I. W. DADSWELL (Austral. J. Exp. Biol., 1935, 13, 33—42).—The total ash contents (H_2O -free basis) of wheats grown in Victoria and New South Wales are in general $<$ comparable data for wheats grown outside Australia.

W. O. K.

Changes in the carbohydrate content of wheat during hardening against drought. I. M. VASSILIEV and N. G. VASSILIEVA (Bull. Acad. Sci. U.R.S.S., 1934, 1340).—Drought-hardening is effected by the temporary maintenance of plants with a reduced H_2O supply until the leaf-tips begin to die back (8 days). During this period the monosaccharide (I) content of the plant increases steadily, sucrose (II) increases at first and decreases later, and hemicellulose (III) decreases in the early stages, subsequently rising rapidly to vals. $>$ those of untreated plants (\bar{U}). The hardened plants, when again receiving normal supplies of H_2O , have permanently lower H_2O and (I) contents and more (III) than \bar{U} . The (II) content falls somewhat immediately after rewating, but subsequently rises $>$ that of \bar{U} .

A. G. P.

Odorous substance of green tea. IV. Odorous substance of dark tea. S. TAKEI, Y. SAKATO, and M. OHO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 21—22; cf. this vol., 267).—Tea-leaf oil contains Δ^6 -hexenaldehyde and Δ^6 -hexenol (I) which are

converted into Δ^6 -hexendi- Δ^6 -hexenylacetal, b.p. $110^\circ/2$ mm., and di- Δ^6 -hexenyl ether, b.p. 228° . Drying affords a condensation product, b.p. 240° (3:5-dinitrobenzoate, m.p. 78°), of (I), which gives dark tea its characteristic odour.

J. L. D.

Pigments of the Mendelian colour types in maize. Chrysanthemin from purple-husked maize. C. E. SANDO, R. T. MILNER, and M. S. SHERMAN (J. Biol. Chem., 1935, 109, 203—211).—Purple maize husks are extracted with MeOH-HCl (I), the extract is cooled, filtered, and the pigment is pptd. with Et_2O . Chrysanthemin (II) is pptd. from dil. HCl solution with $\text{Pb}(\text{OAc})_2$ and the product decomposed with (I). Purification of (II) is completed by formation of the picrate, decomp., and pptn. with Et_2O . Its identity is confirmed by comparison with a synthetic specimen.

H. D.

Components of *Parmelia perlata*, Ach.—See this vol., 749.

Composition of *Salvia miltiorrhiza* (Chinese drug tan-shin).—See this vol., 754.

Saponin and sapogenin of *Chenopodium ambrosioides*, L.—See this vol., 754.

Constitution of miliacin.—See this vol., 753.

Salicaceae. VIII. Distribution of glucosides in the Salicaceae. IX. Physiological study of the glucosides. J. RABATE (Bull. Soc. Chim. biol., 1935, 17, 439—446, 447—458).—VIII. The distribution of the glucosides, sucrose, salicoside, daphneflavonolside, populoside, flavopurposide, salinigriflavonolside, salipurposide, isosalipurposide, piccoside, salidroside, and salireposide in various *Salicaceae* is described.

IX. A criticism of the technique and results of Jowett and Potter (A., 1902, ii, 686) and of Weevers (Jahrb. wiss. Botanik, 1904, 39, 229). Contrary to the results of the first named, the glucoside contents of the stems of male and female *S. purpurea* are almost the same.

A. L.

Indian medicinal plants: *Tinospora cordifolia*, *Solanum xanthocarpum*, and *Fumaria officinalis*. G. P. PENDSE and S. DUTT (Indian J. Med. Res., 1932, 20, 663—670).—Extracts afforded by H_2O and org. solvents from the dried powdered plants are described. *T. cordifolia* contains a waxy substance, $\text{C}_{10}\text{H}_{14}\text{O}_5$, m.p. 173 — 174° , an EtOH -sol. substance (glucoside?), m.p. 76 — 77° , and an intensely bitter principle; *S. xanthocarpum* KNO_3 (1.6—1.9%), sugars (1.6%), solanine, and an oxidising enzyme; *F. officinalis* sugars (8.2%) and traces of alkaloid.

H

Alkaloids of the Chinese drug "Chin-shih-hu."—See this vol., 764.

Alkaloids of *Senecio platyphyllus*, D.C. See this vol., 764.

Localisation of alkaloids in ipecacuanha root. M. WAGENAAR (Pharm. Weekblad, 1935, 72, 513—517).—Staining of the alkaloids (I) by pptn. with $\text{K}_4\text{Fe}(\text{CN})_6$ followed by FeCl_3 after washing out excess reagent, and microdialysis show that (I) is localised in the peripheral cells. The yellow ppt. obtained with picric acid or $\text{K}_2\text{Cr}_2\text{O}_7$ is due to proteins

which resemble gliadin or hordein in being sol. in aq. EtOH. S. C.

Sterol from *Pinus sabiniana*. O. GISVOLD (J. Amer. Pharm. Assoc., 1935, 24, 290).—The non-saponifiable residue from the oil extracted from *P. sabiniana* contained a *sitosterol*, m.p. 137.5° (Ac derivative 127.5°). H. D.

Phytochemistry. CXI. Sterols from *Monarda fistulosa*. O. GISVOLD (J. Amer. Pharm. Assoc., 1935, 24, 214).—The unsaponifiable fraction of oil from wild bergamot leaves yields a sterol, m.p. 130–131° (Ac derivative, m.p. 115–118°). Stigmasterol does not appear to be present. F. O. H.

Volatile oil of *Hyptis mutabilis*. H. W. WERNER (J. Amer. Pharm. Assoc., 1935, 24, 289–290).—The presence of sabinene and caryophyllene is indicated in the steam distillate from *H. mutabilis*. H. D.

Oil of the rose mallow (*Hibiscus moscheutos* × *H. coccineus*) seed. C. BARKENBUS and S. T. THORN (J. Amer. Chem. Soc., 1935, 57, 728–729).—This oil (20%) closely resembles cotton-seed oil, containing the glycerides of oleic (33.12), linoleic (45.53), linolenic (0.06), and saturated (15.6%; mainly palmitic, some stearic, and traces of arachidic) acids, and 1.34% of unsaponifiable matter. R. S. C.

Constitution of fustin and of the wood of *Rhus succedanea*, L.—See this vol., 757.

Starch and related polysaccharides of certain hardwoods. I. Preparation and properties of oak and walnut starch. W. G. CAMPBELL (Biochem. J., 1935, 29, 1068–1080).—A method is described for the quant. isolation of the starch of the sapwood of English oak and walnut. Wood-starch is an acid polysaccharide consisting approx. of 90% of anhydroglucose residues and of an aldobionic acid anhydride (probably glucose glycuronic acid anhydride) which may be partly methylated. The cell walls of oak-sapwood contain a polysaccharide chemically related to that of the cell contents. Wood-starch forms a suitable source of nourishment for the larvæ of *Lyctus* powder-post beetles. P. W. C.

Nitrogen of polysaccharide complex from *Chondrus crispus*. M. R. BUTLER (Biochem. J., 1935, 29, 1025–1027).—The polysaccharide (A., 1934, 1047) has a N content approx. 13% of that originally present in the plant. F. O. H.

[Composition of] the mucilage from psyllium seed (*Plantago psyllium*, L.). E. ANDERSON and M. FIREMAN (J. Biol. Chem., 1935, 109, 437–442).—The mucilage is a mixture of polyuronides composed of *d*-galacturonic acid combined with *l*-arabinose (I). Chains of *d*-xylose mols. (8–35) and an insol. unsaponifiable substance are united to (I). The ash contains K, Ca, Fe, PO₄'''. W. McC.

Nucleic acid of ergot. I. M. GATTY-KOSTYAL and J. TESARZ (Wiadomosci farm., 1934, 61, 17–18 31–32; Chem. Zentr., 1934, ii, 3509).—Ergot on 1.4–1.6% P₂O₅ (I) (calc. on dry matter) distributed thus: lecithin (I), 0.096–0.118%; sol. (I), 1.01–1.14%; nuclein (I), 0.29–0.32%. A

substance (N, 15.21%; P, 8.73%) of the nucleic acid type was isolated. H. N. R.

Origin of the gases in the float of bladder kelp. G. B. RIGG and B. S. HENRY (Amer. J. Biol., 1935, 22, 362–365).—The interior of the float is probably free from bacteria, and the CO therein is a respiratory product. A. G. P.

Mineral nutrition in Victorian fruit trees. F. M. READ and C. E. COLE (J. Austral. Inst. Agric. Sci., 1935, 1, 33–34).—The effects of deficiencies of individual mineral nutrients on the growth of trees are described. The balance of nutrients is more important for growth than are the actual amounts present. Deficiency of one nutrient may result in relatively increased absorption of another, thus intensifying the unbalance. A. G. P.

Distribution of calcium in leafy vegetables. P. C. HSU and W. H. ADOLPH (Chinese Med. J., 1935, 49, 325–327).—Determinations of Ca in inner (I) and outer leaves (II) of certain Chinese vegetable foods show that the Ca content of (II) is from 2 to 20 times that of (I). It is suggested that (II) should be used as food in cases of Ca deficiency. H. T.

Effect of some cations on the permeability of cells to water. E. C. D. BAPTISTE (Ann. Bot., 1935, 49, 345–366).—The permeability of discs of potato and carrot to H₂O is affected by cations in the order K⁺ > NH₄⁺ > Na⁺ > H₂O > Mg⁺⁺ > Ca⁺⁺. A. G. P.

Toxicity of aluminium to seedlings: action of certain ions in eliminating the toxic effects. W. S. EISENMENGER (Plant Physiol., 1935, 10, 1–25).—Org. salts of Al (tartrate, citrate) are toxic to maize, soya beans, and buckwheat, the effect increasing with the concn. applied. Ca(OH)₂ is the best corrective. Ca(NO₃)₂ is less effective. The acidity of the Al salts may be neutralised by KOH, but the toxicity is not so completely eliminated as by Ca(OH)₂. Optimum growth-*p_H* for plants in Al salt-alkali media varies with constituents of the mixture and the proportions in which they occur. Al salts of org. acids are more toxic to plants than are the free acids in solutions of the same *p_H*. A. G. P.

Physiological action of potassium on the vital processes of chlorophyll-containing and chlorophyll-free cells. J. STOKLASA (Věstn. czechoslov. Akad. Zemed., 1934, 10, 146–151; Chem. Zentr., 1934, ii, 3513).—Irradiation with β- and γ-rays from Ra and K preps. favours the production of new plant tissues, even during the night. A. G. P.

Relation of sugar content and odour of clarified extracts of plants to their susceptibility to attack by the Japanese beetle. F. W. METZGER, P. A. VAN DER MEULEN, and C. W. MELL (J. Agric. Res., 1934, 49, 1001–1008).—Plants of which clarified extracts had a fruity odour and a high reducing sugar content were the more susceptible to attack. A. G. P.

Relation of carbohydrate-nitrogen nutrition to disposition of apple to infection by *Erwinia amylovora*. G. K. K. LINK (Phytopath., 1935, 25, 26).—Trees having relatively low carbohydrate (I), and high N contents were susceptible to infection,

whereas those having high (I) and low N were resistant. The susceptibility of the former was maintained throughout the season. A. G. P.

Catalase activity in relation to age and viability of sclerotia of the cotton root-rot fungus. C. J. KING, E. D. EATON, and C. HOPE (J. Agric. Res., 1934, 49, 897—902).—In macerated tissues of root-rot sclerotia (I) catalase activity (II) declines steadily with the age of the (I) until loss of germinative power becomes appreciable. High (II) in (I) of 5—8 weeks old indicates an "after-ripening" process resembling that in seeds. The age and vigour of (I) may be assessed on the basis of determinations of (II). Drying of (I) causes a rapid decline in (II).

A. G. P.

Effect of crown rust on yield, water economy, and composition of oats. H. C. MURPHY (Phytopath., 1935, 25, 28—29).—Rust infection reduced yields and increased H_2O utilisation of oat plants. The composition of grain and husk was not affected, except for slightly increased protein and decreased N-free extractives. In the green plant the % of insol. solids, sol. and insol. ash and N, and the acid-hydrolysable material was increased and that of sol. solids, sucrose, glucose, dextrin, and (notably) fructose declined.

A. G. P.

Carotenoid pigments of uredospores of wheat-stem rust and four of its colour variants. M. NEWTON, H. JOHANSSON, and T. JOHNSON (Phytopath., 1935, 25, 30).—Spectrophotometric examination of naphtha extracts of spores indicates the pigments to be carotenoid in character and in most cases to consist chiefly of carotene. Pigment production in normal is $>$ in subnormal light.

A. G. P.

Metabolism of crown gall and hairy-root bacteria and the composition of crown galls. H. A. CONNER, A. J. RIKER, and W. H. PETERSON (Phytopath., 1935, 25, 11).—In aerated yeast-infusion media crown gall bacteria convert 2% of the glucose fermented into CO_2 and 10—15% into bacterial gum. For hairy-root bacteria the vals. were 20 and 10%, respectively. Small amounts of $AcOH$ and $AcCO_2H$ were also formed. Fresh tomato and raspberry galls contained larger proportions of ash and total N, but less cellulose, starch, pentosans, and sugar, than did contiguous healthy tissue. Differences in $\alpha-NH_2$ -, amide-, NH_3 -, NO_3 -'N, or uronic acid content were insignificant.

A. G. P.

Pathogenic bacteria which induce cell stimulation in plants. J. A. PINCKARD (Phytopath., 1935, 25, 31).—Five species of bacteria causing galls or overgrowths on plants were examined. The optimum growth temp. in all cases approached 28° and the growth produced varied with the C and N sources. Where starch or salts of org. acids were utilised alkalinity developed, whereas other C sources induced acidity. All cultures became acid when N was supplied as oxamide, *l*-tyrosine, or *l*-cystine. Highly reduced potentials occurred in undisturbed liquid cultures.

A. G. P.

Chemical splitting of the tomato "combination-streak" virus complex. M. SHAPOVALOV

(Phytopath., 1935, 25, 33).—Partial differentiation of the components of the complex is obtained by treating infected tomato or tobacco juice with $CoSO_4$, $NiSO_4$ or $ZnSO_4$ at concns. $<$ those producing lytic effects on the whole complex. The two viruses showed relative differences in inactivation by these salts. A. G. P.

Influence of nutrition on host susceptibility to yellow tobacco mosaic. E. L. SPENCER (Phytopath., 1935, 25, 33—34).—Rapidly growing plants were less susceptible than those retarded by excessive N, or excessive P. Susceptibility was high in plants receiving small amounts of K and decreased sharply with increasing supplies of K. Growth retardation was not apparent until the amount of K given was very large.

A. G. P.

Effect of proteoclastic enzymes on purified preparations of tobacco mosaic virus. A. F. ROSS (Phytopath., 1935, 25, 33).—The virus was inactivated by trypsin (I). Heating the digest at 70° for 20 min. resulted in recovery of most of the virus. Permanent inactivation (II) did not occur when enterokinase, $CaSO_4$, $CaCl_2$, $(NH_4)_2SO_4$, $MgSO_4$, and $BaCl_2$ were used as activators for (I). A combination of pepsin and (I) was less effective than (I) alone. Papain and cultures of certain bacteria caused (II). (I) attacked no protein which could be associated with the virus.

A. G. P.

Factors affecting "longevity" in vitro of viruses of tobacco mosaic and of tobacco ring spot. B. M. DUGGAR and D. F. McALISTER (Phytopath., 1935, 25, 15).—The survival of mosaic virus in tobacco extract is favoured by condensation of the extract at low pressure and temp. and by addition of low (antiseptic) concns. of $EtOH$. The ring-spot virus is similarly affected by $EtOH$ and by additions of buffer solutions of pH 5.8—7.0, $PO_4^{'''}$ buffers being more favourable than citrates.

A. G. P.

Factors influencing the activity of tobacco mosaic virus preparations. A. W. PETRE (Contr. Boyce Thompson Inst., 1935, 7, 19—28).—Improvements in the Vinson and Petre Pb-pptn. method (A., 1931, 1201) for preparing the virus are described. The susceptibility of plants to infection is influenced by the relative succulence of growth, but not by the rate of leaf expansion.

A. G. P.

Culture vessel. H. S. HOLDEN (Ann. Bot., 1935, 49, 401).—A shallow culture dish is fitted with a conical flask-like cover. Cultures of micro-organisms, algae, liverworts, etc. can be maintained for an extended period.

A. G. P.

Reaction vessel for measurement of microbiological gas metabolism. A. JANKE and S. KROPACSY (Biochem. Z., 1935, 277, 268—272).—Reactions (I) (e.g., oxidation of $EtOH$ by acetic bacteria) proceeding in the vessel described can be stopped at any desired point, the contents (liquid and gaseous) can be micro-chemically examined, and, if no gas is produced during (I), the rate of consumption of gases can be followed.

W. McC.

Units of measurement in morphological technique. E. AGDUHR (Z. Vitaminforsch., 1935, 4, 136—139).

F. O.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1935.

General, Physical, and Inorganic Chemistry.

Intensity of the electrodeless hydrogen spectrum as conditioned by pressure and discharge-tube dimensions. M. S. McCAY (*J. Elisha Mitchell Sci. Soc.*, 1934, 50, 55). CH. ABS. (e)

Doubly-excited helium atom. H. PRIESTLEY and R. WHIDDINGTON (*Proc. Leeds Phil. Soc.*, 1935, 3, 81—84).—A second double-excitation process in He produced by electron impact has an associated energy of 62.27 volts. This and the previous val. 59.25 volts agree with calc. vals. for the energy levels of doubly-excited He. An angular distribution curve is given for $(2s2p)P$ excitation using 400-volt electrons and compared with the $3P$ distribution for electrons of the same energy. W. R. A.

Zeeman effect in diatomic molecular states having L -uncoupling. J. K. KNIPP (*Physical Rev.*, 1935, [ii], 47, 672—677).—Mathematical. The He mol. is considered. N. M. B.

Perturbed series, especially in C III, B I, and O IV. N. G. WHITEHEAD and J. E. MACK (*Physical Rev.*, 1935, [ii], 47, 677—678; cf. A., 1933, 1220).—Corrections of series limits, based on the use of certain preferential series as indicated by possible extra-configurational perturbations in at. spectral series, are obtained. N. M. B.

Provisional wave-length standards for the extreme ultra-violet. J. C. BOYCE and C. A. RIEKE (*Physical Rev.*, 1935, [ii], 47, 653—657).—Criteria are discussed, and provisional vals. are given for a no. of lines of C, N, O, and A in the range 1850—800 Å. N. M. B.

Efficiency of excitation of the nitrogen first positive bands by electron impact. S. E. WILLIAMS (*Proc. Physical Soc.*, 1935, 47, 420—423).—The upper limit of the effective target area of N_2 for excitation to the triplet levels was determined. The rate of emission of quanta in each of the visible groups of the first positive system was evaluated and was extended to the whole of the first positive system. The cross-sectional area, for excitation by electrons of about 14 volts energy, is $5 \times 10^{-2} \pm 35\%$, in terms of the area of the first Bohr orbit. N. M. B.

Effective rotation temperature of the negative glow in nitrogen. N. THOMPSON (*Proc. Physical Soc.*, 1935, 47, 413—414).—Results previously reported are extended (cf. A., 1934, 711). N. M. B.

Intensity measurements on forbidden lines in the spectra of alkali metals. E. ROSA (*Nuovo*

Cim., 1934, [ii], 11, 380—389; *Chem. Zentr.*, 1934, ii, 3904).—Data are given for the series $2p-m_p$. J. S. A.

Continuous absorption by alkalis. A. THOMA (*Z. Physik*, 1935, 94, 621—648).—Theoretical. A. B. D. C.

Isotope shift in Mg I. R. F. BACHER and R. A. SAWYER (*Physical Rev.*, 1935, [ii], 47, 587—591).—Structure has been observed for several of the Mg I lines in the visible and infra-red, and is attributed to isotope shift. Separations and interpretation are discussed, and indicate that the observed structure cannot be due to mass effect alone. N. M. B.

Absorption spectrum of CaI. R. SAMUEL and M. ZAKI-UD-DIN (*Proc. Indian Acad. Sci.*, 1935, 1, A, 723—726).—Mol. proportions of CaI_2 and Ca heated in a steel bomb for 10—12 hr. at 800—900° and cooled at 0° yield a product containing highly reactive yellowish-brown crystals, giving an indefinite spectrum not containing bands, but showing continuous end-absorption at 2300 Å. attributed to CaI. The energy of the first Ca—I linking, calc. thermochemically, is approx. 2.5 volts. N. M. B.

Band spectrum of zinc. T. S. SUBBARAYA (*Proc. Indian Acad. Sci.*, 1935, 1, A, 663—667; cf. this vol. 3).—A preliminary analysis is given and the relation with the Rayleigh Hg bands is discussed. N. M. B.

Selenium arc spectrum. Se I. J. E. RUEDY and R. C. GIBBS (*Z. Physik*, 1935, 94, 808—809).—Polemical, against Meissner *et al.* (A., 1934, 1280). A. B. D. C.

Selenium arc spectrum. K. W. MEISSNER (*Z. Physik*, 1935, 94, 810—811).—A reply to the above. A. B. D. C.

Molecular spectrum of selenium vapour. I. New system of bands in the ultra-violet. B. ROSEN and M. DÉsirANT (*Bull. Acad. roy. Belg.*, 1935, [v], 21, 436—449).—A new band system for Se vapour is discussed and is due to Se_4 mols. W. R. A.

Emission spectrum in selenium vapour. B. ROSEN and M. DÉsirANT (*Nature*, 1935, 135, 913—914).—A new system of approx. 40 weak, diffuse bands on the short-wave side of the main $1\Sigma-1\Sigma$ system appears at low temp. before the main system becomes visible. It is probably due to the excitation of the Se_2 group in a polyat. mol. of Se. L. S. T.

Influence of an electric field on the absorption spectra of rubidium and caesium. N. T. ZIE and C. S. PIAW (*J. Phys. Radium*, 1935, [vii], 6, 147—153; cf. A., 1934, 823).—The absorption spectra were

photographed in an electric field range 260—1820 volts per cm. The no. of observable lines of the principal series diminishes with increase of field, and new lines for $S-D$ and $S-S$ transitions appear. A Stark effect for the higher members of the principal series and a displacement towards short wave-lengths for forbidden lines of the combinations $S-D$ and $S-S$ were observed. N. M. B.

Hyperfine structure of the red Cd line λ 6438, and hyperfine structure of Sr, Sn, and Mg. H. WESTMEYER (Z. Physik, 1935, 94, 590—596).—Ferchmin and Romanowa's structure for the Cd line (A., 1934, 2) could not be reproduced. The nuclear moment of Sr^{87} is $3/2$, and of Sn^{117} and Sn^{119} $1/2$. A. B. D. C.

Regularity observed in the second spark spectrum of iodine. J. B. SETH (Proc. Indian Acad. Sci., 1935, 1, A, 593—604).—From a special treatment of available data a series of wave-no. pairs giving a system of equal frequency differences is developed and discussed. N. M. B.

Ultra-violet fluorescence spectra of iodine vapour. Resonance spectra. F. DUSCHINSKY, E. HIRSCHLAFF, and P. PRINGSHEIM (Physica, 1935, 2, 439—448).—The resonance lines of I_2 vapour excited by λ 1850—2600 Å. have been investigated at various temp. and pressures. The lines appearing at lower temp. belong to one band system, the lower level of which is the normal state and the upper levels states of greater nuclear separation. When excited by radiation of $\lambda > 2100$ Å. a second series appears of smaller separation. This increases in intensity with rise of temp. and equals the intensity of the first series at 800° . The results are discussed. J. W. S.

Polarisation of the fluorescence bands 2540 and 2650 Å. of mercury vapour. G. ZIELINSKI (Compt. rend., 1935, 200, 1313—1314; cf. A., 1934, 2).—Partial polarisation ($5.5 \pm 0.5\%$) in the plane of excitation is confirmed. N. M. B.

L Spectrum of mercury. (MLE.) Y. CAUCHOIS (Compt. rend., 1935, 200, 1314—1316; cf. this vol., 676).—Data and transitions for 17 weak lines are tabulated. Additional vals. for levels are given. N. M. B.

Absolute intensities in the spectrum of quartz mercury arcs and their variation with temperature changes of the surrounding air. A. J. MADDOCK (Proc. Physical Soc., 1935, 47, 424—432).—Arc watts-intensity variation curves for temp. variation of air surrounding the burner are plotted. Abs. intensities of 30 lines in the range 7000—2300 Å. are tabulated and discussed. N. M. B.

Night light and Northern lights in the long-wave spectral region. L. VEGARD and E. TØNSBERG (Z. Physik, 1935, 94, 413—433).—Measurements are given for red bands photographed at Oslo and Tromsø. Red bands of the night light correspond with the first positive group of N_2 afterglow. A. B. D. C.

Vegard-Kaplan bands in the spectrum of the night sky. J. CABANNES and J. DUFAY (Compt. rend., 1935, 200, 1504—1506).—Bands observed by

the authors correspond with N_2 bands described by Kaplan (this vol., 424). H. J. E.

Variation of relative width of stellar hydrogen lines with spectral type. P. ROSSIER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 32—34).—The width of a stellar line depends on the intensity of the continuous spectrum in its neighbourhood. Passing from a hot star to a more advanced spectral type, the relative density diminishes in the ultra-violet and increases in the visible. The effect on the relative widths of H_α , H_β , H_γ , H_δ , and is determined. A. J. M.

Variation of relative width of stellar calcium and hydrogen lines with spectral type. P. ROSSIER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 34—36).—The width of the Ca K line varies linearly with the spectral interval. A numerical criterion of spectral classification can be based on this. A. J. M.

Ratio of widths of the $\text{H}_\epsilon + \text{H}$ and K lines in stellar spectrograms. P. ROSSIER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 36—37). A. J. M.

Spectral type of some stars of type A. P. ROSSIER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 38—39).—Using the fact that the relative width of the Ca K line varies linearly with spectral interval it is shown that five stars are of a more advanced type than A_0 . A. J. M.

Continuous spectrum of certain stars of the first spectral types. D. BARBIER, D. CHALONGE, and E. VASSY (J. Phys. Radium, 1935, [vii], 6, 137—146; cf. A., 1934, 824).—Using special apparatus, the spectra are photographed and compared with the spectrum of an artificial star consisting of a distant H_2 tube giving a spectrum rich in the ultra-violet and of known energy distribution. Data for 18 stars and their bearing on the constitution of the stellar atm. are given. N. M. B.

Identification of neon in the spectrum of the B stars. M. NICOLET (Bull. Acad. roy. Belg., 1935, [v], 21, 459—466).—A no. of Ne II lines are observed in the spectra of the B stars, 10 *Lacertae*, γ *Cassiopeia*, τ *Scorpii*, β *Cetus Majoris*, and β *Cephei*. W. R. A.

Difference bands in the spectra of the major planets. A. ADEL and V. M. SLIPHER (Physical Rev., 1935, [ii], 47, 651—653).—Absorption bands found in the spectra of Jupiter, Saturn, Uranus, and Neptune, due to gaseous CH_4 , lie at 816, 802, 683, 673, and 584 N. M. B.

Measurements of small light intensities with a counter. I. K. H. KREUCHEN (Z. Physik, 1935, 94, 549—566).—Calibration curves are given for the spectral region 400 to 248 $\text{m}\mu$ using the emitters Al, Zn, Cd, Fe, Cu, and brass. The region from 248 to 185 $\text{m}\mu$ was also considered. Modification of readily oxidised metals with active H_2 increases their sensitivity in the short-wave region. A. B. D. C.

Electrodeless discharges in gases. O. STUHLMAN, jun. (J. Elisha Mitchell Sci. Soc., 1934, 50, 61).—Data for the dependence of the intensity of H_α and on discharge conditions are recorded.

CH. ABS. (e)

Gas discharges in the cloud chamber. H. RAETHER (Z. Physik, 1935, **94**, 567—573).—Discharges from wires and points in H_2 , N_2 , air, and CO_2 were photographed in Wilson's cloud chamber.

A. B. D. C.

Stark splitting of the 6S level of the manganous ion in crystalline fields. K. S. KRISHNAN and S. BANERJEE (Nature, 1935, **135**, 873). L. S. T.

Auger effect and forbidden transitions. H. R. ROBINSON (Nature, 1935, **135**, 826). L. S. T.

Absorption spectra in the ultra-soft X-ray region. V. H. SANNER (Z. Physik, 1935, **94**, 523—530).— L_{III} absorption limits are given for Al(13) and Mg(12), and the M_V limit for Se(34).

A. B. D. C.

Influence of temperature on the intensity of X-ray reflexion from silver. R. ANDRIESEN (Physica, 1935, **2**, 417—424).—For Ag the Debye X-ray reflexion factor M (intensity $\propto e^{-2M}$) varies linearly with temp. at 18—400°. At 400—600° deviations are observed which are attributed to anharmonic linking of the atoms in the crystal lattice.

J. W. S.

Dependence of photophoresis on pressure at high gas pressures. M. REISS (Physikal. Z., 1935, **36**, 410—413).—The photophoretic force of a photo-positive sample of Se was determined for pressures (p) of 1—11 atm. It decreases with increasing p . The Hettner $1/p$ law is obeyed.

A. J. M.

Thermionic properties of tantalum. A. B. CARDWELL (Physical Rev., 1935, [ii], **47**, 628—630; cf. A., 1932, 105).—The photo-electric and thermionic properties of outgassed Ta were investigated simultaneously. Heat treatment at 2200—2500° abs. produced a final stable condition. Corr. thermionic consts. were determined. The photo-electric and thermionic work functions agree, for the same surface, irrespective of thorough outgassing.

N. M. B.

Determination of heats of vaporisation of electrons and their temperature coefficients for molybdenum, tungsten, and tantalum filaments by the cooling method. F. KRÜGER and G. STABENOW (Ann. Physik, 1935, [v], **22**, 713—734).—A method is described for this determination. For Mo the heat of vaporisation (h) of electrons could only be determined over the range 2140—2055° abs., owing to the rapidity with which the element vaporises. The temp. coeff. (k) could not be determined. For Ta and W, h was found over the range 2100—2600° abs. For both, k was positive. The vals. of h extrapolated to 0° abs. agree well in all cases with those calc. from the Richardson equation, but are usually slightly smaller.

A. J. M.

Number of free electrons in a metal. H. FRÖHLICH (Proc. Camb. Phil. Soc., 1935, **31**, 277—280).—Theoretical. The connexion between the no. of free electrons in a metal and valency is discussed.

A. J. M.

Suggested polarisation of electrons. M. HATOYAMA and M. KIMURA (Nature, 1935, **135**, 913—914; cf. A., 1934, 712).—The asymmetry previously reported (A., 1933, 3) could not be confirmed with Au at voltages from 150 to 190 kv.

L. S. T.

Sudden changes in speed and direction shown by the paths of high-energy electrons. L. LEPRINCE-RINGUET (Compt. rend., 1935, **200**, 1524—1526).—Observations are recorded on Wilson-chamber tracks of electrons of 1—10×10⁶ e.v. energy.

H. J. E.

Origin of positive electrons. G. RACAH (Nuovo Cim., 1934, [ii], **11**, 477—481; Chem. Zentr., 1935, i, 11).—Mathematical.

J. S. A.

Momentum of ions leaving a region of ionisation. L. TONKS (Physical Rev., 1935, [ii], **47**, 621—622).—A correction depending on geometrical configuration is examined.

N. M. B.

Ionic hardening. T. NEUGEBAUER (Z. Physik, 1935, **94**, 665—661).—Penetration of the anion into the electron cloud of the cation is used to extend point charge calculations for ionic lattices.

A. B. D. C.

High-velocity particle streams in the vacuum arc. E. C. EASTON, F. B. LUCAS, and F. CREEDY (Elec. Engr., 1934, **53**, 1454—1460).—Relations are given between arc current, mass of metal transported, gas pressure, force between electrodes, and velocity of vapour streams for Fe, Cu, C, W, and other electrodes.

CH. ABS. (e)

Negative proton. G. GAMOW (Nature, 1935, **135**, 858—861).—Indications of the existence of negative protons are discussed.

L. S. T.

Polarisability of the hydrogen molecule ion. G. STEENSHOLT (Z. Physik, 1935, **94**, 770—772).—Theoretical.

A. B. D. C.

Collisions of electrons with nitrogen molecules. R. WHIDDINGTON and E. G. WOODROOFE (Proc. Leeds Phil. Soc., 1935, **3**, 85—87).—The energy losses of electrons in collision with N_2 are 8.95, 12.89, 13.81, and 15.91 volts. Their interpretation in relation to spectroscopic data is discussed.

W. R. A.

Revision of the at. wt. of arsenic. Ratio of arsenic trichloride to iodine. G. P. BAXTER and L. D. FRIZZELL (J. Amer. Chem. Soc., 1935, **57**, 851—855).— $AsCl_3$ was hydrolysed with Na_2HPO_4 , the approx. equiv. of I added, the solution neutralised, and excess or deficiency of I determined by titrating with dil. arsenite or I and starch. At. wt. As 74.91 (I = 126.916) (cf. A., 1933, 442, 659).

M. S. B.

At. wt. of tellurium. III. Analysis of tellurium tetrachloride. O. HONIGSCHMID and H. BAUDREXLER (Z. anorg. Chem., 1935, **223**, 91—100; cf. A., 1933, 761, 1223).—32 argentometric analyses of $TeCl_4$ gave $Te = 127.63 \pm 0.01$, referred to Ag 107.880 and Cl 35.457. This is regarded as a max. val., on account of the liability of $TeCl_4$ to dissociate.

F. L. U.

Isotopes. F. W. ASTON (Nature, 1935, **135**, 686—687).

L. S. T.

Modified Aston-type mass spectrometer and some preliminary results. D. D. TAYLOR (Physical Rev., 1935, [ii], **47**, 666—671).—Ionisation is produced by controlled electron bombardment. The electric field is radial, and the magnetic pole faces are shaped to give the necessary velocity focussing. A special filament assembly, amplifier circuit, and

device for giving a continuous indication α (magnetic field)² are used. Results on the ionisation of N_2 , CO , NH_3 , and N_2H_4 are given. N. M. B.

Band spectroscopic observations of the isotopes of zinc and cadmium. G. STENVINKEL and E. SVENSSON (Nature, 1935, 135, 955; cf. A., 1933, 108).—The existence of Cd^{106} and Cd^{118} is established by band spectrograms of the hydride despite lack of confirmatory evidence for Cd^{118} by mass spectroscopic observations (cf. A., 1934, 937). The band spectrum of Zn hydride shows the Zn isotopes in the following order of decreasing abundance: 64, 66, 68, 67, 65, 63, and 70. The disagreement between spectroscopic and mass spectroscopic observations regarding the existence of isotopes does not indicate untrustworthiness of the former. L. S. T.

Isotopic constitution and at. wts. of hafnium, thorium, rhodium, titanium, zirconium, calcium, gallium, silver, nickel, cadmium, iron, and indium. F. W. ASTON (Proc. Roy. Soc., 1935, A, 149, 396—405).—An account is given of the analyses of 13 elements, some by the use of the favourable arrangement of the anode-ray apparatus previously used for the rare earths (A., 1934, 1150), others by the ordinary discharge with improved technique. The vals. of the chemical at. wts. calc. from photometric measurements are mostly in fair agreement with the International vals. 20 new isotopes were discovered, those of Hf, Th, and Rh being detected for the first time. L. L. B.

Radioactivity of potassium. C. HURST (Nature, 1935, 135, 905).—Klempner's view (this vol., 558) that the radioactivity of K is due to $_{10}K^{40}$ is supported, but a nuclear spin of only 2 or 3 units, and not 4 or 5, is sufficient to increase the half-val. period of the isotope to a reasonable figure. L. S. T.

Investigation of weak radioactive elements in the absence of ultra-radiation. M. PAHL and R. HOSEMANN (Naturwiss., 1935, 23, 318—319).—The activity of K or of Rb, whether determined in the laboratory or at a depth of 800 m., was identical, showing that the radioactivity of weakly active elements is not due to the formation of radioactive elements by bombardment of inactive ones with ultra-radiation. The fact that the natural no. of an Al counter is $>$ that of a brass one is also shown not to be due to the effect of ultra-radiation on the metals. A. J. M.

α -Tracks in presence of strong γ -radiation. D. CAMERON (Nature, 1935, 135, 789).—Under the conditions described, it is possible to observe α -particles in the presence of strong γ -radiation by the Wilson cloud method. L. S. T.

Scattering of protons on protons. W. H. WELLS (Physical Rev., 1935, [ii], 47, 591—596).—Recoil particles from Cellophane bombarded by Po α -particles were used as a source of protons for obtaining large nos. of high-energy proton tracks in H_2 with a Wilson cloud chamber. The velocity distribution of 500 protons is given. From 33 intimate proton-proton collisions in 200,000 tracks, two were within the region of anomalous scattering of α -particles

by H_2 . The closest distance of approach was 6.1×10^{-13} cm. N. M. B.

Spontaneous emission of neutrons by radioelements. I. GUREVICH (Nature, 1935, 135, 956—957).—The neutrons spontaneously emitted by P previously bombarded by neutrons from a Rn+Be source may possess $> 4 \times 10^6$ e.v. Neutron emission is regarded as a secondary and not the primary process suggested by Curie *et al.* (A., 1934, 826). L. S. T.

Velocities of "slow" neutrons. P. B. MOON and J. R. TILLMAN (Nature, 1935, 135, 904).—The induced activity of Ag and Rh bombarded by neutrons retarded by passage through paraffin wax cooled with liquid O is $>$ that obtained with the wax at room temp. With I, the activity is less with the cooled wax, and the difference in behaviour from Ag and Rh indicates that it preferentially absorbs neutrons of velocities different from and probably $>$ those which are effective in other cases. The absorption of "slow" neutrons by a block of I is for an I detector $>$ for detectors of Ag or Rh. L. S. T.

Collisions between neutrons and diplons. C. H. COLLIE, J. H. E. GRIFFITHS, and L. SZILARD (Nature, 1935, 135, 903—904).—The artificial radioactivity produced in spherical detectors of Al, Si, and P by neutrons from a Be+Rn source slowed down by passage through 98.4% D_2O has been compared with that produced after retardation by H_2O . The results indicate that neutrons undergo a greater decrease in velocity on collision with protons than with diplons. L. S. T.

Slowing down of neutrons by protons. J. C. MCLENNAN, E. F. BURTON, and A. PITT (Nature, 1935, 135, 903).—Measurements of the activity produced in a Ag cylinder surrounding a neutron source when both were surrounded by air, H_2O at room temp., and by liquid H indicate that the induced activity is not affected by changes in temp. L. S. T.

Neutron excitation in beryllium. L. EMO (Nuovo Cim., 1934, [ii], 11, 452—460; Chem. Zentr., 1934, ii, 3901).—Neutron emission from Be is attributed to a resonance effect, and begins sharply at a definite range. J. S. A.

Concentration of artificially-produced radioelements by an electric field. F. A. PANETH and J. W. J. FAX (Nature, 1935, 135, 820).—In the bombardment of AsH_3 by slow neutrons from a Be+radio-Th source, the application of an alternating electric field resulted in the collection on the wire electrode of up to 30% of the total activity produced by the neutrons, together with only approx. 0.02% of the total inactive As. The method should be of use whenever thin layers of new radio-elements are required. L. S. T.

Disintegration of nitrogen and boron and possible emission of deuterons. E. POLLARD and W. W. EATON (Physical Rev., 1935, [ii], 47, 597—605).—The detection of nuclear particles by a proportional counter and the investigation of N_2 and B disintegration by α -particles are described. N_2 gave no group ascribable to deuterons; B gave a short-

range group of the expected energy. Particles from both elements were shown to be protons.

N. M. B.

Two new Curie-Joliot processes. H. FAHLENBRACH (Naturwiss., 1935, 23, 288).—Powdered Si, exposed for 18 days to α -rays from Th-B and Th-C, gives a product of half-life 17–18 days. The process is probably $^{14}\text{Si}^{29} + {}^4_2\alpha \longrightarrow {}^{15}\text{P}^{32} + {}^1_1\text{H}^1$; $^{15}\text{P}^{32} \longrightarrow {}^{16}\text{S}^{32} + e^-$. The half-life and absorption coeff. of P^{32} obtained by Fermi by the process $^{16}\text{S}^{32} + {}^0_{-1}\text{n}^1 \longrightarrow {}^{15}\text{P}^{32} + {}^1_1\text{H}^1$ agree with those obtained by the new process. Mg was bombarded with α -rays of range 7.7 cm. in air (from Th-C') for 40 min. Two active products were obtained, one with half-life 2.1 ± 0.2 min., due to Al^{28} : $^{12}\text{Mg}^{25} + {}^4_2\alpha \longrightarrow {}^{13}\text{Al}^{28} + {}^1_1\text{H}^1$; $^{13}\text{Al}^{28} \longrightarrow {}^{14}\text{Si}^{28} + e^-$; another of 7–8 min. Only the first was obtained when shorter-range α -rays from Po were used. The second may be Al^{29} or Si^{27} formed by the processes: $^{12}\text{Mg}^{24} + {}^4_2\alpha \longrightarrow {}^{14}\text{Si}^{27} + {}^0_{-1}\text{n}^1$; $^{14}\text{Si}^{27} \longrightarrow {}^{13}\text{Al}^{27} + e^+$, and $^{12}\text{Mg}^{26} + {}^4_2\alpha \longrightarrow {}^{13}\text{Al}^{29} + {}^1_1\text{H}^1$; $^{13}\text{Al}^{29} \longrightarrow {}^{14}\text{Si}^{29} + e^-$, respectively. The excitation curve gives resonance levels at 4.15 and 4.90 cm. range of α -rays. These are identical with the vals. obtained by Duncanson and Miller (A., 1934, 1284), and ascribed by them to Mg^{25} . A. J. M.

Induced radioactivity. C. D. ELLIS (Nature, 1935, 135, 688–689). L. S. T.

Induced radioactivity. S. C. BISWAS (Current Sci., 1935, 3, 475–477).—Direct attachment of neutrons to Na, Al, and P atoms seems improbable, although this process does appear to be intermediate in the transmutations of heavier elements.

W. R. A.

Atomic physics. (LORD) RUTHERFORD (Nature, 1935, 135, 683–685).—An outline of the discoveries of the last 25 years. L. S. T.

Artificial radioactivity. H. FAHLENBRACH (Z. Physik, 1935, 94, 607–620).—Experiments are described of radioactivity induced in B, Al, and N with Th-B+C and Po. The following half-life periods were obtained: N^{13} 10.73 min., P^{30} 2.89 min., and F^{17} 1.1 to 1.2 min. A. B. D. C.

Production of positrons in different elements. S. DE BENEDETTI (Compt. rend., 1935, 200, 1389–1391).—The no. of positron+electron pairs produced by bombardment of Mg, Al, S, Cu, Zn, Sn, and Pb with Ra-Th γ -rays \propto the square of the at. no., but the no. emitted from C is $>$ this. J. W. S.

Sign and energy of electrons emitted by elements activated by neutrons. E. AMALDI and E. SEGRÉ (Nuovo Cim., 1934, [ii], 11, 452–460; Chem. Zentr., 1934, ii, 3901).—Negative electrons accompanied by γ -rays were detected by a Wilson chamber method. Energy data are given. J. S. A.

Induced β -radioactivity by β -particle bombardment. H. J. WALKER (Nature, 1935, 135, 905–906).—The emission of neutrons and the subsequent positron radioactivity which occur when Li is bombarded by α -particles suggest that proton emission from Li should also be detectable. Delayed emission of “negative” electrons should be observed when Li and B are bombarded by α -particles of suitable

energy. The production of β -radioactive isotopes by proton emission from ^{17}O , ^{21}Ne , etc. is also possible.

L. S. T.

Fermi proton effect in silver. S. KIKUCHI, S. NAKAGAWA, and H. AOKI (Nature, 1935, 135, 905).—The decay curve of Ag activated by neutrons retarded by passage through paraffin wax cannot be expressed as a single exponential curve. L. S. T.

Radioactivity produced by neutron bombardment. E. FERMI (Nuovo Cim., 1934, [ii], 11, 429–441; Chem. Zentr., 1934, ii, 3901).—A summary. The emission of negative electrons only has been observed. J. S. A.

Artificial radioactivity through neutron bombardment. V. E. AMALDI, O. D'AGOSTINO, E. FERMI, F. RASETTI, and E. SEGRE (Ric. Sci. Progr. tecn., 1934, 2, No. 5, 21–22; Chem. Zentr., 1934, ii, 3901).—Detailed results are given for Na, V, Cr, Mn, As, Rb, Rh, Cd, Ir, Au, Th, and U, with chemical evidence for the formation of elements of at. no. $>$ 92 in the case of U. J. S. A.

Investigation of atomic disintegration by means of a double ionisation chamber. B. ZIPPRICH (Naturwiss., 1935, 23, 319–320).—The use of two ionisation chambers, one behind the other, gives greater constancy of experimental conditions, and enables the range and relative no. of particles formed in at. disintegrations to be more accurately determined. A. J. M.

Energy released in certain nuclear transformations. M. L. E. OLIPHANT, A. R. KEMPTON, and (LORD) RUTHERFORD (Proc. Roy. Soc., 1935, A, 149, 406–416).—The accurate determination of the ranges and energies of the swift particles emitted in certain transformations yields data which afford strong evidence of the validity of the laws of conservation of mass-energy, and of momentum, in some at. transmutations in which H^1 , H^2 , H^3 , He^4 , Li^6 , Li^7 , and the neutron are involved. The masses found for Li^6 and Li^7 (6.0143 ± 0.0002 and 7.0148 ± 0.0002 , respectively) are in good agreement with the mass spectroscopic vals. found by Bainbridge. Application of the laws of conservation of momentum and energy gives the mass of H^3 3.0152 ± 0.0002 . L. L. B.

Coincidence counter studies of the variation of intensities of cosmic-ray showers and vertical rays with barometric pressure. E. C. STEVENSON and T. H. JOHNSON (Physical Rev., 1935, [ii], 47, 578–580).—Coeffs. of decrease of intensity with rise of pressure were found. Showers are more sensitive than total cosmic radiation to pressure changes.

N. M. B.

Nature of cosmic radiation. W. F. G. SWANN (Physical Rev., 1935, [ii], 47, 575–577).—If the distribution of energy of the rays entering the atm. is adjusted so as to give an exponential law, the quality of the radiation is independent of altitude, and all phenomena produced by the radiation should increase with altitude \propto the intensity alone. N. M. B.

Cosmic rays. A. H. COMPTON (Nature, 1935, 135, 695–698).—The nature, origin, production, and action of cosmic rays on matter are discussed.

L. S. T.

Secondary effects of cosmic radiation below a water screen. B. ROSSI and S. DE BENEDETTI (*Ric. sci. Progr. tecn.*, 1934, 2, No. 5, 93—94; *Chem. Zentr.*, 1935, i, 15). J. S. A.

New component of cosmic radiation. B. ROSSI and S. DE BENEDETTI (*Ric. sci. Progr. tecn.*, 1934, 2, No. 5, 95, 119—122; *Chem. Zentr.*, 1935, i, 15).—The production of "showers" increases more rapidly with altitude than does the total intensity of the primary radiation, and is attributed to a new component of this latter. J. S. A.

Absorption of cosmic particles in elements of various atomic numbers. G. ALOCCO (*Ric. sci. Progr. tecn.*, 1934, 2, No. 5, 91—93; *Chem. Zentr.*, 1935, i, 194).—No difference was observed in absorption by Cu and by Pb under comparable conditions. H. J. E.

Secondary phenomena of penetrating radiation in lead. I, II. A. DRIGO (*Ric. sci. Progr. tecn.*, 1934, 2, No. 5, 88—89, 89—91; *Chem. Zentr.*, 1935, i, 15, 16).—Results support the views of Rossi *et al.* (cf. preceding abstracts). J. S. A.

Binding energy of atomic nuclei and the system of isotopes. L. SHTRUM (*Physikal. Z. Sovietunion*, 1934, 6, 29—52; cf. A., 1934, 1152).—Analysis of the curve giving the external mass defect shows that the at. nuclei contain only neutrons and protons, but no α -particles. Regularities in nuclear structure are pointed out and new isotopes are predicted. CH. ABS. (e)

Nuclear potential barriers. E. POLLARD (*Physical Rev.*, 1935, [ii], 47, 611—620).—The corr. heights of nuclear potential barriers are derived from experimental data. Barriers differ markedly for different incident particles. The heights of barriers to α -particles increase with at. no., and the nuclear radius at the top \propto (at. wt.)^{1/3}. It is suggested that the anomalies in proton barriers are due to a first-order force effective outside their tops, and that the attraction operative in α -particle collisions is a second-order force. Energies of resonance levels increase approx. linearly with at. no. N. M. B.

Energy of disintegration and a possible structure of the radioactive nuclei. G. J. SIZOO (*Physica*, 1935, 2, 472—482).—When the vals. of the energies of α -ray disintegration or the vals. of the upper limits of the continuous β -ray spectra are plotted against $M - 1.5Z$ (M = mol. wt., Z = at. no.), separate parallel curves are obtained for atoms of odd and even Z , respectively. It is supposed that elements of even Z contain $Z/2$ α -particles and $M - 2Z$ neutrons, whilst odd elements have $(Z - 1)/2$ α -particles, $M - 2Z + 1$ neutrons and 1 proton. J. W. S.

Fundamental paradox of the quantum theory. G. TEMPLE (*Nature*, 1935, 135, 957).—It is deduced that any two operators which represent physical variables must commute. This would make Planck's const. zero. L. S. T.

Non-adiabatic character of variations of nuclear charge. L. GOLDSTEIN (*Compt. rend.*, 1935, 200, 1294—1296).—The effect of the electrons

surrounding the nucleus on processes involving gain or loss of charges by the nucleus is examined.

N. M. B.

Deviations of atomic nuclei from spherical symmetry. H. SCHÜLER and T. SCHMIDT (*Z. Physik*, 1935, 94, 457—468).—The mechanical moments of Eu^{151} , 153 are 5/2, and the ratio of the magnetic moments 151/153 is 2.2. Spherical symmetry of nuclei of Eu, Lu, In, Sb, and Hg are discussed. A. B. D. C.

Eigenfunctions for electrons of heavy elements. L. PINCHERLE (*Nuovo Cim.*, 1934, [ii], 11, 372—379; *Chem. Zentr.*, 1934, ii, 3901).—Mathematical. J. S. A.

Determination of the elementary electric charge. E. SCHOPPER (*Z. Physik*, 1935, 94, 649).—Earlier work by Schopper (cf. this vol., 279) is corr. A. B. D. C.

Electron waves. M. STECK (*Z. Physik*, 1935, 94, 489—495).—De Broglie waves are shown to be high-frequency electromagnetic waves, similar to γ -rays. A. B. D. C.

Van der Waals interaction of hydrogen atoms. L. PAULING and J. Y. BEACH (*Physical Rev.*, 1935, [ii], 47, 686—692).—Mathematical. Interaction at large internuclear distances is discussed by the use of a linear variation function giving a solution to any desired degree of accuracy. N. M. B.

Normal helium atom. J. H. BARTLETT, jun., J. J. GIBBONS, jun., and C. G. DUNN (*Physical Rev.*, 1935, [ii], 47, 679—680).—Mathematical. A least-squares criterion for the merit of approx. wave functions is proposed. N. M. B.

Atomic wave functions for some excited states of helium. W. S. WILSON and R. B. LINDSAY (*Physical Rev.*, 1935, [ii], 47, 681—686).—Mathematical. N. M. B.

Nuclear shells: angular and magnetic momenta of nuclei. P. G. KRUGER (*Physical Rev.*, 1935, [ii], 47, 605—610).—An isotopic system, with proton and neutron shells, for the first 30 elements is examined. N. M. B.

Energy and angular momentum in certain optical problems. R. D'E. ATKINSON (*Physical Rev.*, 1935, [ii], 47, 623—627). N. M. B.

Magnetic moment of the K^{39} nucleus. J. J. GIBBONS, jun., and J. H. BARTLETT, jun. (*Physical Rev.*, 1935, [ii], 47, 692—694).—Mathematical. The calc. val. based on a Hartree wave function is 1.2 nuclear magnetons, compared with 0.38 based on a modified Goudsmit formula. N. M. B.

Ionisation area of He, and Bethe's theory. D. L. WEBSTER, W. W. HANSEN, and F. B. DUVEINECK (*Physical Rev.*, 1935, [ii], 47, 699; cf. A., 1933, 760).—A correction. N. M. B.

Ratio 136/137 in atomic physics. W. N. BOND (*Nature*, 1935, 135, 825).—Vals. of e and e/m are discussed. The most trustworthy val. for e is $(4.7759 \pm 0.0004_3) \times 10^{-10}$ e.s.u. L. S. T.

Mass of the neutrino. W. J. HENDERSON (*Proc. Camb. Phil. Soc.*, 1935, 31, 285—290).—Examination of the shape of the upper portion of the continuous

β -ray spectra curves of Th-C and Th-C'' gives the distribution of energy. Assuming, with Fermi (A., 1934, 579), that the shape of the curve is dependent on the mass of the neutrino, it is shown that this is zero, or at most $\frac{1}{2}$ a very small fraction of the electronic mass. A. J. M.

Equilibrium of black-body radiation. W. HEITLER (Proc. Camb. Phil. Soc., 1935, 31, 242—243).—Theoretical. The no. of electron pairs present in thermodynamic equilibrium and formed from two light quanta of total energy $\leq 2mc^2$ is calc. For temp. $< 10^7$, the density of electrons is zero, but it then increases rapidly to approx. 10^{30} pairs per c.c. at 5×10^9 . A. J. M.

Precision light absorption measurements with prism mirror spectrometers and thermoelements. H. GUDE (Z. Physik, 1935, 94, 816).—A reply to Leiss (this vol., 56). A. B. D. C.

Absorption of light by gaseous chlorine in the region 5040—5320 Å. F. W. JONES and W. SPOONER (Trans. Faraday Soc., 1935, 31, 811—813).—Measurable continuous absorption occurs between λ 5040 and 5320 Å. F. L. U.

Absorption spectrum of liquid hydrogen chloride in the far ultra-violet. R. TRÉHIN and B. VODAR (Compt. rend., 1935, 200, 1663—1665).—Absorption coeff. data for HCl at -90° are recorded for λ 2816—2200 Å., and compared with vals. for aq. HCl. In this there appear to be 2 absorbing mol. species (cf. Tréhin, A., 1933, 111, 1226). H. J. E.

Emission spectrum of the molecule CSe. B. ROSEN and M. DÉsirANT (Compt. rend., 1935, 200, 1659—1661).—Data are recorded for bands observed in a discharge tube containing Se, S, and C, and attributed to CSe ($^1\Pi \rightarrow ^1\Sigma$ transition). H. J. E.

Isotopic shifts in the spectra of diatomic molecules. G. H. DIEKE (Physical Rev., 1935, [ii], 47, 661—665).—Mathematical. Corrections for the dependence of the energy of diat. mols. on the mass of the nuclei are examined. N. M. B.

Isotope effect with bismuth hydride (BiH/BiD). A. HEIMER (Naturwiss., 1935, 23, 287; cf. A., 1931, 664; 1932, 440).—The nuclear vibration consts. of BiH and BiD and the mass ratio of H to D are calc. from a study of the band spectrum. A. J. M.

Blue glow on surfaces at -180° attributed to NH or NH₃ molecules. R. W. LUNT and J. E. MILLS (Trans. Faraday Soc., 1935, 31, 786—791).—Neither at. H nor active N is concerned in the production of the blue glow observed when gases from an a.c. discharge in NH₃ or a mixture of N₂ and H₂ at 1 mm. pressure are led over a surface cooled to -180° . The emission probably arises from two excited NH₂ mols. from the decomp. of N₂H₄ formed in a reaction between two $^1\Delta$ NH mols. and a H₂ mol. in the ground state. F. L. U.

Schuster bands of ammonia. R. W. LUNT, J. E. MILLS, and E. C. W. SMITH (Trans. Faraday Soc., 1935, 31, 792—797).—The Schuster bands can be excited with great intensity in highly purified NH₃ and do not therefore depend on the presence

of O₂ or H₂O. The production of N₂H₄ in discharges is discussed. F. L. U.

Predissociation in the third positive group of carbon monoxide. F. BRONS (Nature, 1935, 135, 873). L. S. T.

Band spectrum of beryllium monoxide. A. HARVEY and H. BELL (Proc. Physical Soc., 1935, 47, 415—419).—A vibrational analysis, interpretation, and expression for certain band heads previously unaccounted for in the ultra-violet are given. N. M. B.

Band spectrum of vanadium oxide. P. C. MAHANTI (Proc. Physical Soc., 1935, 47, 433—445).—Vibrational and rotational analyses and consts. are obtained. N. M. B.

Absorption spectra of alkali dichromates. R. TITEICA (Compt. rend., 1935, 200, 1527—1528).—Absorption max. for aq. Li, Na, K, and NH₄ dichromates occur at λ 3520, 3535, 3575, and 3670 Å., respectively. The bands show structure, with a characteristic frequency of approx. 800 cm.⁻¹, attributed to CrO vibration. H. J. E.

Absorption spectrum of benzene at high temperature. V. HENRI and C. H. CARTWRIGHT (Compt. rend., 1935, 200, 1532—1535).—With rise in temp. from 20° to 460° fine structure disappears progressively in the 4 ultra-violet absorption bands of high frequency, and there is a large increase in general absorption. The phenomena are reversed on lowering the temp. The interpretation is discussed; it is suggested that predissociation produces 2 mols. of C₃H₃ which would not be completely separated. H. J. E.

Ultra-violet absorption spectra of some arylsulphonium salts. M. CHAIX (Compt. rend., 1935, 200, 1537—1538; cf. A., 1933, 1227).—Vals. of the extinction coeff. for SPh₃NO₃ are recorded. Changes occurring on replacing Ph by other groups are reviewed. H. J. E.

Far-ultra-violet absorption spectra of formaldehyde and alkyl derivatives of H₂O and H₂S. W. C. PRICE (J. Chem. Physics, 1935, 3, 256—259).—Absorption spectra of CH₂O and of compounds of the type HOH, ROH, ROR, HSH, RSH, and RSR have been observed in the region 2300—1000 Å. A heat of dissociation of 164 kg.-cal. has been deduced for the C:O linking and an ionisation potential of 10.83 ± 0.01 volt. The influence of dipole moments on ultra-violet absorption spectra and ionisation potentials is discussed. For alcohols and ethers the first ionisation potentials of approx. 10.8 and 10 volts, respectively, are predicted, and for mercaptans and sulphides 9 and 8.5. M. S. B.

Ultra-violet absorption spectra of α - and β -phenylglucosides. D. LEWIS (J. Amer. Chem. Soc., 1935, 57, 898—899).—These spectra are identical. R. S. C.

Ultra-violet absorption spectrum of pepsin. G. L. LAVIN and J. N. NORTHROP (J. Amer. Chem. Soc., 1935, 57, 874—875).—Pepsin has a no. of narrow absorption bands in the region 2500—3000 Å. The band at 2900 Å. is attributed to tryptophan, at

2850 Å. to tyrosine, and bands at 2500—2700 Å. to phenylalanine. M. S. B.

Spectral behaviour of methæmoglobin. R. M. MAYER (Naturwiss., 1935, 23, 288).—An addition to a previous note (this vol., 563). A. J. M.

Composition of Prussian and Turnbull's blues. III. A. K. BHATTACHARYA (J. Indian Chem. Soc., 1935, 12, 143—151).—The absorption spectra of Prussian- (I) and Turnbull's (II) blues have been investigated between λ 2316 and 7228 Å. The absorption curves of (I) and (II) are similar, and the differences diminish as the age of the solutions increases. The results are discussed with reference to the constitutions of (I) and (II). J. G. A. G.

Absorption of sunlight by the earth's atmosphere in the remote infra-red. A. ADEL, V. M. SLIPHER, and E. F. BARKER (Physical Rev., 1935, [ii], 47, 580—584).—Spectroheliometric observations were made for the range 5—21 μ . The long-wave limit of transmission is at 13.5 μ . N. M. B.

Extreme infra-red investigation of hindered rotation in water. C. H. CARTWRIGHT (Nature, 1935, 135, 872).—Measurements of the % transmission and reflexion of H₂O between 52 and 313 μ show that the mols. in H₂O are bound in a quasi-cryst. lattice, and, in agreement with Debye's hypothesis, execute only partial rotation. L. S. T.

Pure rotation spectra of NH₃ and ND₃. R. B. BARNES (Physical Rev., 1935, [ii], 47, 658—661).—Measurements and curves for the range 40—170 μ are given. 10 lines of NH₃ and 13 lines of ND₃ were measured, and expressions for ν are deduced. N. M. B.

Intensities of the vibration-rotation bands of HCl. E. C. KEMBLE (J. Chem. Physics, 1935, 3, 316—317).—A discussion of the disagreement between Bourgin's (A., 1927, 710; 1928, 1076) and Dunham's (A., 1929, 1126) results, and Bartolome's (cf. Mulliken, A., 1934, 942, 1189). M. S. B.

Infra-red spectrum and molecular constants of hydrogen iodide. A. H. NIELSEN and H. H. NIELSEN (Physical Rev., 1935, [ii], 47, 585—586).—The fundamental and first overtone bands of HI were measured under high resolution, and an expression is found for the lines in the positive and negative branches in both bands. The consts. (cf. Colby, A., 1929, 974) are: ν_0 , 2309.58 cm.⁻¹; I_0 , 4.221×10^{-40} g.-cm.²; B , 0.822×10^{-5} ; C , 6.058. N. M. B.

Infra-red absorption spectrum of crystalline sodium nitrite. C. R. BAILEY and J. W. THOMPSON (Nature, 1935, 135, 913).—There appears to be a single linking between the N and each O, and the binding in the NO₂ group is of the same type as in SO₂, corresponding with a vertical angle of approx. 120°. L. S. T.

Atomic vibrations of Y molecules. I. Infra-red spectrum of acetone. C. CORIN (J. Chim. phys., 1935, 32, 241—268).—19 bands have been observed between 2.5 and 0.85 μ , which consist of simple harmonics of the ten fundamental frequencies or their combinations. Agreement with the Raman spectra is found. R. S.

Method of determining the heat of dissociation from a study of the long wave-length limit of the continuous absorption by gas molecules. A. K. DUTTA (Current Sci., 1935, 3, 477—478).—Polemical against Datta *et al.* (this vol., 570).

W. R. A.
Deformation frequencies of heavy acetylenes. Y. MORINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 39—45; cf. this vol., 146).—From the deformation frequencies and force consts. of C₂H₂, the frequencies for C₂HD and C₂D₂ are calc. The cross terms for linking frequencies are discussed. N. M. B.

Influence of temperature on the Raman lines of crystals. L. S. ORNSTEIN and J. J. WENT (Physica, 1935, 2, 503—512).—The intensities of the Raman Stokes and anti-Stokes lines of quartz at various temp. are in accord with theory, but anomalies are encountered with calcite. The intensity of Stokes lines diminishes with rise of temp. The frequency of the Raman lines also diminishes with rise of temp., the effect being greatest at low frequency. The change is correlated to the expansion of the crystal. Explanations are suggested for the broadening of Raman lines with rise of temp. J. W. S.

Raman spectrum of trideuteracetic deuteracid. W. R. ANGUS, A. H. LECKIE, and C. L. WILSON (Nature, 1935, 135, 913).—Known displacements for AcOH are compared with those measured for CD₃CO₂D. The origins of these displacements are tentatively assigned to the C-H, O-H, C-C, or C-O linkings and to the Me or CO₂H groups. L. S. T.

Raman spectra of some deuterium compounds. B. TRUMPY (Nature, 1935, 135, 764).—Raman frequencies of C₂D₂Cl₄ and *cis*- and *trans*-C₂D₂Cl₂ are compared with those of the corresponding H compounds. The isotope effect is clearly determinative in many cases, and indicates the participation of the hydrogens in the different oscillations. An approx. estimate of bond strength gives a val. for D > that of H in these compounds. L. S. T.

Raman spectrum of deuterobenzene. A. KLIT and A. LANGSETH (Nature, 1935, 135, 956).—Data for the Raman spectra of PhD, C₆D₅H, and C₆D₆ are given. All the Raman frequencies of C₆H₆ are lowered by the introduction of D in the mol. Greater isotopic shift is shown between C₆H₆ and PhD than between C₆D₅H and C₆D₆. The Friedel-Crafts reaction C₆H₆ + 6DCl \rightleftharpoons C₆D₆ + 6HCl has been used for the prep. of C₆D₆. L. S. T.

Results of new examinations on the structure of organic molecules. G. VESZI (Techn. Kurir, 1934, 5, No. 9, 1—2).—Raman spectra indicate a Kekule formula for C₆H₆ with trigonal, rather than hexagonal, symmetry. CH. ABS. (r)

Raman effect and constitution of hydrogen peroxide. A. SIMON and F. FEHER (Z. Elektrochem., 1935, 41, 290—293).—The Raman effect has been investigated in 3—99.5% aq. H₂O₂. The H₂O band is observed, even in the most conc. solutions, indicating the linking H \cdot O. A line at 877 cm.⁻¹ corresponds with the O-O vibration. A band at 1421, with two

max. 27 cm^{-1} apart, not previously observed by Venkateswaran (A., 1933, 337), is probably due to a deformation vibration corresponding with the valency angle between H \cdot O and O \cdot O. It practically disappears below 30% H_2O_2 . Another band, at 3410 cm^{-1} , widens with dilution and splits into two max. in 50% H_2O_2 . The line 877, still visible in the 3% solution, disappears on addition of NaOH (0.1—1 equiv.) and the H_2O band only is left. Apparently there is not only dissociation into H \cdot and HO $_2\cdot$, but also a loosening of the O \cdot O linking. In 10% H_2O_2 the 877 line is still faintly visible on addition of NaOH (approx. 1 equiv. to $2\text{H}_2\text{O}_2$), but is strong again on acidifying. M. S. B.

Raman spectrum of tribromosilane. J. M. DELFOSSE and R. GOOVAERTS (Bull. Acad. roy. Belg., 1935, [v], 21, 410—414).— SiHBr_3 gives Raman displacements of 115, 166, 362, 470, 770, 999, and 2236 cm^{-1} ; their assignment is discussed. W. R. A.

Raman spectrum of sulphuric acid. R. M. BELL and M. A. JEFFERSEN (J. Chem. Physics, 1935, 3, 245—247).—8 lines have been found in the Raman spectrum of H_2SO_4 . These vary gradually in frequency, width, and intensity as the concn. varies from 5 to 100%. The results indicate a large concn. of SO_4^{--} at 5—35% and the presence of HSO_4^- up to nearly 100%, but in largest amount in 5—45%. Two of the lines are attributed to SO_2 . The H_2O band first appears at 80% and broadens and increases in intensity with dilution. No lines corresponding with the S \cdot H and O \cdot H linkings were observed. M. S. B.

Raman effect in sulphuric acid-nitric acid mixtures. J. CHÉDIN (Compt. rend., 1935, 200, 1397—1398; cf. this vol., 281).—The Raman frequency of 1400 cm^{-1} of these mixtures is obtained feebly in 99.6% HNO_3 free from H_2SO_4 , and is attributed to N_2O_5 . This is supported by the intensity of this line in solutions of N_2O_5 or P_2O_5 in HNO_3 . In H_2SO_4 - HNO_3 - H_2O mixtures the max. $[\text{H}_2\text{O}]$ for the persistence of this line is the greater the greater is the $[\text{H}_2\text{SO}_4]$. A mixture of 85—90% H_2SO_4 and 10% HNO_3 , after boiling and cooling, shows a Raman line at 2320 cm^{-1} , probably due to $(\text{NO})_2\text{SO}_4$. J. W. S.

Raman spectra of some molecules of the pentatomic type. D. H. RANK and E. R. BORDNER (J. Chem. Physics, 1935, 3, 248—251).—Raman spectra have been determined for nine org. compounds which may be regarded as of the pentat. type if Me is taken as a unit. The spectrum of $\text{CMe}_3\cdot\text{CH}_3\text{D}$ (I) (Whitmore *et al.*, A., 1934, 507), compared with that of CMe_4 , exhibits the various types of isotope effects to be expected for a polyat. mol. The vibrations of (I) are also less degenerate than those of CMe_4 because of the partial destruction of dynamic symmetry. SiMe_4 has a fairly intense line at 863 cm^{-1} which does not fit into the scheme of vibrations for a pentat. mol. Fermi's explanation of similar behaviour in CCl_4 (A., 1931, 1111) probably holds here also. Other Me_4 derivatives show practically complete removal of vibrational degeneracy. M. S. B.

Chemical reactivity and Raman spectra in the eugenol and vanillin group. E. BRINER, B. SUSZ,

and E. PERROTET (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 27—30).—Raman frequencies for eugenol, methyl- and *iso*-eugenol, and vanillin are recorded.

A. J. M.

Raman spectrum of $\Delta^{1:3}$ -cyclohexadiene. G. B. BONINO and R. M. ANSIDEI (Nature, 1935, 135, 873—874).—A comparison of the Raman spectra of $\Delta^{1:3}$ -cyclohexadiene (I) prepared by the Harries-Willstätter and the Crossley methods shows that when prepared by the latter method (I) contains C_6H_6 and cyclohexeno. L. S. T.

Raman effect of oxalic acid in different phases. C. S. S. RAO (Z. Physik, 1935, 94, 536—543).—The cryst. form gives displacements at 473, 851, 1506, 1640, and 1758 cm^{-1} , and in solution 248 (?), 480, 673 (?), 845, 1430, 1656, and 1744 cm^{-1} . The 1430 cm^{-1} displacement is ascribed to the OH. Simultaneous presence of the lines 1650 and 1750 cm^{-1} , ascribed to the $>\text{C}:\text{O}$ linking, indicates that the CO_2H are not identical. Measurements are also given for solutions in EtOH and fatty acids.

A. B. D. C.

Raman spectra of isomeric citronellols and rhodinols.—See this vol., 865.

Fine structure of Rayleigh radiation. II. L. S. ORNSTEIN and P. H. VAN CITTERT (Physica, 1935, 2, 499—502; cf. this vol., 565).—Theoretical. Small deviations from the regular lattice structure lead to general scattering of light with unchanged λ . A strong central component of the spectrum of scattered light should be observed especially with liquids. J. W. S.

Convection currents in an unstable layer of fluid studied by optical methods. K. R. RAMANATHAN and V. N. KELKAR (Current Sci., 1935, 3, 473—475).—Horizontal layers of Et_2O and of CCl_4 on Hg when illuminated by a divergent beam of light reflect patterns which vary with the thickness of the layer.

W. R. A.

Variations in interference colours on copper and steel. F. H. CONSTABLE, M. NAZIF, and H. ELDIN (Nature, 1935, 135, 791).—The colour changes of burnished surfaces of Cu and steel observed at different angles are $>$ expected from the vals. of μ . The colour effects due to scratches on strips of metal cleaned with fine emery paper are described.

L. S. T.

Internal recombination during photo-dissociation of polyatomic molecules. A. N. TERENCE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 482—487).—On irradiation of SnI_4 vapour at 10^{-1} — 10^{-2} mm. pressure with $\lambda\lambda$ 2500—2100 Å. a fluorescence spectrum of I_2 was observed, indicating that I_2 is eliminated from SnI_4 in one act. The process has a marked temp. coeff. indicating an activation energy. The photo-dissociation of BiI_3 also shows a fluorescence, and may resemble that of SnI_4 . H. J. E.

Dependence of the fluorescence spectrum on the viscosity of the solvent. L. A. TUMERMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 471—474).—It is shown for solutions of aesculin, quinine sulphate, rhodamin-B, and Magdala-red in H_2O , EtOH, and glycerol that the fluorescence is independent of the η of the solvent. H. J. E.

Relation between absorption and luminescence spectra in weak dyestuff solutions. V. L. LEVSHIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 474—482; cf. A., 1934, 830).—Measurements are recorded of the absorption and luminescence spectra of solutions of eosin-B in H_2O , isoamyl alcohol, and $COMe_2$, and of erythrosin and rhodamine-6G in H_2O and $COMe_2$. The absorption spectrum changes little, but the intensity of the luminescence spectrum changes considerably, with the solvent, this change depending on the dyes and not on the solvent. H. J. E.

Fluorescence spectra of phaeophorbides. C. DHERÉ and (MLLE.) A. RAFFY (Compt. rend., 1935, 200, 1367—1369).—The fluorescence spectrum of phaeophorbide-*a* (I) and -*b* (II) in Et_2O consists of bands at λ 730 and 670, and 725 and 659 $m\mu$, respectively; in CS_2 the bands in the visible region are λ 679 and 633.5 $m\mu$ for (I) and (II), respectively. F. R. G.

Luminescence phenomena with benzhydrazide and benzenesulphonhydrazides. A. A. M. WITTE (Rec. trav. chim., 1935, 54, 471—475).—Benzhydrazide (I), benzenesulphonhydrazide, and their respective three $(NO_2)_1$ -derivatives and phthalhydrazide showed chemiluminescence on mild oxidation, but some doubt is cast on the purity of the (I). D. R. D.

Sugar charcoal and the fluorescence of acid liquids. III. B. L. VANZETTI (Rend. Sem. Fac. Sci. Cagliari, 1933, 3, 47—50; Chem. Zentr., 1934, ii, 3484; cf. A., 1933, 1280).—The blue fluorescent substance formed by the action of conc. H_2SO_4 on carbohydrates is ultra-filterable, is removed by animal C, and is destroyed by sunlight or by pptn. of H_2SO_4 with Ba salts. The effects of various reagents on the fluorescence are described. Its spectrum is recorded. H. J. E.

Theory of contact resistance. S. KANEKO (J. Electrochem. Assoc. Japan, 1934, 2, 394—397).—Theoretical. CH. ABS. (e)

Relationship between photo-electric conductivity, light absorption, and photographic properties. J. H. DE BOER (Chem. Weekblad, 1935, 32, 327).—The mechanism of the absorption of light by the alkali-metal and Ag halides is compared and contrasted. D. R. D.

Photo-electric effect of caesium oxide cathodes under external fields. R. FLEISCHER and P. GORLICH (Z. Physik, 1935, 94, 597—606).—The long-wave photo-electric max. is displaced towards the red by an accelerating field. A. B. D. C.

Photochemical elementary process in alkali halide crystals. R. HILSCH and R. W. POHL (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1934, [ii], 1, 115—127; Chem. Zentr., 1935, i, 360; cf. this vol., 9).—The no. of coloured centres produced in KBr per light quantum absorbed varies from 0 at low temp. to a max. of 1 at high temp. H. J. E.

Photo-electric behaviour of superposed surface layers at low temperatures. R. SUHRMANN and D. DEMPSTER (Z. Physik, 1935, 94, 742—759).—The selective photo-effect of cathodes formed of at. distributions of alkali metals separated from the metal in bulk by several mol. layers shows fatigue at low

temp. when light of max. spectral sensitivity is used; rise of temp. or illumination with red light removes fatigue. The time variation of fatigue can be quantitatively explained by the presence of active centres of long metastable life. A fall in temp. sharpens the selective max., and shifts the long-wave max. to shorter λ . K atoms separated from K by $C_{10}H_8$ and by K hydride were used as cathodes. A. B. D. C.

Relationships between chemical constitution and dielectric properties. P. DEBYE (Bull. Soc. chim. Belg., 1935, 44, 167—175).—A lecture. J. G. A. G.

Calculation of dipole moments. I. R. KRITSCHEVSKI and J. S. KASARNOVSKI (Z. physikal. Chem., 1935, B, 28, 461—477).—Combination of the thermodynamical and mol.-statistical equations for the heat effect on introducing a dielectric of dielectric const. ϵ and mol. vol. V into an electrostatic field gives $[T^2 V / (\epsilon + 2)^2] (\partial \epsilon / \partial T)_P = -4\pi N \mu^2 / 27k$, where μ is the dipole moment and N , k , and T have their usual significance. This gives good results, much better than Debye's equation, when used to calculate μ for liquids of small ϵ , but fails for polar liquids of high ϵ . It is convenient for determining μ by the dil. solution method with a dipole-free solvent for which $(\partial \epsilon / \partial T)_P \neq 0$. Hedestrand's assumption that for a dil. solution of a polar substance ϵ and d are linear functions of the molar fraction of solute (A., 1929, 647) is incorrect. Equations are derived for the extrapolation to infinite dilution of ϵ and V for a solution. R. C.

Dipole moment of hydrogen chloride and the solvent. S. MIZUSHIMA, K. SUENAGA, and K. KOZIMA (Bull. Chem. Soc. Japan, 1935, 10, 167—168).—The dipole moment (μ , in Debye units) and mol. polarisation of HCl in different media are respectively: in C_6H_{14} at 20° 1.04, 30.0; in C_6H_6 at 10°, 1.20, 38.7, at 20° 1.22, 38.5, at 25°, 1.21, 37.8; in PhMe at 20° 1.24, 39.5; in $CHCl_3$ at 30°, 1.03, 28.9; in Et_2O at 20°, 2.22, 111.3. The high μ in Et_2O is correlated with the Raman spectrum of conc. solutions, which differs from that of HCl gas. R. S. B.

Dielectric constants of air and hydrogen at high pressures. R. McNABNEY, W. MOULTON, and W. L. BEUSCHLEIN (Physical Rev., 1935, [ii], 47, 695—698).—Vals. were measured in the pressure range 71.8—334.7 atm. at 20° and 2500 kilocycles, and the Clausius-Mosotti function was calc. for each pressure. The change with pressure for air is small and irregular, averaging 1.43; for H_2 the val. decreases uniformly from 1.16 at 71.8 atm. to 0.99 at 334.7 atm. N. M. B.

Dielectric properties of heavy water. P. ABADIE and G. CHAMPETIER (Compt. rend., 1935, 200, 1590—1593).—The dielectric const. (ϵ) at 100 m. of H_2O containing 98% D_2O is 79 at 20°, relative to a val. of 81 for H_2O . The dipole moment calc. from the ϵ of solutions in dioxan is 1.87×10^{-18} compared with 1.86×10^{-18} for H_2O . The anomalous dispersion of these solutions at 17 and 28 cm. shows that the intermol. forces between dioxan and D_2O differ from those between dioxan and H_2O . J. W. S.

Dielectric polarisation of phenol. A. R. MARTIN (Nature, 1935, 135, 909).—Data obtained for the polarisation of PhOH in C_6H_6 at 70° are recorded. The behaviour of PhOH is similar to that of the lower alcohols. ∞P_2 is 71.0, giving 1.5 debyes for the dipole moment. L. S. T.

Dielectric polarisation. XII. Dipole moments and structure of thiopyrones and related compounds. F. ARNDT, G. T. O. MARTIN, and J. R. PARTINGTON. **XIII. Dipole moments of simple aliphatic nitriles.** E. G. COWLEY and J. R. PARTINGTON (J.C.S., 1935, 602—604; 604—609).—**XII.** The dipole moments (μ) of 2:6-diphenylthiopyran-4-one (I) (*cis*-form, 1.64; *trans*-form, 1.62), 2:6-diphenylthiopyrone (II) (4.39), and 2:6-diphenylthiopyrone 1-dioxide (III) (0.93) were determined. Vals. in *D* are given in parentheses. For (I), calc. and observed vals. agree. The calc. μ of (II) does not agree with the observed val., showing considerable interaction through the double linking. (III) has a much lower val. than that calc., and obviously behaves differently from (II). The val. for (II) is intermediate between those required by its two possible structures, agreeing with the theory of Arndt (A., 1931, 234) and of Sutton (A., 1934, 1156). Vals. for the heats of combustion measured by Lorenz and Sternitzke (*ibid.*, 1008) support the conclusions reached from the dipole determinations.

XIII. The vals. for μ of MeCN, EtCN, PrⁿCN, and BuⁿCN, all in C_6H_6 solution, are 3.44, 3.57, 3.57, and 3.57 *D*, respectively. These vals. are compared with those obtained for other series of compounds, e.g., the alkyl halides, where μ again remains const. after the Et compound. μ of the aromatic nitriles is discussed, and it is shown that the C-CN group is probably linear in both aliphatic and aromatic nitriles. The relative increase caused by induction in the nitriles is < that in the case of the halides.

A. J. M.

Configurations of disulphoxides of thianthren. T. W. J. TAYLOR (J.C.S., 1935, 625—626).—The configurations assigned to the geometrically isomeric disulphoxides of thianthren on the basis of their dipole moments (μ) (A., 1932, 507) and of the physical properties of the compounds (A., 1934, 781) are probably incorrect. Consideration of the folded structure of these compounds leads to the conclusion that the α -disulphoxide ($\mu=1.7$ *D*) is the *cis*-form, and the β -compound ($\mu=4.2$ *D*) is the *trans*-form.

A. J. M.

Time formation of the dielectric constant of Rochelle salt in an electric field. H. GOEDECKE (Z. Physik, 1935, 94, 574—589).—The dielectric const. of K Na tartrate builds up in three distinct stages: electron polarisation occurs within 10^{-8} sec., followed by polarisation due to ionic movement in 10^{-6} to 10^{-4} sec., and beyond 10^{-4} sec. there is orientation of dipole groups; the last is the primary source of the high dielectric const.

A. B. D. C.

Dielectric constant. V. Anomalous dispersion of lecithin in viscous mineral oils. A. L. FERGUSON, L. O. CASE, and G. H. EVANS (J. Chem. Physics, 1935, 3, 285—290).—A receiver and cell for determining dielectric const. ϵ by the resonance

method is described. In order to determine the microscopic viscosity of solutions of lecithin, measurements of ϵ were made on 5 solutions in very viscous mineral oils at 18° , 25° , and 50° with 6 different frequencies, using the refractometric, resonance, and Wheatstone bridge methods. Comparison of the experimental curves with theoretical Debye curves indicates dispersion, but not of a simple type. A qual. explanation, based on varying viscosity of the components of the solvent, the presence of polar radicals in the solute mols., and the association of the solute, is discussed. M. S. B.

Unipolar interior conductivity of certain crystals. R. DEAGLIO. Note on the above. A. COTTON (Compt. rend., 1935, 200, 1303—1306, 1306).—The vol. conductivity of carborundum, differing relatively to the two opposite directions of the polar axis, was investigated. N. M. B.

Rotatory dispersion of organic compounds. XXV. Open-chain derivatives of arabinose, fructose, and fucose. Optical cancellation in penta-acetyl μ -fructose. W. C. G. BALDWIN, M. L. WOLFROM, and T. M. LOWRY. **XXVI. Acetoin.** T. M. LOWRY and W. C. G. BALDWIN. **XXVII. Menthone and carvomenthone.** T. M. LOWRY and R. E. LISHMUND (J.C.S., 1935, 696—704, 704—708, 709—713).—**XXV.** μ -Fructose penta-acetate shows optical cancellation (cf. A., 1933, 1231). In this case the three asymmetric C atoms have the same relative configuration as those in μ -arabinose tetra-acetate, in which the phenomenon has already been observed, but are of opposite signs. Data are also given for μ -fucose tetra-acetate. Cancellation did not occur with tetra-acetyl-*l*-arabononitrile, *l*-arabinose Et mercaptal, μ -*l*-arabinose tetra-acetate Et mercaptal, or μ -*d*-fructose penta-acetate Et mercaptal, which contain three asymmetric C of similar orientation, but have no C:O attached to the first asymmetric C. It is therefore probable that the C:O is essential to the balance of the opposite partial rotations observed in optical cancellation.

XXVI. CHAcMe.OH (I) exists as an optically active liquid with $[\alpha]_{5461}^{20}$ 6.60° , increasing to 8.04° by fractionation. An optically inactive solid polymeride (II) separates slowly from it without altering $[\alpha]$ of the saturated solution. (II) is dimeric, contains no C:O, and is formulated as a derivative of cyclobutane. The absorption spectrum of the liquid in the homogeneous state and in solution in H_2O , EtOAc, and cyclohexane showed a definite ketonic band at 2750 Å. The racemisation of (I) depends on reversible polymerisation. Acetylation of (II) give a monomeric acetate which shows the ketonic band.

XXVII. The max. of circular dichroism of carvomenthone (III) is displaced by 110° from the max. of absorption in the direction of longer λ , exactly as in the case of camphor (A., 1931, 786). Menthone (IV) and (III) show anomalous rotatory dispersion. The absorption spectra of (III) and (IV) show marked points of contrast. In (III) a negative anomalous rotation with a range of about 2000° is superposed on a positive residual rotation of high frequency. In (IV), anomalous rotation of range $< 200^\circ$ is super-

posed on a composite negative residual rotation which rises steeply with decreasing λ . A. J. M.

Rotatory dispersion of α -halogeno-camphors. J. P. MATHIEU and J. PERRICHET (Compt. rend., 1935, 200, 1583—1585).—The mol. rotations of α -chloro- (I), α -bromo- (II), and α -iodo-camphor (III) have been measured at 2500—6500 Å. The vals. of $[M]_{5461}^c$ for (I) and (II) are in accord with previous data. (III), m.p. 52—54°, decomposes in bright light. For each compound the rotation increases with decreasing λ between 6500 and 3300 Å., and becomes negative at lower λ . The λ for zero rotation does not coincide with the max. of the first absorption band.

J. W. S.

Crossed axial plane dispersion in two organic compounds. A peculiar extinction phenomenon. W. M. D. BRYANT (Amer. Min., 1935, 20, 281—291).—The optic axial angles, approx. temp. coeff., and the $\lambda\lambda$ of uniaxiality of BiPh_2Cl_2 and triphenylethylpyrrolone have been determined. The extinction phenomenon described by Greenwood (A., 1932, 1080) does not depend on rotatory polarisation.

L. S. T.

Kerr effect of chloro-derivatives of methane, ethane, and ethylene. G. SACHSSE (Physikal. Z., 1935, 36, 357—367).—The polarisabilities of the various groupings in the Cl-derivatives of CH_4 , C_2H_6 , and C_2H_4 (viz., C-Cl, C-H, C-C, C=C) are determined. It is shown that these may be added tensorially to find the polarisation ellipsoid of substances containing these groupings. The work of Otterbein (A., 1934, 476) on the polarisabilities of aromatic compounds has thus been extended to aliphatic compounds.

A. J. M.

Refractive index of heavy water. W. J. C. ORR (Nature, 1935, 135, 793).— n for D_2 is < that of H_2 by $(123 \pm 2) \times 10^{-8}$ at 760 mm.

L. S. T.

Active hydrogen. G. R. SCHULTZE (J. Chem. Physics, 1935, 3, 317—318).—A discussion of the validity of the proofs for the existence of H_3 .

M. S. B.

Electronic structure of H_3^+ . C. A. COULSON (Proc. Camb. Phil. Soc., 1935, 31, 244—259).—The structure of H_3^+ is discussed using the method of mol. orbitals of Lennard-Jones, Hund, and Mulliken. Assuming the configuration of the ion to be an equilateral triangle, the val. obtained for the length of side, ρ_0 , at equilibrium, is 0.85 Å., and for the fundamental frequency, ν_0 , 3170 cm^{-1} . The vals. obtained by the perturbation and variational method are compared. All excited levels of H_3^+ are unstable. The configuration of H_3 is probably linear and not triangular.

A. J. M.

Theory of free radicals and organo-alkali compounds. E. A. HYLLERAAS (J. Chem. Physics, 1935, 3, 313—314).—The treatment of the electron affinities of free aromatic radicals by Nilsen (this vol., 283) is not clear and is unsatisfactory.

M. S. B.

Theory of aromatic free radicals. L. PAULING and G. W. WHELAND (J. Chem. Physics, 1935, 3, 315; cf. preceding abstract).

M. S. B.

Valency. R. F. HUNTER and R. SAMUEL (Chem. and Ind., 1935, 467—468; cf. this vol., 431).—A

reply. The authors offer alternative interpretations consistent with their views (A., 1934, 1058). The distinction between the physical definition of stability and chemical reactivity is emphasised. J. G. A. G.

Theory of valency: development and problems. R. SAMUEL (Current Sci., 1935, 3, 461—467).—A review.

Pair linking theory of valency. H. LESSHEIM and R. SAMUEL (Proc. Indian Acad. Sci., 1935, 1, A, 623—662; cf. this vol., 431).—Chemical union is shown to be mainly an effect of the degeneracy due to the electrons, this view leading to an electron-pair linking theory of valency. Spectroscopic evidence is given in support, and in contradiction of a relation between strength of linking and polarity. Degeneracy of the nuclear fields is reduced to an effect determining the polarity.

N. M. B.

Conception of tetrahedral atoms. R. REINICKE (Chem.-Ztg., 1935, 59, 385—388, 405—407).—The arrangement of atoms in crystal lattices accords with the view that chemical linkings are rigidly directed. Considering the atom as the centre of a tetrahedron, the corners and the centres of the faces are the active directions. The no. (≤ 4) of the tetrahedral corners or faces thus active constitutes the valency of the atom; a covalency involves junction by corners, and electrovalency junction of corners with face-centres.

D. R. D.

Constitution of the heterocyclic [ring] $\text{C}_2\text{N}_2\text{O}$. M. MILONE and G. MULLER (Gazzetta, 1935, 65, 241—249; cf. this vol., 684).—The structures of the furazan, azoxime, and oxadiazole rings are discussed from the point of view of quantum mechanics. Energies of formation, link energies, and resonance energies are calc.

O. J. W.

Statistical weights of the rotational levels of polyatomic molecules, including methane, ammonia, benzene, cyclopropane, and ethylene. E. B. WILSON, jun. (J. Chem. Physics, 1935, 3, 276—285).—Theoretical.

M. S. B.

Bond energies and valency angles in simple carbon compounds. W. G. PENNEY (Trans. Faraday Soc., 1935, 31, 734—746; cf. A., 1934, 1158).—Some fundamental C-H exchange integrals are determined and it is shown that the most stable form of the Me radical has plane configuration. The heat of the reaction $\text{H} + \text{Me} = \text{CH}_4$ is calc. to be 106 kg.-cal., in agreement with observation. Calculation of valency angles in substituted methanes indicates that if some or all of the H in CH_4 are replaced by other univalent groups, the resulting deviations from the tetrahedral angle are \pm a few degrees.

F. L. U.

Structure of nuclei of aromatic character. G. B. BONINO (Mem. R. Accad. Sci. Ist. Bologna, Cl. Sci. fis., 1933, [viii], 10, 12 pp.; Chem. Zentr., 1934, ii, 3916).—Theoretical. Modified centric formulæ are proposed.

H. N. R.

Can the ordinary attractive forces between the molecules or atoms of a substance in absence of polarity (dipoles etc.) be accounted for by electrical forces? J. J. VAN LAAR (Chem. Week-

blad, 1935, 32, 337—338).—It is argued that this view is untenable. D. R. D.

Thermochemical consideration of the carbonyl group. P. GOLDFINGER, W. LASAREFF, and M. LETORT (Compt. rend., 1935, 200, 1593—1595).—From thermochemical data it is calc. that the energy of the CO: in aldehydes, ketones, acids, and amides differs from the energy of activation to the $\alpha^3\Pi$ state by amounts which vary according to the groups present. The results are in accord with the frequencies of vibration of the CO: in these groups of compounds. J. W. S.

Calculation of free energy of polyatomic molecules from spectroscopic data. II. A. R. GORDON (J. Chem. Physics, 1935, 3, 259—265).—The methods of calculation previously used for diat. and triat. mols. have been extended to cases where one or more fundamental frequencies are degenerate. New tables are given and calculations made for N_2O , HCN, and C_2H_2 . M. S. B.

Lifetime of free hydroxyl. O. OLDENBERG (J. Chem. Physics, 1935, 3, 266—275).—The life of OH radicals (I) produced by an electric discharge through H_2O vapour and disappearing by chemical reaction after interruption of the discharge, has been investigated. The [OH] was measured by the intensity of the absorption spectrum and its variation with time could be observed. It is concluded that (I) persist up to 1/8 sec. instead of 0.001 sec. as previously supposed. The mode of consumption of (I) and the nature of the processes taking place in the discharge are discussed. M. S. B.

Surface tension of molten metals and alloys. V. Surface tension of Fe-C alloys, Hg_5Tl_2 , and $NaHg_2$, its variation with time in the case of thallium, and surface tension of slags. F. SAUERWALD, B. SCHMIDT, and F. PELKA (Z. anorg. Chem., 1935, 223, 84—90; cf. A., 1933, 1002).—The surface tension (T) of Fe-C alloys has been determined at 1300—1420°, in which range it has a positive temp. coeff., and increases with decreasing C content. Tl, when prepared and examined in a high vac., shows T which does not vary with time. Contact with H_2 causes T to increase with time. Vals. of T for Hg_5Tl_2 , $NaHg_2$, and three slags are given. F. L. U.

Absolute determination of the local strength of X-radiation from a mass-source. A. ROGOZINSKI (J. Phys. Radium, 1935, [vii], 6, 168—174).—Mathematical. N. M. B.

Back scatter for several qualities of X-rays. E. H. QUIMBY, C. D. LUCAS, and W. S. MACCOMB (Radiology, 1934, 23, 7, 43—50).—Data for back scatter from paraffin are recorded. CH. ABS. (e)

Laue symmetry exhibited by orthogonal crystals. W. H. BARNES and A. V. WENDLING (Amer. Min., 1935, 20, 253—259). L. S. T.

Crystal classification and symbolism. D. J. FISHER (Amer. Min., 1935, 20, 292—306). L. S. T.

X-Ray evidence of deformation in a crystal lattice under the action of an electric field. H.

HULUBEI (Compt. rend., 1935, 200, 1530—1532).—Observations on quartz are recorded. H. J. E.

Dendrites, single metal crystals, crystal grains, and the mechanism of grain growth. L. DLOV-GATCH (Rev. Met., 1935, 32, 23—31, 85—89).—Answers to a questionnaire sent to various metallurgists. W. P. R.

Existence of three alum structures. H. LIPSON (Nature, 1935, 135, 912).—X-Ray analysis shows that K, NH_4Me and Cs, and Na alums, previously regarded as isomorphous, have different structures, designated α , β , and γ , respectively. The question whether similar differences of structure exist in other supposedly isomorphous series is raised. Such pseudo-isomorphism is likely to occur only in the cubic system. L. S. T.

Dynamics of molecular crystal lattices. II. Solid nitrogen. V. DEITZ (J. Franklin Inst., 1935, 219, 565—571; cf. this vol., 686).—The distances between the atoms of a mol. of N_2 and its 12 nearest neighbours are calc. Calculation of the lattice energy per atom shows that the repulsion between two N atoms of different mols. in solid N_2 is less steep than that between two Ne or two A atoms. The orientation of mols. for min. lattice potential is deduced. The vibrations of the crystal lattice are considered and the frequencies of the max. Debye and other possible types of oscillation are calc. and checked by comparison of calc. and observed vals. of heat capacity. A. J. M.

Inner equilibria in solid phases. III. A. SMITS (Physikal. Z., 1935, 36, 367—371).—There is no evidence for heterogeneous transformations in solid phases of kinds higher than the first. The transition of NH_4Cl at -30° is discussed. There is no reason for supposing this transition to be of the third kind (cf. this vol., 155). The case of CH_4 is not analogous to that of NH_4Cl , the only point in common being the occurrence of hysteresis. The transition of CH_4 is homogeneous, whilst that of NH_4Cl is heterogeneous. A. J. M.

Orientation and pyroelectricity of crystals of magnesium ammonium phosphates in gall stones. E. PILLET (Compt. rend., 1935, 200, 1365—1367).—The cryst. structure, growth, and pyroelectric properties are described. N. M. B.

Crystallisation of melts. II. J. MEYER and W. PFAFF (Z. anorg. Chem., 1935, 222, 382—388; cf. A., 1934, 478).—The three *allocinnamic* acids give when melted identical liquids which, if filtered through a fine sintered glass filter, can be preserved in sealed vessels at room temp. for a year without solidifying. The liquid can yield crystals of any one of the acids by appropriate seeding. Similar results have been obtained with β -methoxy- and β -ethoxy-phenyl styryl ketones. The substances are therefore polymorphic, not isomeric. F. L. U.

Twinning in α -iron. A. B. GRENINGER (Nature, 1935, 135, 916—917).—Abundant twinning has been observed in α -Fe (C 0.0022, Si 0.0018%) which has been passed slowly through the crit. range, and in α -Fe deformed and then recryst. below the crit.

range. The Widmannstätten figures observed in α -Fe after quenching from above the crit. range are attributed to twinning and macromosaic lattice movements. L. S. T.

Fine structure of X-ray absorption edges of alloys. I. γ -Alloys. R. SMOLUCHOWSKI (Z. Physik, 1935, 94, 775—784).—Kronig's theory is extended to complicated lattice types and alloys. Measurements are given for Cu_5Zn_8 and Ag_5Zn_8 , and the effect of small at. displacements on the fine structure becomes apparent. A. B. D. C.

X-Ray study of recovery and recrystallisation of aluminium single crystals. N. SELJAKOV and E. SOVS (Nature, 1935, 135, 764—765).—X-Ray photographs of single crystals deformed by 5—16% extension are reproduced. Some of the crystals deformed by 10, 12, and 16% extension again become single crystals after recrystallisation, but with an orientation different from that of the deformed crystal. L. S. T.

Diffraction of X-rays by the silver atom. (Factor of structure.) J. LAVAL (Compt. rend., 1935, 200, 1605—1607).—Corresponding vals. of the factor of structure (calc. from the intensity of reflected radiation) and of $\sin\theta/\lambda$ (θ = angle of incidence) are given for 19 reflexion planes of the Ag crystal. The vals. are > those obtained by Chroback (A., 1933, 440). J. W. S.

Crystallographic uniformity of lineage structure in copper single crystals. A. B. GRENINGER (Amer. Inst. Min. Met. Eng., Inst. Metals Div., 1935, Tech. Pub. 596, 9 pp.).—The interpretation of fine structure within individual spots on unsymmetrical back-reflexion Laue photographs of Cu single crystals indicates that such crystals have a crystallographically uniform lineage structure. CH. ABS. (e)

Lattice dimensions of lithium hydride and lithium deuteride. E. ZINTL and A. HARDER (Z. physikal. Chem., 1935, B, 28, 478—480).—The vals. of a for the lattices of LiH and LiD are 4.085 ± 0.001 and 4.065 ± 0.001 Å., respectively, giving mol. vols. of 10.33 and 10.18 c.c. R. C.

Crystal morphology of quartz. IV. Morphology in relation to mineral origin. V. Development of form in β -quartz. G. KALB (Z. Krist., 1935, 90, 163—185).—External morphology only. B. W. R.

Silica framework crystals and their stability fields. M. J. BUERGER (Z. Krist., 1935, 90, 186—192).—Stable SiO_2 at high temp. (tridymite, cristobalite) is loose-packed compared with SiO_2 at low temp. (quartz). The stability of SiO_2 structures is discussed on the basis that the loose packing corresponds with the extra room needed for thermal agitation, and may be maintained at normal temp. if suitable foreign ions occupy the vacant space. B. W. R.

Transformation of aluminium oxide from the β - to the α -form. J. GALLUP (J. Amer. Ceram. Soc., 1935, 18, 144—148).—The conversion $\beta \rightarrow \alpha$ - Al_2O_3 begins in vac. or in H_2 at 1300° and is complete in 10 min. at 1400°. In air and A the conversion does not begin below 1600° and 1650°, respectively.

β - Al_2O_3 crystals have a transition stage before the characteristic α -form appears. It is probable that the expanded lattice structure of β - is due to the inclusion of alkalis and the $\beta \rightarrow \alpha$ change can be brought about only when the conditions permit the escape of the alkalis. J. A. S.

Constitution of lithium nitride. R. BRILL (Z. Elektrochem., 1935, 41, 266—267).—The hexagonal structure found for Li_3N by Zintl *et al.* (this vol., 433) appears to be correct (cf. A., 1928, 108). M. S. B.

Microstructure of active and inactive iron nitrides. G. L. NATANSON (Z. Elektrochem., 1935, 41, 284—290).—In spite of the larger surface of active Fe nitride (cf. Kobosev *et al.*, this vol., 829), X-ray examination indicates that its crystallites are practically the same size as those of the inactive nitride. The action of the activator appears to be the prevention of formation of a closely packed structure by inhibiting recrystallisation of the Fe formed as an intermediate stage in the production of the nitride catalyst from the oxide. A large free surface is thus obtained. M. S. B.

Zinc and cadmium phosphides and arsenides. Zn_3P_2 lattice. M. VON STACKELBERG and R. PAULUS (Z. physikal. Chem., 1935, B, 28, 427—460).— Zn_3P_2 , Zn_3As_2 , Cd_3P_2 , and Cd_3As_2 crystallise in the tetragonal system, with 8 mols. in the unit cell; space-group D_{2h}^{15} . Lattice consts. are recorded. In the co-ordinated lattice the metalloid atoms constitute a slightly deformed closest cubic packing in the tetrahedral interstices of which are the metal atoms. ZnP_2 and CdP_2 form tetragonal crystals, with 8 mols. in the unit cell; space-group D_2^1 or D_2^2 . R. C.

Configuration of the tri-iodide group in ammonium tri-iodide crystals. R. C. L. MOONEY (Z. Krist., 1935, 90, 143—150).—The structure of NH_4I_3 is orthorhombic, a_0 6.64, b_0 9.66, c_0 10.82 Å.; the cell contains 4 mols., space-group $Pmcn$. The I positions are directly located, the NH_4 surmised from analogous data on CsI_3 ; a very nearly linear tri-iodide group is found. B. W. R.

Molecular structure of germanium tetrachloride. L. BROCKWAY (J. Amer. Chem. Soc., 1935, 57, 958—959).—The mol. structure of GeCl_4 has been investigated by electron diffraction (cf. this vol., 18). About the same deviation from additivity of the radii is shown as for SiCl_4 and SnCl_4 . The sharp differentiation between these three and CCl_4 cannot be explained on the basis of gradations in electronegativity of the central atom. The Ge-Cl interat. distance, 2.10 ± 0.03 Å., agrees with Wierl's val. (A., 1931, 665). M. S. B.

Crystal structure of some hexachloro-salts. G. ENGEL (Zentr. Min., 1934, A, 285—286; Chem. Zentr., 1935, i, 18).—The salts $\text{R}^1\text{R}^{IV}\text{Cl}_6$ ($\text{R}^1 = \text{Rb}$, Cs, NH_4 , K, Tl; $\text{R}^{IV} = \text{Ti}$, Se, Zr, Sn, Te, Pt, Pb) are all cubic and of K_2PtCl_6 type structure, except K_2TeCl_6 , which is slightly distorted. Lattice consts. are recorded. J. S. A.

Crystal structure of some alkali tungsten chlorides $[\text{M}_3\text{W}_2\text{Cl}_9]$. C. BROSSET (Nature, 1935, 135, 874).—The NH_4 , Rb, Cs, and Tl compounds

are isomorphous: space-group C_{6h}^2 . $K_3W_2Cl_9$ has a 7.16, c 16.16 Å. and 2 mols. per unit cell. The at. positions are given and the structure of the W_2Cl_9 group, which exists as an ion in the crystals, is illustrated.

L. S. T.

Spinel and the cubic sodium-tungsten bronzes as new examples of structures with vacant lattice points. G. HAGG (Nature, 1935, 135, 874).—X-Ray investigation shows that when $MgO \cdot Al_2O_3$ dissolves Al_2O_3 the O excess is caused by the occurrence of vacant points in the metal lattices. γ - Al_2O_3 accordingly represents a spinel lattice where one ninth of the metal positions are vacant. Similarly, when Fe_3O_4 is oxidised to γ - Fe_2O_3 vacant points occur in the Fe lattice so that 8 out of 9 only are occupied. The lattice dimensions decrease at the same time. In the Na-W bronzes, Na_xWO_3 (x is 1, a is 3.850 Å.), W^{6+} ions are present and the bronze crystallises in a complete perovskite lattice. The deepening of colour from yellow \rightarrow blue \rightarrow red is accompanied by a continual decrease in dimensions and in Na content. As x decreases vacant points occur in the original Na lattice, and in the blue bronze (x 0.3–0.4, a 3.813 Å.) approx. two thirds of the original Na points are unoccupied. W^{6+} ions occur and probably cause the deepening of colour.

L. S. T.

Geometrical and optical properties and crystal structure of tenorite. G. TUNELL, E. POSNJAK, and C. J. KSANDA (Z. Krist., 1935, 90, 120–142).—The cell is monoclinic, a_0 4.653, b_0 3.410, c_0 5.108 Å., β 99° 29', containing 4 CuO; space-group $C2/c$. At. parameters are determined. The interat. distance Cu–O is 1.95 Å., 4 Cu being associated with each O and vice versa.

B. W. R.

Symmetry of the rhombic pyroxenes. T. ITO (Z. Krist., 1935, 90, 151–162).—From certain regularities in the appearance of (hkl) planes in the rotation photograph of $MgSiO_3$ it is suggested that the apparent rhombic nature is due to a twinning of a really monoclinic structure.

B. W. R.

X-Ray study of the structure of the phthalocyanines. I. Metal-free, nickel, copper, and platinum compounds. J. M. ROBERTSON (J.C.S., 1935, 615–621).—The crystals of phthalocyanine and its Cu, Ni, and Pt derivatives are all monoclinic, space-group $P2_1/a$, with 2 centro-symmetrical mols. per unit cell. The mol. consists of a large rigid framework, not distorted by the entrance of a metal atom, and is square, and probably flat. The metal atom and the four surrounding isoindole N atoms are necessarily coplanar. The chemical structure is discussed. The X-ray evidence in conjunction with stereochemical considerations (cf. Linstead, A., 1934, 1114) shows that the whole mol. with the possible exception of the two central NH-H atoms should be coplanar. Intensities of X-ray reflexions are in general agreement with the structure given by Linstead (*loc. cit.*). The mols. have approx. four-fold symmetry. The approx. orientations of mols. in the crystals have been determined.

A. J. M.

Scattering of X-rays by polyatomic liquids. n-Heptane. W. C. PIERCE (J. Chem. Physics, 1935,

3, 252–255).—The application of a Fourier integral analysis to Katzoff's data (this vol., 152) shows that the mol. consists of a zig-zag C chain. The arrangement of the mols. can be determined and is shown to be more random with rise in temp.

M. S. B.

Structure of the surface of oxidised iron. N. A. SCHISCHAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 458–461).—A reply to Finch and Quarrel's criticism (A., 1934, 721).

H. J. E.

Errors of interpretation in the electronic diagrams of organic substances. J. J. TRILLAT and H. MOTZ (Compt. rend., 1935, 200, 1466–1468).—Many org. materials appear to give the same electronic diagrams the data of which are not in accordance with the X-ray data. This is apparently due to the presence of a film of aliphatic compounds which diffract the electrons practically completely. After removal of this film by Et_2O or C_6H_6 the true diagram can be obtained. The possible origin of the film is discussed.

M. S. B.

Electron diffraction at highly polymerised substances. H. MARK, H. MOTZ, and J. J. TRILLAT (Naturwiss., 1935, 23, 319).—The disagreement between electron diffraction patterns and X-ray diagrams for highly polymerised substances is due to the presence of impurities, especially fats and waxes. With careful purification better results are obtained with cellulose.

A. J. M.

Preparation of Rochelle salt crystals to give reproducible measurements. H. KORNER (Z. Physik, 1935, 94, 801–807).—Crystals have been prepared of reproducible piezoelectric modulus, conductivity, and dielectric const.

A. B. D. C.

Frequency-dependence of ferromagnetic permeability as a function of electrical tension. R. SANGER and G. FEJER (Helv. phys. Acta, 1934, 7, 664–665; Chem. Zentr., 1935, i, 362).—Experiments on the fall in permeability of Fe and Ni wires at λ 100–10 cm. are recorded and discussed.

H. J. E.

Hall and magneto-resistance effects. D. SCHOENBERG (Proc. Camb. Phil. Soc., 1935, 31, 271–276).—The assumption, questioned by Kohler (A., 1934, 1298), that the linear Hall effect is perpendicular to the current, has been proved to be correct by experiment with a Bi crystal. The disymmetry of the Hall effect is discussed.

A. J. M.

Limitations of crystal symmetry on physical phenomena with particular reference to diamagnetic magnetostriction. D. SCHOENBERG (Proc. Camb. Phil. Soc., 1935, 31, 265–270).—The calculation is applied to the longitudinal and transverse magnetostriction of a Bi crystal.

A. J. M.

Influence of fibre structure and cooling in magnetic fields on magnetisation. O. DAHL and F. PAWLEK (Z. Physik, 1935, 94, 504–522).—Fibre structure formation in Fe–Ni alloys (40 to 50% Ni) gives anisotropy and technical improvement of magnetisation curves. Cooling in magnetic fields also greatly effects these curves at this [Ni], but not at high [Fe].

A. B. D. C.

Optical constants of rhenium and gallium at the wave-lengths 589 and 436 m μ . H. LANGE (Z. Physik, 1935, 94, 650—654). A. B. D. C.

Plastic properties of single crystals of silver and thallium halides. A. V. STEPANOV (Physikal. Z. Sovietunion, 1934, 6, 312—315).—Plastic properties of AgBr, TiCl, and TlBr resemble those of AgCl and are determined by polarisation properties of the lattice particles. CH. ABS. (e)

Plasticity of rock-salt and the Taylor and Becher-Orowan theories of crystalline plasticity. W. G. BURGERS and J. M. BURGERS (Nature, 1935, 135, 960).—Theoretical. L. S. T.

Survival of the molecular linking in the rock-salt crystal. R. REINICK (Z. physikal. Chem., 1935, B, 28, 411—426; cf. this vol., 17).—Arguments in favour of the survival are developed. Replacing non-directed by directed valencies and spherical atom domains by tetrahedral, each Na atom may be regarded as bound in mol. union to a Cl atom by a three-fold axis of symmetry. It is deduced that the vals. at present accepted for ionic radii are erroneous. The appearance of electrostatic charges in the lattice is probably due merely to the Na and Cl tetrahedra being unable, for spatial reasons, to approach sufficiently close to form the normal neutral mol. In the crystal, therefore, the mol. is equiv. to a dipole. Lattices analogous to the NaCl lattice are treated similarly. R. C.

Exceptions to a rule giving the mol. wt. of a pure liquid. R. LAUTIE (Bull. Soc. chim., 1935, [v], 2, 722—725).—Exceptions to the author's rule (this vol., 435) are discussed. Liquid A, Kr, and Xe contain some diat. mols., whilst polar liquids exhibit association. R. S.

Temperature dependence of the paramagnetism of solid nitric oxide. E. LIPS (Helv. phys. Acta, 1934, 7, 663—664; Chem. Zentr., 1935, i, 362; cf. this vol., 436).—Measurements (63—90° abs.) are recorded. Solid NO has a weak paramagnetism, independent of temp. H. J. E.

Weiss constant of paramagnetic ions in the S-state. I. Aqueous solutions of manganous salts. II. Aqueous solutions of ferric salts. A. BOSE (Proc. Indian Acad. Sci., 1935, 1, A, 605—615, 754—763).—I. Investigations previously reported (cf. A., 1934, 241) are extended, and include MnSO₄. The Curie law is obeyed. The Curie const. of Mn²⁺ is almost the same for all the solutions, irrespective of the nature of the salt and its concn.; the corresponding moment is 29.3—29.4 Weiss magnetons.

II.—The investigations are extended to Fe^{III} salts. Susceptibilities deviate markedly from the Curie and Weiss laws. The connexion of the deviations of χT from its theoretical val. 4.36 with the nature and concn. of the salt, the acid content, and the temp. is examined. The val. 4.36 is approx. reached at high acid concns., indicating that the anomalies are due to hydrolysis. N. M. B.

Properties of paramagnetic substances. Interpretation of fundamental characteristics. G.

DUPOUY (Compt. rend., 1935, 200, 1308—1310).—Experimental data on paramagnetic substances can be explained on the hypothesis that such substances contain, in general, two simple magnetic forms having differing vals. of the magnetic const. θ and C . N. M. B.

Constitution of paramagnetic substances. Transformation points. G. DUPOUY (Compt. rend., 1935, 200, 1385—1387; cf. preceding abstract).—It is concluded that the transformation temp. is independent of the magnetic const. of a mixture, but is dependent only on the transformation temp. of each of the components. The magnetic properties of CoCl₂ solutions confirm the author's theory. An extension of the theory states that when two simple magnetic varieties combine to form several different magnetic species, the masses of each which combine bear whole-no. relations to one another. J. W. S.

Ozone and its magnetic properties. P. LAINE (Ann. Physique, 1935, [xi], 3, 461—554; cf. A., 1934, 477).—In view of previous anomalous results liquid O₃ was investigated. The sp. susceptibility was $(1.4 \pm 0.2) \times 10^{-7}$, and was independent of temp. A reported transformation, on keeping, to a state more paramagnetic than that of O₂ was not observed. The const. paramagnetism of liquid O₃ is attributed to a deformation of the mols. under the influence of an external field. Data on the solubility of O₂ in liquid O₃, the stability of the latter, and its purification were obtained. No evidence of a substance O_n, where $n > 3$, was found. N. M. B.

Magnetic susceptibilities of cobaltic salts and the nature of the cobaltic ion. P. RAY and D. C. SEN (J. Indian Chem. Soc., 1935, 12, 190—193).—The susceptibility of Co^{III} in Co(CN)₃, Co(CN)₃.2H₂O, Co₂(SO₄)₃, (NH₄)₂SO₄.24H₂O, and Co₂(SO₄)₃ corresponds with 13.63, 15.16, 14.29, and 16.05 Weiss magnetons, respectively. The Co^{III} is probably in an excited or metastable state, and no redistribution of electrons, leading to the lowest energy state, occurs during the transformation Co^{III} \rightarrow Co^{II}. J. G. A. G.

Influence of "swelling" on the abnormal unidirectional diamagnetism of graphite crystals. K. S. KRISHNAN and N. GANGULI (Current Sci., 1935, 3, 472—473).—A crystal of graphite was converted into "blue graphite" by H₂SO₄ and HNO₃, washed, and dried and the magnetic susceptibilities in the basal plane and vertical axis were examined. The magnetic anisotropy was diminished from 22 to 1.3×10^{-6} per g. W. R. A.

Surface waves in the electron theory of metals. A. W. MAUE (Z. Physik, 1935, 94, 717—741).—Theoretical. Conductivity due to surface electron waves is investigated. A. B. D. C.

Superconductivity. R. SCHACHENMESER (Z. Physik, 1935, 94, 812—813 and 815).—Criticism of Papapetrou (A., 1934, 949). A. B. D. C.

Superconductivity. A. PAPAPETROU (Z. Physik, 1935, 94, 814).—A reply to the above.

Electrical resistance of pure aluminium at liquid helium temperatures. H. A. BOORSE and H. NIEWODNICZAŃSKI (Nature, 1935, 135, 827—

828).—The electrical resistance of Al containing only spectroscopic traces of Mg, Ca, and possibly Cu is const. between 4.2° and 2.2° abs. L. S. T.

Electrical resistance of cadmium, thallium, and tin at low temperatures. W. J. DE HAAS, J. DE BOER, and G. J. VAN DEN BERG (*Physica*, 1935, 2, 453—459; cf. this vol., 154).—The resistances of Cd, Tl, and Sn wires have been measured between 1° and 20° abs., but above the superconductivity temp. The "ideal" resistance curves for Cd and Sn, calc. by Matthiesen's rule, $\propto T^{4.5}$ and T^4 , respectively. That of Tl cannot be represented by a single power of temp. J. W. S.

Electrical properties of wires of high permeability. E. P. HARRISON, G. L. TURNER, and H. ROWE (*Nature*, 1935, 135, 961).—Wires of Ni-Fe alloys show a pronounced "skin effect" at low audio-frequencies. L. S. T.

Effect of free electrons on the heat-conductivity of silver sulphide. B. M. HOCHBERG (*Physikal. Z. Sovietunion*, 1934, 6, 193—204).—When α -Ag₂S (I) changes to β -Ag₂S the heat-conductivity is doubled, due to the many free electrons in (I). CH. ABS. (e)

Variation of the f.p. of heavy water as a function of pressure. J. TIMMERMANS and L. DEFFET (*Compt. rend.*, 1935, 200, 1661—1663).—Data are recorded for the effect of pressure (1—1051 kg. per sq. cm.) on the f.p. of D₂O (cf. Deffet, this vol., 688). The f.p. of H₂O and D₂O at 1000 kg. per sq. cm. are respectively -8.72° and -4.50°. H. J. E.

Association in the gaseous and liquid state at the b.p. K. BILLIG (*Ber.*, 1935, 68, [B], 591—597).—Theoretical. A comparison of association in the gaseous and liquid states extending to crit. conditions is made. It is rendered highly probable that the b.p. of a substance \propto the product of the association factor and mol. vol. of the liquid. H. W.

Adiabatic demagnetisation of caesium titanium alum. W. J. DE HAAS and E. C. WIERSMA (*Physica*, 1935, 2, 438).—Demagnetisation of Cs₂SO₄.Ti₂(SO₄)₃.24H₂O with an initial field of 25,075 gauss and initial temp. of 1.314° abs. yielded a final temp. (calc.) of 0.0055° abs. J. W. S.

Propane total-heat curve. E. G. RAGATZ (*Petroleum World*, 1934, 31, No. 12, 43—44).—Calc. and experimental data are compared. CH. ABS. (e)

Physical constants of propane. E. R. COX (*Petroleum World*, 1934, 31, No. 12, 44—45, 56).—The physical consts. of C₃H₈ are tabulated. CH. ABS. (e)

Continuation of the saturation curve of water vapour above the critical point. M. JAKOB (*Physikal. Z.*, 1935, 36, 413—414).—The curve of $(\partial C_p / \partial t)_p = 0$ for H₂O at pressures > 225 kg. per sq. cm. forms a direct continuation of the p - T curve for saturated H₂O vapour. The crit. vol. of H₂O obtained from the curve lies between 0.00305 and 0.00320 cu. m. per kg. The C_p - T diagram of H₂O in the neighbourhood of the crit. temp. shows a discontinuity which may be due to a third-order phase change. A. J. M.

Graphical thermodynamics of real gases. E. J. M. HONIGMANN (*Z. Dampfkesselunters.*, 1934, 59, 19—24, 30—35; *Chem. Zentr.*, 1935, i, 363—364).—A discussion and review. H. J. E.

Vapour-pressure curves, m.p., and chemical constants of di- and tri-methylamine and isobutylamine. A. SIMON and J. HUTER (*Z. Elektrochem.*, 1935, 41, 294).—Redetermination of m.p. (cf. this vol., 290) has given the vals. -93.0°, -117.2°, and -84.6°, respectively, in good agreement with those obtained by Wiberg *et al.* (this vol., 574).

M. S. B.

Vapour pressures of magnesium, thallium, and zinc, and the determination of their chemical constants. F. F. COLEMAN and A. EGERTON (*Phil. Trans.*, 1935, A, 234, 177—204; cf. A., 1923, ii, 491).—Sources of error in the determination of v.p. by the effusion method have been investigated. V.-p. data are given for solid Mg and Zn and liquid Tl over the ranges 427—465°, 302—356°, and 574—632°, respectively, and the appropriate $\log p$ - $1/T$ relations derived. The results are in accord with previous measurements in different temp. ranges. Using a graphical method of integration of the thermal data, chemical consts. in close agreement with the theoretical vals. were obtained, viz., Mg 0.47 ± 0.21 , Zn 1.21 ± 0.15 , Tl 2.37 ± 0.28 . Equations giving the v.p. of the metals over a wide range of temp. have been constructed. R. S.

Density of light water: ratio of deuterium to hydrogen in rain water. W. N. CHRISTIANSEN, R. W. CRABTREE, and T. H. LABY (*Nature*, 1935, 135, 870).—Light H₂O prepared by electrolysis natural H₂O and burning the evolved gases has $d <$ that of natural H₂O by approx. 10² parts in 10⁷. Re-electrolysis reduces d again by approx. 14 parts in 10⁷ and a third electrolysis by 12 parts in 10⁷. The product is then almost free from D₂O and at 27° has a difference in d of 127 in 10⁷, indicating that there is 1 mol. of D₂O in 8500 mols. of H₂O in rain-water. Fractional distillation of tap H₂O gave a difference in d of 200 in 10⁷ between the first and last fractions.

L. S. T.

The rectilinear diameter (critical temperature densities). E. MATHIAS (*Compt. rend.*, 1935, 200, 1643—1645).—A review and discussion. H. J. E.

Classification of energy losses according to types of irreversibility. J. VILLEY (*Compt. rend.*, 1935, 200, 1383—1385). J. W. S.

Application of statistical mechanics to the thermodynamics of a gas. (Mlle.) G. SCHOULS (*Bull. Acad. roy. Belg.*, 1935, [v], 21, 396—409).—Using de Donder's formula of general statistical mechanics and taking account of intramol. forces, the thermodynamic energy and entropy of a polyat. gas has been calc. Molar entropies of Cl₂, Br₂, and I₂ at at. pressure and 298° abs. are given. W. R. A.

Metallic binding. P. GOMBAS (*Z. Physik*, 1935, 94, 473—488).—Theoretical. Lattice consts., heat of sublimation, and compressibility are calc. for K. A. B. D. C.

Change of properties of water around 40°. M. MAGAT (*J. Phys. Radium.*, 1935, [vii], 6, 179—

181; cf. A., 1934, 1055).—Curves for compressibility and n , as a function of temp., viscosity, mol. heat at const. vol. and const. pressure, expansion, solubility in C_6H_6 , solubility of Br and Et_2O , and diffraction of X-rays at different temp. all show irregularities in the range 35–45°, suggesting a change of mol. interaction forces. N. M. B.

Pressures of 5000 kg. per sq. cm. II. Absolute determination of compressibility of solid substances. H. EBERT (Physikal. Z., 1935, 36, 388–392; see this vol., 840).—The compressibilities of single crystals of Al, Fe, Au, Pb, Ag, Mg, and polycryst. Cu, manganin, and steel were determined by a comparator method. In general compressibility for single crystals was $>$, but the variation with pressure is $<$, that of the polycryst. substances. A. J. M.

Viscosities of fuming and diluted sulphuric acid and sodium sulphide. V. F. POSTNIKOV and L. L. KUZMIN (Khimstroi, 1934, 6, 527–529).—Data are recorded for fuming H_2SO_4 from –20° to 120° and for Na_2S from 10° to 170°. CH. Abs. (p)

Viscosity measurements of R. O. Herzog and collaborators. L. URBELOHDE (Cellulosechem., 1935, 16, 40).—Polemical. A. G.

Highly polymerised compounds.—See this vol., 728, 730.

Lattice distortion in a copper-beryllium alloy. G. W. BRINDLEY and F. W. SPIERS (Proc. Leeds Phil. Soc., 1935, 3, 73–80).—A Cu-Be alloy (0.72% Be) exhibits lattice distortion attributable to the method of powdering by filing and to the disparity in the size of the atoms in the lattice. The intensities of X-ray reflexions and at. scattering are discussed. W. R. A.

Two intermetallic compounds of beryllium and iron. L. MISCH (Naturwiss., 1935, 23, 287–288).—A ferromagnetic phase, $FeBe_2$, with magnetic transition point 521–524° has been found in the Be-Fe system. The X-ray structure is of the $MgZn_2$ type, 12 atoms in unit cell. Another compound, $FeBe_5$, is also formed, which is not ferromagnetic at room temp., but slightly so at –180°. It has a face-centred cubic lattice, the structure being of the $MgCu_2$ type, 24 atoms in unit cell. A. J. M.

Molecular solid solutions in the system copper-gold. N. V. AGEEV and D. N. SHOYKET (Ann. Physik, 1935, [v], 23, 90–104).—The structure of $AuCu$ and $AuCu_3$ and their solid solutions has been determined by the X-ray method. The lattice structures of the two compounds show that about 10% of the atoms are out of place. With rise of temp. this proportion increases. In solid solutions, temp. and the presence of additional atoms affect the degree of disorder. The theoretical effect of additional atoms is calc. Observed effects are $<$ calc., but this is attributed to temp., the influence of which in solid solutions is $>$ in the pure compounds. The variation of conductivity and hardness of Au-Cu alloys with composition follows a similar course to the variations of the lattice structure. A. J. M.

Crystal growth and nucleus formation. I. N. STRANSKI and R. KAISCHEV (Physikal. Z., 1935, 36,

393–403; cf. A., 1934, 946, 1058, 1059).—Using the simple cubic model, the Thomson-Gibbs equation is shown to express the equilibrium between a crystal and its surroundings. The growth and dissolution of a finite crystal are considered in reference to the work of separation of the lattice constituents from the surface. A. J. M.

Variation of elastic constants of the metallic alloy Ni-Fe on magnetisation. K. NAKAMURA (Z. Physik, 1935, 94, 707–716).—Variation of Young's modulus on magnetisation is small for alloys with $< 30\%$ Ni, but is large at high [Ni]. A. B. D. C.

Solubility of copper in iron and lattice changes during ageing. J. T. NORTON (Amer. Inst. Min. Met. Eng., 1934, Tech. Publ. 586, 9 pp.).—The max. solid solubility of Cu in Fe is 1.4 wt.-%. It decreases with fall of temp. and is const. below 650° (0.35%). The main increase of hardness occurs prior to the pptn. of the Cu-rich phase. At all temp. at which hardening occurs, max. hardness occurs when approx. 20% of the available Cu has been pptd. Complete pptn. decreases the hardness. The chief cause of age-hardening is a pre-pptn. rearrangement of the solid solution. CH. Abs. (e)

Constitution of antimony-tin-zinc alloys. R. BLONDEL and P. LAFFITTE (Compt. rend., 1935, 200, 1472–1474).—Three ternary peritectic points, at 197.5°, 235°, and 395°, respectively, have been observed. $ZnSb$ is the only compound of Zn and Sb which is stable in the presence of Sn. M. S. B.

Superconductivity of alloys. C. J. GORTER (Physica, 1935, 2, 449–452).—The observation that the superconductivity of certain alloys persists at field strengths \gg the magnetic threshold field is reconciled with theory. J. W. S.

Superconducting alloys. K. MENDELSSOHN and J. R. MOORE (Nature, 1935, 135, 826–827).—The magnetic properties of a Pb-Bi alloy (30% Pb) have been investigated at temp. near 0° abs. where the alloy is superconducting. A possible explanation for the phenomena observed is that the threshold val. is high in some parts of the alloy, although in the main this has the same val. as the pure metals. L. S. T.

Fugacities of ethyl alcohol and water in their gaseous mixtures. Deviations from perfect solutions. H. ESSEX and W. R. KELLY (J. Amer. Chem. Soc., 1935, 57, 815–816).—The mol. vols. of 12 gaseous mixtures of $EtOH$ and H_2O , containing 0–99.83% $EtOH$, have been determined at 152.9°, 163.5°, and 173.9°, at pressures 1–5, 6, and 8 atm., respectively. Deviations from perfect solution have been calc. At 1 atm. the solutions are practically perfect. The solutions for which the mol. fraction of the component considered is > 0.2 deviate by $< 2\%$, even at the max. pressures recorded. M. S. B.

Statistical mechanics of fluid mixtures. J. G. KIRKWOOD (J. Chem. Physics, 1935, 3, 300–313).—Theoretical. A statistical treatment of fluid mixtures formally applicable to both real gases and liquids is described. M. S. B.

Densities of aqueous solutions of formaldehyde between 20° and 40°. S. N. DATAR (Current Sci., 1935, 3, 483—484).—Data are given for solutions containing 2.76 and 41.43 g. per 100 c.c. at 5° intervals.

W. R. A.

Densities of aqueous solutions of potassium acetate and *n*-dodecoate. C. R. BURY and G. A. PARRY (J.C.S., 1935, 626—628; cf. A., 1930, 1516).—Data for KOAc at 25° and for K *n*-dodecoate at 25° and 35° are recorded. The *d*-composition curve for the former is smooth, whilst those for the latter show abrupt changes of slope similar to those found for the *n*-octoate.

F. L. U.

Viscosity formula for binary mixtures, the association degrees of constituents being taken into consideration. X. **Viscosity of aqueous solutions of electrolytes.** T. ISHIKAWA and T. BABA (Bull. Chem. Soc. Japan, 1935, 10, 153—167).—Theoretical. The formula for η of Ishikawa (A., 1934, 723) has been applied to the data of Swearingen and Heck (*ibid.*, 591) for C_5H_5N -AcOH mixtures and to aq. salt solutions. "Negative" ($< H_2O$) is considered to be due to the sp. solutional η of the salt ($< \eta_{H_2O}$), and not to the depolymerising action of cations against solvent mols. With no hydration (a) negative η should be observed at all concns.; with slight hydration (b) negative η should be observed at low concns. only, whilst with marked hydration (c) η should be "positive." CsCl, RbCl, and CsNO₃ correspond with (a), RbNO₃, KCl, and KI with (b), 3RbNO₃.H₂O, 3KCl.H₂O, and 2KI.H₂O being formed, whilst NaCl, LiCl, and LiNO₃ correspond with (c) the compounds formed being NaCl.2H₂O, LiNO₃.3H₂O, LiCl.H₂O, LiCl.2H₂O, and 2LiCl.4H₂O.

R. S. B.

Relation of surface tension to other physical properties of liquid mixtures. R. M. CONRAD and J. L. HALL (J. Amer. Chem. Soc., 1935, 57, 863—866).—The compressibility-vol.-% composition diagram for MeOH-CHCl₃ mixtures at 25°, and the corresponding surface-tension diagram, are nearly ideal, although their slight deviations are in strict antibatic relation to each other. Fluidity and v.p. show wide deviations from the normal and have no apparent correlation with any other property. The index of refraction is strictly additive and the max. deviation of *d* from the straight-line function is very small. A simple apparatus for the measurement of compressibility under 2 or 3 atm. is described.

M. S. B.

Thermal dissociation and vapour pressure of boric acid and its volatility in steam. S. BEZZI (Annali Chim. Appl., 1935, 25, 121—122).—The contention that the distillation of H₃BO₃ in a current of steam is due to the formation of complexes of ortho- or meta-boric acid with H₂O in the gaseous phase (this vol., 24) is disputed (cf. A., 1933, 120).

T. H. P.

Determination of the internal latent heat of vaporisation of azeotropic mixtures. III. **Determination of the internal latent heat of vaporisation of liquids.** IV. N. DE KOLOSOVSKI and A. ALMOV. **Determination of the latent heat of vaporisation of azeotropic mixtures.** V. N.

DE KOLOSOVSKI and R. L. THÉODOROVITSCH (Bull. Soc. chim., 1935, [v], 2, 686—689, 690—691, 692—700; cf. A., 1934, 1164).—III. Vals. (*g*) have been determined for C₆H₆-Pr^oOH, PhMe-Pr^oOH, PhMe-Bu^oOH, CS₂-COMe₂, CCl₄-EtOAc, and CHCl₃-HCO₂Me, and the change in entropy ΔS , heat content ΔH , and free energy *A*, calc. for each mixture.

IV. Vals. of *g* are given for HCO₂Et, EtOAc, Pr^oBr (I), Bu^oCl (II), Bu^oBr (III), and the total latent heats of vaporisation λ and v.-p. equations derived for (I), (II), and (III).

V. An apparatus is described in which a weighed amount of the azeotrope is evaporated at the b.p. by a measured electrical current. ΔS , ΔU , and *A* are calc. for 18 mixtures and the variation with temp. of λ and ΔU is deduced for the six mixtures investigated in Section III.

R. S.

Electrical polarisation of concentrated solutions of nitrobenzene with special reference to the validity of the Sugden relation. H. O. JENKINS and L. E. SUTTON (J.C.S., 1935, 609—615).—The polarisation-concn. curves of conc. solutions of PhNO₂ in C₆H₆, CS₂, *n*-C₆H₁₄, cyclohexane, and CCl₄ have been obtained. The curve for PhNO₂ in cyclohexane is normal. The Sugden relation between the total polarisation of solute and the vol. polarisability of the solution (A., 1934, 474) is satisfied by certain solutions, but this is not generally the case. The actual relation depends on both solute and solvent. The method of calculating dipole moments proposed by Goss (A., 1934, 717) is not of general validity owing to the approx. nature of the Raman-Krishnan formula (A., 1928, 348) on which it is based.

A. J. M.

Dielectric properties of alcohols and ether in various solvents. F. H. MÜLLER and P. MORTIER (Physikal. Z., 1935, 36, 371—377).—The mol. polarisation of MeOH, PrOH, and Et₂O in C₆H₁₄, CCl₄, C₆H₆, CS₂ and decalin has been determined at various concns., the curves being extrapolated to infinite dilution. The vals. obtained do not agree with the view that mol. polarisation at infinite dilution is a simple function of the dielectric const. of the solvent. The effect of the solvent on polarisation is discussed with respect to the position of the dipole within the mol.

A. J. M.

Mutual solubility of flavone and its derivatives. T. ASAHINA and K. YOKOYAMA (Bull. Chem. Soc. Japan, 1935, 10, 135—138).—The mutual solubility of flavone and 5:6-dihydroxy-, 5:7:4'-triacetoxy-, 5:6-diacetoxy-, 5-hydroxy-6-methoxy-, and 5:6:7-trimethoxy-flavone has been determined at 80—280°. In contrast to the system primetin-flavone (A., 1934, 365) no solid solutions are formed.

R. S. B.

Solubility of helium in water at 0°, 25°, 50°, and 75° and at pressures to 1000 atm. R. WIEBE and V. L. GADDY (J. Amer. Chem. Soc., 1935, 57, 847—851).—The calc. Bunsen and Ostwald absorption coeffs. are in good agreement with the best known vals., but it is shown that the Ostwald corr. coeff., determined at low pressures, cannot be used to calculate high-pressure solubilities. The min. solubility

for He in H_2O is at approx. 30° , which is $<$ for H_2 or N_2 . No indication of a hydrate was obtained.

M. S. B.

Solubility. XIV. Experimental tests of a general equation for solubility. J. H. HILDEBRAND (J. Amer. Chem. Soc., 1935, 57, 866—871).—An equation for the calculation of solubility from the properties of the components of the solution has been deduced and shown to be applicable to solutions of I, SnI_4 , S, and P in different solvents. Lack of spherical symmetry and presence of dipole moment do not necessarily affect the results. The inequality between the attraction consts. of like and unlike mols. appears to be small.

M. S. B.

Solubilities of certain salts in liquid ammonia. II. Solubility of sodium chloride in liquid ammonia and the saturated vapour pressure of the solution at low temperature. S. ABE, S. SIGETOMI, and R. HARA (J. Soc. Chem. Ind. Japan, 1935, 38, 163—165b).—The solubility (g. NaCl per 100 g. NH_3) falls from 4.20 at -30° to 0.63 at -60° . In combination with previous results (A., 1933, 1240), the data are used to calculate the heat of vaporisation of the saturated solution and the heat of dissolution of NaCl . Below -9.6° the solid phase is $\text{NaCl} \cdot 5\text{NH}_3$; this is formed with the absorption of 11.56 kg.-cal.

J. S. A.

Absorption of fogs from fuming sulphuric acid. H. REMY and C. BEHRE (Kolloid-Z., 1935, 71, 129—145; cf. A., 1934, 955, 1066).—The dependence of the rate of absorption of fogs, produced by blowing air through fuming H_2SO_4 and then saturating the air stream with H_2O , on the SO_3 content of the acid, the H_2SO_4 content of the air, the no. of droplets per c.c., the velocity of the air stream, and the type of absorption vessel, has been determined. F. L. U.

Formation of dew. N. FUCHS (Kolloid-Z., 1935, 71, 145—149).—Condensation of liquid from air saturated with H_2O , or from saturated H_2O vapour alone, occurs at a supersaturation < 0.15 — 0.20% even on "unwettable" solid surfaces. In the latter case droplets are formed, in repeated experiments, always at the same places on the surface. Such condensation centres consist of microscopic wettable impurities. With metals, liquid may separate above the dew point. Supersaturation of 10— 20% is required for dew to separate on the surface of impure liquid mineral oils.

F. L. U.

Adsorption of gases on mercury. R. S. BURDON (Proc. Physical Soc., 1935, 47, 460—470).—A Hg surface was formed in the presence of a gas which was pumped off after an interval, and the Hg surface then made to collapse, causing an evolution of the gas. For air, H_2 , and CO_2 the limiting amount evolved corresponded with a unimol. layer which appears to be retained by the surface for a long period.

N. M. B.

Statistical derivation of Langmuir's adsorption isotherm. R. H. FOWLER (Proc. Camb. Phil. Soc., 1935, 31, 260—264).—Mathematical.

A. J. M.

Adsorption concepts in chemistry. E. K. RIDEAL (Nature, 1935, 135, 737—738). L. S. T.

Interaction of hydrogen with micro-crystalline charcoal. I. R. M. BARRER and E. K. RIDEAL. II. **Activated sorption of hydrogen and methane by carbon.** R. M. BARRER (Proc. Roy. Soc., 1935, A, 149, 231—253, 253—269).—I. The sorption of H_2 on charcoals, for which the cryst. size was determined by X-ray analysis, has been studied. Sorption at 78° , 195° , and 273° abs. shows that the charcoal surface is composite. The total sorption may be represented by the sum of two terms: $x/m - ap/(1+bp) + a'p/(1+b'p)$. Saturation for the first type is reached at low pressures and is caused by active centres due to ash, whilst the second type is due to an ash-free C surface which shows no evidence of active centres. The kinetics of sorption of H_2 , N_2 , and O_2 at low temp. are in agreement with Fick's law. For all gases on ash-free charcoal the relations can be described by $(C_e - C_t)/(C_e - C_i) - b(e^{-at} + 1/9e^{-9at} + 1/25e^{-25at} + \dots)$ and over the later stages of sorption by $\log(C_e - C_t)/(C_e - C_i) = kt$. D_2 is more strongly sorbed than H_2 at 78° abs. Chemisorption of H_2 causes a decrease in the amount of van der Waals adsorption, without altering the velocity. No evidence is found for previously reported discontinuities in the isotherms.

II. Isotherms, isobars, and kinetics for the activated sorption of H_2 by charcoal have been measured between 623° and 1223° abs. Isotherms and kinetics for activated sorption of CH_4 have also been studied. At low pressures the gas phase is H_2 whether equilibrium is approached from the side of CH_4 or H_2 . At higher pressures small quantities of CH_4 are slowly formed; this is detectable when activated sorption is completed. Sorption of H_2 is an activated chemisorption complicated by diffusion. Non-activated diffusion limits the reaction rates above 970° abs. The activation energy varies from 10,000 to 30,000 g.-cal. per g.-mol. at 20% saturation of the surface. The heat change at high temp. is const. at $50,000 \pm 5000$ g.-cal. per g.-mol. At low pressures CH_4 reacts with a C surface according to a unimol. law and const. activation energy (53,400 g.-cal. per g.-mol.).

L. L. B.

Adsorption on measured surfaces of vitreous silica. W. G. PALMER and R. E. D. CLARK (Proc. Roy. Soc., 1935, A, 149, 360—384).—The adsorption of vapours on specially prepared powdered vitreous SiO_2 has been measured. The areas covered by mols. on the surface agree with vals. from other sources. Langmuir's formula has been modified to connect adsorption potential with the amount adsorbed, leading to a new theoretical isothermal. Special experiments were made on the form of the adsorption isothermal at low degrees of adsorption.

L. L. B.

Effect of temperature on adsorption of electrolytes by charcoal. L. LEPIN and G. STRACHOVA (Z. physikal. Chem., 1935, 173, 129—140).—The adsorption of HCl and H_2SO_4 from aq. solution increases with rise of temp., whilst that of HCO_2H and AcOH decreases. This observation supports Schilov's hypothesis (A., 1930, 991) that the adsorption of electrolytes on C depends on a surface reaction between the ions of the electrolyte and the surface C oxide, thus differing entirely from the adsorption of non-electro-

lytes. The temp. coeff. for HCO_2H is somewhat < for AcOH , which is doubtless connected with the fact that almost half the adsorbed HCO_2H reacts with the surface oxide of the C (cf. A., 1931, 1006). Adsorption equilibrium is established more slowly for HCl and H_2SO_4 than for AcOH ; HCO_2H occupies an intermediate position. With HCl and HCO_2H there is evidence of a transition from ionic adsorption at low to mol. adsorption at higher concns. R. C.

Influence of complex formation on the adsorption of copper in ammoniacal solutions by precipitated ferric hydroxide. (MME.) L. S. MATHIEU-LÉVY (Compt. rend., 1935, 200, 1751—1754).—The adsorption passes through a max. with increasing $[\text{NH}_3]$. At low $[\text{NH}_3]$ colloidal $\text{Cu}(\text{OH})_2$ is formed, and this is adsorbed. With increasing $[\text{NH}_3]$ complexes are formed, and the adsorption decreases.

H. J. E.

Absorption of dyes by suspensions of kaolin. A. BOUTARIC and P. COULON (Bull. Soc. Chim. biol., 1935, 17, 620—626).—The adsorption by kaolin of colloidal or semi-colloidal electropositive dyes is greater and more stable to washing than that of electronegative dyes, that of methylen-blue being particularly marked. Addition of aq. H_2SO_4 increases the adsorption of electronegative and decreases that of electropositive dyes. Flocculation of the kaolin increases the adsorption of semi-colloidal dyes.

A. L.

[Adsorption by] humic acids. G. STADNIKOV, K. SISKOV, and A. USCHAKOVA (Kolloid-Z., 1935, 71, 206—214; cf. B., 1929, 231).—The adsorption of $\text{Ba}(\text{OH})_2$ from aq. solution by humic acid is a chemical process in which both phenolic OH and CO_2H groups take part. When OH are methylated adsorption is correspondingly diminished, but when CO_2H are methylated there is no change in absorption, since hydrolysis occurs and MeOH is found in the solution. Similar behaviour is observed with lignin and is characteristic of humic acids.

F. L. U.

Inner adsorption in salt crystals. I. D. BALAREV [with M. VRBANOVA and N. KOLAROV] (Z. anal. Chem., 1935, 101, 161—177).—The slow removal by washing of salts occluded in ppts. is attributed to their occlusion in capillaries of the mosaic structure rather than in superficial adsorption layers. During pptn. in presence of several electrolytes, an orderly preferential adsorption is observed. Isomorphous substances may be held partly by adsorption and partly by mixed crystal formation. Const. composition and elimination of zeolitic H_2O from capillaries are attained only after ageing (inner recrystallisation), which is promoted by subdivision of macro-crystals. Analytical ppts. do not reach stoichiometric composition even after ignition. Kolthoff's views (A., 1932, 457) are criticised. J. S. A.

Adsorption of ovalbumin at the free surface of its solutions when the concentration of the latter varies from 10^{-2} to 10^2 . H. DEVAUX (Compt. rend., 1935, 200, 1560—1563; cf. this vol., 161).—The thickness of films on dil. solution is > that of a unimol. layer, and at const. p_H increases with the concn., but not so rapidly as the latter. The thickness-concn. curve has the characteristics of an

ordinary adsorption curve. A theoretical equation is developed which is in approx. accord with the results.

J. W. S.

Surface tension of solutions. G. JONES and W. A. RAY (J. Amer. Chem. Soc., 1935, 57, 957—958).—By a modification of the capillary rise method, surface tension, σ , may be determined with greater precision than hitherto possible. At very low concn. (< 0.006*N*), σ for aq. KCl is < for H_2O , but rises above the latter val. at higher concn., and is approx. a linear function of concn. This is not in accordance with the equations of Onsager *et al.* (A., 1934, 1068). K_2SO_4 and CsNO_3 give similar results, but sucrose at concn. 0.0005—0.005*M* gives an increased σ . An explanation is given on the basis of the ionic forces. M. S. B.

Surface tension and solvent action of organic liquids. S. PAPKOV (Kolloid-Z., 1935, 71, 204—206).—Org. liquids in which cellulose acetate dissolves or swells have surface tensions in the range 22—30 dynes per cm. for aliphatic and >37 for cyclic compounds.

F. L. U.

Abnormal surface tensions of dilute aqueous phenol solutions. F. SEELICH (Z. physikal. Chem., 1935, 173, 121—128).—Addition of PhOH to H_2O causes a sudden fall in the surface tension, γ . Subsequently γ rises slowly, but this is not due to volatilisation of PhOH . Even the PhOH adsorbed on the wall of the vessel above the surface of the solution is sufficient to cause a considerable fall in γ . It is suggested as a possible explanation that the establishment of equilibrium between associated and non-associated PhOH mols. in solution takes time and that the associated mols. are the more surface active. Apparently the rate of transformation of these is a min. in the adsorbed state.

R. C.

Surface relations of the xanthates. C. C. DE WITT, R. F. MAKENS, and A. W. HELZ (J. Amer. Chem. Soc., 1935, 57, 796—801).—A modification of Ferguson's balanced pressure surface tension apparatus is described. The surface tension, γ , of several xanthate solutions has been determined. The mol. lowering of γ is approx. the same for both Na and K ethylxanthates, and increases in the ascending homologous series from ethyl- to nonyl-xanthates in accordance with Traube's rule. Isomeric forms of K amylxanthate differ considerably in their effect. The relation of the mol. lowering of γ to the efficiency of the normal xanthates (Et to heptyl inclusive) as collectors for malachite and chalcocite in flotation practice is discussed.

M. S. B.

Range of action of surface forces. F. P. BOWDEN and S. H. BASTOW (Nature, 1935, 135, 828).—The resistances to flow of thin ($16\text{--}60 \times 10^{-5}$ cm.) liquid films of 1% NH_4 oleate, H_2O , EtOH , cyclohexane, AcOH , and Et palmitate between parallel surfaces show no evidence of rigidity. Thinner films (approx. 10^{-5} cm.) cooled to within 0.1° of the f.p. behave similarly, η being the same as that of the liquid in bulk. The view that oriented chains of H_2O mols. extend to a distance of 5 \AA from a solid surface is untenable (cf. A., 1934, 721).

L. S. T.

Meaning of the exponential equation between surface pressure and concentration. B. TAMA-

MUSHI (Kolloid-Z., 1935, 71, 150—159; cf. A., 1934, 1304).—The empirical relation $s = kc^{1/n}$ (s = surface pressure, c = concn.) can be regarded as a particular case of the general two-dimensional equation of state, from which it follows that k and n should depend on concn. and temp. Experiments on the variation of the surface pressures of a series of aq. fatty acids with concn. and temp. confirm this conclusion. At very small concns. $n=1$. F. L. U.

Drop-weight method for the determination of electrocapillary curves. S. R. CRAXFORD and H. A. C. MCKAY (J. Physical Chem., 1935, 39, 545—550).—An apparatus for the determination of electrocapillary curves by the drop-wt. method is described. These curves coincide to within 0.2% with those obtained by the use of the capillary electrometer; the method may therefore be applicable to non-wetting solvents for which this is unsuitable. M. S. B.

Formation and structure of uni- and bi-molecular layers of oily substances on metallic surfaces. J. J. TRILLAT and H. MOTZ (Compt. rend., 1935, 200, 1299—1301).—Films of mol. thickness deposited on Au leaf of thickness 50—80 mμ and subjected to 40,000-volt electron beams show diffraction patterns indicating regular mol. orientation which is discussed in relation to the structure of the compounds. Clean films of Ag, Au, Pt, and Al, examined after several months, show similar patterns due to spontaneous accidental contamination. N. M. B.

Mechanism of flotation. Adsorption on particles of talc in aqueous suspension and its flotation. Z. V. VOLKOVA, N. N. SERB-SERBINA, and A. V. SAPOROSHEZ (Kolloid-Z., 1935, 71, 230—234; cf. this vol., 578).—*iso*-Valeric acid (I) is adsorbed by talc particles suspended in H₂O, and at the same time Mg ions pass into the solution. For flotation the optimum concn. of (I) is about 0.5%. An explanation is offered. F. L. U.

Molecular strength of liquids. J. MEYER (Z. physikal. Chem., 1935, 173, 106—114).—Smekal's concept of mol. strength (Naturwiss., 1922, 20, 799) is applied to liquids. The conditions under which the mol. strength of liquids can be directly observed and the influence of temp. are discussed. The importance of eliminating the free surface in such observations is emphasised. R. C.

Ebullioscopic measurements with solutions of ketones and aldehydes in hydrogen fluoride. W. KLATT (Z. physikal. Chem., 1935, 173, 115—120).—The data for aldehydes, ketones, and ketonic acids in anhyd. HF afford no evidence of chemical change other than the formation of solvates, which may dissociate considerably. R. C.

Compressibility of electrolytic solutions. H. FALKENHAGEN and C. BACHEM (Nature, 1935, 135, 830).—The adiabatic compressibilities of strong electrolytes have been measured by a new optical method. The compressibility, k , and concn. are related by $k = Ac + Bc^{3/2}$. The limiting slopes derived from the interionic attraction theory by Glueker agree with the results for 1-1- and 1-2-valent salts, but with electrolytes of higher valency a slope $<$ the expected is obtained. L. S. T.

Influence of evaporation on the migration of salts. K. SCHULTZE (Kolloid-Beih., 1935, 41, 365—392).—The influence of evaporation, vessel wall, and diffusion on the migration of KCl, KNO₃, kainite, and KAl(SO₄)₂ has been studied. The migration is not a sp. property of the salt, since salts previously described as non-migrating, e.g., kainite, can be made to migrate. The diffusion of the salts towards the bulk of the solution and the evaporation of the solution act oppositely, and the degree of dispersion of a disperse phase (as in soil) influences the net result. Erlenmeyer's theory (cf. B., 1934, 214) is criticised. R. S. B.

Aerosols. H. REMY (Chem.-Ztg., 1935, 59, 465—468).—A review of the occurrence, properties, methods of study, and practical applications of aerosols is given. G. H. C.

Preparation and properties of highly concentrated sols. IV. Thorium hydroxide sol. N. R. DHAR and R. N. MITTRA (Kolloid-Z., 1935, 71, 172—176; cf. A., 1933, 123).—Sols containing up to 428 g. of ThO₂ per litre have been prepared. The coagulative effects of KBrO₃+K₂SO₄ are additive, irrespective of the ratio ThO₂/NO₃. KIO₃ and HIO₃ have abnormal coagulating powers, whence it is inferred that their solutions contain I₂O₆". The viscosity (η) and electrical conductivity increase on ageing. The η -concn. curves are very steep. F. L. U.

Influence of temperature, especially above 100°, on inorganic colloids. T. KATSURAI (Kolloid-Z., 1935, 71, 169—172; cf. A., 1934, 729).—Observations of the behaviour of various hydrosols when heated in an autoclave are recorded. F. L. U.

Viscosity and plasticity of disperse systems. IV. Plastic and viscous properties of molten slags and rocks. M. VOLAROVITSCH (Kolloid-Z., 1935, 71, 159—165; cf. this vol., 579).—The viscosity (η) of several molten slags and rocks has been measured in a concentric cylinder apparatus at temp. up to 1400°. A series of Ti slags and basic rocks gave anomalous results attributed to crystallisation of a part of the constituents. Acidic rocks gave higher vals. of η and their η -temp. curves are of the same type as ordinary glass. F. L. U.

Mechanism of emulsification by ultrasonic waves. C. BONDY and K. SOLLNER (Trans. Faraday Soc., 1935, 31, 835—843; cf. A., 1934, 26).—The formation of oil-H₂O emulsions by ultrasonic waves is due to the collapse of cavities of vapour formed by the vibrations. A similar mechanism brings about emulsification when an easily condensable vapour, e.g., steam, is introduced at the interface oil-H₂O. The effect of the presence of gases is discussed. F. L. U.

Influence of gases on mercury emulsions prepared by ultrasonic waves. C. BONDY and K. SOLLNER (Trans. Faraday Soc., 1935, 31, 843—846; cf. preceding abstract).—Ultrasonic waves cause the formation of Hg-H₂O emulsions by driving bubbles of H₂O beneath the Hg surface, where they unite and burst through a thin covering film of Hg, causing its dispersion. Emulsions so formed are quite unstable

in the absence of gases, but are stabilised by H_2 , O_2 , or N_2 , which are adsorbed at the interface.

F. L. U.

Effect of cathode rays on hydrophobic sols. (Miss) M. ANNETTS (J. Physical Chem., 1935, 39, 509—514).—The stability of both positive and negative sols decreases by bombardment with cathode rays, probably due to ionisation of the dispersion medium. The rate of heating of a sol by the rays is slightly > the rate of heating of H_2O under similar conditions. No explanation can be offered on the basis of heat changes in the sol.

M. S. B.

Depolarisation of Tyndall scattering in colloids. I. D. S. SUBBARAMAIA. II. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 1, A, 709—716, 717—722; cf. this vol., 11).—I. The depolarisation is expressed in terms of ρ_u , ρ_v , and ρ_h , where ρ is the ratio of the intensities of the weak and strong components in the transversely scattered light, and u , v , h refer to unpolarised and plane polarised light with the electric vector vertical and horizontal, respectively. Measurements have been made for S- H_2O suspensions, castor oil- H_2O emulsions, As_2S_3 - H_2O solutions, and casein solutions at various p_H vals.

II. Assuming that the total scattering arises from that due to the finite size of the particles assumed spherical and isotropic, and that due to the varying orientations of the actual non-spherical anisotropic particles, the relation $\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v)$ is derived; except for the protein solutions this agrees with the experimental data.

N. M. B.

Influence of alcohol on the viscosity of sols of benzopurpurin and chrysophenin. T. P. PAFKOVA-KVITZEL (Kolloid-Z., 1935, 71, 165—168; cf. A., 1934, 1171).—Addition of EtOH to aq. sols of the above at first reduces the structure-viscosity, which vanishes entirely over a certain concn. range. High EtOH concn. causes a further increase in viscosity without, however, the appearance of rigidity. The effects are attributed to ordered aggregation of mols. at low, and random aggregation at high, concns. of EtOH.

F. L. U.

Stability of emulsions as determined by the distribution of sizes. (Miss) S. BERKMAN (J. Physical Chem., 1935, 39, 527—539).—Distribution curves for C_8H_{18} - H_2O and "stanolax"- H_2O emulsions, with Na oleate as emulsifier, have been obtained. The influence of concn. of emulsifier, age of emulsion, and presence or absence of hydrolysis, on the distribution, has been studied. Integral distribution curves, and the corresponding differential curves, have been obtained, and are shown to reflect in their shape the influence of the various factors concerned.

M. S. B.

Lyophilic behaviour and particle size. F. L. USHER (Kolloid-Z., 1935, 71, 177—179).—When the radius of colloidal Au particles is < 18 m μ their behaviour becomes increasingly lyophilic as their size decreases, as shown by a steadily increasing divergence of the coagulating powers of Li^+ , Na^+ , and K^+ . This supports the view, for which reasons are given, that lyophilic behaviour generally is determined by a high ratio of sol. to insol. constituents of

the surface in contact with the dispersion medium, whether the former are mols., radicals, or ions.

F. L. U.

Coagulation of hydrosols of silver bromide and silver iodide. H. SCHNELLER (Kolloid-Z., 1935, 71, 180—184).—The rate of coagulation of 0.001M sols of AgBr and AgI has been studied in relation to the excess of Ag^+ or halide ion present. A max. of stability is observed with 100% excess of either ion for AgBr, and 30% for AgI. The observations are in agreement with the assumption that below the max. stability the determining factor is the stabilising charge, whereas above the max. instability is due to recrystallisation occasioned by increased solubility.

F. L. U.

Action of alcohol on gum arabic sols studied by the polarisation of diffuse light. C. TOURNEUR (Compt. rend., 1935, 200, 1756—1757).—Sols of gum arabic become turbid on adding EtOH. This change has been followed for varying [EtOH] by measuring the intensity and polarisation of light scattered at 90° by the sol. The results are correlated with the ease of flocculation by electrolytes.

H. J. E.

Lyophilic colloids. XXIV. Specific influences of cations in the auto-complex flocculation of negatively-charged lyophilic colloids (gum arabic sol + neutral salt + alcohol). H. G. B. DE JONG and R. STROOP (Kolloid-Beih., 1935, 42, 96—108; cf. this vol., 32).—The influence of the cation decreases in the order: $Al^{+++} > Ce^{+++} > La^{+++} > Co(NH_3)_6^{+++} > Pb^{++} > UO_2^{++} > Cu^{++} > Cd^{++} > Zn^{++} > Co^{++}$, $Ni^{++} > Mn^{++}$, $Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > Ag > K > Na > NH_4^+ > Li^+$. Assuming that the polarisability of the CO_2 group of gum arabic is > that of H_2O or EtOH, these results can be explained in terms of the charge, radius, and polarisation of the ions.

E. S. H.

Migration studies with colloids. III. Behaviour of gelatin-protected ferric oxide and manganese dioxide sols. F. HAZEL and G. B. KING (J. Physical Chem., 1935, 39, 515—526).—The migration velocities of gelatin-coated Fe_2O_3 and MnO_2 sols have been studied by an ultramicroscopic method for different concns. of gelatin and different p_H . When sufficient gelatin is added to coat the particles these have the properties of the protein. The effect of differences in valency of added electrolytes on the mobility of gelatin-coated hydrophobic sols is much < their effect on adsorption by the uncoated particles. When electrolyte solutions and gelatin of the same p_H are mixed, the $[H^+]$ changes in the direction of the isoelectric point, and the order of the electrolytes in altering p_H is the same as their effectiveness in decreasing the mobility of gelatin-protected particles. This change in acidity is explained by the assumption that salts disperse the protein into smaller particles with the resultant increase in total no. of active groups.

M. S. B.

Highly polymerised compounds.—See this vol., 740, 745.

Colloid chemistry of compounds of sugars and fatty acids, particularly glucose stearate. D. SCHMALTZ (Kolloid-Z., 1935, 71, 234—235).—Glucose monostearate, m.p. 56.5—57°, forms temp.-reversible

thixotropic gels in paraffin oil. It is a good emulsifying agent, giving stable emulsions of the H_2O -in-oil type. F. L. U.

Solubility rules for cellulose derivatives. Cellulose acetate and benzylcellulose. L. CLÉMENT, C. RIVIÈRE, and A. HONNELAITRE (Bull. Soc. chim., 1935, [v], 2, 707—722).—The action of solvents on cellulose acetate and benzylcellulose (I) is related to functional groups in the (I) micelle and in the solvent mol. Viscosity data show that the dispersive power is increased in solvent mixtures containing functional groups present in the micelle (e.g., CO and OH, or C_6H_6 and OH) and also in pure solvents with functional groups in the same mol. Dispersive power is a max. for the first members of a homologous series or for the n -compound of a group of isomeric derivatives. R. S.

Dependence of the viscosity of cellulose esters on the concentration. K. HESS and W. PHILIPPOFF (Ber., 1935, 68, [B], 688—699).—Data for solutions of technical cellulose acetate fractions (I) in AcOH and of cellulose nitrate in amyl acetate are recorded. At low concn., frequently $< 0.1\%$, $\eta_{sp.} \propto c$. At higher concn. breaks occur in the $\eta_{sp.}-c$ and $\eta_{sp.}-t$ curves, but the observations are not directly comparable with those obtained by osmometric measurements. Reproducible results can be secured only if all solutions of an experimental series are prepared from a parent solution. The variability of the relation between viscosity and mol. wt. is illustrated by the behaviour of cellobiose acetate, limit dextrin acetate, and (I), which at similar concn. have the same mol. wt. (calc. with respect to C_6) whereas the η_{sp} vals. are 1 : 10 : 100. H. W.

Sol-gel transformations. I. Inverse sol-gel transformation of methylcellulose in water. E. HEYMANN (Trans. Faraday Soc., 1935, 31, 846—864).—A 1.6% aq. sol of methylcellulose (OMe 35.4%) becomes less viscous with rise of temp., and has min. η at about 46° , above which η rises rapidly and the sol sets to a gel below 50° . The transformation is reversible. The effect of salts is in general to lower the "m.p." of the gel. KI and KCNS raise it, however. The effect is due entirely to the anion, and the ordinary lyotropic series holds good. The vol. increases during the change sol \rightarrow gel. This, and the occurrence of hysteresis, are considered to indicate that gelation is accompanied by partial dehydration of the particles. F. L. U.

Hydrosols of an alcohol-insoluble plant phosphatide ("oil-free planticin"). H. G. B. DE JONG, G. VERBERG, and R. F. WESTERKAMP (Kolloid-Z., 1935, 71, 194—198; cf. following abstract).—This phosphatide, after being freed from $COMe_2$ -sol. impurities, gives clear sols which differ from those of ovoidlecithin and EtOH-sol. soya-bean lecithin in being coagulated by neutral salts with bi- or ter-valent cations in the absence of sensitising substances. The coagulating action of various salts has been studied. F. L. U.

Clear phosphatide sols from commercial phosphatide preparations. H. G. B. DE JONG, G. VERBERG, and R. F. WESTERKAMP (Kolloid-Z.,

1935, 71, 184—194; cf. A., 1931, 908).—Lecithin preps. from egg or soya bean can be obtained as clear sols under the following conditions: (1) sensitising impurities must be removed by pptn. with $COMe_2$ from the Et_2O solution; (2) a solution of the purified lecithin, of concn. $> 5\%$, in EtOH, or better Pr^iOH , must be rapidly mixed with four times its vol. of H_2O at a temp. not below 50° . F. L. U.

Isoelectric point of gelatin. K. S. LJALIKOV, I. R. PROTAS, and G. P. FAERMAN (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 615—622).—The influence of electrolytes on the p_H of the isoelectric point has been studied. Anions depress the p_H , cations exalt it. The charge and hydration of the ions influence the shift. W. R. A.

Electrolytic phenomena related to chemical associations in gelatin. (MLLE.) S. VEIL (Compt. rend., 1935, 200, 1318—1319; cf. A., 1934, 861, 1172).—Fine metallic wires immersed in two separated drops of electrolyte on gelatin form electrolytic systems, the e.m.f. of which depends on the nature of the two electrolytes, and on the concn. for the same electrolyte. N. M. B.

Isoionic point of proteins. G. SANDOR (Compt. rend., 1935, 200, 1371—1372).—In presence of electrolytes the isoionic and isoelectric points of proteins vary with the concn. and nature of the electrolytes. The p_H of serum-albumin, dialysed for 12 days, is const. at 4.8—4.89 at 18° , and independent of the concn., corresponding approx. with the isoionic point. The latter depends on the presence of neutral salts, the ions of which appear to react with those of the protein. The theory that protein chlorides, like strong electrolytes, are always completely ionised is not supported. N. M. B.

Dilatometric study of the denaturation of albumin solutions by heat. F. HAUROWITZ (Kolloid-Z., 1935, 71, 198—204).—The vol. change during denaturation of four different albumins by heat is only 0.01—0.07 c.c. per 100 g. of dried material. It is inferred that the process involves no change in hydration or in the no. of free acid and basic groups. An alternative mechanism is suggested. F. L. U.

Relations between colloidal and constitutive changes of proteins. II. Heat-denaturation of albumin outside the isoelectric region. W. PAULI and W. KOLBL (Kolloid-Beih., 1935, 41, 417—460; cf. A., 1931, 908).—Changes in $[\alpha]_D$, viscosity (η), and p_H for highly purified ovalbumin (I) and serum-albumin (II) have been correlated. From the quantities of acid and alkali needed to arrest coagulation on heating it is inferred that the negative charge on the protein must be somewhat $>$ the positive, which accords with the velocities of the oppositely charged protein ions. A possible explanation is the variation in length of the side-chains, which carry the charge. Heating in the isoelectric region to near the coagulation temp. produces no change in $[\alpha]_D$. Curves for $[\alpha]_D$, η , and Svedberg's coagulation const. at p_H 1—13 show no marked variation except at extreme vals. of p_H . The changes in $[\alpha]_D$ and p_H on heating differ in the alkali and acid regions; for (I) $\Delta p_H = 0$ at approx. p_H 1.5, 4, and 8.5 and for (II) at 2.2, 3, 8, and 13. The inhibition of coagulation by carbamide at

p_H 2—14 is explained by hydrolysis to $(NH_4)_2CO_3$. The changes of p_H with $[\alpha]_D$ suggest the union of carbamide and protein as in the formation of NH_2 -acids; $Na_4P_2O_7$ and Na salicylate act similarly. KCNS and $MgCl_2$ inhibit the coagulation of (II) but not of (I). The mutual coagulation of denatured and native albumin, and the p_H , electrical conductivity, and η of mixtures, have been studied. Native (I) exerts a disaggregating action on (II). R. S. B.

Relations between colloidal and constitutive changes of proteins. III. Casein and edestin. W. PAULI and L. HOFMANN (Kolloid-Beih., 1935, 42, 34—95; cf. preceding abstract).—The variation of $[\alpha]_D$ and η of K caseinate and edestinate with p_H and temp. and the effects of adding neutral salts, carbazide, Na salicylate, and tyophilic colloids have been investigated. Marked differences in the behaviour of the proteins are noted. Edestin forms a stable sol when added to a boiling sucrose solution. Two types of protein association are distinguished, characterised by the formation of compact and loose aggregates, respectively, and accompanied by a corresponding decrease or increase of η . E. S. H.

Modifications of periodic precipitates of the Liesegang type. G. V. STUCKERT (Invest. Labor. Quim. biol. Univ. Cordoba, 1933, 1, 208—213; Chem. Zentr., 1934, ii, 3490).—The influence of PO_4''' , F' , SO_4'' , and CO_3'' on the periodic pptn. of Ca salts in gelatin gel at varying p_H is recorded. H. J. E.

Electrokinetic potential of silver iodide. G. N. GOROCHOVSKY (J. Physical Chem., 1935, 39, 465—475).—The electrokinetic potential (ζ) of AgI sols, prepared in the presence of varying excess of either ion, has been measured electrophoretically. The ζ -concn. curves do not coincide with the endosmotic curves of Lange *et al.* (A., 1929, 758). As the concn. of dispersed AgI diminishes the $[Ag']$ necessary to charge it positively increases, and the isoelectric point is moved further from the point of equivalence in the direction of the excess of Ag' . Dilution by an iso-electrolytic solution also decreases the positive charge of the sol. Change in concn. of the dispersed phase does not cause any change in p_H . M. S. B.

Microscopical determination of electrophoresis velocities and determination of critical concentration of hydrophilic colloids. H. G. B. DE JONG and P. H. TEUNISSEN (Rec. trav. chim., 1935, 54, 460—470).—Two forms of apparatus are described and their use is exemplified by the determination of the concn. of $CaCl_2$, $LiCl$, and $NaCl$ required to flocculate lecithin. D. R. D.

Electrophoresis of sterols. II. Ergosterol. L. S. MOYER (J. Gen. Physiol., 1935, 18, 749—753).—The electrophoretic behaviour of ergosterol suspended in dil. acetate buffer at p_H 3.0—6.0 is identical with that of cholesterol (A., 1934, 1305); this is explained by similarity of preferential adsorption of H' or OH' . F. O. H.

Electrophotophoresis of antimony. G. ISSER and A. LUSTIG (Z. Physik, 1935, 94, 760—769).—Recorded data show that electrophotophoresis is not due to particles surrounded by an ionic cloud. A. B. D. C.

Application of thermodynamics to gas equilibria. A. J. RUTGERS (Z. physikal. Chem., 1935, 173, 73—88).—The mass law has been deduced by a method which utilises an equilibrium box but is valid for dissociations such as $2HCl \rightleftharpoons H_2 + Cl_2$. The reaction isotherm and isochore have also been derived for such reactions. R. C.

Activity coefficients of gases. Application to calculation of effect of pressure on homogeneous chemical equilibria and to calculation of integral Joule-Thomson effects. R. H. NEWTON and B. F. DODGE (Ind. Eng. Chem., 1935, 27, 577—581).—Good agreement with experiment is obtained for the NH_3 synthesis up to 300 atm.; at 600 atm. the agreement is fair, and at 1000 atm. marked deviations occur. The equilibrium const. for the reaction $CO + 2H_2 \rightleftharpoons MeOH$ has been calc. at 250—400° and 0—1000 atm. An approx. method is developed for calculating changes in temp. due to the Joule-Thomson effect. R. S. B.

Statistical theory of regular solutions. A. GANGULI (Current Sci., 1935, 3, 478—479).—Mathematical. W. R. A.

Virial theorem and theory of strong electrolytes. B. N. FINKELSTEIN (Proc. Camb. Phil. Soc., 1935, 31, 281—284).—Theoretical. A. J. M.

Influence of ionic environment on the dissociation of weak electrolytes. H. M. DAWSON (Proc. Leeds Phil. Soc., 1935, 3, 88—91).—Results for two kinetic methods of measuring the dissociation of AcOH in NaCl are compared with those for two potentiometric methods. All indicate that K_c is a max. when the salt solution is about 0.5N. The kinetic methods provide the more consistent results for the influence of ionic environment. W. R. A.

First dissociation constant of carbonic acid. Y. KAUKO and J. CARLBERG (Z. physikal. Chem., 1935, 173, 141—149).—From measurements of the p_H of $NaHCO_3$ solution saturated with CO_2 by potentiometric and colorimetric methods, which give concordant results, and application of the Debye-Huckel theory the val. 3.12×10^{-7} for the first thermodynamic dissociation const. at 18° has been verified. The higher val. obtained by MacInnes and Belcher (A., 1933, 904) is in error owing to uncertainties involved in their extrapolation to infinite dilution. R. C.

Dissociation constant of eugenol. G. G. RAO (J. Indian Chem. Soc., 1935, 12, 161—163).—The dissociation const. of eugenol is approx. 1×10^{-10} from the conductivity at 25° of solutions in aq. NaOH at dilutions between 9 and 48 litres. J. G. A. G.

Temperature variation of ionisation constants in aqueous solution. A. W. WALDE (J. Physical Chem., 1935, 39, 477—484).—The equation given by Harned *et al.* (A., 1934, 732), involves unjustifiable assumptions. M. S. B.

Debye theory of strong electrolytes. S. KANEKO (J. Electrochem. Assoc. Japan, 1934, 2, 348—350).—Theoretical. An expression is derived leading to the same results as those given by Gronwall's equation (A., 1927, 626). CH. ABS. (e)

Determination of ionic activities. S. VON NARAY-SZABÓ and Z. SZABÓ (*Z. physikal. Chem.*, 1935, **173**, 103—105).—Hass and Jelinek's determinations (*A.*, 1933, 26) are of doubtful val., since to derive ionic activities from e.m.f. measurements with cells with transport the precision of measurement must be at least 0.1 mv. and diffusion potentials must be taken into account. R. C.

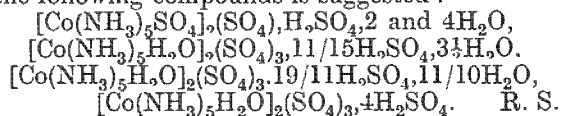
Application of the Debye theory to solutions of cadmium chloride. (MLLE.) M. QUINTIN (*Compt. rend.*, 1935, **200**, 1754—1755; cf. this vol., 826).—The Debye theory may be applied to aq. CdCl_2 ; deviations from calc. vals. occur at lower concns. than for aq. CuSO_4 . H. J. E.

Hydration of ions as a function of their electrostatic potential. H. BRINTZINGER, C. RATANARAT, and H. OSSWALD (*Z. anorg. Chem.*, 1935, **223**, 101—105; cf. this vol., 582).—The hydration of halide ions has been determined from measurements of their dialysis coeff. As with cations, the hydration is a linear function of the potential calc. from the ionic radii. F. L. U.

Composition and hydration of dissolved complex metal-thiocyanate ions. H. BRINTZINGER and C. RATANARAT (*Z. anorg. Chem.*, 1935, **223**, 106—112; cf. *A.*, 1934, 1305).—Dialysis coeffs., ionic wts., potentials, and ionic radii are given for complex (CNS) ions containing Ag, Cu^{I} , Zn, Cd, Co, Ni, Fe^{II} , Mn, Fe^{III} , Al, V, Cr, Th, and Ce. Hydrations are calc. F. L. U.

Hydration of the D' ion in heavy water and the dissociation of deutero-acids. P. GOLDFINGER and W. JEUNEHOMME (*Compt. rend.*, 1935, **200**, 1387—1389).—Existing data suggest that the free energy of the electrostatic action on a solute is about 0.05 kg.-cal. per g.-mol. less in D_2O than in H_2O , but free energy of hydration is greater in D_2O , the difference reaching 1 kg.-cal. per mol. for formation of D_3O^+ . The difference in free energy for acids and deutero-acids is of the same order. J. W. S.

Equilibria between the aquopentamminocobaltic sulphates and their sulphuric acid solutions at 45°. L. O. TAO and W. S. MO (*Bull. Soc. chim.*, 1935, [v], **2**, 911—916; cf. *A.*, 1929, 1409).— H_2SO_4 concns. up to 15*M* have been employed and the equilibria attained after prolonged stirring at 45° studied by Schreinemaker's method. The formation of the following compounds is suggested:



Cuprammonium compounds. III. Electro-metric determination of the complexity constants of cuprammine ions and of the equilibrium between cupro- and cupri-ammonium complexes in presence of copper. Light absorption of cuprammine ions. J. BJERRUM (*Kong. dansk. Vidensk. Selsk., mat.-fvs. Medd.*, 1934, **12**, No. 15, 63 pp.; *Chem. Zentr.*, 1934, ii, 3491—3492).—Results with a Cu amalgam electrode are recorded. Even at

high $[\text{NH}_3]$ the diammine complex is formed. The cuproammines are much more stable than the cupriammines. Absorption curves of $\text{Cu}(\text{NO}_3)_2$ in aq. NH_3 are described. H. J. E.

Refractometric investigation of the formation in aqueous solution of compounds of higher order hitherto regarded as double salts. II. G. SPACU and E. POPPER (*Bul. Soc. Stiințe Cluj*, 1934, **8, 5—128; *Chem. Zentr.*, 1935, i, 5; cf. this vol., 162).—Complex formation has been detected in the systems CuCl_2 — CdCl_2 , NiCl_2 — CdCl_2 , CoCl_2 — CdCl_2 , MnCl_2 — CdCl_2 , BaCl_2 — CdCl_2 , CuSO_4 — K_2SO_4 , CuSO_4 — MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$ — K_2SO_4 , CuCl_2 — KCl , CdCl_2 — KCNS , FeCl_3 — KCl , BaCl_2 — KCl , and BaCl_2 — CaCl_2 , but not in K_2SO_4 — NH_4Cl , KCl — KI , CaCl_2 — KCl , RbCl — KCl , or BaCl_2 — MgCl_2 . J. S. A.**

Oxides of nitrogen. I. Binary system N_2O_4 — N_2O_5 . T. M. LOWRY and J. T. LEMON (*J.C.S.*, 1935, 692—696).— N_2O_4 and N_2O_5 give a simple f.-p. diagram, with eutectic at -15.8° containing 10.8% of N_2O_5 . F. L. U.

Potassium borates. System B_2O_3 — K_2O . A. P. ROLLET (*Compt. rend.*, 1935, **200**, 1763—1765).—Data obtained by thermal analysis are recorded. The compounds B_2O_3 · K_2O (I), m.p. 950° , $2\text{B}_2\text{O}_3$ · K_2O (II), m.p. 815° , $3\text{B}_2\text{O}_3$ · K_2O (III), decomp. before melting, $4\text{B}_2\text{O}_3$ · K_2O (IV), m.p. 857° , and $5\text{B}_2\text{O}_3$ · K_2O (V), m.p. 780° , are formed. Eutectics occur at 787° [(I)–(II)], and 770° [(II)–(III)], and transition temp. at 825° [(III) \rightarrow (IV)] and 780° [(IV) \rightarrow (V)]. H. J. E.

Equilibrium of the reaction between ferric ion and silver. W. C. SCHUMB and S. B. SWEETSER (*J. Amer. Chem. Soc.*, 1935, **57**, 871—874).—The equilibrium $\text{Fe}^{+++} + \text{Ag} \rightleftharpoons \text{Fe}^{++} + \text{Ag}^+$ has been determined at 25° using perchlorates instead of the nitrates employed by others. The mixtures were analysed potentiometrically for Fe^{++} and Ag, using first KMnO_4 and then KSCN . Two series were carried out with a different const. ratio of HClO_4 to $\text{Fe}(\text{ClO}_4)_3$. $\log K + 2.02\mu^{\frac{1}{2}}$ was plotted against μ and extrapolated to zero ionic strength. K is 0.531 and the calc. Fe^{+++} — Fe^{++} electrode potential 0.782 volt. These are $>$ the commonly accepted vals. M. S. B.

Lowering of the ice + potassium sulphate eutectic point. H. MULLER (*Compt. rend.*, 1935, **200**, 1391—1392; cf. *A.*, 1932, 691).—The effects produced by Na_2SO_4 and Li_2SO_4 suggest that these salts are completely ionised. H_2SO_4 lowers the eutectic point almost linearly with concn., but the reduction is not linear with KNO_3 or NH_4Cl . J. W. S.

Mechanism of displacement of noble metals from solutions of their salts by hydrogen under pressure. I. Displacement of palladium from solutions of palladium chloride. II. Displacement of noble metals from solutions of H_2 · PtCl_6 , H_2 · IrCl_6 , Na_3IrCl_6 , and Na_3RhCl_6 . V. V. IPATIEV and V. G. TRONEV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **1**, 622—626, 627—632).—I. In HCl solution the following equilibria are established: H_2 · PdCl_4 , $2\text{H}^+ + \text{PdCl}_4^{--} \rightleftharpoons \text{PdCl}_4^{--} \rightleftharpoons \text{Pd}^{++} + 4\text{Cl}^-$. H_2 gives rise to the reaction $\text{Pd}^{++} + \text{H}_2 \rightarrow \text{Pd} + 2\text{H}^+$. Excess of HCl retards the separation of Pd and dissolves finely

divided Pd. NaCl , MgCl_2 , NiCl_2 , AlCl_3 , and CuCl_2 do not retard the separation, but H_2CrO_4 , FeCl_3 , and HgCl_2 suppress it entirely.

II. The results of similar experiments with H_2PtCl_6 , H_2IrCl_6 , Na_2IrCl_6 , and Na_2RhCl_6 are discussed.

W. R. A.

System bismuth iodide-sodium iodide-water. (MLLE.) M. L. DELWAULLE (Compt. rend., 1935, 200, 1401—1403).—The only double salts formed at 12—60° are $\text{BiI}_3 \cdot \text{NaI} \cdot 6\text{H}_2\text{O}$ and $\text{BiI}_3 \cdot \text{NaI} \cdot 8\text{H}_2\text{O}$.

J. W. S.

Ternary system Na_2SO_4 - NaBrO_3 - H_2O and a sixth possible type of solid solution formation between two components in the Roozeboom classification. J. E. RICCI (J. Amer. Chem. Soc., 1935, 57, 805—810).—The data at 25° (A., 1934, 365) are supplemented by measurements at 10°, 30°, 37.5°, 45°, and 52°. No double compounds are observed, but solid solutions with 2—10% NaBrO_3 at 37.5° and 2—19% at 52° are formed between anhyd. Na_2SO_4 and NaBrO_3 . These solutions may exist in equilibrium with the pure solid components. This is shown to be possible thermodynamically and represents a sixth type in addition to Roozeboom's five types.

M. S. B.

Solid-liquid equilibria in systems of three organic components. I. K. HRYNAKOVSKI and M. SZMYT (Z. physikal. Chem., 1935, 173, 150—163).—The equilibrium diagrams of the systems resorcinol-quinol-NHPhAc, resorcinol- $\text{CO}(\text{NH}_2)_2$ -BzOH, and NHPhAc-salicylic acid-antipyrine have been obtained. With all these systems there is complete miscibility in the molten state and no miscibility in the solid state.

R. C.

Tonometry of saline solutions. J. PERREU (Compt. rend., 1935, 200, 1588—1590; cf. this vol., 579).—The v.p. of aq. solutions of BaCl_2 , MnCl_2 , and $\text{Na}_2\text{S}_2\text{O}_3$ has been determined at 20°; heats of dissolution and differential heats of dilution of solutions of various concns. are also recorded.

J. W. S.

Heats of organic reactions. II. Hydrogenation of some simpler olefinic hydrocarbons. G. B. KISTIAKOWSKY, J. R. RUHOFF, H. A. SMITH, and W. E. VAUGHAN (J. Amer. Chem. Soc., 1935, 57, 876—882).—Heats of hydrogenation of the following homologues of C_2H_4 have been determined at 355° abs., by a method previously described (this vol., 304), with an accuracy of ± 60 g.-cal.: $\text{CHMe}:\text{CH}_2$ —30,115, $\text{CHEt}:\text{CH}_2$ —30,341, *cis*- (b.p. 3.73°, f.p. —139.3°) —28,570, and *trans*-CHMe:CHMe (b.p. 0.96°, f.p. —105.8°) —27,621, $\text{CMe}_2:\text{CH}_2$ —28,389. M. S. B.

Mobilities of organic anions. J. F. J. DIPPEY and F. R. WILLIAMS (Chem. and Ind., 1935, 54, 535—536).—A reply to Vogel (*ibid.*, 487). In the calculation of Λ_0 (this vol., 581), solvent and hydrolysis corrections had been carefully considered, and the vals. of Λ_0 for AcOH, BzOH, and *m*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CO}_2\text{H}$ agree with those found by methods involving mobilities determined by MacInnes (A., 1932, 914). E. W. W.

Measurement of the absolute rates of migration of ions by the method of moving boundaries. I. J. MUKHERJEE, R. MITRA, and A. K. BHATTACHARYYA (J. Indian Chem. Soc., 1935, 12, 177—189).—The velocity of the moving boundary between

equi-conducting aq. solutions of HCl and picric acid at 35° affords vals. of the mobility, *m*, of the picrate ion increasing from 38.3 to 42.2 ($\times 10^{-5}$) cm. per sec. per volt per cm. as the [HCl] is progressively diminished from 0.01*N* to 0.002*N*. The vals. of *m* found for Cl⁻ are markedly < those calc. by Onsager's equation, and during the course of an experiment, *m* of Cl⁻ decreases and that of the picrate ion increases correspondingly. The vals. of *m* probably depend on the potential gradient in the aq. HCl layer, and other significant factors are discussed (cf. A., 1929, 1014).

J. G. A. G.

Transfer of ions in anhydrous acetic acid solution. A. W. DAVIDSON and V. HOLM (Univ. Kansas Sci. Bull., 1933, 21, 463—477).—Transport measurements are recorded for NaOAc and NH_4OAc in AcOH, and for Na Zn acetate and $\text{NH}_4\text{Cu}^{II}$ acetate solutions. For alkali acetates the apparent transport no. of the cation is small, and decreases with dilution. This may be due to complex ion formation. In the double acetates the less positive metal does not migrate towards the anode.

CH. ABS. (e)

Conductivity and hydrolysis of sodium niobates. P. SUE (Compt. rend., 1935, 200, 1739—1741; see below).—Data are recorded. $\text{Nb}_2\text{O}_5 \cdot 3\text{Na}_2\text{O}$ is completely, $7\text{Nb}_2\text{O}_5 \cdot 6\text{Na}_2\text{O}$ strongly, and $\text{Nb}_2\text{O}_5 \cdot \text{Na}_2\text{O}$ slightly hydrolysed.

H. J. E.

Potential dissociation effect. F. MICHELS (Ann. Physik, 1935, [v], 22, 735—747).—The conductivity of AcOH under high potentials has been examined. The influence of concn. on the potential dissociation effect varies with concn. and is considerable at high concns. For KI, LiBr, CoCl_2 , $\text{Co}(\text{NO}_3)_2$, HgCl_2 and CdI_2 in COMe_2 solution the effect increases with duration of collision. It is small with uni-univalent salts, but greater with uni-bivalent salts. The effect is considerable for agar-agar and SiO_2 gel, but negligible for gelatin. With the last, however, variation of frequency is accompanied by large variation in conductivity. Technical semi-conductors show an analogous effect; it is, however, due not to ionic, but to electronic, conduction.

A. J. M.

Neutralisation of aqueous solutions of sodium niobate. P. SUE (Compt. rend., 1935, 200, 1326—1328; cf. A., 1934, 742).—The change in the conductivity during the neutralisation by HCl of solutions of $\text{Nb}_2\text{O}_5 \cdot 3\text{Na}_2\text{O}$ indicates the formation of $6\text{Nb}_2\text{O}_5 \cdot 7\text{Na}_2\text{O}$ and $\text{Nb}_2\text{O}_5 \cdot \text{Na}_2\text{O}$, crystallising with 32 and $7\text{H}_2\text{O}$, respectively.

N. M. B.

Anomalous electrical conductivity. M. USANOVITSCH (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 518—524).—A discussion of the phenomenon of decreasing equiv. conductivity with increasing dilution (*e.g.*, for the systems $\text{AsBr}_3 \cdot \text{Et}_2\text{O}$ or $\text{H}_2\text{O} \cdot \text{H}_2\text{SO}_4$). Compound formation is suggested as a general explanation of the anomalies.

H. J. E.

Electrical conductivity and chemical equilibrium of the electrolyte in gelatin solutions containing sodium, silver, and chlorine ions. W. EHRENBERG and P. WULFF (Kolloid-Beih., 1935, 42, 1—33).—The system has been investigated by measurements of conductivity, p_{H} , and Ag^+ activity, and by

chemical analysis. The conductivity of aq. NaCl is reduced by adding electro-dialysed gelatin (I): the mobility of Cl⁻ is diminished > that of Na⁺. When AgCl is shaken with (I)—NaOH, dissolution occurs and the conductivity rises. Ag₂O also dissolves when shaken with (I), giving rise to a complex univalent anion, (AgG₂)_n. The equilibrium const. for $[G]_n^{2-}[Ag^{+}][AgG_2]^{n-}$ when $n=1$ and ∞ , have been calc. E. S. H.

The antimony electrode. II. A. HOLMQUIST (Svensk Kem. Tidskr., 1935, 47, 102—112; cf. A., 1934, 492).—Measurements in air-free solution show that the potential varies with [Sb⁺⁺⁺] according to the Nernst formula. In HCl solutions more conc. than about 0.05N the solid phase Sb₂O₃ changes to Sb₄O₅Cl₃, as shown by both solubility and e.m.f. determinations. The behaviour in citrate buffers is complicated by formation of an Sb-citrate complex. The effect of O₂ in making the potential more positive appears to be connected with the formation of H₂O₂. H₂O₂ is decomposed by Sb powder, the velocity varying with p_H . R. P. B.

Effect of mechanical agitation on electrode potential. F. O. KOENIG (J. Physical Chem., 1935, 39, 455—463).—The effect of vibration on a Ag electrode in 3N- or 3.5N-KCl saturated with AgCl is to cause an immediate rise of potential to a new const. val. increasing with the frequency of the vibration up to a max. Stirring produces a similar effect which persists if air is replaced by N₂, but the electrode at rest is more positive in air than in pure N₂. The effect is completely inhibited when NaHSO₃ is added, and there is likewise no effect in aq. AgNO₃ of concn. 1tr³—1N. Procopiu's electrokinetic theory of the effect (A., 1931, 687) is discussed and it is shown that the results may be equally well explained as due to irreversible chemical processes. M. S. B.

Electrocapillary curve and its displacement with concentration and temperature. L. A. HANSEN and J. W. WILLIAMS (J. Physical Chem., 1935, 39, 439—453).—A modification of the Lippmann electrometer is described. Electrocapillary curves have been obtained for 1.0, 0.2, and 0.02M-NH₄NO₃ at 25°, 30°, and 75°. In the ascending portion of the curves, when the applied potential ϕ is low, the surface tension σ increases with rise of temp. for the same concn. At higher ϕ the curves cross, and, in the region of the max., σ falls with rise of temp. and the max. is displaced towards lower vals. of ϕ . At still higher vals. of ϕ , σ is depressed by rise of temp. Increase of concn. also decreases σ and shifts the max. towards lower vals. of ϕ . The results are discussed with reference to the decreased adsorption of anions and an increased tendency towards random distribution of solvent dipoles with rise of temp. M. S. B.

E.m.f. of cadmium chloride cells. (MILLER, M. QUINTIN (Compt. rend., 1935, 200, 1579—1580).—The e.m.f. of the cell Cd—Hg amalgam aq. CdCl₂. AgCl|Ag has been measured for [CdCl₂] of 0.001—0.1 mol. per litre at 0—45°. The results suggest that in certain regions there exists, besides the normal reaction, a reaction involving combination of CdCl₂ and AgCl. J. W. S.

Potentials of cells involving moving boundaries. F. D. MARTIN and R. F. NEWTON (J. Physical Chem., 1935, 39, 485—492).—By treating the liquid junction in a cell between two electrolytes with a common ion as a moving boundary, an equation has been deduced for the potential of the cell. Potentials of several such cells, measured immediately after the interruption of the current used to establish the boundary, are not in agreement with the equation. Possible causes have been investigated, but without success. M. S. B.

Electrochemical behaviour of ammonium amalgam under pressure. S. VON NARAY-SZABO and L. SZLATINAY (Z. physikal. Chem., 1935, 173, 89—102).—The decomp. of NH₄ amalgam can be considerably retarded by increase of pressure. The electrode potential, E_1 , at 0° under 30—600 atm. in contact with aq. NH₄Br is a linear function of the logarithm of the c.d., indicating that in the discharge of NH₄⁺ the delayed process which determines the potential of the process as a whole is NH₄⁺ → NH₄. The variation of E_1 with the concn. of the solution is qualitatively similar to what would be expected from Nernst's formula. E does not vary with the p_H unless this is so high as to prevent discharge of NH₄⁺. R. C.

Electrolytic reduction potentials of organic compounds. XXI. Ascending part of the current-voltage curve of electrolysis; "adsorption current." M. SHIKATA (J. Electrochem. Assoc. Japan, 1934, 2, 275—280; cf. this vol., 706).—Observations have been made with a series of azo-, NO₂-, and keto-compounds. The interpretation of the polarographic curves is discussed. CH. ABS. (c)

Titration curves of protein fibres. (MISS) D. J. LLOYD and P. B. BIDDER (Trans. Faraday Soc., 1935, 31, 864—868; cf. A., 1934, 488).—Acid and alkali titration curves of silk fibroin, horsehair, collagen, and solid gelatin have been determined and compared. The isoelectric range decreases in the order named. The curves show a general similarity, and indicate the presence both of salt linkings and of another type of structural cross-linking between the peptide chains. At p_H vals. < 3 and > 11.5 there is a rapid increase in the amount of acid or alkali combining which is not determined by the NH₂-acid constitution, and is accompanied by disruption of the fibre structure. F. L. U.

Surface layers on iron demonstrated by the e.m.f. of the metal immersed in water. S. PROCOPIU and D. UMANSCHI (Compt. rend., 1935, 200, 1395—1396).—Electrolytic Fe kept in H₂O for 20—80 min shows an e.m.f. of -0.11 to 0.17 volt against similar Fe newly immersed. This e.m.f. decreases and becomes zero in 40—90 min. In acidified H₂O the e.m.f. is 0.08—0.1 volt and becomes zero in 30—40 min. As a 250 m μ film of electrolytic Fe dissolves in this acidified H₂O in 20—21 hr., the thickness of the superficial layer to which the abnormal properties are due is about 8 m μ . Cu shows the same effect but to a smaller extent. The phenomenon is attributed to gases adsorbed in the surface. J. W. S.

Passivity of iron and steel in nitric acid solution. V, VI. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 374—382, 383—395).—V. The $[\text{HNO}_3]$ necessary for the appearance of passivity decreases with the vol. of solution used.

VI. Passivity appears at lower $[\text{HNO}_3]$ with increasing thickness of the test-piece. R. S.

Electric phenomena accompanying the formation of organic magnesium compounds. P. BERN (Compt. rend., 1935, 200, 1392—1394).—When electrodes of Mg and Pt are immersed in a solution of EtBr in anhyd. Et_2O , dissolution of 1 g.-atom of Mg liberates about 0.1 coulomb of electricity. The e.m.f. of the cell depends critically on the purity of the Mg. Max. current is obtained with 1 mol. of EtBr per 2 mols. of Et_2O . The conductivity of the solution increases during the reaction. The electrode potential is very low initially (0.1 volt), but increases to a max. of about 2.2 volts, and then falls to 1 volt. These results are in accord with the decomp. potential of MeMgI. J. W. S.

Recombination of hydrogen atoms. II. Relative recombination rates of atomic hydrogen and atomic deuterium. I. AMDER (J. Amer. Chem. Soc., 1935, 57, 856—858).—The rates of recombination of at. H and D have been determined by a dynamic method. $k_{\text{H}} = 2.05 \pm 0.07 \times 10^{-16}$ and $k_{\text{D}} = 1.51 \pm 0.05 \times 10^{-16}$. $k_{\text{H}}/k_{\text{D}} = 1.36 \pm 0.06$, which indicates that the at. diameter and interat. forces for H and D are equal. M. S. B.

Surface influence on certain homogeneous reactions depending on linking mechanism. M. PRETTE (Compt. rend., 1935, 200, 1321—1324).—The rise of reaction temp. and retardation of the rate of reaction of H_2O_2 mixtures, at pressures 300—700 mm., in contact with glass surfaces treated with KCl are discussed. N. M. B.

Addition of ammonia to ethylene.—See this vol., 849.

Effect of gases and vapours on the explosibility of CS_2 -air mixtures. C. RANDACCIO and S. BELLAVIA (Annali Chim. Appl., 1935, 25, 173—179).—The most explosive CS_2 -air mixture, containing 352—378 g. of CS_2 per cu. m., may be rendered harmless by addition of 55% of inert gas "burnt air," i.e., CO ,— 4N_2 . T. H. P.

Role of methyl and methylene radicals in the decomposition of methane. L. S. KASSEL (J. Amer. Chem. Soc., 1935, 57, 833—834).—The kinetics of CH_4 decomp. are best explained by the CH_3 mechanism (cf. A., 1932, 1209) rather than by the Me mechanism of Rice *et al.* (this vol., 191) based on the use of Te mirrors. M. S. B.

Action of bromine on butadiene. G. B. HEISIG and J. L. WILSON (J. Amer. Chem. Soc., 1935, 57, 859—863).—The rate of reaction between equiv. amounts of butadiene and Br has been determined in small, medium, and large spheres on glass and paraffin surfaces. The rate increases until the v.p. of $\alpha\beta$ -dibromobutene formed is reached and the walls are covered by a unimol. layer: it then becomes const. The results indicate a wall reaction, where, however,

the wall is covered with the condensed product of the reaction. M. S. B.

Kinetics of the decomposition of gaseous glyoxal. E. W. R. STEADIE, W. H. HATCHER, and J. F. HORWOOD (J. Chem. Physics, 1935, 3, 291—295).—The reaction at 410—450° is homogeneous and of the first order, but C and tar are deposited and the results are variable. Three modes of decomp. appear to occur. If $(\text{CHO})_2$ is an intermediate product in the oxidation of C_2H_4 , it must be oxidised and not decomposed during the reaction, since no appreciable quantities of C or tar are formed. M. S. B.

Thermal decomposition of acetone vapour. C. A. WINKLER and C. N. HINSHELWOOD (Proc. Roy. Soc., 1935, A, 149, 340—354).—The kinetics of the decomp. of COMe_2 have been re-investigated by a method involving the measurement of the rate of disappearance of the unchanged COMe_2 . The reaction is first order for initial pressures >100 mm., and the new velocity coeffs. are given by $\log_e k = 34.34 - 68,000/RT$. The products of reaction at various stages have been analysed and the intermediate formation of keten has been studied quantitatively. In the range 100—2.5 mm. the curve of $1/t_{1/2}$ against initial pressure shows a composite form similar to that shown by the curves for N_2O and certain aldehydes. The energy of activation falls slightly at lower pressures. The influence of surface and vessel size shows the reaction to be almost entirely homogeneous. L. L. B.

Thermal decomposition of acetaldehyde. C. A. WINKLER and C. N. HINSHELWOOD (Proc. Roy. Soc., 1935, A, 149, 355—359).—A study of the influence of surface and vessel size yields no evidence that the reaction $\text{MeCHO} = \text{CH}_2 + \text{CO}$ is appreciably heterogeneous, or that it depends on a chain mechanism. Chemical analysis shows that the rate of reaction of MeCHO can be followed accurately by the rate of pressure increase. L. L. B.

Applications of the transition state method to calculation of reaction velocities, especially in solution. M. G. EVANS and M. POLANYI (Trans. Faraday Soc., 1935, 31, 875—894).—The reaction velocity coeff. of a chemical reaction, excepting a chain reaction or one the velocity of which is determined by the rate of energy supply, can be put $= k/K^{\ddagger}$, where K is the "equilibrium const. of the transition state" and v is the thermal velocity of the representative point of the reacting system at the top of the energy barrier. The special case of the effect of hydrostatic pressure on reaction in solution is worked out in detail. F. L. C.

Orientation effects in bimolecular reactions. J. M. STURTEVANT (J. Chem. Physics, 1935, 3, 295—299).—Theoretical. Deviations from Bronsted's limiting formula for bimol. ionic reactions in solution cannot be explained by variations with concn. of electrostatic orientation effects due to lack of symmetry in the ions, as suggested by La Mer *et al.* (A., 1931, 1132). M. S. B.

Kinetics of the alkaline hydrolysis of ethyl carbonate and of potassium ethyl carbonate.

N. F. MILLER and L. O. CASE (J. Amer. Chem. Soc., 1935, 57, 810—814).—The rate of reaction between Et_2CO_3 and KOH has been measured at 25° and 35°. A bimol. followed by a unimol. reaction takes place, $\text{Et}_2\text{CO}_3 + \text{KOH} \rightarrow \text{KETCO}_3 + \text{EtOH}$ and $\text{KETCO}_3 + \text{H}_2\text{O} \rightarrow \text{KHCO}_3 + \text{EtOH}$. Both velocity coeffs. have been determined by two methods which give satisfactory agreement. The temp. coeffs. for the two reactions for the 10° interval are 2.06 and 3.46, respectively. M. S. B.

Velocity of hydrolysis of dithionic acid. J. MEYER (Z. anorg. Chem., 1935, 222, 337—344).—Hydrolysis of $\text{H}_2\text{S}_2\text{O}_5$ proceeds as a unimol. reaction between 60° and 100°. It is catalysed by H^+ and the velocity $\propto [\text{H}^+]$. The temp. coeff. for 10° decreases from 3.7 at 60° to 2.7 at 100°. The undissociated mol. alone undergoes hydrolysis. F. L. M.

Kinetics of reaction between potassium thiocyanate and iodine in aqueous solution. R. O. GRIFFITH and A. McKEOWN (Trans. Faraday Soc., 1935, 31, 868—875).—The reaction has been studied in acetate, phosphate, oxalate, and phthalate buffers, in none of which is a simple kinetic equation obeyed. A possible mechanism is suggested. F. L. U.

Reaction of hydrogen chloride with methyl alcohol. C. N. HINSHELWOOD (J.C.S., 1935, 599—601).—The difference in the activation energies involved confirms that the mechanism of the interaction of H halides with simple alcohols differs from that of the esterification of carboxylic acids. Data are given for the reaction between HCl and MeOH. J. W. S.

Factors determining velocity of reactions in solution. Molecular statistics of the esterification of carboxylic acids. C. N. HINSHELWOOD and A. R. LEGARD (J.C.S., 1935, 587—596).—From a study of the rates and energies of activation (E) of 15 esterification reactions, it is concluded that for a series of alcohols the changes in rate are determined, not by the const. P in the formula $\text{rate} = PZ e^{-E/RT}$, but by variations in E . Similarly for a series of acids. In general large vals. of E are associated with large vals. of P . On changing from a non-ionic catalyst to H^+ , P increases by about 10^4 , but differences between individual non-ionic catalysts seem to depend on the val. of E . Steric hindrance appears to depend on high E rather than on purely geometric factors. No positive evidence is obtained that the rate of esterification reactions depends on quantum-mechanical transition probabilities, or that the smallness of P in such reactions is connected with smallness of such probabilities rather than with the necessity for accurate orientation of the mols. at the moment of reaction. J. W. S.

Action constant, heat capacity, and energy of activation in the saponification of the esters of *o*-phthalic, 3- and 4-nitro-*o*-phthalic acids. G. SEMERANO (Gazzetta, 1935, 65, 252—272; cf. A., 1931, 1241).—Velocity coeffs. for 0—100° have been measured, and energies of activation calc. The stereokinetics of the reactions are discussed. O. J. W.

Rate of decomposition of some *p*-substituted nitrosoacetanilides in benzene. W. S. M. GRIEVE and D. H. HEY (J.C.S., 1935, 689—691).—The stability of substituted PhN_2 salts follows the order $p\text{-OMe} > p\text{-Cl} > p\text{-Br} > p\text{-Me} > \text{H} > m\text{-Me}$, the reverse of the order for substituted Na benzenediazotates. Substituted nitrosoacetanilides, which may be in tautomeric equilibrium $\text{Ar}\cdot\text{N}(\text{Ac})\cdot\text{NO}$ \rightleftharpoons $\text{Ar}\cdot\text{N}(\text{N}=\text{O})\cdot\text{OAc}$, follow the order of stability $p\text{-Cl} > p\text{-Br} > \text{H} > p\text{-Me}$, but the differences in the unimol. velocity coeff. for the decomp. are small. J. W. S.

Complex formation between polynitro-compounds and aromatic hydrocarbons. I. Finite reaction rates. D. L. HAMMICK and G. SIXSMITH (J.C.S., 1935, 580—584).—Crystallisation of a mixture of 1 mol. of Me 4 : 6 : 4' : 6'-tetranitrodiphenate with 4 mols. of indene (I) yields the compound $2\text{C}_{16}\text{H}_{10}\text{O}_{12}\text{N}_4\cdot\text{C}_9\text{H}_8$ (II), m.p. 159° (corr.), which does not react with Br in CCl_4 solution, but is decomposed into its constituents on recrystallisation from MeOH in absence of excess of (I). The rate of formation and decomp. of (II) in solution have been investigated and the equilibrium consts. of the steady state reached evaluated on the supposition that in solution combined (I) is mainly in the form of (II). J. W. S.

Oxidation velocities of some unsaturated hydrocarbons with peracetic acid in acetic acid solution. J. STUURMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 450—452).—The bimol. coeffs. (k) for the reaction between unsaturated hydrocarbons and AcO_2H in AcOH have been determined at 25–8°, the reaction being $>\text{C}:\text{C}< + \text{AcO}_2\text{H} = \text{O} < \text{C} < + \text{AcOH}$. AcO_2H was determined by liberation of I from KI. Replacement of H by Me increases $\log k$ by the same amount in all cases, but this does not hold for replacement of H by Ph. R. S. B.

Kinetics of the nitration of benzene. F. H. COHEN and J. P. WIBAUT (Rec. trav. chim., 1935, 54, 409—427).—The reaction in Ac_2O is of the first order with respect to C_6H_6 and third order to HNO_3 catalysed by HNO_3 , when effects of reaction with solvent were eliminated (formation of AcNO_3 and other products). Velocity coeffs. were found for 0°, 18°, and 25° and activation energies calc. AcNO_3 does not nitrate C_6H_6 in Ac_2O , nor does HNO_3 in glacial AcOH. HNO_3 nitrates C_6H_6 in CCl_4 in presence of a trace of Ac_2O , but the reaction is stopped by much Ac_2O . D. R. D.

Detonation of nitrogen iodide, $\text{NI}_3\cdot\text{NH}_3$. W. E. GARNER and W. E. LACHEM (Nature, 1935, 135, 832).—When moist $\text{NI}_3\cdot\text{NH}_3$ is suspended over P_2O_5 and the vessel evacuated by a Hg-vapour pump, the crystals detonate as soon as they are dry. Decomp. into I and permanent gases occurs without detonation if the pressure of the latter is kept $> 2 \times 10^{-3}$ cm. At room temp., decomp. is complete in 12—24 hr. At –20°, there is little reaction until H_2O is removed, after which the pressure rises linearly. As I condenses on the vessel the rate of gas evolution decreases and pressure ultimately becomes const., although some $\text{NI}_3\cdot\text{NH}_3$ is still undecomposed. The residue

then detonates when a high vac. is effected. The thermal reaction is retarded by H_2O and by the easily condensable products of decomp., and on removal of these $NI_3 \cdot NH_3$ detonates spontaneously. This accounts for its extreme sensitivity to a blow which creates fresh, unstable surfaces. L. S. T.

Mechanism of the thermal decomposition of active and inactive iron nitrides. N. I. KOBOSEV, B. V. JEROFEJEV, and S. I. SLUCHOVSKI (Z. Elektrochem., 1935, 41, 274—284).—The kinetics of the decomp. of Fe_2N (I), activated by Al_2O_3 for NH_3 synthesis, and of inactive Fe_2N (II) and Fe_3N (III) have been investigated at 300—600°. The reaction is not autocatalytic and the velocity of decomp. of (I) is 5—6 times that of (II) and (III). The surface N is present as adsorbed NH_3 . In (II) and (III) diffusion takes place from the interior to the surface, but in (I) this is restricted by the action of Al_2O_3 . As a result the mechanism of the reaction in (II) and (III) undergoes a sharp change at about 400°, but not in (I). The surface of (I) is about 8 times that of (II). The velocity coeffs. ($\times 10^{-8}$) of surface decomp. are (I) 6.9, (II) 8.4, (III) 27.8, and the true activation energies, when allowance has been made for the diffusion energy, are practically the same. Al_2O_3 has, therefore, practically no direct action on the Fe catalyst in NH_3 synthesis, but acts by increasing the surface as a result of its influence on the crystal lattice (cf. Natanson, this vol., 812). It probably inhibits diffusion by its adsorption on the diffusion centres, and similarly inhibits the recrystallisation of Fe during formation of the nitride. Nitride decomp. does not appear to take place at definite active centres, but over the whole surface. M. S. B.

Supercooling capacity of water and linear velocity of crystallisation of ice in aqueous solutions. G. TAMMANN and A. BÜCHNER (Z. anorg. Chem., 1935, 222, 371—381).—Purified H_2O can be supercooled 14—19° with a cooling rate of 0.4—1.0° per min., and nearly pure D_2O slightly less. Powdered cryst. quartz and powdered vitreous SiO_2 diminish the supercooling possible by 6—7°, whilst corundum has no effect. The velocity of crystallisation of ice has been measured for a no. of solutions of electrolytes and non-electrolytes. At low concns. HCl , $NaCl$, $NaOH$, and sucrose increase the velocity. F. L. U.

Decomposition of nitric esters at low temperatures. LAMBREY (Mem. Poudres, 1934—1935, 26, 101—118).—Full details are given of results already noted (A., 1934, 1312). The rate of decomp., r , of guncotton (I) (60%) + glyceryl trinitrate (40%) at 30° is $>$ that of (I) at 36.5°. For pentaerythritol tetranitrate r is negligible at 43°. J. G. A. G.

Kinetics of the decomposition of diphenyliodonium iodide. C. J. M. FLETCHER and C. N. HINSHELWOOD (J.C.S., 1935, 596—599).—The activation energy for decomp. of $Ph_2I \cdot I$ is 26,300 g.-cal. for the solid state and 27,000 g.-cal. (uncorr. for change in viscosity) for solutions in PhI . Solubility data for $Ph_2I \cdot I$ in PhI are given for 0—95°. The rates of reaction observed are discussed in relation to different activation mechanisms. J. W. S.

Reaction rates of solid-liquid interfaces. C. V. KING (J. Amer. Chem. Soc., 1935, 57, 828—831).—The experimental results of Fage *et al.* (Proc. Roy. Soc., 1932, A, 135, 828—831) on fluid motion near a solid surface have been applied to the comparison of the rate of convection of fluid towards the surface with the rate of dissolution of Mg and Zn in acids under identical conditions. The results indicate that convection is negligible and that the acid reaches the metal surface by diffusion. Nernst's diffusion theory is criticised and modifications are suggested. M. S. B.

Mechanism of ionisation of hydrogen at a platinum electrode. J. HORIUTI and M. POLANYI (Mem. Manchester Phil. Soc., 1935, 78, 47—54).—The rate of ionisation of D_2 in $EtOH-KOH$ was determined. If the rate is expressed in terms of first order reaction consts., $k \propto (\text{pressure})^{-\frac{1}{2}}$, but in $EtOH-KOH$ solution only. The rate increases with rise of temp. according to Arrhenius' law. The activation energy of the ionisation process is slightly $> 10,200$ g.-cal. A. J. M.

True activation energy of the desorption of the ketonic group from graphite. V. SIHVONEN (Suomen Kem., 1935, 8, B, 28).—A summarising discussion (cf. A., 1934, 978). R. S. B.

Catalysis of ester hydrolysis by D_3O^+ ions. J. C. HORNEL (Nature, 1935, 135, 909).—Determinations of the rate of hydrolysis of $MeOAc$ in H_2SO_4 solutions show that the ratios of the catalytic coeffs. in heavy and light H_2O are $k_{D_3O^+}/k_{H_3O^+} = 1.86$ at 15° and 1.68 at 25°. These ratios are practically equal to those found for the inversion of sucrose (A., 1934, 1075). L. S. T.

Effect of electrolytes on the rate of hydrolysis of diethyl acetal. L. C. RIESCH and M. KILPATRICK (J. Physical Chem., 1935, 39, 561—569).—The primary kinetic salt effect in the hydrolysis of Et_2 acetal by strong acids in aq. solution has been determined for $NaClO_4$, $LiCl$, $NaCl$, KCl , $LiNO_3$, NH_4NO_3 , KNO_3 , $C_6H_5Me \cdot SO_3Na$, and $PhSO_3Na$. The average val. of k_{35}/k_{25} is 3.395 and the heat of activation is independent of the electrolyte concn. within the limits of experimental error. M. S. B.

Magnetic investigations of the mechanism of oxidation. O. BAUDISCH (Ber., 1935, 68, [B], 769—775).—Many examples are cited in favour of the view that the intermediate, intensely coloured, labile products obtained by the catalytic oxidation of nitrogenous compounds with $Fe(CN)_5$ compounds are $Fe \cdot NO$ derivatives which exert a very marked influence on the magnetic state of the central atom and play a part in the mechanism of oxidation. H. W.

Catalytic hydrogenation of unsaturated organic compounds by means of selenium. M. YOKOYAMA and M. KOTAKE (Bull. Chem. Soc. Japan, 1935, 10, 138).—Unsaturated org. acids, e.g., oleic acid, when heated with Se at 300° for 1—1.5 hr. are partly reduced. R. S. B.

Reaction between nitrous oxide and hydrogen on platinum. J. K. DIXON and J. E. VANCE (J. Amer. Chem. Soc., 1935, 57, 818—821).—The reac-

tion on smooth Pt wire has been studied at 260–271° by a flowing method. The rate approx. \propto the N_2O pressure and is nearly independent of the H_2 pressure. H_2O inhibits the reaction slightly. The energy of activation is 23,100 g.-cal. The possible factors governing the rate of reaction are discussed.

M. S. B.

Reaction velocity and quantity of catalyst. J. SIRKIN and V. G. VASSILIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 513–517).—Bredig and Berneck's observations on the effect of the quantity of Pt on the rate of decomp. of H_2O_2 (A., 1900, ii, 213), were confirmed, using Pt deposited on SiO_2 gel. The same wt. of Pt distributed over varying amounts of gel has approx. the same activity. The application of the chain theory to surface reactions is suggested.

H. J. E.

Effect of salts and gelatin on the catalytic decomposition of hydrogen peroxide by activated sugar charcoal. D. FOWLER and J. H. WALTON (Rec. trav. chim., 1935, 54, 476–480).—Gelatin (0.1%) inhibits the decomp., and the effect is enhanced by $NaNO_3$, KCl , $BaCl_2$, K_2HPO_4 , and KH_2PO_4 at low concns. At higher salt concns., the velocity is increased. The first three salts exert no effect alone. The temp. coeff. of the reaction is slightly >1 .

D. R. D.

Effect of arsenic on corrosion of iron by sulphuric acid.—See B., 1935, 498.

Effects of fluorides on thermal synthesis of calcium aluminates. II. S. NAGAI and T. YOSHURA (J. Soc. Chem. Ind. Japan, 1935, 38, 157–160B; cf. A., 1934, 49).—The interaction of $CaCO_3 + Al_2O_3$ (1:1) at 1000–1350° is accelerated by the presence of 1% of CaF_2 , the temp. of reaction being lowered by 100–150° at the lower temp. The ratio $CaO : Al_2O_3$ is at first >1 , but afterwards decreases as the reaction is completed.

J. A. S.

Catalytic oxidation action of colloids. III. Y. SHIBATA and K. YAMASAKI (Bull. Chem. Soc. Japan, 1935, 10, 139–144).—Au and Ag sols have scarcely any influence on the O_2 uptake-time curve of alkaline pyrogallol at 25°. Pt sol greatly accelerates O_2 absorption in the order of effectiveness: sol prepared by reduction of H_2PtCl_6 by $CH_3O >$ Bredig sol $>$ sol prepared by reduction by illuminating gas. The red Pt sol prepared by reducing H_2PtCl_6 with CO gives irreproducible results, but the black sol formed from it gives results similar to those for the other Pt sols.

R. S. B.

Influence of a metal surface on the kinetics of oxidation of ethane. E. A. ANDREEV (Compt. rend. Acad. Sci., U.R.S.S., 1935, 1, 610–615).—Oxidation of a stoichiometric $C_2H_6-O_2$ mixture in a quartz vessel exhibits an upper pressure limit for the combustion. Experiments were made at 61 and 91 mm. at 652°. The curve showing the kinetics of the combustion at 61 mm. can be divided into three sections: (a) C_2H_6 oxidises with increase of pressure and H_2O and CO are formed in large quantities; (b) pressure remains const. for a time; then there is a flash followed by diminution in pressure due to CO being oxidised to CO_2 ; (c) slow oxidation of CO .

At initial pressure of 91 mm. no explosive oxidation of CO is evidenced, indicating that the kinetics are different in spite of good agreement for the final val. of CO_2 . Introduction of metal wire accelerates the reaction. The oxidation of a hydrocarbon presumably takes place in two stages; the first stage being the formation of CO , aldehydes, etc. which are ultimately converted into CO_2 .

W. R. A.

Hydrogenation by adsorbed hydrogen atoms. K. S. ABLEZOVA and S. Z. ROGINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 490–493).—At. H adsorbed on a relatively inactive Cu or Ni film at -180° will hydrogenate C_2H_4 . No reaction was observed with H adsorbed on glass. On treating a Ni film at -180° in succession with at. H and C_2H_4 , and warming, no gas evolution took place at room temp. C_2H_6 was evolved at a higher temp. Intermediate compound formation is suggested.

H. J. E.

New type of promoter. K. S. ABLEZOVA and S. Z. ROGINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 487–490).—In preparing Ni or Pt catalyst for the hydrogenation of C_2H_4 by evaporation of a Ni or Pt wire in vac., a much greater activity of the metal film resulted if evaporation took place in presence of a small amount of gas. Fresh quantities of gas were added as clean-up by the metal occurred. O_2 , N_2 , or H_2 was equally effective as promoter. The role of the added gas is discussed.

H. J. E.

Zinc oxide as catalyst. A. SCHLEEDÉ, M. RICHTER, and W. SCHMIDT (Z. anorg. Chem., 1935, 223, 49–83).—The catalytic activity of differently prepared specimens of ZnO in promoting decomp. of $MeOH$ has been studied in relation to their fluorescence and sp. surface. ZnO prepared by heating $Zn(NO_3)_2$ shows red fluorescence and is almost inactive, whereas that prepared by heating hydrated ZnO or $ZnCO_3$ is very active but shows no fluorescence. By varying the conditions of prep. specimens with intermediate properties can be obtained. The active products have a looser structure with greater internal surface than the inactive.

F. L. U.

Synthesis of higher paraffins from water-gas. Use of promoters for activating iron-copper catalyst.—See B., 1935, 484.

Synthesis of benzene from carbon monoxide by catalytic reduction under atmospheric pressure. III. Influence of gas velocity.—See B., 1935, 484.

Catalytic properties of rhenium. M. S. PLATONOV, S. B. ANISSIMOV, and V. M. KRASCHENINNIKOVA (Ber., 1935, 68, [B], 761–765).—At 15–20°/1 atm. finely-divided Re causes very slow hydrogenation of maleic acid or cyclohexene (I). At 150°, reduction of (I) in presence of Re-clay (II) is very slow, whereas at 250° cyclohexane is produced. C_6H_6 is unaffected by (II) at 100° or 150°, whereas at 200° partial decomp. occurs with evolution of CH_4 . At 250°, $PhNO_2$ is appreciably reduced to NH_2Ph , whilst at 300° the reaction is violent. Max. production of NH_3 from NO (50.4%) is observed at 400°, free N_2 being also produced. $MeCHO$ is formed from $EtOH$ in 11–12% yield at 300° and 14% yield at 600°, the

curve of the contact process appearing to exhibit 2 maxima. With rise of temp. the % of CH_4 in the gases increases; CO first increases and then slowly diminishes. As oxidising catalyst Re has the disadvantage of yielding readily volatile oxides.

H. W.

Electrolytic production of heavy water. Y. HORI (J. Electrochem. Assoc. Japan, 1934, 2, 290—297).—Processes are reviewed. Electrolysis in 4 stages of H_2O containing 0.07% D_2O gave a concn. of 66.7% D_2O . CH. ABS. (e)

Influence of the cation on the electrolytic formation of persulphate. O. ESSIN and E. ALFIMOVA (Z. Elektrochem., 1935, 41, 260—265).—The electrolytic production of the persulphates of K, NH_4 , Al, Na, Mg, and Zn has been studied. The results are in agreement with previous observations (A., 1933, 34; 1934, 38) on the dependence of current yield on the concn. of SO_5^{2-} , SO_4^{2-} , and $\text{S}_2\text{O}_8^{2-}$. The cations have, in general, a catalytic influence on the different reactions taking place at the anode. M. S. B.

Electrolytic production of lithium.—See B., 1935, 502.

Electrodeposition of copper-nickel-zinc alloys from cyanide solutions.—See B., 1935, 554.

New electrolytic experiment. P. JOLIBOIS (Compt. rend., 1935, 200, 1469—1470).—If, in the electrolysis of aq. CuSO_4 or aq. AgNO_3 , the cathode is raised approx. 1 mm. above the surface of the solution and a sufficiently high potential is applied to cause a spark discharge to cross the gap, $\text{Cu}(\text{OH})_2$ and Ag_2O , respectively, are deposited in the cathode solutions. It is concluded that the separation of Cu and Ag observed under ordinary conditions is due to a secondary reaction with the H_2 from the electrolytic decomp. of H_2O . With the arrangement described H_2 escapes. The experimental result supports the theory of the existence of an envelope of H_2O around the ions. M. S. B.

Electrodeposition of silver from iodide solutions.—See B., 1935, 555.

Existence of an oxide film on gold. W. J. MULLER and E. LOW (Ber., 1935, 68, [B], 989—991).—Observation of a Au anode under the polarising microscope during electrolysis in 5N-HCl with a Pt gauze cathode shows the metal to be covered with a strongly reflecting or absorbing layer which is removed during electrolysis; its disappearance is followed by a non-polarising, strongly reflecting secondary film which by analogy with observations on chemical passivity can consist only of a Au oxide or hydroxide. Similar observations of a clean Au surface show the metal to acquire slowly an oxide film when exposed to air. H. W.

Cadmium-zinc alloy plating from acid sulphate solutions.—See B., 1935, 555.

Alkali zincate storage battery with the cathode filled with zinc powder.—See B., 1935, 507.

Electrolytic separation of tantalum. M. L. HOLT (Z. Elektrochem., 1935, 41, 303—304).—Repetition of the experiments of Isgarischev *et al.* (A., 1934, 852) failed to give any separation of Ta

from solutions of the composition employed by them. M. S. B.

Theory of chromium electrodeposition.—See B., 1935, 554.

Behaviour of sodium sulphite in the cathodic discharge of hydrogen ions. F. TODT (Z. Elektrochem., 1935, 41, 270—273).—The increase in the velocity of dissolution of Fe, observed on the addition of Na_2SO_3 (I) (cf. A., 1934, 973), takes place at $p_{\text{H}} < 7-8$ only, and becomes more marked as the p_{H} diminishes. (I) also increases the current strength between Fe and Pt or Cd and Pt electrodes, and acts as a poison towards the H electrode under similar conditions. These results may be explained by the oxidising action of (I) on H^+ . Fe with a high C content is much more readily dissolved than pure or even technical Fe at the same p_{H} . This is apparently due to smaller polarisability, and therefore greater facility for the discharge of H^+ at the C surface. M. S. B.

Influence of high-frequency field on the combustion of an acetylene-air mixture. V. ROSSICHIN and V. TIMKOVSKI (Nature, 1935, 135, 916).—An increase in field frequency results at first in a decreased effect of the field in reducing the velocity of combustion and then, at a frequency of 1.8×10^7 sec.⁻¹, in accelerating the velocity of combustion. In the region of ultra-short λ , the acceleration increases and finally reaches 20% at the frequency 3.4×10^7 sec.⁻¹. This effect is due presumably to a kind of resonance energy exchange between the electrons and mols. of a reacting mixture. L. S. T.

Photochemical hydrogen-oxygen reaction. H. A. SMITH and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1935, 835—840).—The photochemical combination of H_2 and O_2 by λ 1719—1725 and 1850—1862 Å. has been reinvestigated (cf. A., 1930, 871). O_3 , H_2O_2 , and H_2O were obtained with the shorter λ and O_3 and H_2O_2 with the longer. H_2O formation in the latter case was not observed, due to incomplete absorption. The effect of pressure has also been studied and a possible reaction mechanism is discussed. M. S. B.

Formation of hyponitrous acid as an intermediate compound in the oxidation of ammonia to nitrous acid.—See this vol., 787.

Influence of water on the sensitivity of photographic emulsions. A. CHARRIOU and (Mlle.) S. VALETTE (Compt. rend., 1935, 200, 1528—1530).—The sensitivity of rapid emulsions for blue rays is reduced to $\frac{1}{2}$ of its initial val. by soaking for 30 min. in H_2O . The effect is less marked for yellow and red rays and is much less on soaking in EtOH or C_2Me_2 instead of H_2O . Condensation of H_2O in aerial photography may reduce the speed of emulsions. H. J. E.

Mechanism of photographic development. Induced reduction of silver halides by sodium sulphite in presence of organic developers and influence of alkali on the reaction. K. M. PANDALAI (J.S.C.I., 1935, 54, 169—172T; cf. A., 1934, 39).—Quinol is oxidised, during the development of Ag halides, to benzoquinone (I), which reacts with

alkali sulphite to re-form quinol. (I) has no action, by itself, on Ag halides, but reduction is considerable in the presence of Na_2SO_3 . Time and temp. have no great effect on the reaction. Na_2CO_3 , alone, has a strongly accelerating influence on the reduction, but, in presence of Na_2SO_3 also, high concns. seem unfavourable. The function of the alkali is probably to increase the velocity of ionisation of the developers and maintain the physico-chemical equilibrium in the developing bath, functioning also as halogen absorbents. Some results are also given for other developers and oxidation products. The formation of quinolsulphonic acid as an intermediate product during quinol development has been proved by its isolation as the Na salt.

J. L.

Micellar theory of the latent image. F. WEIGERT (Phot. Korr., 1934, 70, Suppl. 11, 41—51; Chem. Zentr., 1935, i, 187; cf. A., 1932, 29).—A summary.

J. S. A.

Photographic activity of irradiated ergosterol.—See this vol., 857.

Photochemical reaction between iodine and oxalate. N. R. DHAR, A. K. BHATTACHARYA, and B. L. MUKERJI (J. Indian Chem. Soc., 1935, 12, 151—160).—The reaction between excess of $\text{K}_2\text{C}_2\text{O}_4$ and aq. I in the absence of KI is unimol. in the dark and semi-mol. in homogeneous radiation of λ 3125—3536 and 8500—8750 Å., and is greatly retarded by adding KI. The velocity, V , varies as powers of the absorbed light between 0.33 and 1.25, and this index and the temp. coeff., k , diminish as the acceleration produced by the radiation increases. A val. of k 8.85 has been found for the dark reaction, and in general k diminishes as λ decreases. V is increased and k is lowered by stirring the reaction mixture. The absorption of light by oxalate solutions is increased by adding I.

J. G. A. G.

Photochemical reaction between ethylene iodide and iodine in carbon tetrachloride solution. D. S. NARAYANAMURTI (J. Indian Chem. Soc., 1935, 12, 173—176).—The data of Schumacher and Wiig (A., 1931, 180) are consistent with every collision between I atoms in solution resulting in the formation of I_2 mols.

J. G. A. G.

Sensitivity of organic substances to X-rays. G. KOEGL (Fortschr. Röntgenstr., 1934, 50, 381—383; Chem. Zentr., 1935, i, 380).—Measurements with 1:4- and 1:5- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$, 1:4-, 1:5-, and 2:5- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$, and on 1:2- and 2:1-benzoquinone diazide show the effect of X-rays to be determined by the no., nature, binding, and position of the elementary constituents of the mol.

H. J. E.

Comparison between the oxidising effect of X-rays and the electric discharge on diamond and graphite. V. SIHVONEN (Suomen Kem., 1935, 8, B, 26—27).—O., at 0.04 mm., activated by X-rays or by an electric discharge for 1—3 hr., does not oxidise diamond (I) at room temp., and there is no surface corrosion. There is no reaction between (I) at room temp. and CO_2 at 0.02 mm. when activated by X-rays for 1.5 hr. With graphite (II) under the same conditions irradiation causes oxidation. Direct

exposure of the (II) in presence of O_2 gives CO_2 , but when the grains are screened by Pb, CO predominates. With coarsely powdered (II) the yield of oxidation products is increased.

R. S. B.

Chemical effects of radioactive rays. O. WERNER and V. SENFTNER (Angew. Chem., 1935, 48, 331—335).—A summary of published work.

E. S. H.

Heavy hydrogen and heavy water. E. A. HYLLERAAS (Tids. Kjem., 1935, 15, 7—11).—A review.

R. P. B.

Preparation of stable lithium iodide. Y. D. GNESIN and L. S. DOROSINSKI (Khim. Farm. Prom., 1934, No. 5, 30—32).—The cryst. LiI, after centrifuging, is fused in a SiO_2 vessel at 245—263°. This treatment insures stability.

CH. ABS. (e)

Reactions between dry inorganic salts. II. E. B. THOMAS and L. J. WOOD (J. Amer. Chem. Soc., 1935, 57, 822—827).—Previous X-ray measurements (A., 1934, 265) have been extended to cover the 18 possible double decomp. of the halides of the alkali metals in such mixtures as $\text{NaCl} + \text{KBr} \rightarrow \text{NaBr} + \text{KCl}$. 15 go to completion in the direction of diminution of the mean cube edge, and for these the algebraic sum of the heats of formation is always positive. It is invariably a member of the stable pair which has the highest m.p. of the four components concerned. In the stable pair also the heavier cation and anion unite to form one member and the lighter the other. In the case of $\text{KBr} + \text{RbCl} \rightarrow \text{KCl} + \text{RbBr}$ the average cube edge on the two sides of the equation is the same, and the X-ray data can be best explained by assuming a homogeneous solid solution of all four ions. The reactions $\text{KBr} + \text{RbI}$ and $\text{RbCl} + \text{CsBr}$, in which the algebraic sums of the heats of formation of reciprocal pairs are practically zero, do not go to completion in either direction.

M. S. B.

Borophosphates of copper and lead ($\text{M}^{\text{II}}\text{BPO}_5$). D. CHIRON and D. GRISCHOTT (Atti R. Accad. Lincei, 1935, [vi], 20, 391—394).—By fusion of the metallic oxide with B_2O_3 and P_2O_5 at 1100° the pure compounds CuBPO_5 and PbBPO_5 have been prepared. The corresponding Zn and Cd compounds contain ZnO and CdO, respectively.

O. J. W.

Salt-like properties of halogens. Products of the action of bromine on silver salts.—See this vol., 857.

Preparation of anhydrous perchlorates of magnesium and alkaline-earth metals by reactions between solids. G. F. SMITH and V. R. HARDY (Z. anorg. Chem., 1935, 223, 1—16).—By heating a finely-ground mixture of NH_4ClO_4 with MgCO_3 for 12 hr. at 250° and 1—10 mm. a 95% yield of $\text{Mg}(\text{ClO}_4)_2$ may be obtained. The yields of the Ba, Sr. and Ca compounds under similar conditions were 75%, 90%, and < 30%, respectively. Mixtures of NH_4ClO_4 with the oxides at 160° gave low yields. The yield increases with stability of the intermediate metal ammine perchlorate.

F. L. U.

Alkaline-earth metal ammine perchlorates. G. F. SMITH and E. G. KOCH (Z. anorg. Chem., 1935, 223, 17—27; cf. preceding abstract).—*Ammine*

perchlorates of Ca, Sr, and Ba having the following nos. of NH_3 mols. have been prepared: Ca 2, 4, 6; Sr 2, 6, 7; Ba 2, 6. The existence of di- and hexammine Mg perchlorates is confirmed. Dissociation pressures, solubility in Et_2O , and vals. of d_4^{25} are recorded. In all the hydrated perchlorates H_2O can be completely displaced by a stream of dry NH_3 , the hexammine salt being formed in each case. F. L. U.

Calcium aluminate. IV. Properties of aluminium hydroxide crystallising from calcium aluminate solutions. G. ASSARSSON (Z. anorg. Chem., 1935, 222, 321—336; cf. A., 1933, 1119).—Hydrated Al_2O_3 crystallising from aq. Ca aluminate has been examined chemically, microscopically, and by X-rays. Very unstable solutions give a granular ppt. containing about 4 mols. H_2O between 5° and 50° , the proportion decreasing to about 3 as 90° is approached. From less unstable solutions flakes, needles, plates, or spherites are obtained according to the conditions. All specimens show the structure of hydrargillite, except the needles, which appear to contain 4 mols. of H_2O . Optical data are recorded. F. L. U.

Ammoniates of alkaline-earth nitrates. M. A. PORTNOV and A. M. JURAYEV (Z. anorg. Chem., 1935, 223, 45—48; cf. this vol., 159).—Nitrates of Ca, Sr, and Ba form compounds below 0° with 4 and 8 mols. of NH_3 . They are unstable at room temp. F. L. U.

Boron arsenate. G. E. R. SCHULZE (J. Amer. Chem. Soc., 1935, 57, 883).—A discussion of the possible reasons for the differences between the author's (A., 1933, 1004; 1934, 352) and Schumb and Hartford's vals. (this vol., 180) for d and n of BaAsO_4 . M. S. B.

Synthesis of emerald. A. AMSTUTZ and A. BORLOZ (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 39—41).—The solubility of SiO_2 , BeO , and Al_2O_3 in molten BeF_2 has been investigated. Two types of apparatus are proposed for obtaining large crystals of emerald. A mixture of BeF_2 , SiO_2 , BeO , Al_2O_3 , and traces of Cr_2O_3 falls periodically on to a small crystal in an electric furnace. The BeF_2 acts as a flux, and is continually driven off at the temp. of the furnace, leaving silicates of Be and Al with Cr_2O_3 . In the second apparatus a cyclic process is used in which the BeF_2 is condensed and used again. A. J. M.

Reduction of carbonic acid by means of nascent hydrogen. M. QURESHI and N. H. EFFENDI (J. Osmania Univ. Coll., 2, reprint).—Na and K amalgams, Ca, and Ba reduce aq. CO_2 solutions to HCO_2H . On prolonged reaction traces of CH_2O are formed. Mg gives no HCO_2H . All the above metals reduce a 10% solution of HCO_2H to CH_2O fairly rapidly. The reduction of HCO_2H to CH_2O (detected by Schryver's test) can be used for detecting 1 part in 10,000 of HCO_2H , if the presence of HCl is avoided. Ultra-violet light has no effect on the reduction of the CO_2 solutions. O. J. W.

Per-compounds. III. Persilicates. F. KRAUSS and C. OETTER (Z. anorg. Chem., 1935,

222, 345—370; cf. A., 1934, 741).—The following compounds and their properties are described: $\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$; $\text{Li}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$, with and without H_2O ; $\text{BaSi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, $3\text{H}_2\text{O}$; $\text{CaSi}_2\text{O}_5 \cdot \text{H}_2\text{O}$, $4\text{H}_2\text{O}$; $\text{SiO}_2 \cdot \text{H}_2\text{O}$ with and without $2\text{H}_2\text{O}$. Attempts to prepare K, Mg, and Zn salts were unsuccessful. F. L. U.

Zirconium pyrophosphate. A. KARL (Compt. rend., 1935, 200, 1668—1669).— $\text{ZrP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ is sol. in conc. aq. alkali carbonates at the b.p., the solution depositing crystals of the type $\text{ZrP}_2\text{O}_7 \cdot 4\text{M}_2\text{CO}_3$ (I). Zr is not pptd. from solutions of (I) by aq. NH_3 or by alkali oxalates. The Zr is partly pptd. by H_2O_2 . (I) is decomposed by acids, forming ZrP_2O_7 . H. J. E.

Oxyhalides of lead. A. BAROUT (Atti R. Accad. Lincei, 1935, [vi], 20, 384—390).—Thermal analysis of the various systems at 250 — 900° shows the existence of the following compounds: $\text{PbCl}_2 \cdot x\text{PbO}$ ($x=1, 2, 4$), $\text{PbBr}_2 \cdot x\text{PbO}$ ($x=1, 2, 6$), and $\text{PbI}_2 \cdot x\text{PbO}$ ($x=2, 4, 6$). O. J. W.

Preparation of anhydrous titanium trichloride. M. BILLY and P. BRASSEUR (Compt. rend., 1935, 200, 1765—1767).— TiCl_4 is reduced by heating in a sealed tube at 340° with pptd. Sb, prepared by adding Zn to a HCl solution of SbCl_3 , washing, and drying in CO_2 at 50° . The product is washed in a CO_2 atm. successively with CCl_4 and dry Et_2O to remove TiCl_4 and SbCl_3 , respectively. The yield is theoretical. H. J. E.

Chloronitrides, nitrides, and hydroxynitrides of phosphorus. P. RENAUD (Ann. Chim., [xi], 3, 443—512).—The subject is reviewed historically, and the prep. of $(\text{PNCl}_2)_3$ (I) is described. X-Ray examination of the orthorhombic crystals gives a 14.30, b 6.25, c 13.03 Å. (I) polymerises during distillation, the more rapidly the lower is the temp., and the polymeride undergoes a process analogous to cracking at 400° . The thermal polymerisation of (I) in sealed tubes at 150° , 160° , 185° , and 200° has been studied and the increase of n [in $(\text{PNCl}_2)_n$] with time of heating t determined cryoscopically. H_2O favours the production of non-gelatinous polymerides, whilst high temp. and the existence of a temp. gradient yield gums. The variation of m.p. with n and t is plotted. Insol., infusible gums having the mechanical properties of rubber are produced at 200° . A transition temp. between amorphous and partly cryst. forms can be observed thermally and by X-rays, whilst mechanical transition to a brittle form occurs at -47° . The behaviour of the gums is discussed in relation to the theory of gels. The polymerides react vigorously with Na_2O_2 . H_2O reacts slowly with (I), but yields H_2O -sol. additive products with the polymerides, which decompose giving HCl. Black, impure $(\text{PN})_n$ is formed when (I) is heated with Na. Previous work on the interaction of NH_3 and PCl_3 is critically reviewed. A yellow, insol. powder (II) consisting of $(\text{PN})_n$ with adsorbed NH_3 and NH_4Cl is obtained by heating PCl_3 with NH_4Cl or by passing NH_3 into PCl_3 . The chemical properties and analysis of (II) are described. When heated in vac., (II) gives an insol., greyish-black powder of $(\text{PN})_n$ which is infusible, non-combustible,

and non-volatile up to 1000°. (PN)_n reacts vigorously with Na and molten nitrates, and gives a 90% yield of cryst. PNO₂H₂ (III) after refluxing with H₂O for 15 days. The cryst. properties of (III) have been studied: *a*—*b* 7.57, *c* 7.60 Å.; mol. wt. 79; *d* 1.775; m.p. 195°; decomp. 210°. The m.p., *d*, and cryst. properties of (III) are practically identical with those of NH₄H₂PO₄, but analysis indicates the formula given. R. S.

Explosive reaction of bismuth with perchloric acid. D. G. NICHOLSON and J. H. REEDY (J. Amer. Chem. Soc., 1935, 57, 817—818).—When Bi is heated in 70% HClO₄ below 100° it dissolves slowly with the formation of small amounts of chloride in solution. At about 110° a brownish coating, which explodes violently on further heating, is formed. This is not Bi(ClO₃)₃, nor an active form of Bi comparable with "active Sb," and apparently it is not due to impurities. Attempts to determine the composition of the brown coating were unsuccessful. M. S. B.

alloTelluric acid. M. PATRY (Compt. rend., 1935, 200, 1597—1599; cf. this vol., 593).—Crude *allo*-telluric acid (I) formed by heating orthotelluric acid in a sealed tube is a mixture owing its properties to a complex acid (H₂TeO₄)_n, sol. in HNO₃ and in EtOH. The EtOH solution on evaporation yields the compound (EtHTeO₄)_n, a very hygroscopic white powder, sol. in H₂O and insol. in Et₂O, C₆H₆, and CHCl₃. Prolonged heating of the solution under reflux gives a 20% yield of the compound (Et₂TeO₄)_n, insol. in cold H₂O but sol. in Et₂O. The EtOH solution, when treated with Na, ppts. NaH₃Te₂O₈·1.5H₂O. (I) prepared by prolonged heating at 150—305° contains the *anhydride* TeO₃. J. W. S.

Tellurates. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 864—866).—The existence of Ag₆TeO₆·3H₂O and Ag₆Te₂O₉·3H₂O has been confirmed. Bi₂(TeO₄)₃, UO₂TeO₄·2Na₂TeO₄·4H₂O, BeTeO₄·7Be(OH)₂, and Ce₂(TeO₄)₃ have been prepared by the action of Na₂TeO₄ on the nitrates or chlorides. R. S.

Formula of ferromagnetic chromic oxide. A. MICHEL and J. BENARD (Compt. rend., 1935, 200, 1316—1318).—Differential thermal analysis of the product formed by heating CrO₂Cl₂ shows the formation of a ferromagnetic oxide CrO₂, and a solid solution of O₆ in Cr₂O₃, decomp. at higher temp. into green Cr₂O₃ and O₂. N. M. B.

Behaviour of chromic oxide towards alkali halogenate solutions. I. Reaction system chromic oxide-bromate. R. LYDEN (Z. anorg. Chem., 1935, 223, 28—32).—Strongly ignited Cr₂O₃ (insol. in acids) dissolves readily on warming with aq. KBrO₃. For complete dissolution 6 mols. KBrO₃ for 5 mols. Cr₂O₃ are required. The reaction is represented by: 2Cr⁺⁺⁺ + BrO₃⁻ + 5H₂O = 2H₂CrO₄ + Br⁻ + 6H⁺. F. L. U.

Reaction tungstic oxide-carbon-chlorine. G. W. SEARS and F. LOHSE (J. Amer. Chem. Soc., 1935, 57, 794—796).—WO₂Cl₂, WOCl₄, and probably WCl₆ are successively produced and free O₂ is evolved. C acts as a catalyst and does not disappear so long as a current of Cl₂ is maintained. C may therefore be used to catalyse the extraction of W from its ores by

Cl₂. Cl₂ was removed from the residual gases by Hg before O₂ was determined. M. S. B.

Identification of the 12-heteropoly-acids and their salts by means of X-ray powder photographs. J. W. ILLINGWORTH and J. F. KEGGIN (J.C.S., 1935, 575—580; cf. A., 1934, 479).—The crystal structures of the hydrates of a no. of 12-heteropoly-acids and of their NH₄ and alkali-metal salts have been investigated. They generally crystallise with 29 or 5H₂O. The following compounds have been prepared: K₃AsW₁₂O₄₀, Cs₃AsW₁₂O₄₀, (NH₄)₃HSiMo₁₂O₄₀, K₃KSiMo₁₂O₄₀, Rb₃HSiMo₁₂O₄₀, Cs₃HSiMo₁₂O₄₀, Tl₃HSiMo₁₂O₄₀, (NH₄)₃HMnMo₁₂O₄₀, Cs₃HMnMo₁₂O₄₀. Attempts to prepare metamolybdic acid, 12-boro-, -stanni-, -chromo-, -antimono-, and -vanado-molybdates were unsuccessful, and Mo and W were the only metals which could be placed in the outer sheath of the 12-acid. J. W. S.

Iron, even when impure, is not oxidised by pure air at saturated humidity. P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 742—745).—Extraneous material has been excluded by the employment of bacteriological technique. Carefully cleaned commercial Fe or Fe partly plated with Sn remains bright in air saturated with H₂O under these conditions. The origination of rust in depressions or scratches is attributed to the presence of extraneous material. R. S.

Autoxidation of the hydroxides of iron, manganese, and cobalt. O. LIÉVIN and J. HERMAN (Compt. rend., 1935, 200, 1474—1477).—An apparatus for measuring the rate of oxidation by O₂ of Fe(OH)₂, Mn(OH)₂, and Co(OH)₂, respectively suspended in alkaline solution, is described. The oxidation to Fe₂O₃ is very rapid and appears to follow a simpler course than that of the other two. Mn(OH)₂ oxidation stops at a stage intermediate between Mn₂O₃ and MnO₂. The max. for Co(OH)₂, Co₂O₃, is attained much more slowly than in the other two cases. The oxidisability of Co(OH)₂ appears to depend on the colour of the original ppt. M. S. B.

Spectroscopically pure γ-ferric oxide in colloidal aggregation as a biological indicator. Preparation of γ-Fe₂O₃·H₂O, and γ-Fe₂O₃. O. BAUDISCH (Svensk Kem. Tidskr., 1935, 47, 115—119).—Pure O₂-free C₅H₅N through which a stream of CO₂ is passed is treated with a Congo-neutral solution of spectroscopically pure FeCl₃. After keeping for 12 hr. under CO₂, the yellow crystals of [(FeCl₂)(C₅H₅N)₄] (I) are washed with C₅H₅N and dried. Through a 2% solution of (I) in pure H₂O, a current of O₂ or air is passed until γ-Fe₂O₃·H₂O is quantitatively pptd. The air-dried product is dehydrated by heating in a quartz test-tube at 240—260° until it is converted into the ferromagnetic γ-Fe₂O₃. The applications of the latter in biology are discussed.

Palladium-hydrogen. W. KRAUSE and L. KAHLENBERG (Trans. Electrochem. Soc., 1935, 68, 35—55).—Pd foil shrinks and thickens on repeated hydrogenation. The hydrogenation rate is a max. after 12 absorptions at 0°, three at 25°, and a single absorption above 56°. The total absorption decreases linearly up to 82°, above which it falls rapidly, whilst the

hydrogenation rate after 1 min., expressed as % of the total, is a max. at 56°. For succeeding time intervals, the rate is approx. const. up to 75°, but falls rapidly at higher temp. The linear dimensions of Pd foil have been determined after each successive expansion due to hydrogenation and contraction due to dehydrogenation until after ninety operations there was no further change, when the Pd was almost cylindrical in shape. The d and the total H_2 absorbed per g. now became const., whilst the Pd_2H reduced H_2SO_4 to H_2S and H_3PO_4 to PH_3 and exhibited pyrophoric properties. R. S.

Quantitative spectral analysis. H. TRICHÉ (Compt. rend., 1935, 200, 1538—1541).—A spark is established between a metal electrode to be examined and a metal sheet not containing the metal to be detected. On the other side of the sheet is a spark gap (in the same circuit) to a comparison electrode. The two sparks are focussed simultaneously on the spectrograph slit. Methods of matching are described. H. J. E.

Use of flame spectra in chemical analysis. H. W. LOHSE (Canad. J. Res., 1935, 12, 519—532).—As a method of quant. analysis spectra of flames produced by atomising aq. solutions by means of an air- C_2H_2 jet have been studied. Errors in the results are largely due to plate variation. Changes in pressure of C_2H_2 may also be significant, since a variation of 1 cm. of H_2O in the pressure gives a change of several % in the line intensity of Ca and Na. Results have been compared for several minerals using chemical and flame spectra methods, the discrepancies being of the same order as those due to plate variation. R. S. B.

Micro-chemical analysis. M. RAEDER (Tids. Kjem., 1935, 15, 14—16).—A review. R. P. B.

Solutions for colorimetric standards. IV. Ferric chloride. M. G. MELLON and C. T. KASLINE (Ind. Eng. Chem. [Anal.], 1935, 7, 187—189).—Data are given for the transmission of $FeCl_3$ solutions in the visible region at different HCl concns. Optimum vals. are $[FeCl_3]$ 0.5—0.02M, $[HCl]$ 5.0—0.05M. J. S. A.

Qualitative chemical analysis. V. MACRI (Boll. Chim. Farm., 1935, 74, 345—349).—Various modifications of the accepted method for the separation of the metals into groups are described, with special reference to methods for separating and detecting the alkali metals without going through the group separation for the other metals. The following method is preferred. The solution, or the liquid obtained on extraction of the solid with hot H_2O , is acidified, if not already acid, with dil. HNO_3 . If either $Ba(NO_3)_2$ or dil. H_2SO_4 produces a ppt., excess of the reagent is added. The filtrate is evaporated nearly to dryness with aq. $Ba(OH)_2$, evolution of NH_3 indicating NH_4 . The residue is extracted with H_2O and the Ba pptd. by addition of $(NH_4)_2CO_3$ or CO_2 . The solution is acidified with HCl, and evaporated to dryness. LiCl is extracted by means of EtOH-Et₂O and the residue tested for K and Na. D. R. D.

Titrimetric determination of water in organic liquids using acetyl chloride and pyridine. D. M.

SMITH and W. M. D. BRYANT (J. Amer. Chem. Soc., 1935, 57, 841—845).—The reaction of $AcCl$ and C_5H_5N with H_2O to form 2 mols. of titratable acid as C_5H_5N salts is much more rapid than the corresponding reaction with EtOH to form 1 mol. each of acid and ester. It can thus be used as a basis for the determination of H_2O in many org. compounds, including fatty acids. Substances interfering with the method are discussed. M. S. B.

Determination of moisture in liquid ammonia.—See B., 1935, 492.

Influence of acid in potentiometric chloride titration. L. GUZELJ (Z. anal. Chem., 1935, 101, 257—269).—The electrode potential at the equivalence point is considerably depressed (up to 0.1 volt) and the titre slightly raised ($> 1\%$) in presence of acids. The effect is \propto [acid], and approx. \propto the strength of the acid, i.e., greatest for HNO_3 , small for $AcOH$. J. S. A.

Volumetric determination of chlorides and sulphates in a mixture containing both, with the help of an adsorption indicator. M. B. RANE and K. R. APTE (J. Indian Chem. Soc., 1935, 12, 204—207).— $CdSO_4$ may be titrated directly with $Ba(OH)_2$, using fluorescein (I) as indicator. Cl^- and SO_4^{2-} in the same solution are determined by titrating successively with $AgOAc$, and $Ba(OH)_2$ after adding $Mg(OAc)_2$, using (I) as indicator (cf. A., 1932, 923). Acid solutions are first exactly neutralised with aq. NH_3 . J. G. A. G.

Volumetric micro-determination of chloride and potassium ions. Application of potassium method to sea-water. B. BULLOCK and P. L. KIRK (Ind. Eng. Chem. [Anal.], 1935, 7, 178—180).— Cl^- is determined by titration with 0.005N- $AgNO_3$, using dichlorofluorescein as indicator. 2 vols. of $COMe_2$ are added to make the end-point more distinct. For determination of K, excess of aq. $PtCl_4$ is added and the solution evaporated to dryness. The residue is washed with 80% EtOH (I) saturated with K_2PtCl_6 (II), then with 20% NH_4Cl , and finally with (I) until free from NH_4Cl . Mg powder + H_2O is added, reducing (II) to Pt, and Cl^- in the solution is titrated as above. J. S. A.

Volumetric determination of halides. Use of dichlorofluorescein as adsorption indicator. K. BAMBACH and T. H. RIDER (Ind. Eng. Chem. [Anal.], 1935, 7, 165—166).—Dichlorofluorescein may be used as indicator for titration of Cl^- , Br^- , or I^- with $AgNO_3$ in EtOH or aq.-EtOH solution. J. S. A.

Detection and colorimetric determination of micro-quantities of bromide. V. A. STENGER and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1935, 57, 831—833).—The determination of very minute quantities of Br^- may be made with phenol-red by oxidation with $Ca(OCl)_2$ in borax buffer at pH 8.7—8.8. A colour change, due to the formation of bromophenol-blue, is obtained, and can be best observed and measured by changing to pH 5.0—5.4 by the addition of suitable buffers. M. S. B.

Determination of minute amounts of bromide in presence of very great excess of chloride. F. L. HAHN (Mikrochem., 1935, 17, 222—235).—(1) Free

Br is liberated by chloramine-*T* in acetate-buffered solution at 5.5–5.6 in presence of fluorescein, which is thus brominated to cosin with only inconsiderable chlorination. 10^{-6} g. of Br may be so determined in presence of 0.1 g. of Cl. (2) Small $[\text{Br}']$ has a large effect on the potential of the calomel electrode. From measurement of potential in the solution under examination, using a Pt wire-Hg-Hg₂Cl₂ or a liquid Hg-aq. Hg₂(ClO₄)₂ electrode, $[\text{Br}']$ may be compared with that of known solutions.

Microchemical detection of iodine. S. AUGUSTI (Mikrochem., 1935, 17, 113–117).— I^- gives with a solution of $\text{Hg}(\text{NO}_3)_2$ in aq. NH_3 (i.e., $\text{Hg}_2\text{N}\cdot\text{NO}_3$) a yellow ppt. of $\text{Hg}_2\text{N}\cdot\text{I}$; sensitivity 2.2×10^{-7} g. A brown ppt. is given by $< 9 \times 10^{-6}$ g. of I^- with dil. aq. $\text{NaOCl} + 1\%$ aq. MgSO_4 . J. S. A.

Iodide determination in acid solution. G. JÓNAS (Magyar gyo. Tars. Ert., 1934, 10, 526–539; Chem. Zentr., 1935, i, 443).—Oxidation of I^- with Cl_2 in HCl solution ($> N$) yields ICl . In determining I^- , CCl_4 and $3N\text{-HCl}$ are added, and the I^- is converted into ICl with aq. NH_2Cl (stabilised with $\text{Na}_2\text{B}_2\text{O}_7$). The end-point is shown by the decolorisation of the violet CCl_4 solution. The HCl solution is then diluted with H_2O to 0.2–0.3 *N*, the ICl is destroyed by adding KI , and the liberated I titrated with $\text{Na}_2\text{S}_2\text{O}_3$. The mean of the NH_2Cl and $\text{Na}_2\text{S}_2\text{O}_3$ titrations is taken. Large amounts of Br^- do not interfere. Ag^+ , Hg^{2+} , Pb^{2+} , or Bi^{3+} may be present. In presence of Fe^{2+} , the Cl titration gives the $\text{Fe}^{2+} + \text{I}^-$, and the $\text{Na}_2\text{S}_2\text{O}_3$ titration gives the I^- . H. J. E.

Determination of fluorine in phosphatic material.—See B., 1935, 493.

Determination of oxygen in water by syringe pipettes.—See B., 1935, 528.

Determination of ozone. A. MACHE (Compt. rend., 1935, 200, 1760–1762).—At high $[\text{O}_3]$ (e.g. 40 mg. per litre), Juliard and Silberschartz' method (A., 1928, 978) is exact. The fluorescein method (A., 1919, ii, 198) is suitable for low $[\text{O}_3]$ if the is strictly const. H. J. E.

Adsorption indicator in the volumetric determination of sulphates. A colloido-chemical study. M. P. V. IYER (J. Indian Chem. Soc., 1935, 12, 164–167).—The colour changes observed during the titration by $\text{Ba}(\text{OH})_2$ of MgSO_4 and MnSO_4 , but not other sulphates, in the presence of Na fluoresceinate (cf. A., 1932, 923) are due to the pptn. of $\text{Mg}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$ at alkaline vals. and the concomitant adsorption of fluoresceinate ions. The fading of the colour on ageing is correlated with growth of the particles of the ppt., and the nature of the adsorption process is discussed. J. G. A. G.

Sensitive reaction for thiosulphate ion. A. BLANCK (Z. anal. Chem., 1935, 101, 194).— $\text{CuSO}_4 + \text{AcOH}$ are added, and the solution is heated from above. In presence of $\text{S}_2\text{O}_3^{2-}$ a black ring of CuS is produced. PO_4^{3-} , CNS^- , CN^- , $\text{Fe}(\text{CN})_6^{4-}$, and S^{2-} interfere. J. S. A.

Determination of sulphuric acid in clouds, as present in burner gases etc.—See B., 1935, 492.

Rational procedure for use of selenium in the Kjeldahl method. V. V. ILLARIONOV and N. A. SOLOVJEVA (Z. anal. Chem., 1935, 101, 254–257; cf. this vol., 596).— H_2SeO_3 dissolved in H_2SO_4 (0.005 g. of Se per c.c.) + $\text{CuSO}_4 + \text{K}_2\text{SO}_4$ is used as catalyst. J. S. A.

Determination of nitrogen trioxide in nitrosyl-sulphuric acid.—See B., 1935, 492.

Direct titration of soluble orthophosphates with lead acetate in presence of dibromofluorescein as adsorption indicator. A. W. WELLINGS (Analyst, 1935, 60, 316–318; cf. A., 1933, 798).—The aq. PO_4^{3-} is made neutral or slightly acid with HNO_3 . The procedure for the subsequent titration is described. E. C. S.

Photometric investigation of ceruleomolybdate determination of phosphate in waters. R. J. ROBINSON and H. E. WIRTH (Ind. Eng. Chem. [Anal.], 1935, 7, 147–150).—The methods of Atkins and of Truog and Meyer (cf. A., 1929, 1158) are more suited to very low $[\text{PO}_4^{3-}]$ than the Bell-Doisy method, but are subject to a large neutral salt effect. J. S. A.

Fajans' titration method. E. J. KOCSIS and L. POLLAK (Acta Lit. Sci. Univ. Hung. Francisco Joseph., 1934, 4, 147–155).—A review of applications of the method in determining PO_4^{3-} , MoO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, $\text{Fe}(\text{CN})_6^{4-}$, Hg^{2+} , Zn^{2+} , and coloured halide solutions. Suitable indicators are recorded. CH. ABS. (e)

Detection of arsenic in presence of antimony. N. A. TANANAEV and V. D. PONOMAREV (Z. anal. Chem., 1935, 101, 183–185).—As compounds are reduced to AsH_3 (detected with HgCl_2 paper) by $\text{Sn} + \text{HCl}$, whilst Sb is deposited as the metal. 0.01% of As in Sb may be so detected. J. S. A.

Determination of very small amounts of carbon monoxide in air.—See B., 1935, 526.

Micro-alkalimetry. II. Micro-determination of alkali carbonates. J. MIKA (Z. anal. Chem., 1935, 101, 270–278).—The solution is titrated nearly to completion, stirring with a stream of air free from CO_2 . Dissolved CO_2 is then removed completely by prolonged passage of air (15 min.), and titration completed to a permanent tint at p_{H} 5.0. Me-red is used as indicator, and matched against a Na_2HPO_4 -citric acid buffer. J. S. A.

Volumetric determination of potassium by the cobaltinitrite method. C. S. PRYER (J.S.C.I., 1935, 54, 157–158T).—Error may be introduced through the presence of NH_4^+ in some brands of A.R. $\text{Co}(\text{NO}_3)_2$ (cf. this vol., 317). C. W. G.

Gravimetric determination of silver. P. SPACU (Bul. Soc. Stiinte Cluj, 1934, 7, 568–570; Chem. Zentr., 1934, ii, 3531).—The neutral or feebly acid (HNO_3) AgNO_3 solution is treated with KCN until the pptd. AgCNS redissolves. Conc. $[\text{Co en}_2(\text{CNS})_2][\text{CNS}(\text{trans})]$ (I) is added to the hot solution and the orange-red $[\text{Ag}(\text{CNS})_2][\text{Co en}_2(\text{CNS})_2]$ (Ag 20.78%) is washed with 1% aq. KCN containing 0.5% of (I), with 96% EtOH , and with Et_2O and dried in vac. at room temp. H. J. E.

Indirect microchemical detection of alkaline-earth metals on hot cathodes of oxide [dull

emitter] valves. H. FRITZ (Mikrochem., 1935, 17, 191—209).—The valves are opened and filled with O_2 -free N_2 . The filament is heated, converting free Ba into Ba_3N_2 , and is then cut out and distilled with aq. Na_2CO_3 . NH_3 in the distillate is determined colorimetrically with Nessler's reagent. The amount of free metal so found is many times > that required for a unimol. layer. J. S. A.

Drop methods for identification of cations in presence of phosphate ion. N. A. TANANAEV and V. A. SCHULEPOVA (Z. anal. Chem., 1935, 101, 179—182).—Removal of PO_4''' is necessary only for the detection of Ca, Sr, and Ba, and may be effected with either $(NH_4)_2MoO_4$ or Na_2WO_4 . J. S. A.

Quantitative spectral analysis of calcium and barium in light alloys and solutions. H. TRICHE (Compt. rend., 1935, 200, 1665—1667).—Tests are described on the spectroscopic detection of Ca and Ba, using $\lambda\lambda$ 3933.67 and 3891.78 Å., respectively. The influence of temp., concn., and the addition of foreign substances on the relative intensities was studied. H. J. E.

Volumetric determination of beryllium. B. S. EVANS (Analyst, 1935, 60, 291—293).—Be is pptd. as $Be(OH)_2$, which is exactly neutralised with HCl. A known vol. of 0.1N-HCl is added, the excess of which is determined by liberating I from aq. $KIO_3 + KI$ in presence of $NaHCO_3$ and titrating with 0.1N- As_2O_3 . The separation of Be from a large amount of Pb is described. E. C. S.

Micro-determination of magnesium. G. CREUSS-CALLAGHAN (Biochem. J., 1935, 29, 1081—1085).—Mg 20×10^{-6} g. in 3 c.c. of solution can be determined by pptn. with 8-hydroxyquinoline, hydrolysis of the Mg complex, bromination with excess of Br, and volumetric determination of free Br. The error is $\pm 10\%$. The presence of 4 times as much Ca causes no error with 50×10^{-6} g. of Mg in 3.5 c.c. J. N. A.

Micro-detection of magnesium and aluminium with alkannin and naphthazarin. Relation of alkannin to naphthazarin. J. V. DUBSKY and E. WAGNER (Mikrochem., 1935, 17, 186—190).—Blue alkaline EtOH solutions of alkannin (I) (0.05%) and of naphthazarin (II) (0.03%) give bulky blue ppts. with 0.05 mg. of Mg. The purple solution of (II) made alkaline with $(CH_3-NH_2)_2$ gives a blue colour with 0.35×10^{-6} g. of Mg. Al gives violet ppts. with (I) and (II) in presence of NH_3 . J. S. A.

Qualitative micro-analysis by electrolysis and spectrography. A. SCHLEICHER (Z. anal. Chem., 1935, 101, 241—254).—Metals present in 0.1—2 c.c. of solution are deposited electrolytically on a thin Cu wire or C point cathode, and are identified from their most sensitive spectral lines in the interrupted arc, using the enriched deposit on a C point cathode as electrode. By electrolysis first from HCl, and then adding aq. NH_3 , a separation is made into (a) metals electro-deposited from acid (Hg—Pt in the electrochemical series); (b) metals deposited from acid and alkaline solution (Cd—Ge); (c) those deposited from NH_3 solution (Zn—Al). Determination of the concn. at which spectral lines appear on progressive concn.

or dilution affords a measure of the concn. of the metals present. J. S. A.

Detection of cadmium as selenide. P. KRUMHOLZ and O. KRUH (Mikrochem., 1935, 17, 210—214).—Cd is pptd. as red-brown CdSe by addition of Na_2Se to the NH_3 -KCN solution in presence of Cu, Ni, Co, or Zn in large excess. Confusion of CdS with flavianic or rubianic acids from $H_2S + (CN)_2$ is thus avoided. J. S. A.

Limits for spectroscopic detection of cadmium and palladium in silver.—See B., 1935, 552.

Volumetric determination of lead in alloys containing tin, antimony, and copper.—See B., 1935, 501.

Determination of traces of lead in drinking water.—See B., 1935, 527.

Colorimetric determination of traces of copper with sodium diethyldithiocarbamate. E. LAGET (Ann. Chim. Analyt., 1935, [iii], 17, 145—147).—The interfering white cloudiness due to hydrolysis of Na diethyldithiocarbamate is best avoided by working in 50% EtOH, and 10^{-7} — 10^{-4} g. of Cu may then be determined. The method may be used in the presence of Zn, Cd, and traces of Fe and Mn, but aq. NH_3 should then be added. A. G.

Reaction of copper with benzidine and new method of determining traces of copper. A. TETTAMANZI (Atti R. Accad. Sci. Torino, 1934, 69, I, 197—203; Chem. Zentr., 1935, i, 115).—The reaction between benzidine and Cu in presence of KI is due to liberated I. Free I may be so detected at a concn. of 1 in 500,000. J. S. A.

Micro-determination of copper. F. HECHT and R. REISSNER (Mikrochem., 1935, 17, 127—134).—In the micro-analysis of minerals Cu may be accurately determined with benzoinoxime, salicylaldoxime, or, best, with 5:7-dibromo-8-hydroxyquinoline. J. S. A.

p-Aminophenol hydrochloride as reagent for copper and iron cations. S. AUGUSTI (Mikrochem., 1935, 17, 118—126).—A 2% solution of $p-OH-C_6H_4-NH_2 \cdot HCl$ in EtOH gives blue-violet ppts. with Cu^{++} and Fe^{+++} ; sensitivity 0.2×10^{-7} g. of Cu, 0.06×10^{-7} g. of Fe. Other heavy metals do not interfere. J. S. A.

Modified iodometric method of determining copper. H. W. FOOTE and J. E. VANCE (J. Amer. Chem. Soc., 1935, 57, 845—847).—Addition of a sol. thiocyanate near the end-point of the usual iodometric titration of Cu increases the sharpness of the end-point and the accuracy of the method. When the titration is complete the Cu ppt. is white. M. S. B.

Determination of copper in pharmaceutical specialities containing copper and iron.—See B. 1935, 523.

(A) Potentiometric determination of mercury. G. SPACU and I. G. MURGULESCU. (B) Volumetric determination of mercury. G. SPACU and V. ARMEANU (Bul. Soc. Științe Cluj, 1934, 7, 552—558, 621—630; Chem. Zentr., 1934, ii, 3530—3531).—(A) The Hg solution is treated with excess of KI and

titrated with $[\text{Cu en}_2](\text{NO}_3)_2$ solution (I), $[\text{HgI}_4][\text{Cu en}_2]$, (II) being formed. An amalgamated Pt wire serves as indicator electrode. The solubility of (II) is 1.34×10^{-4} .

(B) Hg^{I} salts are oxidised with aqua regia, Cl being eliminated by SO_2 or KHSO_3 . The solution is then titrated with (I), the first drop of which in excess gives a violet colour (cf. A., 1929, 901, 1259). Halides, SO_4^{II} , CNS^{I} , and nitrates of NH_4 , Mg, and the alkaline earths do not interfere. CN^{I} must be removed.

H. J. E.

Volumetric determination of mercury. M. SCHTSCHIGOL (Khim. Farm. Prom., 1934, No. 3, 29—32).—0.2—0.4 g. of the sample is dissolved in H_2O and 20—30 c.c. of 30% NaOH , treated with 5—10 c.c. of glycerol, and filtered. The ppt. is washed and dissolved in 15 c.c. of hot HNO_3 . The solution is diluted, KMnO_4 being added until pink and then FeSO_4 until colourless, and titrated with 0.1N- NH_4CNS .

CH. ABS. (e)

Titrimetric determination of manganese. J. LEROIDE and A. BRULLET (Bull. Soc. chim., 1935, [v], 2, 740—742).— KMnO_4 is added to a solution of MnSO_4 and K_2SO_4 (50 g.) or Na_2SO_4 in boiling H_2O (500 c.c.) until a permanent pink coloration is obtained.

R. S.

Sensitive polarographic test for the absence of rhenium in manganous salts. J. HEYROVSKY (Nature, 1935, 135, 870—871).—A method for the detection of 2×10^{-8} g. of ReO_4^{I} is described. Commercial Mn salts contain < 1 part of Re in 10^6 of Mn.

L. S. T.

Quantitative separation of iron and cobalt. P. SPACU (Compt. rend., 1935, 200, 1595—1597).—Treatment of a hot solution containing Fe^{III} and Co^{II} with $\text{C}_6\text{H}_5\text{N}$ separates all the Fe as $\text{Fe}(\text{OH})_3$, whilst the Co remains in solution and can be determined as $[\text{Co}(\text{C}_6\text{H}_5\text{N})_4(\text{CNS})_2]$.

J. W. S.

Drop reaction for ferricyanide. E. STORFER (Mikrochem., 1935, 17, 170—173).—Neutral solutions of $[\text{Fe}(\text{CN})_6]^{\text{III}}$ give with $[\text{CuR}_3]\text{Cl}$ [$\text{R} = \text{CS}(\text{NH}_2)_2$] a violet or grey ppt. of $[\text{CuR}_3]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$. 100,000-fold excess of $[\text{Fe}(\text{CN})_6]^{\text{III}}$ does not interfere. Limiting concn. of $[\text{Fe}(\text{CN})_6]^{\text{III}}$, 1 : 100,000.

J. S. A.

Determination of ferrous and manganous oxides in steel by means of mercuric chloride.—See B., 1935, 499.

Detection of iron, lead, and tar in dust samples.—See B., 1935, 526.

Vanadous sulphate as a reducing agent. I. P. C. BANERJEE (J. Indian Chem. Soc., 1935, 12, 198—203).— $\text{VSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (I), which is less easily oxidised by air than VSO_4 , is prepared by electrolysis, between Pb electrodes, of vanadyl sulphate in H_2SO_4 containing $(\text{NH}_4)_2\text{SO}_4$; the anolyte is $2\text{H}_2\text{O} : 1\text{H}_2\text{SO}_4$. The solution is preserved under H_2 . The strong reducing properties of (I) are illustrated by numerous reactions described. Fe^{III} is determined by direct titration using KCNS as internal indicator. Fe^{II} is first oxidised to Fe^{III} with KMnO_4 or H_2O_2 and aq. NH_3 . Cr^{III} is determined by oxidising with Na_2O_2 to CrO_4^{II} , neutralising with H_2SO_4 , adding excess of (I),

and back titrating with standard Fe^{III} alum using KCNS as indicator. Cu^{II} is determined, in the presence of excess of KCNS and a little FeSO_4 , by direct titration with (I); the Cu is pptd. as CuCNS . J. G. A. G.

Volumetric determinations in strongly alkaline solutions. I. Titration of cobalt with ferricyanide. O. TOMIČEK and F. FREIBERGER (J. Amer. Chem. Soc., 1935, 57, 801—804).—Co can be rapidly and simply titrated, potentiometrically, with $\text{K}_3\text{Fe}(\text{CN})_6$ in presence of alkalis, preferably aq. NH_3 . The solution must be kept below 10° and in an atm. of CO_2 . The method is not affected by large amounts of Ni^{II} , Cu^{II} , Zn^{II} , $\text{AsO}_4^{\text{III}}$, Fe^{II} , CrO_4^{II} , MoO_4^{II} , or VO_3^{I} , or by Fe^{III} if the concn. is not too great. Mn and $\text{AsO}_3^{\text{III}}$ must be absent. M. S. B.

Determination of cobalt in steel.—See B., 1935, 551.

Determination of chromium, aluminium, and iron, and the complete analysis of chromites. K. N. TODORVIĆ and V. M. MITROVIĆ (Bull. Soc. Chim. Yougoslav., 1934, 5, 219—227).—Chromite (0.2—0.3 g.) is fused with $\text{Na}_2\text{B}_4\text{O}_7$ — Na_2CO_3 — K_2CO_3 , and the melt is extracted with H_2O ; Cr is determined iodometrically, and Fe by the Zimmermann—Reinhardt method. A second portion of ore is fused with Na_2O_2 , and Al_2O_3 + Cr_2O_3 + Fe_2O_3 determined; the Al_2O_3 content is calc. by difference. R. T.

Determination of chromium and nickel in ferrous alloys containing manganese and more than 1% of carbon.—See B., 1935, 499.

Detection of germanium in blende. G. PICCARDI (Annali Chim. Appl., 1935, 25, 179—194).—Chemical and X-ray analysis prove unsatisfactory for detecting small amounts of Ge in blende, but a spectroscopic method described gives good results.

T. H. P.

Microchemical detection of bismuth, antimony, and gold. A. SA (An. Farm. Bioquim., 1934, 5, 3—7; Chem. Zentr., 1934, ii, 3531).—To a drop of the acid solution is added (in testing for Au) a small crystal of NaBr or (for Bi or Sb) a small crystal of KI , followed by 2-aminopyridine. Bi gives a scarlet ppt. (lamellæ and H-formed crystals), and Sb an orange-yellow ppt., the crystals being larger than for Bi. The limits of detection for Sb and Bi are 1.2, 7.5×10^{-6} g., respectively. Au gives yellow-red rectangular lamellæ and H-formed crystals. In presence of Ag, Pb, Hg, Cu, Cd, Sn, or Au, Bi must first be separated by NaOH and KCN . H. J. E.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXVIII. Separation of rare earths from earth acids. W. R. SCHOELLER and E. F. WATERHOUSE (Analyst, 1935, 60, 284—291; cf. A., 1934, 1192).—For the separation of large amounts of rare earths (I) from the earth acids (II) Schoeller and Powell's modification (J.C.S., 1921, 119, 1927) of Smith's HF method (A., 1884, 111) is recommended. For small quantities, the bulk of (II) is removed by hydrolysis with tartaric acid (III), (I) are pptd. with tannic acid in presence of NH_3 , the ppt. is fused with KHSO_4 , and the melt is either extracted with aq. $\text{H}_2\text{C}_2\text{O}_4$ (IV) or is dissolved in (III) and pptd. with (IV). E. C. S.

Industrial importance of m.p., and apparatus for their determination. J. A. SCARROW (Canad. Chem. Met., 1935, 19, 98).—The apparatus, intended for the determination of m.p. $< 300^\circ$, is trustworthy at temp. $> 50^\circ$. A brass block has a vertical thermometer socket and inclined tubes for the capillaries for the samples. It is inserted in a hole in a piece of asbestos board supported by a brass ring and shielded from draughts by a Pyrex glass sleeve.

C. I.

Leads and the formula in electric calorimeter calibration. W. P. WHITE (Rev. Sci. Instr., 1935, [ii], 6, 142—143).—A formula for calculation of the energy lost in the leads is deduced.

C. W. G.

Application of low-temperature calorimetry to radioactive measurements. F. SIMON (Nature, 1935, 135, 763).—The possibility of using the increased sensitivity of calorimetric measurement resulting from the use of very low temp. for radioactive measurements is illustrated.

L. S. T.

Thermal ratios and measurement of the tube apparatus for exothermic heterogeneous gas catalysis. W. LEITENBERGER (Chem. App., 1934, 21, 113—116, 121—123, 133—135; Chem. Zentr., 1934, ii, 3536).—Theoretical.

R. N. C.

Dispersion curves of some reflecting power standards of use in the microscopic study of metallic minerals. J. ORCEL and P. FASTRE (Compt. rend., 1935, 200, 1485—1488).—By a photo-electric method previously described (Bull. Soc. Franç. Min., 1930, 53, 301), the reflecting powers for different $\lambda\lambda$ have been determined for the following standards: diamond, blende, galena, grey Cu, Si, and pyrites.

M. S. B.

Measurement of spectral distribution of intensity of fluorescence of Röntgen screens and intensifiers. H. FUNK and H. STEPS (Z. tech. Physik, 1934, 15, 301—306; Chem. Zentr., 1935, i, 113).—A photometer for weak fluorescent or phosphorescent sources is described. The spectrum of the fluorescent light is independent of the λ of the X-rays.

J. S. A.

Bollenrath optical dilatometer. W. KOCH (Metallwirts., 1934, 13, 671—672; Chem. Zentr., 1935, i, 149; cf. B., 1934, 765).—An improved form is described. The reported allotropic transition of Bi at 75° does not occur.

J. S. A.

Use of photographic plates with thick emulsion layers in studying the distribution of radioactive elements in natural objects. V. I. BARANOV and S. I. KRETSCHMER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 543—549).—A review of the technique and its applications.

H. J. E.

Selenium-sulphur rectifier photo-electric cell. G. P. BARNARD (Proc. Physical Soc., 1935, 47, 477—501).—The construction of a new type of cell, its theory, an investigation of its physical behaviour, and equations for its performance are given.

N. M. B.

Use of photo-electric apparatus in chemistry.—See B., 1935, 558.

X-Ray goniometer for the investigation of crystal structures of solidified gases. W. H. KEESOM and K. W. TACONIS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 375).—The method has been developed for those cases in which the Debye-Scherrer method yields insufficient data. Single crystals are grown by very slow crystallisation of liquid, and two exposures are made on the same film of the camera, in the second the film being continuously moved in the direction of the camera axis, as in Weisenberg's goniometer. For C_2H_4 the rhombic cell contains 2 mols., a 6.46, b 4.87 c 4.14 Å. at -175° ; d 0.717.

R. S. B.

Automatic high-pressure cloud chamber. W. M. BRUBAKER and T. W. BONNER (Rev. Sci. Instr., 1935, [ii], 6, 143—145).—A mixture of CH₄ and EtOH at 20 atm. is used.

C. W. G.

Electron diffraction camera. L. H. GERMER (Rev. Sci. Instr., 1935, [ii], 6, 138—142).

C. W. G.

Calculation of p_H values. W. R. ATKIN and F. C. THOMPSON (J. Soc. Leather Trades Chem., 1935, 19, 140—148).—Methods of calculation applicable to various acids, bases, and salts are given.

D. W.

Powder method of electronography. N. A. SCHISCHAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 461—463).—A process of fractional sedimentation of powders in a 1 m. long air tube is described. All particles above 0.1—1 μ in size settle in 20 min. The remaining suspended material is collected on a thin celluloid film as a holder, and exposed to the cathode beam, satisfactory powder photographs being obtained.

H. J. E.

Electrometric titration. Device for automatically stopping at a predetermined end-point. W. E. SHENK and F. FENWICK (Ind. Eng. Chem. [Anal.], 1935, 7, 194—197).—The sharp change in e.m.f. between two dissimilar electrodes at the end-point is utilised to operate a valve relay device controlling the burette.

J. S. A.

Direct reading p_H meter for glass, quinhedrone, and hydrogen electrodes. A. HEMINGWAY (Ind. Eng. Chem. [Anal.], 1935, 7, 203—205).

J. S. A.

Completely superconducting galvanometer. E. F. BURTON, H. G. SMITH, and F. G. A. TARR (Nature, 1935, 135, 906).

L. S. T.

Rapid practical method of demagnetisation involving high frequency. C. W. DAVIS (Nature, 1935, 135, 790—791).—The method can be used for determining the magnetic properties of powders, for testing Fe and steel bars, and in processes involving magnetic separation of ores.

L. S. T.

Apparatus for carbon dioxide determination according to Pettenkoffer. P. S. TUTUNDZIC (Bull. Soc. Chim. Yougoslav., 1934, 5, 151—154).

R. T.

Automatic pipette for rapid delivery. W. T. FORSEE, jun., P. J. THOMPSON, and C. B. POLLARD (Ind. Eng. Chem. [Anal.], 1935, 7, 156).

J. S. A.

Improved slow-combustion pipette for gas analysis. D. J. PORTER and D. S. CRYDER (Ind. Eng. Chem. [Anal.], 1935, 7, 191—192).—The gas is

led through a Pt capillary containing a concentric Pt wire, on to an electrically heated Pt spiral.

J. S. A.

Burette assembly for standard reducing solutions. C. J. SCHOLLENBERGER (Ind. Eng. Chem. [Anal.], 1935, 7, 199).

J. S. A.

Gas analysis apparatus.—See B., 1935, 530.

Construction of glass helices for fractionating column packing. E. E. ROPER, G. F. WRIGHT, J. R. RUHOFF, and W. R. SMITH (J. Amer. Chem. Soc., 1935, 57, 954—955).—Details are given for making helices for the column of Wilson *et al.* (cf. A., 1933, 926).

R. S. C.

High-speed oil-diffusion pump. H. W. EDWARDS (Rev. Sci. Instr., 1935, [ii], 6, 145—147).—Stream lines on the high-pressure side and baffles on the low-pressure side enable a speed of 50 litres per sec. to be reached at a pressure of 10^{-4} mm.

C. W. G.

Possible improvement of Walpole's comparator blocks. M. DÉRIBÉ (Ann. Chim. Analyt., 1935, [iii], 17, 149—150).—Tubes of rectangular cross-section are suggested.

A. G.

Rotating sphere viscosimeter for liquids. A. GUILLET (Compt. rend., 1935, 200, 1522—1524; cf. this vol., 467).—Theoretical.

H. J. E.

Apparatus for measuring the viscosity of liquids at high pressures. C. C. MASON (Proc. Physical Soc., 1935, 47, 519—520).—An instrument covering a wide range of viscosities, suitable for determining the pressure coeff. of viscosity and investigating temp. effects, is described.

N. M. B.

Circulatory stirrer. W. PFLUGBEIL (Chem.-Ztg., 1935, 59, 389).—The liquid is caused to pass vertically up a glass cylinder surrounding the stirrer and to flow downwards in the outer portion of the beaker, or alternatively it may be made to circulate in the opposite direction. This vertical circulation ensures efficient mixing of liquids of different density.

D. R. D.

Manometer for measuring small pressure differences in gases and vapours at any initial pressure. H. SCHULTES and K. NEUMANN (Chem. Fabr., 1935, 8, 197—198).—Pressure changes are measured by the displacement of an air bubble in a horizontal capillary, using a modification of Henry's method (Compt. rend., 1912, 155, 1078). The method is suitable for measuring rates of adsorption.

H. J. E.

Emergency stopper for nitric acid bottles. D. HARRIS (Ind. Eng. Chem. [Anal.], 1935, 7, 162).—Al foil may be used; it undergoes no corrosion.

J. S. A.

Manometric manostat. G. B. BACHMAN (Ind. Eng. Chem. [Anal.], 1935, 7, 201).—An electrically operated device is described.

J. S. A.

Filtration of hot solutions. G. R. YOHE (Ind. Eng. Chem. [Anal.], 1935, 7, 206).—The liquid is maintained at const. level in the filter by an electrically heated siphon.

J. S. A.

Simple laboratory stirrer for use on vacuum line. G. T. AUSTIN (Ind. Eng. Chem. [Anal.], 1935, 7, 206).—A simple air turbine is described.

J. S. A.

Extraction test-tube. H. BARSCH (Z. anal. Chem., 1935, 101, 194—195).—A stoppered test-tube, with a side tap, is described.

J. S. A.

Apparatus for fractional solidification. R. PADMANABHAN (J. Indian Chem. Soc., 1935, 12, 197).—The apparatus operates at low temp., and H_2O is excluded. An immersion filter, *F*, is placed in the mixture, *M*, in a wide test-tube, *T*, surrounded by the freezing bath, and the stem of *F* passes through a cork *C* attached to the top of *T* by wide rubber tubing. A $CaCl_2$ tube and thermometer also pass through *C*. After part of *M* has solidified, the excess of pressure in *F* is changed to a deficiency and the fluid portion of *M* is thus removed.

J. G. A. G.

Pressures of 5000 kg. per sq. cm. I. Fundamental determination of the effective cross-section of the pressure balance. H. EBERT (Physikal. Z., 1935, 36, 385—388).—The construction of a differential pressure balance and the determination of the effective cross-section are described.

A. J. M.

Simple lecture apparatus for demonstration of the Peltier effect. H. ČECH (Physikal. Z., 1935, 36, 415—416).

A. J. M.

Equivalents. F. H. VAN LEENT (Chem. Weekblad, 1934, 31, 777—778).—The author advocates the extended use of equiv. wts. rather than at. and mol. wts., and of formulæ such as K_2O , Mn_2O_7 rather than $KMnO_4$, particularly in the teaching of chemistry.

H. F. G.

Chinese influence on Western alchemy. W. H. BARNES (Nature, 1935, 135, 824—825).

L. S. T.

Origin of chemistry: definition of flame. J. R. PARTINGTON (Nature, 1935, 135, 916).—Historical.

L. S. T.

Geochemistry.

Recent development of geochemistry. W. VAN TONGEREN (Chem. Weekblad, 1935, 32, 304—317).—A review.

D. R. D.

Sampling apparatus and composition of air in the stratosphere. A. LEPAPE and G. COLANGE (Compt. rend., 1935, 200, 1340—1342).—An automatic sampling globe, with arrangements for recording time, pressure, and temp. of sampling, is described.

The O_2 is determined by absorption and circulation over heated Cu in a special apparatus.

N. M. B.

Jugoslavian iodine-containing mineral waters. S. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1934, 5, 155—177).—Petroliferous strata in Jugoslavia are located along the former sea-coast. Analytical data are given for the mineral H_2O of these strata.

R. T.

Mineral water of Strumicka Banja. D. KENIG (Bull. Soc. Chim. Yougoslav., 1934, 5, 179—187).—Analytical data are recorded. R. T.

Deuterium content of naturally occurring water. A. J. EDWARDS, R. P. BELL, and J. H. WOLFENDEN (Nature, 1935, 135, 793).—The increase in d following the electrolysis of tap- H_2O gives a val. of 6220 ± 300 for H/D . L. S. T.

Physico-chemical variables in a Minnesota lake. H. J. COSTING (Ecol. Monog., 1933, 3, 493—533).—Local and daily variations in pH , total CO_2 and free CO_2 contents of lake- H_2O are recorded. Soil samples from areas filled in by decomp. of plant residues consisted largely of marl (I) with a low % of org. matter (II). High (II) in the substratum was usually accompanied by a still higher (I) content. CH. ABS. (p)

Slovenian mineral springs and travertine. S. PRAT, J. HAMACKOVA, and J. VOLKO-STAROHORSKY (Sborn. Masaryk. Akad. Prace, 1934, 8, No. 5, 1—19; Chem. Zentr., 1935, i, 42).—The influence of physical and biological factors on the mineral content of spring waters, and on the rate and structure of sediment deposition, is discussed. J. S. A.

Iodine mineral waters in Yugoslavia. S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1934, 5, 155—177).—Analyses of I waters in petroleum-bearing strata are given. C. W. G.

Carbonated spring water from Burgenland. E. DITTLER and R. DWORZAK (Chem. Erde, 1935, 9, 269—285).—Analysis shows considerable Na, Mg, SO_4 , and free CO_2 . The Mg is probably derived from the underlying serpentine. L. J. S.

Heavy water content of French and other mineral waters. K. HANSEN, E. RUSTUNG, and J. HVEDING (J. Pharm. Chim., 1935, [viii], 21, 538—541).—The % of D_2O in various medicinal waters, determined by d (flotation method) after purification by repeated distillation (κ 1.1— 3.89×10^{-6} ohms $^{-1}$), is the same as that in ordinary H_2O . J. W. B.

Data in oceanographical chemistry. N. M. CARTER, E. G. MOBERG, T. SKOGSBERG, and T. G. THOMPSON (Proc. 5th Pacific Sci. Congr., 1934, 1933, 2123—2127).—A review and discussion of methods of reporting data. CH. ABS. (e)

Diffusion and reactions in solids. P. ESKOLA (Bull. Comm. geol. Finlande, 1934, No. 104, 144—156; Chem. Zentr., 1935, i, 192).—A discussion of solid reactions under pressure with reference to petrological problems. H. J. E.

Chemical structure of the earth. I. I. SASLAVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 537—543).—A discussion of data. H. J. E.

Age of uraninite and monazite from the pegmatic seams in North Carelia. A. N. LABUNTZOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 646—648).—The Pb from uraninite (U 61.14, Pb 18.10%) has a mean at. wt. of 206.06 corresponding with the at. wt. of its isotope Ra-6. From this the age of uraninite is 2.125×10^6 years. From the at. wt. of Th contained in monazite the age of the monazite is 2.114×10^6 years. W. R. A.

Analysis and optical properties of thoreaulite. J. MELON (Bull. Acad. roy. Belg., 1935, [v], 21, 473—475).—Thoreaulite (Ta_2O_5, SnO_2) gave on analysis Ta_2O_5 72.83, SnO_2 21.88, SiO_2 1.85, Fe_2O_3 0.50, Al_2O_3 1.02, CaO 1.28%, and traces of Nb_2O_5 , Sb_2O_5 , MnO , and MgO . The mineral has high refractive index, is clinorhombic, and has hardness 6 and d 7.6—7.9. W. R. A.

Structures of vermiculites and their collapse by dehydration. J. W. GRUNER (Amer. Min., 1934, 19, 557—575).—The formula is $(OH)_2(Mg, Fe)_3(Si, Al, Fe)_4O_{19.4}H_2O$. The crystal is monoclinic holohedral (a_0 5.3, b_0 9.2, c_0 28.57—28.77 Å.; probable space-group C_{2h}^2 ; 4 mols. per unit cell). The structure consists of $(OH)_4Mg_6(Si, Al)_8O_{20}$ sheets with alternate layers of $8H_2O$ occupying a space 4.9 Å. thick. Half the H_2O can be driven off at 110° without essential change in the powder diagrams, but at 750° a collapse of the talc structure occurs. CH. ABS. (e)

Porphyry from the Gulf of Bothnia. P. ESKOLA (Bull. Comm. géol. Finlande, 1934, No. 104, 111—127; Chem. Zentr., 1934, ii, 3493).—The minerals are described. H. J. E.

Mineralogy and genesis of the Mayville iron ore of Wisconsin. J. E. HAWLEY and A. P. BEAVAN (Amer. Min., 1934, 19, 493—514).—The characteristics of the ore deposit are described and discussed. CH. ABS. (e)

Geological geophysical prospecting for bituminous shale deposits in the Lower Volga area, particularly in the Obshchi Suirt district. N. M. POPOV. Prospecting for bituminous shale in the Ozinki-Tshair Lower Volga district. I. I. KROMM (Bit. Shale and Tech. Utilisation, 1932, 45—71, 82—88).—Analyses are recorded and discussed. CH. ABS. (e)

Content of rare elements in igneous rocks. E. TROGER (Chem. Erde, 1935, 9, 286—310).—The average contents of Ti, Mn, Ba, Sr, Zr, Cr, Li, V, Ni, P, S, F, and Cl given by published analyses are tabulated for different types (acid to basic) of rocks. L. J. S.

Minor chemical constituents of some igneous rocks. G. A. HARCOURT (J. Geol., 1934, 42, 585—600).—Spectroscopic data for 14 granites are recorded. Ba, Sr, Mn, B, and Cr were found in nearly all; Sn, Pb, and Ag were present in half, and Co in one specimen. CH. ABS. (e)

X-Ray study of narsarsukite, $Na_2(Ti, Fe)Si_4O_{11}$. B. E. WARREN and C. R. AMBERG (Amer. Min., 1934, 19, 546—548).—The mineral is tetragonal (a 10.74, c 7.90 Å.; 4 mols. per unit cell; space-group S_6^2 , C_4^2 , or C_4^1). CH. ABS. (e)

Unmixing of chalcopryrite from sphalerite. N. W. BUERGER (Amer. Min., 1934, 19, 525—530).—Polished sections 1 mm. thick were heated in vac. at 200—500° and cooled rapidly. At 350—400° small blebs of chalcopryrite (I) appeared in the sphalerite (II) in the region of the larger masses, indicating the unmixing of a solid solution of (I) in (II). CH. ABS. (e)

Synthesis of spinels. A. BAZILEVICH (Min. Suir., 1934, 9, No. 9, 25—30).—The powdered oxide mix-

ture was formed into cubes and heated for 2 hr. at the following optimum temp.: $\text{MgO}, \text{Al}_2\text{O}_3$, 1600—1750°; $\text{MgO}, \text{Cr}_2\text{O}_3$, 1600—1700°; $\text{MgO}, \text{Fe}_2\text{O}_3$, 1350°; forsterite, formed in presence of SiO_2 , 1400—1600°. At higher temp. vitrification occurs. Al spinel has abrasive properties equal to those of pumice stone. It is a promising refractory material. CH. ABS. (e)

Pyrites in quartz. F. BRECH (Nature, 1935, 135, 917).—Unusual features of Brazilian quartz containing pyrites inclusions are described. L. S. T.

Chemical composition of tschewkinite. I. P. ALIMARIN (Compt. rend. Acad., Sci. U.R.S.S., 1935, 1, 648—653).—The empirical formula, $\text{R}^{\text{II}}\text{R}^{\text{III}}\text{R}^{\text{IV}}\text{O}_{10} \cdot x\text{H}_2\text{O}$, is derived from analysis. W. R. A.

Spectral analysis of tektites. E. PREUSS (Chem. Erde, 1935, 9, 365—418; cf. A., 1934, 988).—Tektites and SiO_2 -glass from various localities were examined by the method of Mannkopf and Peters (A., 1931, 991). No definite conclusion as to the origin of these bodies can be reached. L. J. S.

Petrogenesis of the Franconian Wellenkalk. P. SCHMITT (Chem. Erde, 1935, 9, 321—364).—Descriptions with chemical analyses of the limestones and dolomites of the Wellenkalk (Triassic) formation. L. J. S.

X-Ray examination of turquoise. K. F. MAYER (Chem. Erde, 1935, 9, 311—317).—X-Ray powder photographs of turquoise from several localities and of artificial material show similar patterns. A somewhat similar pattern is also shown by wavellite and chalcociderite. L. J. S.

X-Ray examination of turquoise and other phosphates. H. JUNG (Chem. Erde, 1935, 9, 318—320).—A discussion of the preceding paper. L. J. S.

Copper minerals of Kinsenda (Belgian Congo). I. Bornite-chalcocopyrite associations. M. GYSIN (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 24—27).—The deposits consist of lamellæ of chalcocopyrite separated by grains of bornite. The genesis of the minerals is discussed. A. J. M.

Constitution of sepiolite from Ampandrandava. H. LONGCHAMON (Compt. rend., 1935, 200, 1607—1610).—From the composition, cryst. structure, and physico-chemical properties, the formula $(\text{Mg}, \text{H}_2)_3\text{Si}_4\text{O}_{11} \cdot \text{H}_2\text{O} \cdot z\text{H}_2\text{O}$ is suggested for this compound, the term $z\text{H}_2\text{O}$ representing the zeolitic H_2O . J. W. S.

Properties of sepiolite from Ampandrandava. H. LONGCHAMON (Compt. rend., 1935, 200, 1331—1333; cf. preceding abstract).—Curves for dehydration and transition of form are given and discussed. N. M. B.

Constitution of senonian phosphates from Syria. L. CAYEUX (Compt. rend., 1935, 200, 1553—1555).—The forms of phosphates from three localities have been examined and are discussed with reference to the origin of the deposits. J. W. S.

Orthitic granites of South-West Karamazar. A. L. LISOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 588—592).—A discussion of the geological structure of the region. H. J. E.

Orthites in mid-asiatic rocks. N. POROKOPENKO (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 532—536).—The occurrence of the minerals is described. H. J. E.

[Description of various minerals.] R. KOECHLIN (Zentr. Min., 1934, A, 256—266; Chem. Zentr., 1934, ii, 3493).—Data are recorded for laurionite, zeophyllite, phosphosiderite, euclase, and other minerals. H. J. E.

Nickel deposits associated with diabase in Nassau. F. AHLFELD (Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg, 1933, 68, 93—122; Chem. Zentr., 1934, ii, 3494).—The deposits are described. Their origin and development are discussed. H. J. E.

Occurrence of vivianite in the District of Columbia. J. H. BENN (Amer. Min., 1935, 20, 311—312).—The vivianite occurs at Washington as small blue masses embedded in clay. It is associated with limonite and muscovite. L. S. T.

Amphibole from the Purcell sills, British Columbia. H. M. A. RICE (Amer. Min., 1935, 20, 307—309).—Partial analyses and optical properties of the two different types of amphibole which occur in the Purcell sills are recorded. L. S. T.

Mineragraphy and X-ray analysis of stainierite from the Swansea mine, Goodsprings, Nevada. S. R. B. COOKE and D. J. DOAN (Amer. Min., 1935, 20, 274—280).—X-Ray data show that the Co in the ore is present as stainierite (I), $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the cryst. form of heterogenite, with which it has sometimes been confused. (I) occurs in the ore as two varieties, one cryst. and anisotropic and the other cryptocryst. and isotropic. X-Ray data show no essential differences between the two varieties. Both are slowly sol. in cold HCl. The crude ore contains 1.23% of Co. L. S. T.

Granite, pegmatite, and replacement veins in the Sheahan Quarry, Graniteville, Missouri. C. TOLMAN and S. S. GOLDBICH (Amer. Min., 1935, 20, 229—239).—The granite (I), pegmatite (II), and replacement veins are genetically related. (I) consists of quartz, albite, orthoclase, microcline, and a small amount of accessory minerals. Secondary minerals include magnetite, muscovite, fluorite, sericite, chlorite, calcite, hæmatite, and pyrite. (II) is complex. Perthite and quartz represent the magmatic stage, whilst hydrothermal minerals are topaz, muscovite, albite, beryl, biotite, rutile, cassiterite, sericite, fluorite, pyrite, chalcocopyrite, and galena. Chemical analyses for (I), perthite, beryl, and muscovite are given. L. S. T.

Alteration of the lavas surrounding the hot springs in Lassen Volcanic National Park, California. C. A. ANDERSON (Amer. Min., 1935, 20, 240—252).—The blue-black basalts, the grey pyroxene andesites, and the pale grey dacites are all bleached and decomposed to white, and rarely to yellow, brown, and red, products. Opal (I) accompanied by minor amounts of kaolin (II) and alunite is the chief product in the altered exteriors of lava fragments where active decomp. is taking place. The muds from the hot spring basins usually contain

more (II). Tridymite, residual in part, but largely secondary, is also formed. The various types of alteration products appear to be related to the concn. of the H_2SO_4 . A high concn. favours the formation of (I) and a low concn. that of (II).

L. S. T.

Johannite from Joachimsthal and Colorado. M. A. PEACOCK (Z. Krist., 1935, 90, 112—119).—A morphological study.

B. W. R.

Pectolite. M. A. PEACOCK (Z. Krist., 1935, 90, 97—111).—Triclinic symmetry, found by X-ray examination, is confirmed.

B. W. R.

Distribution of selenium in nature. L. W. STROCK (Amer. J. Pharm., 1935, 107, 144—157).—The Se contents of magmatic rocks, sulphides of hydrothermal origin, caliche, sea- H_2O , sedimentary Fe ores, and pyrites are given and the biological and geological significance of the Se absorption by plants and $\text{Fe}(\text{OH})_3$ is discussed (cf. B., 1934, 418).

E. H. S.

Chemico-mineralogical characters of the tertiary eruptive rocks of Kabylie de Collo (Dept. of Constantine, Algeria). M. ROUBAULT (Compt. rend., 1935, 200, 1488—1490).—All the rocks are rich in quartz and consist of the types occurring generally in North Africa.

M. S. B.

Bowlingite. (Mlle.) S. CAILLIERE (Compt. rend., 1935, 200, 1483—1485).—Two specimens of bowlingite (I), a hydrated silicate of Fe, Mg, and Al, have been examined chemically and the results compared with an analysis of saponite (II). The analogy is confirmed by thermal and X-ray analysis. On dehydration by calcination, recrystallisation begins at 810° and indications of the X-ray diagram of enstatite appear. The change is complete at 910° and the product becomes slightly magnetic. At higher temp. still the definite formation of magnetite is observed. The products of calcination of (II) are similar. (I) is apparently a fibrous variety of (II). A sample of diabantite behaved similarly in all respects to (I).

M. S. B.

Measurement of geological time. A. HOLMES (Nature, 1935, 135, 680—683).—Mainly a discussion of the application of radioactive methods to the determination of the age of igneous rocks.

L. S. T.

Isotope ratio in petroleum. N. S. FILIPPOVA (J. Chem. Physics, 1935, 3, 316; cf. Dole, A., 1934, 853, 1185).—The H_2O obtained by burning a motor-petroleum from Machach-Kala in a calorimetric bomb contained 1.5 parts of D per 5000 of H compared with 1 : 5000 in distilled H_2O . If the O_2 used for combustion had an increased concn. of heavy O_2 the val. given for the ratio would have to be reduced.

M. S. B.

Petrographic characters of the Permian coals of the Belgian Congo. A. DUPARQUE (Compt. rend., 1935, 200, 1490—1492).—The coals are very similar in character to bituminous Westphalian coals and stand between spore or cuticle coals and cannel coal.

M. S. B.

Microscopic structure of coals of the Kousnetz basin. M. D. ZALESKI and H. T. TSCHIRKOVA (Bull. Acad. Sci. U.R.S.S., 1934, 1319—1324).—The coal described is an old earthy peat composed mainly of a brownish-red jelly-like material with dispersed micrococci and fragments of modified wood (*Dadoxylon mungaticum*, Zal., and, probably, *Mesopitys Tchihatcheffi*, Goeppert).

T. H. P.

Classification of coals. W. A. BONE (Nature, 1935, 135, 910—911).—A criticism of the Stopes nomenclature.

L. S. T.

Classification of coals. R. LESSING (Nature, 1935, 135, 911).—A reply to criticism (cf. above).

L. S. T.

Evaluation of experimental data for slate and greywacke soils. R. GANSSEN and K. UTESCHER (Mitt. Lab. preuss. geol. Landesanst., 1934, 20; Chem. Zentr., 1935, i, 42).—A method is given for calculating the transport of individual soil components.

J. S. A.

Organic Chemistry.

Electronic theory and organic chemistry. II. Structure of open-chain unsaturated organic compounds. V. RASUMOVSKI (Bull. Soc. chim., 1935, [v], 2, 762—788).—The electronic theory of valency previously developed (this vol., 431) is applied in detail to various unsaturated open-chain hydrocarbons and cyclic systems, especially in relation to the reactivity of the various possible electromerides. The following phenomena are discussed on this basis, predictions in all cases being in harmony with experimental data: the greater reactivity of C_2H_4 than of C_2H_2 in additive reactions; *cis-trans* isomerism of C_2H_4 derivatives; the isomerisation of $\text{CHPr}^2\text{:CH}_2$ and $\text{CPr}^2\text{:CH}$ contrasted with the stability of $\text{CMe}_2\text{:CH}_2$; the greater reactivity of C_2H_4 and of cyclohexane than of C_6H_6 , and the smaller stability of cyclooctatetraene; the greater reactivity of C_6H_6 than of $(\text{CPh}_2)_2$ or of $\text{C}_5\text{H}_5\text{N}$;

the order of free radical stability $\text{Me} < \text{CHPh}_2 < \text{CPh}_3$, and the orientation of substitution in C_6H_6 and C_{10}H_8 .

J. W. B.

Isomerisation of *n*-heptane. G. CALINGAERT and D. T. FLOOD (J. Amer. Chem. Soc., 1935, 57, 956).—Pyrolysis of *n*- C_7H_{16} by AlCl_3 at 100° gives a mixture containing 1% of *n*- C_6H_{14} and 4% of 3-methylhexane, but no other isomeric heptane.

R. S. C.

Index of unsaturation of ethylenic compounds. VOLMAR and WAGNER (Bull. Soc. chim., 1935, [v], 2, 826—844).—Using Farnsteiner's gravimetric method (Br in Et_2O at -10° and weighing the additive Br compound) as a standard, the various lit. methods for determination of the index of unsaturation have been tested with ethylenic hydrocarbons ($\text{C}_{16}\text{H}_{32}$), alcohols ($\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$), bromides ($\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{Br}$), and acids (oleic, linoleic,

and $\text{CHPh}:\text{CH}:\text{CO}_2\text{H}$) and diallylbarbituric acid. The following are the main conclusions. I must be added at 15–25°, and Br at < 0°. Addition of I without a catalyst (Margosches *et al.*, A., 1924, ii, 575) is often incomplete, and is useless when negative groups are present, since these greatly reduce the activity of the double linking. Hübl's method ($\text{I}-\text{HgCl}_2$) is applicable for small indices, but fails in presence of acids containing >1 double linking, and cannot, therefore, be used for drying oils. SCN is more reactive than I and is satisfactory for ethylenic hydrocarbons, but gives low vals. in other cases. Wijs' method (ICI) is satisfactory for open-chain derivatives, but not for bromides. Of methods using IBr that of Hanus (A., 1902, ii, 112) is best, but is not applicable to aromatic unsaturated acids. Winkler's method (A., 1925, ii, 446) is satisfactory for the usual oils, soaps, and resins, but the presence of two non-miscible phases is an objection and it gives low results with aromatic compounds. The method of Volmar *et al.* (B., 1928, 236) is trustworthy in all cases, requires no blank determination, and is capable of use in micro-determinations.

J. W. B.

Action of bromine on butadiene.—See this vol., 827.

$\alpha\epsilon$ -Dibromo-*n*-pentane. A. MÜLLER (Ber., 1935, 68, [B], 1013).—The contamination of $\alpha\epsilon$ -dibromo-*n*-pentane with PhCN described by Johnson (A., 1934, 55) is due to removal of H_3PO_4 previous to heating the product of the action of 1-benzoylpiperidine and PBr_5 with HBr . If the directions of von Braun *et al.* (A., 1905, i, 341) are followed, the product reacts readily with Mg .

H. W.

Bromo-derivatives of olefines C_8 to C_{11} . M. TUTOR (Compt. rend., 1935, 200, 1418–1420).—Reaction does not occur between the olefines and HCl at 20°, whilst with HI the change is not sufficiently rapid to avoid dissociation leading to polyhalogenated compounds. Saturation of olefines with dry HBr at 0°, followed by treatment of the product with ice- $\text{H}_2\text{O}-\text{Et}_2\text{O}$, washing with aq. K_2CO_3 at 0°, and desiccation with CaCl_2 , leads to the following compounds: β -bromo- γ -methylheptane, b.p. 69°/12 mm.; δ -bromo- $\beta\delta$ -dimethylhexane, b.p. 67°/15 mm.; β -bromo- $\epsilon\epsilon$ -dimethylhexane, b.p. 64°/15 mm.; δ -bromo- $\beta\delta$ -dimethylheptane, b.p. 80°/15 mm.; ϵ -bromo- $\beta\epsilon$ -dimethylheptane, b.p. 83°/16 mm.; β -bromo- $\beta\gamma\epsilon$ -trimethylhexane, b.p. 79°/15 mm.; δ -bromo- $\beta\delta$ -dimethyloctane, b.p. 93°/15 mm.; δ -bromo- $\beta\delta\zeta$ -trimethylheptane, b.p. 83°/15 mm.; δ -bromo- $\beta\delta\eta$ -trimethyloctane, b.p. 98°/11 mm. The monobromides are readily hydrolysed to the corresponding alcohols, the b.p. of which are about 40–50° > those of the olefines. Separation of mixtures of olefines with saturated and benzenoid hydrocarbons of similar b.p. is effected by the action of HBr followed by hydrolysis and distillation, whereby the corresponding alcohol is readily isolated; benzenoid and saturated hydrocarbons are not attacked and are separated by use of HNO_3 . Olefines suspended in very dil. H_2SO_4 are converted by $\text{KBr}-\text{KBrO}_3$ into non-distillable dibromides which are sufficiently pure to be useful in separations.

H. W.

Natural and synthetic $\Delta^{\beta(\gamma)}$ -hexenol. S. TAKEI, T. IMAKI, and Y. TADA (Ber., 1935, 68, [B], 953–956).—Sorbic acid is reduced by $\text{Na}-\text{Hg}$ in H_2O to hydrosorbic acid (*p*-iodophenacyl ester, m.p. 92°), the Et ester, b.p. 165–168°, of which is converted by Na and EtOH into Δ^{β} (or Δ^{γ})-hexenol, b.p. 153–156° (4'-iododiphenylurethane, m.p. 155–156°). Et sorbate similarly affords a Δ^{γ} -hexenol (4'-iododiphenylurethane, m.p. 148°; 3:5-dinitrobenzoate, m.p. 28°). The identity of these hexenols with that obtained from the leaves of fresh green tea (probably *trans*- Δ^{γ} -hexenol) is excluded by the differences in odour and the physical consts. of their derivatives.

H. W.

Symmetrical pentanetriol. L. BLANCHARD and R. PAUL (Compt. rend., 1935, 200, 1414–1415).—4-Pyrone is hydrogenated incompletely and with difficulty in presence of Pt-black or of Ni as customarily obtained. In presence of Ni prepared by Raney's technique it is rapidly transformed into tetra- and thence into hexa-hydropyrone (I), b.p. 90°/19 mm., which affords $\alpha\gamma\epsilon$ -tribromopentane, b.p. 143°/25 mm., with HBr at 100°. (I) is unattacked by Ac_2O at 200°. Treatment of (I) with an insufficiency of HBr and subsequently with KOAc at 130–140° gives a mixture of acetates hydrolysed by $\text{Ba}(\text{OH})_2$ to *n*-pentane- $\alpha\gamma\epsilon$ -triol, b.p. 188–189°/11 mm. (phenylurethane, m.p. 154°).

H. W.

Polarimetric determination of mannitol. M. FREREJACQUE (Compt. rend., 1935, 200, 1410–1412).—Use of As_2O_3 in the polarimetric determination of mannitol (I) is convenient but not highly accurate, since the increments in rotation are small. In presence of >2 MoO_3 per mol. (I) has $[\alpha]_{\text{D}}^{20} +169^\circ$. For the determination of (I) in wines etc. the liquid is treated with C and Pb subacetate and centrifuged. After removal of excess of Pb by H_2S and of H_2S by air, the solution is centrifuged and polarised. An aliquot portion is then treated with $N\text{-H}_2\text{SO}_4$ and 0.1*N*-molybdate and again polarised. The operation in acid solution avoids errors due to mannose or fructose.

H. W.

Polymerisation and ring-formation. XXIV. **Cyclic and polymeric formals.** J. W. HILL and W. H. CAROTHERS. XXV. **Macrocyclic esters.** XXVI. **meta- and para-Rings.** E. W. SPANAGEL and W. H. CAROTHERS (J. Amer. Chem. Soc., 1935, 57, 925–928, 929–934, 935–936; cf. A., 1934, 392).—XXIV. $\text{CH}_2(\text{OBU})_2$ and polymethylene glycols afford α -polyformals, which at 230–250°/low pressure give β - (I) and ω -forms (II). The monomeric (I) are indistinguishable in odour from the corresponding carbonates; e.g., the 17-membered rings have a musk-like odour, but the dimerides are odourless. $\text{CH}_2(\text{OBU})_2$ with $\text{OH}[\text{CH}_2]_3\text{OH}$ (III) and $\text{OH}[\text{CH}_2]_4\text{OH}$ affords relatively volatile cyclic monomerides. That from (III) is 6-membered (cf. the sugars) and does not polymerise, but the higher membered cyclic monomerides polymerise. The ω -polymerides can be drawn into tough, elastic, oriented (X-ray diagrams) fibres. The following *poly-methylene formals* are described: (α) monomerides, tetra-, b.p. 112–117°, and penta-methylene, b.p. 40–44°/11 mm., and triethylene glycol, m.p. 18–

20°; (b) dimerides, deca-, m.p. 93–94°, penta-, m.p. 55–56°, hexa-, m.p. 71–72°, nona-, m.p. 68–69°, and tetradeca-methylene, m.p. 103.5–104°; (c) ω -polymerides, penta-, m.p. 38–39°, hexa-, m.p. 38°, nona-, m.p. 54–55°, deca-, m.p. 56–57°, tetradeca-, m.p. 68–69°, and octadeca-methylene, m.p. 71–72°, and triethylene, a syrup, of which the last is most readily depolymerised (70%).

XXV. Depolymerisation of linear polyesters is rapidly effected by heating to a carefully controlled temp. at 1 mm. with various inorg. catalysts. Mono- and/or di-meric cyclic esters are formed in yields often of 60–75% in 1–2 hr. The following monomerides are described, data in parentheses referring to the corresponding dimerides: (a) *succinates*: *tri*-, b.p. 94–100°/2 mm., m.p. 81° (138°), *tetra*-, b.p. 95–96°/2 mm., m.p. 42° (121°), *penta*-, b.p. 88–89°/1 mm., m.p. 19° (87°), *hexa*-, b.p. 108–110°/2 mm., m.p. –15° (110°), *hepta*-, b.p. 116–118°/1–2 mm., m.p. 49° (86°), *octa*-, m.p. 71° (101°), *nona*-, m.p. 71°, *deca*-, b.p. 135–140°/2 mm., m.p. 58° (109°), *dodeca*-, b.p. 156–159°/2 mm., m.p. 12°, *trideca*-, b.p. 154°/1–2 mm., m.p. 13°, *tetradeca*-, b.p. 167°/2 mm., m.p. 11°, and *octadeca-methylene*, b.p. 199–201°/2 mm., m.p. 13°; *ethylene* (m.p. 131°); (b) *adipates*: *hexa*-, b.p. 117°/2 mm., m.p. 70°, and *nona-methylene*, b.p. 144–146°/2 mm., m.p. 26°; *triethylene glycol*, b.p. 162°/2 mm., m.p. 59°; (c) *azelates*: *ethylene*, m.p. 52° (145°), *tetra*-, b.p. 123–124°/2 mm., m.p. 9°, and *hexa-methylene*, m.p. 59°; (d) *sebacates*: *ethylene*, b.p. 119–123°/2 mm., m.p. 42° (81°), *tri*-, b.p. 130–133°/2 mm., m.p. 7° (110°), *tetra*-, b.p. 136–138°/2 mm., m.p. 6°, *penta*-, b.p. 159–160°/2 mm., m.p. 37°, and *hexa-methylene*, m.p. 47°, and *diethylene glycol*, b.p. 156–157°/2 mm., m.p. 15°; (d) *heptamethylene suberate*, b.p. 158–160°/1–2 mm., m.p. 47°; *ethylene decamethylenedicarboxylate*, b.p. 139–141°/2 mm., m.p. 18° (96°), and *brassyate*, b.p. 139–142°/1 mm., m.p. –8° (146°); *decamethylene octadecanedicarboxylate*, m.p. 60°. 9–13-membered rings are formed in poorest yields; with higher members there are indications of alternations, with lower yields for rings with an even no. of atoms. Depressions in $[M_n]$ are greatest for 9–14-membered rings, but are occasionally 0 for large rings. Other physical data, including odour, are discussed.

XXVI. m -C₆H₄(O·CH₂·CO₂H)_n and polymethylene glycols at 190–210° give resinous, polymeric *esters* (I), m -C₆H₄(O·CH₂·CO₂)₂(CH₂)_n; the *nonamethylene* polymeride is cryst., m.p. 35–40°. p -C₆H₄(O·CH₂·CO₂Et)₂ with glycols and a trace of SnCl₄ at 190–210° gives polymeric *p*-ring *esters* (II) [as (I)]; the *tetra*-, *hexa*-, and *deca-methylene* esters have m.p. 45–50°, 50–55°, and 60–65°, respectively. Depolymerisation by 1–2% of SnCl₄ at 270°/1 mm. affords the following monomeric, cryst. esters [the m.p. given first is that of the *m*-ring ester (I), that given second of the *p*-ring ester (II), and the figures in parentheses the corresponding pure yields %]: *ethylene*, m.p. 100°, – (21, 0); *tri*-, m.p. 134°, – (24, 0), *tetra*-, m.p. 112°, 140° (16, 12), *hexa*-, m.p. 115°, 124° (35, 12), *nona*-, 86°, – (35, –), and *deca-methylene*, m.p. 86°, 58° (35, 18). The smallest *m*- and *p*-rings obtainable have 13 and 16 members, respectively. R. S. C.

Fission of ethyl thiosulphite S₂(OEt)₂. A. MEUWSEN and H. GEBHARDT (Ber., 1935, 68, [B], 1011–1013).—Treatment of S₂(OEt)₂ with NaOEt in warm EtOH causes separation of S and formation of Et₂ sulphonylate (I), S(OEt)₂, b.p. 23–24°/17 mm., the action appearing catalytic. (I) is immediately decomposed by KOH–MeOH with separation of S. It immediately decolorises Br in CCl₄ and is converted by prolonged treatment with O₂ into Et₂SO₃.

H. W.

alloTelluric acid [esters].—See this vol., 834.

Reaction between esters of organic acids and magnesium isopropyl chloride. II. Ethyl acetate and propionate. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1935, [v], 2, 816–824).—EtOAc reacts with MgPr^{is}Cl (3 mols.) in Et₂O to give a 93% yield of C₃H₈, the other products depending partly on the method of isolation. Decomp. with NH₄Cl or dil. H₂SO₄ and distillation under reduced pressure gives OH·CMePr^{is}·CH₂·COPr^{is} (I) (65%) (semicarbazone, m.p. 116–117°; lit. 109°) [dehydrated by I to CMePr^{is}·CH·COPr^{is} (II); hydrolysed by aq. KOH to COMePr^{is} (III)], and small amounts of (II), (III), EtOAc, and EtOH. Decomp. with NH₄Cl and distillation at atm. pressure affords (III) (60%) and (II); when decomp. is effected with dil. H₂SO₄ (II) is the main product, small amounts of (III) and of CH₂Ac·COPr^{is} (IV) also being obtained. (IV) is obtained in 12% yield under prescribed conditions. With MgEtBr (II) gives β -dimethyl- ϵ -isopropyl- Δ^2 -n-hepten- ϵ -ol, b.p. 60–64°/1 mm. (III) with MgPr^{is}Cl gives a 70% yield of (I), in agreement with the suggested mechanism of these reactions. EtCO₂Et and MgPr^{is}Cl and decomp. with NH₄Cl and distillation under atm. pressure give 73% of C₃H₈ and 48% of COEtPr. In accordance with the suggested mechanism approx. the same % of gas is evolved by the action of MgRX on the ketone, the corresponding ester, or the ketol. J. W. B.

Synthesis of β -chloropropionic acid by condensation of carbonyl chloride with ethylene. A. L. KLEBANSKI and K. K. TSCHEVITSCHALOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 42–47).—Interaction of C₂H₄ and COCl₂ is investigated under many different conditions of temp., pressure, solvents, and catalysts. With AlCl₃ in CS₂ at < 0°, CH₂Cl·CH₂·CO₂H and acrylic acid are formed.

J. L. D.

Catalytic hydrogenation of unsaturated organic compounds by means of selenium.—See this vol., 829.

Reduction [debromination] of fatty acid bromides. W. KIMURA (Fettechem. Umschau, 1935, 42, 78–80).—5*N*-H₂SO₄–MeOH solution in conjunction with Zn is convenient for the debromination of fatty acid bromides to form the corresponding unsaturated Me esters. E. L.

Simultaneous reactions in the pyrolysis of ricinoleic esters and especially of castor oil. I. Mechanism of and optimum conditions for ricinoleic scission. A. BARBOT (Bull. Soc. chim., 1935, [v], 2, 895–910).—In the pyrolysis of castor oil two reactions are superimposed: (a) dehydration to $\Delta^6\alpha$ -

and Δ^8 -linoleic acids, which then undergo spontaneous polymerisation to a spongy residue and (b) fission into ricinoleic acid (I) and *n*-heptaldehyde (II), and the further scission products, undecenoic acid (III), $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$, C_8H_{16} , and, probably, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_8\cdot\text{CHO}$, and myristic, palmitic, stearic, and oleic acid. The effect of varying conditions on the relative importance of the two decomp. is studied in detail by analysis of the products at various stages. At 185–190° a little H_2O is evolved, but decomp. into (II) and (III) begins sharply at 285–290°. This temp. and the yields obtained are almost independent of pressure, but (b) increases much more rapidly than (a) with rise of temp.. Hence rapid distillation at $> 500^\circ/15\text{--}35\text{ mm.}$ (conditions prescribed) affords much increased yields of (II) (23–24% of the wt. of the oil, i.e., 82–83% of the theoretical) and (III) (10–14%), although the higher temp. slightly reduces the yield of (III) by favouring its polymerisation. Evolution of H_2O increases 9-fold at the moment of formation of the spongy polymeride. To explain the results it is suggested that (I) exists in the tautomeric forms

$$\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H} \rightleftharpoons \text{C}_6\text{H}_{13}\cdot\text{CH}\langle\text{CH}_2\text{O}\rangle\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$$

the former undergoing dehydration and the latter scission in various ways.

J. W. B.

Ether-like compounds. XVI. Influence of oxygen in the atomic chain on esterification and hydrolysis. M. H. PALOMAA and K. R. TUKKIMAKI (Ber., 1935, 68, [B], 887–892).—Examination of the esterification, $\text{OR}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H} + \text{MeOH} \xrightleftharpoons[k_2]{k_1}$

$\text{OR}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Me} + \text{OH}$, catalysed by HCl when $\text{R}=\text{Me}$, Et , Pr^a , Pr^b , Bu^a , or Bu^b and $n=1, 2, 3$, or 4 , shows that k_2 is at a pronounced min. when $n=2$. The nature of R has little influence on k_2 or k_1 or on the temp. coeffs. Within the limits $n=1\text{--}4$ the latter are nearly equal and about the same as that of $\text{Pr}\cdot\text{CO}_2\text{H}$. The effect of the ratio $\text{H}_2\text{O}\text{--}\text{MeOH}$ in the solvent has been examined. Two extreme cases are recognised, in the first of which the rate of reaction is parallel to that of the mol. concn. of the solvent participating in the change or of its components, whereas in the second the influence of the solvent remains approx. the same over a wide variation of concn. The difference is ascribed to constitutive factors, notably α -substitution. Substances which in a definite reactive solvent fall into the second category are probably solvatised in a high degree.

H. W.

Preparation of acetylenedicarboxylic acid from fumaric acid. C. MUSANTE (Gazzetta, 1935, 65, 199–200).—From $(\text{CHBr}\cdot\text{CO}_2\text{H})_2$ (I) prepared from fumaric acid, the latter is removed by treating an Et_2O extract with aq. KOH , and acidifying the aq. solution. The pure (I) is then treated with $\text{KOH}\text{--}\text{EtOH}$ in the usual way.

E. W. W.

Alkaline ceritartrates. M. FOUCHET (Bull. Soc. chim., 1935, [v], 2, 701–707).—Oxidation (O_2) of a solution of cerous *d*-tartrate in $2N\text{--KOH}$ (free from K_2CO_3) and evaporation of the solution at $< 50^\circ/\text{vac.}$ affords *K d-ceritartrate* (I) $+ 6\text{H}_2\text{O}$, $[\alpha]^{16} + 137.5^\circ$

(crystallographic data), from which ceritartronic acid is liberated by AcOH . The corresponding *K l-ceritartrate*, $[\alpha]^{16} - 137.3^\circ$, is similarly prepared. On the basis of its cryst. form and $[\alpha]$ the structure $[\text{CO}_2\text{K}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{CO}_2\text{K})\cdot\text{O}\cdot\text{Ce}\cdot\text{O}]_n$ is suggested for (I).

J. W. B.

Synthesis of ascorbic acid and its identity with vitamin-C. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 59–63).—Synthetic ascorbic acid, prepared according to Reichstein *et al.* (A., 1934, 511), is identical with the natural product in properties and therapeutic activity.

F. R. S.

E. Fischer's allomucic acid. T. POSTERNAK (Naturwiss., 1935, 23, 287).—An equimol. mixture of *d*- and *l*-talomucic acids (A., 1892, 299; 1894, i, 218) is identical with the acid which Fischer (A., 1891, 1193, 1444) regarded as allomucic acid and as having the annexed structure. The acid of this structure is as yet unknown; the author expects to obtain it by the oxidation of *d*-allonic acid (A., 1911, i, 14).

H. G. M.

Mechanism of aldehyde, ketone, and ester condensations. K. BODENDORF (Ber., 1935, 68, [B], 831–832; cf. A., 1934, 991).—Mainly a reply to Tschelincev (this vol., 472). An electronic explanation of the mechanism is given.

H. W.

Determination of formaldehyde. J. H. NORRIS and G. AMPT (J. Soc. Chem. Ind. Victoria, 1933, 33, 801–810).—10 ml. of aq. CH_2O (approx. 4%) is treated with excess of $\text{NH}_4\text{Cl} + 25\text{ ml. of } 0.5N\text{--NaOH}$ in a stoppered flask. The excess of alkali is titrated back to 7.5 of aq. $(\text{CH}_2)_6\text{N}_4$ using cresol-red or bromothymol-blue.

J. S. A.

Reduction of carbonic acid by means of nascent hydrogen.—See this vol., 833.

Thermal oxidation of formaldehyde. R. SPENCE (Nature, 1935, 135, 961–962).—Packing with powdered Pyrex glass changes the course of the polymerisation and decomp. of CH_2O . The gaseous product is almost exclusively CO_2 instead of CO and H_2O .

L. S. T.

Thermal decomposition of acetaldehyde.—See this vol., 827.

Attempts to apply the Tschitschenko reaction to unsaturated aldehydes. E. V. ZAPPI and R. A. LABRIOLA (Anal. Asoc. Quím. Argentina, 1934, 22, 133–142).— $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ with $\text{Al}(\text{OEt})_3$ under varying conditions yields polymerides. $\text{CH}_3\cdot\text{CH}\cdot\text{CO}_2\text{CH}_3\cdot\text{CH}\cdot\text{CH}_3$ was not produced.

F. R. G.

Ethers of hydroxyaldehydes and their acetals. P. SCHORIGIN and V. KORSCHAR (Ber., 1935, 68, [B], 838–844).—Addition of geraniol to NaOEt in EtOH followed by removal of EtOH and treatment of the product with boiling $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})_2$ in presence of Cu powder gives $\beta\beta$ -diethoxyethyl geranyl ether (glycollaldehyde geranyl ether *Et*, acetal), b.p. $144^\circ/8\text{ mm.}$ Similarly, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})_2$, NaOH , and the requisite phenol at 100° and subsequently at $160\text{--}170^\circ$ yield the following aryl $\gamma\gamma$ -diethoxy-*n*-propyl ethers, $\text{R}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, in which $\text{R}=\text{C}_6\text{H}_5$, C_6H_4 , C_6H_3 , C_6H_2 , C_6H , C_5H_5 , C_5H_4 , C_5H_3 , C_5H_2 , C_5H , C_4H_4 , C_4H_3 , C_4H_2 , C_4H , C_3H_3 , C_3H_2 , C_3H , C_2H_2 , C_2H , C_1H .

Ph (I), b.p. 126°/6 mm., *o*-C₆H₄Me, b.p. 165°/18 mm., *m*-C₆H₄Me, b.p. 150°/5 mm., *p*-C₆H₄Me, b.p. 137°/5 mm., α -C₁₀H₇, b.p. 145°/2 mm., β -C₁₀H₇ (II), b.p. 166°/2 mm., m.p. 24—25°, CH₂Ph (III), b.p. 114°/2 mm., *isoamyl*, b.p. 111°/6 mm. Dil. acids decompose the acetals, R·O·CH₂·CH₂·CH(OEt)₂ + H₂O = R·OH + CH₂·CH₂·CHO + 2EtOH, and Ac₂O causes acetolysis. H₂SO₄, ZnCl₂ in boiling AcOH, or heating at 250° effects condensations of the type, R·O·CH₂·CH₂·CH(OEt)₂ → R·O·CH₂·CH₂·CHO → OR·CH₂·CH₂·CH(OH)·CH(CH₂·OR)·CHO → OR·CH₂·CH₂·CH·C(CH₂·OR)·CHO → OR·CH₂·CH₂·[CH·C(CH₂·OR)]₂·CHO etc. Thus (I) yields the compound (IV) C₆₃H₅₈O₈, in which the presence of 1 CHO is quantitatively established. Titration with Br indicates the presence of about 5 double linkings, the deficiency being due to incomplete elimination of H₂O from OH·CH·CH as established according to Zerevitinov. When treated with red P and conc. HI (IV) gives PhOH and a hydrocarbon CH₂Me·CH[·CMe·CH]₃·CMe₂, b.p. 185—195°/2 mm. The substances C₆₀H₆₂O₇ and C₃₉H₃₂O₄ are obtained from (III) and (II), respectively.

H. W.

Thermal decomposition of acetone vapour.—See this vol., 827.

Action of mixed organomagnesium compounds on aliphatic α -ethylenic ketones. J. COLONGE (Bull. Soc. chim., 1935, [v], 2, 754—761).— $\alpha\delta$. Addition of a Grignard reagent to the conjugated system in aliphatic α -ethylenic ketones ·C''·C'·C=O is favoured by an alkyl substituent on the C' of the olefinic radical, but when C'' is so substituted (with or without α -substitution) only the normal formation of a *tert*-alcohol is observed. These conclusions are based on the following results: Me α -methyl- Δ^2 -propenyl ketone with MgMeI affords only $\beta\gamma$ -dimethyl- Δ^2 -*n*-penten- β -ol (I), b.p. 53—54°/13 mm. (dehydrated by distillation at 760 mm. to the diene, b.p. 106—108°), but with MgMeBr (I) and a 20% yield of Me $\alpha\beta$ -dimethyl-*n*-butyl ketone are obtained; MgBuBr similarly gives (I) and Me $\alpha\beta$ -dimethyl-*n*-hexyl ketone, b.p. 195—196° (corr.)/755 mm. (semicarbazone, m.p. 99—100°). CMeEt·CMe·COMe with the appropriate MgRX gives only the *tert*-alcohol and thus are obtained $\beta\gamma\delta$ -trimethyl- Δ^2 -*n*-hexen- β -ol, b.p. 60—61°/5 mm. (reduced catalytically to $\beta\gamma\delta$ -trimethyl-*n*-hexan- β -ol, b.p. 57—58°/5 mm.), $\gamma\delta\epsilon$ -trimethyl- Δ^3 -*n*-hepten- γ -ol, b.p. 70—72°/5 mm., $\delta\epsilon\zeta$ -trimethyl- Δ^4 -*n*-octen- δ -ol, b.p. 79—80°/4 mm., and $\epsilon\zeta\eta$ -trimethyl- Δ^5 -*n*-nonen- ϵ -ol, b.p. 93—94°/5 mm. CHPr·CMe·COMe with MgMeBr affords mainly $\gamma\delta$ -dimethyl- Δ^2 -*n*-octen- γ -ol, b.p. 81—82°/11 mm., and a little Me α -methyl- β -ethyl-*n*-amyl ketone isolated as its semicarbazone, m.p. 120°. CMeBu·CH·COBu with MgEtBr gives only $\beta\beta\epsilon\zeta$ -pentamethyl- γ -ethyl- Δ^5 -*n*-hepten- γ -ol, b.p. 106—108°/12 mm.

J. W. B.

Influence of hydrogen sulphite solutions on xylose. G. MENZINSKY (Ber., 1935, [B], 822—824).—Xylose is converted by aq. Ca(HSO₃)₂ or aq. NaHSO₃ at 130° under pressure into xylonic acid (brucine salt, m.p. 170—172°, $[\alpha]^{20}_{\text{D}}$ -37·37° in H₂O; double compound of Cd salt with CdBr₂). H. W.

3L

Reducing powers of physiologically-important carbohydrates. A. P. WEINBACH and D. B. CALVIN (Science, 1935, 81, 407—408).—The relative and actual reducing vals. of various carbohydrates have been compared using 5 of the newer methods for the determination of glucose (I). The order of reducing power for all methods per unit wt. of carbohydrate is fructose (II) or glucose (I) > arabinose (III) > galactose (IV) > lactose (V) > maltose (VI); the order per mol. is (II) or (I) > (V) > (VI) or (IV) > (III). L. S. T.

Carbohydrates and furfuraldehyde. I. H. BREDERECK (Ber., 1935, 68, [B], 777—783).—The methods employed in the prep. of CHPh. derivatives are not applicable to furfurylidene compounds. Condensations of carbohydrates with furfuraldehyde (I) at high temp. in presence of CaCl₂, ZnCl₂, etc. are unsatisfactory on account of ready resinification. Small yields are obtained when the components are heated in CO₂ under slightly diminished pressure and these increase to 80% when the liberated H₂O is removed in a small Soxhlet apparatus filled with CaCl₂. (I), as employed, is faintly acid to litmus, doubtless due to HCl which is essential for condensation. α -Methylglucoside and (I) at 160—165°/100—200 mm. yield 4 : 6-furfurylidene- α -methylglucoside (II), m.p. 153—154°, $[\alpha]^{25}_{\text{D}}$ +84·4° in H₂O, and a substance, m.p. 215—217°. Treatment of (II) with Ac₂O·C₅H₅N affords 4 : 6-furfurylidene- α -methylglucoside 2 : 3-diacetate, m.p. 112—113°, hydrolysed by HCl-EtOH and then converted by CPh₃Cl in C₅H₅N into 6-triphenylmethyl- α -methylglucoside 2 : 3-diacetate, m.p. 163—164°, $[\alpha]^{25}_{\text{D}}$ +78·0° in CHCl₃, whence 6-triphenylmethyl- α -methylglucoside 2 : 3 : 4-triacetate, m.p. 138°. (II), MeI, and Ag₂O in COMe₂ give 4 : 6-furfurylidene-2 : 3-dimethyl- α -methylglucoside, m.p. 119—120°, $[\alpha]^{25}_{\text{D}}$ +98·4° in CHCl₃, hydrolysed to 2 : 3-dimethyl- α -methylglucoside, m.p. 82—85°, $[\alpha]^{25}_{\text{D}}$ +150·2° in H₂O. α -Methylmannoside and (II) similarly afford 2 : 3 : 4 : 6-difurfurylidene- α -methylmannoside, m.p. 182—184°, $[\alpha]^{25}_{\text{D}}$ +42·45° in CHCl₃, and 4 : 6-furfurylidene- α -methylmannoside (III), m.p. 153—154°, $[\alpha]^{25}_{\text{D}}$ +64·5° in CHCl₃. Treatment of (III) with Ac₂O·C₅H₅N followed by hydrolysis with 0·5% HCl-EtOH leads to α -methylmannoside 2 : 3-diacetate, m.p. 142—143°, $[\alpha]^{25}_{\text{D}}$ +32·9° in H₂O. Repeated treatment of (III) with MeI and Ag₂O in COMe₂ followed by hydrolysis and action of CPh₃Cl in C₅H₅N affords triphenylmethyl-dimethyl- α -methylmannoside, m.p. 176°, $[\alpha]^{25}_{\text{D}}$ +8·1° in CHCl₃, whereas less drastic methylation leads similarly to triphenylmethylmethyl- α -methylmannoside, m.p. 182—183°.

H. W.

Differentiating behaviour of α - and β -methylglucoside towards *p*-toluenesulphonyl chloride and pyridine. K. HESS and H. STENZEL (Ber., 1935, 68, [B], 981—989; cf. this vol., 68).—Treatment of α -methylglucoside (I) with *p*-C₆H₄Me·SO₂Cl (II) in C₅H₅N at 20° (16 days) gives non-cryst. α -methylglucoside 2 : 3 : 4 : 6-tetra-*p*-toluenesulphonate (III), $[\alpha]^{19}_{\text{D}}$ +44·7° in CHCl₃, +42·0° in COMe₂. With the same ratio of (I) and (II) but at 75° (2 days), the products are 4-chloro- α -methylglucoside 2 : 3 : 6-tri-*p*-toluenesulphonate (IV), m.p. 134—135° $[\alpha]^{19}_{\text{D}}$ +39·1° in CHCl₃, $[\alpha]^{25}_{\text{D}}$ +32·1° in COMe₂, $[\alpha]^{25}_{\text{D}}$ +42·7° in C₆H₆,

and at 80° (4 days) 4:6-dichloro- α -methylglucoside 2:3-di-*p*-toluenesulphonate (V), m.p. 119—120°, $[\alpha]_D^{25} +97.2^\circ$ in C_5H_5N , $[\alpha]_D^{25} +102.5^\circ$ in $CHCl_3$, $[\alpha]_D^{25} +100.5^\circ$ in $COMe_2$. β -Methylglucoside (VI) and (II) quantitatively afford β -methylglucoside 2:3:4:6-tetra-*p*-toluenesulphonate, m.p. 183—184°, $[\alpha]_D^{25} -6.9^\circ$ in $CHCl_3$, $[\alpha]_D^{25} -9.8^\circ$ in $COMe$, or under modified conditions, 4-chloro- β -methylglucoside 2:3:6-tri-*p*-toluenesulphonate, m.p. 186—187°, $[\alpha]_D^{25} -17.7^\circ$ in $CHCl_3$, $[\alpha]_D^{25} -18.9^\circ$ in $COMe_2$, $[\alpha]_D^{25} -31.8^\circ$ in C_5H_5N (max. yield 43.7%) or 4:6-dichloro- β -methylglucoside 2:3-di-*p*-toluenesulphonate, m.p. 147.5—148°, $[\alpha]_D^{25} +23.3^\circ$ in $CHCl_3$, $[\alpha]_D^{25} +35.9^\circ$ in $COMe_2$, $[\alpha]_D^{25} +19.2^\circ$ in C_5H_5N (max. yield, 15.6%). Chlorination is effected by replacement of $O\cdot SO_2\cdot C_6H_4Me$ by Cl , $R\cdot O\cdot SO_2\cdot C_6H_4Me + C_5H_5N\cdot HCl \rightarrow RCl + C_5H_5N\cdot p\text{-}C_6H_4Me\cdot SO_3H$. (III) and (IV) are smoothly transformed into (V) by $C_5H_5N\cdot HCl$ in C_5H_5N , whereas (I) is unaffected. The constitution of (V) follows from its identity with the product of Helferich *et al.* (A., 1925, i, 792). (IV) and NaI in $COMe_2$ give 4-chloro-6-iodo- α -methylglucoside 2:3-di-*p*-toluenesulphonate, m.p. 127—128°, $[\alpha]_D^{25} +107.6^\circ$ in $CHCl_3$, $+96.5^\circ$ in $COMe_2$, $[\alpha]_D^{25} +120.5^\circ$ in C_6H_6 , in which both halogen atoms are stable towards $AgOAc$ in $AcOH$ at 100°. Since (V) does not react with NaI under these conditions, Cl in (IV) is probably in position 4. Unexpectedly, cellulose resembles (I) in its behaviour towards (II), whereas starch is similar to (VI).

H. W.

Detection of small amounts of invert sugar in the presence of sucrose. VON MORGENSTERN (Zentr. Zuckerind., 1934, 42, 824—825).—Hydrolysis of sucrose (I) during the determination of invert sugar (II) by Cu_2O pptn. is prevented by the presence of buffers and NH_2 -acids. Although the pptn. of Cu_2O is delayed, Barford's reagent serves for the qual. detection of (II) in presence of (I) if buffered with $NaOAc$ and glycine.

A. G. P.

Synthesis of α -maltosides and their behaviour towards diastase. B. HELFERICH and S. R. PETERSEN (Ber., 1935, 68, [B], 790—795).—Maltose octa-acetate, $PhOH$, and $ZnCl_2$ at 100° give phenyl- α -maltoside hepta-acetate (I), m.p. 184—184.5°, $[\alpha]_D^{25} +170.2^\circ$ in $CHCl_3$. *o*-Tolyl- α -maltoside hepta-acetate (II), m.p. 188.5—190°, $[\alpha]_D^{25} +161.4^\circ$ in $CHCl_3$, prepared similarly, passes when irradiated and treated with Br in $CHCl_3$ containing $NaHCO_3$ into ω -bromo-*o*-tolyl- α -maltoside hepta-acetate (III), m.p. 198.5—199.5° (corr.), $[\alpha]_D^{25} +160.2^\circ$ in $CHCl_3$, which is converted by $AgOAc$ in boiling $COMe_2-H_2O$ into saligenin- α -maltoside hepta-acetate (IV), m.p. 191—192° (corr.), $[\alpha]_D^{25} +154^\circ$ in $CHCl_3$. *p*-Tolyl- α -maltoside hepta-acetate (V), m.p. 159.5—161.5°, $[\alpha]_D^{25} +166^\circ$ in $CHCl_3$, and *p*-tolyl- β -maltoside hepta-acetate, m.p. 160.5—162° (corr.), $[\alpha]_D^{25} +46^\circ$ in $CHCl_3$, are produced simultaneously. (V) is transformed by successive treatments with Br and $Ag_2O-COMe_2-H_2O$ into *p*-hydroxymethylphenyl- α -maltoside hepta-acetate (VI), m.p. 175.5—177.5° (corr.), $[\alpha]_D^{25} +173^\circ$ in $CHCl_3$. The maltosides obtained by the action of $NaOMe$ in anhyd. $MeOH$ on (I), (II), (IV), and (VI) are amorphous; they have $[\alpha]_D^{25} +198^\circ$, $[\alpha]_D^{25} +186^\circ$, $[\alpha]_D^{25} +168.5^\circ$, and $[\alpha]_D^{25} +208^\circ$ in H_2O , respectively. *p*-Hydroxydiphenyl- β -maltoside

hepta-acetate has m.p. 131—134° (corr., decomp.) after softening, $[\alpha]_D^{25} +45.5^\circ$ in $CHCl_3$. Treatment of (III) with NH_3 in $MeOH-H_2O$ and of the product with stearyl chloride in $C_5H_5N-CHCl_3$ affords *o*-aminomethylphenyl- α -maltoside octastearate, m.p. 85—87°, $[\alpha]_D^{25} +48.0^\circ$ in $CHCl_3$, transformed by NH_3-MeOH at 170° into *o*-stearamidomethylphenyl- α -maltoside (VII), $[\alpha]_D^{25} +55.4^\circ$ in abs. $EtOH$. The maltosides are resistant towards diastase of malt; the slight fission observed being due to the presence of α -glucosidase; the formation of maltose could not be detected. (VII) behaves similarly although only colloiddally sol. in H_2O ; enlargement of the aglucone of the α -maltosides is too external to render the substrate "starch-like" towards diastase.

β -Melibiose octa-acetate is converted by $HBr-AcOH$ at 0° into non-cryst. acetobromomelibiose (VIII), transformed by $MeOH-H_2O$ into β -melibiose hepta-acetate, m.p. 193° (corr.), $[\alpha]_D^{25} +119^\circ$ to $+125.8^\circ$ in $CHCl_3$. (VIII) and Ag_2O in anhyd. $MeOH$ give methyl- β -melibioside hepta-acetate, m.p. 158—160° after softening, $[\alpha]_D^{25} +92.7^\circ$ in $CHCl_3$.

H. W.

Cymarose. R. C. ELDERFIELD (Science, 1935, 81, 440—441).—Oxidation of cymarose (I) with 50% HNO_3 yields a hydroxymethoxyglutaric acid (II) characterised by its *di*-*N*-methylamide, m.p. 138°, $[\alpha]_D^{25} -55.3^\circ$. The lactone of (II) has m.p. 150—152°, $[\alpha]_D^{25} -1.2^\circ$. The OMe of (I) is on the third C of the deoxyhexose chain.

L. S. T.

Schardinger's dextrins from starch. K. FREUDENBERG and R. JACOBI (Annalen, 1935, 518, 102—108).—Schardinger's α - (I) and β - (II) -dextrin are individual products, but his sparingly-sol. "schlamm" is an additive compound of (I) and (II) which crystallises under certain conditions. To these are added γ - (III), δ - (IV), and ϵ - (V) -dextrin which occur in small amount and, in part, have possibly not been obtained homogeneous. The confusion in the lit. is caused by the difficulty of separating these mixtures, their power of forming additive compounds with acids, H_2O , $EtOH$, and other solvents, and the false vals. for mol. wt. when determined in the customary manner. The following consts. are recorded: (I) $[\alpha]_D^{25} +148^\circ$ in H_2O ; $[\alpha]_{578}^{25} +153^\circ$ to $+167^\circ$ and then $+70^\circ$ in 50% H_2SO_4 (acetate, $[\alpha]_D^{25} +107.5^\circ$ in $CHCl_3$); (II), $[\alpha]_D^{25} +158^\circ$ in H_2O , $[\alpha]_{578}^{25} +165^\circ \rightarrow 171^\circ$ $+70^\circ$ in 50% H_2SO_4 (acetate, $[\alpha]_D^{25} +121^\circ$ in $CHCl_3$); (III), $[\alpha]_D^{25} +160^\circ$ in H_2O , $[\alpha]_{578}^{25} +165^\circ \rightarrow +170^\circ \rightarrow +69^\circ$ in 50% H_2SO_4 (acetate, $[\alpha]_D^{25} +137^\circ$ in $CHCl_3$); (IV), $[\alpha]_D^{25} +166^\circ$ in H_2O (acetate, $[\alpha]_D^{25} +126^\circ$ in $CHCl_3$); (V) $[\alpha]_D^{25} +171^\circ$ in H_2O (acetate, $[\alpha]_D^{25} +158^\circ$ in $CHCl_3$). (I) appears to be a penta- and (II) a hexa-saccharide. (I) and (II) appear to contain about 0.6% OMe . Variation of $[\alpha]_{578}^{25}$ during hydrolysis of (I), (II), and (III) shows the presence of a readily-hydrolysed β union belonging to the anhydride termination of the chain-formed oligosaccharide. The assumption that this is of the same type as in β -glucosan is qualitatively but not quantitatively satisfactory. A β union within the chain is excluded. (I) is best separated as acetate by $EtOAc$ from the other acetates and (II) in the free state from H_2O .

H. W.

Determination of relative mol. wts. of the members of polymeric-homologous series of cellulose derivatives. L. I. MIRLAS (Iskus. Volokno, 1934, 5, No. 6, 5—10).—A discussion of the relation between mol. wt. and η . CH. ABS. (e)

Colloid chemistry of compounds of sugars and fatty acids, particularly glucose stearate.—See this vol., 821.

Solubility rules for cellulose derivatives. Cellulose acetate and benzylcellulose.—See this vol., 822.

Dependence of the viscosity of cellulose esters on the concentration.—See this vol., 822.

Addition of ammonia to ethylene. C. E. SUN (J. Chinese Chem. Soc., 1935, 3, 1—5).—From calculations of the energies of activation it is concluded that NH_3 will not add easily to C_2H_4 , that a primary amine will decompose more easily into a *sec.*-amine than into a hydrazine, and that this decomp. will occur long before its decomp. into C_2H_4 .

J. W. S.
Chlorinated ethylamines. New type of vesicant. K. WARD, jun. (J. Amer. Chem. Soc., 1935, 57, 914—916).— $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ with SOCl_2 in CHCl_3 or its hydrochloride with SOCl_2 in C_6H_6 or PCl_5 in CHCl_3 gives *-trichloroethylamine*, an oil (hydrochloride, m.p. 130—131°; picrate, m.p. 136.5—137°). The following revised data are given: $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NH}_2$ (best obtained from $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ and SOCl_2) hydrochloride, m.p. 144°, and picrate, +0.5 H_2O , m.p. 107—110°; $\beta\beta'$ -dichlorodiethylamine picrate, m.p. 112—113°. The Cl_3 - but not the Cl - or Cl_2 -base is strongly vesicant. The Cl in these bases is reactive. $\beta\beta'$ -Diamylthiol-diethylamine, b.p. 214°/25 mm., is described.

R. S. C.
Relation between the behaviour of ethylamine, propylamine, and butylamine and their p_H . A. TETTAMANZI (Atti R. Accad. Sci. Torino, 1934, 69, I, 369—377; Chem. Zentr., 1935, i, 190; cf. A., 1934, 993).—Triethylamine (I) forms with aq. solutions of bivalent metals partly products of alcoholysis (II) and partly additive products. In abs. EtOH with Co^{II} halides only (II) are formed. Mono- and di-ethylamine behave similarly in EtOH, but do not form compounds in H_2O . Compound formation is correlated with the p_H of the H_2O solutions. (I) reacts with NaOH forming crystalline compounds with (I) : Na ratios of 1 : 1.5 and 1 : 2.

H. J. E.
Preparation of β -diethylaminomethylbutanol. S. I. SERGIEVSKAJA, A. A. KROPACHEVA, and I. LIPOVICH (Khim. Farm. Prom., 1934, No. 5, 13—15).—Et α -ethylhydracrylate is converted successively into $\text{CH}_2\text{Cl}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ and $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, which is then reduced to $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{OH}$.

CH. ABS. (r)
True methylcholines. A. SIMONART (J. Pharm. Exp. Ther., 1935, 54, 105—130).—A criticism of Hunt's work (cf. A., 1934, 875) with choline derivatives.

M. T.
 β -Methylcholine and its acetyl ester. R. T. MAJOR and J. K. KLINE (J. Pharm. Exp. Ther., 1935,

54, 131—135).—Methylcholine chloride and acetyl- β -methylcholine, previously described and used by different investigators, were almost certainly, with a few exceptions, not as pure as the compounds prepared by the authors. M. T.

Deamination of chitin and glucosamine. P. SCHORIGIN and N. N. MAKAROVA-SEMLJANSKAJA (Ber., 1935, 68, [B], 965—969).—Chitosan (I) reacts vigorously with liquid N_2O_4 at -10° and even in presence of CCl_4 as diluent extensive destruction of (I) occurs; unless action is very carefully conducted (I) is completely dissolved with production of oligosaccharides. NH_2 of chitin (II) appears so protected against chemical reagents by Ac that the latter cannot be removed without degradation of (II). Deamination of glucosamine under the conditions of Zechmeister *et al.* and treatment of the product (III) with $\text{NHPh}\cdot\text{NH}_2$ gives small amounts of a product which does not depress the m.p. of phenylglucosazone (IV); if the syrup is evaporated in vac. only traces of (IV) are produced. Oxidation of (III) with HNO_3 affords $\text{H}_2\text{C}_2\text{O}_4$, which is not produced from glucose (V) or mannose (VI) under similar conditions. The absence of fructose in (III) is established by its non-reaction with $\text{NPhMe}\cdot\text{NH}_2$. (III) yields a *hexosediphenylhydrazone*, m.p. 144—145°, $[\alpha]_D +28.8^\circ$ in MeOH, whereas *d*-mannose- and *d*-glucose-diphenylhydrazones have m.p. 150°, $[\alpha]_D +11.6^\circ$ in MeOH and m.p. 156°, $[\alpha]_D +13.6^\circ$ in MeOH, respectively. The carbohydrate is therefore not (V) or (VI) but another monosaccharide, probably Fischer's chitose. H. W.

Methyl ethers of chitin. P. SCHORIGIN and N. N. MAKAROVA-SEMLJANSKAJA [with V. ANURJEVA] (Ber., 1935, 68, [B], 969—971).—Chitin (I) is methylated with much greater difficulty than cellulose and 45 treatments with $\text{Me}_2\text{SO}_4\text{--NaOH}$ give a product with 9.34% OMe (1 OMe=14.28%). The material retains the structure of (I) and combined AcOH is almost unchanged. The difficulty is attributed to the failure of (I) to swell in alkali and is partly overcome by use of more conc. NaOH and mechanical stirring. After pre-swelling in conc. HCl, products with 16.07% OMe are obtained after 15 treatments in which (I) is probably very appreciably degraded. H. W.

Acetylation of chitin. P. SCHORIGIN and E. HAIT (Ber., 1935, 68, [B], 971—973).—Acetylation of chitin (I) with Ac_2O in presence of AcOH and H_2SO_4 proceeds only to a small extent since (I) does not swell in the mixture. Addition of HClO_4 is useless. Better results are obtained by use of HClO_4 and ZnCl_2 or of conc. $\text{HCl}\text{--Ac}_2\text{O}$. Complete acetylation is secured by passing dry HCl through (I) suspended in Ac_2O , but the *I* val. of the product indicates considerable degradation of (I). The products are sol. in HCO_2H and 50% *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ solution in a degree which increases with the degree of acetylation. They dissolve immediately in HNO_3 (*d* 1.5) and the solutions give ppts. of chitin acetate nitrate when diluted with H_2O . H. W.

Steric series. XXII. Configuration of alanine. K. FREUDENBERG and M. MEISTER (Annalen, 1935, 518, 86—96; cf. A., 1934, 767).—Re-examination of the configurative relationship of *l*(+)-lactic acid (I) to (+)-alanine in the light of more recent

rules (*loc. cit.*) confirms the previous conclusion (A., 1924, i, 1173). (I) is converted into (—)-*carbethoxy-l(+)-lactic acid*, b.p. 98°/0.45 mm., $[\alpha]_{578}^{20} -43.6^\circ$, $[\alpha]_{546}^{20} -49.2^\circ$, transformed into (—)-*carbethoxy-l(+)-lactyl chloride* (II), b.p. 79°/11 mm., $[\alpha]_{578}^{20} -14.0^\circ$, $[\alpha]_{546}^{20} -14.9^\circ$, whence (EtOH + C₅H₅N) *Et* (—)-*carbethoxy-l(+)-lactate* (III), b.p. 93°/11 mm., $[\alpha]_{578}^{20} -40.9^\circ$, $[\alpha]_{546}^{20} -46.0^\circ$, and *Ph* (—)-*carbethoxy-l(+)-lactate*, b.p. 123°/0.6 mm., $[\alpha]_{578}^{20} -35.1^\circ$, $[\alpha]_{546}^{20} -39.8^\circ$. (—)-*Carbethoxy-l(+)-lactidimethylamide*, b.p. 91°/0.45 mm., $[\alpha]_{578}^{20} -5.6^\circ$, from (II) and NHMe₂ in Et₂O, from (III) and NHMe₂ at 80°, or from OH·CHMe·CO·NMe₂ and ClCO₂Et in C₅H₅N (corresponding dl-form, m.p. 20°), and (—)-*carbethoxy-l(+)-lactanilide*, m.p. 101–102°, $[\alpha]_{578}^{20} -49.5^\circ$ in EtOH (corresponding dl-form, m.p. 79°), are described. EtBr is transformed by (NH₄)₂SO₃, NH₃, and H₂O at 110° followed by treatment with PCl₅ into *ethanesulphonyl chloride*, b.p. 61–65°/11 mm., which with *Et* l(+)-*lactate* in Et₂O–C₅H₅N affords *Et* (—)-*ethanesulphonyl-l(+)-lactate*, b.p. 93°/12 mm., $[\alpha]_{578}^{20} -44.3^\circ$, $[\alpha]_{546}^{20} -50.0^\circ$. (—)-*Ethanesulphonyl-l(+)-lactic acid*, $[\alpha]_{578}^{20} -28.5^\circ$, $[\alpha]_{546}^{20} -32.3^\circ$, is converted by SOCl₂ into (—)-*ethanesulphonyl-l-lactyl chloride*, b.p. 84°/0.03 mm., $[\alpha]_{578}^{20} -43.4^\circ$, $[\alpha]_{546}^{20} -47.7^\circ$, whence *Ph* (—)-*ethanesulphonyl-l(+)-lactate*, b.p. 145°/0.16 mm., $[\alpha]_{578}^{20} -46.3^\circ$, $[\alpha]_{546}^{20} -52.4^\circ$, (—)-*ethanesulphonyl-l(+)-lactidimethylamide*, b.p. 128°/0.1 mm., $[\alpha]_{578}^{20} -2.5^\circ$ in Et₂O (corresponding dl-compound, m.p. 40°), and (—)-*ethanesulphonyl-l(+)-lactanilide*, m.p. 75°, $[\alpha]_{578}^{20} -70.4^\circ$, $[\alpha]_{546}^{20} -79.4^\circ$ in EtOH (corresponding dl-substance, m.p. 98°). *Et* azidopropionate, $[\alpha]_{578}^{20} -20.1^\circ$, is converted by successive treatments with H₂–Pt sponge and ClCO₂Et–K₂CO₃ into *Et* (—)-*carbethoxy-l(+)-aminopropionate*, b.p. 123°/11 mm., m.p. 38°, $[\alpha]_{578}^{20} -4.4^\circ$ in hexane. Similarly, *Ph* l(—)-*azidopropionate*, b.p. 105.0°/0.6 mm., $[\alpha]_{578}^{20} -81^\circ$, $[\alpha]_{546}^{20} -8.9^\circ$, yields *Ph* (—)-*carbethoxy-l(+)-aminopropionate*, m.p. about 40°, $[\alpha]_{578}^{20} -24.0^\circ$, $[\alpha]_{546}^{20} -27.2^\circ$ in EtOH (dl-compound, m.p. 70°). (—)-*Carbethoxy-l(+)-aminopropiondimethylamide*, b.p. 97°/2 mm., $[\alpha]_{578}^{20} -13.7^\circ$, $[\alpha]_{546}^{20} -15.5^\circ$ (corresponding dl-compound), l(—)-*azidopropionanilide*, $[\alpha]_{578}^{20} +105^\circ$, (—)-*carbethoxy-l(+)-aminopropionanilide*, m.p. 131°, $[\alpha]_{578}^{20} -56.1^\circ$, $[\alpha]_{546}^{20} -64.9^\circ$ in EtOH (corresponding dl-compound, m.p. 151°), and *carbethoxy-l(+)-alanine*, $[\alpha]_{578}^{20} -4.5^\circ$ in Et₂O–hexane (9:11) (corresponding dl-compound, m.p. 84°), are described. *Et* (—)-*ethanesulphonyl-l(+)-amidopropionate*, b.p. 119°/0.2 mm., $[\alpha]_{578}^{20} -25.5^\circ$ (corresponding dl-substance), is hydrolysed to (—)-*ethanesulphonyl-l(+)-alanine*, m.p. 82–83°, $[\alpha]_{578}^{20} -7.1^\circ$ in Et₂O–hexane (7:3) (r-acid, m.p. 82–83°). dl- α -*Ethanesulphonamidopropionyl chloride* has m.p. 61°. *Ph* l(+)- α -*ethanesulphonamidopropionate*, m.p. 93°, $[\alpha]_{578}^{20} +47.6^\circ$, $[\alpha]_{546}^{20} -54.3^\circ$ in EtOH (dl-compound, m.p. 97°), l(+)- α -*ethanesulphonamidopropiondimethylamide*, m.p. 82–83°, $[\alpha]_{578}^{20} -29.3^\circ$, $[\alpha]_{546}^{20} -33.0^\circ$ in EtOH (dl-substance, m.p. 81°), and l(+)- α -*ethanesulphonamidopropionanilide*, m.p. 112°, $[\alpha]_{578}^{20} -61.9^\circ$, $[\alpha]_{546}^{20} -70.7^\circ$ in EtOH (dl-compound, m.p. 131°), are described. H. W.

Amino-acids. VIII. Condensation of creatinine with aromatic aldehydes and syntheses of *N*-methylamino-acids. U. DEULOFEU and G. MENDIVELZUA (Ber., 1935, 68, [B], 783–789; cf. A.,

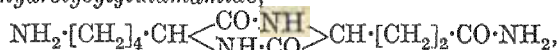
1934, 1216).—Creatinine (I) is readily condensed with aromatic aldehydes by Ac₂O and NaOAc, acetylated products (II) being obtained in varying yield. These, which are insol. in alkali, are reduced by Na–Hg to the corresponding H₂-derivatives. Ac attached to N is very resistant to alkaline hydrolysis and is not removed during reduction. The products are readily hydrolysed by acid to the corresponding substituted creatinines. (II) are hydrolysed by conc. Ba(OH)₂ to the corresponding NHMe-acids. Thus are obtained: 2-acetyl-5-benzylidenecreatinine, m.p. 208°, 2-acetyl-5-benzylcreatiniine, m.p. 135°, 5-benzylcreatiniine, m.p. 282°, and phenyl-*N*-methylalanine, sublimates 253–255°: 2-acetyl-5-p-acetoxymethylidenecreatiniine, m.p. 225–226°, 2-acetyl-5-p-hydroxybenzylcreatiniine, m.p. 162°, *N*-methyltyrosine, m.p. 265° when slowly heated or m.p. 318° when rapidly heated, and 5-p-hydroxybenzylcreatiniine, m.p. 230°; 2-acetyl-5-p-methoxybenzylidenecreatiniine, m.p. 201°, 2-acetyl-5-p-methoxybenzylcreatiniine, m.p. 137°, and 5-p-methoxybenzylcreatiniine, m.p. 270°; 2-acetyl-5-m-acetoxymethylidenecreatiniine, m.p. 182°, 2-acetyl-5-m-hydroxybenzylcreatiniine, m.p. 164°, 5-m-hydroxybenzylcreatiniine, m.p. 229°, and m-hydroxyphenyl-*N*-methylalanine, m.p. 268° or m.p. 292° when slowly or rapidly heated, respectively: 2-acetyl-5-m-methoxybenzylidenecreatiniine, m.p. 181°; 2-acetyl-5-o-acetoxymethylidenecreatiniine, m.p. 209°, 2-acetyl-5-o-hydroxybenzylcreatiniine, m.p. 153°, and o-hydroxyphenyl-*N*-methylalanine, m.p. 207° or m.p. 226°, when slowly or rapidly heated, respectively: 2-acetyl-5-o-methoxybenzylidenecreatiniine, m.p. 195°, and 2-acetyl-5-o-methoxybenzylcreatiniine, m.p. 159°; 2-acetyl-5-3'-acetoxymethyl-4'-methoxybenzylidenecreatiniine, m.p. 223°, and 2-acetyl-5-3'-hydroxy-4'-methoxybenzylcreatiniine, m.p. 185°: 2-acetyl-5-veratrylidenecreatiniine, m.p. 215°, and 2-acetyl-5-veratrylcreatiniine, m.p. 127°; 2-acetyl-5-piperonylidenecreatiniine, m.p. 240° after softening at 235°, and 2-acetyl-5-piperonylcreatiniine, m.p. 164°. When heated with *p*-OH·C₆H₄·CHO at 150–155°, (I) affords *di-p*-hydroxybenzylidenecreatiniine, m.p. 265°. H. W.

Preparation of glutamine. H. B. VICKERY, G. W. PUCHER, and H. E. CLARK (J. Biol. Chem., 1935, 109, 39–42).—The method of Schulze and Bosshard (A., 1883, 658) of prep. from beetroot is modified in detail, and 80% of the glutamine content isolated. E. W. W.

Multivalent amino-acids and peptides. I. Synthesis of quadrivalent amino-acids and their derivatives. II. Synthesis of derivatives of lysylglutamic acid. J. P. GREENSTEIN (J. Biol. Chem., 1935, 109, 529–540, 541–544).—I. Three tetrapolar NH₂-acids are synthesised. Et₃ aconitate and NH₃–EtOH (saturated at 0°) at 100° give *anhydrominotricarballyltetra-amide*, CO<CHR·NH>CO (R=NH₂·CO·CH·CH₂·CO·NH₂), m.p. 232° (decomp.), hydrolysed by 5*N*-NaOH at 100° to α -aminotricarballylic acid, m.p. 196° (decomp.) [Cu salt; carbobenzyloxyglycyl, m.p. 72° (decomp.)], and glycyl derivatives, m.p. 195° (decomp.)]. $\alpha\gamma\delta$ -Triamino- Δ^7 -pentenoic acid hydrochloride, m.p. 171–173° (decomp.), is obtained by boiling the Bz₂ derivative with conc. HCl. α -Bromo- ϵ -benzamidoheptenoic acid and K ethylxanthate

give the substance $\text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{S}_2 \cdot \text{COEt}$, m.p. 112—114°, which, when heated first with NH_3 -EtOH and then with Zn-HCl , gives ϵ -benzamido- α -thiol-*n*-hexoic acid hydrochloride, m.p. 123° after softening at 117° (corresponding acid, m.p. 158°), which is oxidised by $\text{FeCl}_3\text{-NH}_3$ to α -disulphido-di- ϵ -amino-hexoic acid, m.p. 207° (decomp.) [corresponding $\epsilon\epsilon'$ -di-guanidino-, m.p. 178—180° (decomp.), and -di(phenyl-carbamido)-acid, m.p. 81°, resolidifies, decomp. 140°].

II. Me lysylglutamato with $\text{NH}_3\text{-MeOH}$ at 0° gives anhydrolsylglutamamide,



(hydrochloride, m.p. 242°), and with $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{OMe}$ affords α -amino- ϵ -guanidinohexoylglutamic acid, m.p. 95° (decomp.), hydrolysed by hot conc. HCl to the mono-peptide.

R. S. C.

Rotatory power of ricinoleamide. E. ANDRÉ and C. VERNIER (Bull. Soc. chim., 1935, [v], 2, 809—816).—Repeated saturation of an EtOH solution of castor oil with NH_3 at 0° and prolonged keeping affords successive crops of the ricinoleamide which have been fractionally crystallised. The fraction from the later NH_3 treatment of the mother-liquor has a higher $[\alpha]_D^{20} + 3^\circ 6'$, than that of the first crop, m.p. 65.5—67°, $[\alpha]_D^{20} + 2^\circ 35'$, thus indicating the presence of two ricinoleic acids (possibly *dl*- and *d*-) of different rotatory power.

J. W. B.

Thiocarbamide. G. A. KIRKHOFF and E. A. AKONIANZ (Khim. Farm. Prom., 1934, No. 3, 17—18).—An improved prep. is described.

CH. ABS. (r)

ψ -Halogenes. XXIX. Preparation, reactions, and tautomerism of cyanates and of cyanic acid. L. BIRCKENBACH and H. KOLB. XXX. Raman effect and the constitution of the cyanate residue. J. GOUBEAU (Ber., 1935, 68, [B], 895—912, 912—919; cf. A., 1933, 1281; 1934, 1332).—XXIX. The following compounds are described: $\text{Hg}(\text{NCO})_2$ (I); $2\text{Hg}(\text{NCO})_2 \cdot \text{KOCN} \cdot \text{KOAc}$ (II); $3\text{Hg}(\text{NCO})_2 \cdot 2\text{KOCN}$ (III); $\text{Hg}(\text{NCO})_2 \cdot \text{KCl}$ (IV); $\text{Hg}(\text{OCN})_2 \cdot \text{KCl}$ (V) (also $+ \text{H}_2\text{O}$); $2\text{Hg}(\text{OCN})_2 \cdot \text{KOCN} \cdot \text{KOAc}$ (VI); $3\text{Hg}(\text{OCN})_2 \cdot 2\text{KOCN}$ (VII); $2\text{AgNCO} \cdot \text{KOCN}$ (VIII); NMe_4 cyanate (IX). These are colourless cryst. compounds freely sol. in H_2O [with exception of (VIII)] which become grey or brown in sunlight. The *O*-cyanates, unless decomposed by hot H_2O , are transformed thereby into *N*-cyanates. Investigation of the constitution of the cyanates is based on Raman spectrum (see below) and chemical evidence. The production of Me 2-iodocyclohexylallophanate (X) from *O*-cyanates and of Me 2-iodocyclohexylcarbamate (XI) from *N*-cyanates, I, cyclohexene, and MeOH has been further examined. Pure AgNCO or (I) afford exclusively (XI). (II), (III), (IV), (V), (VI), (VII), and (VIII) yield with equiv. amounts of I (X) and (XI) in proportion about 20:1 to 5:1. Mixtures of AgNCO or (I) with K salts sol. in MeOH give (X). Formation of (X) requires brine and, in all cases, hasty termination of the reaction hinders its formation. Production of (X) does not take place from (III) if I is in 10% excess or from other complexes in presence of a greater excess. During the production of (X) and (XI)

2-iodocyclohexyl Me ether and MeOCN are also formed. $\text{Pb}(\text{OCN})_2$ scarcely reacts with I and does not form (X). (IX) reacts smoothly with formation of (X). The following schemes are proposed: $\text{R} \cdot \text{NCO} + \text{I} \rightarrow \text{INCO} (+ \text{C}_6\text{H}_{10}) \rightarrow \text{C}_6\text{H}_{10}\text{I} \cdot \text{NCO} (+ \text{MeOH}) \rightarrow \text{C}_6\text{H}_{10}\text{I} \cdot \text{NH} \cdot \text{CO}_2\text{Me}$ and $\text{INCO} (+ \text{MeOH}) \rightarrow \text{HNCO}$. $\text{R} \cdot \text{OCN} + \text{I} \rightarrow \text{I} \cdot \text{OCN} (+ \text{C}_6\text{H}_{10}) \rightarrow \text{C}_6\text{H}_{10}(\text{I} \cdot \text{NCO}) + \text{HO-CN} \rightarrow \text{C}_6\text{H}_{10}\text{I} \cdot \text{NH} \cdot \text{CO} \cdot \text{O} \cdot \text{C} \cdot \text{N} \rightarrow \text{C}_6\text{H}_{10}\text{I} \cdot \text{NH} \cdot \text{CO} \cdot \text{N} \cdot \text{C} \cdot \text{O}$ and $\text{I} \cdot \text{OCN} (+ \text{MeOH}) \rightarrow \text{C}_6\text{H}_{10}\text{I} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO}_2\text{Me}$ and $\text{I} \cdot \text{OCN} (+ \text{MeOH}) \rightarrow \text{HO-CN} \rightarrow \text{HNCO}$. Investigation of the reaction between cyanic acid (XII) and MeOH gives the following results. (XII) obtained from AgNCO or (I) and H_2S or HCl in MeOH yields (XI) exclusively. If isolated and distilled and then treated with MeOH it gives (X) and (XI), dilution with Et_2O favouring the formation of (X). (XII) from cyanuric acid behaves analogously. (XII) from KOCN , (II), (III), (IV), (V), (VI), (VII), and (IX), Pb cyanate, and mixtures of AgNCO and K salts invariably affords predominately (X) sometimes mixed with small amounts of (XI). (X) is not formed by subsequent addition of (XII) to (XI).

XXX. The Raman spectrum of the cyanate residuo definitely establishes its existence in 2 differing forms according to its partner. In the undoubtedly heteropolar alkali salts and the Pb salt the oxynitrile form occurs. In purely homopolar form in the acid and esters and in metallic salts in which for other reasons a transition to homopolar union must be assumed the ketimide form is present. Both forms are detected only in the Hg salts, particularly in those of complex nature, thus conforming the views of Hantzsch according to which formation of isomeric salts is possible only with certain heavy metals such as Hg. In all other cases the Raman spectrum indicates the presence of only one of the two possible forms.

H. W.

Determination of cacodylates. S. BABICH (Khim. Farm. Prom., 1934, No. 5, 27—29).—The material is decomposed with H_2SO_4 and MnO_2 , and diluted to 100 c.c. Tile's reagent ($\text{NaH}_2\text{PO}_4 + \text{HCl}$) is added to ppt. As, and the ppt. is dissolved in a measured vol. of I solution and NaHCO_3 . Excess of I is titrated with $\text{Na}_2\text{S}_2\text{O}_3$.

CH. ABS. (e)

Interchange of heavy atoms in organo-metallic methyls. A. LEIGH-SMITH and H. O. W. RICHARDSON (Nature, 1935, 135, 828—829).—Using radioactive isotopes as indicators evidence has been obtained indicating that Pb and Bi deposited on a metal surface can exchange with the Pb in PbMe_4 and the Bi in BiMe_3 in Et_2O at room temp. The exchange process occurs mainly between atoms of the same at. no. and without disruption of the mol.

L. S. T.

1-Methyl- Δ^2 - and - Δ^3 -cyclopentenes and their derivatives. M. GODCHOT, M. MOUSSERON, and R. RICHAUD (Compt. rend., 1935, 200, 1599—1601).—The mixture, b.p. 65—76°, obtained by action of $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ on *dl*-1-methylcyclopentan-3-ol, yields on fractionation *dl*-1-methyl- Δ^2 -cyclopentene (I), b.p. 66.5—67°/766 mm., oxidised to α -methylglutaric acid, and 1-methyl- Δ^3 -cyclopentene, b.p. 74.5—75.5°/766 mm., oxidised to β -methylglutaric acid. If optically active 1-methylcyclopentan-3-ol is dehydrated

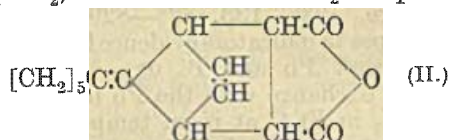
(H_2SO_4), the fractionated product yields d-1-methyl- Δ^2 -cyclopentene (II), b.p. 66.5—67°/766 mm., $[\alpha]_{546}^{20} +89.13^\circ$, and 1-methyl- Δ^3 -cyclopentene, b.p. 75—76°/766 mm. (I) yields a chlorohydrin, and 2-methyl-epoxycyclopentane, (III), b.p. 115—116°/760 mm. Oxidation (KMnO_4) of (I) gives cis-1-methylcyclopentane-2:3-diol, b.p. 107—108°/16 mm. (diphenylurethane, m.p. 181—182°; CMe_2 derivative). With $\text{H}_2\text{O}-\text{HCl}$ at 110°, (III) yields trans-1-methylcyclopentane-2:3-diol, b.p. 112°/18 mm. (diphenylurethane, m.p. 238—239°). (II) is oxidised by BzO_2H to an active 2-methyl-2-epoxycyclopentane, b.p. 114—115°/760 mm., $[\alpha]_{546}^{20} +15.96^\circ$, hydrated to an active trans-1-methylcyclopentane-2:3-diol, $[\alpha]_{46}^{20} -3.85^\circ$.

E. W. W.

Oxidation of 1-ethyl- Δ^1 -cyclohexene and of β -methyl- Δ^2 -butene with selenium dioxide. A. GUILLEMONAT (Compt. rend., 1935, 200, 1416—1418).—Treatment of 1-ethyl- Δ^1 -cyclohexene (I) with SeO_2 in AcOH affords a difficultly separable mixture of acetate and ketone. Addition of SeO_2 to a cold solution of (I) in AcOH containing a little Ac_2O and subsequent boiling of the mixture leads to 1-ethylcyclohexenyl acetate, b.p. 89—90°/15 mm. (yield 37%), hydrolysed to 1-ethylcyclohexen-6-ol, b.p. 82—83°/12 mm., which is oxidised to 1-ethylcyclohexen-6-one, b.p. 78—80°/15 mm. (semicarbazone, m.p. 174—175°). Similarly, β -methyl- Δ^2 -butene yields β -methyl- Δ^2 -buten- α -yl acetate, b.p. 148—150°/760 mm., hydrolysed to β -methyl- Δ^2 -buten- α -ol, b.p. 136—138°/760 mm., which is reduced (PtO_2) to β -methylbutan- α -ol, b.p. 127—128°/760 mm. The Raman spectra of all these compounds are recorded.

H. W.

Diels-Alder reaction in the fulvene series. E. P. KOHLER and J. KABLE (J. Amer. Chem. Soc., 1935, 57, 917—918).—cyclopentadiene with cyclohexanone or pentanone and NaOMe in MeOH give cyclohexylidene- (I) (45% yield), yellow, b.p. 78—80°/25 mm. (with air gives an amorphous peroxide; polymerises, when kept, to a colourless dimeride, depolymerised by distillation), and cyclopentylidene-cyclopentadiene (48%), orange, b.p. 55—57°/2 mm. (I) gives a maleic anhydride adduct (II), m.p. 132°, which dissociates (cryoscopy; isolation of maleic anhydride) in AcOH and C_6H_6 , but can be hydrogenated (PtO_2) in EtOAc to the H_2 -compound, in



which the cyclic ethylenic linking has been reduced, since ozonisation gives cyclohexanone. The additive products from diphenyl- and dimethyl-fulvene are also largely dissociated (cryoscopy) in AcOH and C_6H_6 , but are hydrogenated, best in dioxan, to the H_2 -compounds, m.p. 213° (giving COPh_2 with O_3) and 128°, respectively.

R. S. C.

Physical requisites for chemical reaction of aromatic compounds. G. HARADA (J. Electrochem. Assoc. Japan, 1934, 2, 341—348).—A discussion of the changes of potential energy of the aromatic nucleus.

CH. ABS. (e)

Kinetics of nitration of benzene.—See this vol., 828.

Synthesis of benzenoid hydrocarbons. J. F. DURAND (Bull. Soc. chim., 1935, [v], 2, 824—826).—The general reaction $\text{C}_6\text{H}_5\text{X} + \text{R}\cdot\text{OH} \rightarrow \text{C}_6\text{H}_4\text{RX} + \text{H}_2\text{O}$ in presence of ZnCl_2 , H_2SO_4 , P_2O_5 , etc. should be known as Liebmann's reaction (A., 1882, 171).

J. W. B.

Preparation and properties of benzene- d_6 [hexadeuterobenzene]. P. I. BOWMAN, W. S. BENEDICT, and H. S. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 960).— C_6H_6 and D_2O in presence of Ni-kieselguhr at 200° give an equilibrium mixture containing deuterobenzenes (I), as shown by ultra-violet absorption, the shift being approx. const. for each D introduced. Separation of C_6H_6 -(I) mixture and reheating with pure D_2O causes formation of more (I). Four operations give C_6D_6 (> 99% pure), d_{15}^{20} 0.9417.

R. S. C.

Direct alkylation of olefines under the catalytic influence of phosphorus pentoxide. B. W. MALISHEV (J. Amer. Chem. Soc., 1935, 57, 883—884).—Olefines and aromatic hydrocarbons condense in presence of dispersed P_2O_5 -lampblack, stabilised by cresol, best at 200—250°/1—40 atm. C_6H_6 and C_2H_4 thus give PhEt (23.1% crude, 18.2% pure), $\text{C}_6\text{H}_4\text{Et}_2$ (42.3%; mixture), $\text{C}_6\text{H}_3\text{Et}_3$ (24.4%; mixture), and higher homologues (8.5%; including C_6Et_6). *iso*-Butylene (I) gives PhBu (47.9), $\text{C}_6\text{H}_4\text{Bu}_2$ [17; including *p*- $\text{C}_6\text{H}_4\text{Bu}_2$ (12%)], and higher homologues (11%). PhMe and C_3H_6 give much *p*-cymene, and C_{10}H_8 and C_2H_4 a mixture of $\text{C}_{10}\text{H}_7\text{-Et}$ and $\text{C}_{10}\text{H}_6\text{Et}_2$. P_2O_5 does not polymerise lower olefines under the above conditions; on the contrary, diisobutylene gives the same products as does (I). Higher olefines, however, give naphthenes.

R. S. C.

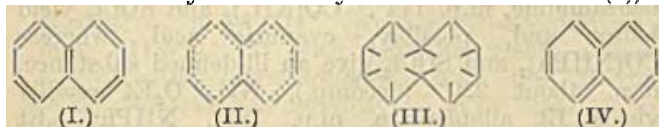
Oxidation of organic substances with selenium dioxide. J. J. POSTOVSKI and B. P. LUGOVKIN (Ber., 1935, 68, [B], 852—856).—Benzil is formed in 17% or 35% yield when stilbene or tolane is heated with SeO_2 at 235° or 280°, respectively. In the latter case oxidation is due to the direct addition of O to the triple linking. $\text{CPh}\cdot\text{CH}$ in absence of solvent is transformed into BzOH. $\text{CPh}_2\cdot\text{CPh}_2$ is not oxidised at 220—230°, whilst Se is not produced by the action of SeO_2 on hexaphenylbutene at 260°. Anthracene is readily converted at 165—170° into anthraquinone (yield 76%), whereas phenanthrene at 250° gives only 3% of phenanthraquinone. The influence of ring structure on CH_2 is illustrated by the production of COPh_2 in 87% yield from CH_2Ph_2 at 200—210°, whereas under the same conditions fluorene gives only 5% of fluorenone. SeO_2 has no action on EtOAc at its b.p., whereas it transforms Ac_2O into $\text{CHO}\cdot\text{CO}_2\text{H}$ in 17% yield.

H. W.

Internal energy relationships of organic compounds. VI. Fission in the hexaphenylethane and sugar series on the basis of the double linking rule. O. SCHMIDT (Ber., 1935, 68, [B], 795—801).—It is considered that in the C_2Ph_6 and sugar series double linkings are present at the moment of fission which, according to rule, weaken the C-C union in position 3 to the double linking. The necessary

energy of dissociation is approx. afforded by the heat of solution of the radicals produced; in the CPh_3 series these radicals are stable under the experimental conditions whereas in the sugar series further changes immediately ensue. H. W.

Raman effect and problems of constitution. VIII. **Symmetry of the naphthalene molecule.** K. W. F. KOHLRAUSCH (Ber., 1935, 68, [B], 893—895).—The infra-red and Raman spectra of C_{10}H_8 are in harmony with the symmetrical structures (I),



(II), or (III) but not with the unsymmetrical constitution (IV). H. W.

Synthesis of methylcholanthrene. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1935, 57, 942—946; cf. this vol., 480).— $p\text{-C}_6\text{H}_4\text{BrMe}$, $(\text{CH}_2\text{O})_3$, and HCl in presence of $\text{AlCl}_3\text{-ZnCl}_2$ (specified conditions of prep. only) at $40\text{--}50^\circ$ give 8% of 4-bromo-2:5-di(chloromethyl)toluene, m.p. 125° (reduced by Zn dust and alkali to 5-bromo- ψ -cumene), and 74% of a mixture, b.p. $106\text{--}108.5^\circ/4\text{ mm.}$, of 4-bromo-2- and -3-chloromethyltoluene (in the proportion 1:1.8), which with $\text{CH}_2(\text{CO}_2\text{Et})_2$ and NaOEt affords a mixture (88% yield), b.p. $166\text{--}170^\circ/2\text{ mm.}$, of esters, hydrolysed by $\text{Ba}(\text{OH})_2$ to a mixture (I), m.p. $147\text{--}150^\circ$, of 2-bromo-5-methyl-, m.p. $159\text{--}161^\circ$ (decomp.) (oxidised by KMnO_4 to 4-bromoisophthalic acid), and 5-bromo-2-methyl-benzylmalonic acid, m.p. (impure) $160\text{--}162^\circ$. (I) in hot H_2O gives 92% of a mixture (II), b.p. $168\text{--}172^\circ$, of β -4-bromo- m - and β -4-bromo- o -tolylpropionic acid; incompletely hydrolysed (I) at 190° gave 70% of (II) and the Et esters, b.p. $129^\circ/1.5\text{ mm.}$, of (II), which by hydrolysis and ring-closure gave the same products as did (II). The acid chlorides from (II) with AlCl_3 in CS_2 afford a 94% yield of 7-bromo-4-methyl-, m.p. 154° , and 4-bromo-7-methyl-1-hydrindone (III), m.p. 95° , each obtained also from the corresponding pure component of (II) and each reduced (Clemmensen) to 4-bromo-7-methyl-hydrindene, b.p. $100^\circ/2\text{ mm.}$, $265^\circ/757\text{ mm.}$ The Grignard reagent of (III), prepared by MgEtBr in N_2 with $\alpha\text{-C}_{10}\text{H}_7\text{-COCl}$, affords a good yield of 4- α -naphthoyl-7-methylhydrindene, an oil, which at $405\text{--}410^\circ$ (bath) in 25 min. gives methylcholanthrene (IV), m.p. $178.5\text{--}179^\circ$ (corr.) [picrate, m.p. $182\text{--}182.5^\circ$ (corr.)]. (III) and $\beta\text{-C}_{10}\text{H}_7\text{-COCl}$ give 4- β -naphthoyl-7-methylhydrindene (45% yield), m.p. 114° , and 7-methyl-8:9-dimethylene-1:2-benzanthracene (V), m.p. 187.5° (corr.) [picrate, m.p. $164.5\text{--}165.5^\circ$ (corr.)]. (IV) (over-all yield from $\text{C}_6\text{H}_4\text{BrMe}$ 11%) is identical (absorption; carcinogenic) with the substance from dehydronorcholene. (V) is not carcinogenic.

R. S. C.

Azulene. K. S. BIRRELL (J. Amer. Chem. Soc., 1935, 57, 893—895).—Azulene (I) [from guaiene (II)], when hydrogenated (2.7 mols.) and ozonised, gives HCO_2H (formed by oxidation of a terminal Me group), $\text{Pr}^n\text{CO}_2\text{H}$, an acid (III), $\text{C}_{14}\text{H}_{21}\text{-CO}_2\text{H}$, and an acid ($\text{C}_6\text{H}_4\text{Ph-CO-CH}_2$ ester, m.p. 132°), probably α -methyl-

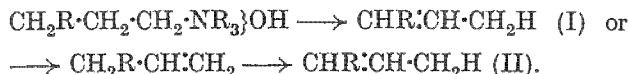
glutaric acid. (I) thus probably has the formula of Ruzicka *et al.* (A., 1931, 1302). After absorption of 4 mols. of H_2 , ozonolysis gives HCO_2H and (III). (II) (probably a mixture) and KMnO_4 give COMe_3 and $\text{H}_2\text{C}_2\text{O}_4$. A reaction mechanism for this oxidation and azulene formation is discussed. The Na (IV) and K (V) derivatives of (I) are probably as annexed. (IV) and aq. Et_2O give a hydrocarbon, m.p. 141° , probably $\text{C}_{30}\text{H}_{38}$. Carboxylation and oxidation of (V) gives COMe_3 , AcOH , and probably $\text{H}_2\text{C}_2\text{O}_4$. The $\text{C}_6\text{H}_4\text{Ph-CO-CH}_2$ esters of adipic acid and $(\text{CHMe-CO}_2\text{H})_2$ have m.p. 148° and 146° , respectively.

R. S. C.

Constitution and reactivity. VIII. **Substitution in aromatic compounds as a polar phenomenon or as a homopolar coupling effect.** K. LAUER (J. pr. Chem., 1935, [ii], 142, 243—251; cf. A., 1933, 60, 277, 395, 829).—Schmidt's theory of aromatic substitution (this vol., 73) may have a better theoretical foundation than Robinson's theory of polarity, but, unlike the latter, does not satisfactorily explain experimental results, e.g., the nitration and sulphonation of PhNO_2 etc. The reaction of NH_2OH with $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ to form 2:4-dinitroaniline and dinitro- m -phenylenediamine, the formation of $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$ from PhNO_2 and alkali, the action of NaNH_2 on $\text{C}_5\text{H}_5\text{-N}$, the formation of p -nitrophenylcarbazole, and the oxidising action of SO_3 (see this vol., 863), all involve substitution in positions which on Schmidt's theory should be unreactive, but are explicable on Robinson's. Schmidt's theory does not explain substitution in CH_2PhCl , CHPhCl_2 , and CPhCl_3 and fails in practice because it assumes that the aromatic mol. reacts in the (stationary) state deduced theoretically; variation of results with substituent and with solvent shows that this is not the case. Schmidt's classification of substituents is invalid.

E. W. W.

Influence of poles and polar linkings on the course pursued by elimination reactions. XXII. **Wagner rearrangement in the Hofmann degradation.** C. K. INGOLD and M. A. T. ROGERS (J.C.S., 1935, 722—725).— γ -Elimination with accompanying Wagner rearrangement, involving the migration of the β -H (I) is demonstrated in the thermal decomp. of onium salts by substitution of CO_2Et for γ -H in order to distinguish (I) from β -elimination followed by prototropic change with migration of the γ -H (II):



$\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (prep., A., 1927, 650, modified) is converted by SOCl_2 into $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, which condenses with $\text{CH}_2(\text{CO}_2\text{R})_2\text{-NaOEt-EtOH}$ to give only $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OEt}$, isolated as β -ethoxyethyltrimethylammonium iodide, m.p. $156\text{--}158^\circ$, but with $\text{CH}_2\text{Ph-CN}(\text{CO}_2\text{Et})_2$ is obtained *Et benzyl- β -dimethyl-aminoethylmalonate* (III) (hydrochloride, m.p. $131\text{--}132^\circ$), converted by MeI-MeNO_2 into its methiodide (IV), m.p. $103\text{--}130^\circ$, whence the Cl' , OH' (V), CO_3'' (VI), and OEt' (VII) derivatives were obtained in

solution. Thermal decomp. of (V) at 140—170° (N₂) gives NMe₃, (III), α -benzyl- γ -butyrolactone (VIII), b.p. 182°/15 mm. (oxidised by 3% KMnO₄ to benzylsuccinic acid), and α -benzyl- γ -butyrolactone- α -carboxylic acid (IX), m.p. 87—88° (best obtained by thermal decomp. in presence of excess of NaOH). Decomp. of (VI) (CO₂) gives (VIII), and (IV) gives a little (III), NMe₃I, NMe₃EtI, the Et ester of (IX), and Et iso- α -benzylcrotonate (X), b.p. 144—148°/19 mm., hydrolysed to iso- α -benzylcrotonic acid (XI), m.p. 107° (Ag salt; amide, m.p. 82—83°) (gives MeCHO on ozonolysis). Thermal decomp. of (VII) at 150—210° gives (X) by mechanism (I):

$\text{CH}_2\text{Ph}\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{CH}_2\text{NMe}_3\text{OEt}$ (VII) \longrightarrow $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CHMe}$ (X), and the production of the iso-acid (X) in the elimination $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CH}_2\text{Br} + \text{OH}' \longrightarrow$ (X) suggests that this also involves γ -H elimination and Wagner rearrangement. Saturation of (VIII) in EtOH with HBr and hydrolysis of the Br-ester (20% aq. EtOH-NaOH) affords (XI). J. W. B.

Production of aromatic amines by hydrogenation. I. Catalysts and conditions of hydrogenation. K. YOSHIKAWA, T. YAMANAKA, and B. KUBOTA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 23).—Reduction of PhNO₂ with H₂ is facilitated by Ni catalysts poisoned with thiophen or sulphates. Cu increases the rate and lowers the temp. of reduction. The life of the Ni-Cu catalyst is shorter the higher is the temp., and is lengthened by Al₂O₃. J. L. D.

Constitution and reactions of thiocarbonyl tetrachloride. II. Reaction with primary arylamines, phenols, and reducing agents. J. M. CONNOLLY and G. M. DYSON (J.C.S., 1935, 679—681).—The compounds obtained by interaction of NH₂Ar and CSCI₄, previously described as NHAr·CCl₂·SCI (A., 1934, 883), are actually NHAr·S·CCl₃ (I), since they react with 4 mols. of NH₂Ar' in inert solvents: (I) + 4NH₂Ar' \longrightarrow NH₂Ar', HCl + 2HCl + NHAr·S·C(NHAr')₃ \longrightarrow NH₂Ar', HCl + S + NAr'C(NHAr')₂, HCl. Thus S-anilinotrichloromethylthiol [(I), R=Ph; previously designated anilinodichloromethylchlorothiol] with NH₂Ph in ligroin affords, after basification, NPh:C(NHPh)₂; S-*p*-toluidinotrichloromethylthiol. (I), R=*p*-C₆H₄Me, similarly affords tri-*p*-tolylguanidine. PhNCS with Cl₂-CHCl₃ affords NPh:CCl₂, b.p. 209°, converted by *p*-C₆H₄Me·NH₂ in boiling C₆H₆ into NPh:C(NH·C₆H₄Me)₂. (*p*-C₆H₄Me·NH₂)₂CS with HgO in C₆H₆ at 40° affords di-*p*-tolylcarbodi-imide, converted by NH₂Ph in boiling C₆H₆ into *as*-phenyldi-*p*-tolylguanidine. CSCI₄ reacts similarly with phenols, and thus, from the appropriate phenol, are prepared S-*phenoxy*-, b.p. 196°/760 mm. (decomp.), -*p*-tolyl-*oxy*-, b.p. 183°/755 mm. (decomp.), -2-chlorophenoxy-, b.p. 180°/756 mm. (decomp.), -*s*-xylyloxy- (unstable), and -diphenyl-*yl*-2-*oxy*-, m.p. 58°, -trichloromethylthiol, all of type OR·S·CCl₃. These are reduced (Zn dust-AcOH) to give MeSH, and react with an excess of NH₂Ar in inert solvents to give the corresponding triarylguanidine hydrochloride in 40—50% yield. Good yields of ArNCS are obtained by addition of CSCI₄ to NH₂Ar dissolved in HCl-SnCl₂. Examples

are given, and an improved prep. (64% yield) of CSCI₂ is described. J. W. B.

Action of thionyl chloride on anilides, carbamides, and urethanes. W. H. WARREN and F. E. WILSON (Ber., 1935, 68, [B], 957—960; cf. A., 1931, 339).—*NN'*-Diphenylformamidine, m.p. 135°, is obtained from HCO·NHPh and SOCl₂, if the solution is preserved previously to distillation of the excess of the latter. NHPhAc and SOCl₂ give ill-defined results whereas NHPhBz and SOCl₂ afford *NN'*-diphenylbenzamidine, m.p. 144°. CO(NH₂)₂ and SOCl₂ yield biuret and, possibly, cyanuric acid, whereas CO(NHPh)₂ and SOCl₂ give an ill-defined substance, m.p. about 220° (decomp.). NH₂·CO₂Et readily yields Et allophanate, m.p. 188°. NHPh·CO₂Et with cold SOCl₂ affords (PhNCO)₂, whereas tars are produced if the mixture is heated. H. W.

N-Methylation of acetanilides. E. THIELEPAPE [with A. FULDE] (Ber., 1935, 68, [B], 751—753).—NHPhAc is treated with Na in C₆H₆ and subsequently with Me₂SO₄ or MeI, thereby giving *N*-methylacetanilide, m.p. 100° (corr.). Similar treatment of *p*-OMe·C₆H₄·NHAc affords *p*-methoxy-*N*-methylacetanilide, b.p. 183°/18 mm., m.p. 57° (corr.). H. W.

Action of nitrous acid on dimethylaniline. III. J. C. EARL and A. W. MACKNEY (J. Proc. Roy. Soc. New South Wales, 1935, 68, 58—60; cf. A., 1934, 998).—*p*-NO·C₆H₄·NMe₂, HNO₃ with glacial AcOH at 33° during 90 min. gives principally 2:4-(NO₂)₂·C₆H₃·NMe₂, also *p*-NO₂·C₆H₄·NMe₂ and *p*-NO₂·C₆H₄·NMe·NO. F. N. W.

Benzoates of N- β -hydroxyethylaniline. P. SCHORIGIN and V. BELOV (Ber., 1935, 68, [B], 833—837).—NHPh·CH₂·CH₂·OH and BzCl in NPhMe₂ give the corresponding *ON*-Bz₂ derivative (I), m.p. 92—93° (yield about 79%), converted into β -anilinoethyl benzoate (II), m.p. 77—78°, identical with the product of von Auwers (A., 1904, i, 736). The constitution of (II) follows from the identity of its Me derivative (picrate, m.p. 164°) with that prepared from NHPhMe and CH₂Cl·CH₂·OBz or from NaOBz and CH₂Cl·CH₂·NPhMe (von Braun *et al.*, A., 1920, i, 29). Under very mild conditions (I) is hydrolysed to a substance, C₁₅H₁₅O₂N, m.p. 74—75°, regarded either as 2-hydroxy-2:3-diphenyloxazolidine or the unstable *N*-benzoate of β -hydroxyethylaniline. The *N*-benzoate of Clemo *et al.* is (II). H. W.

Peracetic acid oxidation of acetyl derivatives of aromatic amines. D. BIGLAVI and C. ALBANESE (Gazzetta, 1934, 65, 249—252).—Treatment of NHRAc, where R = Ph, *p*-C₆H₄·NO₂, *p*-C₆H₄Br, *p*-C₆H₄Me, and 1:2:5-C₆H₂Me₃, with AcOH-H₂O₂ yields RNO₂, no azoxy-compound being formed. The mechanism ·NHAc \rightarrow ·N(OH)Ac \rightarrow ·N(OH)₂ + AcOH, is suggested. E. W. W.

Metal ammine salts from benzidine sulphate. A. TETTAMANZI (Atti R. Accad. Sci. Torino, 1934, 69, I, 225, 230; Chem. Zentr., 1935, i, 190).—Cryst. additive compounds of sulphates of Co, Ni, Cd, Mn, Zn, and Fe^{II} with benzidine are described. They are insol. in H₂O but more sol. in EtOH. H. J. E.

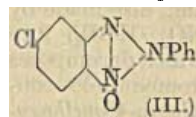
Alkylated ethylenediamine derivatives. II. Reaction between Grignard compounds and $\alpha\beta$ -bisbenzylidenediaminoethane. J. VAN ALPHEN and (MISS) J. L. ROBERT (Rec. trav. chim., 1935, 54, 361—365; cf. this vol., 337).—Bisbenzylidene-ethylenediamine (I) with MgPhBr in Et₂O gives $\alpha\beta$ -bisbenzylidene-ethylenediamine, m.p. 105.5° (dihydrochloride, cryst.; bisphenylcarbamido-derivative, m.p. 218°), and α -amino- β -benzylidene-ethylenediamine, b.p. 201.5°/20 mm., m.p. 25.5° [bisphenylcarbamido-derivative, m.p. 203°; benzylidene derivative, m.p. 66°; 2:4-dinitrophenyl derivative, m.p. 111° (phenylcarbamido-derivative, m.p. 211.5°)]. (I) with MgEtBr yields α -amino- β -(α -phenylpropyl)aminoethane, b.p. 139°/20 mm. (bisphenylcarbamido-derivative, m.p. 200°), and $\alpha\beta$ -bis-(α -phenylpropylamino)ethane, b.p. 210°/25 mm. (dihydrochloride, cryst.; bisphenylcarbamido-derivative, m.p. 186.5°). F. R. G.

Preparation of 2:4:6-triaminotoluene and related amines by catalytic hydrogenation. F. HEIN and F. WAGNER (Ber., 1935, 68, [B], 856—864).—Chemical reduction of 1:2:4:6-C₆H₂Me(NO₂)₃ is satisfactory for the production of salts of 1:2:4:6-C₆H₂Me(NH₂)₃, but the isolation of the free base (I) therefrom is difficult owing to its unusual susceptibility to air. Catalytic reduction (Pd—BaSO₄ or Pd—MgO; less advantageously, Pd—SiO₂ gel or Pd—C) in EtOH (apparatus described) yields (I), m.p. 121° in bath preheated to 115°, which is resistant to air when dry. Diazotisation of (I) does not occur homogeneously and depends on the concn. Coupling of (I) with SO₃H·C₆H₄·N₂Cl occurs quantitatively with production of the compound, (NH₂)₃C₆Me(N₂·C₆H₄·SO₃H)₂, solutions of which are intensely yellow and obey Beer's law. The salt C₆H₂Me(NH₂)₃·H[(SCN)₄Cr(NH₃)₂] is too sol. to permit analytical application. Under similar conditions only 1 NO₂ of 2:4:6-trinitro-3-*tert*-butyltoluene is reduced, probably that *para* to Bu^t. Two NO₂ of 2:4:6-trinitro-*m*-xylene are affected whilst 3-nitro-*o*-toluidine is reduced. H. W.

Carbonitrosohydrazines. III. Hydrazo- and azo-hydroxamic acids. A. QUILICO and R. JUSTONI (Gazzetta, 1935, 65, 201—214).—In the prep. of arylhydrazinoformhydroxamic acids (I) (A., 1934, 401) from carbonitrosohydrazines (II) and NH₂OH (III), improved yields are obtained by using large excess of (III) at 14—15°. The Ph compound (IV) so prepared has new m.p. 179°. From (IV) an azo-compound was not isolated, but *p*-tolylhydrazinoformhydroxamic acid (V) treated with H₂O₂—AcOH yields *p*-tolueneazoformhydroxamic acid (VI), m.p. 125° (decomp.) [NH₄ salt (VII), decomp. 144°]. When (V) is treated with NH₃ in EtOH and the solution exposed to the air, (VII) is readily obtained; and similarly the NH₄ salt, m.p. 156° (decomp.), of *p*-chlorobenzeneazoformhydroxamic acid (VIII) (*loc. cit.*). (V) with boiling 20% HCl gives *p*-C₆H₄Me·NH₂ and (III). HNO₂ reconverts (I) into (II). (I) with Ac₂O yields benzene- (IX), *p*-toluene- (X), and *p*-chlorobenzene- (XI) azocarbonamides. Conc. HCl converts (X) and (XI), respectively, into substances, C₆H₁₀ON₃Cl, m.p. 171°, and C₇H₇ON₃Cl₂, m.p. 191°; (IX) is, however, decomposed. (VI) and (VIII)

similarly treated give substances, C₈H₁₀O₂N₃Cl, m.p. 169° (decomp.), and C₇H₇O₂N₃Cl₂, m.p. 180° (decomp.). E. W. W.

1-Chloro-3:4-dinitrobenzene series. II. A. MANGINI and C. DELIDDO (Gazzetta, 1935, 65, 214—228).—Impure 5-chloro-2-nitrophenylhydrazine (I) (A., 1934, 177) as obtained from 1:3:4-C₆H₃Cl(NO₂)₂ (II) prepared from *m*-C₆H₄Cl·NO₂ contains chloro-nitrophenylhydrazines of m.p. 200—204° and 140°, which it is suggested are derived from 1-chloro-2:3- and -3:6-dinitrobenzene. (I) with ClCO₂Et in C₅H₅N yields *Et* α -5-chloro-2-nitrophenylhydrazine- β -carboxylate, m.p. 134—135°. With PhNCS, (I) in C₅H₅N gives γ -phenyl- α -5-chloro-2-nitrophenylisothiosemicarbazide, C₆H₃Cl(NO₂)₂·NH·N·C(SH)·NHPh, m.p. 190—192° (decomp.); this forms Ag, Hg, Cd, Cu, and Pb salts, and has the *syn* configuration; with COCl₂ in PhMe it



yields 5-anilino-3-(5'-chloro-2'-nitrophenyl)-1:3:4-thiadiazol-2-one, m.p. 187—188°. α -Phenyl- β -5-chloro-2-nitrophenylhydrazine (*loc. cit.*) with Ac₂O gives 5-chloro-2-phenylbenzo-1:2:3-triazole 1-oxide (III), m.p. 138—139.5°. (II) with semicarbazide gives 5-chloro-2-nitrophenylsemicarbazide, NO₂·C₆H₃Cl·NH·CO·NH₂, m.p. 214—216° (decomp.), identified by prep. from (I) and carbamide. (II) with benzidine gives NN'-bis-(5'-chloro-2'-nitrophenyl)benzidine, m.p. 252—253° (decomp.), whilst *p*-C₆H₄(NH₂)₂ gives N-5'-chloro-2'-nitrophenyl-*p*-phenylenediamine [hydrochloride, m.p. 250—258°; Ac derivative, m.p. 220—221° (decomp.)]; N'-benzylidene and -*o*-, -*m*-, and -*p*-nitrobenzylidene derivatives, m.p. 148—149°, 219—220.5° (decomp.), 220—221°, and 198.5—200°, respectively.] E. W. W.

Transformation of dialkylidenecyclohexanones into the corresponding dialkylphenols. I. Dibenzylidenecyclohexanone to 2:6-dibenzylphenol. R. WEISS and J. EBERT (Monatsh., 1935, 65, 399—404).—Dibenzylidenecyclohexanone (I) with HBr and Ac₂O in AcOH at > 40° is converted into 2:6-dibromo-2:6-dibenzylcyclohexanone, m.p. 139—141°; at 52—55° the product is 2:6-dibenzylphenyl acetate (II), m.p. 74—77°, hydrolysed (KOH—EtOH) to 2:6-dibenzylphenol (A., 1929, 552), m.p. < 30°. (II) with Br in AcOH gives 4-bromo-2:6-dibenzylphenol, m.p. 74—77°, and with diazotised *p*-nitroaniline, 4'-nitro-4-hydroxy-3:5-dibenzylazobenzene, m.p. 169—171°. (I) is prepared from cyclohexanone and PhCHO in abs. EtOH (HCl); in KOH—EtOH a substance, C₃₃H₃₀O, m.p. 172—175°, is formed. E. W. W.

Interaction of thionyl chloride with phenol. C. COURTOT and T. Y. TUNG (Compt. rend., 1935, 200, 1541—1543; cf. A., 1932, 506; 1934, 177).—The interaction of SOCl₂ with PhOH is represented by 3PhOH + 2SOCl₂ = (C₆H₄·OH)₃·S·Cl + SO₂ + 3HCl, but in the presence of AlCl₃ as dehydrating agent, only a trace of SO₂ is evolved, the H₂O produced by the reaction reacting with the AlCl₃ instead of the SOCl₂. P₂O₅ may also be used as a dehydrating agent, in which case the main product is the compound (C₆H₄·OH)₃·S·O·PO(OH)·OPh, m.p. 217—218°, also obtained by the action of OPh·PO(OH)₂ on (C₆H₄·OH)₃·S·Cl, m.p. 265—268° (corr.) [lit. 261—262°

(decomp.). The compound $(C_6H_4 \cdot OH)_3S \cdot NO_3$, m.p. 169—170°, with $H_2SO_4-HNO_3$ (60:40) affords a $(NO_2)_2$ -derivative, m.p. 213° (decomp.). The compound $(C_6H_4 \cdot OBz)_3S \cdot Cl$ has m.p. 53—54° (cf. A., 1933, 389; 1934, 69). H. G. M.

Aromatic fluoro-compounds. XX. Fluorophenols. G. SCHIEMANN, with W. WINKELMULLER, E. BAESLER, and E. LEY [and, in part, M. SEYHAN] (J. pr. Chem., 1935, [ii], 143, 18—28).—4-Fluoro- α -naphthylamine diazotised yields 4-fluoro- α -naphthol, m.p. 115°. *o*-, *m*-, and *p*-fluoroanisole with $AlCl_3$ in C_6H_6 give *o*-, *m*-, and *p*-fluorophenol; the last is also obtained from *p*-fluorophenetole. 2-Fluoro- and 2:3'-difluoro-4'-methoxydiphenyl ether similarly give 2-fluoro-, m.p. 69—72°, b.p. 198—200°/22 mm., and 2:3'-difluoro-, b.p. 156—157°/9 mm., 4'-hydroxydiphenyl ether. (I) and Br in $CHCl_3$ yield 4-bromo-2-fluoroanisole, m.p. 16°, b.p. 96°/14 mm., also made by converting 4-bromo-*o*-anisidine (HNO_2 , $HBFe_4$) into 5-bromo-*o*-anisole diazonium fluoride, which decomposes at 152°. *o*-Fluorophenol and *p*-bromoanisole condense (K_2CO_3 , Cu, C_5H_5N) to 2-fluoro-4'-methoxydiphenyl ether, b.p. 160.5—161.5°/12 mm. 2:3'-Difluoro-4'-methoxydiphenyl ether has m.p. 28.5°, b.p. 161.0°/10 mm. E. W. W.

Bromination of substances containing two aromatic nuclei. II. Bromination of phenyl and tolyl esters of *m*- and *p*-nitrobenzoic acids. G. V. JADHAV and Y. I. RANGWALA (Proc. Indian Acad. Sci., 1935, 1, A, 616—619; cf. this vol., 339, 746).—The appropriate nitrobenzoates (I) heated with 1 or 2 mols. of Br yield 4-bromophenyl *p*-, m.p. 181°, 4-bromo-*o*-tolyl *p*-, m.p. 183—184°, 4-bromo-*m*-tolyl *p*-, m.p. 145—146°, 4-bromophenyl *m*-, m.p. 122° (the above were also prepared from the respective bromophenols and nitro-acid chlorides), and (probably) 4:5-dibromo-*o*-tolyl *p*-, m.p. 139—140° (depresses m.p. of 4:6-isomeride), -nitrobenzoate. (I) heated with Br and fuming HNO_3 (8 hr.) give (probably) 4:5-dibromo-*o*-, m.p. 170°, and 3:5:6-tribromo-*p*-, m.p. 193—194°, -tolyl *m*-nitrobenzoate. *p*-Tolyl *p*-nitrobenzoate with Br and conc. HNO_3 at 110—120° (2 hr.) yields 3:5- or 2:5-dibromo-*p*-tolyl *p*-nitrobenzoate, m.p. 165°, converted by Br and conc. HNO_3 at 150—160° (2 hr.) into 3:5:6-tribromo-*p*-tolyl *p*-nitrobenzoate, m.p. 194—195°. F. R. G.

Mononitration of α -naphthol and α -naphthyl methyl ether, and mono-reduction of 2:4-dinitro- α -naphthol. H. H. HODGSON and E. W. SMITH (J.C.S., 1935, 671—674).—In agreement with Pictet *et al.* (Chem. Zentr., 1903, ii, 1109) and contrary to Bell (A., 1933, 499) $(OH)_2N(OAc)_2$ (I) with α - $C_{10}H_7 \cdot OH$ in $AcOH$ < 7° affords a 34% yield of its 2- NO_2 -derivative (II); α - $C_{10}H_7 \cdot OAc$ similarly gives a 45% yield of (II) and some 2:4- $(NO_2)_2$ -derivative (III), but α - $C_{10}H_7 \cdot OMe$ affords mainly its 4- NO_2 -derivative (IV), also obtained by the action of $Me_2SO_4-K_2CO_3$ on 4-nitro- α -naphthol. Reduction (Fe—50% $AcOH$) of (IV) and acetylation of the product gives 4-acetamido- α -naphthyl Me ether, converted by (I)— $AcOH$ at 18—20° into its 3- NO_2 -derivative, m.p. 246°. Further nitration (at 70°) of either (IV) or the 2- NO_2 -compound gives the 2:4- $(NO_2)_2$ -derivative. Reduction of (III) with $SnCl_2$ —

HCl — $EtOH$ at < 30° gives the hydrochloride, m.p. 175° (decomp.), of 2-nitro-4-amino- α -naphthol (V), m.p. 160° (decomp.) [*N*-Ac, m.p. 250° (decomp.) (lit. m.p. 238°) (*Me* ether, m.p. 214°), and *N*-Bz derivative, m.p. 230° (decomp.)]. Diazotisation of (V) gives 2-nitro-4-diazonaphthalene 1-oxide (VI), m.p. 163° (decomp.), converted (Sandmeyer) into 4-chloro-2-nitro- α -naphthol, m.p. 155°. (VI) with β - $C_{10}H_7 \cdot OH$ in acid solution gives 2-nitro-1-naphthol-4-azo- β -naphthol, m.p. 233° (decomp.), and with $OK \cdot CS_2Et$, hydrolysis to the mercaptan, and oxidation with $K_3Fe(CN)_6$, it gives 3:3'-dinitro-4:4'-dihydroxydiphenyl disulphide, m.p. 197° (decomp.). (V) with aq. HNO_3 at room temp. gives 2:3-dinitro-4-amino- α -naphthol, m.p. 130°, and with Cl_2 , Br-, or $I-CHCl_3$, it affords, respectively, its 3-*Cl*-, m.p. 120° (hydrochloride), 3-*Br*- (VII), m.p. 123°, and 3-*I*-derivative, m.p. 138°. 2-Bromo-4-nitro- α -naphthylamine is reduced (Fe—50% $AcOH$) and acetylated to the corresponding 4-acetamido-compound, m.p. 230°, nitrated to 2-bromo-3-nitro-4-acetamido- α -naphthylamine, m.p. 300°, which gives (VII) when boiled with 10% $NaOH$. J. W. B.

Alkaline-earth compounds of guaiacol and *p*-cresol. V. P. SUMAROKOV (Lesokhim. Prom., 1933, 2, No. 3, 34—36).—The prep. and properties of the Ba and Ca salts are described. CH. ABS. (r)

Chemical activity of the naphtholic hydrogens of 1:7-dihydroxynaphthalene. L. PALFRAY and A. LEMAN (Compt. rend., 1935, 200, 1328—1331).—No difference in activity was observed between the two OH groups. The Bz_2 derivative, m.p. 101—105°, and diphenylurethane, m.p. 203—204°, of 1:7- $C_{10}H_6(OH)_2$ are described. F. R. G.

Optically active naphthalenesulphoxyacetic acids. F. GAJOWCZYK and J. SUSZKO (Ber., 1935, 68, [B], 1005—1011; cf. A., 1932, 1288).—1- $C_{10}H_7 \cdot SH$ and $CH_2Cl \cdot CO_2H$ in alkaline solution afford 1-naphthylthiolacetic acid, m.p. 111° (corresponding amide, m.p. 147°), oxidised by 30% H_2O_2 in $AcOH$ at room temp. to *r*-naphthalene-1-sulphoxyacetic acid (I), $C_{10}H_7 \cdot SO \cdot CH_2 \cdot CO_2H$, m.p. 151° (decomp.). Repeated crystallisation of (I) and cinchonidine from $COMe_2$ containing 3% of H_2O affords cinchonidine 1-naphthalene-1-sulphoxyacetate, m.p. 190—191° (decomp.), $[\alpha]_D^{20} -296.7^\circ$ in $CHCl_3$, whence 1-naphthalene-1-sulphoxyacetic acid, m.p. 151° (decomp.), $[\alpha]_D^{20} -459^\circ$ in $EtOH$, which is not racemised by prolonged contact with 5% $NaOH$ at 20°. Treatment of the residual acid from the above resolution with strychnine in $EtOH$ leads to strychnine d-naphthalene-1-sulphoxyacetate, m.p. 148—150° (decomp.), $[\alpha]_D^{20} +174^\circ$ in $CHCl_3$, whence d-naphthalene-1-sulphoxyacetic acid, m.p. 150—151° (decomp.), $[\alpha]_D^{20} +456^\circ$ in $EtOH$. 2-Naphthylthiolacetic acid (amide, m.p. 134°) is similarly oxidised to *r*-naphthalene-2-sulphoxyacetic acid, m.p. 144° (decomp.), resolved by cinchonine in C_6H_6 into 1-naphthalene-2-sulphoxyacetic acid, m.p. 144—146° (decomp.), $[\alpha]_D^{20} -171^\circ$ in 99.5% $EtOH$ [cinchonine salt, m.p. 141° (decomp.), $[\alpha]_D^{20} +43^\circ$ in 99.5% $EtOH$], and d-naphthalene-2-sulphoxyacetic acid, m.p. 143—145° (decomp.), $[\alpha]_D^{20} +168^\circ$ in 99.5% $EtOH$ (cinchonine salt, m.p. 156—158° (decomp.), $[\alpha]_D^{20} +175^\circ$ in 99.5% $EtOH$). H. W.

Salt-like properties of halogens. Products of the action of bromine on silver salts. M. I. USCHAKOV and V. O. TCHISTOV (Ber., 1935, 68, [B], 824—830; cf. A., 1934, 1187).—Immediate decolorisation is observed when equiv. solutions of Br and AgNO₃ in MeOH are mixed and the amount of pptd. AgBr increases with time owing to the reducing action of MeOH. Determination of the oxidising power of the solution shows that reaction is $\text{Br}_2 + \text{AgNO}_3 \rightarrow \text{AgBr} + \text{BrNO}_3$; $2\text{BrNO}_3 + \text{AgNO}_3 \rightleftharpoons \text{AgBr} + \text{Br}(\text{NO}_3)_2$. The isolation of BrNO₃ from MeOH solution appears impossible, but the compound, BrNO₃·2C₅H₅N, m.p. 78—78.5° in a sealed capillary, is obtained when Br in CHCl₃ is gradually added to AgNO₃ in C₅H₅N-CHCl₃ at 0°. With cyclohexene it yields 2-bromocyclohexyl nitrate, b.p. 125—126°/15 mm., and bromocyclohexyl Me ether mixed with dibromocyclohexane. Ag salts of carboxylic acids and Br yield compounds (I) of positive Br⁺, reaction proceeding to completion in presence of a large excess of Ag salt, when (I) are periodically removed, for example, by addition of cyclohexene or when the C₅H₅N complexes of the Ag salts are used. The following 2-bromocyclohexyl esters are described: benzoate, m.p. 64—64.5°; m-nitrobenzoate, m.p. 81.5°; acetate, b.p. 108—111°/12 mm.; propionate, b.p. 126—128°/11 mm.; n-butyrate, b.p. 140°/10 mm., 145°/14 mm. Addition of Cl₂ and cyclohexene to a suspension of AgOBz in CCl₄ at -10° leads to 2-chlorocyclohexyl benzoate, m.p. 50.5—51.5°. H. W.

Relationship between absorption and valency in the chemistry of organic colouring matters. Halochromic dyes. P. RUMPF (Bull. Soc. chim., 1935, [v], 2, 882—894).—It is suggested that the coloured forms of all halochromic colouring matters are due to the presence of a central carbonium (ter-covalent C) or immonium (dicovalent N) cation rather than to quinonoid forms. Various dyes of the di- and tri-phenylmethane, phthalein, and diphenylamine groups are discussed on this basis. The colour of the anthocyanin group may also be due to the carbonium condition of C in position 2 rather than to an oxonium salt, and the oxidation-reduction systems of indo-phenol, safranin, and related types are consistently explained. The polar effects of substituents are also discussed. J. W. B.

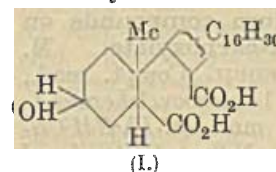
Triphenylmethane series. II. Photochemical behaviour and optical activity of triphenylmethyl derivatives. I. LIFSCHITZ (Rec. trav. chim., 1935, 54, 397—408; cf. A., 1934, 403).—3-Methoxy-9-phenylfluorene (I) (modified prep.), m.p. 125° (lit. 84°), +C₆H₆, m.p. about 116° (decomp.), and +CCl₄, photosensitive, gives the chloride, m.p. 119—120°, not photosensitive, which with SH·CH₂·CO₂H in CS₂ readily gives 3-methoxy-9-phenylfluorene-9-thioglycollic acid, m.p. 156°, resolved by brucine into the l-acid, m.p. 98—100° [brucine salt, m.p. 131° (decomp.)]. When illuminated, this is largely racemised, but gives also traces of (I) and a substance, m.p. 184—185°. Illumination probably produces [C₁₉H₁₂·OMe]⁺ and [SH·CH₂·CO₂H]⁻. 9-Phenylfluorene-9-thioglycollic acid, m.p. 149.5°, gives, when illuminated, a small amount of a substance, m.p. 187°, possibly 9-fluorene peroxide. Attempts to prepare a perchlorate of (I) failed. R. S. C.

Saligenin. G. A. KIRKHOF and A. D. STEPANOV (Khim. Farm. Prom., 1934, No. 3, 14—15).—The reduction of salicylamide, both with Na-Hg in 96% EtOH, and electrolytically, using a Hg cathode, is described. CH. ABS. (r)

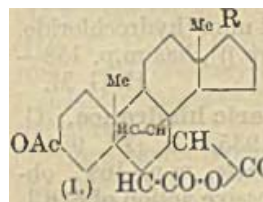
Irradiation of ergosterol. I. L. FRANCESCONI and F. OPISSE (Annali Chim. Appl., 1935, 25, 124—135).—From the physical properties and colour reactions of the products obtained by exposing dry ergosterol, in the cold and in presence of CO₂, to the light from a Hg-vapour lamp for 1—32 hr., the proportions of lumisterol, vitamin-D₂, and suprasterol are deduced. The best conditions for obtaining vitamin-D₂ are given. T. H. P.

Photographic activity of irradiated ergosterol and its nature. II. L. FRANCESCONI and L. BALDISERA (Annali Chim. Appl., 1935, 25, 136—148).—Pure ergosterol does not affect a photographic plate, but after irradiation either in the dry state and in presence of CO₂ or in EtOH, it acts on the plate more vigorously than autunite. The activity persists for a long time. The phenomenon is chemical, O taken up by the irradiated material being partly released in active form. Irradiation of santolin with ultra-violet light produces similar results. T. H. P.

Stereochemistry of sterols and bile acids. H. LETTRE (Ber., 1935, 68, [B], 766—767).—Cholesterol is transformed through cholestanol-6-one into β-chlorocholestan-6-one, oxidised by HNO₃ to a chlorodicarboxylic acid which is hydrolysed to the OH-acid (I). Treatment of (I) with boiling Ac₂O gives the lactonic acid, C₂₇H₄₄O₄, m.p. 211—213°; OH at C 3 and CO₂H at C 5 are therefore in the cis-position to one another. Chenodeoxycholic acid (II) is oxidised by NaOBr to a OH-tricarboxylic acid (III), which readily gives a lactonic dicarboxylic acid (IV). (II) is a derivative of cholic acid, and is hence derived from cis-decahydronaphthalene. Me at C 10 and H at C 5 are cis to one another and CO₂H at C 5 in (III) is trans to these substituents. Lactone formation shows that OH at C 7 is cis to CO₂H at C 5. (IV) is also derived from biliobanic acid, the product of the action of NaOBr on cholic acid (V). OH at C 7 in (V) and in (II) are sterically similar and trans to Me at C 10 and H at C 5. H. W.



Transformation products of ergosteryl acetate-maleic anhydride. H. H. INHOFFEN (Ber., 1935, 68, [B], 973—981; cf. A., 1934, 186, 769).—The action of MgMeI under defined conditions on ergosteryl acetate-maleic anhydride [(I); R=C₉H₁₇] gives an enol-lactone (II), $\text{X} \left\{ \begin{array}{l} \text{CH}_2\text{C}(\text{CH}_2) \\ \text{CH}-\text{CO} \end{array} \right\} \text{O}$ (X=C₃₀H₄₆O₂), m.p. 195° (corr.), which reduces NH₃-Ag solution but does not give the Legal reaction. A small amount of a product (III), $\text{X} \left\{ \begin{array}{l} \text{C}:\text{CMe} \\ \text{C}:\text{CMe} \end{array} \right\} \text{O}$, m.p. 246° (corr.), is also obtained the yield of which can be greatly increased by modified conditions. If elimin-



ation of H_2O is avoided the primary product (IV), $\text{X} \begin{matrix} \text{[CH}\cdot\text{CMe(OH)} \\ \text{[CH}\cdot\text{CMe(OH)} \end{matrix} > \text{O}$, m.p. 275—277°, is obtained, converted by hot Ac_2O into (III). Alkaline hydrolysis of (II) yields a complex mixture from which are isolated a sparingly sol. acidic substance, m.p. 290—295° (decomp.), transformed by CH_2N_2 into a Me ester or ether, $\text{C}_{34}\text{H}_{50}\text{O}_5$, m.p. 195—196° (corr.) [acetate, $\text{C}_{36}\text{H}_{52}\text{O}_4$, m.p. 205—206° (corr.)], and a freely sol., neutral product, $\text{C}_{33}\text{H}_{50}\text{O}_4$, m.p. 121—123° (corr.), which does not react with CH_2N_2 but is converted by boiling Ac_2O into the acetate, $\text{C}_{35}\text{H}_{52}\text{O}_5$, m.p. 129—131° (corr.). Exhaustive hydrogenation (Pt sponge in AcOH) of (II) yields the H_6 -derivative (V), $\text{C}_{35}\text{H}_{56}\text{O}_4$, m.p. 215—217° (corr.), hydrolysed to a OH-acid, transformed by boiling Ac_2O into (V) and a neutral product, m.p. 201—202° (corr.), which also yields (V) when acetylated. Reduction of (II) in presence of Pd and COMe_2 yields the dihydroenol-lactone (VI), m.p. 182° (decomp.) (cf. I; $\text{R}=\text{C}_9\text{H}_{19}$), also obtained by treating 22-dihydroergosteryl acetate-maleic anhydride (VII) with MgMeI in Et_2O . Ozonisation of (VI) followed by oxidative fission of the ozonide with CrO_3 - AcOH gives a neutral product (VIII), $\text{C}_{35}\text{H}_{50}\text{O}_9$, m.p. 304—305° (corr., decomp.), and an acid substance of which the Me ester (IX), m.p. 307—308° (corr.), is identical with that obtained by the ozonisation of (VII). (VIII) is converted into (IX) by the successive action of boiling 80% AcOH and CH_2N_2 . H. W.

Sterol from *Pinus sabiniana*.—See this vol., 797.

Action of organomagnesium compounds on ethyl 1-aminocyclohexane-1-carboxylate. M. GODCHOT and (Mlle.) G. CAUQUIL (Compt. rend., 1935, 200, 1479—1481).—*Et* 1-aminocyclohexane-1-carboxylate (I), b.p. 110°/15 mm. (N-Ph-NH-CS-derivative, m.p. 258—259°; N-2:4-dinitrophenyl derivative, m.p. 168°; forms a compound, m.p. 265°, with CS_2), obtained from the acid (A., 1906, i, 425), reacts with MgMeI (5 mols.) forming 1-aminocyclohexyldimethylcarbinol, b.p. 145°/11 mm. (hydrochloride, m.p. 138°), 1-hydroxycyclohexylisopropyl alcohol, m.p. 82°, b.p. 125°/15 mm. (cf. A., 1909, i, 796), and 3:6-bis-pentamethylene-2:5-dimethyl-3:6-dihydropyrazine (II), m.p. 212°. The formation of (II) is explained by the self-condensation of the intermediate compound 1-aminocyclohexyl Me ketone (III), b.p. 105°/10 mm. (hydrochloride, m.p. 195°), obtained from (I) with 3 mols. of MgMeI . (III) with KOEt-EtOH affords (II). Similarly (I) and 3 mols. of MgEtBr afford 1-aminocyclohexyl Et ketone, b.p. 132—133°/12 mm. (hydrochloride, m.p. 230°), and (I) and MgPhBr give mainly 1-aminocyclohexyl Ph ketone, m.p. 126—127° (hydrochloride, m.p. 258—260°), and some 1- α -hydroxybenzhydrylcyclohexanol (A., 1913, i, 485). Di-1-cyanocyclohexylamine (A., 1914, i, 671) formed spontaneously from α -amino- α -cyanocyclohexane, b.p. 105°/12 mm. [hydrochloride, m.p. 199° {lit. 187—189° (decomp.)}], has m.p. 138—139°. H. G. M.

Overcoming two cases of steric hindrance. G. WITTE and H. PETRI (Ber., 1935, 68 [B], 924—927).—Me 1-benzhydryl-8-naphthoate, m.p. 168°, obtained from the acid by the successive action of SOCl_2 and MeOH or by means of CH_2N_2 in Et_2O , is unaffected

by MgPhBr but is converted by LiPh in Et_2O into 1-benzhydryl-8-hydroxydiphenylmethylnaphthalene (I), m.p. 200—201° (K derivative). (I) is easily transformed by MeOH-HCl into 1-benzhydryl-8-methoxydiphenylmethylnaphthalene (II), m.p. 247—248° (slight decomp.), and by HCl in CHCl_3 followed by AcCl into 1-benzhydryl-8-chlorodiphenylmethylnaphthalene, decomp. 140—142°. Reduction of (I) by ZnCl_2 in AcOH-HCl containing a trace of HI affords 1:8-dibenzhydrylnaphthalene, m.p. 243°, also obtained by successive treatments of (II) with Na-K and MeOH . Similarly, 9:9-diphenylacenaphthone-10-one is indifferent towards MgPhBr but is readily transformed by LiPh into 10-hydroxy-9:9:10-triphenylacenaphthene, m.p. 169—170°, whence 10-methoxy-, m.p. 174—175°, and 10-chloro-, decomp. 165°, -9:9:10-triphenylacenaphthene. H. W.

Complex formation between polynitro-compounds and aromatic hydrocarbons.—See this vol., 828.

Relations between constitution and substantivity of cotton-substantive "naphthols." H. KRZIKALLA and B. EISTERT (J. pr. Chem., 1935, [ii], 143, 50—58).—The substantivity of "Naphthol AS" (2-hydroxy-3-naphthanilide) (I) is usually ascribed to the $\cdot\text{CO}\cdot\text{NH}_2$. "Homonaphthol AS" (2-hydroxy-3-naphthylacetanilide) (II) (see below), which gives yellower dyes than (I), is little more substantive than $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and the *N*-Me derivative of (I) has also low substantivity; that of (I) is therefore ascribed to an enol structure, $\text{C}_{10}\text{H}_6(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{NPh}$. This is supported by the low substantivity of β -naphthol-3-sulphonanilide (A., 1931, 479). The action of CH_2N_2 on (I) yields, however, only 2-methoxy-3-naphthanilide, m.p. 154°. (II) is prepared as follows. 2-Hydroxy-3-naphthoyl chloride (new m.p. 100—101°) with CH_2N_2 gives 2-hydroxy-3-naphthoyldiazomethane (III), m.p. 128—129° (decomp.); attempts to combine this with NH_2Ph yielded only 5:6-benzo-3-coumaranone (IV) [obtained in quant. yield from (III) heated in EtOH with HCl]. 2-Acetoxy-3-naphthoyl chloride (new m.p. 98°) yields 2-acetoxy-3-naphthoyldiazomethane (V), m.p. 122—123° (decomp.), converted by HCl in AcOH into 3-chloroacetyl- β -naphthol, m.p. 151° [which in $\text{C}_2\text{H}_5\text{N}$ gives (IV)]. With NH_2Ph , (V) yields 2-hydroxy-3-naphthylacetanilide (II), m.p. 215—216°. This is hydrolysed (KOH) to 2-hydroxy-3-naphthylacetic acid (+ H_2O ; sinters at 150°, chars at 240°) (p-nitrobenzeneazo-derivative), which with P_2O_5 in xylene forms 2-hydroxy-3-naphthylacetolactone (5:6-benzo-2-coumaranone), m.p. 128—129°. 2-Hydroxy-3-naphthmethyl-anilide with CH_2N_2 gives the 2-*OMe*-compound, m.p. 96—97°. E. W. W.

Nitration of lactones Ia and IIb. [Lactones of the isomeric 2-phenyl-3- α -hydroxybenzylcyclopropane-1-carboxylic acids.] F. SCHENCK (Ber., 1935, 68, [B], 920—924; cf. A., 1932, 1029).—Under defined conditions lactone Ia is transformed by AcNO_3 in Ac_2O into the lactone (I) of 2-*p*-nitrophenyl-3- α -hydroxybenzylcyclopropane-1-carboxylic acid Ia, m.p. 134—135°, whilst a larger proportion of AcNO_3 affords a dinitrolactone Ia, m.p. 199—200°, which is hydrolysed to the corresponding acid, decomp.

185° (*Me* ester, m.p. 191—192°). (I) is similarly converted into 2-*p*-nitrophenyl-3- α -hydroxybenzylcyclopropane-1-carboxylic acid Ia (II), decomp. 168° [*Me* ester (III), m.p. 167—167.5°], transformed by H_2SO_4 -AcOH at 15—20° into (I). Lactone IIb similarly yields the lactone (IV) of 2-*p*-nitrophenyl-3- α -hydroxybenzylcyclopropane-1-carboxylic acid, m.p. 154—155°, whence 2-*p*-nitrophenyl-3- α -hydroxybenzylcyclopropane-1-carboxylic acid IIb (V), m.p. 174° (*Me* ester, m.p. 130—131°), reconverted by Ac_2O or H_2SO_4 -AcOH into (III). Since (II) is converted into (IV) by Ac_2O , NO_2 is attached to the same Ph and in the same position in (I), (II), (IV), and (V) and the *para* position follows from the production of *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ by the oxidation of (I) with KMnO_4 . Since (III) is transformed by H_2SO_4 -AcOH followed by KOH-EtOH into α -*p*-nitrobenzylidene- γ -phenyl- Δ^2 -butenoic acid, m.p. 212—213.5°, NO_2 is substituted in the 2-Ph group. H. W.

Preparation of substituted *o*-aroylbenzoic acids in the identification of aromatic hydrocarbons. H. W. UNDERWOOD, jun., and W. L. WALSH (J. Amer. Chem. Soc., 1935, 57, 940—942).—Aromatic hydrocarbons (I) may be identified by conversion [Friedel-Crafts; technique for 0.4 g. of (I) described] into *o*-aroylbenzoic or -tetrachlorobenzoic acids, followed, if necessary, by ring-closure to anthraquinone derivatives. The following have been prepared: *o*-4-*n*-butyl-, m.p. 97—98°, *o*-2:4-diethyl-, m.p. 114—116°, and *o*-2:4:6-triethylbenzoylbenzoic acid, m.p. 129.5—130.5°; 3:4:5:6-tetrachloro-2-2':3'-, m.p. 177.5—178.5°, -2':4'-, m.p. 222—224°, -2':5'-dimethyl-, m.p. 244—246°, and -4'-ethylbenzoylbenzoic acid, m.p. 172—173°; 5:6:7:8-tetrachloro-2:3-dimethylanthraquinone. R. S. C.

(A) 1:9-Benzanthrone-8-carboxylic acid and dibenzanthronedicarboxylic acid from 8-bromo-1-naphthoic acid. H. G. RULE, W. PURSELL, and (in part) A. J. G. BARNETT. (B) Cyclisation of 1:9-benzanthrone-8-carboxylic acid to 8:11-ketobenzanthrone, and of dibenzanthronedicarboxylic acid to diketodibenzanthrone. L. A. BIGELOW and H. G. RULE (J.C.S., 1935, 571—572, 573—575).—(A) *Me* 8-bromo-1-naphthoate and *o*- $\text{C}_6\text{H}_4\text{I}\cdot\text{CO}_2\text{Me}$ heated together with Cu-bronze at 215—220° afford (with other products) the *Me*₂ ester (I), m.p. 132—133°, of 8-*o*-carboxyphenyl-1-naphthoic acid, m.p. 231—232°, which is obtained, together with some *Me* 8-*o*-carboxyphenyl-1-naphthoate (II), m.p. 150—151°, by hydrolysis with KOH-EtOH. (I) with conc. H_2SO_4 at 100° gives 1:9-benzanthrone-8-carb-

proved], decarboxylated by Cu-bronze in boiling quinoline to benzanthrone (IV). Fusion of (III) with 10 parts of KOH at 225—230° affords dibenzanthronedicarboxylic acid (V), which is a blue vat dye. (V) is decarboxylated by Cu-bronze in quinoline to dibenzanthrone, which gives the same absorption spectrum as violanthrone-A separated from crude violanthrone (Maki, B., 1933, 261).

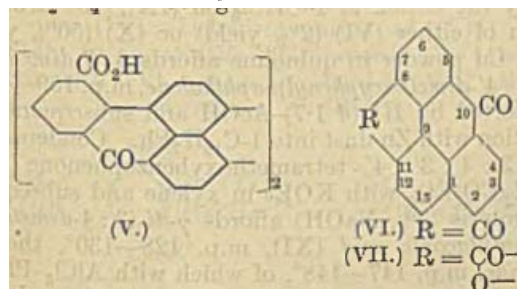
(B) The products obtained by treatment of (I) with H_2SO_4 (d_4^{20} 1.823) vary with the temp. of reaction. At 15—40° *Me* 1:9-benzanthrone-8-carboxylate, m.p. 159—160°, is obtained in almost quant. yield, with slight hydrolysis to (III), which is obtained in 90% yield at 100°. At 120—170° (IV) is obtained in small yield with partial dehydration to 8:11-ketobenzanthrone (VI), m.p. 327—328°, which at >135° is formed together with (?) the lactone (VII), m.p. 355—356°, of 11-hydroxybenzanthrone-8-carboxylic acid (separation difficult). Much loss by sulphonation occurs at >160°. (VII) is prepared free from (VI) by oxidation of (III) with CrO_3 - H_2SO_4 , and (VI) is best prepared by addition of P_2O_5 to (III) dissolved in *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 200°. Similar dehydration of (V) gives diketodibenzanthrone (purple-blue vat dye). Neither decarboxylation nor methylation of (VII) could be effected. All m.p. in (b) are corr. J. W. B.

Occurrence of norstictic acid in *Parmelia acetabulum*.—See this vol., 905.

Methylcholanthrene from cholic acid. L. F. FRESER and M. S. NEWMAN (J. Amer. Chem. Soc., 1935, 57, 961).—Cholic acid (I) is oxidised to dehydrocholic acid, which is hydrogenated (PtO_2) to impure 3:7-dihydroxy-12-ketocholanic acid, pyrolysed (260—330°) to a mixture, which with Se at 320—330° affords methylcholanthrene in 5.4% over-all yield. R. S. C.

Isolation of 3-hydroxy-6-ketoallocholanolic acid from pig's bile.—See this vol., 773.

Syntheses with cyclic ketonic esters. I. Synthesis of 1-methylcyclohexane-2-acetic-1-carboxylic acid and related compounds. C. K. CHUANG, Y. L. TIEN, and Y. T. HUANG. II. Synthesis of cyclohexane-1:2-diacetic acid and related compounds. C. K. CHUANG and C. M. MA (Ber., 1935, 68, [B], 864—870, 871—876).—I. *Et* 1-methylcyclohexan-2-one-1-carboxylate (improved prep.) does not condense with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in presence of piperidine or KOEt, but is transformed by Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ into *Et* 2-hydroxy-1-methylcyclohexane-1-carboxylate-2-acetate (I), b.p. 169—170°/10 mm. (corresponding non-cryst. acid). (I) is dehydrated by SOCl_2 in $\text{C}_6\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$ to the unsaturated ester, $\text{C}_8\text{H}_{14}\text{O}_4$, b.p. 144—156°/10 mm., hydrolysed by KOH-MeOH to the *Me* *H* ester (II), $\text{C}_{11}\text{H}_{16}\text{O}_4$, m.p. 133—134° (*Ag* salt; corresponding anilide, m.p. 146.5—147.5°), and by KOH-EtOH to the *Et* *H* ester (III), $\text{C}_{12}\text{H}_{18}\text{O}_4$, m.p. 92.5—93° (anilide, m.p. 107—108°). (II) is catalytically reduced to 1-carbomethoxy-1-methylcyclohexane-2-acetic acid (IV), m.p. 59—60°, the corresponding *Et* *H* ester (V), m.p. 79—81°, being obtained similarly from (III). Hydrolysis of (IV) or (V) affords 1-methylcyclohexane-1-carboxylic-2-acetic acid (VI), m.p. 163—164° (anilide, m.p. 164—165°; dianilide, m.p. 186—187°), also obtained by treating (I)



oxylic acid (III), m.p. 273° [also by the action of cold conc. H_2SO_4 on (II), the constitution of which is thus

successively with HBr and Zn dust in AcOH and hydrolysing the product. Attempts to isomerise (VI) by boiling with Ac_2O or distillation in high vac. were unsuccessful.

II. Et cyclohexan-2-one-1-carboxylate is transformed by Na and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 into Et₂ cyclohexan-2-one-1-carboxylate-1-acetate, b.p. 168—170°/8.8 mm., which does not yield ketonic derivatives. It is converted by boiling conc. HCl followed by esterification into Et cyclohexan-2-one-1-acetate (VII), b.p. 131—133°/9.8 mm. (semicarbazone, m.p. 191—193°; phenylhydrazone, m.p. 134—135°); cyclohexan-2-one-1-acetic acid has m.p. 39—41°. (VII) with Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 affords Et₂ 1-hydroxycyclohexane-1:2-diacetate (VIII), b.p. 132—134°/0.5 mm.; (VII) does not condense with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in presence of piperidine. Dehydration of (VIII) by SOCl_2 in $\text{C}_5\text{H}_5\text{N}\cdot\text{EtOH}$ yields the unsaturated ester, b.p. 129—135°/0.5 mm., hydrolysed to a cyclohexene-1:2-diacetic acid, m.p. 164—166° after softening at 155°, reduced (Pt-sponge-EtOH) to a mixture (IX) of *cis*- and *trans*-cyclohexane-1:2-diacetic acids from which a homogeneous material could not be obtained by crystallisation or isomerisation. (IX) with NH_2Ph at 180—190° yields a product from which *trans*-cyclohexanediacetmonoanilide, m.p. 179°, is derived, whence *trans*-cyclohexane-1:2-diacetic acid, m.p. 167°.

H. W.

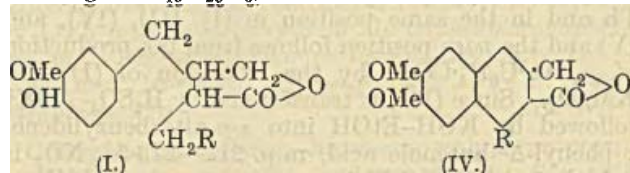
Derivatives of o-piperonal. T. S. STEVENS (J.C.S., 1935, 725—726).—3:4-Dibromopyrocatechol methylene ether in CHCl_3 is converted by 38% $\text{CH}_2\text{O}\cdot\text{AcOH}\cdot\text{H}_2\text{SO}_4$ at 40° (2 weeks) and hydrolysis of the Ac derivative formed into 2:3-dibromo-5:6-methylenedioxybenzyl alcohol, m.p. 115°, reduced (3% Na-Hg in boiling 70% MeOH) to 2:3-methylenedioxybenzyl alcohol, b.p. 165°/30 mm., m.p. 34—35°, oxidised (KMnO_4) to o-piperonylic acid. J. W. B.

α-Aminoketones. II. Experiments based on Gabriel's synthesis. J. PASCUAL and R. R. REBOLLO (Anal. Fis. Quím., 1934, 32, 374—381).—The chloride (I) (improved prep.) of phthalimidoacetic acid (Me ester, m.p. 115—116°) with $\text{CHNa}(\text{CO}_2\text{Et})_2$ in C_6H_6 yields a compound, $\text{C}_{17}\text{H}_{17}\text{O}_7\text{N}$, and an acid, $\text{C}_{15}\text{H}_{12}\text{O}_6\text{N}_2$, as well as Et phthalimidoacetylmalonate. Et γ-phthalimidoacetoacetate (cf. Pfähler, A., 1913, i, 750) with NaOEt and MeI in C_6H_6 yields Et γ-phthalimido-α-methylacetoacetate (?), m.p. 79—80°. (I) with $\text{CH}_2\text{Ph}\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ gives Et phthalimidoacetylbenzylmalonate (cf. *loc cit.*), hydrolysed by conc. HCl at 120° to an unidentified compound (decomp. 170°) containing 31.6% Cl. F. R. G.

5-Chloro-3:4-dimethoxycinnamic acid and some of its esters. R. M. HANN (J. Washington Acad. Sci., 1935, 25, 220—222).—5-Chloroveratraldehyde when heated with malonic acid, $\text{C}_5\text{H}_5\text{N}$, and $\text{C}_5\text{H}_{11}\text{N}$ (steam-bath) affords 5-chloro-3:4-dimethoxycinnamic acid, m.p. 126—127° [Me, m.p. 63°. Et, m.p. 165°, phenacyl, m.p. 132°, p-fluoro-, m.p. 135° (I), p-chloro-, m.p. 137°, and p-bromo-phenacyl ester, m.p. 132°]. All m.p. except (I) are corr. H. G. M.

Constituents of natural phenolic resins. I. Matairesinol. R. D. HAWORTH and T. RICHARDSON. II. "Sulphite-liquors lactone." R. D. HAWORTH, G. SHELDRIK, and (in part) C. R. MAVIN

(J.C.S., 1935, 633—636, 636—644).—I. Analytical data for matairesinol (I) + EtOH, m.p. 74—76°, and anhyd., m.p. 117—118°, $[\alpha]_D^{18} -48.6^\circ$ in COMe_2 (lit. -4.89°), and its Me_2 (II), m.p. 127—128°, $[\alpha]_D^{18} -35.6^\circ$ in CHCl_3 [Br_2 -derivative, m.p. 126—127°, $[\alpha]_D^{18} -38.4^\circ$ in CHCl_3 ; $(\text{NO}_2)_2$, m.p. 179—180°, $[\alpha]_D^{18} -126.6^\circ$ in CHCl_3 , by cold conc. $\text{HNO}_3\cdot\text{AcOH}$, and $(\text{NO}_2)_4$ -derivative, m.p. 202—203°, $[\alpha]_D^{19} -161.6^\circ$ in COMe_2 , by cold fuming HNO_3 , or boiling conc. HNO_3], and Et₂ ether (III), m.p. 97—98°, agree best with the composition $\text{C}_{20}\text{H}_{22}\text{O}_6$ (Easterfield *et al.*, J.C.S., 1910, 95, 1028, give $\text{C}_{19}\text{H}_{20}\text{O}_6$). Oxidation of (II) and (III)



with 3% $\text{KMnO}_4\cdot\text{EtOH}\cdot\text{NaOH}$ (CO_2 stream) affords, respectively, veratric acid and 3-methoxy-4-ethoxybenzoic acid (yield > 50%). Oxidation of (II) with $\text{Pb}(\text{OAc})_4\cdot\text{AcOH}$ effects ring-closure to give a 10—15% yield of a mixture (separated by fractional crystallisation from $\text{MeOH}\cdot\text{CHCl}_3$) of the lactone (IV),

m.p. 254—255°, of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid (less sol.) and the isomeric lactone (V), m.p. 215—216°, of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid. Hence (I) has the structure assigned [$\text{R} = 3:4\text{ C}_6\text{H}_3(\text{OMe})_2$].

II. Dimerisation of 3:4-dimethoxyphenylpropionic acid in Ac_2O at 100° affords the anhydride (VI), m.p. 305—306°, of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)naphthalene-2:3-dicarboxylic acid, m.p. 232—234° (Me_2 , m.p. 166°, and Et_2 , m.p. 127—128°, esters), which is obtained together with veratroylveratric acid by oxidation of the Me_2 ether (VII) of "sulphite-liquors lactone" (VIII) (Erdtmann, A., 1934, 1352). Condensation of Na β-3:4-dimethoxybenzoylpropionate with veratraldehyde in Ac_2O at 100° gives the lactone (IX), m.p. 140—147°, resolidifying and remelting 153°, of β-3:4-dimethoxybenzoyl-α-3':4'-dimethoxybenzylidenepropionic acid, m.p. 175°, converted by boiling $\text{MeOH}\cdot\text{HCl}$ into the Me ester, m.p. 177—178°, of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)naphthalene-3-carboxylic acid (X), m.p. 222—223° (Br_1 -m.p. 295—296°, shrinks at 280—285°, and Br_2 -, m.p. 260°, -derivatives), which is obtained by hydrolysis, or by the action of $\text{I}\cdot\text{CHCl}_3$ on (IX). Decarboxylation of either (VI) (2% yield) or (X) (50% yield) with Cu powder in quinoline affords 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)naphthalene, m.p. 159—160°, converted by HI (d 1.7)— AcOH and subsequent distillation with Zn dust into $\text{I}\cdot\text{C}_{10}\text{H}_7\text{Ph}$. Condensation of 3:4:3':4'-tetramethoxybenzophenone and $(\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ with KOEt in xylene and subsequent hydrolysis (5% NaOH) affords γ-di-(3:4-dimethoxyphenyl)itaconic acid (XI), m.p. 128—130°, the anhydride, m.p. 147—148°, of which with $\text{AlCl}_3\cdot\text{PhNO}_2$ gives 1-keto-5:6-dimethoxy-3-(3':4'-dimethoxyphenyl)indene-2-acetic acid, m.p. 216—217° [semicarbazone (not analysed), m.p. 254° (decomp.)], reduced (H_2 -

Pd-C-AcOH) to 5:6-dimethoxy-3-(3':4'-dimethoxyphenyl)hydrindene-2-acetic acid, m.p. 169—170°. Condensation of $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ with veratrole (2 mols.) in $\text{AcOH}\text{--}\text{H}_2\text{SO}_4$ at $< 15^\circ$ and subsequent hydrolysis (10% $\text{KOH}\text{--}\text{MeOH}$) affords $\gamma\gamma$ -di-3:4-dimethoxyphenyl-n-propane- $\alpha\beta$ -dicarboxylic acid, m.p. 177—178° [also obtained in small yield by catalytic reduction of (XI)], the anhydride (AcCl) of which is converted by $\text{AlCl}_3\text{--PhNO}_2$ at 0° into 4-keto-6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid (XII), m.p. 200—201° (90% yield) [semicarbazone, m.p. 244—245° (decomp.)], the *Et* ester (XIII), m.p. 130—131°, of which is reduced ($\text{Zn}\text{--}\text{Hg}\text{--}\text{HCl}$) to 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid, m.p. 184—185° (Br_2 -derivative, m.p. 190—191°), dehydrogenated (Se at 280°) to the corresponding naphthalene. With $\text{Br}\text{--}\text{CHCl}_2$ (XIII) gives a 3:6'- Br_2 -derivative, m.p. 146—147°, converted by NPhEt_2 at 180—190° into *Et* 4-hydroxy-6:7-dimethoxy-1-(6'-bromo-3':4'-dimethoxyphenyl)-naphthalene-2-carboxylate (XIV), m.p. 193—195°, converted (repetition unsuccessful) by $\text{H}_2\text{--Pd}\text{--C}$ in boiling EtOH into (?) the debrominated ester, m.p. 228°. (XIV) with 40% CH_2O in conc. $\text{HCl}\text{--AcOH}$ at 100° gives the lactone, m.p. 319—320°, of 4-hydroxy-6:7-dimethoxy-1-(6'-bromo-3':4'-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid. (XIII) with $\text{HCO}_2\text{Et}\text{--Na}$ in C_6H_6 affords *Et* 3-aldehyde-4-keto-6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-1:2:3:4-tetrahydronaphthalene-2-carboxylate, m.p. 165°, reduced by 4% $\text{Na}\text{--Hg}$ in 0.2% NaOH at 100° (CO_2 stream) to the corresponding 4-hydroxy-3-hydroxymethyl-acid, m.p. 200°, converted by heating at 200° , or by boiling 10% H_2SO_4 , into the α -form, m.p. 186—187°, of the lactone (XV) (*B*, $\text{R}=\text{Me}$) of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-3-hydroxymethyl-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid. Similar condensation of (XIII) with $\text{Et}_2\text{C}_2\text{O}_4$ ($\text{KOEt}\text{--}\text{C}_6\text{H}_6$) affords the lactone (XVI) + H_2O , m.p. 212—213°, of 4-hydroxy-6:7-dimethoxy-2-carboxy-1-(3':4'-dimethoxyphenyl)-1:2:3:4-tetrahydronaphthalene-3-glycollic acid [*Et*₂ ester, m.p. 145—146°, hydrolysed to a carboxylic acid, m.p. 212—213°, which depresses the m.p. of the hydrated form (XVI)], converted at $215^\circ/12\text{ mm.}$ into an acidic compound, m.p. 285°. When heated at 215° (10 min.) (XVI) gives the stereoisomeric β -form, m.p. 209—210°, of (XV). Dehydrogenation of the β -form with $\text{Pd}\text{--black}$ at 220—230°, or the action of $\text{Pb}(\text{OAc})_4\text{--AcOH}$ at 70° on either the α - or β -form, gives (IV) (above), converted by $\text{NaOBr}\text{--NaOH}$ and subsequent treatment with AcCl into (VI). Dehydrogenation of (VII) with $\text{Pb}(\text{OAc})_4$ or Se at 255—260° affords (V) (above), isomeric with (IV), but also oxidised to (VI). Hence (VII) has the structure *A* [$\text{R}=\text{Me}$; $\text{R}'=3:4$ -

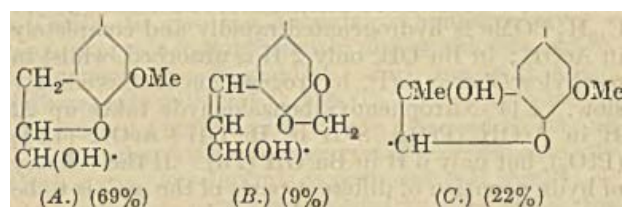
KMnO_4 to 5-methoxy-4-ethoxy-2-(3'-methoxy-4'-ethoxybenzoyl)benzoic acid identical with that obtained by Vanzetti *et al.* (A., 1934, 1099) from isoolivil.

J. W. B.

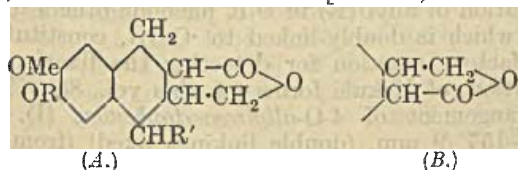
Condensation of oxalic esters with β -methyltricarballic ester. C. K. CHUANG and C. M. MA (Ber., 1935, 68, [B], 882—886).— $\text{Me}_3\beta$ -methyltricarballic ester and $\text{Me}_2\text{C}_2\text{O}_4$ condense in presence of NaOMe to *Me*₂4:5-diketo-2-methylcyclopentane-1:2:3-tricarboxylate (I), m.p. 176—177.5°; the corresponding *Et* esters do not appear to behave similarly. (I) affords *Na*₂, *Ag*₂, and *Cu* derivatives. With $o\text{--C}_6\text{H}_4(\text{NH}_2)_2$ it yields the compound, $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_2$, m.p. 249—251° (decomp.). The monoxime, m.p. 147—149° (decomp.), monophenylhydrazone, m.p. 154—155°, and monosemicarbazone, m.p. 140—141° (decomp.), are described.

H. W.

Lignin. XIV. K. FREUDENBERG, F. SOHNS, and A. JANSON (Annalen, 1935, 518, 62—85).—Finely divided pine wood is extracted with boiling $\text{EtOH}\text{--}\text{C}_6\text{H}_6$, the product is ground under H_2O and treated with 4% NaOH in absence of air, and submitted to alternate treatments with boiling 1% H_2SO_4 or 7% $\text{H}_2\text{C}_2\text{O}_4$ and Schweitzer's solution. The lignin (I) thus obtained is about 66% of that present in the wood (as determined analytically); the residue is similar in nature. (I) contains 16% of OMe and yields 0.9—1.1% of CH_2O when treated with mineral acid, thus confirming the presence of $\text{CH}_2\text{O}_2\cdot$ in (I). After methylation, (I) contains 29% OMe and yields only traces of CH_2O . Since similar treatment of piperonylic acid yields small amounts of veratric acid, it appears that $\text{CH}_2\text{O}_2\cdot$ is replaced by OMe during methylation. (I) contains OH which cannot be methylated, but is capable of acetylation; the presence of $\text{CRR}'\text{Me}\cdot\text{OH}$ thus indicated is confirmed by the formation of 6% of AcOH when (I) is oxidised by CrO_3 . The analytical data are in harmony with the presence of the arrangements *A*, *B*, and *C* in the proportions given:



Incomplete treatment of pine wood with NaHSO_3 does not appear to give lignin- β -sulphonic acid. The α -acid (II) thereby obtained contains less S than the technical product examined by Klason. Titration of (II) shows the presence of 1 phenolic OH and 1 SO_3H in 3 and 5 units, respectively. It is probable that OH results from ring opening and is possibly independent of the no. of SO_3H groups. Addition of $(\text{NH}_4)_2\text{CO}_3$ enables the yield of protocathechuic acid (III) obtained by treatment of (I) with molten KOH to be increased to 10%. Since under the experimental conditions about 50% of (III) is destroyed, this corresponds with about 25% of the amount theoretically obtainable. Hemipinic acid similarly gives about 75% of (III). Polymeric coniferyl alcohol



$\text{C}_6\text{H}_3(\text{OMe})_2$] and (VIII) is *A* ($\text{R}=\text{H}$), confirmed by oxidation of its *Et*₂ ether, m.p. 178—179°, with

(IV) behaves qualitatively and quantitatively similarly to (I). Ozonisation of (I) gives about 20% of $\text{H}_2\text{C}_2\text{O}_4$, but mainly other acids sol. in H_2O . Methyl-lignin (V), particularly in AcOH , is more readily attacked yielding $\text{H}_2\text{C}_2\text{O}_4$ and acids, one of which appears to be $\text{CO}_2\text{H}\cdot\text{C}_4\text{H}_5\text{O}_2(\text{OH})_2$. (V) is oxidised by KMnO_4 , appears indifferent to HIO_4 , and affords CBr_4 with OBr' . (IV) resembles (I) in its behaviour towards O_3 . Mild treatment of cryst. monomeric coniferyl alcohol with $\text{C}_5\text{H}_5\text{N}$ and Ac_2O gives a product with the same composition, whereas more drastic treatment (also methylation) is accompanied by loss of H_2O . (IV) has 12.5% of total OH of which 7% is phenolic OH. The mechanism of polymerisation is discussed. (IV) reacts with NaHSO_3 . The main points of distinction between (III) and (I) are the higher degree of oxidation of (I) and its lack of phenolic OH. Comparison of (IV) and (I) indicates that nuclear condensation rather than side-chain polymerisation is the primary process in the formation of (I).

Emphasis is laid on the distinction between analytical (I), (I) as isolated from wood, and (I) as existing in wood. It is considered that the part of pine (I) investigated belongs to the type of guaiacylglycerol, including coniferaldehyde, acetylguaiacylcarbinol, and analogues of similar degree of oxidation. The uniformity in the properties of (I) isolated by different methods suggests that it exists as such pre-formed in the wood and that the formation and polymerisation of the coniferyl system are physiological processes. This view is supported by the behaviour of methylated or non-methylated wood towards O_3 . In beech wood the physiological process appears less advanced.

H. W.

Method of microhydrogenation. K. H. SLOTTA and E. BLANKE (J. pr. Chem., 1935, [ii], 143, 3—17).—The micro-apparatus of Smith (A., 1932, 619), for hydrogenating 1—3 mg. of material, is adapted and described. It is confirmed that carotene takes up 22 H (cf. *loc. cit.*; A., 1933, 254, 1151). $\beta\text{-C}_{10}\text{H}_7\text{-COMe}$ is hydrogenated rapidly and completely in AcOH ; in $\text{Bu}^\text{t}\text{OH}$, only 2 H is absorbed, whilst in methylcyclohexane (I), hydrogenation is exceedingly slow. 4-(4'-Nitrophenoxy)benzaldehyde takes up 22 H in AcOH (PtO_2), 8 H in $\text{Bu}^\text{t}\text{OH}+\text{AcOH}$ (4:1) (PtO_2), but only 6 H in $\text{Bu}^\text{t}\text{OH}$ (Pd). If the velocity of hydrogenation of different parts of the mol. is to be compared, a less active catalyst and an unfavourable solvent are employed. Thus the curve for coprostenone in $\text{AcOH}+(\text{I})$ (PtO_2) shows no discontinuity, whilst in isomyl ether (Pd) it shows that slower hydrogenation of $>\text{C}:\text{O}$ accompanies faster hydrogenation of $>\text{C}:\text{C}<$.

E. W. W.

Coloured hydrocarbons of the rubene type. I. A. WILLEMART (Bull. Soc. chim., 1935, [v], 2, 867—882).—Mainly a more detailed account of results previously summarised (this vol., 612, 616). $\text{OH}\cdot\text{CPhBu}\cdot\text{C}:\text{CPh}$ (I) (*Me ether*, m.p. 46°) is converted by 3% H_2SO_4 in Bu_2O into *Ph* β -phenyl- β -tert.-butylvinyl ketone, m.p. 68° (also by boiling the corresponding Cl-compound in EtOH) (*oxime*, m.p. $128-129^\circ$). $\text{OH}\cdot\text{CPh}_2\cdot\text{C}:\text{CBu}^\text{t}$ (II) similarly affords

$\beta\beta$ -diphenylvinyl *Bu* ketone, m.p. 66° (*oxime*, m.p. $128-129^\circ$). The steric effect of *Bu* is evident in the conversion of (I) into the ketone, and into its chloride [94% in 98 hr.; (II) gives 98% in 1.25 hr.] and may explain the failure of such chlorides to form a rubene.

J. W. B.

Behaviour of β -*p*-dimethylaminobenzoin with alcoholic hydrogen chloride. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 955).— $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHPh}\cdot\text{OH}$ and hot $\text{HCl}\cdot\text{EtOH}$, with or without CuSO_4 , give $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{COPh}$ (I) and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COPh}$ (II). (II) and $\text{Sn}\cdot\text{HCl}$ yield (I). Benzoin and benzanisoin do not react similarly.

R. S. C.

Oxime of β -*p*-dimethylaminobenzoin. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 955—956).— β -*p*-Dimethylaminobenzoin, $\text{NH}_2\text{OH}\cdot\text{HCl}$, and NaOAc in hot EtOH give the *anti*-phenyl *oxime*, m.p. 184° , which with SOCl_2 in CHCl_3 gives PhCHO and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$.

R. S. C.

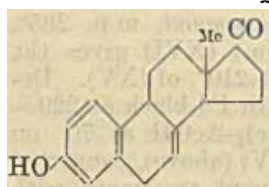
Isomeric form of benzildihydrazone. Preparation of the dihydrazones of benzil and its derivatives. J. VAN ALPHEN (Rec. trav. chim., 1935, 54, 443—446).— Bz_2 and hot 10% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot\text{EtOH}$ give mono- and a trace of di-hydrazone (II). (II) is best prepared by boiling 2:3-diphenyl-5:6-dihydropyrazine with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot\text{EtOH}$, when it is accompanied by a small quantity of an *isomeride*, m.p. 197° (decomp.), 230° (decomp.; block), or 260° (instantaneous). 2:3-Di-*p*-anisyl- and -*di-p*-tolyl-5:6-dihydropyrazine, m.p. 179° , give similarly the known anisil- and tolil-dihydrazones.

R. S. C.

Dimesityl diketones and their derivatives. I. $\alpha\alpha$ -Dimesityl- $\alpha\alpha$ -pentanedione and its dibromo-derivatives. T. KAO (J. Chinese Chem. Soc., 1935, 3, 56—59).— $\alpha\alpha$ -Dimesityl- $\alpha\alpha$ -pentanedione, m.p. $133-134^\circ$, results from the Friedel-Crafts condensation of mesitylene and glutaryl chloride; with Br it gives a brown liquid (not identified) and $\beta\beta$ -dibromo- $\alpha\alpha$ -dimesityl- $\alpha\alpha$ -pentanedione, m.p. $98-99^\circ$.

F. N. W.

Constitution of equilin. J. W. COOK and E. ROE



(Chem. and Ind., 1935, 501—502).—The nearly identical absorption spectra curves of equilin (I) and œstrone together with previous work (this vol., 752) establish the annexed formula for (I).

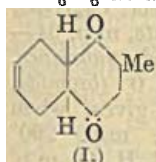
F. N. W.

Chelation. II. Stabilisation of Kekulé forms in *o*-hydroxyacetophenones. W. BAKER and (Miss) O. M. LOTHIAN (J.C.S., 1935, 628—633).—Migration of allyl (R) in *O*-R phenolic ethers to the *o*-C, which is doubly-linked to $\cdot\text{C}\cdot\text{OR}$, constitutes a satisfactory reaction for detecting the fixation, by chelation, of Kekulé forms (cf. this vol., 85). Thus rearrangement of 4-*O*-allylresacetophenone (I), b.p. $156-157^\circ/9$ mm. (double linkings fixed) (from resacetophenone, anhyd. K_2CO_3 , and RBr in boiling COMe_2), at $210-215^\circ$ gives 3-allylresacetophenone (II), m.p. 133° (85% yield), converted by Me_2SO_4 —10% aq.

KOH at 30° into its 4-*O*-*Me* ether, m.p. 61°, and by Me_2SO_4 -20% aq. KOH in COMe_2 into its *Me*, ether (III), b.p. 169—170°/15 mm. Similar methylation of (I) affords 2-*O*-methyl-4-*O*-allylresacetophenone, b.p. 171°/9 mm., m.p. 31° (chelation impossible) (also by allylation of isopæanol), which rearranges normally to give 2-*O*-methyl-5-allylresacetophenone (IV), m.p. 136° (60% yield) [4-*O*-methyl ether, m.p. 88—89°, not identical with (III)]. The structure of (II) follows from its reduction (H_2 -PdCl₄-EtOH) to 3-*n*-propylresacetophenone (V), m.p. 127—128°, identical with a specimen synthesised as follows: 7-hydroxy-4-methylcoumarin with $\text{RBr-K}_2\text{CO}_3\text{-COMe}_2$ affords its 7-*O*-allyl ether, m.p. 101°, converted by rearrangement at 210° into 7-hydroxy-4-methyl-8-allylcoumarin, m.p. 193—194°, hydrolysed by 20% aq. NaOH to 2-allylresorcinol, b.p. 155—160°/11 mm., reduced (H_2 -PdCl₄-EtOH) to 2-*n*-propylresorcinol, m.p. 106°. This by condensation with $\text{MeCN-ZnCl}_2\text{-HCl}$ in Et_2O and hydrolysis of the ketimine gives (V). (II) with $\text{RBr-K}_2\text{CO}_3$ in COMe_2 gives 4-*O*-allyl-3-allylresacetophenone, m.p. 34.5°, rearranged to 3:5-diallylresacetophenone (VI), m.p. 89—90°; similar allylation of (IV) gives 2-*O*-methyl-4-*O*-allyl-5-allylresacetophenone, m.p. 79°, rearranged and methylated to 3:5-diallylresacetophenone *Me*₂ ether, b.p. 178—179°/13 mm. (semicarbazone, m.p. 135—136°), identical with a specimen obtained by the action of $\text{Me}_2\text{SO}_4\text{-K}_2\text{CO}_3$ on (VI) in COMe_2 . Orientation of (V) establishes the constitution of 5-*n*-propylresacetophenone (Rosenmund *et al.*, A., 1933, 953).

J. W. B.

Condensation of butadiene with alkylbenzoquinones. C. K. CHUANG and C. T. HAN (Ber., 1935, 68, [B], 876—882).—Butadiene and toluquinone in C_6H_6 at 110 afford butadienetoluquinone (I), m.p.



79—81° (monoxime, m.p. 155° after darkening at 150°). The constitution of (I) is deduced from its isomerisation by a trace of HBr in AcOH to 2-methyl-5:8-dihydronaphtha-1:4-quinol (II), m.p. 170° after darkening at 165°, which is readily sol. in alkali, gives a diacetate (III), m.p. 103—104° [also obtained from (I) and boiling Ac_2O], but does not react with NH_2OH . Reduction of (I) with Zn dust and AcOH gives dihydrobutadienetoluquinone, m.p. 85—86° (dioxime, m.p. 235—237°). Catalytic hydrogenation (Pt-sponge) of (II) yields 2-methyl-5:6:7:8-tetrahydronaphtha-1:4-quinol, m.p. 163—165° [diacetate, m.p. 100—101°, also obtained by hydrogenation of (III)], oxidised by FeCl_3 to 2-methyl-5:6:7:8-tetrahydronaphtha-1:4-quinone, m.p. 50—52°. A similar condensation could not be effected with xyloquinone.

H. W.

Quinones. III. Preparation of α -naphthaquinone by hydrolysis of 4-nitroso- α -naphthol. C. L. TSENG and M. HU (J. Chinese Chem. Soc., 1935, 3, 60—66; cf. A., 1934, 1005).—Controlled acid hydrolysis (A., 1934, 1005) of 4:1-NQ- $\text{C}_{10}\text{H}_6\text{-OH}$ (modified prep.) gives α -naphthaquinone, m.p. 121.5—124.5° (lit. 126°, 125°, and 123—124°) in 22% yield.

F. N. W.

Enantiomorphous natural dyes. H. BROCKMANN and H. ROTH (Naturwiss., 1935, 23, 246).—Alkannin (I), m.p. 149° (from *Alkanna* roots), is lævo-

rotatory, whilst shikonin (II), m.p. 147° (from *Shikon* roots) (A., 1922, i, 946), is dextrorotatory and is the optical enantiomorph of (I). Treatment with MeOH-HCl converts (I) and (II) into the same optically-inactive OMe-derivative, m.p. 105° (cf. A., 1935, 217). On the basis of numerous degradation experiments the annexed structural formula is proposed for (I) and (II).

H. G. M.

Constitution and reactivity. X. Reaction kinetics of sulphonation by sulphuric acid containing water. K. LAUER and R. ODA (J. pr. Chem., 1935, [ii], 142, 258—272).—The velocity of sulphonation of anthraquinone (cf. A., 1933, 69) by 89.5—100% H_2SO_4 at temp. from 160° to 130° is determined, and velocity coeffs. (*k*) are calc. Graphs connecting *k* with concn. (*C_s*) of H_2SO_4 at various temp. (*T*) resemble those of v.p. against *C_s*. When *q* and α (cf. *loc. cit.*) are plotted against *T* or *C_s*, irregular graphs are obtained, but if $\log k$ is plotted against $1/T$, a series of straight lines for each val. of *C_s* results. From the tangents of the angles made by these with the $1/T$ axis, *q* and $\alpha \times 10^{-10}$ at varying *C_s* are calc. *q* falls from 37,900 at 89.5% to 35,500 at 93.3%, and to 27,500 at 100%; $\alpha \times 10^{-10}$ from 224 to 41.7 and to 1.0. From this it is deduced that in the sulphonation of anthraquinone there are two simultaneous reactions: attack by H_2SO_4 , and attack by SO_3 . The former will show greater *q* and α than the latter, and these therefore fall as *C_s* increases, since this brings an increasing decomp. of H_2SO_4 to give SO_3 . Factors of this kind may explain the different behaviour of H_2SO_4 and HNO_3 in aromatic substitution.

E. W. W.

Ring structure of thymidine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1935, 109, 623—630; cf. this vol., 610).—Triphenylmethylthymidine (detailed prep.) gives a 3-*p*-toluenesulphonate (I), $[\alpha]_D^{25} +29.5^\circ$ in COMe_2 , in which the *p*- $\text{C}_6\text{H}_4\text{Me-SO}_3$ is shown to be attached to a sec. C by the rate of reaction with NaI in COMe_2 to give the 3-iodide. Thymidine gives a mixture of toluenesulphonylthymidine chloride and di-*p*-toluenesulphonylthymidine, which reacts at about the same rate with NaI as does (I). Thymidine is thus a pyranoside, and the PO_3H_2 are attached to C3 and C6 of the deoxyribose of deoxyribosenucleic acid, for which a complete formula is proposed. If the PO_3H_2 of ribosenucleic acid are attached to C3 and C2, the readier hydrolysis of this acid by alkali and the loss of one PO_3H_2 (that on C2) by the action of acid are explained.

R. S. C.

Fulvic acid, a metabolic product of *Penicillium*.—See this vol., 786.

Constituents of *Nephromopsis stracheyi* f. *ectocarpisma*, Hue. I. M. ASANO and T. AZUMI (Ber., 1935, 68, [B], 995—997).—Prolonged maceration of the thalli with cold Et_2O gives *l*-usnic acid, m.p. 201—202°, $[\alpha]_D^{19} -510.8^\circ$, caperatic acid, m.p. 131—132°, $[\alpha]_D^{19} -21.7^\circ$ in CHCl_3 (Me_2 ester, m.p. 57—58°), *l*-lichesteric acid, m.p. 121—123°, $[\alpha]_D^{19} -31.9^\circ$ in CHCl_3 , *nephromopsis acid* (I), $\text{C}_{19}\text{H}_{34}\text{O}_4$, m.p. 137°, $[\alpha]_D^{19} -85.1^\circ$ in CHCl_3 (*Me* ester, m.p. 60—

61°), and an acid (II), $C_{19}H_{36}O_4$ or $C_{19}H_{32}O_4$, m.p. 106—107° (*Me* ester, m.p. 38—40°). When oxidised with $KMnO_4$ in $COMe_2$ (I) gives very small amounts of higher fatty acids. When treated with red P and HI (*d* 1.7) at 190—200° and subsequently with Zn and AcOH, it yields α -methyl- β -*n*-tetradecylsuccinic acid. (I) is therefore probably a stereoisomeride or diastereoisomeride of dihydroprotolichestic acid. (II) appears closely related to protolichestic acid.

Components of Iceland moss. V. Reduction of dihydroprotolichestic acid and of lichestic acid. M. ASANO and T. ASUMI (Ber., 1935, 68, [B], 991—994; cf. A., 1932, 931).—Although unsaturated, lichestic acid does not absorb H in presence of Pt or Pd. It is transformed by red P and HI (*d* 1.7) at 200° followed by de-iodination with Zn and AcOH into α -methyl-*n*-heptadecic (λ -isostearic) acid (I), b.p. about 170°/1 mm., m.p. 48—49° (*amide*, m.p. 104—104.5°; *anilide*, m.p. 86—86.5°; *p*-toluidide, m.p. 82—83°). Lichesterylic (γ -keto- α -methyl-*n*-heptadecic) acid and $N_2H_4 \cdot H_2O$ in boiling EtOH afford 4-methyl-6-*n*-tridecylpyridazinone,

$CO \left\langle \begin{array}{c} CHMe \cdot CH_2 \\ NH \end{array} \right\rangle N \cdot C_{13}H_{27}$, m.p. 66°, converted by NaOEt in EtOH at 170—180° into (I). *n*-Pentadecyl iodide and $CMcNa(CO_2Et)$, yield *Et*, methyl-*n*-pentadecylmalonate, b.p. 197—207°/2 mm., hydrolysed to methyl-*n*-pentadecylmalonic acid, m.p. 95.5—96.5°, decomp. about 175°, which passes into (I) when heated. *d*-Protolichestic acid,

$\begin{array}{c} O \cdot CH(C_{13}H_{27}) \\ CO - C(CH_3) \end{array} > CH \cdot CO_2H$, m.p. 104—106°, from European Iceland moss, is catalytically hydrogenated to dihydro-*d*-protolichestic acid, m.p. 104—106° (converted by CH_2N_2 into the *Me* ester, m.p. 51.5—52.5°), which, with red P and HI (*d* 1.7) at 190—200° affords α -methyl- β -*n*-tetradecylsuccinic acid, m.p. 133—135°. H. W.

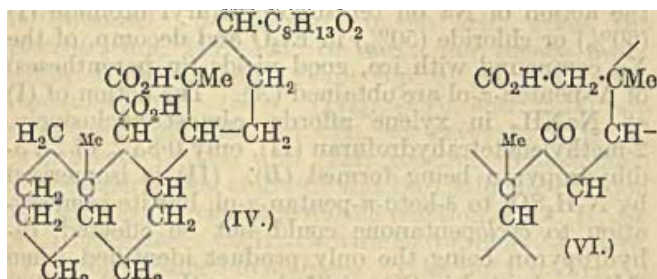
Bitter principles of the Colombo root. I. K. FEIST, P. RINTELEN, and E. KUNTZ (Annalen, 1935, 517, 119—133; cf. A., 1908, i, 100).—Columbin (I), m.p. 182° (decomp.); the m.p. is a poor criterion of homogeneity, is $C_{22}H_{44}O_7$. It contains 1 OH (Zerevitinov) (*acetate*, m.p. 228°), cannot be etherified with CH_2N_2 , and does not give a colour with $FeCl_3$. Probably 4 O are present in lactone groups. OMe and OEt are absent and $\cdot O_2CH_2$ is doubtful. $\cdot CHO$ or $\cdot CO$ could not be detected. Treatment of (I) with acids or alkalis leads to chasmanthin (II), $C_{20}H_{42}O_7$, m.p. 265° or m.p. 212°, $[\alpha] \pm 0^\circ$. The mixed m.p. of the two forms is intermediate between that of each. Both forms without change of composition pass into (II), m.p. 246°, which is mainly obtained from Colombo root (extraction described). Neither form reacts with CH_2N_2 or with reagents for $\cdot CO$ or $\cdot CHO$. Chasmanthin diacetate has m.p. 275°. Treatment of (II) with NaOH and Me_2SO_4 gives chasmanthin *Me*, ether (III), m.p. 271° [obtained similarly from (I) with unexplained loss of 2 C and 2 H], which does not give an Ac or Bz derivative and with the Zerevitinov method gives indecisive results. Catalytic hydrogenation of (I) causes absorption of 4 H_2 with loss of 2 C and 2 H, whereas that of (II)

leads to consumption of 3 H_2 , both operations giving hydrochasmanthic acid (III), $C_{20}H_{28}O_7$, m.p. 259°. (III) appears to be a lactonic acid. With CH_2N_2 it gives a *Me*, ester, m.p. 172°. OH of (II) appears intact in (IV), which with NaOH and Me_2SO_4 gives the *Me*, ether, m.p. 189°. When heated in vac. (I) gives (II) and a product (V), $C_{19}H_{22}O_4$, provisionally designated V-columbin (vacuum columbin). Under similar conditions, (II) does not pass into (V). Conversion of (I) into (V) is accompanied by loss of OH and of a lactone group, but a lactone ring persists. Attempted acetylation or methylation of (V) was fruitless. A connecting link between (I) and (V) appears to exist in decarboxycolumbin (VI), $C_{21}H_{24}O_5$, m.p. 143°, obtained by heating (I) at 192° or by prolonged boiling with H_2O . Treatment of (VI) with boiling Ac_2O affords iso-V-columbin, $C_{19}H_{22}O_4$, m.p. 208°, also obtained by treating (V) with alkali. Catalytic hydrogenation of (V) gives hydro-V-columbin, $C_{19}H_{30}O_4$, m.p. 186°, which is not isomerised by alkali. Ozonisation of (I) leads to the acid (VII), $C_{17}H_{20}O_8$, m.p. 263° (decomp.) (also +2 H_2O); the *Me*, m.p. 242°, and *Et*, m.p. 236.5°, esters are described. (VI) is oxidised with difficulty, but is transformed by fuming HNO_3 into an acid, m.p. 234° (*Me* ester, $C_{18}H_{21}O_8 \cdot NO_2$, m.p. 228°). Ozonisation of (III) gives a substance, m.p. 257°, probably identical with (VII). H. W.

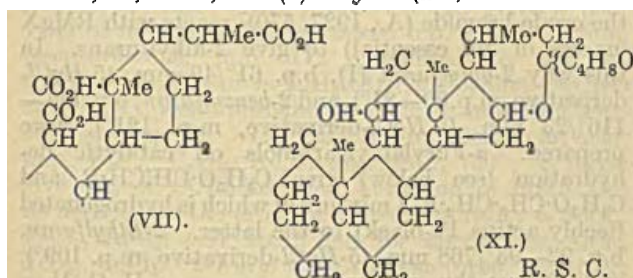
Slash-pine (Pinus caribaea, Morelet). I. Fatty constituents of the phloem. J. A. HALL and O. GISVOLD (J. Biol. Chem., 1935, 109, 585—595).—The ligroin (b.p. 60—70°) extract of the phloem of *P. caribaea* contains a sterol, $C_{29}H_{50}O$, m.p. 137—138°, $[\alpha]^{25} -23.4^\circ$ in $CHCl_3$ (*Ac* derivative, m.p. 126°, $[\alpha]^{25} -29.7^\circ$ in $CHCl_3$; digitonide) (also obtained from the seeds of *P. sabimiana*), an isocetyl alcohol, $C_{16}H_{34}O$, m.p. 74—75°, $[\alpha]^{25} +9.8^\circ$ in $CHCl_3$ (*acetate*, m.p. 64—65°) (OH not *tert.*), an unsaturated substance, $C_{30}H_{56}O_3$, b.p. 170—172°/0.005 mm., α 0° (*bromide*, m.p. 123—125°; no active H), and gives, when hydrolysed, a phytosterolin, $C_{29}H_{50}O$, m.p. 290° [giving with $HCl \cdot C_5H_{11} \cdot OH$ a sterol, $C_{29}H_{50}O$, m.p. 136—137°, $[\alpha]^{25} -24^\circ$, and a sugar (phenylosazone, m.p. 204°)], *n*- $C_5H_{11} \cdot CO_2H$, oleic, linoleic, palmitic, and behenic (*p*-bromophenacyl ester, m.p. 91—92°) acids. R. S. C.

Sarsasapogenin. II. J. C. E. SIMPSON and W. A. JACOBS (J. Biol. Chem., 1935, 109, 573—584; cf. A., 1934, 896).—Since sarsasapogenin (I), $C_{27}H_{44}O_3$ (lit. $C_{26}H_{42}O_3$), m.p. 199.5—200° (from EtOH), 194—195° (from EtOAc), gives Diels' hydrocarbon and ketones, $C_6H_{13} \cdot COMe$ (II) and $C_8H_{14}O_3$, it probably has a sterol structure. (I) or sarsasapogenone (III), m.p. 223—224° (modified prep.; slowly acetylated by cold AcOH), with NaOBr gives a mixture of acids, mostly a dibasic acid (IV), $C_{27}H_{42}O_6$, m.p. 280° (decomp.) (*Me*, m.p. 216—217°, and *Me H* ester [obtained from (V) by $O \cdot 1N \cdot NaOH$], m.p. 224—225°). (I) and $CrO_3 \cdot AcOH$ or (III) and $H_2SO_4 \cdot CrO_3$ give (IV) and a keto-acid (VI), $C_{27}H_{40}O_5$, m.p. 161—162° [*Na* salt; *Me* ester, m.p. 123—124°, catalytically hydrogenated (1 mol.) to an amorphous product; *Br*-derivative, m.p. 197° (decomp.); *oxide* (by BzO_2H), m.p. 191—192°; no colour with $C(NO_2)_4$]. Relative

rates of hydrolysis of the esters indicate the formulae shown for (VI) (but containing one ethylenic linking) and (IV). (IV) and HNO_3 (d 1.5) give a dibasic *lactonic acid* (VII) [also obtained in poor yield from (V)], $\text{C}_{22}\text{H}_{32}\text{O}_6$, m.p. 295° , which with CH_2N_2 gives



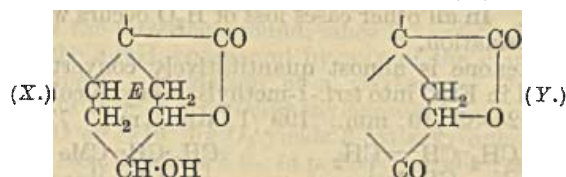
the Me_2 ester (VIII), $\text{C}_{25}\text{H}_{38}\text{O}_6$, m.p. $171-172^\circ$. The lactone group is readily opened by $0.1N$ -alkali. (VIII) is difficultly hydrolysed and with $0.5N$ - NaOH gives the Me H ester, m.p. $213-215^\circ$, reconverted into (VIII) by CH_2N_2 . Since (II) is a Me ketone, (VII) possibly has the structure shown, but with OH on C15, 16, or 17, and (I) may be (IX).



Oxidation of oleanolic and acetyloleanolic acid.

W. AUMULLER, W. SCHICKE, and E. WEDEKIND (Annalen, 1935, 517, 211-228).—Oleanolic acid (I) (modified prep.) and KMnO_4 in hot $\text{H}_2\text{SO}_4\text{-COMe}_2$ give oily acids and δ -hydroxyoleanono- γ -lactone (II), $\text{C}_{30}\text{H}_{46}\text{O}_4$, m.p. 304° [Ac derivative, m.p. 233° (oxime, m.p. 258°)], with either δ -hydroxyoleanolo- γ -lactone, $\text{C}_{30}\text{H}_{48}\text{O}_4$, m.p. $328-330^\circ$ [Ac_2 derivative (III), m.p. 292°], or δ -keto-oleanono- γ -lactone (IV), $\text{C}_{30}\text{H}_{44}\text{O}_4$, m.p. 286° (dioxime, an oil), identical with the diketone obtained (cf. Kitasato, A., 1934, 1223) from (I) and CrO_3 . (II) and CrO_3 in cold AcOH give (IV). Acetyloleanolic acid (V) and KMnO_4 give similarly acids and δ -hydroxyacetyloleanolo- γ -lactone, $\text{C}_{32}\text{H}_{50}\text{O}_5$, m.p. 337° [Ac derivative=(III)], oxidised by $\text{CrO}_3\text{-AcOH}$ to δ -ketoacetyloleanolo- γ -lactone (VI), $\text{C}_{32}\text{H}_{48}\text{O}_5$, m.p. 286° [oxime, m.p. 232° (decomp.)], also obtained (*loc. cit.*) from (V) and cold CrO_3 . (V) and CrO_3 at 80° give (VI), an acid, $\text{C}_{27}\text{H}_{40}\text{O}_7$ (Ac derivative, m.p. 300°) (A., 1933, 213), now termed acetylviscolic acid, and ketoacetyloleanolic acid, $\text{C}_{32}\text{H}_{50}\text{O}_5$, m.p. 284° (Me ester, m.p. 245°). (II) and CrO_3 at 80° give a small amount of a neutral substance, m.p. about 318° , and an acid, $\text{C}_{30}\text{H}_{44}\text{O}_7$, m.p. 303° (Me ester, m.p. 219° ; oxime, m.p. 190°). (IV) gives similarly a neutral substance, $\text{C}_{28}\text{H}_{38}\text{O}_6$, m.p. 315° , and viscolic acid, $\text{C}_{25}\text{H}_{36}\text{O}_6$, m.p. 303° (Me ester, m.p. 238°). Viscolic acid and alkaline KMnO_4 give an oily acid (Me_3 ester, $\text{C}_{28}\text{H}_{42}\text{O}_9$, m.p. 191°). The oxidations of (I) and (V) are interpreted as addition of 2 OH to the $\gamma\delta$ -ethylenic linking and

subsequent formation of γ -lactone, with or without subsequent oxidation of the new OH in ring E , and, sometimes, of the OH in ring A . Thus, e.g., (II) contains the grouping (X) and (IV) (Y).



R. S. C.

Constituents of *Datura stramonium*.—See this vol., 905.

Raman spectra of isomeric citronellols and rhodinols. Y. R. NAVES, G. RUS, and J. ALLARD (Compt. rend., 1935, 200, 1112-1114).—Physical characteristics of pure citronellol (from three sources) (I), rhodinol (II), citronellic acid (III) and citronellal (IV) are recorded. Raman spectra prove that l -(I), (I) (from the Et ester), and (III) are mixtures of $\text{CH}_3\text{CMc}[\text{CH}_2]_3\text{CHMe}\cdot\text{CH}_2\text{R}$ (A) and $\text{CMc}_2\text{CH}\cdot[\text{CH}_2]_2\text{CHMe}\cdot\text{CH}_2\text{R}$ (B) forms, (B) predominating, whilst (IV), (II), and (I) [obtained by reduction of (IV)] are found in (B) form only.

F. N. W.

Cardiostimulant effect of Japan camphor: a transformation product in the body, d -trans-7-aldehydroapocamphor, as the true active substance. K. TAMURA, G. KIHARA, and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1935, 11, 161-163).— α -apoCamphor-7-carboxylic acid was separated into the *trans*-, m.p. 250° , $[\alpha]_D +3.17^\circ$, and the *cis*-form, m.p. 273° , $[\alpha]_D -67.2^\circ$, and by reduction of its chlorides, d -trans-, m.p. $195-196^\circ$, and d -cis- κ -ketocamphor, m.p. 205° , have been obtained. The action of the *trans*-compound on the heart was $>$ that of the *cis*-compound, contrary to its action as a convulsant poison. d -trans- α -apoCamphor-7-carboxylic acid was isolated from the urine of a dog poisoned with camphor.

H. G. R.

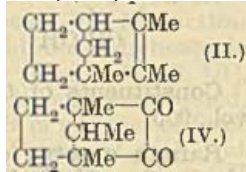
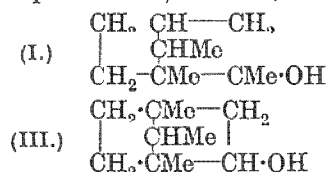
Two new transformation products of camphor in the animal organism. Y. ASAHINA and M. ISHIDATE (Ber., 1935, 68, [B], 947-953).—Tamura's discovery (see preceding abstract) is supported by the isolation of *trans*- π -apoCamphor-7-carboxylic acid from the urine of dogs to which it has been administered. Oxidation of campherol with CrO_3 and KMnO_4 and distillation of the neutral product with steam yields α - (I), m.p. $47-48^\circ$ (semicarbazone, m.p. $235-236^\circ$), and β - (II), m.p. $42-45^\circ$ (semicarbazone, m.p. $220-223^\circ$), -santenone. (I) is oxidised to *cis*-allosantenic acid, m.p. $151-152^\circ$. *trans*- π -Hydroxycamphor, m.p. 233° , is converted into the corresponding hydrazone, m.p. about 100° (acetate, m.p. 217°), oxidised by HgO in presence of KOH to inactive *teresantalol*, b.p. $97-98^\circ/10\text{ mm.}$, m.p. 118° ; this with 10% H_2SO_4 at 100° gives inactive apocamphenecarbinol, m.p. about 146° , oxidised by CrO_3 to (I) and (II), thus probably indicating the mode of production of the latter in the organism.

H. W.

Wagner transformation with tertiary alcohols. *tert*-2-Methylsantenol. G. KOMPPA and G. A. NYMAN (Annalen, 1935, 517, 105-119).—Wagner

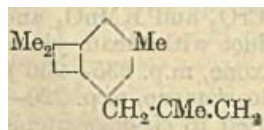
transformation accompanies dehydration of *tert.*-alcohols of the pentosean system only when both bridge-C7 and C1 lying between that to which OH is attached and the bridge C are loaded with substituents. In all other cases loss of H₂O occurs without transformation.

Santenone is almost quantitatively converted by MgMeI in Et₂O into *tert.*-1-methylsantenyl alcohol (I), b.p. 82—83°/10 mm., 199°/1 atm., m.p. 77—79°



(*phenylurethane*, m.p. 134—135°). Treatment of (I) with KHSO₄ at 170° yields 1-methylsantene (II), b.p. 151—152°, ozonised in AcOH at a diketone, b.p. 125—127°/14 mm. [*disemicarbazone*, C₁₂H₂₀O₂N₆, m.p. 230—231.5° (decomp.)], which reddens fuchsin-H₂SO₃, gives CHBr₃ with OBr', and does not give appreciable amounts of acid products when oxidised with Ag₂O. (II) is transformed by 50% H₂SO₄ in AcOH at 50—55° followed by hydrolysis into *sec.*-4-methylsantenol (III), b.p. 198—200°, m.p. 33—34.5° (*acetate*, b.p. 92—93°/10 mm.; *phenylurethane*, m.p. 81—82°). Cautious oxidation of (III) with CrO₃ affords 4-methylsantenone (IV), b.p. 199—199.5° (*semicarbazone*, m.p. 217—218°; *hydrazone*, b.p. 86—87°/1.37 mm., and its *Ac* derivative, m.p. 153—154°). (IV) is converted by a large excess of SeO₂ in boiling EtOH into 4-methylsantenone-quinone (V), m.p. 53—54.5° (*quinoxaline* derivative, m.p. 83.5—84.5°). Oxidation of (III) with alkaline KMnO₄ leads to 1:2:3-trimethylcyclopentane-1:3-dicarboxylic (*mesantenic*) acid, m.p. 239—240° (*anhydride*, m.p. 95—96°; corresponding *anilic*, m.p. 180—181°, and *toluidic*, m.p. 205—206°, *acid*). The occurrence of a Wagner transformation during the hydration of (II) is also established as follows. Catalytic hydrogenation (*Skita*) of (II) gives 1-methylidihydrosantene (VI), b.p. 159—160°. If, however, 4-methylsantenol is transformed into the corresponding *chloride*, b.p. 87°/10 mm., m.p. 73—75°, which is reduced by Na and EtOH, 4-methylsantenone, b.p. 152—154°, results, and differs from (VI). H. W.

Constitution of caryophyllene. L. RUZICKA



(*Chem. and Ind.*, 1935, 509).—A review of the products of the degradation of caryophyllene leads to the annexed constitution.

H. W.

Ledum camphor and the constitution of the ledenes. G. KOMPPA (*Suomen Kem.*, 1935, 8, B, 19—20).—Ledol (I), C₁₅H₂₆O, a *tert.*-alcohol, is dehydrated (KHSO₄) to ledene (II), and with Pd-H₂ gives dihydroledene, which shows that it is saturated. Dehydrogenation of (II) with Se gives cadalene, and with O₃ it affords CH₂O [which shows that in (I), OH and Me are linked to the same C] and a ketone which decomposes when distilled in a high vac. J. L. D.

Essential oil of *Calythrix tetragona*.—See B., 1935, 573.

Stability of the hydrofuran ring. III. Mechanism of the rearrangements accompanying the rupture of the ring in tetrahydrofurfuryl derivatives. Preparation of Δ⁸-penten-α-ol. R. PAUL (*Bull. Soc. chim.*, 1935, [v], 2, 745—754).—By the action of Na on tetrahydrofurfuryl bromide (I) (60%) or chloride (50%) in Et₂O and decomp. of the Na compound with ice, good yields (in parentheses) of Δ⁸-penten-α-ol are obtained (A). The action of (I) on NaNH₂ in xylene affords, almost exclusively, 2-methylenetetrahydrofuran (II), only 0.83% of 2:3-dihydropyran being formed (B). (II) is isomerised by N-H₂SO₄ to δ-keto-*n*-pentan-α-ol, but its isomerisation to cyclopentanone could not be effected, dihydropyran being the only product identified when (II) was heated in CO₂ at 350°, or with Al₂O₃ at 380° in N₂. The mechanism of these reactions is discussed on the basis of the electronic theory of Prévost *et al.* (A., 1931, 670), according as to whether X in C₄H₇O·CH₂X is a positive (A) or negative (B) group. J. W. B.

Preparation of α-alkylfurans. R. PAUL (*Compt. rend.*, 1935, 200, 1481—1483).—Furfuryl chloride [or the crude bromide (A., 1927, 570)] reacts with RMgX (excess of Mg essential) to give 2-alkylfurans. In this way 2-butylfuran (I), b.p. 61°/49 mm. (5-HgCl-derivative, m.p. 80—81°), and 2-benzylfuran, b.p. 114—116°/23 mm. (5-HgCl-derivative, m.p. 121°), were prepared. α-Furylalkylcarbinols on catalytic dehydration (see below) give C₄H₃O·CH·CH·R and C₄H₃O·CH₂·CH₂·R, a mixture of which is hydrogenated (feebly active Pt-black) to the latter. 2-Ethylfuran, b.p. 92—93°/768 mm. (5-HgCl-derivative, m.p. 109°), and (I) were thus prepared. H. G. M.

Orientation in the furan series. IX. Friedel-Crafts reaction with 2-furfuraldehyde. H. GILMAN, N. O. CALLOWAY, and R. R. BURTNER. X. **Anomalous Friedel-Crafts reactions.** H. GILMAN and R. R. BURTNER (*J. Amer. Chem. Soc.*, 1935, 57, 906—907, 908—912; cf. A., 1934, 300).—IX. Furfuraldehyde (I) and Pr⁶Cl-AlCl₃ give 2:4-CHO·C₄H₃O·Pr⁶ (II), since oxidation and bromination gives 5-bromo-4-isopropyl-2-furoic acid, m.p. 103—104°, also obtained by hydrolysis of its *Et* ester, b.p. 141—144°/17 mm. (from *Et* 4-bromofuroate, Pr⁶Cl, and AlCl₃), and by oxidation (Ag₂O) of 5-bromo-4-isopropyl-2-furfuraldehyde (synthesised from 5-bromofurfuraldehyde and Pr⁶Cl). When the acid is treated successively with Br (0.65 mol.) at 125—140°, hot H₂O, alkaline Ag₂O, and K₃Fe(CN)₆, it yields 5-bromofuran-2:3-dicarboxylic acid and thence (by HgCl₂) 5-bromo-3-furoic acid. 4-*iso*Propyl-2-furoic acid with Cu-bronze in quinoline at 220—240° gives 3-isopropylfuran, b.p. 111—112° (2-HgCl-derivative, m.p. 90°), or by replacement of the CO₂H 4-isopropylfuran-2-mercurichloride, m.p. 119—120°.

X. (I) with BuⁿCl, Bu⁶Cl, or BuⁿCl gives (AlCl₃) 2:5-CHO·C₄H₃O·Buⁿ (III), b.p. 93—95°/13 mm. (*semicarbazone*, m.p. 205°), oxidised to the known acid (IV) (*amide*, m.p. 121°), which was converted into 2-*tert.*-butylfuran (5-HgCl-derivative, also obtained directly from the acid by replacement of the CO₂H), and obtained also from (IV) by way of the acid chloride. *Et* 5-bromo-2-furoate with BuⁿCl (AlCl₃-CS₂) gives

Et 5-bromo-4-tert.-butyl-2-furoate (V), b.p. 148—152°/13 mm. (3% yield), hydrolysed (KOH-EtOH) to the acid, m.p. 164°, which is reduced by Zn dust and aq. NH_3 to 4-tert.-butyl-2-furoic acid, m.p. 89°, whence, by way of the chloride, 4-tert.-butyl-2-furfuraldehyde (VI), b.p. 93—95°/13 mm. (semicarbazone, m.p. 187°), is obtained. *n*-isoPropyl-2-furoic acid gives the chloride, b.p. 117—121°/16 mm., and thence 5-iso-propyl-2-furfuraldehyde (VII), b.p. 91°/11 mm. (semicarbazone, m.p. 159°). (III), (VI), and (VII) are unaffected by AlCl_3 in CS_2 , so that the differing orientation of (II) and (III) remains unexplained. The isomerisation of $\text{Bu}^\alpha\text{Cl}$ and Bu^βCl during reaction is paralleled by cleavage during reaction of $n\text{-C}_5\text{H}_{11}\text{Cl}$, $n\text{-C}_6\text{H}_{13}\text{Cl}$, and $n\text{-C}_{18}\text{H}_{37}\text{Br}$ with *Et* 5-bromo-2-furoate, (V) being obtained in all cases. Like BuCl , $n\text{-C}_6\text{H}_{11}\text{Cl}$ with (I) affords 5-(? tert.)amyl-2-furfuraldehyde (poor yield), b.p. 95—98°/15 mm. (semicarbazone, m.p. 196°), oxidised to the oily acid (α -naphthalide, m.p. 201°). Furan is more aromatic than C_6H_6 in being more readily alkylated, but $p\text{-OMe-C}_6\text{H}_4\text{-CHO}$ and Pr^βCl with AlCl_3 in CS_2 give a 22.4% yield of 4-methoxy-3-isopropylbenzaldehyde, b.p. 146—150°/16 mm. (oxidised to the known acid), and PhCHO gives a poor yield of *m*-isopropylbenzaldehyde, b.p. 95—97°/2 mm. [semicarbazone, m.p. 172°; oxidised to oily $m\text{-C}_6\text{H}_4\text{Pr}^\beta\text{-CO}_2\text{H}$ and $m\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$], whilst PhCHO and $\text{Bu}^\alpha\text{Cl}$ yield probably a little *m*-tert.-butylbenzaldehyde, b.p. 140—150°/13 mm., oxidised to an acid, m.p. 123°. C_6H_6 , Ac_2O , and SnCl_4 (60°; 8 days) give 4% of COPhMe . For acylation of furan and its derivatives the order of decreasing utility is SnCl_4 , FeCl_3 , AlCl_3 , and TiCl_4 , but for alkylations AlCl_3 , FeCl_3 , SnCl_4 . 2-Furyl CH_2Cl ketone (prep. by AlCl_3 ; 21%) has b.p. 127—129°/27 mm. R. S. C.

Friedel-Crafts reaction with nitro-compounds.

H. GILMAN, R. R. BURTNER, N. O. CALLOWAY, and J. A. V. TURCK, jun. (J. Amer. Chem. Soc., 1935, 57, 907—908).— Me_2 furan-2 : 3-dicarboxylate, Ac_2O , and SnCl_4 in C_6H_6 give *Me*₂ 2-acetofuran-3 : 4-dicarboxylate, m.p. 108°. In the following Friedel-Crafts reactions NO_2 was replaced by Cl or reduced, or no reaction occurred. 2-Nitrofuran and EtCOCl give 5-chloro-2-propionylfuran, m.p. 55°, but *Et* 5-nitro-2-furoate does not react. PhNO_2 with Bu^βBr or Pr^βBr and AlCl_3 at room temp. (30 days) give *o*- and *p*- $\text{C}_6\text{H}_4\text{Cl-NH}_2$ (more rapidly with Bu^βBr , if heated), but MeBr and EtBr do not react. R. S. C.

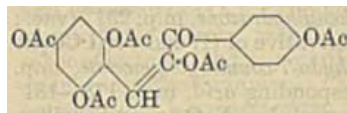
Oxidation and reduction phenomena observed in catalytic dehydration of furylalkylcarbinols. R. PAUL (Compt. rend., 1935, 200, 1118—1120).—Furfuryl alcohol heated (390°) with Al_2O_3 in N_2 yields 2-methylfuran and furfuraldehyde; similarly 2-furylmethylcarbinol gives 2-ethyl- and 2-vinyl-furan and 2-furyl *Me* ketone, and 2-furyl-*n*-propylcarbinol gives 2-*n*-propylfuran, 2-furyl Pr^α ketone, and α -2-furyl- Δ^2 -butene. F. N. W.

Dibenzofuran [diphenylene oxide]. IV. Orientation and relative aromaticities of the 2-, 3-, and 4-dibenzofuryl radicals. H. GILMAN, W. G. BYWATER, and P. T. PARKER (J. Amer. Chem. Soc., 1935, 57, 885—887; cf. this vol., 91).—The NO_2 -derivative, m.p. 100°, formed as by-product from

diphenylene oxide (I) and fuming HNO_3 in AcOH , is a mixture, containing the 2- NO_2 -compound, since reduction and acetylation gives some 2-NHAc-compound. The hydroxydiphenylene oxide (II), m.p. 138—139°, formed from resorcinol and WO_3 at 500—550° is the 3-OH-compound, since it is also obtained from the 3- NH_2 -compound by way of the diazonium borofluoride. Oxidation of a mixture of Grignard reagents from 2-bromodiphenylene oxide and $\text{Bu}^\alpha\text{Br}$ in Et_2O at -10° by O_2 yields 2-hydroxydiphenylene oxide, m.p. 134°. *Pb* 2-, m.p. 158.5—159.5°, 3-, m.p. 125—126°, and 4-benzofuryltriphenyl, m.p. 99—100°, with HCl give (I). (I) is thus more aromatic than C_6H_6 . By analogy the $(\text{OH})_2$ -derivative formed with (II) is probably the 3 : 7-compound. 4-Acetamidodiphenylene oxide and Br give the 1-Br-4-NHAc-compound, whence the 1-Br-compound, m.p. 67°, is obtained. 1-Substitution also occurs with 4-hydroxydiphenylene oxide and Br or PhN_2Cl , but is rare. 1 : 2 : 3 : 4-Tetrahydrodiphenylene oxide is sulphonated in the 7-position. R. S. C.

Tannins and similar compounds. XXVIII. Transformations of anthocyanidins and catechins. K. FREUDENBERG, KARIMULLAH, and G. STEINBRUNN (Annalen, 1935, 518, 37—61; cf. A., 1934, 779).—Reasons are advanced for considering the natural tannins to be formed by autocondensation of catechins. Doubts are expressed with regard to Russell's syntheses (A., 1934, 416, 1107, 1362) of definite flavanols and pinacols and on the identity of his amorphous, synthetic products with individual, natural tannins.

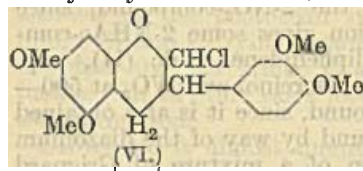
According to conditions pelargonidin chloride (I) is transformed by $\text{C}_5\text{H}_5\text{N}$ and Ac_2O into monomeric ψ -pelargonidin penta-acetates, m.p. 146° (II), m.p. 165° (III), or m.p. 168° (IV), or into a trimeric penta-acetate,



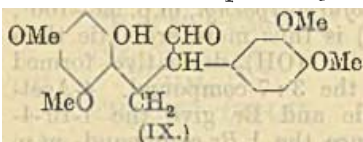
m.p. 224° (decomp.), which cannot be hydrogenated and does not afford (I) when treated with HCl . (II) and (III) are dimorphous forms, of which (III) is the more stable. (II), (III), and (IV) give the same H_2 -derivative, m.p. 148° (PtO_2 in AcOH). Probably (II) and (IV) are *cis-trans* isomerides (cf. A). Fisetinidin chloride (V) affords two ψ -fisetinidin penta-acetates, $\text{C}_{25}\text{H}_{22}\text{O}_{11}$, m.p. 107° and 149°, respectively, which give amorphous products when hydrogenated and are re-converted into (V) by AcOH-HCl . β -Resorcaldehyde and ω : 4-diacetoxyacetophenone are converted by HCl in EtOAc into 4' : 3 : 7-trihydroxyflavylum chloride, which passes when treated with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ into 4' : 3 : 2(?) : 7-tetra-acetoxyflavene, m.p. 135—136°, which yields only amorphous products when hydrogenated. Cyanidin chloride yields ψ -cyanidin hexa-acetate, m.p. 156° (also obtained from natural cyanidin), which yields two H_2 -derivatives, m.p. 151° and 173°, respectively, and possibly a third isomeride, m.p. 145—148°.

The optically active chloride (VI) is transformed by MeOH at room temp. into pentamethyl-d-isocatechin (VII), m.p. 78.5°, $[\alpha]_D^{25} + 132.5^\circ$ in CCl_4 , in good yield. Pentamethyl-dl-isocatechin has m.p. 125°. Tetra-

methylethyl-*d*-isocatechin, m.p. 123°, $[\alpha]_{578}^{17} +123^\circ$ in $C_2H_2Cl_4$, and the corresponding *dl*-*comp*ound, m.p. 116°, are described. Acetyl-tetramethyl-*d*-isocatechin (VIII), from (VI) and KOAc in



AcOH or from (VI) and AcOH in C_6H_5N , has m.p. 151°, $[\alpha]_{578}^{7.5} +202^\circ$. (VIII) is converted into (VII) by HCl-MeOH at room temp. Acetyltetramethyl-*dl*-isocatechin,



m.p. 168°, gives a Br_1 -derivative, m.p. 149°. (VI) with NaOAc in boiling $COMe_2-H_2O$ or with $CaCO_3$ in $COMe_2-H_2O$ at room temp. gives the aldehyde (IX), m.p. 136.5°, $[\alpha]_{578}^{37.5} +57.3^\circ$ in CCl_4 (oxime, m.p. 168°; acetate, m.p. 99.5°, $[\alpha]_{578}^{20} -125^\circ$ in $C_2H_2Cl_4$), which does not give the colour reactions for CHO and in which phenolic OH cannot be detected by $FeCl_3-EtOH$. The corresponding optically inactive aldehyde, m.p. 127°, its monoacetate, m.p. 110°, and (?) triacetate, m.p. 167°, are described.

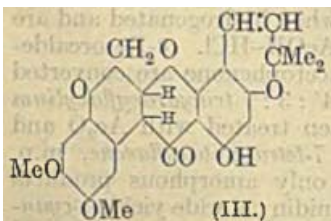
H. W.

Chemistry of the anthocyanins. R. ROBINSON (Nature, 1935, 135, 732—736).—A summary.

L. S. T.

Natural coumarins. XIV. New synthesis of angelicin (from *Angelica archangelica*, L.). E. SPATH and M. PAILER (Ber., 1935, 68, [B], 940—943; cf. A., 1934, 779).—Umbelliferone does not react with HCN or KOH- $CHCl_3$ but is converted by successive treatments with $(CH_2)_8N_4$ in AcOH at 100° and boiling HCl into umbelliferone-8-aldehyde (I), m.p. 189—191° [phenylhydrazone, m.p. 231° (vac.; decomp.)]. The Na derivative of (I) and CH_3I-CO_2Et at 100° give *Et* 8-aldehydo-7-coumaryloxyacetate, m.p. 157° (vac.); the corresponding acid, m.p. 178—181° (decomp.), is transformed by NaOAc and boiling Ac_2O into angelicin, m.p. 138—139.5°. H. W.

Synthesis of rotenone and its derivatives. V. Constitution of apotoxocarol. R. G. HEYES and A. ROBERTSON (J.C.S., 1935, 681—684).—In an attempted synthesis of dehydroapotoxocarol (I), Me 4:5-dimethoxy-2-cyanomethylphenoxyacetate and phloroglucinol condense ($ZnCl_2$) to 4:5-dimethoxyphenoxyacetic acid-2-phloroacetophenone (II) (+ $2H_2O$), m.p. 215° (decomp.), and phloroglucinol Me₂ ether similarly affords -2-(2':4'-O - dimethyl)phloroacetophenone, m.p. 196—197°, neither compound undergoing cyclisation. (I) forms a diacetate, m.p. 202°, and with NaOH is



converted into (II). In the formation of apotoxocarol by hydrolytic fission (NaOH) of toxicarol (III), $COMe_2$ is formed; this is considered to arise from a 2:2-dimethyl- Δ^3 -chromen residue in (III), and reasons for the formula (III) are advanced.

F. R. S.

Constitution of pyrroline. A. TREIBS and D. DINELLI (Annalen, 1935, 517, 170—172).—Pyrroline

(I) is $NH<\begin{matrix} CH_2\cdot CH \\ CH_2\cdot CH \end{matrix}$ since ozonisation of the hydrochloride in H_2O and oxidation of the product with H_2O_2 leads to $NH(CH_2\cdot CO_2H)_2$. Ozonisation of (I) in CCl_4 gives ill-defined results. Treatment of (I) with CS_2 in CCl_4 yields the dithiocarbamate, $C_6H_{14}N_2S_2$, m.p. 201° (sealed tube). (I) and 1:2:4- $C_6H_3Br(NO_2)_2$ yield 1-2':4'-dinitrophenylpyrroline, m.p. 124.5°, well adapted to the identification of (I). H. W.

Tschitschibabin condensation of butaldehyde and ammonia. E. BERGMANN (Chem. and Ind., 1935, 534—535).—Correction of misprinted formulae given by Haskelberg (this vol., 628). E. W. W.

Iridium dipyridinobromo-compounds. (MME.) M. DELÉPINE-TARD (Compt. rend., 1935, 200, 1477—1478).— C_5H_5N and K_3IrBr_6 afford pyridinium dipyridinoiriditetrabromide, $[Ir(C_5H_5N)_2Br_4](C_5H_5N)H$ (I), and the salt, $[Ir(C_5H_5N)_2Br_4]K\cdot H_2O$ (II). (I) is more readily obtained by heating C_5H_5N with M_3IrBr_6 (cf. A., 1923, i, 944), and with aq. NH_3 and NH_4Br affords the salt $[Ir(C_5H_5N)_2Br_4]NH_4\cdot H_2O$ (III), which does not lose H_2O at 100°. (III) is converted into (II) by treatment with KOH and KBr: the corresponding Rb and Cs salts (each + H_2O) can similarly be obtained, whilst the Ag and Tl salts are obtained from (III) by double decomp. with $AgNO_3$ -aq. NH_3 and Tl_2SO_4 , respectively. The salts of the alkali metals are oxidised (HNO_3 , Cl_2 - or $Br-H_2O$) forming compounds of the quadrivalent Ir base, $Ir^{IV}(C_5H_5N)_2Br_4$, reconverted into the tervalent condition by reducing agents. When an aq. solution of (III) is refluxed for 6 hr. the aquo-compound, $Ir(H_2O)(C_5H_5N)_2Br_3\cdot 3H_2O$ (IV), is obtained. This is a ψ -acid, dissolves in alkalis and aq. NH_3 , and is re-pptd. by addition of acids. When the NH_3 from a solution of (IV), $AgNO_3$, and NH_3 is allowed to evaporate, the compound, $[Ir(C_5H_5N)_2(OH)Br_3]_3H_2Ag$, is obtained, whilst from HNO_3 medium the salt $[Ir(C_5H_5N)_2Br_3(NO_3)]Ag\cdot 3H_2O$, is obtained. This series of Br-derivatives is similar to that of the corresponding Cl-derivatives of Ir, and is considered to be the *trans*-dipyridino-series. On no occasion have two isomeric derivatives been isolated. H. G. M.

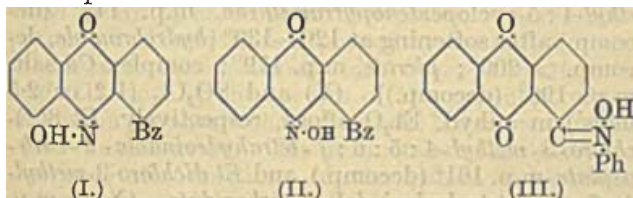
Optically active silver complexes. F. HEIN and H. REGLER (Naturwiss., 1935, 23, 320).—The variations in $[\alpha]$ (in $CHCl_3-C_5H_5N$) of fractions of α -bromod-camphor- π -sulphonate of the Ag complex with 8-hydroxyquinoline, $[Ag(C_9H_6N\cdot OH)_2]$, indicate the presence of optically active stereoisomerides.

F. O. H.

Polymembered heterocyclic compounds. VII. Preparation of 7- to 18-membered saturated and unsaturated cyclic imines by reduction of thioisoximes. L. RUZICKA, M. HURBIN, M. W. GOLDBERG, and M. FURTER (Helv. Chim. Acta, 1935, 18, 659—667; cf. A., 1934, 82).—cycloHexanoneisoxime is converted by P_2S_5 in xylene at 100° into cyclohexanonethioisoxime, b.p. 123—128°/0.1 mm., m.p. 107—109°, which is not readily reduced by Zn dust and alkali but is converted electrolytically into hexamethyleneimine. cycloHeptanonethioisoxime has m.p. 82—83°. cycloPentadecanone is transformed by HN_3 into cyclopentadecanoneisoxime, m.p. 133°, whence the thioisoxime and pentadecamethyleneimine,

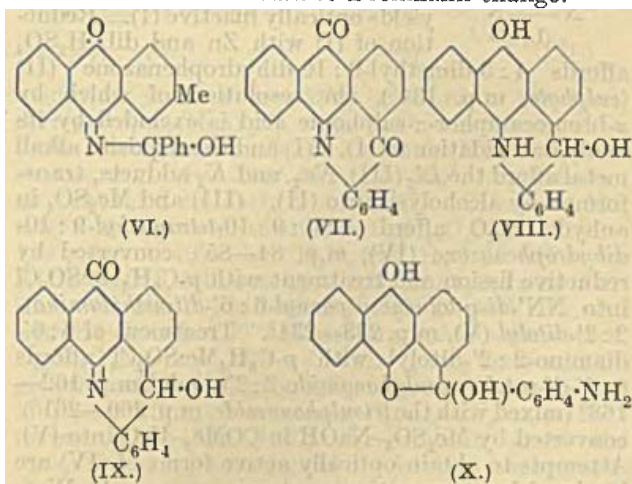
b.p. 112—115°/0.2 mm., m.p. 50—51°. *cycloheptadecanethioisooxime*, m.p. 110—111°, is electrolytically reduced to *heptadecamethyleneimine*, b.p. 142—147°/0.5 mm., m.p. 64—66° (tartrate; acetate, m.p. about 68°). Norcivetone is transformed successively into the isooxime, m.p. 112—113°, *thioisooxime*, m.p. 93—94°, and Δ^7 (or/and Δ^8)-*dehydrohexadecamethyleneimine*, b.p. 120—121°/0.15 mm., m.p. 36—37° (*picrolonate*, m.p. 199—200°). Civetone is converted by HN_3 and HCl in C_6H_6 into *civetoneisooxime*, m.p. 121—122°, or by excess of HN_3 into the *tetrazole*, $\text{CH}[\text{CH}_2]_7\text{C}\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot\text{N}$, m.p. 90—91°. *Civetoneisothioisooxime*, b.p. 210—220°/0.15 mm., m.p. 119—120°, is reduced by Na and AcOH in EtOH to Δ^2 -*dehydroheptadecamethyleneimine*, b.p. about 128°/0.1 mm., m.p. 28—29° (*picrolonate*, m.p. 196—197°; *succinate*, m.p. 120°). Compounds with poly-membered ring systems are characterised by a more or less pronounced odour of musk, which is purest with the lactones, followed by the ketones and other compounds. The abs. val. of d of cyclic imines is closer to that of the hydrocarbons than of the ketones, but variation of d from member to member of a series is most similar with imines and ketones. H. W.

Isomerism of oximes of 1-aroylantraquinones and benzoylenemorphanthridone. V. R. SCHOLL and E. J. MULLER [with E. STIX] (Ber., 1935, 68, [B], 801—814).—Treatment of 1-benzoylantraquinone with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and Na_2CO_3 in boiling EtOH affords mainly α -(anti)- (I) accompanied by small and varying amounts of β -(syn)-1-benzoylantraquinoneoxime (II), decomp. about 210° after softening and γ -(anti)-*Ph* 1-antraquinonyl ketoxime (III), decomp. about 218°.



(II) is isomerised to (I) rapidly in boiling PhNO_2 , more slowly in boiling AcOH . In contrast to (I) and (III), it cannot be etherified by $\text{HCl}\text{--}\text{EtOH}$. (I) and (II) are readily converted by boiling $\text{HCl}\text{--}\text{PhNO}_2$ into benzoylenemorphanthridone (IV). These facts and the similarity of (II) to 1-benzoyl-2-methyl-antraquinoneoxime (V) enable the *syn* structure to be assigned to (II). (III) cannot be converted into (IV). It is transformed into a red vat by $\text{Na}_2\text{S}_2\text{O}_4\text{--}\text{NaOH}$, from which it is regenerated by air. It readily suffers the Beckmann transformation, giving anthraquinone-1-carboxyanilide, and hence has configuration (III). (V) is not etherified by 2% $\text{HCl}\text{--}\text{EtOH}$, whilst with 8% $\text{HCl}\text{--}\text{EtOH}$ at 150° it is largely de-oximated to 1-benzoyl-2-methylantraquinone. (V) is transformed by boiling $\text{HCl}\text{--}\text{PhNO}_2$, possibly owing to liberated NH_2OH , into 2-hydroxy-2-phenyl-3-methyl-6 : 7-benzoylene- $\beta\beta'$ -benzo-2-pyrrolene (VI), m.p. 266—267°, the constitution of which follows from its ready reduction to 2-phenyl-3-methyl-6 : 7-benzoylene- $\beta\beta'$ -benzopyrrole. Anthraquinone-1-carb-

oxyl chloride is converted by AlCl_3 and 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$ in boiling CS_2 into *mesityl anthraquinonyl ketone*, m.p. 167°, the *oxime*, m.p. 202—203°, of which is closely similar to (I) in prep. and reactions. It is transformed by $\text{HCl}\text{--}\text{EtOH}$ into *Et anthraquinone-1-carboxylate*, reaction being probably due to primary de-oximation rather than to Beckmann change.

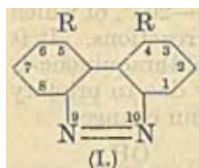


Benzoylenemorphanthridone (VII) is converted by boiling $\text{KOH}\text{--}\text{EtOH}$ into two H-compounds giving red and blue solutions, respectively, in alkali which can be separated from one another by means of their differing behaviour towards air. The former, also obtained from (VII) by the protracted action of $\text{Na}_2\text{S}_2\text{O}_4$ in boiling NaOH , is rapidly transformed by air into 9-hydroxy-5 : 10-benzoylenemorphanthridine (VIII), decomp. 254—257°, readily oxidised by CrO_3 to (VII), and is therefore (IX). The latter, incipient decomp. about 235°, closely resembles the anthraquinol-1-carboxylactones and is regarded as the *lactol* of 1-o-aminobenzoylantraquinol (X). *O-Acetyl-9-anilino-anthran-10-ol-1-carboxylactam*, m.p. 251—252° after softening, is incidentally described. H. W.

Action of hydrazine on cyclic ureides (parabanic acid). R. FOSSE, P. E. THOMAS, and P. DE GRAEVE (Compt. rend., 1935, 200, 1260—1264).—Parabanic acid (I) in aq. solution with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and $\text{NHPh}\cdot\text{NH}_2$ gives, respectively, *oxalurhydrazide* (II), m.p. 198° (decomp.), and *oxalurphenylhydrazide* (cf. J.C.S., 1888, 53, 556). (I) and (II) with xanthhydrol in AcOH give *dixanthylparabanic acid*, m.p. 214°, and *xanthylloxalurhydrazide*, cryst. (II) and $\text{R}\cdot\text{CHO}$ give the *oxalurhydrazones* of PhCHO , m.p. 215° (decomp.), CH_2O , m.p. 212° (decomp.), and MeCHO , m.p. 224° (darkens at 220°). F. R. G.

Configuration of 4 : 5-disubstituted phenanthrene and phenazone derivatives. G. WITTIG and O. STICHNOTH (Ber., 1935, 68, [B], 928—935; cf. A., 1933, 944).—With the object of elucidating the steric relationships of phenanthrene derivatives, 4 : 5-disubstituted derivatives of phenazone have been investigated, since they are more readily accessible and probably similarly constructed. 1 : 2 : 3- $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NO}_2$ (improved prep.) is converted by Cu powder at 180—190° and finally at 225—235° into 6 : 6'-dinitro-2 : 2'-ditolyl, m.p. 107—108° (yield 81%), which is electro-

lytically reduced to 4:5-dimethylphenazone [(I) R=Me], m.p. 112—113°. The salts of (I) with optically active OH·CHPh·CO₂H, lactic or tartaric acid are too unstable to permit resolution, whereas the α-bromocamphor-π-sulphonate, m.p. 164—167°, [α]_D +52.0° in MeOH, yields optically inactive (I). Reduction of (I) with Zn and dil. H₂SO₄



affords 4:5-dimethyl-9:10-dihydrophenazone (II) (sulphate, m.p. 134°), the resolution of which by α-bromocamphor-π-sulphonic acid is excluded by its ready autoxidation to (I). (I) and the requisite alkali metal afford the Li₂ (III), Na₂, and K₂ adducts, transformed by alcoholysis into (II). (III) and Me₂SO₄ in anhyd. Et₂O afford 4:5:9:10-tetramethyl-9:10-dihydrophenazone (IV), m.p. 84—85°, converted by reductive fission and treatment with p-C₆H₄Me·SO₂Cl into NN'-di-p-toluenesulphonyl-6:6'-di(methylamino)-2:2'-ditolyl (V), m.p. 233—234°. Treatment of 6:6'-diamino-2:2'-ditolyl with p-C₆H₄Me·SO₂Cl affords 6:6'-di-p-toluenesulphonamido-2:2'-ditolyl, m.p. 162—163° (mixed with the trisulphonamide, m.p. 260—261°), converted by Me₂SO₄-NaOH in COMe₂-H₂O into (V). Attempts to obtain optically active forms of (IV) are hindered by its sensitiveness to air. H. W.

Pyrrole derivatives with attached isocyclic ring. Bz-Tetrahydroindoles and cyclopentenopyrroles. A. TREIBS and D. DINELLI (Annalen, 1935, 517, 152—169).—Attempts to introduce a single N·OH group into cyclohexanone (I) were unsuccessful. Similarly treatment of Et cyclohexanone-2-carboxylate with amyl nitrite and HCl gives Et dinitrosocyclohexanone-2-carboxylate, whereas reaction does not occur with NaNO₂ and AcOH. cyclo-Hexanone-2-carboxylic acid and NaNO₂ in AcOH-H₂O afford non-cryst. oximinocyclohexanone (II), which decomposes when distilled, but is identified by transformation into dioximinocyclohexane, m.p. 189—190°, and by reduction to octahydrophenazine, m.p. 108° [hydrochloride, m.p. 159—160° after softening at 150°; picrate, m.p. 165° (decomp.)]. (II) with CH₂Ac·CO₂Et and Zn dust at 70—80° gives Et 2-methyl-4:5:6:7-tetrahydroindole-3-carboxylate, m.p. 134° (yield 20%); 2-methyl-4:5:6:7-tetrahydroindole-3-carboxylic acid, m.p. 170° (decomp.), passes at 180° into 2-methyl-4:5:6:7-tetrahydroindole, b.p. 105—107°/10 mm. COEt·CH₂·CO₂Et similarly affords Et 2-ethyl-4:5:6:7-tetrahydroindole-3-carboxylate, m.p. 130° (yield 20%), whence 2-ethyl-4:5:6:7-tetrahydroindole-3-carboxylic acid, m.p. 178° (decomp.), and non-cryst. 2-ethyl-4:5:6:7-tetrahydroindole, which is very sensitive to air and does not give a picrate. 3-Acetyl-2-methyl-4:5:6:7-tetrahydroindole, m.p. 203° (hydrobromide, decomp. 156°; hydrochloride), is obtained similarly from CH₃Ac₂. Reduction of OH·N·CMe·CH₂·CO₂Et (III) and ketone (IV) by Zn dust in aq. AcOH at 70—80° does not give a tetrahydroindole, whilst in anhyd. media the yield is 0.8—1.6%, increased to 16% by use of a large excess of (IV). By use of isolated (III) at the b.p. the yield may attain 46%. Thus (I) and (III) in anhyd. AcOH afford Et 3-methyl-4:5:6:7-tetrahydroindole-3-carboxylate (V), m.p. 110° (also obtained, accompanied by

Et₂ 2:5-dimethylpyrrole-3:5-dicarboxylate, when CH₂Ac·CO₂Et in AcOH is treated with NaNO₂ and the solution used directly for the condensation). (V) yields 3-methyl-4:5:6:7-tetrahydroindole-2-carboxylic acid, m.p. 130° (decomp.), and 3-methyl-4:5:6:7-tetrahydroindole (VI), m.p. 58° [picrate, m.p. 149° (decomp.)]. (V) is dehydrogenated by Se at 270—300° to skatole. Et oximinopropionylacetate, m.p. 62°, and (I) (4 mols.) yield Et 3-ethyl-4:5:6:7-tetrahydroindole-2-carboxylate, m.p. 189°, whence 3-ethyl-4:5:6:7-tetrahydroindole-2-carboxylic acid, m.p. 129° (decomp.), which passes at 135°/vac. into 3-ethyl-4:5:6:7-tetrahydroindole (VII), m.p. 52°. (VII) gives the aldehyde reaction in cold solution and does not appear to form a picrate. (III) and cyclopentanone yield Et 3-methyl-4:5-cyclopentenopyrrole-2-carboxylate, m.p. 147°, in small amount; 3-methyl-4:5-cyclopentenopyrrole-2-carboxylic acid, m.p. 143—145° (decomp.), passes at 150°/vac. into 3-methyl-4:5-cyclopentenopyrrole (VII), m.p. 28—29° (picrate, m.p. 109°). (VI) is converted by anhyd. HCN and HCl in anhyd. Et₂O into 3-methyl-4:5:6:7-tetrahydroindole-2-aldehyde (VIII), m.p. 170°, which condenses with cryptopyrrolealdehyde (IX) in AcOH at 100° to 3-methyl-4:5:6:7-tetrahydroindole-3':5'-dimethyl-4'-ethylpyrrolenine-2:2'-methene, m.p. 169° (hydrobromide, m.p. 225°; picrate, m.p. 200—201°; Cu salt, C₃₆H₄₆N₄Cu, m.p. 230°), which appears to undergo a porphyrin synthesis. (VI) and HCO₂H containing HBr give di-3-methyl-4:5:6:7-tetrahydroindylmethine, m.p. 172° [hydrobromide, m.p. 235° (decomp.)]; picrate, m.p. 212° (decomp.)], also obtained from (VIII) and opsopyrrolecarboxylic acid. Et 2:3:4-trimethylpyrrole-5-carboxylate, m.p. 126°, is obtained in 7% yield from COMeEt, (III), and Zn dust in boiling AcOH. (VIII) and (IX) afford 3:3':5'-trimethyl-4'-ethyl-4:5-cyclopentenopyrromethine, m.p. 142° (decomp.) after softening at 120—130° [hydrobromide, decomp. > 200°; picrate, m.p. 179°; complex Cu salt, m.p. 196° (decomp.)]. (V) and SO₂Cl₂ (1.2 or 2.5 mols.) in anhyd. Et₂O afford, respectively, Et 8(?)chloro-3-methyl-4:5:6:7-tetrahydroindole-2-carboxylate, m.p. 161° (decomp.), and Et dichloro-3-methyl-4:5:6:7-tetrahydroindole-2-carboxylate (X), m.p. 155°. (X) is hydrolysed to the corresponding acid, m.p. 167° (decomp.), which when heated yields a substance, C₂₈H₂₅O₂N₃·HCl, decomp. 230°. Br in AcOH transforms (V) into Et (8?)bromo-, m.p. 158° (decomp.), or Et dibromo- (XI), m.p. 121° (decomp.), -3-methyl-4:5:6:7-tetrahydroindole-2-carboxylate. Et bromohydroxy-3-methyl-4:5:6:7-tetrahydroindole-2-carboxylate, m.p. 130° (decomp.) after becoming red at 110°, is obtained from (XI) and H₂O in AcOH.

H. W.

γ-Triazines. XXVIII. Dihydroxyphenyltriazine and its derivatives. A. OSTROGOVICH (Gaz-zetta, 1935, 65, 229—241).—Correction and extension of work of Elzanowski (Diss., Fribourg, 1898). 2:4-Dihydroxy-6-phenyl-1:3:5-triazine, m.p. 293—294°, prepared by dissolving benzoylbiuret in dil. KOH, and, later, adding AcOH (A., 1930, 1193), is anhyd. (crystallographic data); its hydrochloride has 1 or 0.5H₂O. The Na (+H₂O, +6H₂O, or +7/3H₂O, + MeOH), Na₂ (+2EtOH), Ag (+0.5H₂O, or +H₂O), Ag₂ (+H₂O), Ba (+3H₂O), Mg (+10H₂O), and Pb salts,

and a complex, $[\text{Cu}(\text{NH}_3)_4(\text{OH})_2](\text{C}_9\text{H}_6\text{O}_2\text{N}_3)_2$ (crystallographic data), are described. E. W. W.

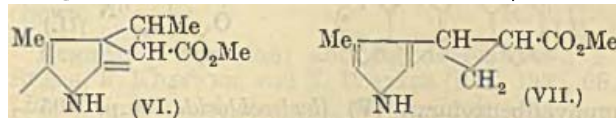
Synthetic *d*-, *l*-, and *dl*-9-araboflavin. R. KUHN and F. WEYGAND (Ber., 1935, 68, [B], 1001—1005).—The *oxalates*, m.p. 190—191°, 190—191°, and 164—165°, respectively, of *d*-, *l*-, and *dl*-arabinoamine are described. (I) and $\text{O}-\text{C}_6\text{H}_4(\text{NO}_2)_2$ in 80% EtOH at 135° afford 1-nitro-2-*d*-1'-arabitylamino-benzene, m.p. 187—188° (tetra-acetate, m.p. 126—127°), reduced (PtO_2 -80% EtOH) and then condensed with alloxan to 9-*d*-araboflavin (II), m.p. 296° (decomp.), $[\alpha]_D^{25} + 83.5^\circ$, $+75.5^\circ$, $+64.0^\circ$ in 0.1*N*-NaOH ($c=0.503$, 0.251, and 0.126, respectively), $[\alpha]_D^{17} - 175^\circ$ in 0.1*N*-NaOH + $\text{Na}_2\text{B}_4\text{O}_7$ (tetra-acetate, m.p. 265—266°). Similarly are obtained 1-nitro-2-*l*-1'-arabitylamino-benzene, m.p. 187—188° (tetra-acetate, m.p. 126—127°), and 9-*l*-araboflavin (III), m.p. 296° (decomp.), $[\alpha]_D^{17} - 82.5^\circ$, -74° , and -68° in 0.1*N*-NaOH ($c=0.678$, 0.339, and 0.169, respectively), $[\alpha]_D^{15} + 174^\circ$ in 0.1*N*-NaOH + $\text{Na}_2\text{B}_4\text{O}_7$ (tetra-acetate, m.p. 265—266°). 1-Nitro-2-*dl*-1'-arabitylamino-benzene, m.p. 168—169° (tetra-acetate, m.p. 146—147°), 9-*dl*-araboflavin, m.p. 296°, and its tetra-acetate, m.p. 273—274°, are obtained by admixture of the requisite optical antipodes in equal amount. (II) and (III) do not promote the growth of rats on a vitamin- B_2 -free diet. H. W.

[Pyridyl]-substituted barbituric acids.—See B., 1935, 524.

Chlorophyll. LVI. Action of diazoacetic esters on some chlorophyll derivatives. H. FISCHER and H. MEDICK. LVII. Synthesis of deoxyphyllerythroaetioporphyrin. H. FISCHER and J. HOFMAN [with E. STROBEL] (Annalen, 1935, 517, 245—273, 274—277; cf. this vol., 763).—LVI. $\text{CHN}_2\cdot\text{CO}_2\text{Me}$ (I) (and the Et ester) adds on to the vinyl group of chlorophyll derivatives to give cyclopropane derivatives, as is proved by oxidation of the products to methylmaleinimidecyclopropanecarboxylic acid (II), and by the spectra of the products, which retain the porphyrin characteristics, but show removal of the unsaturation. The products are susceptible to many of the reactions of the parent substances. Derivatives without the vinyl group do not react. CH_2N_2 adds only extremely slowly. It is thus proved that chlorophyll (II), protoporphyrin, and phaeophorbide-*a* and -*b* contain the vinyl group. Possible structures for the phaeophorbides are discussed, but certain statements in the lit. require revision before a decision can be reached. (II), hæmin (IV), and bacteriopheophorbide are thus very closely related. The "oxo-reaction" is now explained thus:

$\text{R}\cdot\text{CH}:\text{CH}_2 + \text{HI} \longrightarrow \text{R}\cdot\text{CHMeI} \longrightarrow (-2\text{H by I})$
 $\text{R}\cdot\text{CHMe}\cdot\text{OH} \longrightarrow \text{RAc}$. The structures given below are confirmed by spectral analysis. Protoporphyrin Me_2 ester (best obtained by CH_2N_2 in $\text{C}_5\text{H}_5\text{N}$; 2 days) adds 2 mols. of (I) at 100° (2 hr.) to give the substance (V), $\text{C}_{42}\text{H}_{46}\text{O}_8\text{N}_4$, m.p. 193—194° (cryst. Zn and amorphous Cu salts), stable to $\text{HBr}\cdot\text{AcOH}$ at 45°, oxidised by CrO_3 and aq. H_2SO_4 to hæmatic acid and (II), m.p. 205°. Methylphaeophorbide-*a* adds 1 mol. of (I) to give a poor yield of a substance, $\text{C}_{39}\text{H}_{42}\text{O}_7\text{N}_4$, m.p. about 220°, probably constituted as (VI), giving with $\text{HI}\cdot\text{AcOH}$ at 65° the isomeric porphyrin derivative, as (VII), m.p. 242°. (VI) with 25% HCl gives a sub-

stance (VIII), $\text{C}_{37}\text{H}_{40}\text{O}_5\text{N}_4$, m.p. 243° (oxime, m.p. 225°), also obtained from pyropheophorbide-*a* and (I). Catalytic (Pd) hydrogenation of (VIII) in COMe_2 is very slow, and re-oxidation leads mainly to (VIII); hydrogenation in AcOH is somewhat faster, and re-



oxidation gives a 30—35% yield of a porphyrin derivative, $\text{C}_{37}\text{H}_{38}\text{O}_5\text{N}_4$, m.p. 243°, which with CrO_3 yields methylethylmaleinimide and (II) (with substances, m.p. 110—111° and 149—150°, respectively), also obtained similarly from (VIII). Chlorin- e_6 Me_3 ester and (I) give the substance, $\text{C}_{40}\text{H}_{46}\text{O}_8\text{N}_4$, m.p. 187—189°, also obtained by CH_2N_2 in $\text{C}_5\text{H}_5\text{N}\cdot\text{MeOH}$ or by $\text{KOH}\cdot\text{MeOH}$, followed by CH_2N_2 in Et_2O , from (VI). This with Na_2CO_3 in boiling $\text{C}_2\text{H}_5\text{N}$ gives (VIII), and with $\text{HI}\cdot\text{AcOH}$ at 50° affords the porphyrin derivative, $\text{C}_{40}\text{H}_{44}\text{O}_8\text{N}_4$, m.p. 235°. Chlorin- e_4 Me_2 ester and (I) give the substance, $\text{C}_{38}\text{H}_{44}\text{O}_6\text{N}_4$, m.p. 184°, and rhodin-*g* Me_3 ester affords a substance, $\text{C}_{40}\text{H}_{44}\text{O}_9\text{N}_4$, m.p. 241° (oxime, m.p. 194—196°). Protohæmin gives the "oxo-reaction," a poor yield of a ketonic (oxime) substance being obtained. (I) does not react with meso-, hæmato-, tetramethynæmato-, or ketorhodo-porphyrin, mesoporphyrinogen, mesochlorin, mesorhodin, an ozonide of aetioporphyrin (another prep. reacted), dihydrophaeophorbide-*a*, phaeoporphyrin- a_5 , phylloerythrin, or dimethylphaeopurpurin-7. Phaeopurpurin-18, however, reacts.

LVII. 2-Formyl-4-methyl-3-bromovinylpyrrole-5-carboxylic acid and hæmopyrrole with HBr at 0° give *o*-carboxy-4 : 4' : 5'-trimethyl-3'-ethyl-3-bromovinylpyrromethene hydrobromide, decomp. 285° after discoloration from 170°, which with cryptopyrrole-methene-I in molten $(-\text{CH}_2\cdot\text{CO}_2\text{H})_2$ gives a mixture of aetioporphyrin with a little deoxyphyllerythroaetioporphyrin, m.p. 360° (block), separable with difficulty by adsorption on talc and perfusion with Et_2O .

R. S. C.

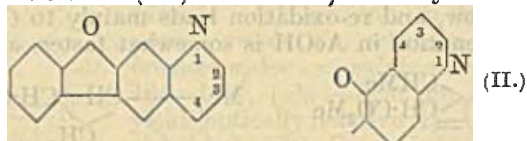
Phthalocyanines. I. Metal-free, nickel, copper, and platinum compounds.—See this vol., 813.

Nucleic acid of ergot.—See this vol., 797.

Constitution of the heterocyclic ring, $\text{C}_2\text{H}_2\text{O}$.—See this vol., 810.

Benzofuroquinolines. E. MOSETTIG and R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 902—905).—2-Aminodibenzofuran (modified prep.) gives (Skraup) benzofuro-3 : 2-*g*- (I) (32%), m.p. 168—169° (hydrochloride, m.p. 216—233°), and -2 : 3-*f*-quinoline (II), m.p. 106—107° (hydrochloride, m.p. 266—285°). The structure of (I) is proved by the degradation given below and that of (II) follows. Hydrogenation ($\text{Cu}\cdot\text{Cr}\cdot\text{BaO}$ in decalin; 100—150°; 1500—1800 lb.) affords the 1 : 2 : 3 : 4- H_4 -derivatives, m.p. 111—112° {hydrochloride, m.p. 196—226°; Bz, m.p. 198—200°, and *N*-Me derivative (prep. by MeI and NaOAc in EtOH at 100°), m.p. 56—57° [hydrochloride, m.p. 195—200° (decomp.); methiodide (III), m.p. 207—209°]}, and m.p. 80—81° {hydrochloride, m.p. 255—235°; Bz, m.p. 158—159°, and *N*-Me derivative, m.p.

72—73° [hydrochloride, m.p. 204—209° (decomp.); methiodide (IV), m.p. 193—194°], respectively. Emde degradation of (III) affords 3- γ -dimethylamino-*n*-



propyldibenzofuran (V) (hydrochloride, m.p. 195—197°; picrate, m.p. 164—165°; methiodide, m.p. 210—211.5°), identical with the synthetic product (A., 1922, i, 746). Dibenzofuran, $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 give β -3-dibenzofurylpropionic acid, m.p. 185—187° (lit. 184—185°). γ -3-Dibenzofurylbutyric acid, purified by way of the Et ester (distills in high vac.) and *K* salt, m.p. 114—115°, gives the hydrazide, m.p. about 118—120° (lit. 122—123°), which affords the urethane, m.p. 72—74° (and a substance, m.p. 140—160°), whence were obtained the azide (and a substance, m.p. 220—222°), 3- γ -amino-*n*-propyldibenzofuran hydrochloride (96% yield), m.p. 228—231° (lit. 219—220°), and (by $\text{HCO}_2\text{H}-\text{CH}_2\text{O}$ at 130—160°) (V). (IV) affords (Emde) 1- γ -dimethylamino-*n*-propyldibenzofuran (hydrochloride, m.p. 168—169°; picrate, m.p. 128—129.5°; methiodide, m.p. 237—238°). Physiological activity is in the order: (I), (II) < H_4 -derivatives < (III), (IV). The substances do not cause death in effective doses. All m.p. are corr.

R. S. C.

Hydrolysis of ergotinine and ergoclavine. W. A. JACOBS and L. C. CRAIG (J. Amer. Chem. Soc., 1935, 57, 960—961; cf. this vol., 504, 764).—Hot HCl destroys the lysergic acid fraction of ergotinine, giving amorphous products, *l*-phenylalanine, and *d*-proline. Ergoclavine with alkali gives NH_3 , lysergic acid, $\text{CH}_2\text{Pr}-\text{CO}-\text{CO}_2\text{H}$, and leucine, and with acid only partly racemised *l*-leucine and another NH_2 -acid, but not proline.

R. S. C.

Ergotocin. Active principle of ergot responsible for the oral effectiveness of some ergot preparations on human uteri. M. S. KHARASCH and R. R. LEGAULT (J. Amer. Chem. Soc., 1935, 57, 956—957).—Ergotoxine, ergotamine, and sensibamine are ineffective when administered orally in 2 mg. doses to human mothers and in 2—4 mg. doses induce unpleasant side-reactions and caused uterine contraction in only 5 out of 15 cases. Some ergot preps. (U.S.P. method) (I) are ineffective. A dextrorotatory base, ergotocin (II), m.p. 155° (decomp.) [red picrate, m.p. 195—197° (decomp.); some salts sol. in 10 parts of H_2O], is present only in effective (I) and is responsible for the whole of this efficiency; the immediately effective dose of pure (II) for man is 0.3 mg. orally equiv. to 3—4 g. of crude defatted ergot or 0.1 mg. intravenously. (II) is fairly sol. in H_2O , is not pptd. by Meyer's reagent in concn. < 1:7500, and does not liberate NH_3 with hot alkali.

R. S. C.

Alkaloids of jaborandi leaves. VI. Synthesis of *r*-homopipilic acid. N. A. PREOBRASHENSKI, A. M. POLJAKOVA, and V. A. PREOBRASHENSKI. VII. Resolution of the unstable ethylparaconic (*r*-pipilic) acid into its optical antipodes. N. A. PREOBRASHENSKI and V. A. PREOBRASHENSKI. VIII. Synthesis of *d*-homopipilic acid. N. A. PREO-

BRASHENSKI, A. M. POLJAKOVA, and V. A. PREOBRASHENSKI (Ber., 1935, 68, [B], 844—847, 847—849, 850—852; cf. A., 1934, 632).—VI. Treatment of *r*-pipilic acid (I) with PBr_3 , H_2 (+Pd), I, KCN, H_2SO_4 , and HCl in succession leads to *r*-homoisopipilic acid. Inversion is shown to occur during prolonged heating or distillation in vac., under the influence of PBr_3 , or by prolonged boiling with acids, but not with the remaining reagents if the changes are effected at low temp. The synthesis is effected as follows: (I) is transformed by SOCl_2 into *r*-pipilic chloride, b.p. 98°/0.3 mm., converted by H_2 -Pd in C_6H_6 into *r*-pipilaldehyde, b.p. 92°/0.2 mm., which is reduced ($\text{Al}-\text{Hg}$ in Et_2O) to the corresponding alcohol (II), b.p. 117.8°/0.05 mm. (II) and SOCl_2 in presence of $\text{C}_5\text{H}_5\text{N}$ afford *r*-pipilic chloride, b.p. 92°/0.8 mm., whence the corresponding iodide, nitrile, b.p. 125—130°/0.1 mm., and *r*-homopipilic acid, m.p. 100—101°.

VII. (I) is resolved into its optical antipodes by crystallisation of the brucine or cinchonine salts from H_2O . The vals., m.p. 121.2—122.2°, $[\alpha]_D^{18} +54.60^\circ$ in H_2O , and m.p. 120—121.8°, $[\alpha]_D^{18} -54.00^\circ$ in H_2O , are recorded for the *d*- (II) and *l*-acids, respectively.

VIII. (II) with SOCl_2 gives *d*-pipilic chloride, converted by CH_3N_2 in Et_2O into *d*-pipilic CHN_2 ketone (III), m.p. 106—108°. Addition of (III) in H_2O to a mixture of $\text{Na}_2\text{S}_2\text{O}_4$ and Ag_2O in H_2O affords *d*-homopipilic acid, the identity of which with the material from natural sources is established by converting it into *d*-homopipilic CH_2Cl ketone, m.p. 88.5—89.2°.

H. W.

[Simplification of Pictet's synthesis of nicotine.] J. B. WIBAUT (Ber., 1935, 68, [B], 768).—Spath *et al.* (this vol., 635) have overlooked the work of Wibaut *et al.* (A., 1928, 1386; 1933, 77, 1312).

H. W.

Sophora alkaloids. IX. Thermopsine. A. OREKHOV and H. GUREVITSCH [with T. OKOLSKAJA] (Ber., 1935, 68, [B], 820—822; cf. this vol., 635).—Attempts to degrade thermopsine (I) by the action of KOH or Ag_2O on its methiodide were unsuccessful, (I) being almost quantitatively recovered. Emde's method is also inapplicable. (I) does not add CNBr in boiling C_6H_6 . The attempted Hofmann degradation of tetrahydrothermopsine methiodide, m.p. 261—262° (decomp.), gives unchanged base. (I) in 50% H_2SO_4 is reduced at a Pb cathode to the base $\text{C}_{15}\text{H}_{28}\text{ON}_2$, m.p. 112—113°, $[\alpha]_D^{18} +55.9^\circ$ in MeOH , which contains 1 OH (Zerevitinov) and, apparently, NH. Reduction of (I) is accompanied by ring fission.

H. W.

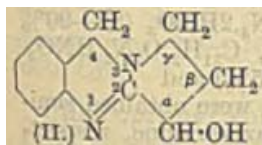
Alkaloids of Convolvulus pseudocantabricus. III. Constitution of convolvine and isolation of two new bases. A. OREKHOV and R. KONOVALOVA [with E. EREMINA] (Ber., 1935, 68, [B], 814—819; cf. A., 1934, 908).—Convolvine (I) (nitrate, m.p. 115°) is $\text{C}_{16}\text{H}_{24}\text{O}_4\text{N}$ (not $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}$). Alkaline hydrolysis of (I) yields 3:4- $\text{C}_6\text{H}_3(\text{OMe})_2\text{CO}_2\text{H}$ and nortropine, m.p. 159—161°. Treatment of (I) with MeI in COMe_2 gives convolvamine (II), m.p. 109—110°, and its methiodide, m.p. 275—276°. (I) is therefore veratroylnortropine. (I) constitutes 90% of the alkaloidal mixture of the seeds of *C. pseudocantabricus*, whereas (I) and (II) are present in about equal proportion in the foliage. Convolvidine (III), probably $\text{C}_{32}\text{H}_{42}\text{O}_8\text{N}_2$ or

$C_{33}H_{44}O_8N_2$, m.p. 192—193°, optically active, is isolated from crude (I) owing to its very sparing solubility: Alkaline hydrolysis of (III) affords 3 : 4- $C_6H_3(OMe)_2 \cdot CO_2H$ and an *alkamine*, m.p. 274—276° (*picrate*, m.p. 229—231°). *Convolvicine*, C_5H_8N or $C_{10}H_{16}N_2$, b.p. 250—260°/1 atm. (*picrate*, m.p. 200—202°), is obtained from the mother-liquors from the hydrochlorides of (I) and (II). H. W.

Alkaloids of han-fang-chi. K. K. CHEN and A. L. CHEN (J. Biol. Chem., 1935, 109, 681—685).—Han-fang-chi, *Cocculus diversifolius* (or *japonicus*) (2.3% of total alkaloids), yields to EtOH mainly tetrandrine, $C_{32}H_{24}O_2(OMe)_4(NMe)_2$, m.p. 217—218°, $[\alpha]_D^{25} +252.4^\circ$ in $CHCl_3$ [*dihydrochloride*, m.p. 263°, decomp. 266°, $[\alpha]_D +224.2^\circ$ in H_2O ; *dihydrobromide*, m.p. 270° (decomp. from 258°), $[\alpha]_D^{25} +200.7^\circ$ in H_2O ; *dinitrate*, decomp. 208° (softens at 205°), $[\alpha]_D +211.2^\circ$ in H_2O ; *oxalate*, decomp. 165—170° (softens at 147.5—148.5°); *dipicrate*, decomp. 235—242°; *diflavinate*, decomp. 248—250° (cf. A., 1932, 1048)]. M.p. are corr. R. S. C.

Structure of vasicine. II. **Synthesis of deoxyvasicine.** W. E. HANFORD and R. ADAMS. III. **Position of the hydroxyl group.** R. C. MORRIS, W. E. HANFORD, and R. ADAMS (J. Amer. Chem. Soc., 1935, 57, 921—924, 951—954; cf. this vol., 365).—II. γ -Phenoxybutyryl chloride (prep. by $SOCl_2$), b.p. 154—156°/20 mm., gives the *amide*, m.p. 113°, and with $o\text{-NO}_2 \cdot C_6H_4 \cdot CH_2 \cdot NH_2$ in C_6H_6 the *o-nitrobenzylamide*, m.p. 75—76°, hydrogenated (PtO_2 ; EtOH; 2—3 atm.) to γ -phenoxybutyryl-*o*-aminobenzylamide, m.p. 97.5—98°, which at 270°/1.5 mm. gives H_2O and 2- γ -phenoxypropyl-3 : 4-*dihydroquinazoline*, m.p. 111.5—112.5°. With HBr it gives the γ -Br-compound, converted by alkali into deoxyvasicine (I), m.p. (+ $2H_2O$) 77° (0.5 H_2O ; prep. over H_2SO_4 in vac.) 88—89°, and (anhyd.; hygroscopic; prep. over P_2O_5 in vac.) 96.5—97.5° (*benzylidene* derivative, m.p. 161—163°, often 157—159°). γ -Chlorobutyryl-*o*-nitrobenzylamide, m.p. 73°, with KOH in C_6H_6 at 50° affords N-*o*-nitrobenzylpyrrolidone (14%), m.p. 100°, hydrogenated (PtO_2 ; EtOH; 1 atm.) to the *o*- NH_2 -compound, m.p. 63—65°, which distils unchanged at 245—255° and could not be converted into (I). γ -Chlorobutyrylbenzylamide, m.p. 68°, affords quantitatively N-benzylpyrrolidone, b.p. 122.5—123°/2 mm., which with conc. HCl at 100° gives γ -benzylaminobutyric acid hydrochloride, hygroscopic, m.p. 158—161°.

III. Contrary to Ghose *et al.* (A., 1933, 77), vasicine (II) does not react with 3% H_2O_2 , but with 30% H_2O_2 at 60—70° gives some of the compound (III), m.p. 213—214°, shown below to be 2 : 3- α -hydroxytrimethylene-4-quinazoline. The substance, m.p. 168°, was not obtained and was probably the equimol. mixture of (II) and (III), which has m.p. 168—170°. (III) and $SOCl_2$ give 2 : 3- α -chlorotrimethylene-4-quinazoline, m.p. 109°, reduced by Zn dust and AcOH to (I). (I) and 3% H_2O_2 at 50—60° give 2 : 3-trimethyl-



ene-4-quinazoline (IV), m.p. 110—110.5° (*benzylidene* derivative, m.p. 137—139°), which is synthesised thus. $o\text{-NH}_2 \cdot C_6H_4 \cdot CO \cdot NH_2$ (prep. from the ester and liquid NH_3 at 200°/1200 lb.) affords *o*- γ -phenoxybutyryl-*o*-amino-

benzamide, m.p. 150°, which at 230—235° loses H_2O to give 2- γ -phenoxypropyl-4-quinazoline, m.p. 181°, converted by HBr into the γ -Br-compound, which with hot KOH-EtOH affords (IV). (IV) and $Pb(OAc)_4$ give (III). (II) thus has almost certainly the formula shown. R. S. C.

Peganine (vasicine) and its derivatives. E. SPATH, F. KUFFNER, and N. PLATZER (Ber., 1935, 68, [B], 935—940; cf. this vol., 635).—Treatment of $o\text{-NO}_2 \cdot C_6H_4 \cdot CH_2Cl$ with pyrrolidine in boiling EtOH yields 1-*o*-nitrobenzylpyrrolidine, b.p. (bath), 100—115°/1 mm., reduced by $SnCl_2$ and fuming HCl to 1-*o*-aminobenzylpyrrolidine, m.p. 31—32°, identical with deoxyhexahydropeganine. Reduction of peganine (I) with Na and isoamyl alcohol gives dihydropeganine (pegan-3-ol), m.p. 132—133°, and pegane. Treatment of (I) with Ac_2O at 100° yields *O*-acetylpeganine, m.p. 122—123° (vac.), readily hydrolysed to (I). Boiling Ac_2O converts (I) into N-acetylpegadiene (II), $C_{13}H_{12}ON_2$, m.p. 163—164.5° (cf. Ghose *et al.*, A., 1933, 77), hydrolysed to pegadiene, $C_{11}H_{10}N_2$, m.p. 210—211° (vac.), re-converted by boiling Ac_2O into (II). H. W.

Cactus alkaloids. XIV. Anhalidine. E. SPATH and F. BECKE (Ber., 1935, 68, [B], 944—945; cf. this vol., 635).—Anhalidine, m.p. 131—133° (isolation from *Anhalonium Lewinii* described) is formed by treatment of anhalamine with MeI in MeOH followed by Na_2CO_3 and is therefore 8-hydroxy-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline. H. W.

Synthesis of tropinone, ψ -pelletierine, lobelamine, and related alkaloids under physiological conditions. C. SCHOPF and G. LEHMANN (Annalen, 1935, 518, 1—37; cf. A., 1932, 1046; 1934, 1373).—The formation of tropane alkaloids in the cell can be satisfactorily explained if tropinone (I) is assumed to be an intermediate product (cf. Robinson, A., 1917, i, 581, 876). It is shown that (I) is formed in good yield from $(\cdot CH_2 \cdot CHO)_2$, NH_2Me , HCl, and $CO(CH_2 \cdot CO_2H)_2$ at p_H 3—11 and 20—25°. (I) is not produced from tropinonedicarboxylic acid (II) by KOH used in its isolation. At p_H 13, (II) is formed in large amount. $CH_3Ac \cdot CO_2H$ cannot replace $CO(CH_2 \cdot CO_2H)_2$. The hypothesis that $CO_2Me \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2H$ (III) is the initial material in the biosynthesis of cocaine and its analogues is supported by the observation that (III), $(\cdot CH_2 \cdot CHO)_2$, and NH_2Me at p_H 5 afford Me tropinone-carboxylate (IV) in good yield. Reduction of (IV) and esterification of the OH thus produced leads to the alkaloids. Attempts to convert succindialdioxime (V) into $(\cdot CH_2 \cdot CHO)$ by $EtNO_2$ in dioxan at $< 15^\circ$ yield a compound (succindialdehyde Et_2 acetal or 2 : 5-diethoxytetrahydrofuran), b.p. 65—72°/12 mm. $(\cdot CH_2 \cdot CHO)_2$ is best obtained by passing N_2O_3 into (V) suspended in H_2O . Glutardialdehyde (VI) is obtained by ozonolysis of cyclopentene or, preferably, from *trans*-cyclopentane-1 : 2-diol and $Pb(OAc)_4$.

At p_H 3—13, preferably p_H 3—7, ψ -pelletierine (VII) is formed in good yield from (VI), NH_2Me , and $CO(CH_2 \cdot CO_2H)_2$. In contrast with observations in the tropinone series, comparatively large yields of (VII) are obtained at p_H 13, doubtless owing to the relative instability of primarily-formed ψ -pelletierinedicarboxylic acid in alkaline solution. (VII) cannot be

formed from COMe₂ in the plant unless an undetected enzyme which catalyses the condensation is present.

By analogy, lobelanine (VIII),

$\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Bz}) \\ \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Bz}) \end{smallmatrix} \text{NMe}$, is regarded as the primary product of the biogenesis of *Lobelia* alkaloids. (VIII) is formed in good yield from (VI), NH₂Me, and CH₂Bz·CO₂H in feebly acid solution within a very narrow range. At *p*_H 7 the yield is very small, whilst at *p*_H 9, 11, or 13 only traces of (VIII) cannot be detected as the sparingly sol. hydrochloride. In alkaline solution the amount of basic product is very little and the only neutral product is CPhMe. At *p*_H 3 (VIII) is almost completely stable, whereas at *p*_H 5 it suffers noticeable decomp., increasing with the alkalinity of the solution; the effect is not sufficiently pronounced to account for the influence of *p*_H in the synthesis of (VIII). (·CH₂·CHO)₂, NH₂Me, and CH₂Bz·CO₂H at *p*_H 3, 4, 5, 7, and 9 afford 2:5-diphenacyl-1-methylpyrrolidine (IX), m.p. 62° (hydrochloride, m.p. 205—206°), in good yield and its formation is well marked at *p*_H 11 and 13. Unlike (VIII), (IX) is almost completely stable in neutral or feebly alkaline solution. The constitution of (IX) is established by degradation of its methiodide, m.p. 186° (corresponding methochloride), to β-dimethylamino-αζ-dibenzoyl-Δ^ε-hexene, m.p. 110°, the methiodide, m.p. 204—205°, of which passes into αζ-dibenzoyl-Δ^{εε}-hexadiene (X), m.p. 192° after softening at 185°. (X) is hydrogenated (Pd-CaCO₃ in MeOH) to αβ-dibenzoylhexane, m.p. 94° (semicarbazone, m.p. 203—204°), identical with that obtained from suberyl chloride and C₆H₆. The max. yield (83%) of 2:5-diacetoxy-1-methylpyrrolidine, m.p. 57—58° [picrate, m.p. 176—177° (decomp.)], from (·CH₂·CHO)₂, NH₂Me, HCl, and CH₂Ac·CO₂H is obtained at *p*_H 5 and 20—22°. H. W.

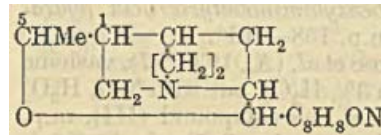
Iodobismuthates of quinine and hydrocupreine esters. A. MIHALOVICI and L. VON ULLMANN (Curierul farm., 1934, 4, No. 3, 1—5; No. 4, 1—6; Chem. Zentr., 1935, i, 214).—An amorphous product is obtainable only by pptn. at great dilution. Hydrolysis is avoided by repeated washing with fresh H₂O.

H. J. E.

Hydrocupreine aminoalkyl ethers. K. H. SLOTTA and R. BEHNISCH (Ber., 1935, 68, [B], 754—761).—NMe₂·CH₂·CH₂·OH is transformed by SOCl₂ in C₆H₆ into β-dimethylaminoethyl chloride, b.p. 109°/759 mm. [hydrochloride (I), m.p. 201°]. (I), NaOEt, and hydrocupreine in boiling EtOH afford β-dimethylaminoethylhydrocupreine, m.p. 103°. The following compounds are analogously obtained: β-diethylaminoethyl chloride, b.p. 146—147°/750 mm. (hydrochloride, m.p. 212°), and β-diethylaminoethylhydrocupreine, m.p. 120° (sulphate, m.p. 215°); β-diethylamino-n-propyl chloride, b.p. 59—60°/16 mm., and the non-cryst. β-diethylamino-n-propylhydrocupreine, which passes over P₂O₅ at 80°/high vac. into a cryst. modification, m.p. 124° (sulphate, m.p. 196°); γ-diethylaminoisobutyl chloride, b.p. 35—37°/12 mm. (picrate, m.p. 151°), and γ-diethylaminoisobutylhydrocupreine, softens at 80—90° (sulphate, m.p. 228°); γ-dimethylaminoisooamyl chloride, b.p. 50—53°/12 mm., and γ-dimethylaminoisooamylhydrocupreine, m.p. (indef.) 70—80° (trisulphate, m.p. 216°); tetramethyl-di-

aminoisopropyl chloride, b.p. 68—70°/12 mm. (picrate, m.p. 170°), and non-cryst. tetramethyldiaminoisopropylhydrocupreine [sulphate, m.p. (indef.) 85—90°]. All the ethers exhibit the bactericidal and antimalarial actions of their components in a greatly diminished degree, showing that the most active components can yield inactive mols. if their union produces compounds of mol. wt. beyond the optimal. OPh·[CH₂]₅·Br and NH₂Et₂ at 140° yield Ph ε-diethylamino-n-amyl ether, b.p. 166°/13 mm. (hydrochloride, m.p. 115°), which is converted by conc. HCl at 160° into PhOH and ε-diethylamino-n-amyl chloride, b.p. 85—90°/12 mm., which very rapidly passes into 1-ethylpiperidine ethochloride, m.p. 275° (picrate, m.p. 241°; aurichloride, m.p. 249°), also obtained by treating 1-ethylpiperidine with EtI and the product with AgCl. Tetramethyldiaminoisopentanol gives the corresponding chloride in which Cl is very mobile. Di-β-chloroethylamine hydrochloride is stable, but the base polymerises very readily. H. W.

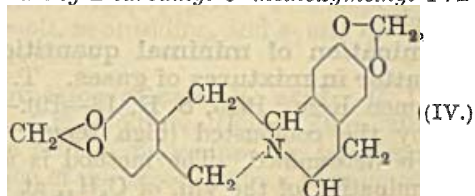
Third hydroxy-base derived from quinidine. T. DOMANSKI and J. SUSZKO (Rec. trav. chim., 1935, 54, 481—491).—Quinidine and conc. HCl or HBr give, besides α-isoquinidine (I) (A., 1933, 517), difficultly separable γ-isoquinidine (II), C₂₀H₂₄O₂N₂, m.p. about 70°, [α]_D¹⁵ +51.1° in EtOH [dintrate, m.p. 196°, [α]_D¹⁸ +50° in H₂O; oxalate, m.p. 185—188° (decomp.), [α]_D¹⁸ -56.9° in H₂O; hydriodide, m.p. 180—183°; H tartrate (III), m.p. 160—161° (decomp.); picrate, m.p. 183—193°; methiodide (IV), m.p. 227—235°, [α]_D¹⁵ +(?-12° in EtOH; dimethiodide, m.p. 241—242° (decomp.), [α]_D²² -95° in EtOH; perbromide, B.HBr₃, m.p. 213—216°, regenerates (II) at once with dil. aq. alkali; N-oxide, +3H₂O, m.p. about 80—100°, decomp. 160°]. (III) at 120° gives γ-isoquinicine, m.p. 113°, [α]_D²⁴ -40° in EtOH (N-NO-derivative, m.p. 103—105°, decomp. about 140°), yielding with cold MeI-Et₂O the N-Me derivative, an oil [dintrate, m.p. 155° (decomp.); methiodide, m.p. 90—100°, decomp. > 205°, [α]_D¹⁸ -11° in EtOH], also obtained from (IV) and hot 10% KOH. (II) in 10—25% AcOH at 100° gives γ-hydroxydihydroquinotoxin, m.p. 110—118°, [α]_D¹⁵ -15° in EtOH (H tartrate, m.p. about 60°; N-NO-derivative, m.p. 65—80°, [α]_D¹⁵ -17° in EtOH; p-nitrophenylhydrazone, m.p. about 90°), in H₂SO₄ (d 1.80) at 70—80° (1.75 hr.) gives β-isoquinidine (V), and in 60% HBr at 100° yields bromodihydrocupreidine [dihydrobromide, m.p. 288° (decomp.)]. (II) is probably an intermediate between (III) and (V), differing from them sterically at C1 and C5, and having the annexed formula. R. S. C.



Degradations in the brucine series. T. T. CHU (Annalen, 1935, 517, 290—294).—11-Amino-brucine (nitrate, decomp. > 200°) and HNO₃ give a cacotheline derivative, C₂₁H₂₂O₇N₄·2HNO₃ (80—90% yield), and a purple substance, C₂₁H₂₂O₉N₂·HNO₃. Substances, C₂₁H₂₀O₈N₄·HNO₃ (95%) and C₂₁H₂₀O₇N₅·HNO₃ (100% yield), were obtained similarly from 11-oximino- and diazo-brucine, respectively. CrO₃ gives mixtures. Oxidation of the

above products with Br-HBr or Cl₂ at 100° or of their catalytic hydrogenation products gives no colourless, H₂O-sol. degradation product. R. S. C.

Protopine and allied alkaloids. II. New synthesis of the berberine ring-system, and of a ring-homologue of the aporphine alkaloids. T. S. STEVENS (J.C.S., 1935, 663—667).—β-Piperonyl-ethylamine (I) and the lactone (II) of 1:2:4:5-CH₂O₂:C₆H₂(CH₂·OH)·CH₂·CO₂H give 6-hydroxy-methylhomopiperonyl-β-piperonylamine (III), m.p. 176°. (I) with 1:2:4:5-CH₂O₂:C₆H₂(CH₂Cl)·CH₂·CN forms 6-β-piperonyl-ethylaminomethylhomopiperonyl-nitrile, m.p. 77—79°, and with 1:2:4:5-CH₂O₂:C₆H₂(CH₂Br)·CH₂·CO₂Me yields 3-keto-6:7-methylenedioxy-2-β-piperonyl-ethyl-1:2:3:4-tetrahydroisoquinoline, m.p. 144—146°, which could not be dehydrated, and bis-(6-carboxymethylhomopiperonyl)-β-piperonyl-ethylamine, m.p. 225—230° (decomp.). 6-Methoxymethylhomopiperonyl-β-piperonyl-ethylamine, m.p. 103—105°, and PCl₅ afford 2:3:10:11-bismethylenedioxyprotoberberinium chloride. (III) and POCl₃ give a product, reduced (Zn) to a base "A," probably 6:7:3':4'-bismethylenedioxy-8:6'-methylene-1:2:3:4-tetrahydroproto-papaverine, m.p. 188° (p-nitrobenzoyl derivative, decomp. 285°). "A" and Me₂SO₄, followed by KBr, afford 6:7:3':4'-bismethylenedioxy-8:6'-methyleneprotolaudanosine methobromide (+H₂O), m.p. 210—220° (decomp.), which with MeOH-KOH forms the methine, m.p. 101° [hydrochloride, m.p. 170—174°; methobromide (+2H₂O), decomp. 275°]. (II) is reduced (Zn) to 6-methylhomopiperonylic acid, m.p. 148—151°, which with (I) affords 6-methylhomopiperonyl-β-piperonyl-ethylamine, m.p. 158—160°. The amide is cyclised and reduced to 6:7:3':4'-bismethylenedioxy-6'-methyl-1:2:3:4-tetrahydroproto-papaverine, m.p. 92—94° [picrate, m.p. 240° (decomp.)], which differs from "A." The base (IV) and CNBr followed by NaOMe yield 6:7:3':4'-bismethylenedioxy-2-carbamyl-6'-methoxymethyl-1:2:3:4-



tetrahydrotopapaverine, m.p. 75—80°, which with POCl₃ and subsequent hydrolysis is converted in small yield into "A."

6:7:3':4'-Bismethylenedioxy-2-methyl-1:2:3:4-tetrahydrotopapaverine (picrate, decomp. 210°) is prepared from Me₂SO₄ and the cyclisation product of homopiperonyl-β-piperonylamine; the 2-benzenesulphonyl compound, m.p. 110—113°, is similarly obtained. Aceto-6-bromo-β-piperonyl-ethylamide, m.p. 125°, and 6-bromohomopiperonylic acid [Me ester, m.p. 84°; amide, m.p. 181°; nitrile, m.p. 65—67°, oxime, m.p. 166—167° (decomp.)] do not condense with CH₂O. F. R. S.

Chloropropyl yohimboate and its derivatives. D. E. Worrall (J. Amer. Chem. Soc., 1935, 57, 900).—The following are prepared: α-chloro- [from

CH₂(CH₂Cl)₂, m.p. 110—111° [H sulphate, decomp. 283°; apo-form, m.p. 105—106° (decomp.)], α-diethyl-amino-, m.p. indef. > 75° (dihydrochloride, m.p. 192—193°; methiodide, m.p. 195—196°; apo-form, m.p. 95—96°), and α-piperidino-propyl, m.p. 107—108°, cetyl, a gum (hydrochloride, m.p. 238°), and benzyl yohimboate, m.p. 77—78° (hydrochloride, m.p. 253—254°). R. S. C.

Stereochemistry of tervalent arsenic. I. G. KAMAI (Ber., 1935, 68, [B], 960—965).—Addition of AsMeEtI to a solution of Mg and p-C₆H₄Br₂ yields p-bromophenylmethylethylarsine (I), b.p. 132—133°/8 mm., which gives an additive compound with CuBr and a cryst. arsonium salt with CH₂BrBz. p-Bromophenyl-p-tolylmethylethylarsine (II), b.p. 211—215°/9 mm., is obtained from p-C₆H₄Me·AsMeI and p-C₆H₄Br·MgBr. Attempts to convert (I) or (II) into the corresponding acids failed on account of their non-reactivity with Mg. p-Tolylethyl-n-propylarsine is oxidised by KMnO₄ to p-carboxyphenylethyl-n-propylarsine oxide hydrochloride, m.p. 119—120° (converted by H₂S into p-carboxyphenylethyl-n-propylarsine sulphide, m.p. 142°), which is reduced by SO₂ in presence of I to p-ethyl-n-propylarsinobenzoic acid (III), AsEtPr·C₆H₄·CO₂H, m.p. 58—59° (NH₄ and Ba salts; compound with HgCl₂, m.p. 69—70). p-Carboxyphenylmethylethyl-n-propylarsonium iodide has m.p. 154—156°. (III) gives strychnine, m.p. 145—147°, [α]_D²⁰ -29.88° in CHCl₃, and quinine, m.p. 194—195°, [α]_D²⁰ -71.45°, salts, but evidence of resolution is not obtained. H. W.

Organic selenium compounds. Chemical properties of some arylselenonium compounds.

Preparation of diarylselenonium acetates. D. G. FOSTER (Rec. trav. chim., 1935, 54, 447—460; cf. A., 1934, 539).—SePh₂Br₂ or SePh₂Cl₂ and AgOAc in Et₂O or C₆H₆ gives the acetate (I), OH·SePh₂·OAc, m.p. 81—82°, which loses AcOH when kept or heated in vac., and absorbs Ac₂O vapour to form the diacetate, SePh₂(OAc)₂, m.p. about 132°. SePhEtBr₂ or SePhEtCl₂ and AgOAc in cold Et₂O or C₆H₆ afford SePhEt, PhSeO₂H, and AcOH; when heated, however, SePhEt, SePh₂, and AcOH are produced, probably by decomp. of SePh₂O, produced from the monoacetate. SePh₂O and Ac₂O give (I), but (p-C₆H₄Me)₂SeO and (p-C₆H₄·OEt)₂SeO give the diacetates, m.p. 88—90° and 81—82°, respectively; SePhMeO and p-C₆H₄Br·SeEtO probably react, but give no definite products. CH₂R·SePhO (R=H or Me), when distilled/high vac. or heated in conc. aq. solution, decompose thus: (a) CH₂R·SePhO → SePh·CH₂R (II) + PhSeO₂H + RCHO; (b) PhSeO₂H + (II) → Se₂Ph₂ + RCHO + H₂O. Reaction (b) can be realised alone. SePh₂Br₂ and NaOEt give SePh₂, MeCHO, and EtOH, but SePhEtBr₂ and NaOEt give probably SePhEtO, since the final products are SePhEt, PhSeO₂H, Se₂Ph₂, and MeCHO. SePhBu^aBr₂ and NaOBu react similarly. The following are incidentally described: Ph Bu^a, b.p. 105°/5 mm. (dibromide, m.p. 84°), n-amyl, b.p. 116°/5 mm. (dibromide, m.p. 88—90°, and n-hexyl selenide, b.p. 133°/5 mm. (dibromide, m.p. 95°); phenyl-ethyl-, m.p. 181—183°, and methyl-selenonium oxide, m.p. 53—54°, hygroscopic. R. S. C.

Influence of the stibino-group on the reactivity of nuclear chlorine. C. B. BISWELL and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 913—914).— SbO_3H_2 has less influence than AsO_3H_2 on the reactivity of aromatic Cl. 3-Chlorophenylstibinic acid (from $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$) [chloride, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SbOCl}_5$, m.p. 82° after sintering (NH_4Cl additive compound, m.p. $87\text{--}89^\circ$)] does not react with NH_2Ph , is unchanged by $6N\text{-NaOH}$ at 100° , and affords at 50° the 5- NO_2 -acid (I) [chloride, m.p. 250° (NH_4Cl additive compound, m.p. 250°)], and thence the 5- NH_2 - and (by $6N\text{-KOH}$ at 97°) 5- OH -acids. The above acids are amorphous, m.p. $> 250^\circ$. (I) and the appropriate amine in PhNO_2 or, better, $\text{C}_5\text{H}_{11}\text{OH}$ with, best, polished Cu, give 5-nitro-2-anilinophenylstibinic acid, decomp. 250° , and the 2-alkylamino-acids, substituted by Pr^a , decomp. 220° , Bu^w , decomp. 170° , Bu^s , decomp. 200° , $n\text{-amyl}$, decomp. 120° , and $isoamyl$, decomp. 200° . R. S. C.

Ultracentrifugal study of gliadin. L. KREJCI and T. SVEDBERG (J. Amer. Chem. Soc., 1935, 57, 946—951).—Gliadin, which is stable from p_H 1.46 to 12, is shown by centrifuging to be heterogeneous, being composed at p_H 2.23 and 20° of whole and half-mols. (mol. wt. 34,500 and 17,250; dissymmetry nos. 1.92 and 1.21, respectively), but solely of whole mols. at lower p_H and higher temp. The least sol. fraction contains mostly whole, the most sol. almost entirely half-mols. The sedimentation const. of the main constituent is 2.10×10^{-13} . R. S. C.

Attempts to isolate dihydroxyproline-alanine from gelatin hydrolysates. O. H. EMERSON and C. L. A. SCHMIDT (Proc. Soc. Exp. Biol. Med., 1934, 32, 291—296).—No definite cryst. compound corresponding with dihydroxyproline-alanine was isolated from the phosphotungstic acid ppt. from the Van Slyke technique. R. N. C.

Relations between colloidal and constitutive charges of proteins. II. Heat-denaturing action of albumin. III. Casein and edestin.—See this vol., 822, 823.

Titration curves of protein fibres.—See this vol., 826.

Dilatometric study of the denaturation of albumin solutions by heat.—See this vol., 822.

Isoionic point of proteins.—See this vol., 822.

Chromatographic adsorption and its applications. E. LEDERER (Chim. et Ind., 1935, 33, 1072—1078).—The development of the method and its application to the separation of numerous org. compounds are reviewed. R. S.

Detection of elements in organic compounds. I. Simultaneous detection of carbon, hydrogen, and mercury. II. Improved sodium fusion test for the detection of sulphur, nitrogen, iodine, bromine, and chlorine. C. L. TSENG (J. Chinese Chem. Soc., 1935, 27—32, 33—38).—I. Usual tests do not detect Hg in many org. compounds. The method recommended is to heat the compound with CuO , C and H being detected as usual, whilst the Hg is deposited on the cooler parts of the tube. This is subsequently treated with I vapour, when the Hg is converted into HgI_2 .

II. The sample is made into a pellet with excess

of lactose with addition of EtOH if necessary, and is dropped into the melted Na, which is then submitted to an exhaustive series of tests for S, N, and halogens. J. W. S.

Determination of organic halogens. I. Parr bomb method. C. L. TSENG, M. HU, and M. C. CHIANG (J. Chinese Chem. Soc., 1935, 3, 39—51).—Modified procedures are described for determination of halogens by the Parr bomb method. Solutions containing I are reduced by SO_2 before gravimetric determination as AgI . Details are given of the separation of F as CaF_2 . J. W. S.

Combination of catalysts to reduce digestion time in determination of nitrogen. I. In organic compounds. C. F. POE and M. E. NALDER (Ind. Eng. Chem. [Anal.], 1935, 7, 189).—Quickest digestion was obtained with $\text{CuSO}_4 + \text{HgO} + \text{Se}$. Addition of H_2O_2 has little effect. J. S. A.

Rapid determination of iodine value. W. RZUČIČKA (Mikrochem., 1935, 17, 215—221).—A solution of 5—10 mg. of material in EtOH or COMe_2 is treated with 2 c.c. of $0.2N\text{-I} + 20$ c.c. of H_2O . The excess of I is titrated back with $0.05N\text{-Na}_2\text{S}_2\text{O}_3$. J. S. A.

Ebulliometric determination of the degree of decomposition of an organic substance. W. SWIENTOSŁAWSKI (Nature, 1935, 135, 829).—The lowering of the b.p. of azeotropic mixtures of certain org. liquids produced by small amounts of H_2O is used as the basis of a method for determining with an accuracy of 0.001% the amounts of H_2O resulting from the partial decomp. of some org. compounds. L. S. T.

Ebulliometric determination of the amount of a substance adsorbed on the surface of solid substances. M. WOJCIECHOWSKI (Nature, 1935, 135, 830).—The principle underlying the above method has been used to investigate the amount of substances adsorbed on the surfaces of glass or of metals. At 18° , the amounts of C_6H_6 adsorbed on 1 sq. cm. of glass and Cu are 0.00026 and 0.00034 mg., respectively. L. S. T.

Determination of minimal quantities of organic matter in mixtures of gases. T. E. BREHMER (Suomen Kem., 1935, 8, B, 18—19).—The CO_2 formed by the combusted (high temp.; catalyst) material is determined. The method is applied to the determination of the v.p. of C_6H_{14} at -77° and -72° , and of PhMe at -40° to -54° , and gives vals. close to those recorded in the lit. J. L. D.

Determination of formic, acetic, propionic, and oleic acids. S. I. SUCHANOVSKI and E. V. ROGINSKAJA (Lesokhim. Prom., 1934, 3, No. 5—6, 26—29).—The mixture of acids is evaporated with PbO to separate EtCO_2H . PbSO_4 is pptd. from the filtrate with H_2SO_4 and filtered, excess of H_2SO_4 being removed with Ba(OH)_2 . The solution, containing salts of HCO_2H and AcOH , is extracted with gasoline in presence of a saturated solution of CaCl_2 and NaCl . The aq. part is neutralised and evaporated to dryness, and the residue fused with KOH and CuO for the determination of AcOH . HCO_2H is determined in a separate sample by the Skala method or by oxidising with HgO . Oleic acid is determined by difference.

CH. ABS. (e)

Detection of organic compounds by means of drop reactions. IX. Detection of acetic acid and methyl ketones by formation of indigotin. F. FEIGL, R. ZAPPERT, and S. VASQUEZ (*Mikrochem.*, 1935, 17, 165—169; cf. this vol., 507).—The solution containing AcOH is evaporated to dryness with CaCO_3 . The residue is dry-distilled, and the COMe_2 formed brought into contact with paper moistened with an alkaline solution of $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$, forming indigotin. Sensitivity 0.06 mg. of AcOH. Me ketones may be detected by warming with a drop of the same reagent and extracting with CHCl_3 . A blue coloration indicates the presence of Ac. J. S. A.

Identification of small quantities of formaldehyde. R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (*Compt. rend.*, 1935, 200, 1450—1454).— CH_2O reacts with $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ (I) and HCl at 100° to give methylenedi- β -naphthol (II), m.p. 191—195° (decomp.) (cf. A., 1893, i, 100), which with POCl_3 affords dinaphthoxanthene (*ibid.*, 222). This with Br affords a dinaphthopyrylium bromide (cf. A., 1901, i, 604), converted by HCl into the chloride, which gives a platinichloride. Thus 0.1 mg. of CH_2O at a dilution of 1:10⁵ can be pptd. and characterised microchemically by the use of the foregoing reactions. Glyoxylic acid combines with (I) and HCl more slowly than does CH_2O , and forms a compound, m.p. 215° , with cryst. properties different from those of (II).

H. G. M.

Colour test for the identification of mono-, di-, and tri-nitro-compounds. R. W. BOST and F. NICHOLSON (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 190—191).— $(\text{NO}_2)_2$ - and $(\text{NO}_2)_3$ -compounds of the C_6H_6 series give a blue and a blood-red colour, respectively, with COMe_2 -5% KOH. $(\text{NO}_2)_1$ -compounds give no coloration, nor do highly substituted derivatives.

J. L. D.

Sensitive test for *p*-phenylenediamine. O. HEIM (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 146).— $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (0.0005 mg.) with a trace of NH_2Ph in dil. $\text{AcOH-K}_2\text{S}_2\text{O}_8$ gives a blue-green colour. Aminophenols, *m*-anisidine, and *o*- and *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ do not interfere.

J. L. D.

Determination of salicylic acid. R. L. RAIGORODSIKA and E. S. BINOVA (*Farm. Zhur.*, 1934, 137—140).—The acid is determined by treatment with I and titration of the excess, or by a bromometric modification of Kolthoff's method.

CH. ABS. (e)

Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. I. Colour reaction between the phospho-18-tungstic acid reagent and thiol compounds. K. SHINOHARA (*J. Biol. Chem.*, 1935, 109, 665—679).—The effect of varying the conditions on the colorimetric determination (± 0.37 and 2%, respectively) of cysteine (> 0.0048 mg.) and $\text{SH-CH}_2\text{-CO}_2\text{H}$ by $\text{P}_2\text{O}_5(\text{WO}_3)_{18}\cdot 3\text{H}_2\text{O}$ is measured. The best results are obtained at p_H 5 (maintained by a NaOAc buffer). Excess of halides should be avoided, H_2SO_4 being used for hydrolysis of proteins or HCl being neutralised by LiOH. CN^- interferes by retarding the development of colour. H_2S may be removed in a stream of CO_2 or N_2 .

R. S. C.

Separation of large amounts of tyrosine from cystine. F. R. GREENBAUM (*Amer. J. Pharm.*, 1935, 107, 162—173).—Tyrosine is removed from aq. solution by adding NH_3 ; the cystine is then isolated by adjusting the p_H to 1.72—2.0.

E. H. S.

Determination of small amounts of pyridine in presence of nicotine and ammonia. L. BARTA (*Biochem. Z.*, 1935, 277, 412—415).—The colour developed on addition of $\text{C}_5\text{H}_5\text{N}$ (I) to a mixture of BrCN and $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ is used for the colorimetric determination of (I) down to concns. of 1 in 10⁶. A solution containing (I), nicotine (II), and NH_3 in citrate buffer (p_H 3) on steam-distillation yields only (I), which can then be determined in the distillate. (I) may be determined in (I)-(II) mixture by pptn. of (II) with silicotungstic acid, making alkaline, and distilling, the (I) content of the distillate being then obtained colorimetrically.

P. W. C.

Determination of tryptophan. T. TOMIYAMA and S. SHIGEMATSU (*Proc. Soc. Exp. Biol. Med.*, 1934, 32, 446—449).—The blue colour produced by tryptophan with HCl and Ehrlich's reagent is matched with that resulting from the reduction of phosphomolybdic acid with $\text{NH}_2\text{-C}_{10}\text{H}_6\text{-SO}_3\text{H}$ (eikonogen) and NaHSO_3 .

Microchemistry of antipyrine. M. WAGENAAR (*Pharm. Weekblad*, 1935, 72, 642—644).—Antipyrine gives characteristic ppts. or colorations with the following reagents (sensitivity given in parentheses): NaCl, HNO_3 violet (2 mg.), HCl- NaNO_2 sea-green cryst. (0.1 mg.; 1:300), $\text{K}_3\text{Fe}(\text{CN})_6$ (0.1 mg.; 1:200), $\text{K}_3\text{Fe}(\text{CN})_6$ (0.2 mg.; 1:200), Na nitroprusside and acid (0.1 mg.; 1:200), PtCl_4 (0.2 mg.; 1:200), PtCl_4 -NaI dark red crystals. Optical and crystallographic properties are given.

S. C.

Microchemical reactions on pyrimidone. M. WAGENAAR (*Pharm. Weekblad*, 1935, 72, 612—615).—Pyrimidone (I) gives characteristic cryst. ppts. with the following reagents (sensitivity given in parentheses): NaCl (0.1 mg.), KHgI_3 (0.05 mg. in concn. 1:200), KClO_3 , KI- ZnI_2 (0.2 mg.; 1:100), PtCl_4 (0.1 mg.; 1:100), $\text{AuCl}_3\text{-HNO}_3$ (0.05 mg.; 1:100), picric acid (0.1 mg.; 1:200), $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$ (0.1 mg.; 1:200), KI-I (0.02 mg.; 1:200), chinosol (II) (0.2 mg.; 1:100). (II) gives no ppt. with antipyrine (III) and may be used for detecting 1% of (I) in (III).

S. C.

Determination of pilocarpine and its salts. J. A. SANCHEZ (*Rev. Centr. Estud. Farm. Bioquim.*, 1934, 24, 48—51; *Chem. Zentr.*, 1934, ii, 3535).—The amount of alkali necessary to open the lactone ring is measured acidimetrically.

R. N. C.

Colorimetric determination of small quantities of morphine. R. HOFMANN and N. POPOVICI (*Pharm. Zentr.*, 1935, 76, 346—348).—In the absence of other reducing substances morphine (I) may be determined by addition of 2 c.c. of a solution of silicomolybdic acid to 25 c.c. of a solution of (I) (0.2—10 mg.) in 1% HCl, addition of 5 c.c. of 5% aq. NH_3 , and colorimetric comparison (yellow light filter) of the blue colour produced with that obtained from a 0.1% solution of (I) in 1% HCl. Examples are given, the error varying from 0.1 to 2%.

J. W. B.

Biochemistry.

Determination of gaseous metabolism. H. WOLLSCHITT and G. KRAMER (Arch. exp. Path. Pharm., 1935, 178, 378—389).—A modified form of Haldane apparatus and its application are described.

F. O. H.

Conditions of foetal respiration in the goat. J. BARCROFT, R. H. E. ELLIOTT, L. B. FLEXNER, F. G. HALL, W. HERKEL, E. F. MCCARTHY, T. MCCLURKIN, and M. TALAAT (J. Physiol., 1934, 83, 192—214).—The O_2 -dissociation curve for the blood of the pregnant goat moves to the right of the normal, and that of the foetus to the left, the max. divergence occurring at 18—19 weeks. The movements are due to fall of p_H in the case of the curve of the mother, and to specificity of haemoglobin in the case of that of the foetus.

R. N. C.

Methylene-blue and anoxaemia. G. CRISLER (Amer. J. Physiol., 1935, 110, 580—581).—Methylene-blue augments the symptoms of anoxaemia by formation of methaemoglobin.

R. N. C.

Arterialisation of blood. IV. Balance of oxygen tension between alveoli and blood and the diffusion constant. H. SARRE (Z. Biol., 1935, 96, 352—363; cf. this vol., 371).—The "diffusion const." of O_2 can be calc. from equations for the difference in average O_2 tension between alveolar and arterial blood and successfully applied to conditions due to incomplete balance of O_2 tension and to changes in depth of respiration or in partial pressure of O_2 .

F. O. H.

Oxygen equilibrium of haemoglobin and its structural interpretation. L. PAULING (Proc. Nat. Acad. Sci., 1935, 21, 186—191).—It is suggested that the haemoglobin mol. contains 4 interacting haem groups arranged at the corners of a square, and on this basis equations are derived each containing only 2 consts. The first represents data on O_2 equilibrium at const. p_H , the second the change in O_2 equilibrium with change in p_H .

H. T.

Haemoglobin function in the developing chick. F. G. HALL (J. Physiol., 1934, 83, 222—228).—Haemoglobin from the chick embryo has an O_2 affinity $>$ that from the mature fowl. The val. changes progressively in chicks during incubation and early growth, suggesting that embryonal haemoglobin is different from that of latter life.

R. N. C.

(A) Use of Ringer-Locke solutions containing haemoglobin as a substitute for normal blood in mammals. W. R. AMBERSON, J. FLEXNER, F. R. STEGGERDA, A. G. MULDER, M. J. TENDLER, D. S. PANKRATZ, and E. P. LAUG. (B) Oxygen consumption with haemoglobin-Ringer solution. A. G. MULDER, W. R. AMBERSON, F. R. STEGGERDA, and J. FLEXNER. (C) Influence of p_H on the elimination of haemoglobin by the perfused frog's kidney. M. D. WEBSTER, F. L. ENGEL, E. P. LAUG, and W. R. AMBERSON (J. Cell. Comp. Physiol., 1934, 5, 359—382, 383—397, 399—413).—(A) Substitution of Ringer-Locke solutions containing haemoglobin (I) permits life in animals for many hr. (I) slowly passes from blood vessels into urine and lymph. In addition

to transporting O_2 (I) produces a colloidal osmotic pressure which maintains a normal fluid balance in all tissues except kidneys.

(B) Animals surviving on (I)-Ringer-Locke solutions have a normal O_2 utilisation.

(C) Elimination of (I) from perfused frog kidney is large at p_H 5.5 and small at 7.8. In the more acid solutions there is either an increased permeability of glomerular capillaries or dissociation of (I) which acting as a cation below its isoelectric point permeates the capillary membranes more easily.

A. G. P.

Physical chemistry of proteins. XII. Solubility of human haemoglobin in concentrated salt solutions. A. A. GREEN, R. J. COHN, and M. H. BLANCHARD (J. Biol. Chem., 1935, 109, 631—634).—Horse carboxyhaemoglobin (I) is pptd. at lower ionic strengths than human (I), the vals. of β and K_s in the salting-out equation being lower. The solubility of cryst. human (I) in conc. $PO_4^{'''}$ buffers has been determined.

H. G. R.

Haemoglobin and solids of the blood of Australian aborigines and whites. H. S. H. WARDLAW, H. C. BARRY, I. W. McDONALD, and A. K. MCINTYRE (Austral. J. Exp. Biol., 1935, 13, 1—7).—Whites in central Australia and aborigines in natural surroundings showed a lower haemoglobin and total solids content than whites in Sydney. In the whites the increase of blood-solids resulting from exercise was much $>$ in the blacks.

W. O. K.

Blood-pigment. XVII. Human haemoglobins. XVIII. Globin and its haemaffinic groups. XIX. Methaemoglobin and its compounds with hydrogen peroxide, cyanides, fluorides, and sulphides. F. HAUROWITZ (Z. physiol. Chem., 1935, 232, 125—145, 146—158, 159—164; cf. A., 1931, 857, 972).—XVII. In man there are three distinct haemoglobins, foetal (I), adult (II), and muscle-haemoglobin (III) (myoglobin). The existence of a fourth special haemoglobin in pernicious anaemia is not established. The blood of new-born infants contains 70—85% of (I) and 30—15% of (II). (I) was obtained in cryst. form. The Fe content and O_2 capacity of (I) and maternal haemoglobin (IV) is the same; the O_2 affinity differs. In solution the O_2 affinity of (IV) is greater, in the intact corpuscles that of (I). (III) is not identical with any of the blood-pigments and is characterised by its high affinity for O_2 . The different vals. of O_2 affinity are caused by binding of the same haemin to different globins, or by specificity of the corpuscles in which the haemoglobin occurs.

XVIII. It is assumed that all globins have a special at. group in common which can fix O_2 reversibly. Since the isoelectric point of globin (V) (p_H 6.8—6.9) is $<$ that of methaemoglobin (VI) (p_H 7.0) in spite of the loss of 2 CO_2H from (VI) in formation of (V), the haemin-Fe of (VI) is probably bound to an acid group of (V). I-KI inhibits the power of (V) to couple with haemin more than various other reagents. This suggests a haemaffinic SH group. Most of the (V)-S is present as cystine or cysteine.

XIX. Like HCN, HI, and H_2S , H_2O , reacts quickly with brown (acid), and slowly with red (alkaline) methæmoglobin. To change the brown into the red type requires 1 mol. of H_2O_2 per Fe atom. The complex with H_2O_2 contains Fe^{III} . All the reagents affect the prosthetic group since the absorption spectrum is altered. They are presumably attached to the Fe^{III} atom. Types of co-ordination compounds are suggested for the complexes formed. J. H. B.

**Action of picric acid on globin and hæmoglo-
globin.** A. BOLLIGER and E. GOULSTON (Austral. J. Exp. Biol., 1935, 13, 23—26).—Globin picrate obtained from globin prepared by the method of Hamsik (A., 1930, 630) or directly from hæmoglobin and picric acid forms a well-defined but amorphous compound containing 25.5% of picric acid.

W. O. K.

**Hæmoglobinuria caused by injection of hæmo-
globin.** T. MINATOYA (Tohoku J. Exp. Med., 1934, 24, 11—20).—Intravenously injected globin or horse hæmoglobin is excreted in the urine of rabbits as such. Autogenous hæmoglobin was not detected.

CH. ABS. (p)

**Measuring red blood-cells with special refer-
ence to a new diffraction apparatus.** A. PILPER (Lancet, 1935, 228, 1152—1153).

L. S. T.

**Blood-proteins of children. II. Distribution
in the same specimen of blood of hydrolysable,
amide-, humin-, basic amino-, and monoamino-
nitrogen of the whole blood, red cells, and serum-
proteins.** A. BERNHARD, J. S. LEOPOLD, and I. J. DREKTER (Amer. J. Dis. Children, 1934, 48, 819—829; cf. this vol., 230).—Comparative data for children and adults are recorded.

CH. ABS. (p)

**Validity of rapid determinations of the osmotic
pressure of protein solutions.** H. S. WELLS, D. G. MILLER, jun., and B. M. DRAKE (J. Clin. Invest., 1935, 14, 1—6; cf. A., 1934, 674).—Serum is osmotically stable within the temp. range 10—37° for a sufficient time to permit determinations of osmotic pressure. Membranes previously described are completely impermeable to serum-proteins over a wide range of permeability vals.

CH. ABS. (p)

**Determination of the colloidal osmotic pressure
in blood-serum and similar fluids.** A. KEYS and H. TAYLOR (J. Biol. Chem., 1935, 109, 47—53).—A true equilibrium method and osmometer are described requiring 2 ml. of colloid solution, single determinations being obtained with 0.5 ml.

P. W. C.

**Behaviour of plasma-colloids in recovery from
brief severe work and the question as to the per-
meability of the capillaries to protein.** A. KEYS and H. TAYLOR (J. Biol. Chem., 1935, 109, 55—67).—The O_2 capacity, serum-protein, and serum colloidal osmotic pressure of the blood of normal young men before and after exercise to exhaustion in a treadmill are investigated. Although large increases in O_2 capacity and even larger increases in serum-protein were obtained, the colloid osmotic pressure generally decreased, due probably to a change in the mean size of the protein mol. From an application to the data of a method of analysis by

successive approximations, it appears that about 400 ml. of filtrate containing about 1% of protein left the blood during work and that at the same time between 5 and 20 ml. of new red cells entered the active circulation.

P. W. C.

**Solubility of plasma-proteins. II. Depend-
ence on p_H , temperature, and lipin content in
concentrated solutions of potassium phosphate.
Fractional precipitation of the proteins.** A. M. BUTLER, H. BLATT, and H. SOUTHGATE (J. Biol. Chem., 1935, 109, 755—767; cf. A., 1933, 293).—Variations in temp. (20—30°), p_H (5.4, 6.5, 7.7), or concn. of lipins do not appreciably affect the solubility of proteins (I) (from horse-plasma) in the solutions. Constituents of (I) are separated by fractional pptn. (at p_H 6.5) with the following mol. concns. of $KH_2PO_4 + K_2HPO_4$: 1.25 fibrinogen, 1.25—1.5 67% of the euglobulin (II), 1.5—2.4 30% of the (II) and 80% of the pseudoglobulin (III), 2.4—2.58 albumin (IV) and (III), 2.58—3.0 (IV).

W. McC.

**Behaviour of pathological sera in the ultra-
centrifuge.** A. S. McFARLANE (Biochem. J., 1935, 29, 1175—1201).—The results of centrifugal analysis of the proteins (I) in a wide variety of pathological sera are given, together with clinical data. The proportion of globulin to albumin in most cases is > in normal sera; this appears to be a general effect. The proportion of the third constituent X of normal sera varies more widely in these sera, and some react more readily to dilution. There is evidence of other constituents in some of the sera (malignant disease; myeloma). An unknown cause affects the sedimentation rates of the (I) in some sera; in others, there is evidence of the presence of polydisperse (I) mols.; this is associated with the presence of (I) in the urine.

F. A. A.

**Ultracentrifugal analysis of normal and patho-
logical serum fractions.** A. S. McFARLANE (Biochem. J., 1935, 29, 1209—1226).—Globulin (I) fractions, obtained from normal human and animal sera by $(NH_4)_2SO_4$ pptn., are heterogeneous, still contain-
ing albumin (II), but pathological human and anti-
diphtheritic horse sera give practically pure (I). (I) and (II), separated by cataphoresis, are nearly homo-
geneous. ψ -Globulin separated by electrodialysis
resembles (I) in mol. wt. Euglobulin appears to be
polydisperse. The new mol. species found in patho-
logical sera retain their individuality after $(NH_4)_2SO_4$
treatment.

F. A. A.

**Pectin-phenomenon of blood and its physico-
chemical basis.** W. ZIEGELMAYER (Kolloid-Z., 1935, 71, 214—230).—Addition of apple-pectin (I) to fresh equine or human blood accelerates contraction of the clot and expression of serum, which latter can then exert a similar, though weaker, action on fresh blood. The clot, in spite of greater shrinkage, is softer when formed in presence of (I) and is easily re-dispersed in H_2O . The max. effect is obtained with 10% of (I), and increases with acidity.

F. L. U.

**Vapour pressure of human blood by Hill's
thermoelectric method. Apparatus and tech-
nique.** R. W. CULBERT (J. Biol. Chem., 1935, 109, 547—563).—Hill's method is elaborated. The aver-

age val. of the v.p. of children's blood, ranging from 1 month to 12 years, is equiv. to 0.9029 ± 0.0016 g. of NaCl per 100 g. of H_2O , a significant difference being noted between the sexes. H. G. R.

Critical temperature of serum. IX. Ionic equilibrium as a function of temperature and p_H . P. L. DU NOUY and V. HAMON (Ann. Inst. Pasteur, 1935, 54, 442—460; cf. A., 1933, 293).—Normal serum (horse, sheep, ox) heated under conditions to minimise loss of CO_2 has a fairly const. p_H up to 56° ; at approx. 60° a decrease (average 0.05) occurs. When loss of CO_2 is not prevented, the val. returns to normal or even higher levels at 60 — 62° . With dil. sera, the decrease commences at approx. 55° and attains a min. at approx. 60° . With sera acidified to p_H 6.80—6.90, the decrease approaches zero, whilst at p_H 5.4 an increase (approx. 0.05 p_H) occurs. Heating to 62° does not modify the buffering power of serum. F. O. H.

Temperature of serum and Kottmann reaction. P. SIMONIN and J. R. HELLUY (Compt. rend. Soc. Biol., 1935, 118, 1554—1558).—The intensity of the Kottmann reaction in serum is not increased by heating under a layer of paraffin. R. N. C.

Nature of difference in phospholipin content of oxalated and heparinised plasma. L. H. SCHMIDT (J. Biol. Chem., 1935, 109, 449—453).—The difference in plasma-phospholipin between oxalated and heparinised blood is due to a contraction in vol. of the erythrocytes on addition of oxalate. H. D.

Colorimetric determination of small amounts of cholesterol in blood and other biological fluids. M. NORIEGA DEL AGUILA (Bol. Soc. Quim. Peru, 1935, 1, No. 3, 73—74).—0.1 c.c. of blood etc. is hydrolysed with cold 0.5% NaOH in 50% EtOH, to decompose the esters of cholesterol, which is extracted with Et_2O , and determined by means of the colour reaction with $CHCl_3$, Ac_2O , and H_2SO_4 , known solutions of cholesterol being used as standards. E. L.

Distribution of lactate between the corpuscles and the plasma in blood. S. C. DEVADATTA (Quart. J. Exp. Physiol., 1934, 24, 295—303).—The ratio, R , of lactate (I) concn. in the corpuscles to that in the plasma is 0.6—0.9 in the blood of resting animals, and 0.5—0.6 in that of fatigued animals. This change is not due to a delay in the diffusion of (I) from the plasma into the corpuscles, or to the presence, either in the corpuscles or plasma, of some indiffusible substance determined as (I). R is increased by increased partial pressure of CO_2 , by decreased partial pressure of O_2 , and by increased $[H^+]$. Hence "(I) shift" analogous to the "Cl" shift" occurs during each respiratory cycle. R is reduced by increased concn. of (I) in the whole blood. There are at least three variables which determine the distribution of (I) between the corpuscles and plasma: partial pressure of O_2 and of CO_2 and concn. of (I) in the whole blood. The increased blood-(I) level of fatigued individuals is $>$ sufficient to account for the fall of R observed in these circumstances.

NUTR. ABS. (b)

Micro-method for determination of the individual or total ketonic substances in blood.

O. CANTONI (Biochem. Z., 1935, 277, 448—450).—The method is described for the determination individually or collectively of $COMe_2$, CH_3Ac-CO_2H , and β -hydroxybutyric acid. P. W. C.

Determination of bilirubin in animal and human serum. R. HELLER (Z. ges. exp. Med., 1933, 87, 17—21; Chem. Zentr., 1934, ii, 3535).—Bilirubin (I) is not present in the blood of normal or splenectomised rabbits, guinea-pigs, or rats. The method of Ernst and Forster is untrustworthy for the determination of (I) in lipochrome-rich blood. R. N. C.

Apparatus for determination of urea in blood-serum. R. BIOT (Semana med., 1934, 41, I, 1867—1871; Chem. Zentr., 1934, ii, 3997).— N_2 is liberated by NaOBr and measured volumetrically. J. S. A.

Determination of alkali reserve, (A) by the method of Van Slyke, (B) by the method of Van Slyke and Cullen. R. A. TREULES (Semana Med., 1934, II, 913—915, 1469).—(A) Use of petrolatum to protect blood from contact with air may be omitted if the plasma is subsequently saturated with air containing 5% CO_2 or with alveolar air from the operator.

(B) If blood is taken without exposure to air the treatment with 5% CO_2 may be omitted.

CH. ABS. (p)

Clinical determination of phosphorus in blood. J. C. J. BURKENS (Nederl. Tijds. Geneesk., 1934, 78, 4944—4950; Chem. Zentr., 1935, i, 277).—A discussion, with reference to changes after sampling.

H. J. E.

Evidence of adsorption experiments on the forms of calcium and inorganic phosphorus in blood-serum. D. M. GREENBERG and C. E. LARSON (J. Biol. Chem., 1935, 109, 105—121).—Adsorption experiments with variously prepared $BaSO_4$ powders, permutit, and kaolin gave no evidence of either a citrate-like Ca compound or a specifically adsorbable Ca—P complex in blood-serum, all the characteristics attributed to these hypothetical substances being obtainable under proper conditions with merely Ca^{++} and PO_4^{---} . P. W. C.

Forms of calcium and inorganic phosphorus in human and animal sera. IV. Reply to Greenberg and Larson. H. R. BENJAMIN (J. Biol. Chem., 1935, 109, 123—129).—The statement of Greenberg and Larson (see above) that the $BaSO_4$ prep. described previously (A., 1933, 521) adsorbs Ca^{++} is rebutted on the grounds that it was impossible to remove all the Ca from a serum ultra-filtrate by repeated additions of $BaSO_4$, and the alternative theory suggested by these authors is rejected as not in accordance with facts previously described, and is not able to account for low-P rickets. The hypothesis that the adsorbable Ca is in the form of a Ca—P complex is re-affirmed. H. D.

Blood-calcium after injections of blood-serum of parathyroidectomised animals. C. Y. CHOI (J. Chosen Med. Assoc., 1934, 24, 89).—Injection of serum from parathyroidectomised animals into normal rabbits tended to decrease the blood-Ca.

NUTR. ABS. (m)

Determination of inorganic sulphate in human blood-serum. W. S. HOFFMAN and R. CARDON (J. Biol. Chem., 1935, **109**, 717—727).—The serum (4 c.c.) is freed from PO_4''' and protein by treatment with FeCl_3 in dil. HCl , aq. NH_3 , and NH_4OAc , and SO_4'' is determined by pptn. with benzidine hydrochloride in COME_2 , the benzidine sulphate being subsequently oxidised with excess of $0.1N\text{-KMnO}_4$. Excess of $0.1N\text{-Na}_2\text{C}_2\text{O}_4$ is then added and the excess titrated with $0.02N\text{-KMnO}_4$. The vals. given by other methods are 35—300% too high. Normal serum contains SO_4'' equiv. to 0.34—1.09 mg. of S per 100 c.c. The vals. agree with those of Denis (A., 1922, ii, 225). W. McC.

Determination of bromine in blood and sera. C. O. GUILLAUMIN and B. MEREJKOWSKY (Bull. Soc. Chim. biol., 1935, **17**, 485—501).—A modification of the method of Damiens (A., 1920, ii, 768) is employed for the determination of Br in 1 c.c. of serum with an accuracy of 2×10^{-6} g. The serum of normal individuals contains 8—9 mg. of Br per litre. A. L.

Results of repeated determinations of the blood-cerebrospinal fluid barrier. H. W. LOVELL and J. R. BROWN (Proc. Soc. Exp. Biol. Med., 1934, **32**, 516—520).—In patients given Br' *per os* for 5 days, a state of equilibrium is established between blood- and cerebrospinal fluid-Br' for 9 days after cessation of Br' ingestion. The permeability quotient rises with the passage of time; it does not vary widely when blood-Br' is high. R. N. C.

Clotting of blood. III. Indefinite fluidity of blood in body-vessels, and the relation between setting time and syneresis of blood clot. S. PRAKASH (Allahabad Univ. Stud., 1935, **11**, 431—442).—The fluidity of blood is maintained in the body by the const. swing between the acid and alkaline range. Syneresis is inhibited by substances which inhibit the setting. H. G. R.

Calcium metabolism in the first phase of blood-clotting. I. Action of oxalate in the second phase of blood-clotting. H. SCHEURING (Biochem. Z., 1935, **277**, 437—447).—Thrombin (I) is a colloidal Ca compound, and during its formation in serum Ca is converted from the ionised into the colloidal condition. $\text{H}_2\text{C}_2\text{O}_4$ thus has a double action, inhibiting (I) formation by Ca pptn. and leading to the degradation of formed (I) by Ca removal. P. W. C.

Effect of nicotine on the blood-coagulation time in rabbits. S. KANOWOKA (Tohoku J. Exp. Med., 1934, **24**, 307—312).—The effect was variable and not influenced by loss of the adrenaline-secreting mechanism. CH. ABS. (p)

Variations in the time of coagulation [of blood] by X-rays. R. REDING (Compt. rend. Soc. Biol., 1935, **119**, 342—344).—Irradiation by X-rays is followed by an immediate retardation of the coagulation of the blood, which then develops into an acceleration and finally a further retardation. This is most pronounced in cases of cancer. H. G. R.

Hæmolysis by solanine and cholesterologenesis, studied *in vitro*. V. DE LAVERGNE and P. KISSEL

(Compt. rend. Soc. Biol., 1935, **118**, 1551—1552).—Cholesterol liberation during hæmolysis by solanine is masked by its pptn. owing to the low p_H of the solution. R. N. C.

Hæmolysis by saponin and cholesterologenesis, studied *in vitro*. V. DE LAVERGNE and P. KISSEL (Compt. rend. Soc. Biol., 1935, **118**, 1553—1554).—Neutral or alkaline saponin solution causes liberation of cholesterol (I) during hæmolysis similar to that caused by H_2O , but < that from the action of hæmolysins. In acid solution (I) is pptd. as it appears. R. N. C.

Hæmolytic action of lecithins. B. S. LEVIN (Compt. rend. Soc. Biol., 1935, **119**, 80—82).—The hæmolytic action of pure, freshly-prepared lecithins is effective at greater dilutions than the anti-hæmolytic action. The anti-hæmolytic action of commercial lecithins is masked by the hæmolytic action of the impurities present. R. N. C.

Kinetics of hæmolytic systems. VII. Disappearance of lysin during stromatolysis. E. PONDER (Biochem. J., 1935, **29**, 1263—1272; cf. A., 1934, 1380).—The reaction of saponin (I) with erythrocyte stroma is completed before either of the components of the reaction is used up; the final amount of (I) is a linear function of its initial concn. The curves of reaction are not described by the ordinary kinetic equations and it is concluded that the velocity coeff. varies. The quantity of (I) disappearing for a given quantity of stroma and that used up by stroma for complete hæmolysis of an equiv. amount of erythrocytes are independent of temp. H. D.

Hæmolysing action of the smokes of tobacco and other plant products on the blood *in vitro*. F. BATTELLI, D. ZIMMET, and P. GAZEL (Arch. Sci. phys. nat., 1934, **16**, Suppl., 185—186).—Tobacco smoke hæmolyses the blood of animals and men *in vitro* to an irregular extent. All other plant smokes examined had the same effect. H. D.

Anti-hæmolytic action of liver extract. E. ROSENTHAL and J. PATAI (Z. klin. Med., 1934, **127**, 284—285; Chem. Zentr., 1934, ii, 3975).—Liver extract inhibits hæmolysis of red corpuscles by NHPh-NH_2 , the action being due to its hypotonic character. R. N. C.

Viscosity and precipitation [in immune sera]. M. COPPO (Compt. rend. Soc. Biol., 1935, **119**, 175—177).—The antibody content of an immune serum rises as the quantity of antigen required to produce max. η falls. Max. η is higher for sera pptd. at higher dilutions. The rate of increase \propto the antibody content. For each antibody concn. there is a corresponding antigen concn. that gives a min. val. of η . R. N. C.

Serological studies of azo-proteins. Antigen-containing azo-compounds with aliphatic side-chains. K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1934, **59**, 751—768).—Notable specificity is exhibited in the reactions of short-chain compounds containing CO_2H . Succinic acid can be differentiated from malonic or glutaric acid. Reactions of compounds with longer chains, although sp.

to a certain extent, depend mainly on the physico-chemical properties of long aliphatic chains. The influence of halogen, OH, and NH_2 groups on serological specificity is examined. Inhibition reactions permit observation of the specificity of *cis-trans*-isomerides.

CH. ABS. (p)

Serological specificity of peptides. II. K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1934, 59, 769—780; cf. A., 1932, 957).—When examined by inhibition reactions immune sera exhibited high specificity and permitted distinction between peptides of similar structure.

CH. ABS. (p)

Action of temperature and adsorption on the elements controlling the reactions of flocculation and deviation of the complement. R. D. DE LA RIVIERE and N. KOSOVITCH (Compt. rend. Soc. Biol., 1935, 119, 42—43).—Successive rapid chilling and heating of the antigen-antibody flocculate causes it to dissociate, and also produces deviation of the complement, neither of these reactions being produced by either chilling or heating alone. The antibodies of heated serum are not adsorbed by kaolin or C, both of which, however, adsorb them from active serum, and also the substances controlling the Wassermann reaction from syphilitic serum if they have previously been in contact with the antigen.

R. N. C.

Vitamin-C and alexin. E. HARDE and A. E. THOMSON (Compt. rend., 1935, 200, 1425—1427).—Evidence is adduced in favour of alexin being a compound of ascorbic acid and proteins and, possibly, of lipins.

H. W.

Contractile factors of the chromosome micelle. D. M. WRINCH (Nature, 1935, 135, 788—789; cf. this vol., 231).—A discussion of the contractile factors which this micelle may be expected to possess. They include attraction between acidic and basic groups, variation in the no. of such groups within the mol. due to changes in p_H , and intramol. folding as in keratin.

L. S. T.

Carnosine and anserine in mammalian skeletal muscle. W. A. WOLFF and D. W. WILSON (J. Biol. Chem., 1935, 109, 565—571).—Both carnosine and anserine (I) are present in the muscle of the dog, cat, deer, gnu, and opossum. (I) has been isolated from the llama.

H. G. R.

Glyoxalines of some foodstuffs. M. LOEPER, A. LESURE, and A. MOUGEOT (Compt. rend. Soc. Biol., 1935, 119, 173—175).—The glyoxaline (I) contents of a no. of foodstuffs of animal origin are given. (I) is higher in prepared than in fresh foods.

R. N. C.

Lipochromes of marine animals. V. Astacene from fish-livers. N. A. SØRENSEN (Tids. Kjem., 1935, 15, 12—13).—Astacene was isolated from the liver oil of *Regalecus glesne* and *Lophius piscatorius* (cf. A., 1934, 1246).

F. O. H.

Body-oil of "Aburazame" (*Squalus sucklii*, Girard). M. TSUJIMOTO (Fettechem. Umschau, 1935, 42, 69—70).—Samples (A, B) of pale oil, each obtained by boiling out the mixed body-flesh of two fishes (one male and one female) had respectively: d_4^{25} —, 0.9163; n_D^{20} 1.4800, 1.4760; acid val. 3.16, 0.84;

sap. val. 178.1, 167.3; I val. (Wijs) 173.7, 167.8; unsaponifiable matter 4.87, 8.20. The respective fatty acids had m.p. 33°, 33—34°; neutralisation val. 192.2, 188.3; I val. 187.1, 178.1; Et_2O -insol. bromides 63.5%, 53.9% (Br content of 71.27%). Me ester fractionation indicated that the bulk of the acids from (B) were C_{18} to C_{22} acids, the bulk of the C_{20-22} acids being highly unsaturated; C_{16} acids occur in small amount, and only very little, if any, acids below C_{16} were present. The unsaponifiable matter (m.p. 37—38°) included batyl and selachyl alcohols, and (?) small amounts of chimyl and more unsaturated alcohols. The characteristics of the liver oils (sap. val. 161.2—168.9, I val. 122—137.9, unsaponifiable matter 9.8—16.23%) from the four fishes are also detailed separately. No oil could be separated from the flesh of *Centroscyllium ritleri*, Jordan and Fowler ("Korokozamé").

E. L.

Seasonal variations of fats in the organisms of *Pyrhocoris apterus*. C. MACIUCA (Compt. rend. Soc. Biol., 1935, 119, 224—225).—Fat is max. in autumn and min. in spring, i.e., three months later than the corresponding max. and min. for glucose and glycogen.

R. N. C.

Compounds between muscle-proteins and dextrans. IV. Polysaccharoproteins. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1935, 277, 1—14).—Myosin (I) gives both irreversible and reversible complex compounds with dextrin (II). The influence of the method of prep. of (I), the purity and concn. of (I), the p_H and the concn. of (II) on the formation of these complex compounds is investigated.

P. W. C.

Chemical groups of protein which possess affinity for polysaccharides. Experiments with organic solvents. S. J. VON PRZYŁECKI and H. RAFAŁOWSKA (Biochem. Z., 1935, 277, 416—419).—The adsorbability of P-free dextrin at the H_2O -solvent interface (16 org. solvents little sol. in H_2O and possessing groupings known to be present in the protein chain were used) was determined, and it was found that in the formation of complexes resembling the polysaccharoproteins the NH_2 -group was especially important.

P. W. C.

Polysaccharoclupeins. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1935, 277, 420—423).—When 1% solutions of clupein are mixed with solutions of starch, glycogen, or dextrin and the p_H is suitably adjusted, a ppt. of the polysaccharoprotein is obtained, neither solution individually giving a ppt. at this p_H . Sucrose and raffinose do not give these ppts. The NH_2 -groups of the arginine of clupein are probably used in forming these complexes.

P. W. C.

Dextrino-guanidine. S. J. VON PRZYŁECKI and H. RAFAŁOWSKA (Biochem. Z., 1935, 277, 424—425).—Guanidine forms complex compounds with dextrin and starch, but not with sucrose or raffinose.

P. W. C.

Chemical and histological studies of bones and teeth of new-born infants. K. U. TOVERUD and G. TOVERUD (Acta paediat., 1933, 16, 459—467).—The average Ca content of the ash of the parietal bone

of full-term infants of mothers on average good diet during pregnancy was 39.74% as against 38.43% for infants of mothers on deficient diet. Similar but smaller differences were obtained for the ribs. For premature infants all figures were lower but the same difference was noted. The ash-P did not reflect the dietary difference. A bone with low ash and low Ca from birth is probably more disposed to the development of a rachitic or osteoporotic process during deficient post-natal feeding than a normal bone.

NUTR. ABS. (b)

Muscle-potassium in man. A. LEULIER, B. POMMÉ, and A. BERNARD (Compt. rend. Soc. Biol., 1935, 119, 201—202).—Vals. are given for the K of the various muscles in amputated legs. R. N. C.

Copper content of human and animal organs. W. GERLACH (Virchow's Archiv, 1934, 294, 171—197).—The Cu content of human liver is 0.003—0.013 mg. per g. of fresh tissue (average 0.0075 mg.). The vals. for foetal livers are 0.015—0.25 mg. (average 0.0679 mg.), with no definite parallelism between age and Cu content. In and at the end of pregnancy there is no relationship between Cu of the foetal livers and the no. and development of blood-forming foci. In the 1st year of life Cu of livers progressively diminishes, being about 0.02 mg. at the end of the 1st year, and between 5 and 15 years the normal level for adults is reached. Between the ages of 5 months and 80 years there is no evidence of sex differentiation. The average Cu content of placenta from normal or still births is 0.0032 mg. per g. In cirrhosis of livers the average Cu is 0.0383 mg. and in typical Laennec cirrhosis normal to 0.18 mg. Vals. are given for livers from other diseases. The spleen is poor in Cu, vals. for ages from 5 foetal months upwards being 0.0001—0.010 mg. (average 0.0026 mg.). No very high vals. are found and there is no definite relationship between the Cu content of the spleen and that of the liver, although the val. for spleen is higher in cases of cirrhosis. The average Cu of the lungs is 0.0025 mg. and of the kidneys 0.00298 mg. The vals. for heart, brain, pancreas, skin, and bones are 0.001—0.006 mg. In adult eyes the vals. are 0.0004—0.0166 mg. and in foetal eyes 0.00022—0.0277 mg. Vals. are given for Cu content of liver, spleen, kidney, and lung of animals of different species suffering from different diseases.

NUTR. ABS. (m)

Occurrence of strontium and barium in human organs and excreta. W. GERLACH and R. MÜLLER (Virchow's Archiv, 1934, 294, 210—212).—Samples of bones and of different organs from 63 cases, varying in age from foetus to old age, were examined spectroscopically and Sr was invariably detected. The amount varied with the Ca content of the tissues, and was between 0.01 and 0.1×10^{-6} per g. fresh substance. Ba could not be detected in human bones. Similar results were obtained with a no. of bones from animals, wild and domesticated. The relationship of Ba to Ca in faeces is very variable.

NUTR. ABS. (b)

Osmotic pressure of fixing solutions. J. Z. YOUNG (Nature, 1935, 135, 823—824).—With marine animals, fixatives should be made up in salt solutions similar to those found in the animal's blood to prevent

distortion or bursting of the cells through the entrance of H_2O .

L. S. T.

Colouring matter of the domestic cocoon. VII. Colouring matter of the green cocoon, *Bombyx mori*, var. *Seihaku*. VIII. Quercetin glucoside from mulberry leaves. M. OKU (J. Agric. Chem. Soc. Japan, 1934, 10, 1014—1028, 1029—1038; cf. A., 1934, 204).—VII. The green cocoon (2.5 kg.) was extracted with 70% EtOH, and EtOH was expelled from the extract. The Et₂O extraction of the residue gave a flavone-like substance, in addition to bombilupsol. An orange ppt., obtained with Pb(OAc)₂ from the Et₂O-insol. part, was decomposed with 7% HCl, and the filtrate neutralised with NaOH; it gave a yellow ppt. (11.4 g.) of bombycin, which was hydrolysed by 5% H₂SO₄ to mol. proportions of glucose, aglucone, and bombycetin, C₂₀H₁₉NO₇ (I), a yellowish-brown powder, m.p. 170—180°. The absorption spectrum of (I) resembles that of quercetin.

VIII. Mulberry leaves were extracted with 80% EtOH, the chloroplast pigments were removed with Et₂O, Pb(OAc)₂ was added to the aq. solution. From the yellow ppt., isoquercitrin, m.p. 220—221°, was isolated in a yield, based on air-dried leaves, of approx. 0.05%.

CH. ABS. (e)

Behaviour of aqueous solution of the domestic cocoon. XX. Resistance of sericin to alkali. H. KANEKO and Y. NAKAZAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 997—1000; cf. this vol., 511).—The aq. solution of sericin (I) was heated under reflux. To 10 c.c. of (I) were added 5 c.c. of 0.4M-CuCl₂ and 4 c.c. of 10N-NaOH, the solution being diluted to 50 c.c. and filtered. 10 c.c. of the filtrate were acidified with AcOH and titrated iodometrically. Sericin-A was more resistant to alkali than sericin-B.

CH. ABS. (e)

Antigenic differences between the venoms of the tiger-snake *Notechis scutatis* and the black tiger-snake *Notechis scutatis*, var. *niger*. C. H. KELLAWAY and F. E. WILLIAMS (Austral. J. Exp. Biol., 1935, 13, 17—21).—The thrombin-free venoms of the tiger-snake and the black tiger-snake differ in their antigenic and immunological properties, but not sufficiently to justify their separation into two distinct species.

W. O. K.

p_H and acid-neutralising power of saliva. B. C. SOYENKOFF and C. F. HINCK, jun. (J. Biol. Chem., 1935, 109, 467—475).—Ordinary human saliva had p_H 6.64; that stimulated by paraffin had p_H 7.13. The titration curve of the former showed buffering above p_H 4.

H. D.

Galactose in the thoracic lymph of the dog. M. FAY and P. S. WHARTON (J. Biol. Chem., 1935, 109, 695—701).—Injection of galactose (I) into the duodenum results in the appearance of (I) in the blood and thoracic lymph, the proportion which appears increasing with the rate of absorption of (I), but < 0.5% of the (I) is absorbed by way of the thoracic duct. During the absorption the concn. of (I) in thoracic lymph is > in femoral blood. Blood-glucose usually increases, but sometimes decreases, following injection of (I).

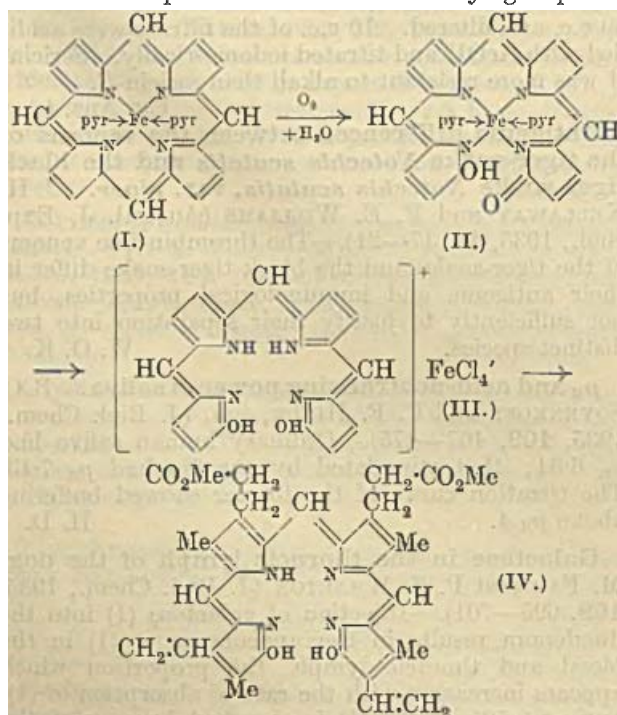
W. McC.

Composition of pure gastric juice. F. HOLLANDER (Amer. J. Digest. Dis. Nutrition, 1934, 1, 319—329).—A review. CH. ABS. (p)

Gastric acidity as influenced by pyloric closure and stenosis. R. ELMAN and C. T. ECKERT (Arch. Surg., 1934, 29, 1039—1046).—Pyloric stenosis leads to high gastric acidity and interference with the normal neutralisation of acids produced in the stomach. Closure of the pylorus delays neutralisation, which is re-established on opening. CH. ABS. (p)

Inhibition of gastric secretion by oil of peppermint. H. NECHELES and J. MEYER (Amer. J. Physiol., 1935, 110, 686—691).—Oil of peppermint applied locally to secreting mucosa causes a suppression of acid flow which is not associated with any relative increase in buffer activity. R. N. C.

Transformation of hæmin into bile-pigments. R. LEMBERG (Biochem. J., 1935, 29, 1322—1336).—The "green hæmins" prepared by oxidation of pyridinehæmochromogen (I) (Warburg and Negelein, A., 1930, 1199), for which the name verdohæmochromogen (II) is now suggested, are not related to the chlorophyll-hæmins, but are characterised as pyridinehæmochromogens of isobiliverdin. The compound is formed by oxidative scission of the porphyrin nucleus of the hæmochromogen. The "green ester" of Warburg and Negelein is identified as the ferri-chloride of biliverdin Me₂ ester (III), which is transformed into the biliverdin ester (IV) and identified by m.p. and mixed m.p. with an authentic specimen from gall-stone bilirubin. Mesohæmin gives a similar series of compounds in which the vinyl groups are



replaced by Et. It is suggested that the formation of bile-pigments in the animal body proceeds similarly, yielding biliverdin (dehydrobilirubin) which is later reduced to bilirubin, and that the unsaturated

side-chains of bilirubin and biliverdin are vinyl groups as in hæmin.

P. W. C.

Oxidase system of milk and cytochrome. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, 119, 337—339).—Previous conclusions that the enzymic and oxidising systems of raw, fresh milk consist of dehydrogenases and oxidases activating mol. O₂ are confirmed. H. G. R.

Relation of the reductase test to the bacterial content of milk. J. MÜLLER (Z. Fleisch- u. Milchhyg., 1934, 45, 85—87; Chem. Zentr., 1935, i, 493).—The influence of bacteria on the reductase test is so marked as to render it valueless by itself.

H. N. R.

Relation between quantity and fat content of milk. B. VON H. SZABO (Mezög.-Kutat., 1934, 7, 180—185; Chem. Zentr., 1935, i, 493).—There is a linear relationship between quantity and fat content of cows' milk; an increase of 0.25% in fat corresponds with an annual decrease of 300 kg. in quantity. Improved feeding may cause a considerable increase in quantity but affects fat content only slightly. Milk-secretion is controlled mainly by the activity of the gland cells; increased activity increasing their permeability and hence the H₂O content of the milk.

H. N. R.

Influence of soya-bean cake on milk production and the quality of butter. E. TAKAHASHI, K. IGUCHI, K. MITAMURA, and K. SHIRAHAMA (Pub. S. Manchuria Railway Co., 1934, 66 pp.).—Soya-bean cake fed to stock at the rate of 20, 35, and 50% of the production ration (calc. on the Hansson standard) caused progressive increase in milk yield and no ill effects on quality of milk or health of the cow, but at the highest level the butter was too soft.

NUTR. ABS. (b)

Passage into milk of some diffusible substances (urea, sodium chloride, methylene-blue). E. LESNÉ, G. DREYFUS-SÉE, and LARDÉ (Acta pædiat., 1933, 16, 539—541).—No evidence was obtained of the passage into human milk of substances such as urea or NaCl when consumed in excess or of methylene-blue when given to the extent of 0.15 g.

NUTR. ABS. (b)

Factors influencing the utilisation of cow's milk. J. H. HESS, H. G. PONCHER, and J. WOODWARD (Amer. J. Dis. Children, 1934, 48, 1058—1071).—Milk treated by a process of base exchange (B., 1934, 39) retains sufficient Ca and P to maintain positive Ca and P balances in growing infants receiving 100 c.c. of milk per kg. body-wt. per day. The increased efficiency of utilisation of treated milk is due to the increased proportion of ultra-filterable Ca, greater ash alkalinity, and the formation of a fine flocculent curd by the action of rennin.

CH. ABS. (p)

p_H of the contents of the duodenum. G. LOEWY (Compt. rend. Soc. Biol., 1935, 119, 286—287).—After a meal, the p_H of the duodenal contents of the dog varies between 4.69 and 6.25. H. G. R.

Urinary protein. C. A. SAGASTUME and R. A. CRESPI GHERZI (Rev. Fac. Cienc. quim., La Plata, 1934, 9, 49—57).—Sulphosalicylic acid is at least as sensitive as CCl₃-CO₂H or HNO₃ in detecting protein-

uria, and has the advantage that it less readily forms a ppt. with mucin. F. A. A.

Behaviour of urinary proteins in the ultra-centrifuge. A. S. McFARLANE (Biochem. J., 1935, 29, 1202—1208).—An indication, similar to that found in the sera (cf. this vol., 879), of a polydisperse albumin fraction was found in the urinary protein from 5 patients. Globulin, although high in the sera, was absent from 3 of the urines. F. A. A.

High porphyrin excretion in the new-born: theory of hæmatogenous nature of icterus neonatorum. L. HEROLD (Arch. Gynakol., 1934, 158, 213—215).—A high excretion of porphyrin was found from the 2nd to the 6th day after birth, with a max. of about 8×10^{-6} g. per day. This is attributed to hæmoglobin destruction. NUTR. ABS. (b)

Calcium and ammonium excretion in urine of rabbits. M. A. LOGAN (J. Biol. Chem., 1935, 109, 481—487).—Unlike the cat, the rabbit excretes more Ca^{++} than normal during fasting; this increase is depressed by feeding NaHCO_3 and accentuated by feeding NH_4Cl . In the latter case the extra Ca^{++} appears to be excreted at the expense of skeletal tissue, although an equiv. amount of P is not excreted. H. D.

Presence in egg-white and in rice-polishing concentrate, low in vitamin- B_2 , of an anti-pernicious anæmia principle. D. K. MILLER and C. P. RHOADS (New England J. Med., 1934, 211, 921—924).—The thermostable dietary factor which, together with the heat-labile enzyme present in gastric secretion, is required for normal hæmatopoiesis occurs in egg-white and concentrates from rice polishings. The identity or otherwise of this factor with vitamin- B_2 is unproved. CH. ABS. (p)

Chemical composition of liver preparations. J. ERDOS (Biochem. Z., 1935, 277, 337—341).—A method is described for the separation of an active antianæmic prep. from liver, the active principle being pptd. as the Ag salt, analysis of which corresponds with $\text{C}_{650}\text{H}_{720}\text{O}_{36}\text{N}_{30}\text{S}_3\text{P}_2\text{Ag}_3$. The mol. contains 6 free NH_2 -groups and on hydrolysis 18 further NH_2 are liberated. P. W. C.

Evaluation of liver and stomach preparations. J. ERDOS (Biochem. Z., 1935, 277, 342—348).—The max. decrease in erythrocyte count in dogs after injection of $\text{NHPh}\cdot\text{NH}_2$ occurs after 48—72 hr., whereas if antianæmic preps. are first administered (orally or subcutaneously) the max. decrease occurs 48 hr. later still. P. W. C.

Nature of hæmatopoietic substance occurring in liver. H. D. DAKIN and R. WEST (J. Biol. Chem., 1935, 109, 489—522).—Commercial liver extract is pptd. with $\text{Ca}(\text{OAc})_2$ in 75% EtOH and the filtrate is pptd. with Reinecke acid, which is removed from an EtOH solution of the ppt. as its NPhMe_2 salt, and the active material is salted out repeatedly with $(\text{NH}_4)_2\text{SO}_4$. From an aq. solution of the ppt. further purification is achieved by pptn. with MgSO_4 and NaCl, Reinecke, picric, or flavianic acid. The purified product (I) is approx. 1% of the liver extract. On hydrolysis with 20% HCl it yields histidine < 0.1%, arginine 14%, lysine 5%, leucine 15%,

hydroxyproline 10%, monoaminodicarboxylic acids 41—45%, glycine 5%. The NH_2 -hexose (II) present is not isolated by pptn. with $\text{Hg}(\text{OAc})_2$; the Elson-Morgan determination of glucosamine (A., 1934, 175) is tentatively adapted to its determination and gives a val. of 15%. Phenylglucosazone is obtained from (II); $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ gave no osazone either before or after hydrolysis. No purine bases were present in the hydrolytic products of (I). Peptic digestion of (I) was slight, whilst that by erepsin was almost complete. H. D.

Antitryptic activity of synovial fluid in patients with various types of arthritis. W. F. HOLMES, jun., C. S. KEEFER, and W. K. MYERS (J. Clin. Invest., 1935, 14, 124—130).—Synovial fluid contains antitrypsin. It may be extracted with CHCl_3 , and is reduced in quantity when there are a large no. of cells. CH. ABS. (p)

Inhibition of tryptic digestion of cartilage by synovial fluid from patients with various types of arthritis. C. S. KEEFER, W. F. HOLMES, jun., and W. K. MYERS (J. Clin. Invest., 1935, 14, 131—135).—Synovial antitrypsin probably limits the destruction of cartilage by the enzymes of purulent exudates. CH. ABS. (p)

Significance of concentration and dilution tests in Bright's disease. A. S. ALVING and D. D. VAN SLYKE (J. Clin. Invest., 1934, 13, 969—998).—The d of urine is examined in relation to urea clearance and the interpretation of concn. and dilution tests. The principal factor in determining d is the concn. of mineral salts. CH. ABS. (p)

Calcinosis. W. D. W. BROOKS (Quart. J. Med., 1934, 3, 293—319).—In a case of severe generalised calcinosis (girl aged 15 years) serum-Ca was 12.2 mg., plasma-inorg. PO_4^{---} 7.7 mg. per 100 ml., and phosphatase 0.33 unit. All the bones showed diminished Ca. There was increased retention of both Ca and P. Treatment with Na_2HPO_4 resulted in equilibrium in Ca metabolism, reduction of blood-Ca, and mobilisation of abnormal Ca deposits. NUTR. ABS. (m)

Glycolysis in cancer tissue. I. C. FRISCH and R. WILLHEIM (Biochem. Z., 1935, 277, 148—151).—Glycolysis inhibited by addition of benzoquinone becomes again evident on adding boiled juice of mouse-carcinoma tissue. P. W. C.

Properties of the causative agent of a chicken tumour. X. Chemical properties of chicken tumour extracts. XI. Composition of extracts containing the active principle. A. CLAUDE (J. Exp. Med., 1935, 61, 27—40, 41—57).—A protein and a phospholipin are the principal constituents of the active material. CH. ABS. (p)

Effect of active gonadotropic substances from pregnancy urine on collum carcinoma. E. STOCKL (Z. Krebsforsch., 1934, 41, 292—301; Chem. Zentr., 1935, i, 263).—Injection of "pregnyl" (I) in carcinomatous women does not increase excretion of gonadotropic substances or of hormones in the urine. Very high doses of (I) increase growth of connective tissues and inhibit tumour growth. Genital bleeding is favourably influenced. R. N. C.

Effect of anterior pituitary and pineal hormones on the growth of inoculation tumours. P. ENGEL (Z. Krebsforsch., 1934, 41, 281—291; Chem. Zentr., 1935, i, 264).—Growth of inoculation tumours in mice is increased by the growth hormone of the anterior pituitary; the effect is abolished by pineal extract. Growth is inhibited by this extract or the gonadotropic pituitary hormone, the effects of which are additive when they are injected together. Mouse sarcoma is less easily influenced by hormones than mouse carcinoma. R. N. C.

Carcinogenic action of synthetic 1:2-benzpyrene. P. RONDINI and A. CORBELLINI (Atti R. Accad. Lincei, 1935, [vi], 21, 128—133).—1:2-Benzpyrene, made by a modification of Cook and Hewett's method (A., 1933, 601), is one of the most powerful carcinogenic agents when administered externally or subcutaneously to rats and mice. T. H. P.

Tumour-growth inhibiting factor from normal human connective tissue. J. J. MORTON and D. N. BEERS (J. Exp. Med., 1935, 61, 59—66).—Active material occurs in extracts of fresh connective tissue (rectus sheath) but not of muscle. CH. ABS. (p)

Ætiology of convulsions in early infancy. S. GRAHAM (Acta pædiat., 1933, 16, 572—579).—There is a greater incidence of infantile convulsions in the winter and spring months; serum-Ca is frequently reduced but Ca × P is rarely < 30. Administration of CaCl₂ is often successful. NUTR. ABS. (b)

Cystinuria. III. Metabolism of serine. E. BRAND and G. F. CAHILL (J. Biol. Chem., 1935, 109, 545—546).—Cystine excretion in cystinuria is unchanged by feeding *dl*-serine alone or with *l*-cystine. H. G. R.

Composition of serum-proteins in Bence-Jones albuminuria. K. LANG (Arch. exp. Path. Pharm., 1935, 178, 372—377).—Bence-Jones protein (I) is rich in tyrosine (II) (8.21%) and tryptophan (III) (3.60%) but poor in histidine (0.30%). The corresponding serum-proteins (euglobulin, pseudoglobulin, albumin-I, but not albumin-II) differ considerably from the normal in their composition in that they approach (I), i.e., have a high content of (II) and (III). F. O. H.

[Composition of] Bence-Jones protein. H. O. CALVERY and R. H. FREYBURG (J. Biol. Chem., 1935, 109, 739—743).—The ash, H₂O, total N, NH₂-N, P (nil), S, amido-N, humin-N (nil), tyrosine, tryptophan, cystine, arginine, lysine, aspartic and glutamic acid contents of two samples of the protein (from the same patient) are given. Some of the vals. are very close to those for serum-globulin. W. McC.

Factors determining the effect of exercise on blood-sugar in the diabetic. R. RICHARDSON and A. L. CASE (J. Clin. Invest., 1934, 13, 949—961). CH. ABS. (p)

Eczema and the hydrogen-ion concentration in blood-plasma. K. EDEL (Nederl. Tijds. Geneesk., 1934, 78, 3673).—In patients suffering from eczema the *p*_H of the blood-plasma varies from 7.15 to 7.45. There is no correlation between degree of *p*_H disturbance and intensity of disease. Changing the *p*_H

by feeding K Na tartrate or H₃PO₄ does not influence rate of recovery. NUTR. ABS. (m)

Effect of muscular work on metabolism in diseases of the extrapyramidal system. I. Effect on lactic acid metabolism. II. Effect on gas metabolism. H. SUGIMOTO and T. MIYAMOTO. III. Effect on colloid osmotic pressure of the blood. T. MIYAMOTO and H. SUGIMOTO (Tôhoku J. Exp. Med., 1934, 24, 215—224, 225—237, 238—248).—I. Blood-lactic acid is approx. 30% > normal in cases of disease. The increase following muscular work is accentuated and the return to normal is prolonged. Treatment with atropine and harmine causes a return, in these factors, towards normal.

II. Basal metabolism is only slightly increased. Variations in O₂ consumption, O₂ deficit, and R.Q. during exercise are examined.

III. Serum-protein concn., colloid osmotic pressure, and pressure per unit serum-protein are normal in diseased patients. The increase in all vals. after work is > normal and the return to original levels is prolonged. CH. ABS. (p)

Excretion of creatine substances in fever. F. LIEBEN and E. ASRIEL (Biochem. Z., 1935, 277, 159—164).—The excretion of creatine (I) by rabbits after injection of 2:4-dinitrophenol without and with subcutaneous injection of (I) and administration of arginine, histidine (II), and glycine (III) is investigated. In this type of fever, excretion of (I) is increased, the excretion quotient after administration of (I) is decreased, and after (II) and (III) both total (I) and urinary (I) are increased. P. W. C.

Phosphate and creatine metabolism in fever. W. W. PAYNE (Biochem. J., 1935, 29, 1310—1317).—In cases of juvenile general paralysis undergoing malaria treatment, the following changes occur. During rise of temp. the PO₄^{'''}, creatine (I), and creatinine in the blood decrease and the PO₄^{'''} and (I) in urine may even disappear. The reverse change occurs as the temp. falls. When the fever is stopped by administration of quinine, the blood-PO₄^{'''} and (I) decrease. The renal threshold for PO₄^{'''} in children appears to be between 1.8 and 3.2 mg. per 100 ml., but no evidence of a threshold for (I) was obtained. It is suggested that during rise of temp. a rapid breakdown of phosphagen and formation of hexose phosphate occur in muscle, the process being reversed when the temp. falls. P. W. C.

Chemical nature of the so-called syphilis antigen. Animal immunisation experiments. T. RÓNAI (Z. Immunitats., 1932, 75, 125—142).—The Kiss cholesterol-free phosphatide prep., coupled with pigs' serum, produces *in vivo* antisera which react with immunising preps. and with cholesterol-containing heart extract. The reactivity to syphilis serum and the antibody-producing power are removed by preliminary adsorption with Al(OH)₃. Sera of rabbits immunised with the Kiss prep., but not the Al(OH)₃-adsorbed extracts, react with these extracts. R. N. C.

Orientation and pyroelectricity of crystals of magnesium ammonium phosphates in gallstones.—See this vol., 811.

Behaviour of blood-choline in pallid and florid hypertension. Chemical method of determination of choline in small quantities of blood. H. BOHN, W. SCHLAPP, and K. STERN (Z. klin. Med., 1934, 127, 226—232; Chem. Zentr., 1934, ii, 3534—3535).—Blood-choline is depressed in hypertension the depression in pallid being > that in florid hypertension. Choline is extracted by diluting with EtOH, removing any ppt., concn., and dialysis into H₂O; it is then determined by the method of the Roman. R. N. C.

Determination of pressor substances in blood in pallid hypertension. H. BOHN and W. SCHLAPP (Z. klin. Med., 1934, 127, 233—242; Chem. Zentr., 1934, ii, 3535).—The pressor substances are extracted by adding the blood to 5 vols. of EtOH, decanting after 2 hr., evaporating the EtOH at 37°, and repeated pptn. from EtOH until the solution is protein-free. R. N. C.

Effect on renal efficiency of lowering arterial blood-pressure in cases of essential hypertension and nephritis. I. H. PAGE (J. Clin. Invest., 1934, 13, 909—915).—Reduction of blood-pressure by NaSCN, by colloidal S, or spontaneously did not affect the efficiency of kidneys. CHEM. ABS. (p)

Protein content of subcutaneous oedema fluid in heart disease. R. G. BRAMKAMP (J. Clin. Invest., 1935, 14, 34—36).—The protein content of the fluid in cases of congestive heart failure varied from 0.03 to 0.54%. CH. ABS. (p)

Idiopathic hyperproteinæmia. C. L. COPE and H. K. GOADBY (Lancet, 1935, 228, 1038—1040).—A case of generalised oedema in an otherwise healthy man, due to low plasma-protein concn., is described. L. S. T.

Mandelic acid in the treatment of urinary infections. M. L. ROSENHEIM (Lancet, 1935, 228, 1032—1037).—The bacteriostatic powers *in vitro* of a no. of org. acids on the growth of *B. coli* have been compared with that of β -hydroxybutyric acid (I). Benzoylactic acid had the greatest effect, whilst β -hydroxypropionic and lævulic acids were satisfactory. Mandelic acid compares favourably with (I), is non-toxic, and is excreted unaltered in the urine. Clinical trials showed it to be effective in cases of urinary infection. L. S. T.

Phosphatase content of blood-serum in jaundice. C. H. GREENE, H. F. SHATTUCK, and L. KAPLOWITZ (J. Clin. Invest., 1934, 13, 1079—1087).—Phosphatase (I) occurred in bile and was increased in serum during jaundice. Bile-(I) is probably hepatic in origin. Part of the serum-(I) may be derived from liver and not from bone. CH. ABS. (p)

Naturally occurring porphyrins. I. Isolation of coproporphyrin-I from urine in a case of atophan cirrhosis. II. Isolation of a hitherto undescribed porphyrin occurring with an increased amount of coproporphyrin-I in fæces in familial hæmolytic jaundice. III. Coproporphyrin-I from fæces in untreated cases of pernicious anæmia. C. J. WATSON (J. Clin. Invest., 1935, 14, 107—109, 110—115, 116—118).—II. The

new porphyrin had some of the characteristics of deuteroporphyrin.

III. Coproporphyrin-I occurred in fæces in cases of pernicious anæmia. None was detected during remission with liver therapy, or in other types of anæmia or in normal fæces. CH. ABS. (p)

Effect of loss of bile on some elements of the blood. G. LÖWY (Compt. rend. Soc. Biol., 1935, 119, 178—179).—Removal of bile by anastomosis of the bile duct and the urethra in the dog causes a temporary fall in red-cell count, but hæmoglobin, Ca, and cholesterol show no significant variations. Fibrin shows a slight rise. R. N. C.

Basal metabolism and iodine content of the blood in myelogenous leucæmia: influence of di-iodotyrosine. R. DASSEN and E. B. DEL CASTILLO (Semana méd., 1934, II, 1854—1855).—Basal metabolism and blood-I are increased in leucæmia but revert to normal after administration of di-iodotyrosine. CH. ABS. (p)

Specific dynamic action of foodstuffs in the endogenous forms of obesity and its influencing by the thyrotropic hormone. A. SYLLA (Z. klin. Med., 1934, 127, 396—414; Chem. Zentr., 1935, i, 103).—Five cases of "hypophyseral" corpulence were influenced favourably by the thyrotropic hormone. R. N. C.

Lipin metabolism and electrolytes in obesity. N. P. SOLOTAREVA, G. SCHAAL, L. N. GOLDMANN, and E. J. ZVILICHOVSKAJA (Acta med. scand., 1934, 83, 596—609).—Obesity is associated with an excessive storage of fat in cells and tissues and with a quant. change in blood-lipins and electrolytes. The lecithin and cholesterol contents of serum are always considerably > in normal men and the ratios cholesterol: lecithin and K:Ca become sub-normal. Administration of thyreoidin causes a decrease of wt. and a return of these ratios to normal vals.

Calcium and phosphorus content of the skeleton and blood-serum in simple senile osteoporosis. E. RUTISHAUSER and A. MAULBETSCH (Beitr. path. Anat., 1934, 94, 332—344).—Bones (ribs, vertebræ, and femurs) from cases of senile osteoporosis did not differ from the normal either in ash content or in Ca and P. Blood-Ca and -inorg. P were also normal. NUTR. ABS. (b)

Clinical significance of determinations of total serum-calcium. M. C. EHRSTROM (Acta med. scand., 1934, Suppl. 58, 182 pp.).—Results of analyses of 20 normal and 140 pathological sera are given. Normal serum-Ca varies widely from day to day and from hr. to hr. The variations are not related to time of day or food intake. Sera from patients suffering from a variety of diseases show much the same variations as do normal sera. These facts explain the lack of agreement in the lit. concerning serum-Ca in normal and abnormal conditions. Day curves of serum-Ca should be given rather than isolated figures. NUTR. ABS. (m)

Blood-glutathione in cases of pellagra. J. NITZULESCU, I. ORNSTEIN, and M. TEODORU (Bull. Soc. Chim. biol., 1935, 17, 227—231).—The variation of

blood-glutathione in cases of pellagra falls very close to the normal variations. P. W. C.

Alterations in mineral constituents of anterior horn cells in experimental poliomyelitis. W. E. PATTON (Amer. J. Path., 1934, 10, 615—627).—Nerve-cell destruction in poliomyelitis involves three stages: (i) oedema with diminution of inorg. contents of the cell, (ii) granulation with hypermineralisation, (iii) acidophilic necrosis with decrease in mineral content. CH. ABS. (p)

Utilisation of oxygen by the uterus in the rabbit. J. BARCROFT, L. B. FLEXNER, E. F. MCCARTHY, and T. McCLURKIN (J. Physiol., 1934, 83, 215—221).—The % saturation with O₂ of the venous blood from the uterus falls progressively during the later stages of pregnancy, and rises sharply after parturition. R. N. C.

Specific dynamic action of protein, fat, and carbohydrate during pregnancy. H. WYANDT and F. L. DUNN (Biochem. Z., 1935, 277, 15—16).—During pregnancy the sp. dynamic action of protein and to a smaller extent that of glucose does not differ essentially from that of normal women. The influence of fat is more uniform and increases during the whole period of pregnancy. P. W. C.

Ætiology of acute rheumatism. (A) B. SCHLESINGER, A. G. SIGNY, and W. W. PAYNE. (B) B. SCHLESINGER, A. G. SIGNY, and C. R. AMES [with J. E. BARNARD] (Lancet, 1935, 228, 1090—1095, 1145—1149).—(A) Streptococcal precipitins can be demonstrated in the blood of rheumatic patients following acute streptococcal throat infections. The nucleoprotein and globulin fractions of the bacterial substance provide the best antigens for demonstrating the reaction. The relationship of hæmolytic streptococcal infection to acute rheumatism is reviewed.

(B) Evidence supporting the view that the virus elementary bodies obtained by high-speed centrifugation of pericardial exudates represent the infective agent of acute rheumatism has been obtained.

L. S. T.

Late rickets with chronic nephritis and glycosuria. R. DEBRE, J. MARIE, F. CLERET, and R. MESSIMY (Arch. Méd. Enfants, 1934, 34, 597—606).—Typical clinical and X-ray appearances of late rickets in a girl aged 11 are described. Fasting blood-sugar was normal, but high after glucose; the blood-fats were also increased. Blood-urea was normal, serum-Ca low, and -P rather low. Three possible explanations are: (1) a glycosuria due to gross renal damage; (2) true renal glycosuria; (3) a renal glycosuria with acidosis. NUTR. ABS. (b)

Variations in serum-protein fractions during an attack of rinderpest and the effect of the plane of nutrition thereon. (Ann. Rept. Dept. Vet. Sci. Tanganyika, 1933 [1934], 42—48).—The different protein fractions of the serum undergo definite changes during the course of rinderpest. The plane of nutrition may affect the composition of serum. On poor dry pasture the serum has a lower protein content than on fresh grass. The ratio of albumin to globulin is higher on the poor ration. These changes can

probably be correlated with those occurring during an attack of rinderpest, since stock often go off their food at that time. NUTR. ABS. (b)

Lactic acid and glutathione contents of the blood of schizophrenic patients. J. M. LOONEY and H. M. CHILDS (J. Clin. Invest., 1934, 13, 963—968).—The less easy removal of lactic acid from the tissues in schizophrenic than in normal patients may be partly due to a lowered content of glutathione. CH. ABS. (p)

Nitrogen balance and the O : N ratio in experimental scurvy. I. L. D. KASOHEVNIK and S. A. EIDMAN (Biochem. Z., 1935, 277, 401—411).—The development of scurvy in guinea-pigs on a scorbutic diet is divisible into three periods, an initial period in which the body-wt. increases, the urinary N decreases, and the urinary oxidation coeff. (O : N) increases considerably, a second period in which the body-wt. decreases steadily but the urinary N increases considerably and the O : N ratio remains high, followed by the third period characterised by negative N balance and rapid loss in body-wt. P. W. C.

Formation of intercellular substance by administration of ascorbic acid in experimental scurvy. V. MENKIN, S. B. WOLBACH, and M. F. MENKIN (Amer. J. Path., 1933, 10, 569—575).—Ascorbic acid produces the same reparative process as does orange juice. CH. ABS. (p)

Carbohydrate metabolism. II. Role of the thyroid gland. J. A. JOHNSTON (Amer. J. Dis. Children, 1934, 48, 1015—1029; cf. A., 1934, 211).—Impaired carbohydrate oxidation is associated with hyperthyroidism. If glycogen storage is maintained, injected carbohydrate is oxidised more readily than in normal cases owing to improved glycogenolysis. Delayed oxidation in cretinism is due to decreased glycogenolysis and administration of thyroid extract results in a sparing action on proteins due to increased availability of glycogen and greater oxidation of fat. CH. ABS. (p)

Calorigenic action of *d*- and *l*-thyroxine. W. T. SALTER, J. LERMAN, and J. H. MEANS (J. Clin. Invest., 1935, 14, 37—39).—*d*- and *l*-Thyroxine are equally effective in relieving human myxoedema. CH. ABS. (p)

Clinical significance of the level of blood-iodine in Graves' disease and toxic goitre and the therapeutic action of tissue hydrolysates. L. A. JAKOBSSON and F. S. TSCHERNJAK (Acta med. scand., 1934, 84, 147—156).—Blood-I in various forms of hyperthyroidism (0.023—0.033 mg. per 100 ml.) is > in healthy persons (0.018—0.020 mg.). A case of myxoedema gave 0.015 mg. There is no correlation between basal metabolic rate or severity of symptoms and blood-I level in hyperthyroidism, and injection of hydrolysates of endocrine organs and tissues has no definite effect on clinical symptoms or blood-I. NUTR. ABS. (m)

Carbohydrate metabolism in human hypothyroidism induced by total thyroidectomy. I. Glucose-tolerance curve and fasting serum-sugar concentration. D. R. GILLIGAN, M. I. ABRAMS, and B. STERN. II. Blood-sugar response to insulin.

M. I. ABRAMS and D. R. GILLIGAN (Amer. J. Med. Sci., 1934, 188, 790—796, 796—800).—The response of the sympathetic adrenal system to insulin is normal in hypothyroidism. There is no antagonism between the internal secretion of the normal thyroid gland and the pancreas. NUTR. ABS. (m)

Action of iodine in hypothyroidism. E. DELCOURT-BERNARD (Rev. belge Sci. méd., 1934, 6, 749—762).—In goitre with hypothyroidism, equiv. amounts of I given as Lugol's solution and di-iodotyrosine (I) cause increase in pulse-rate, O_2 consumption, and basal metabolic rate. Lugol's solution causes sometimes an increase, sometimes a decrease in basal metabolic rate in hypothyroidism without goitre. In myxoedema, Lugol's solution and (I) increase basal metabolic rate and pulse rate, but not so effectively as thyroxine. NUTR. ABS. (m)

Purified protein derivative, a standardised tuberculin for uniformity in diagnosis and epidemiology. F. B. SEIBERT, J. D. ARONSON, J. REICHEL, L. T. CLARK, and E. R. LONG (Amer. Rev. Tuberc., 1934, 30, 707—768).—A review. CH. ABS. (p)

Preparation and biological properties of the active principle of tuberculin (β -tuberculin). I. II. Sensitisation tests. III. Allergy and immunity relations in tuberculosis. P. KALLÓS and E. NATHAN. IV. Further sensitisation tests. P. KALLÓS and C. ZOBOLI (Acta med. scand., 1934, 83, 130—164, 165—168, 169—196, 197—211; Chem. Zentr., 1935, i, 94).—I. β -Tuberculin (I) is obtained from the collodion ultrafiltrate from tubercle bacilli cultures by dissolving and re-pptg. with $EtOH-Et_2O$, is hygroscopic, optically active, protein-free, and sol. in feebly alkaline solution, and is probably a nuclein derivative. It provokes sp. skin-reactions in tuberculous guinea-pigs, and anaphylaxis followed by desensitisation in the isolated tuberculous uterus. It reacts with the sera of skin-tuberculous animals, and with lung-tuberculous patients. Old tuberculin does not give these reactions.

II. Guinea-pigs are not sensitised by pre-treatment with (I), but the skins of rabbits are locally sensitised to subsequent intravenous injection of (I).

III. Tuberculin allergy is closely dependent on tuberculosis immunity.

IV. Guinea-pigs are sensitised by (I) if horse-serum is used as restrainer. If collodion suspension is used as restrainer the anaphylactic reaction occurs only with a non-adsorbed solution of (I), which hence has the properties of a hapten. R. N. C.

Physiology of whales. A. H. LAURIE (Nature, 1935, 135, 823).—Direct observations indicate that whales do not fill their lungs with H_2O when diving, thus preventing caisson sickness (cf. A., 1933, 844). L. S. T.

Degree of constancy in human basal metabolism. F. G. BENEDICT (Amer. J. Physiol., 1935, 110, 521—530).—The physiological functions in a well-conditioned man in complete muscular and mental repose, at least 12 hr. after food, are uniform from day to day. Ingestion of much carbohydrate increases the R.Q. for one day, but does not affect

O_2 consumption. An emotional disturbance causes an increase in metabolism lasting several days.

R. N. C.

Basal metabolism of American-born Chinese girls and of American girls of the same age. C. C. WANG (Amer. J. Dis. Children, 1934, 48, 1041—1049).—No differences were observed. CH. ABS. (p)

Respiratory metabolism of *Galleria mellonella* (bee moth) during metamorphosis at different constant temperatures. F. CRESCITELLI (Anat. Rec., 1934, 60, Suppl., 35—36).—The level of the respiratory metabolism is a function of temp. Total O_2 consumption or CO_2 production is at a min. at 30° .

NUTR. ABS. (b)

Respiratory quotient of developing grasshopper embryos (*Melanoplus differentialis*). E. J. BOELL (Anat. Rec., 1934, 60, Suppl., 47).—In the first 5 days of embryonic life R.Q. is about unity. In the next 5 days it falls to 0.75 and remains about this level for a further 10 days, after which, as the embryo enters the diapause, it falls to 0.70.

NUTR. ABS. (b)

Chemical changes associated with metamorphosis in a beetle (*Tenebrio molitor*, L.). A. C. EVANS (J. Exp. Biol., 1934, 11, 397—401).—Noticeable changes take place in the distribution of carbohydrates, fatty acids, unsaponifiable matter, and N during the metamorphosis of the mealworm.

NUTR. ABS. (b)

Metabolic rate of developing amphibia with special reference to sexual differentiation. I. A. WILLS (Anat. Rec., 1934, 60, Suppl., 63).—There is increased O_2 consumption during the period of metamorphosis. No significant difference was found between the average metabolic rates of males and females at the time of sexual differentiation or at metamorphosis. NUTR. ABS. (b)

Growth of blow-fly larvæ on blood and serum. II. Growth in association with bacteria. R. P. HOBSON (Biochem. J., 1935, 29, 1286—1291; cf. A., 1934, 226).—Infected *Lucilia* larvæ grow better on muscle than on blood, the difference disappearing on adding yeast autolysate to the blood. The period of slow growth is lengthened by transferring them each day to sterile blood. On transference of aseptic larvæ to a vitamin-B-deficient diet growth is at first normal and declines later, showing that the site of bacterial synthesis of vitamin-B is the blood and not the intestines. The growth-promoting effect of yeast is due to the presence of $HPO_4^{''}$ and K^+ ; blood is deficient in P. The larvæ grow readily on blood infected with pure cultures of various bacilli isolated from the intestines and blown meat. H. D.

Fat-soluble growth factor required by blow-fly larvæ. I. Distribution and properties. R. P. HOBSON (Biochem. J., 1925, 29, 1292—1296).—Muscle-oil, wool-wax, wheat-germ oil, egg yolk, cod-liver oil, and butter contain growth-promoting power for blow-fly larvæ which runs parallel with the sterol content and is present in the unsaponifiable residues. Growth-promoting power is not associated with the presence of vitamin-A, -D, and -E. H. D.

Oxygen consumption in perfused dog's liver. N. FIESSINGER, H. BÉNARD, and G. SYLLABA (Compt. rend. Soc. Biol., 1935, **119**, 182—183).—The O_2 consumption of the surviving perfused liver is 800—1100 c.c. per kg. per hr. It is not affected by glucose, insulin, glycine, or antelobin. It is lowered by 0.001*N*-KCN, the action of which is antagonised by $Na_2S_2O_4$. R. N. C.

Gaseous metabolism of frog kidney. F. O. SCHMITT, R. S. KERR, and E. D. BUEKER (Amer. J. Physiol., 1935, **110**, 539—544).—Vals. are given for the O_2 consumption and R.Q. of frog's kidney in Ringer's solution with or without HCO_3' or PO_4''' . Glucose increases O_2 consumption slightly without affecting the R.Q., whilst phloridzin decreases them both, and neutral-red and phenol-red are without effect. R. N. C.

Respiratory quotient of frog's muscle under conditions of rest and work. C. L. GEMMILL (J. Cell. Comp. Physiol., 1934, **5**, 277—289).—The R.Q. of resting frog's muscle (0.81) indicates a mixed metabolism. During stimulation the val. rises (0.94) as a result of increased utilisation of protein and/or carbohydrate (I). It is probably not exclusively a combustion of (I). A. G. P.

An oxidative reserve as source of anaerobic carbon dioxide in heart-muscle. W. O. FENN (J. Cell. Comp. Physiol., 1934, **5**, 347—358).—Anaerobic CO_2 exceeds the pre-formed CO_2 after correction for O_2 in solution or in combination with hæmoglobin. A. G. P.

Connexion between muscle metabolism and weather. III. Experiments at high altitudes. O. RIESSER, G. KUNZE, and K. GALLE (Biochem. Z., 1935, **277**, 349—364).—Experiments on the changes of muscle metabolism (measured in terms of changes of P_2O_5 and glycogen contents) in rabbits originally carried out at sea-level (this vol., 387) are repeated at an altitude of 3500 m. As before, an attempt is made to correlate abnormal variations with changes in weather conditions. P. W. C.

Co-ordination of chemical processes in muscle. V. Phosphate transfer through phosphopyruvic acid. T. MANN (Biochem. Z., 1935, **277**, 380—382).—Inhibition of glycogenolysis by addition to muscle of $CH_2I \cdot CO_2H$ or NaF leads to deamination of adenosinetriphosphoric acid which is itself inhibited in exactly the same way by either phosphoglyceric or phosphopyruvic acid or by $AcCO_2H + PO_4'''$. P. W. C.

Glutathione in the aestivation of *Helix aperta*, Born. F. DULZETTO (Atti R. Accad. Lincei, 1935, [vi], **21**, 195—198).—This organism becomes lethargic in May and active again with the first autumnal rains. In August the foot contains reduced glutathione (I), which is localised in the muscles, whereas in the hepato-pancreas and albumen glands (I) occurs in the oxidised form. In October the foot shows no sensible increase of reduced (I), which is absent from the hepato-pancreas, but apparent in the albumen glands. T. H. P.

Tyrosine content of tissues after intravenous injection. F. B. KING, R. SIMONDS, and M. AISNER

(Amer. J. Physiol., 1935, **110**, 573—579).—Tyrosine injected intravenously in the dog disappears rapidly from the blood. Urea-N shows no significant rise that would suggest deamination, whilst phenols increase only in the thyroid, adrenals, and pancreas. R. N. C.

Availability of *d*- and *l*-homocystine for growth purposes. H. M. DYER and V. DU VIGNEAUD (J. Biol. Chem., 1935, **109**, 477—480; cf. A., 1933, 1074).—*d*- and *l*-Homocystine support growth of rats on a cystine-deficient diet equally well. H. D.

Effect of addition of small amounts of cystine to a diet deficient qualitatively in protein on metabolism. K. KLAPPER (Biochem. Z., 1935, **277**, 376—379).—The high urinary C : N and vacate O : N ratios brought about in white rats by feeding a diet sufficient in caloric val. but deficient in essential NH_2 -acids cannot be rendered normal by adding small amounts of cystine to the diet, the latter leading to a further increase in these ratios and to increased retention of N. P. W. C.

Pig's blood as human food in China. W. PENG-CHU (J. Chinese Chem. Soc., 1935, **3**, 67—77).—The biological val. of dialysed dried pig's blood is about half that of caseinogen. F. N. W.

"Lipotropic" effect of protein. C. H. BEST, M. E. HUNTSMAN, and J. H. RIDOUT (Nature, 1935, **135**, 821—822; cf. A., 1934, 920).—The power of proteins and choline and betaine to decrease the fat content of liver is discussed. Experiments on rats indicate that the effect of slight or moderate undernutrition on the deposition of liver-fat has been unduly emphasised (cf. this vol., 523). A slight change in body-wt. does not affect liver-fat balance. L. S. T.

Results of feeding lecithin and pancreas in depancreatized dogs on the liver-fat and its saponifiable and unsaponifiable fractions. E. P. RALLI, G. FLAUM, and R. BANTA (Amer. J. Physiol., 1935, **110**, 545—551).—Pancreas combined with cod-liver oil (I) is more effective than egg-lecithin (II) with (I) in preventing the deposition of liver-fat. (II) alone produces a slightly lower liver-fat than pancreas alone. Sugar excretion is diminished slightly by (II) and increased by pancreas. In normal dogs total liver-fat is < in depancreatized dogs. R. N. C.

Significance of the liver in the metabolism of lipins. IV. Lipins in the blood and bile in cases of oral administration of glucose to rabbits. Y. ASODA (Japan J. Gastroenterol., 1934, **6**, 42—45; cf. A., 1934, 1393).—Injection or feeding of glucose to rabbits lowers the blood-cholesterol and -lecithin and increases these lipins in bile. Liver regulates the level of blood-lipins by excretion into the bile. CH. ABS. (p)

Exchange of lipins in the umbilical circulation at birth. E. M. BOYD and K. M. WILSON (J. Clin. Invest., 1935, **14**, 7—15).—Phospholipins (I) and cholesterol are regularly absorbed by the fetus at birth. The fatty acids of (I) in the foetal circulation are more saturated than those of the maternal circulation. CH. ABS. (p)

Fat metabolism in infants. L. E. HOLT, jun., H. C. TIDWELL, and C. M. KIRK (*Acta paediat.*, 1933, 16, 165—176).—Different fats are compared both as regards their ease of assimilation and their fate after absorption. Mineral intake is inversely related to fat retention. Decreasing the size of fat particles did not favour assimilation. Increasing the volatile acid fraction of the fat did not cause clinical disturbances and the shorter-chain fats were more completely absorbed. Unsaturated fat was far better absorbed than saturated, unsaturation being much more important than m.p. The more saturated character of faecal fat on mixed-fat diets is due to selective absorption of unsaturated fat. Intravenous administration of emulsified fat has diagnostic and therapeutic val. **NUTR. ABS. (b)**

Ketosis. VI. Quantitative studies on β -oxidation. J. S. BUTTS, C. H. CUTLER, L. HALLMAN, and H. J. DEUEL, jun., with H. BLUNDEN (*J. Biol. Chem.*, 1935, 109, 597—613).— δ -Oxidation was observed in the increase in the production of ketonuria after administration of *n*-octoic acid (I) in place of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ (II), whereas with butyric (III) or *n*-hexoic (IV) acid the vals. are practically identical. α -Oxidation is small since administration of valeric acid is followed by slight ketonuria. After administration of (I), (III), or (IV), 70—75% of the ketonic substances consists of β -hydroxybutyric acid (V), the val. being slightly lower after (I) and 85—95% after (V). The female animal is more susceptible to ketonuria after feeding the above acids than the male. **H. G. R.**

Urinary excretion of ketones and ammonia in minimum endogenous protein metabolism. H. TRIMBACH (*Arch. internat. Physiol.*, 1934, 39, 417—433).—The classification of animal species according to their excretion of ketones or NH_3 per unit of body-wt. when on a strict carbohydrate (I) diet is the same as that of their heat production. Since ketonuria exists when the calorific requirements of the organism are met by (I), it may be ketogenic, but other evidence suggests that it may, according to circumstance or perhaps simultaneously, be ketogenic or antiketogenic. **NUTR. ABS. (m)**

Ketogenesis during fasting. H. TRIMBACH (*Arch. internat. Physiol.*, 1934, 39, 462—501).—The hyperketonuria which appears to be the rule in the young is an exception in the case of the adult and is observed only in a very limited no. of species. During prolonged fasting there is no systematic variation in the daily excretion of ketones, indicating no tendency to a more complete oxidation of fat. There is no relation between ketonuria and NH_3 excretion in fasting. **NUTR. ABS. (b)**

Effect of ingestion of alkali on ketone excretion during inanition. H. TRIMBACH (*Arch. internat. Physiol.*, 1934, 39, 502—515).—Administration of NaHCO_3 during prolonged fasting and in amounts which cause the urine to become alkaline never diminishes ketogenesis and may cause an increase. **NUTR. ABS. (m)**

Physiological ketogenesis. P. H. FLEURET (8ème Réunion, Assoc. Physiol. Nancy, May, 1934).—In the goat, rabbit, and dog there is no const. level

of excretion of ketones (I) for a given diet. Starvation reduces excretion of (I) in the goat and rabbit and usually in the dog, although there may occasionally be an increase. In the goat, proteins more easily increase production of (I) than do carbohydrates (II), and (II) more easily than fats. The rabbit has less tendency to increased production than the goat. There is no relationship between reaction of the urine and the excretion of (I), which may be formed not only by β -oxidation, but also from MeCHO .

NUTR. ABS. (m)

Nitrogen metabolism. II. Effect of an alkalinising salt, sodium citrate, on endogenous nitrogen metabolism on a fat diet. IV. C. ZUMMO (*Arch. internat. Physiol.*, 1934, 40, 129—139).—The administration of Na citrate to dogs on a fat diet led to a diminution in the N excretion. The urinary N excretion found in one case was as low as that observed when the animal was transferred from a fat to a carbohydrate diet. **NUTR. ABS. (b)**

Excretion of inulin by the dogfish, *Squalus acanthias*. J. A. SHANNON (*J. Cell. Comp. Physiol.*, 1934, 5, 301—310).—The inulin (I) clearance is > that of xylose (II). The discrepancy is abolished by phloridzin, and hence is attributable to the active reabsorption of (II). The creatinine clearance is much > that of (I) and is a function of the plasma concn. both in the presence of (I) and in that of (II). **A. G. P.**

Oxidation occurring after ingestion of galactose in the dog. J. H. ROE, A. GILMAN, and G. R. COWGILL (*Amer. J. Physiol.*, 1935, 110, 531—538).—The R.Q. of normal fasting dogs is not raised by ingestion of 2 g. of galactose (I) per kg., but a delayed elevation occurs with 5 g. per kg. In depancreatized dogs this does not occur. The observations suggest that (I) is not oxidised as such, but is converted into glucose. **R. N. C.**

Carbohydrate metabolism in hypophysectomised frogs. E. SILAIEVA (*J. Cycle med.*, 1933, 3, 259—267).—For 5 days after total hypophysectomy an increased blood-sugar was observed in frogs; after that time it fell continuously until the animals died. The glycogen content of the liver and muscles followed the blood-sugar curve, and the processes of oxidation and glycolysis in the liver were considerably diminished. A slight temporary hypoglycaemia occurred immediately after the operation. **NUTR. ABS. (b)**

Relationship between tissue growth, glycolysis, and oxygen tension. E. KNAKE (*Z. Chirurg.*, 1934, 243, 633—654).—The growth of embryonic connective tissue (chicken) is increased in an atm. of 5% of O_2 , retarded in 0.2%, and uninfluenced in 66%. In pure O_2 the growth rate is unchanged for 3 or 4 days; thereafter the cells are permanently injured. Epithelial tissue growth is retarded in pure O_2 , but the cells are not injured; reduction of O_2 to < 5% injured the cells. The optimal conditions for growth probably depend on glycolysis and oxidation and differ for different tissues. **NUTR. ABS. (b)**

Liver-glycogenesis. P. BARREDA (*Arch. exp. Path. Pharm.*, 1935, 178, 333—341).—Formation of sugar occurs in surviving glycogen-poor or -rich liver-

tissue (rat) in PO_4 or HCO_3 buffer at p_{H} 7.4, and is increased by addition of pyruvic or lactic acid. Glycogenesis probably occurs to some extent, but the concomitant glycogenolysis masks it so that only an increase in total carbohydrate is detectable. Addition of insulin alone has no significant action, but sugar + insulin tends to increase glycogenesis. F. O. H.

(A) Lactic acid formation in liver. (B) Concentrations of lactic acid in blood and liver of rabbits. P. A. BOTT and D. W. WILSON (J. Biol. Chem., 1935, 109, 455—462, 463—466).—(A) The CuSO_4 - $\text{Ba}(\text{OH})_2$ filtrate of liver gives a bad endpoint in the Friedemann (A., 1927, 800) determination of lactic acid (I). Saturation of the filtrate from the pptd. proteins with $(\text{NH}_4)_2\text{SO}_4$ and extraction with Et_2O continuously for 3 hr., removal of the latter, and determination of (I) in the aq. residue gives good results. The glycolytic activity of liver is decreased by mincing and destroyed by freezing in liquid air; that of muscle is uninfluenced by mincing.

(B) Well-fed rabbits show a rise in blood- and liver-(I) under amytal anaesthesia which is correlated with their increased muscular activity. Fasting animals show smaller rises. Blood-(I) is always > liver-(I). H. D.

Absorption of glucose from the colon. W. W. EBELING (Arch. Surg., 1934, 29, 1039—1046).—Absorption of glucose depends on the concn. and vol. of the solution placed in the colon. Use of hypertonic solutions may be harmful owing to abstraction of H_2O . CH. ABS. (p)

Effect of introduction of hydrochloric acid into the duodenum on intestinal absorption of glucose. E. DE KOKAS and G. DE LUDANY (Compt. rend. Soc. Biol., 1935, 119, 283—285).—An increased absorption of glucose of the order of 20% was observed.

H. G. R.

(A) Effect of irradiation with mixtures of ultra-violet and visible light on carbohydrate metabolism. (B) Effect of irradiated oats on carbohydrate metabolism. L. PINCUSSEN (Strahlenther., 1934, 51, 537—540, 685—688).—(A) When white rats fed on a diet of bread and oats were irradiated, even a small amount of ultra-violet light in the radiation had a notable effect in increasing the carbohydrate reserves.

(B) The feeding of oats which had been irradiated with visible and ultra-violet light to rats on a rachitogenic diet not only prevented the appearance of rickets, but also caused a rise in the ratio of carbohydrate to lactic acid in the blood, liver, and muscles. The R.Q. of the muscle tissues was also raised in the rats which had received the irradiated oats.

NUTR. ABS. (b)

New aspects of deficiencies in nutrition. D. HUNTER (Lancet, 1935, 228, 1025—1032).—A lecture.

L. S. T.

Physico-chemical properties of fruits and the effect of apple diet on acid-base balance. H. MARYNOWSKA-KAULBERSZ (Acta pædiat., 1933, 16, 19—227).—The juice of citrous fruits, when administered to dogs, produced a change towards acidosis in the alkali reserve of the blood, whereas with apple

juice the reverse was the case. With the citrous juice the change in the p_{H} of the digestive tract was much > with apple juice. With children, an apple diet again tended towards an alkalosis. Neither these results, nor the fact that apple pulp has little or no absorptive capacity for tetanus toxin, explain the beneficial effect of an apple diet in the treatment of infantile diarrhoea. NUTR. ABS. (b)

Effect of a diet extremely low in sodium chloride on the composition of urine and blood and on blood-volume in healthy persons. R. STOHR (Z. ges. exp. Med., 1934, 95, 55—66).—Two subjects were kept for 51 and 36 days on low-NaCl diets. At first there was a rapid fall in NaCl output, later a stationary low output, and finally a slight increase accompanied by a rise in blood-Cl' and serum-albumin, a decrease of globulin, and a loss of wt. (8 kg. and 1.6 kg.). After addition of a small amount of NaCl to the diet the output of NaCl increased, but did not equal the intake; blood-Cl' fell, but not to the original val. NUTR. ABS. (b)

Effect of diet poor in inorganic salts on the albino rat, edestin being the source of dietary protein. P. P. SWANSON, G. H. TIMSON, and E. FRAZIER (J. Biol. Chem., 1935, 109, 729—737; cf. A., 1933, 90).—The diet (ash 0.27%) does not produce such pronounced changes in the composition of the blood as does the corresponding diet (ash 0.5%) in which caseinogen is the source of dietary protein, there being no sp. erythropoietic effect and no polycythæmia. The size of the erythrocytes is reduced only slightly, and their hæmoglobin concn. is not so greatly reduced. Severe diuresis accompanied by polydipsia occurs with the first diet and growth is greatly retarded, whereas, with the second, diuresis is only slight. W. McC.

Effect of deprivation of water on the composition of animal tissues. B. HAMILTON and R. SCHWARTZ (J. Biol. Chem., 1935, 109, 745—753).—In puppies, almost complete removal of H_2O from the diet results in loss of extracellular fluid and concn. of electrolytes in the body-fluids. The losses of H_2O (per 100 g. of fat-free dry substance) and of base are: skin 43, 24, muscle 35, 22, brain 14, 0, liver 13, 0, kidneys (about) 9%, 0. No loss of K from any tissue occurs. W. McC.

Determination of the state of hydration of the body by the amount of water available for dissolution of sodium thiocyanate. L. A. CRANDALL and M. X. ANDERSON, jun. (Amer. J. Digest. Dis. Nutr., 1934, 1, 126—131).—The method is applied to experimentally dehydrated and superhydrated dogs and human beings with oedema as well as to normal animals and man. It depends on the fact that after intravenous injection of aq. NaCNS, its concn. in the blood-serum becomes relatively const. in about 2 hr. and then decreases very slowly until elimination is completed in about 6 days. The quantity of fluid available for the dissolution of the NaCNS is calc. from the concn. in the blood-serum 2—4 hr. after the injection of 15—20 mg. per kg. The vals. obtained, calc. as a % of body-wt. or preferably (for man) as litres per sq. m. of body-surface, are compared with normal vals. NUTR. ABS. (b)

Calcium and phosphorus exchange in young growing pigs. L. S. SPILDO (Beretn. Forsogslab. Kobenhavn. 1933, No. 151, 246 pp.; Bied. Zentr., 1934, A, 5, 193—194).—When ultra-violet light is excluded, rations having a high (2.5) P_2O_5 : CaO ratio produce in young growing pigs "ostitis fibrosa" combined with osteoporosis. Osteoporosis occurs with a ratio of approx. 0.4. The min. requirement for growth only is 7 g. of CaO and 13 g. of P_2O_5 daily. The optimum ratio with favourable light conditions is 1.6.

A. G. P.

Silicigenous functions of silicoderms. A. LABBE (Compt. rend., 1935, 200, 1880—1882).— SiO_2 is used metabolically by silicoderms. The morphology of the process is described.

R. S. C.

Narcosis. III. K. H. MEYER and H. HEMMI (Biochem. Z., 1935, 277, 39—71).—The lipin and adsorption theories of narcosis are critically reviewed. No parallelism exists between adsorbability and narcotic activity. Experiments with a series of alcohols up to $C_{18}H_{35}OH$ lead to the view that narcosis occurs when any chemically indifferent substance reaches a certain molar concn. in the lipin alcohols of the cell substance. This concn. depends on the kind of animal or cell, but not on the chemical nature of the narcotic. The degree of activity in the gaseous condition is compared with that in aq. solution, and an explanation given for the fact that $CHCl_3$ is more strongly narcotic in air and less strongly in aq. solution than is CCl_4 .

P. W. C.

Physical chemistry of blood during narcosis. I. R. BACHROMEJEV and L. PAVLOVA (Arch. exp. Path. Pharm., 1935, 178, 390—395).—With the stimulating stage of $CHCl_3$ narcosis in dogs, the serum-Ca and -K fall and rise, respectively; with Et_2O both levels rise. With complete narcosis by $CHCl_3$, Et_2O , chloral hydrate, urethane, morphine, and $MgSO_4$ and also with asphyxia, Ca and rate of coagulation increase, whilst K and velocity of sedimentation of erythrocytes decrease; alkalisation of the blood has the opposite effect. A return to normal vals. occurs during recovery.

F. O. H.

Ether apnoeas. A. E. GUEDEL and D. N. TREWEEK (Anesthesia and Analgesia, 1934, 13, 263—264).—The effect, on respiratory activity, of varying the CO_2 supply in Et_2O anaesthesia is examined.

CH. ABS. (p)

Initial effect of some anaesthetic substances on the movements of cilia and smooth muscle. G. H. W. LUCAS (Anesthesia and Analgesia, 1934, 13, 206—211).—Some narcotics (Et_2O , C_2H_4) produce initial stimulation of movement prior to the depression. Others ($CHCl_3$) induce depression from the beginning.

CH. ABS. (p)

Analgesia and anaesthesia with special reference to such substances as trichloroethylene and vinesthene (divinyl ether). D. E. JACKSON (Anesthesia and Analgesia, 1934, 13, 198—204).—Properties and means of administration are described.

CH. ABS. (p)

Effects of preoperative medication and anaesthesia on movements of the small intestines. H. E. CARLSON (Anesthesia and Analgesia, 1934, 13,

221—226).—Comparison is made of the action of atropine and morphine in Et_2O and N_2O anaesthesia.

CH. ABS. (p)

Effect of barbiturates and morphine. J. T. HALSEY (Anesthesia and Analgesia, 1934, 13, 204—205).—Effects of injection of neonal, dial, and morphine after Et_2O anaesthesia are described.

CH. ABS. (p)

Influence of the anion combined with cocaine on the anaesthetic activity of the alkaloid. J. REGNIER and R. DAVID (Compt. rend., 1935, 200, 1428—1430).—At p_H 4 the anaesthetic activities of solutions of cocaine citrate, lactate, tartrate, sulphate, phosphate, hydrochloride, hydriodide, thiocyanate, formate, acetate, salicylate, benzoate, and phenylacetate are in the ratio 0.2, 0.4, 0.6, 0.8, 1, 1, 1.2, 1.5, 2.5, 2.9, 4, 5, 12. The alkaloidal salt behaves therefore as an entity.

H. W.

Influence of yohimbine on the action of morphine and of chloral hydrate on blood-sugar. S. YAMACHI (Folia Pharmacol. Japon., 1934, 19, No. 1, 44—53).—Yohimbine (I) in dosages which only slightly increase the blood-sugar decreases the hyperglycaemia caused by morphine or chloral hydrate. (I) also increases the decline in blood-sugar following poisoning by the drugs.

CH. ABS. (p)

Mechanism of the action of strychnine or the combination of it with cardiac tonics on the isolated heart of *Rana esculenta*. K. IBA (Folia Pharmacol. Japon., 1934, 19, No. 1, 18—31).—The action of strychnine varies with the concn. used. It acts synergistically with digitalin, *g*-strophanthin, helleborin, rhodealin, and pentamethylenetetrazole. With adrenaline there is potentiation.

CH. ABS. (p)

Pharmacological investigations of yolk-sac vessels of the chick embryo. I—III. T. NAKANO (Folia Pharmacol. Japon., 1934, 19, No. 1, 102—120).—I. Caffeine, Ba, tetrahydro- β -naphthylamine, and eserine constricted, whereas cocaine, $NaNO_2$, and pilocarpine dilated, the vessels. The effects increased with age. Differences in action on veins, arteries, and capillaries are shown.

II. Quinine, optochin, cinchonine, eucupine, vuzin, quinidine, and cinchonidine are similarly compared.

III. Li dilated and NH_4^+ and Sr^{++} usually constricted vessels. Ca^{++} and K^+ always caused constriction. Mg^{++} constricted in small and dilated in large concns.

CH. ABS. (p)

Action of ephedrine quaternary halide compounds. C. PAK and B. E. READ (Chinese J. Physiol., 1935, 9, 1—16).—Methylephedrine methiodide and bromide, $OH\cdot CHPh\cdot CHMe\cdot NMe_3X$, exert a weak stimulating effect on the sympathetic ganglion cells of pithed dogs and cats (about 1/40 of that of NMe_4I), a weak reversible atropine-like action, but no curare-like action. Large doses paralysed the ganglia of the autonomic nervous system.

W. O. K.

Pharmacological action of ephedine. K. K. CHEN, R. C. ANDERSON, I. J. FREIHAGE, and T. Q. CHOU (Chinese J. Physiol., 1935, 9, 17—20).—Ephedine, $C_8H_{18}O_3N_2$, m.p. 87° , lowers blood-pressure in cats, contracts isolated guinea-pig's uterus, and aug-

ments peristaltic movement of rabbit's isolated small intestine, sometimes preceded by a slight inhibition.

W. O. K.

Pharmacological action of fritimine. K. K. CHEN, C. L. ROSE, R. C. ANDERSON, and T. Q. CHOU (Chinese J. Physiol., 1935, 9, 21—26).—Fritimine, $C_{38}H_{62}O_3N_2$, m.p. 167° , lowers the blood-pressure in anaesthetised cats, temporarily depresses respiration, increases blood-sugar in rabbits, contracts the guinea-pig's uterus, and inhibits rabbit's isolated small intestine.

W. O. K.

Influence of some sympathetic depressant poisons as ergotoxine, thymoxyethyl-dimethylamine, and thymoxyethylallylamine on the excretion of sodium chloride and water by the kidneys. K. ARIMA (Folia Pharmacol. Japon., 1934, 19, No. 1, 26—43).—Ergotoxine in all dosages decreases the NaCl and H_2O excreted. Thymoxyethyl-dimethylamine (I) in moderate and -diallylamine (II) in small dosages produce similar effects. (I) in large or small and (II) in moderate dosages stimulate NaCl and H_2O excretion.

CH. ABS. (p)

Toxicity and sympathetic-inhibitory action of corynantheine. E. ROTHLIN and RAYMOND-HAMET (Arch. exp. Path. Pharm., 1935, 178, 305—307).—Corynanthine (I) and corynantheine (II) (A., 1933, 1313) possess the same adrenaline-inhibitory activity but the toxicity of (II) is twice that of (I), properties to be correlated with the difference of OMe in their constitution.

F. O. H.

Antagonism of drugs in iris epithelium cultures. I, II. K. SANJO (Folia Pharmacol. Japon., 1934, 19, No. 1, 54—63).—I. Convallamarin (I) acts antagonistically to certain drugs of the quinine group in their depressant action on cultures of iris epithelium. The antagonism resembles that between atropine and muscarine.

II. (I) is similarly antagonistic to sinomenine, parasinomenine, emetine, and cephaeline.

CH. ABS. (p)

Pharmacology of a new aromatic guanidine derivative. II. Influence on organs of circulation. A. KURODA (Folia Pharmacol. Japon., 1934, 19, No. 1, 18—31).—The vasodilator action of 3:4-dihydroxybenzyl, phenoxyethyl-, *p*-methoxybenzyl-, *p*-hydroxyphenyl-, and α -phenylethyl-guanidine is examined.

CH. ABS. (p)

Acidosis of guanidine intoxication. A. S. MINOT, K. DODD, and J. M. SAUNDERS (J. Clin. Invest., 1934, 13, 917—932).—The acidosis is due to increased production and defective metabolism of lactic acid. Alkalinising Na salts are dangerous because of the lowered effectiveness of Ca^{++} in hyperguanidinæmia. Combined with Ca medication, $NaHCO_3$ administration is satisfactory.

CH. ABS. (p)

Preparation of ergometrine. H. W. DUDLEY (Pharm. J., 1935, 134, 709).—Defatted powdered ergot is extracted with industrial EtOH (denatured with 5% MeOH) which has been made alkaline by the addition of conc. aq. NH_3 . The extract is conc. in a vac. to small vol., rendered slightly acid (dil. H_2SO_4), and concn. is continued until all the alcohol is removed. After separation from residual fat the aq. concentrate is made faintly alkaline

(Na_2CO_3), filtered, made strongly alkaline (Na_2CO_3), and extracted with $CHCl_3$. The $CHCl_3$ extract is conc. in vac., when crude ergometrine (this vol., 655) separates. The pure alkaloid, recrystallised from COMeEt, decomposes at $161-162^\circ$. Its solution in EtOH is dextrorotatory. Directions for making the cryst. H_2O -sol. hydrochloride are given.

H. W. D.

Ergotocin. Active principle of ergot responsible for the oral effectiveness of some ergot preparations on human uteri.—See this vol., 872.

Active constituents of ergot. M. R. THOMPSON (J. Amer. Pharm. Assoc., 1935, 24, 24—38, 185—196).—There appears to be present in aq. extracts a new alkaloid which is more sol. in H_2O than is ergotoxine or ergotamine and also differs from these by the rapidity and extent of its action after oral administration (cf. Dudley and Moir, this vol., 655).

F. O. H.

Pharmacodynamic action of the benzylcholines. J. LAMBILLON (Compt. rend. Soc. Biol., 1935, 119, 317—318).—Compared with β -methylcholine the nicotine-like activity is increased and the muscarine-like activity decreased.

H. G. R.

Response of the leech to acetylcholine. C. F. A. PANTIN (Nature, 1935, 135, 875).—A sensitive test for acetylcholine is its power to contract the longitudinal muscle of the body-wall of *Hirudo medicinalis*.

L. S. T.

Circulatory-active (adrenaline-like) substances in liver extracts. F. GRABE, O. KRAYER, and K. SEELKOPF (Klin. Woch., 1934, 13, 1381—1383; Chem. Zentr., 1935, i, 106).—Minced liver is extracted with MeOH after exposure to the air for 24—100 hr., and the conc. extract pptd. with $COMe_2$, filtered, and the $COMe_2$ evaporated in vac. The pressor effect of this extract is due to tyramine (I), which can be isolated as the benzoate. (I) is also probably responsible for the pressor effect of commercial liver extract. The effect is absent from extract of fresh liver.

R. N. C.

Pressor substances from body-fluids of man in health and disease. I. H. PAGE (J. Exp. Med., 1935, 61, 67—96).—Extracts of human blood-plasma, ascitic and cerebrospinal fluids contain a powerful pressor substance (I) having the properties of an org. base. Plasma-colloids hold the (I) in a bound state. The amount of (I) is not increased in patients with hypertension of varied pathogenesis.

CH. ABS. (p)

Depressor extracts of human blood and the vascular action of extracts of rabbit and dog blood. I. H. PAGE (J. Exp. Med., 1935, 61, 87—102).—EtOH extracts of plasma from arterial or venous blood of rabbits differ from those of human plasma in possessing a depressor action. This action is not antagonised by atropinisation. Plasma extracts of dogs have no vascular effect. Ultrafiltrates of rabbit plasma are actively vasodepressor, but those of human and dog-plasma are without action. These effects resemble those of adenylic acid (I) rather than of histamine. Human plasma, ascitic and spinal fluids on keeping yield extracts having a depressor and a constrictive action on kidneys. Histamine, choline, and adenosine depress the level of blood-pressure >

they constrict the kidney-vol. (I) has the reverse action.

CH. ABS. (p)

Demonstration of the fourth depressor substance in human urine and blood. F. LANGE (Deut. Arch. klin. Med., 176, 1—13; Chem. Zentr., 1935, i, 262).—Extracts of blood and of urine that are adenosine- and histamine-free, injected in cats simultaneously with atropine to inhibit choline action, still provoke a fall of blood-pressure. The activities of blood extracts inversely \propto those of urine extracts from the same subjects. Both extracts from cases of hypertonia show respectively the min. and max. effects; urine extracts from normal subjects and arterio-sclerotics show moderate activity.

R. N. C.

Colloidal characteristics of the anaphylactic reaction *in vitro*. II. Variation of the proportion antigen-antibody. A. LUMIERE and P. MEYER (Bull. Soc. Chim. biol., 1935, 17, 219—226).—When to the serum of a sensitised rabbit is added an amount of antigen too small to lead to the formation of a visible ppt., there is an increase in viscosity representing an increase in the vol. of the protein particles.

P. W. C.

Biochemical properties of curro-saponin. C. A. SAGASTUME and L. P. PONCE (Rev. Fac. Cienc. quim., La Plata, 1934, 9, 29—34; cf. A., 1932, 647).—Solutions of curro-saponin kept in contact with animal charcoal completely lose their hæmolytic properties. A decrease in the acidity of the inactivated solutions was noted, but there was no diminution in the foam-producing properties.

F. A. A.

Pharmacology and therapeutics of "brom-salizol" (bromosaligenin). D. I. MACHT and F. DUNNING (J. Lab. Clin. Med., 1934, 20, 127—140).—The action on smooth muscle is examined.

CH. ABS. (p)

Pharmacology of camphoric acid derivatives: relationship between chemical constitution and pharmacodynamic action. II. Action on blood-pressure and respiration. Y. FUJIMOTO (Folia Pharmacol. Japon., 1934, 19, No. 1, 1—17).—The action of various compounds on blood-pressure and respiration in urethane-anæsthetised rabbits is related to their chemical constitution.

CH. ABS. (p)

Gametocidal action of plasmoquin. W. KIRUTH and F. SCHONHOFFER (Klin. Woch., 1934, 13, 875—876; Chem. Zentr., 1935, i, 266).—The work of Kritschewski and Pines (this vol., 395) is adversely criticised.

A. G. P.

Experimental intoxication by benzene vapour. Concentration of the poison in the blood and rate of disappearance. M. PERONNET (J. Pharm. Chim., 1935, [viii], 21, 503—513).—The amount of C_6H_6 in the blood of guinea-pigs put into a C_6H_6 -containing atm. is nearly \propto the time (up to 20 min.) spent by the animal in this atm. Symptoms of acute intoxication appear when the blood contains 2.60—2.80 mg. of C_6H_6 per 100 g. When the animal is removed into fresh air, the C_6H_6 disappears rapidly from the blood mainly by exhalation (nearly half of the C_6H_6 disappears in the first 5 min.). The urine of animals exposed to C_6H_6 vapour contains excess of PhOH,

although no excess could be detected in the blood. PhOH injected into a rabbit disappeared almost completely from the blood after 5 min. H. G. M.

Ammoniophanæresis in the course of experimental cantharidine nephritis in the dog. M. POLONOVSKI, G. BIZARD, and P. BOULANGER (Compt. rend. Soc. Biol., 1935, 119, 197—198).—Urinary NH_3 and urea fall after injection of cantharidine, the fall being less const. and less marked than in U nephritis. Ammoniophanæresis remains normal. R. N. C.

Toxic nephritis following exposure to carbon tetrachloride and smoke fumes. S. F. DUDLEY (J. Ind. Hyg., 1935, 17, 93—110).—Chronic CCl_4 poisoning is accompanied by grave renal disorders.

H. G. R.

Potassium ferrocyanide poisoning and injury to the kidneys. L. POPPER (Wien. klin. Woch., 1934, 47, 1119—1120; Chem. Zentr., 1935, i, 107).—The toxicity of $K_4Fe(CN)_6$ is due to $Fe(CN)_6^{4-}$ and not to the formation of HCN. Physiological effects on kidneys are described.

A. G. P.

Experimental hepatonephritis in rabbits. I. Modification of the formation of urea by uranium nitrate. II. Comparative values of blood-urea and -indoxyl. III. Comparative determination of the retention of nitrogen by blood and tissues in the rabbit. M. EOK and J. DESBORDES (Bull. Soc. Chim. biol., 1935, 17, 341—343, 344—347, 348—350).—I. Large doses (4—6 mg. U per kg.) cause death as quickly as do small doses (< 2 mg. per kg.) but the serum-urea at the time of death in the former case is decreased, due to hepatic lesions, whereas in the latter case it is increased above normal.

II. Determination of blood-indoxyl forms a better method of following U nephritis than blood-urea since the former vals. are not affected by the size of dose.

III. Normal variation vals. are given for the N_2 separable by NaOBr and for the total non-protein-N in the blood and in the $CCl_3 \cdot CO_2H$ filtrate of muscle of the rabbit.

P. W. C.

Possible influence of rare gases on physiology. F. S. ORCUTT and R. M. WATERS (Anesthesia and Analgesia, 1934, 13, 238—239).—Absence of He and A from an atm. rich in O_2 (90—98%) is not the cause of the intolerance of rats for such atm.

CH. ABS. (p)

Influence of ionised air on normal subjects. L. P. HERRINGTON (J. Clin. Invest., 1935, 14, 70—80).—Ionised air produced by passage over pressed MgO at 950° and filtered so that air may be of either polarity was without effect.

CH. ABS. (p)

Influence of variations of atmospheric ozone on the biological activity of solar radiation. R. LATARJET (Compt. rend., 1935, 200, 1437—1439).—A mathematical expression is developed governing the effect of the selective absorption of atm. O_3 on the relative intensity of the various solar radiations in the extreme ultra-violet.

H. W.

Blood picture, reproduction, and general condition during daily exposure to illuminating gas. I. R. WILLIAMS and E. SMITH (Amer. J. Physiol., 1935, 110, 611—615).—Hæmoglobin and the cell-

plasma ratio increase in rats exposed daily to air containing a sublethal % of illuminating gas.

R. N. C.

Analysis of the effects of carbon monoxide and of cyanides on the [animal] cell by means of vital stains. P. MAKAROV (*Protoplasma*, 1934, 20, 530—554; *Chem. Zentr.*, 1935, i, 252).—The action of CO on epithelial cells of frog intestine results in inhibition of O_2 respiration, cessation of granule formation, gelatinisation of the nucleus, reduction of oxidation-reduction indicators, disappearance of glycogen, and destruction of chondriosomes. HCN inhibits O_2 respiration and prevents the utilisation of intracellular energy, but in other respects its action differs from that of CO.

A. G. P.

Toxicology of hydrocyanic acid. P. R. ORELLA (*Rev. Fac. Cienc. quim.*, La Plata, 1934, 9, 93—102).—Contrary to the findings of Sensi and Revello (A., 1926, 1058) HCN may be detected in the organs of animals killed by respiring HCN as well as in those of animals killed by ingestion of cyanides, and the production of HCN in viscera of normal animals, either by putrefactive changes or by the action of the reagents used, was not observed. Advantages of ammoniacal $AgNO_3$ as an absorbent for HCN are described.

F. A. A.

Chemo-toxicology of hydrocyanic acid. C. GERIN (*Boll. Chim. Farm.*, 1935, 74, 305—307).—Mustard oil (I) in large quantities protects human viscera from putrefaction. It does not form HCNS when distilled with excess Na_2CO_3 in a current of CO_2 , but traces of HCN appear; in presence of $(NH_4)_2S$, (I) is transformed into HCNS. The presence of HCNS in putrefied viscera cannot therefore serve as an indication of HCN poisoning.

R. N. C.

Mottled [tooth] enamel. J. S. WALKER (*J. Amer. Dental Assoc.*, 1933, 1867—1871).—The presence of > 2.7 p.p.m. of F in H_2O causes mottling.

CH. ABS. (p)

Effect of organic dietary constituents on chronic fluorine toxicosis in the rat. P. H. PHILLIPS and E. B. HART (*J. Biol. Chem.*, 1935, 109, 657—663).—Ingestion of 78—84 mg. of F per kg. of body-wt. per day completely inhibits growth. A high-fat-low-carbohydrate diet with or without the addition of lactates, glycerol, or lactic acid does not alter the effect.

H. G. R.

Pulmonary lesions experimentally produced by introduction of aluminium oxide and of borosilicate glass. W. S. LEMON and G. M. HIGGINS (*Amer. Rev. Tuberc.*, 1934, 30, 548—560).—Lesions caused by Al_2O_3 or borosilicate were unlike those caused by SiO_2 . Neither substance circulated in the blood-stream.

CH. ABS. (p)

Effect of calcium, strontium, and barium chloride on tissue oxidation. H. G. O. HOLCK (*Skand. Arch. Physiol.*, 1934, 70, 273—294).— $CaCl_2$ depresses the respiration of all tissues and has a stabilising effect on gastric muscle, after the first depressant action. $SrCl_2$ and $BaCl_2$ are equally depressant but $< CaCl_2$ except in cardiac muscle, where $SrCl_2$ is ineffective and $BaCl_2$ stimulates slightly. Hence the toxic effect of Ba salts seems not to be due

to interference with physiological oxidation. $CaCl_2$, $BaCl_2$, and $SrCl_2$ decrease the p_H to the same slight extent. KCl does not modify the depressant results obtained. The succinodehydrogenase system of horse muscle is not affected by $CaCl_2$ or $Ca(NO_3)_2$. The lactic-dehydrogenase system of rabbit and guinea-pig muscle shows depression with $CaCl_2$, less with $BaCl_2$, and least with $SrCl_2$.

NUTR. ABS. (m)

Toxicity and fixation of magnesium thiosulphate in the organism. R. E. CARRATALA and C. L. CARBONESCHI (*Semana med.*, 1934, 41, II, 25—29; *Chem. Zentr.*, 1935, i, 107).—Use of MgS_2O_3 in HCN poisoning is examined. The characteristic effects of Mg^{++} on the nervous system were observed after injection.

A. G. P.

(A) **Biology of the precipitating action of the mucus of Boro fish, *Pisoodonophis boro* (Ham. Buch.).** S. L. HORA. (B) **Chemistry of the action.** S. RAYCHAUDHURI and B. MAJUMDAR (*J. Proc. Asiatic Soc. Bengal*, 1934, 29, 271—274, 275—283).—(A) Coagulation of mud in estuary H_2O is attributed to the slime excreted by the Boro fish.

(B) The slime has p_H 5.0 (approx.) and coagulates $Fe(OH)_3$ sol and clay suspensions but not Au sols except in the presence of electrolytes. Colloidal particles of slime are positively charged but do not affect the charge on clay particles.

CH. ABS. (p)

Biological action of metals irradiated by means of a mercury-quartz lamp. J. M. GOLDBERG (*Acta med. skand.*, 1934, 83, 212—218; *Chem. Zentr.*, 1935, i, 265).—The oligodynamic (bactericidal) action of Ag, Cu, and Hg, after irradiation in NaCl or Ringer's solution, was $>$ that of Au or Fe similarly treated. The solution after contact with the metals has a stimulant effect on the frog heart.

A. G. P.

Surface inactivation of catalase. L. A. ROSENBLUM (*J. Biol. Chem.*, 1935, 109, 635—642).—Catalase solution is inactivated in the presence of glass beads by adsorption on the surface. Catalase is also adsorbed out of solution without inactivation by quartz.

H. G. R.

Absorption spectra of melanins. G. FLORENCE, J. ENSELME, and M. POZZI (*Bull. Soc. Chim. biol.*, 1935, 17, 268—282).—Absorption curves are given for the melanins of horse sarcoma and *Vicia faba* and of their hydrolysis products and of the products obtained from tyrosine, tyramine, and adrenaline by the action of tyrosinase.

P. W. C.

Variation of the absorption spectra of tyrosine, tyramine, adrenaline, thyroxine, and di-iodo-tyrosine with the p_H of the medium. G. FLORENCE, J. ENSELME, and M. POZZI (*Bull. Soc. Chim. biol.*, 1935, 17, 283—289).—With tyrosine (I), the more alkaline is the medium, the greater is the absorption in the ultra-violet, whilst with tyramine, thyroxine, and adrenaline, the spectrum is not changed by variation in p_H and in all cases it resembles the spectrum of (I) in acid solution. Di-iodotyrosine at p_H 2 has a spectrum resembling that of (I) at p_H 7.4, but the absorption is slightly greater.

P. W. C.

Spectrographic study of the reaction of tyrosinase on tyrosine and related substances. G. FLORENCE, J. ENSELME, and M. POZZI (*Bull. Soc.*

Chim. biol., 1935, 17, 290—313).—Tyrosinase acts on tyrosine (I), tyramine, and adrenaline but not on di-iodotyrosine and thyroxine. The reaction with (I), when followed in terms of changes of absorption, can be divided into 2 phases, an increase in absorption (formation of red substance) followed by a decrease in absorption (pptn. of melanin). Only the first phase is obtained in the reaction adrenaline-tyrosinase and only the second with tyramine-tyrosinase.

P. W. C.

Determination of α -amylase. S. JOZSA and W. R. JOHNSTON (Ind. Eng. Chem. [Anal.], 1935, 7, 143—146).—Jozsa and Gore's method (cf. B., 1930, 389) is improved, and the α -amylase in fluids is measured in "liquefon" units (cf. this vol., 782). The technique involves neither a restricted range of concns. nor the use of empirical consts. (cf. A., 1933, 425).

J. L. D.

Enzymic transformation of phosphoglyceric acid into pyruvic acid by embryos of *Sorghum saccharatum*. C. ANTONIANI (Atti R. Accad. Lincei, 1935, [vi], 21, 192—195).—*Sorghum* embryos transform Na phosphoglycerate into AcCO_2H , the yield of the latter being 25—27% of the theoretical.

T. H. P.

Kinetics of the reversible reaction between hexosediphosphoric acid and dihydroxyacetone-phosphoric acid. O. MEYERHOF (Biochem. Z., 1935, 277, 77—96).—This thermodynamic equilibrium is influenced in the direction of synthesis by increase of concn. of enzyme, substrate, and by addition of ions and proteins. The action of ions is especially pronounced, $0.001M\text{-Mg}^{++}$ causing considerable displacement of equilibrium. The requirements of the van t'Hoff isochore are obeyed in all cases. The initial velocity at different substrate concns. is not \propto to these but is the same for a given enzyme concn. The reaction in both directions appears to be unimol. and it must be assumed that it is determined by some unimol. intermediate reaction, probably the conversion of the Harden-Young ester into a labile hexosediphosphoric ester.

P. W. C.

Activation of pancreatic juice by calcium at different temperatures. M. GUILLAUMIE (Compt. rend. Soc. Biol., 1935, 119, 146—149).—The velocity of activation of pancreatic juice by Ca increases with temp. Tryptic activity increases less rapidly than curdling power at first, rising suddenly later to its max.

R. N. C.

Ultra-violet absorption spectrum of pepsin.—See this vol., 805.

Crystalline carboxypolypeptidase. M. L. ANSON (Science, 1935, 81, 467—468).—A cryst. H_2O -insol. protein which attacks chloroacetyltyrosine and pepsin digests even in presence of CH_2O has been isolated from ox pancreas. Recrystallisation frees the globulin from proteinase but does not change its carboxypolypeptidase activity.

L. S. T.

Influence of salts of different buffer mixtures on proteolytic and peptolytic processes. E. MASCHMANN and E. HELMERT (Biochem. Z., 1935, 277, 97—121).—The velocity of hydrolysis of gelatin and Witte's peptone in citrate, acetate, and veronal-

acetate-HCl buffer solutions by papain (with and without its impurity "X") in presence and absence of HCN, cysteine, reduced glutathione, ascorbic acid, $\text{K}_4\text{Fe}(\text{CN})_6$, hæmoglobin, papain impurity X-Fe, and other Fe salts is investigated. In general, the reaction proceeds more quickly in citrate than in the other buffer solutions but the difference decreases the older is the enzyme solution.

P. W. C.

Influence of various arsenical compounds on papain. E. MASCHMANN (Biochem. Z., 1935, 277, 139—147).—The influence of 8 ter- and 7 quinquivalent therapeutically important As compounds on the hydrolysis of gelatin by papain is investigated in citrate and acetate buffer solutions, the amounts of enzyme and substrate being varied. The different enzyme preps. and kinds of gelatin did not influence the result, but the type of buffer used had considerable effect. Thus arsenophenylglycine inhibited the hydrolysis in citrate, but accelerated in acetate, buffer.

P. W. C.

Stabilisation of carboxylase solutions. O. VON SCHOENEBECK (Biochem. Z., 1935, 277, 451).—Addendum to the author's earlier paper (with Neuberger) (this vol., 401). For stabilisation of enzymes, whereas previous workers treated the animal or vegetable tissue with anhyd. glycerol, the author in this case stabilises by adding glycerol (up to 50%) to the aq. maceration extract prepared in the usual way.

P. W. C.

Inactivation of zymase or carboxylase by diazomethane. F. AXMACHER (Klin. Woch., 1934, 13, 776; Chem. Zentr., 1935, i, 92).—Dried yeast ($\text{COME}_2\text{-Et}_2\text{O}$), treated with CH_2N_2 , was unable to ferment sugars or AcCO_2H . Top and bottom yeasts behaved similarly. Glucose fermentation was the most sensitive.

A. G. P.

Changes in metabolic products of pure culture yeasts on repeated propagation. E. SCHILD and R. WEBER (Woch. Brau., 1935, 52, 161—165).—Fermented worts obtained as a result of successive cultivations of the same yeast show small variations in composition; no regularities can be traced through these variations, although there appears to be a tendency for esters to diminish in amount. Ester formation is independent of NH_2 -acid fermentation, but depends on the character and physiological condition of the yeast.

I. A. P.

Discrepancies in the value of the aerobic reducing intensity of the yeast cell and starfish egg. L. V. BECK (Science, 1935, 81, 469—470).—Independently of whether a cytoplasmic p_R val. of 6.0 or the more probable val. of 7 be assumed, the aerobic reducing intensity of Fleischmann's yeast cells estimated from the reaction of penetrating oxidation-reduction indicators is more negative than the val. estimated from the reaction of the naturally-occurring oxidation-reduction system cytochrome-C.

L. S. T.

Behaviour of glycine-alcohol towards yeast shaken with oxygen. F. LIEBEN and S. MOLNAR (Biochem. Z., 1935, 277, 165—170).—The system NH_2 -acid-MeCHO on addition to yeast shaken with O_2 differs from the system NH_2 -acid-EtOH in that with the former, both components are utilised by the

yeast. The absorption of glycine is increased in the presence of both MeCHO and EtOH whereas the absorption of EtOH is inhibited by the presence of glycine. P. W. C.

Proteins of yeast (*Saccharomyces cerevisiae*). F. A. CSONKA (J. Biol. Chem., 1935, 109, 703—715).—The N, P, S, cystine (I), tryptophan, tyrosine, arginine, histidine (II), and lysine contents of the fractions of brewers' and bakers' yeasts obtained by treatment with Et₂O and successive extraction with H₂O, 10% aq. NaCl, and 0.2% aq. NaOH are given. Acid hydrolysis of yeast attacks (I) and (II). The amount of coagulable protein obtained from yeast changes with the duration of treatment with Et₂O, reaching a max. at about 20 hr. and then decreasing. W. McC.

Effect of ultra-violet irradiation on certain yeasts, particularly *Schizosaccharomyces octosporus*, Beijerinck. A. DELAFONT (Compt. rend. Soc. Biol., 1935, 119, 133—134). R. N. C.

Formation and distribution of bios. K. SUCHORUKOV, E. KLING, and D. KLIASCHKO (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 524—531).—Light of short λ is necessary for bios formation, which is inhibited by NO₃⁻ and enhanced by NH₃-N; glucose has no effect. Bios is liberated during the autolysis of proteins; plants enrich the soil with it, whence it is utilised by organisms which cannot effect its synthesis. P. G. M.

Relation between the phosphorus content of soil and the yield of mycelium of *Aspergillus niger*. A. SARTORY, R. SARTORY, J. MEYER, and F. ARNOLD (Compt. rend. Soc. Biol., 1935, 119, 304—306).—P₂O₅ in the mycelium of young cultures \propto that available, the assimilation decreasing in the adult cultures, proteolysis causing a loss of P from mycelium. Conditions are given for satisfactory operation of Niklas' method for determination of soil fertility. H. G. R.

Action of alkaloids on the invertase produced by *Aspergillus niger*. G. MEZZADROLI and A. AMATI (Atti R. Accad. Lincei, 1935, [vi], 21, 46—50).—Secretion of invertase by *A. niger* grown in sucrose-Raulin solution is enhanced by small amounts of quinine or strychnine, but retarded by caffeine. The activity of the ready-formed enzyme is depressed by all three compounds, most by strychnine. T. H. P.

Biochemistry of micro-organisms. XLV. Metabolic products of *Penicillium Charlesii*, G. Smith. IV. *l*- γ -Methyltetronic acid. Formation and structure of ramigenic and verticillic acids. P. W. CLUTTERBUCK, H. RAISTRICK, and F. REUTER (Biochem. J., 1935, 29, 1300—1309).—*l*- γ -Methyltetronic acid (I), C₅H₆O₃, is formed as a metabolism product when *P. Charlesii* is grown on a synthetic medium containing glucose and can be isolated through the Hg salt. This acid on keeping in solutions containing COMe₂ readily gives first isopropylidenebis- γ -methyltetronic acid, C₁₃H₁₆O₆, m.p. 172°, α _D²⁰ -39°, dibasic, and on longer keeping acetonylisopropylidenebis- γ -methyltetronic acid, C₁₉H₂₀O₆, m.p. 171°, identical with ramigenic acid (II) (Me₁ derivative, m.p. 199°). Verticillic acid (III),

C₂₆H₃₀O₁₁.H₂O, on mild hydrolysis gives 1 mol. of (II) and 2 mols. of (I). By using EtOH instead of COMe₂ for separation of the polysaccharide fraction, it was shown that carolic, carolinic, carlic, and carlosic acids, and (I) are true metabolism products, whilst the (II) and (III) of the earlier experiments (A., 1934, 452) must be regarded as artefacts arising from (I)+COMe₂. A new method for synthesis of (I) is described. P. W. C.

Physiology of *Rhizoctonia solani*, Kuhn. III. Susceptibility of different plants as determined by seedling infection. IV. Effect of a toxic substance produced by *R. solani*, when grown in liquid culture, on the growth of wheat, carrots, and turnips. W. NEWTON and N. MAYERS (Sci. Agric., 1935, 15, 393—398, 399—401).—III. The susceptibility of various plants grown in infested soil differed widely. Turnips and carrots produced stunted growth but no evidence of infection. Resistance of plants grown in inoculated agar culture differed from that in infected soil.

IV. A heat-stable toxin is secreted by *R. solani* during growth and is present in the mycelium. Sterilised extracts of old cultures of the organism are much more toxic to turnip and carrot than to wheat. A. G. P.

Aerobic respiration in *Spirostomum ambiguum* and the production of ammonia. H. SPECHT (J. Cell. Comp. Physiol., 1934, 5, 319—333).—Manometric measurement of respiration of *S. ambiguum* yields different vals. for O₂ consumption and CO₂ production according to the presence or absence of HCl in the respiration vessel. This is attributed to the production of NH₃ by the protozoan. A. G. P.

Decomposition of pentosans and pentoses by micro-organisms. L. M. HOROVITZ-VLASSOVA and N. V. NOVOTELNOV (Zentr. Bakt. Par., 1935, 91, II, 468—481).—Ability to decompose pentosans is associated principally with fungi (*Aspergillus*, *Penicillium*, etc.). The pentoses formed are acted on by certain moulds, e.g., *Aspergillus*, with the formation of citric, oxalic, and other org. acids, and also by bacteria. Acid hydrolysates of cottonseed and sunflower husk are decomposed by *B. lactis aerogenes* forming lactic acid, AcOH, and CO₂, and by *B. esterificans* to yield, principally, PrCO₂H and CO₂. The general use of oil-seed press-cakes for the production of org. acids is discussed. A. G. P.

Cellulose-decomposing, sporing bacteria of the groups *Bacillus omelianski* and *B. macerans*. V. MEYER (Zentr. Bakt. Par., 1935, II, 92, 1—33).—An organism is isolated which, in protein-free media, decomposes cellulose (I) only when living in symbiosis with other organisms (notably *B. coli*). Addition of protein permits decomp. of (I) without symbiosis, and with production of HCO₂H, AcOH, CO₂, and H₂. The mechanism of the symbiosis is examined. A. G. P.

Assay of preparations of lactic acid bacteria. G. TIXIER and J. BECK (Bull. Soc. Chim. biol., 1935, 17, 252—267).—Methods for assessing the biological val. of pharmaceutical preps. of these organisms in

terms of bacteriological counts and lactic acid production are described.

P. W. C.

Vitamin and nitrogenous food requirements of the true lactic acid bacteria. S. ORLA-JENSEN (Nature, 1935, 135, 915).—All the lactic acid bacteria, *Streptococci* as well as rod-shaped forms, require an alkali-stable substance related to bios for their growth. The rod forms require, in addition, lactoflavin and possibly another activator. The *Thermobacteria* show as narrow requirements as regards N food as do higher animals, but the *Streptobacteria* are satisfied with NH_4 salts and a trace of cysteine, whilst the *Streptococci* require only NH_4 salts as the source of N.

L. S. T.

Utilisation of the "complete" antigen by living *B. ærtrycke*. A. BOIVIN and L. MESROBEANU (Compt. rend. Soc. Biol., 1935, 119, 209—211).—The antigen is utilised by the *S* and *R* forms of *B. ærtrycke* when it forms the sole source of nutrition. The fatty acid fraction is apparently utilised more readily than the polysaccharide fraction. The antigen probably serves as a reserve carbohydrate supply for the bacteria.

R. N. C.

Respiration and fermentation of pathogenic bacteria. IV. Oxygen respiration and hydrogen peroxide production of pneumococcus. A. FUJITA and T. KODAMA (Biochem. Z., 1935, 277, 17—31).—The optimal p_{H} for the respiration of pneumococcus (which does not contain the oxidation enzyme) is 7.1 and the influence of ions (especially of cations) is very pronounced, addition of K^+ , Ca^{++} , and especially of Mg^{++} effecting considerable increase. NH_4OH ($10^{-4}M$) completely inhibits the action of catalase but has no effect on the respiration of pneumococcus. The ratio of O_2 used to H_2O_2 formed is the same for all substrates, 80% of the used O_2 being converted into H_2O_2 . H_2O_2 reacts with AcCO_2H , AcCHO , and $\text{CO}(\text{CH}_2\text{OH})_2$. The greater is the virulence of the organism, the greater is the production of H_2O_2 . During respiration of pneumococcus, hæmoglobin is converted into methæmoglobin. Decrease of respiration by H_2O_2 is inhibited by addition of AcCO_2H or catalase.

P. W. C.

Nitrifying bacteria in activated Paris mud. H. WINOGRADSKY (Compt. rend., 1935, 200, 1886—1888).—Three groups of nitrifying bacteria are described.

R. S. C.

Pigment formation by bacteria. C. A. SAGASTUME and A. A. SOLARI (Rev. Fac. Cienc. quim., La Plata, 1934, 9, 1—5).—The addition of certain sugars, or Fe^{+++} , to the media favours the production of a red pigment (extractable by EtOH) by *Rhodococcus roseus*.

F. A. A.

Pigment of *Bacillus violaceus*. I. Production, extraction, and purification of violacein. W. C. TOBIE (J. Bact., 1935, 29, 223—227).—Growth and pigmentation of *B. violaceus* is increased by passage of O_2 through the culture. The amount of pigment obtained is markedly influenced by the quality of the peptone used in the medium. The isolation of violacein is described.

A. G. P.

Species of *Salmonella* producing a water-soluble pigment. M. W. DESKOWITZ and L. BUCHBINDER (J. Bact., 1935, 29, 293—298).—The organism (probably a variant of *S. enteritidis*) produced a yellow pigment most readily in media containing certain brands of peptone.

A. G. P.

Decomposition of salts of organic acids by bacteria of the genus *Salmonella*. A. A. HAJNA (J. Bact., 1935, 29, 253—258).—Nearly all members of this genus utilise N as NH_4 salts, P as PO_4^{+++} , and C as org. acids. Mg salts favour growth. Ability to utilise particular acids varied with species and with strains of individual species. Mucic acid was decomposed in nearly all cases.

A. G. P.

Culture of *B. tuberculosis* and BCG in different evolutionary states (granular, filamentous, and acid-resisting and non-acid-resisting bacilli) by means of lysates obtained by repeated freezing. E. GRASSET (Compt. rend. Soc. Biol., 1935, 119, 261—265).—By submitting living *B. tuberculosis* and BCG to repeated freezing, products of microbial lysis are obtained from which the various evolutionary forms may be developed.

H. G. R.

Chemical nature of the lipid hapten from tubercle bacilli killed by heat. M. A. MACHEBŒUF, G. LEVY, and M. FAURE (Compt. rend., 1935, 200, 1547—1549; cf. A., 1934, 564, 929).—Phosphoaminolipins have no hapten activity. Active material contains P but no N, is sol. in CHCl_3 , insol. in COMe_2 , and slightly sol. in MeOH , and loses its activity rapidly in alkaline and slowly in acid (p_{H} 3.0) media.

A. G. P.

Oxytrophs and oxytrophic organisms. A. LVOV (Compt. rend. Soc. Biol., 1935, 119, 87—90).—The term "oxytrophic" is applied to organisms requiring other org. compounds besides org. N compounds for growth.

R. N. C.

Determination of lipins in micro-organisms. O. TURPENEN (Suomen Kem., 1935, 8, B, 17—18).—The true lipin content of *Geotrichoides* cannot be obtained merely by extraction with solvents, because of the mechanical structure of the material. Extraction is facilitated by previous treatment with hot 5*N*- NaOH or HCl , after which the presence of fats cannot be demonstrated histologically in the sample.

J. L. D.

Balance of nitrogen determinable by the Kjeldahl method in aerobic cultures of micro-organisms. III. Role of ammonia. M. LEMOIGNE and R. DESVEAUX (Bull. Soc. Chim. biol., 1935, 17, 210—218).—The loss of N occurring in cultures of micro-organisms during ageing is due to oxidation of NH_3 to N_2 .

P. W. C.

Purification of vaccine lymph by X-rays. B. S. LEVIN (Compt. rend., 1935, 200, 1441—1443).—By use of a Cr anticathode vaccine lymph can be freed by X-rays from bacteria without sensibly affecting its activity.

H. W.

Action of ether, chloroform, sodium fluoride, phenol, and saponin on the virus of infectious anæmia. L. BALOZET (Compt. rend. Soc. Biol., 1935, 119, 162—165).—The virus is destroyed rapidly by 1% of saponin, and slightly attacked by 0.1% of

PhOH, higher concns. of which also destroy it rapidly. It is not affected by Et_2O , CHCl_3 , or NaF .

R. N. C.

Oxidation-reduction phenomenon of methylene-blue in transmissible lysis. G. PETROVANO (Compt. rend. Soc. Biol., 1935, 119, 218—219).—The transformation undergone by *B. coli* in transmissible lysis is not oxido-reductive. The lytic principle alone is chemically inactive and incapable of fixing free O_2 .

R. N. C.

Photo-sensitisation of a streptococcus. D. BROCC-ROUSSEU (Compt. rend. Soc. Biol., 1935, 119, 272—273).—The antiseptic action of sulphamido-chrysoidine hydrochloride is markedly increased by sunlight.

H. G. R.

Bactericidal action of azochloroamide (N,N-dichloroazodicarbonamide). F. C. SCHMELKES and E. S. HORNING (J. Bact., 1935, 29, 323—331).—Azochloroamide is more effective in the presence of org. matter (e.g. serum) than other Cl compounds examined. Its action is restricted by actively reducing substances, e.g., hæmoglobin.

A. G. P.

Bactericidal properties of sodium formaldesulphoxylate in vivo. I. M. RABINOWITZ, A. C. CORCORAN, J. A. DAVIDSON, and L. J. RHEA (Canad. Med. Assoc. J., 1934, 31, 534—535).—Satisfactory treatment of Hg poisoning is recorded.

CH. ABS. (p)

Biological properties of carvacrol. D. GARDNER and M. L. CASELLI (Compt. rend., 1935, 200, 1430—1432).—The bactericidal action of carvacrol (I) towards *Staphylococcus aureus* is very much more pronounced than that of thymol or menthol. The Na derivative (II) of (I) is more active than the $\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3$ compound, particularly in aq. solution. The action of (I) towards Kedrewski's paratuberculosis bacillus, of (I) and (II) towards *B. coli*, and the toxic power of (I) have been investigated.

H. W.

Effect of various therapeutic agents, especially of the caffeine group, on bacterial agglutination. K. WATANABE (Tohoku J. Exp. Med., 1934, 24, 111—117).—The agglutination of *Eberthella typhosa* by the corresponding rabbit antiserum was unaffected by quinine, salicylic acid, "Thyroprotein," "Pituglandol," cocaine, pilocarpine, atropine, and nicotine but was inhibited by caffeine- NaOBz and theobromine- Na salicylate or $-\text{NaOAc}$.

CH. ABS. (p)

Physiology of parathyroid glands. VII. Responses of normal human kidneys and blood to intravenous parathyroid extract. R. ELLSWORTH and J. E. HOWARD (Bull. Johns Hopkins Hosp., 1934, 55, 296—308; cf. A., 1933, 320).—Intravenous injection of parathormone caused an immediate increase in urinary PO_4''' and p_{H} , an increase in Cl' , and, occasionally, a diuresis. Urea clearance was unchanged. The inorg. P of the plasma decreased somewhat and serum-Ca showed variable changes. The hormone has a fundamental influence on P metabolism.

CH. ABS. (p)

Alterations in liver-glycogen following thyroid, iodine, and glucose feeding. W. D. FRAZIER and H. FRIEMAN (Surgery, Gynæcol., Obstet., 1935, 60, 27—29).—Addition of thyroid extract to a productive

diet for guinea-pigs results in a depletion of liver-glycogen which is not prevented by administration of I or glucose.

CH. ABS. (p)

Effect of thyroid and thyroxine on the concentration of creatine in the heart, muscle, liver, and testes of the albino rat. M. BODANSKY (J. Biol. Chem., 1935, 109, 615—622).—After feeding of thyroid or thyroxine, cardiac hypertrophy and diminution of total creatine (I) by 20—50% was observed, death from heart failure being probably related to the lowering of phosphocreatine. (I) in muscle may be reduced by 50% depending on the duration of the symptoms. There was a slight increase in (I) of the testes, but no change in the liver.

H. G. R.

Effect of alkali on the absorption of a peptide of thyroxine from the gastro-intestinal tract. W. O. THOMPSON, P. K. THOMPSON, and L. F. N. DICKIE (J. Clin. Invest., 1934, 13, 933—947).—The peptide, containing I 48% with N:I ratio 0.48—1.0, had little effect on basal metabolism when administered by mouth in aq. suspension, but when dissolved in dil. aq. NaOH was as effective as Na thyroxine.

CH. ABS. (p)

Effect of thyroidectomy and thyroxine on the response of the denervated heart to injected and secreted adrenaline. M. E. McK. SAWYER and M. G. BROWN (Amer. J. Physiol., 1935, 110, 620—635).—The response of the denervated heart of the cat to injected and secreted adrenaline is lowered by thyroidectomy and restored by sufficient thyroxine to restore metabolism to its normal level.

R. N. C.

Adrenaline content of the blood and variations in blood-sugar. F. MEYTHALER and K. WOSSIDLO (Arch. exp. Path. Pharm., 1935, 178, 320—329).—The diminution in blood-sugar (I) in men due to insulin is accompanied by an increase in the adrenaline (II) content of the peripheral blood before the "crit. point" [(I)=0.07—0.08%] is reached. Even during the post-hyperglycæmic fall in (I) (i.e., with vals. up to > 0.3%) following injection of glucose, the blood-(II) is > normal.

F. O. H.

Protective action of adrenaline. F. MEYTHALER (Arch. exp. Path. Pharm., 1935, 178, 330—332).—The so-called "emergency function" of adrenaline in conditions such as hypoglycæmia, asphyxia, shock, etc. is discussed and the conception of a definite "crit. point" of the blood-sugar is criticised (cf. preceding abstract and this vol., 901).

F. O. H.

Adrenaline and vagal tonus. II. A. CROCETTA (Boll. Soc. ital. Biol. sperim., 1933, 8, 1714—1717).—Vagotomy in new-born puppies does not produce adrenalinæmia. Asphyxia or bleeding provokes a discharge of adrenaline as in adult dogs.

R. N. C.

What part of the melanophore system in *Fundulus* is acted on by adrenaline? G. H. PARKER (J. Cell. Comp. Physiol., 1934, 5, 311—318).—Adrenaline causes an accumulation of pigment in the melanophores of *Fundulus* by direct action on the colour cells and not by nerve stimulus.

A. G. P.

Influence of oxidation-reduction systems on adrenaline action. K. TERAI (Folia Pharmacol.

Japon., 1934, 19, No. 1, 79—89).—Adrenaline action on various organs of mouse, rabbit, and toad is prevented by benzoquinone and scarcely affected by quinol. CH. ABS. (p)

Chologogue action of secretin and derivatives. J. LA BARRE and R. GOFFIN (Compt. rend. Soc. Biol., 1935, 119, 311—313).—Secretin and excretin but not incretin augment the secretion of bile, probably due to a direct stimulation of the liver. H. G. R.

Crystalline insulin. VI. Influence on liver-glycogen. M. BURGER and H. KOHL. **VII. Influence on "residual carbon" and lactic acid of the blood.** M. BURGER, F. HORN, and V. RUPPERT (Arch. exp. Path. Pharm., 1935, 178, 269—281, 282—294).—VI. Intraperitoneal injection of 1 c.c. of physiological aq. NaCl into narcotised, fasting dogs diminishes liver-glycogen (I) by 17% within 6 hr. and injection of insulin (II) (0.02—0.03 mg. per kg.) under parallel conditions, by 55%. The depletion of (I) increases the difference between the blood-sugar levels of jugular vein and liver capillaries, storage of carbohydrate occurring in the muscles.

VII. Injection of (II) (0.02 mg. per kg.) into normal dogs produces a rapid fall of approx. 0.15% in the "residual C" of the blood due more to disappearance of fat than of sugar. A similar phenomenon occurs with diabetics with doses of 0.010—0.015 mg. per kg.; with 0.0025 mg. per kg. the sugar-C falls but "residual C" and, more especially, the fat-C increase. With small or large doses of (II), the blood-lactic acid increases to an extent dependent on dose and fall in blood-sugar. F. O. H.

Fall in blood-sugar in men after intravenous administration of insulin. F. MEYTHALER and E. KLEINEIDAM (Arch. exp. Path. Pharm., 1935, 178, 315—319).—Determinations at 1—2-min. intervals indicate that the blood-sugar (I) does not diminish steadily but gives a zig-zag curve. A parallelism between this curve and that of the pulse rate indicates an intermittent compensatory release of adrenaline (due to a sympathetic nervous mechanism); a definite "crit. point" of adrenaline release does not occur (cf. Cannon *et al.*, Amer. J. Physiol., 1924, 69, 48).

F. O. H.

Secondary action of insulin on hypercholesterolaemic rabbits. A. I. LEWIN (Arch. exp. Path. Pharm., 1935, 178, 308—314).—Simultaneous enteral administration of cholesterol (I) to rabbits has no influence on the hypoglycaemic symptoms produced by insulin. With cholesterolaemia due to feeding of (I), however, the symptoms do not appear, although the normal fall in blood-sugar occurs: with such animals, withdrawal of blood favours the reappearance of the symptoms. F. O. H.

Peripheral action of insulin in normal animals. N. B. LAUGHTON and A. B. MACALLUM (Biochem. J., 1935, 29, 1257—1262).—The max. tolerated doses (M.T.D.) of certain inhibitors to different stages in the metabolism of glucose are given for rabbits and the effects of insulin (I) in antagonising their effects observed. The M.T.D. of KCN, urethane, and NaF produce hyperglycaemia which temporarily neutralises the action of 1 rabbit unit of (I) per 2 kg. body-wt.

The M.T.D. of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ only delays the effects of (I). (I) exerts no antagonistic action to hyperglycaemia produced in these ways; however it inhibits that produced by adrenaline and hence it is concluded that this is not due to a mobilisation of liver-glycogen but to the sp. action in the respiratory cycle and intermediate stages of glucose metabolism. (I) exerts its max. effect on the reaction between AcCO_2H and glycerophosphoric acid. H. D.

Effect of bacteria on insulin. M. SAHYUN and P. BEARD (J. Lab. Clin. Med., 1934, 20, 160—164).—The activity of insulin is destroyed by *Proteus vulgaris*, but is not affected by *E. coli*. CH. ABS. (p)

Influence of adrenaline, pituitrin, and ephetonin on the absorption of insulin. V. CLAUSEN (Diss., Copenhagen, 1934, 144 pp.).—When adrenaline (I) was combined with insulin (II) [0.1—0.2 ml. of (I) 1:1000 to 5 ml. of (II)=200 international units] the rate of absorption of (II) was retarded by the local action of (I); the immediate effect on blood-sugar (III) was therefore < and the later effect > that of (II) alone. With a normal or moderately high fasting (III), injection of (II) and (I), given at the same time as food, gave an improved (III) curve, but if the fasting (III) was high, the injection had to precede a meal by 1—2 hr. to give good results. In the treatment of diabetes (5 cases) good results were got in 3 that showed a normal fasting (III) with (II), and were liable to (II) convulsions. In 2 cases with high fasting (III), sugar tolerance was improved by combined (II) and (I) treatment. Pituitrin had a similar effect, but ephetonin had none. NUTR. ABS. (b)

Relation of the pituitary gland to the action of insulin and adrenaline. O. COPE and H. P. MARKS (J. Physiol., 1934, 83, 157—176).—The response of the adrenals to insulin hypoglycaemia in the dog after removal of the pituitary is normal, but the liberated adrenaline (I) does not restore the blood-sugar (II) to normal, although the liver contains ample reserve of glycogen (III). The elevation of (II) by (I) is also diminished. These changes are not reversed by administration of thyroid. Conversely, injection of pituitary extract increases resistance to insulin and response to (I), which effects are not prevented by thyroidectomy. This suggests the presence in the pituitary of a principle rendering liver-(III) susceptible to the mobilising action of (I).

R. N. C.

Effect of a chronic enrichment of the organism with insulin on the steadiness of the thyroid secretion. V. S. SIMNITZKI and A. L. KOMENDANTOVA (Virchow's Archiv, 1934, 293, 448—457; Chem. Zentr., 1935, i, 103).—Repeated daily injections of insulin over a period of 20—45 days in rabbits causes a lowering of the thyroid function, considered to be the result of increased carbohydrate assimilation and reduction of the protein exchange controlled by the thyroid. R. N. C.

Effects of thyro-parathyroidectomy and carbohydrate intake on the action of anterior pituitary extracts. O. H. GAEBLER (Amer. J. Physiol., 1935, 110, 584—592).—Antuitrin-G (I) produces large calorogenic responses in thyro-parathyroidectomised

dogs which cannot be explained as toxic effects. The effect on N storage is \times in normal dogs. H_2O storage followed by diuresis occurs through the action of (I). Fat oxidation is increased during the post-absorptive periods of the two days following (I) injection, whether the carbohydrate (II) intake is moderate or high, and also when (II) equiv. to the rise in metabolism is added to the diet at the time of injection, but not when the (II) added is equiv. to twice the rise.

R. N. C.

Separation of a thyrotropic from the gonadotropic substances of the pituitary. R. O. GREEP (Amer. J. Physiol., 1935, 110, 692—699).—The thyrotropic substance is pptd. from the pituitary extract with $BzOH$. It is destroyed by heat together with the gonadotropic substances, and is not present in extracts of placenta, or urine or serum of pregnancy.

R. N. C.

Effect of extracts of posterior pituitary on liver-glycogen. P. GOMORI and J. CSOMAY (Magyar Orvosi Arch., 1934, 35, 277—281).—Oxytocin (orasthin) and vasopressin (tonephin), injected into rats, produced an approx. equal decrease in liver-glycogen which was not, in either case, due to histamine.

NUTR. ABS. (b)

Effect of the pressor principle of the posterior lobe of the pituitary body on the liver-fat after the feeding of choline chloride. B. MUKERJI and H. B. VAN DYKE (Chinese J. Physiol., 1935, 9, 69—75).—Oral administration of choline chloride (0.2—0.5 g. per kg. body-wt. *per diem*) to rabbits did not prevent the acute increase in liver-fat following a single large dose of pitressin.

W. O. K.

Relation of the posterior lobe of the pituitary gland to anæmia and to blood formation. E. C. DODDS and R. L. NOBLE (Nature, 1935, 135, 788).—Rabbits injected subcutaneously with 150 mg. of $COMe_2$ -picric acid extract of the lobe or with 40 c.c. of standard B.P. pituitary extract develop a severe macrocytic anæmia. A marked leucocytosis is often associated. A reticulocyte response commences soon after the appearance of the anæmia. The results suggest the possibility that the control of blood destruction by the reticulo-endothelial system may reside in the posterior lobe of the pituitary gland.

L. S. T.

Posterior lobe of the pituitary gland: its relationship to the stomach and to the blood picture. E. C. DODDS, G. M. HILLS, R. L. NOBLE, and P. C. WILLIAMS (Lancet, 1935, 228, 1099—1100).—Chronic gastric ulcers in the acid-bearing area of the stomach are produced by the subcutaneous injection in rabbits of standard B.P. pituitary extract or of the $COMe_2$ -picric acid extract of the lobe. Injection of the extract appears to produce a temporary inhibition of HCl secretion so that the stomach does not react to histamine stimulus. Extracts prepared from spleen, liver, testes, pancreas, thyroid, etc. have no action on the blood or stomach picture.

L. S. T.

Relation of the pituitary, hypothalamus, and the autonomic nervous system to carbohydrate metabolism. L. DAVIS (Ann. Surg., 1934, 100, 654—666).—Hyperglycæmia and glycosuria do not

follow pancreatectomy in the cat which has bilateral hypothalamic lesions situated in the tuber cinereum. Stimulation of the superior cervical and stellate ganglia in the cat causes hyperglycæmia and glycosuria, but not after bilateral symmetrical lesions of the pons or section of the splanchnic nerves. The probable relationship of this part of the brain to pancreatic diabetes is discussed. NUTR. ABS. (b)

Effects of pituitary implants and extracts on the genital system of the lizard. L. T. EVANS (Science, 1935, 81, 468—469).—The morphological changes accompanying the injection of human pregnancy urine extract and sheep pituitary extract in male and female lizards are described. Metabolism, general activity, and moulting are also increased.

L. S. T.

Sex hormones and pituitary growth. P. ENGEL (Klin. Woch., 1934, 13, 1540—1541; Chem. Zentr., 1935, i, 102).—Injection of sex hormones simultaneously with pituitary extract in rats does not inhibit the action of the growth hormone.

R. N. C.

Synthesis of folliculin in female [rats] with A-avitaminosis. B. A. KUDRJASHOV (Arch. exp. Path. Pharm., 1935, 178, 295—304).—With severe A-avitaminosis, the œstrous cycle is not markedly changed, whilst administration of gonadotropic pituitary prep. (prolan) induces œstrus. Hence A-avitaminosis has no effect on the production of folliculin by the ovaries or on the action of prolan.

F. O. H.

œstrin content of pregnancy urine and placenta of the chimpanzee. E. ALLEN, A. W. DIDDLE, and J. H. ELDER (Amer. J. Physiol., 1935, 110, 593—595).—Both œstrone and œstriol appear in the urine of chimpanzees at various stages of pregnancy, and in the placenta at full term.

R. N. C.

Influence of œstrin on the pituitary-gonad complex of the immature female rat. C. E. LANE (Amer. J. Physiol., 1935, 110, 681—685).—œstrin at first stimulates the pituitary to increased gonadotropic hormone secretion. The liberation of the follicle-stimulating hormone is then inhibited. Formation of the luteinising hormone or of a similarly-acting substance from the pituitary is greatly increased.

R. N. C.

Hormones of the corpus luteum. H. PENAÜ and H. SEIGNNET (J. Pharm. Chim., 1935, [viii], 21, 485—495).—The lipin-sol. hormone of the corpus luteum may be assayed by determining the min. quantity required to produce a certain action on the uterus of the immature rabbit following administration of folliculin.

W. O. K.

Vitamins: their specific and non-specific actions. P. KARRER (Bull. Soc. chim., 1935, [v], 2, 917—937).—A lecture.

Utilisation of energy-producing nutriment and protein in white and yellow corn and in diets deficient in vitamin-A, -D, and -B₂. W. W. BRAMAN, A. BLACK, O. G. KAHLENBERG, Le R. VORIS, R. W. SWIFT, and E. B. FORBES (J. Agric. Res., 1935, 50, 1—37).—Yellow corn contains more vitamin-A than does white corn, whilst the latter is

superior in digestibility and food energy. Rats fed on a vitamin-*D*-deficient diet are inferior to those on a complete diet as regards appetite, gain of fat and energy, and elimination of C in the urine. Deficiency of vitamin-*B*₂ does not affect the digestibility of protein, but it depresses fat and protein synthesis and energy storage; it also increases the C:N ratio in the urine. P. G. M.

Possibility of local vitamin deficiency. S. BALACHOVSKI (Presse méd., 1934, 42, 1404—1407).—Colloidal carotene in the form of the crude unsaponifiable fraction of carrot lipins, applied locally, relieved superficial eye lesions, gingivitis, etc.

CH. ABS. (p)

Lactic bacilli as a possible source of vitamin-*B*. R. LECOQ and H. VILLETTE (Compt. rend. Soc. Biol., 1935, 119, 274—275).—*B. bulgaricus* in a diet containing 66% of sucrose increases the vitamin-*B* requirements of the pigeon. H. G. R.

Lactic bacilli and alimentary unbalance. R. LECOQ (Compt. rend. Soc. Biol., 1935, 119, 276—277; cf. preceding abstract).—Pigeons receiving *B. bulgaricus* in a diet low in sugar develop symptoms of polyneuritis similar to those observed with lactose. H. G. R.

Flavin balance in animals. F. VIVANCO (Naturwiss., 1935, 23, 306).—With normal rats the excretion of flavin (I) in the faeces is approx. twice that in the urine, the total being $3-5 \times 10^{-3}$ g. per rat daily. With *B*₂-avitaminosis for 4—6 days, the liver, kidney, and heart have only 30% of the normal (I) content whilst after 14 days the urine is (I)-free and growth ceases; even at death, however, the organs contain approx. one third the normal content of (I). Ingestion of (I) produces growth prior to replenishment of reserve depots. F. O. H.

Vitamin-*C* content of Chinese foods and drugs. Y. F. CHU and B. E. READ (Chinese J. Physiol., 1935, 9, 47—61).—A large no. of Chinese fruits, vegetables, and medicinal herbs have been examined. W. O. K.

Biological synthesis of ascorbic acid. B. C. GUHA and A. R. GHOSH (Nature, 1935, 135, 871; cf. this vol., 416).—The liver-tissues of the ox, cat, and fowl do not convert mannose (I) into ascorbic acid (II) *in vitro*. Intravenous and subcutaneous injection of (I) in rats increases the (II) content in all tissues investigated. Intravenous injection of glucose (III) increases the (II) content of the adrenal gland. Embryonic guinea-pig tissue at an early stage of development, and ovarian tissue of the pregnant guinea-pig and of the adult non-pregnant monkey can also convert (I) into (II) at pH 7.4 in a phosphate-buffered Ringer-Locke solution at 37°. Replacement of (I) by (III) does not lead to an appreciable synthesis of (II). Although (III) is the ultimate precursor of (II), it has probably to pass through an intermediate stage of (I) or some (I)-like configuration. L. S. T.

Determination of ascorbic acid by titration. E. W. McHENRY and M. L. GRAHAM (Nature, 1935, 135, 871—872).—The increased ascorbic acid (I) titration val. against phenol-indophenol obtained after heating various foodstuffs is probably due to the liberation

of combined (I) from an ester. Hence simple extraction and titration of certain plant tissues measures only free (I). An amount of reversibly-oxidised (I) may also escape measurement. Ox adrenal tissue contains little combined (I) and none of the reversibly-oxidised acid. Acid fruits contain only free (I).

L. S. T.

Sensitive drop reaction for ascorbic acid. H. TAUBER (Mikrochem., 1935, 17, 111—112).—Plant or animal tissue is macerated with 8% AcOH, and a drop of the liquid is applied to $K_3Fe(CN)_6$ on filter-paper. < 0.003 mg. of ascorbic acid (I) reduces $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$, giving a blue colour on adding a drop of aq. $Fe_2(SO_4)_3$. Large amounts of cysteine, glutathione, and pyrogallol interfere, as do sugars after hydrolysis. The oxidised form of (I) may be reduced with H_2S before testing. J. S. A.

Removal of sterols from material containing vitamin-*D*. S. NATELSON and A. E. SOBEL (J. Biol. Chem., 1935, 109, 687—694; cf. A., 1934, 1099).—PhOH, borneol, cholesterol (I), and ergosterol (II) yield K salts of sulphates insol. in Et_2O and light petroleum whereas vitamin-*D* (III) (e.g., in cod-liver oil), calciferol, irradiated (I) and (II) do not. *h* ergosteryl sulphate when irradiated dry with or without subsequent boiling with H_2O acquires no anti-rachitic activity but does if it is first boiled with H_2O . Sterols are separated from (III) by conversion into K salts of sulphates, the mixture being then extracted with light petroleum which dissolves (III). W. McC.

Change of activity of crystalline vitamin-*D* and its quantitative spectrographic determination. L. FUCHS and J. VAN NIEKERK (Biochem. Z., 1935, 277, 32—38).—Cryst. vitamin-*D* on long keeping in air in the dark suffers a partial decomp., becoming yellowish in colour, the absorption in the ultra-violet simultaneously decreasing and the prep. no more being completely sol. in C_6H_6 . After such keeping, the vitamin-*D* content calc. from the absorption spectrum approximates closely to that obtained from animal experiments. All standard preps. of the vitamin require therefore standardisation from time to time by the absorption method. P. W. C.

Irradiation of ergosterol. I.—See this vol., 857.

Vitamin-*D* injury in fowls. O. SEIFRIED and E. HEIDEGGER (Tierärztl. Rundsch., 1933, 39, 172; Bied. Zentr., 1934, A, 5, 194).—Excessive feeding of vitamin-*D* to hens results in abnormal Ca storage and a condition corresponding to hypervitaminosis-*D* in mammals. Hens are the less sensitive. Deficiency of -*D* also leads to excessive Ca storage.

A. G. P.

Antihæmorrhagic vitamin of the chick. H. DAM (Biochem. J., 1935, 29, 1273—1285; cf. A., 1934, 1271).—A factor preventing hæmorrhage in the chick (vitamin-*K*) is found in hog-liver fat, hen's egg yolk, hemp seed, and vegetables, occurring in the easily sol. non-sterol fraction of the non-saponifiable residue. Vitamin-*A*, -*D*, and -*E* are ineffective in preventing hæmorrhage. The factor is not destroyed by heating at 100° for 12 hr. The statement of McFarlane (A., 1931, 659) that caseinogen prevents hæmorrhage is disputed. H. D.

Reversibility of the vernalisation process. M. F. GAVRILOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 561—563).—Vernalisation in the cotton plant, as indicated by a change in p_H of the isoelectric point from 6.0 to 5.6, takes place in 10—15 days. The process is reversible if the time is prolonged.

P. G. M.

Seasonal changes in the composition of the pecan during fruit development. C. J. B. THOR and C. L. SMITH (J. Agric. Res., 1935, 50, 97—121).—In the period between blossoming and August (Texas), the growth of the pecan is characterised by the formation of structural matter. During the subsequent filling of the kernels, materials contributing to the formation of oil, and probably of protein, are derived from sources outside the fruit. Accumulation of sugars, occurring later, is due to translocation from the husk.

A. G. P.

Physiology of apple varieties. A. H. FINCH (Plant Physiol., 1935, 10, 49—72).—The starch (I) and total carbohydrate (II) contents, (I):N ratio, and (II):N ratio in terminal shoots of apples were highest in fruitful shoots of biennial-bearing trees, next highest in regularly but shyly-bearing trees, and lowest in unfruitful trees. Terminal growth, accumulation of (I), and formation of xylem began earlier in more fruitful trees. Summer wood formation in the xylem is associated with (II) accumulation. A relatively large no. of parenchymatous cells and a low fibre: parenchyma ratio in the xylem coincided with a high (II)—low N type of composition. Fewer cells and high ratio are associated with low (II) and high N in the shoot. The composition of terminal shoots in individual varieties may serve as an index of the cultural requirements of the trees.

A. G. P.

Synthesis of tropinone, ψ -pelletierine, lobeline, and related alkaloids under physiological conditions.—See this vol., 873.

Growth, organic nitrogen fractions, and buffer capacity in relation to hardness of plants. S. T. DEXTER (Plant Physiol., 1935, 10, 149—158).—Winter wheat plants of high N contents did not harden when exposed to a temp. of 2° in darkness. Low N—high carbohydrate (I) plants of winter wheat, winter rye, winter barley, winter oats, and cabbage hardened well under these conditions. Leaves of cabbage having low (I) and high N although not hardening at 2° became more alkaline and had better buffer capacity both before and after exposure than did corresponding plants having high (I) and low N. Hardening in darkness was more effective at a const. low temp. than at alternating temp. Under the latter conditions (2—20°) plants accumulated more sol. N and less sugar than when maintained at 2°. Low-temp. storage, irrespective of the hardening process, induces an increase in sol. N, a decrease in respiratory rate (unrelated to sugar changes or enzymic activity), and, usually, an increase in sugars.

A. G. P.

Osmotic quantities of plant cells in given phases. A. URSPRUNG (Plant Physiol., 1935, 10, 133).—The appropriate use of terms is discussed.

A. G. P.

Rôle of sugar in the osmotic value of wheat. W. H. FUCHS (Planta, 1935, 23, 340—348).—The osmotic activity of sugars in wheat seedlings is examined in relation to winter hardening.

A. G. P.

Linkage between output of electrical energy by polar tissues and [plant] cell oxidation. H. F. ROSENE and E. J. LUND (Plant Physiol., 1935, 10, 27—47).—Direct relationships are established between the $[O_2]$ of the atm. in contact with roots of *Allium cepa* and the regional and total potential gradient in the root tissue.

A. G. P.

Respiration of barley plants. I. Determination of carbohydrates in leaves. II. Carbohydrate concentration and carbon dioxide production in starving leaves. E. W. YEMM (Proc. Roy. Soc., 1935, B, 117, 483—504, 504—525).—I. Aq. solutions containing glucose, fructose, sucrose, and maltose are analysed by use of the iodometric and Hagedorn-Jensen methods before and after hydrolysis with (a) H_2SO_4 , (b) invertase. The presence of non-sugar substances in plant leaf extracts vitiates results and corrections must be made by means of control tests after removal of all sugars by yeast fermentation. Non-sugars affect the iodometric results > the Hagedorn-Jensen method. Starch is determined by means of taka-diastase, a similar test for non-sugars being applied.

II. Production of CO_2 by barley leaves in the initial stages of starvation is > accounted for by the loss of carbohydrates. Subsequently non-carbohydrate material (probably protein) also undergoes oxidation. The rate of decomp. of furanose sugars in the leaf is > that of pyranose types.

A. G. P.

Esterification of phosphate in the respiratory breakdown of sugar in higher plants. M. S. RAO (Nature, 1935, 135, 909—910).—Evidence that in the breakdown of sugar by fermenting peas combination of the sugar with H_3PO_4 is a necessary step, is presented.

L. S. T.

Temperature-absorption characteristics during germination in seeds of differing structure and biochemical composition under varying concentrations of oxygen and water supply. B. N. SINGH and R. K. TANDON (Proc. Indian Acad. Sci., 1935, 1, B, 496—518).—Absorption of H_2O by seeds is influenced by temp., aeration, and H_2O supply simultaneously, but to extents which differ in intensity and direction according to seed type (starchy, proteinaceous, or oily).

A. G. P.

Carbon dioxide balance [in plants] at higher light intensities. E. S. MILLER and G. O. BURR (Plant Physiol., 1935, 10, 93—114).—Many potted plants in a closed system reduce the $[CO_2]$ of their atm. to 0.01 vol.-% and maintain this in light intensities of about 2000 f.c. At high temp. (36°) the CO_2 balance of some plants rises above this val. At more moderate temp. the balance is independent of temp. CO_2 balance is controlled by the concn. of dissolved CO_2 and not by the total CO_2 (free and HCO_3^-). Plants growing in CO_2 are not in energy balance since the R.Q. may not be unity. Liberation of CO_2 by succulents and xerophytes is caused by high temp. rather than by light.

A. G. P.

Assimilation of carbon dioxide by leaves in different regions of the spectrum. E. K. GABRIELSEN (*Planta*, 1935, 23, 474—478).—The assimilatory activity of *Sinapis* leaves is highest in the red-orange region of the spectrum and decreases steadily towards the violet. The % utilisation of light energy is < that of *Chlorella*. A. G. P.

Effect of carbon dioxide on the p_H and certain nitrogen fractions of the sugar-beet plant. J. M. FIFE and V. L. FRAMPTON (*J. Biol. Chem.*, 1925, 109, 643—655).—When the plant is subjected to an increased concn. of CO_2 , of the juice is reversibly increased. The reactions are not local, do not depend on the partial pressure of CO_2 , but are caused by an increase in NH_3 from fission of acid amides. H. G. R.

Relationship between nitrogen fertilisation and chlorophyll content in pineapple plants. R. K. TAM and O. C. MAGISTAD (*Plant Physiol.*, 1935, 10, 159—168).—In nearly all cases, increased applications of N fertiliser resulted in an increased concn. of total chlorophyll in the leaves. A. G. P.

Fluorescence spectra of chlorophyll-*a* and -*b* in ether solution. F. P. ZSCHEILE, jun. (*Protoplasma*, 1935, 22, 513—517).—Apparatus and technique are described. A. G. P.

Effect of orange juice on the growth of *Laminaria* gametophytes. P. W. CARTER (*Nature*, 1935, 135, 958—959).—The addition of orange juice to sea- H_2O stimulates the formation of filamentous gametophytes and also the production of sexual organs of *L. saccharina*, Lamour. L. S. T.

Growth-stimulating and -inhibiting action of dyes on plants. J. SELLEI (*Arch. Pharm.*, 1935, 273, 285—288).—Although very dil. solutions of various dyes greatly increase the growth of various plants (control given H_2O only), more conc. solutions exert a strong growth-retarding influence. Such growth-stimulation is related to the photochemical action of dyes which can sensitise the plant to light, even when the soil is deficient in nutritive salts. J. W. B.

Germination hormone in *Gramineae*. N. CHOLODNY (*Planta*, 1935, 23, 289—312).—A growth-promoting substance (I) occurs in the starchy tissue of the endosperm of maize, oats, etc. during the early stages of germination. Formation of (I) probably begins immediately after the first absorption of H_2O by the endosperm, and proceeds more rapidly than in any other plant organ. It occurs in seeds which have lost, naturally or artificially, their germinative power, and is probably due to enzyme activity. Production of (I) is related to starch hydrolysis. (I) formed in the endosperm is rapidly absorbed by the developing embryo. Physiological responses of root-tips and coleoptiles to (I) are similar to those to auxin. A. G. P.

Activation of cambial growth by pure hormones. R. SNOW (*Nature*, 1935, 135, 876; cf. this vol., 418).—Strong cambial growth can be activated in young decapitated sunflower seedlings by solutions of pure auxin-*a* and of pure β -indolylacetic acid at concns. of 1 or 2 in 10^6 . L. S. T.

Lichen substances. LI. Occurrence of norstictic acid in *Parmelia acetabulum*, Ach. Y. ASAHINA and F. FUJIKAWA (*Ber.*, 1935, 68, [B], 946—947).—The acid present in *P. acetabulum* Ach. from Europe is identified as norstictic acid, which (not salizic acid) is found in *Stereocaulon salacinum*. H. W.

Constituents of roots of Ch'ai Hu (*Bupleurum falcatum*, L.). Y. CHI and C. MA (*J. Chinese Chem. Soc.*, 1935, 3, 78—85).—Steam-distillation of the EtOH-sol. portion of the roots gives a volatile essential oil, b.p. 130—157°/2 mm., whilst oleic, linoleic, palmitic, stearic, and lignoceric acids together with glucose, saponin, and an alcohol (*bupleurumol*), $C_{37}H_{64}O_2$, m.p. 163—164° (*acetate*, m.p. 174—175°), are found in the non-volatile fraction. F. N. W.

Constituents of European *Datura stramonium* cultivated in China. T. Q. CHOU (*Chinese J. Physiol.*, 1935, 9, 77—82).—From the stem and leaves hyoscyne, hyoscyamine, and atropine were isolated and also two neutral compounds, *datugen*, $C_{13}H_{20}O_2$, m.p. 295°, $[\alpha]_D +41.6^\circ$ in $CHCl_3$, and *datugenin*, $C_{16}H_{22}O_5$, m.p. 265°, $[\alpha]_D +75^\circ$ in $CHCl_3$. W. O. K.

Occurrence of anabasine in *Nicotiana glauca*, R. Grah. (Solanaceae). C. R. SMITH (*J. Amer. Chem. Soc.*, 1935, 57, 959—960).—The roots contain NH_3 , C_5H_5N , and 1% of anabasine. R. S. C.

Microchemical test for protein-grains in plant-cells. R. H. DASTUR and U. K. KANITKAR (*Current Sci.*, 1935, 3, 432).—Sections of plant-tissue are treated with 2 c.c. of 0.5% aq. Na β -naphthaquinone-sulphonate, 1 c.c. of 1% Na_2CO_3 , and 4 drops of 1% phenolphthalein for 30 hr. and then transferred to a mixture of AcOH (50%) and NaOAc (5%), washed for $\frac{1}{2}$ min., treated with 4% aq. $Na_2S_2O_3$ for 5 min., washed, dehydrated, and mounted in glycerol. This method detects proteins and NH_2 -acids. A reagent containing 0.2 g. of *o*-benzoquinone in 20 c.c. of 95% EtOH mixed with 1 c.c. of 1% aq. Na_2CO_3 specifically stains proteins. W. O. K.

Isolation and distribution of nitrogen in dilute alkali-soluble proteins of healthy Valencia and Washington navel oranges. W. B. SINCLAIR, E. T. BARTHOLOMEW, and R. D. NEDVIDEK (*J. Agric. Res.*, 1935, 50, 173—180).—Small differences are found in the total N and in the NH_3 fraction of the proteins of the two varieties. In both cases the NaOH-sol. proteins have relatively high proportions of basic and amide-N. A. G. P.

Determination of the nitrogenous fractions in vegetative tissue of the peach. O. W. DAVIDSON and J. W. SHIVE (*Plant Physiol.*, 1935, 10, 73—92).—Dormant or slowly growing peach stems yielded no HCN when treated by Robinson's method (A., 1929, 1345). Appreciable amounts were obtained from rapidly growing stems. Hydrolysis of cyanogenetic glucosides by enzymes reaches a max. at p_H 5.5—5.7. Decomp. by boiling with H_2SO_4 is never complete. In Sessions and Shive's method for determining NH_3 -N (A., 1929, 960), glucoside-N may be partly or wholly converted into NH_3 during aeration with NaOH. This conversion is prevented by addition of sol. Fe salts to the peach extract. Recovery of NH_3 by the

Sessions—Shive method at room temp. is $>$ that by vac. distillation at 60° in presence of borax. If emulsin in peach tissue is destroyed quickly, no loss of N occurs during drying of stem material. In roots the loss is small. A. G. P.

Determination of amino-nitrogen in plant extracts. N. W. STUART (Plant Physiol., 1935, 10, 135—148).—High vals. for $\text{NH}_2\text{-N}$ by the Van Slyke method are attributed to gas liberated by reaction of acid derivatives of phenols (e.g., tannins) or of substances sol. in 80% EtOH and in H_2O (pigments, lipins, etc.) with the HNO_2 . Distillation of the material with solid CaO under reduced pressure gives more satisfactory results. A. G. P.

Determination of ammonia- and amide-nitrogen in plant-tissue. G. W. PUCHER, H. B. VICKERY, and C. S. LEAVENWORTH (Ind. Eng. Chem. [Anal.], 1935, 7, 152—156).—The dried tissue (drying conditions described) with $\text{NaOH-Na}_2\text{B}_4\text{O}_7$ at 40° and p_{H} 6.5 in a vac. yields NH_3 which is a measure of the NH_4 salt-N, and is determined nephelometrically ($\pm 3\%$) with Nessler's reagent. Glutamine affects the determination to some extent, but not allantoin, adenine, or asparagine. A previously hydrolysed sample (cf. A., 1931, 537) treated as above affords a measure of the amide-N. J. L. D.

Bitter principles of the Colombo root.—See this vol., 864.

Phlobaphens. I. Acid phlobaphen of the Spanish (edible) chestnut. E. MULLER and J. ZELLNER (Biochem. Z., 1935, 277, 383—393).—From the tannin extract of the chestnut, conditions are given for the pptn. of a phlobaphen (I) of const. composition corresponding with a min. empirical formula $\text{C}_{27}\text{H}_{20}\text{O}_{16}$. (I) on treatment with Ac_2O gives a *Ac* derivative, together with a *compound*, $\text{C}_{18}\text{H}_{10}\text{O}_{10}$, resembling diacetyllagic acid, and on oxidation with H_2O_2 in alkaline solution gives a *product*, $\text{C}_{14}\text{H}_6\text{O}_8 \cdot 2\text{H}_2\text{O}$, decomp. 400° [*Ac* derivative, m.p. $310\text{--}315^\circ$ (decomp.)]; *phenylhydrazone*, $\text{C}_{14}\text{H}_6\text{O}_{10} \cdot \text{C}_6\text{H}_5\text{N}_2$, which resembles but is not identical with ellagic acid. Reduction of (I) by Zn dust gives anthracene and C_{10}H_8 but no fluorene, whilst KOH fusion gives protocatechuic and succinic acids and pyrogallol. P. W. C.

Biochemistry of Salix. V. Relationship of salipurposide to naringoside and isohesperidoside. VI. *Salix nigricans*, Sm. VII. *Salix repens*, L. J. RABATÉ (Bull. Soc. Chim. biol., 1935, 17, 314—318, 319—327, 328—340).—V. Salipurpol is identical with naringetol. Naringoside is identical with isohesperidoside and differs from salipurposide only by the presence of a mol. of rhamnose.

VI. The leaves of *S. nigricans* contain *salicoside*, m.p. 202° , $[\alpha]_{\text{D}} -62.29^\circ$, and the bark *piceoside*, m.p. 195° , $[\alpha]_{\text{D}} -87.26^\circ$. The branches while very young contain only salicoside, after 1 year contain 1/3 salicoside and 2/3 piceoside, and later only contain piceoside. The leaves contain *salinigriflavonololide*, m.p. 292° , $[\alpha]_{\text{D}} -9.5^\circ$ in $\text{C}_6\text{H}_5\text{N}$, of which the aglucone after alkaline fusion gives protocatechuic acid.

VII. The formula attributed to salireposide, a

glucoside from the bark of *S. repens*, by Wattiez (A., 1931, 1100) is criticised, salirepol, m.p. 106° , the prosthetic group of the debenzoylated glucoside, being shown to be hydroxysaligenol. P. W. C.

Biochemistry of the peach tree. Persica vulgaris, L. Persicoside. C. CHARAUX and J. RABATÉ (J. Pharm. Chim., 1935, [viii], 21, 495—503, and Compt. rend., 1935, 200, 1689—1691).—*Persicoside* (I), $\text{C}_{22}\text{H}_{24}\text{O}_{11}$, m.p. $258\text{--}260^\circ$ (depending on the mode of determining it), $[\alpha]_{\text{D}} -112.8^\circ$ in EtOH, is obtained by extraction of the bark of peach trees with hot EtOH. No naringenin nor any of the glucoside reported by Karigone *et al.* (cf. J. Pharm. Soc. Japan, 1929, 49, 97, 937) was detected. (I) is hydrolysed by dil. H_2SO_4 and by emulsin to glucose and hesperitin (II), m.p. 228° , which on alkaline fusion gives phloroglucinol and hesperetic acid and is identical with the substance obtained by hydrolysis of hesperidoside. The flavanone structure of (II) is confirmed. H. G. M.

Saccharides of camomile flowers. II. Biochemical examination of the organs of the fresh plant. C. BÉGUIN (Pharm. Acta Helv., 1934, 9, 140—143; Chem. Zentr., 1935, i, 270; cf. A., 1933, 544).—Only the flowers contain the heteroside previously described. The assimilation products are found mainly in the leaf-bearing stems. H. J. E.

Spectrophotometry in the ultra-violet and its application to biological analysis. A. CHEVALLIER (Bull. Soc. Chim. biol., 1935, 17, 530—547).—A lecture.

Ammonium picrate for preliminary fixation in intra-vital staining. A. V. LEONTOVITSCH (J. Physiol. U.S.S.R., 1934, 17, 430—432).—Suitable NH_4 picrate is prepared by heating 230 g. of picric acid, 1750 c.c. of H_2O , and 130 c.c. of 25% aq. NH_3 under reflux for 1 hr., and air-drying the cryst. product separating on cooling. R. T.

Enzymic histochemistry. XIV. Micro-determination of chlorine in tissues. K. LINDERSTRÖM-LANG, A. H. PALMER, and H. HOLTER (Z. physiol. Chem., 1935, 231, 236—230, and Compt. rend. Trav. Lab. Carlsberg, 1935, 21, No. 1, 5 pp.; cf. A., 1934, 1260).—After ashing, the tissue-Cl is determined by electrometric titration. J. H. B.

Volumetric determination of chlorine in biological fluids rich in lipins. B. DREVON (Bull. Soc. Chim. biol., 1935, 17, 136—155).—By using the method of Sundermann and Williams (A., 1931, 974) loss of Cl' due to the presence of lipins is avoided. A. L.

Method for preparing biological materials for phosphorus determinations. H. W. GERRITZ (Ind. Eng. Chem. [Anal.], 1935, 7, 116—118).—Urine is digested with hot conc. $\text{H}_2\text{SO}_4\text{-HClO}_4$ in < 0.5 hr. to give a clear solution in which P is determined as accurately as with the $\text{H}_2\text{SO}_4\text{-HNO}_3$ ashing technique. J. L. D.

Micro- and submicro-determination of iron. J. LAVOLLAY (Bull. Soc. Chim. biol., 1935, 17, 432—438).—Fe in biological liquids may be determined by pptn. with 8-hydroxyquinoline at p_{H} 5.0. A. L.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1935.

General, Physical, and Inorganic Chemistry.

Intensity measurements in the fine structure of the Balmer line H_{α} . L. S. ORNSTEIN, H. LINDEMAN, and J. A. VREESWIJK, jun. (*Physica*, 1935, 2, 541—550). M. S. B.

(A) After-effect of a glow discharge in lowering the striking potential in nitrogen, hydrogen, and air. (B) Cause of lowering of striking potential at low pressures. G. MACIUC (*Bul. Fac. tiințę Cernauti*, 1933, 7, 59—75, 250—294; *Chem. entr.*, 1935, i, 527).—(A) The lowering observed by Badareu in N_2 is due to charging of the glass walls by the first discharge.

(B) Data for the effect of wall charges in lowering the striking potential are recorded. The effect disappears when the walls are rendered conducting and earthed. H. J. E.

New nitrogen afterglow spectrum. J. KAPLAN (*Nature*, 1935, 135, 1034—1035; cf. *A.*, 1934, 1051).—A new afterglow spectrum obtained by passing a current of low density through N_2 is reproduced. The relative intensity of the Vegard-Kaplan bands, emitted by the metastable mol., is markedly enhanced. The new spectrum supports the view that radiations from the night sky agree closely with these bands. L. S. T.

Excitation and emission in the nitrogen band spectrum. G. O. LANGSTROTH (*Proc. Roy. Soc.*, 1935, A, 150, 371—381).—The results of measurements of the intensities of 9 additional second positive N bands for various exciting electron energies between 14 and 160 e.v. are discussed (cf. *A.*, 1934, 1150). No dependence of the relative intensities on the energy of the exciting electrons was found except at low energies, and it is concluded that interaction between the exciting electron and the vibrating nuclei is improbable. The agreement of the observed intensities with those calc. from the excitation and emission probabilities is only approx. The discrepancies are ascribed to neglect of anharmonicity in the theoretical model. L. L. B.

Oxygen afterglow. (LORD) RAYLEIGH (*Proc. Roy. Soc.*, 1935, A, 150, 34—36).—Stoddart's failure to obtain the afterglow in moist O_2 is ascribed to the use of an unstable type of discharge. The electrodeless ring discharge should be employed. L. L. B.

Intensity distribution and half-value width of neon lines. I. W. SCHÜTZ. II. W. SCHÜTZ, H. SCHILLBACH, and K. KRÄMER (*Physikal. Z.*, 1935, 36, 403—406, 406—409).—I. The intensity distribution of the Ne lines for different vals. of the ratio of the

dispersion width to Doppler width, and the relation between the total width and both these, are calc. A. J. M.

Absolute output of the Na D line by excitation by electron collision. W. CHRISTOPH (*Ann. Physik*, 1935, [v], 23, 51—60).—A photo-electric process, using the opposing-field method of Haft (*A.*, 1933, 439) with lowest possible pressure to avoid absorption losses, was employed. The val. obtained is $>$ that of Ornstein. A. J. M.

Emission spectro-photographic determinations of aluminium in the ash of biological material. R. LINDEMANN (*Z. Physik*, 1935, 95, 6—29).—A low-voltage arc was used to determine the Al content of organs, bones, and gall-stones. A. B. D. C.

Spectrum of Cu III. L. BLOCH and E. BLOCH (*Compt. rend.*, 1935, 200, 2017—2019).—Data are classified. H. J. E.

Emission bands of selenium. R. K. ASUNDI and Y. P. PARTI (*Current Sci.*, 1935, 3, 548). A. B. D. C.

Multiplets and terms in the first two spectra of niobium. W. F. MEGGERS and B. F. SCRIBNER (*J. Res. Nat. Bur. Stand.*, 1935, 14, 629—647).—Results are reported for the principal multiplets in the Nb I and Nb II spectra. Sextet and quadruplet terms occur in the Nb I and quintet and triplet terms in the Nb II spectra. The normal states of neutral and singly ionised Nb atoms are $(4d^45s)^6D$ and $(4d^4)^5D$, respectively. J. W. S.

Higher terms in the spectrum of Ag II. W. P. GILBERT (*Physical Rev.*, 1935, [ii], 47, 847—850).—Complete measurements and classifications, extending available data, are tabulated for the range 500—11,000 Å. The ionisation potential is 21.4 volts. N. M. B.

Atomic energy states of tellurium, Te III. S. G. KRISHNAMURTI (*Current Sci.*, 1935, 3, 547). A. B. D. C.

Emission spectrum of Te_2 . E. OLSSON (*Z. Physik*, 1935, 95, 215—220).—Isotope displacements are used to improve the vibration level formula. A. B. D. C.

Absorption of light in caesium vapour in the presence of helium. H. J. J. BRADDICK and R. W. DITCHBURN (*Proc. Roy. Soc.*, 1935, A, 150, 478—486).—The absorption of light in Cs vapour is progressively reduced by the addition of He, for He pressures up to 20 cm. About 3 cm. of He reduces it to half-val. at 3150 Å., and about 2 cm. to half-val. at

2250 Å. The mol. absorption of Cs in the region 3430—3530 Å. is completely suppressed by the addition of a small amount of He. L. L. B.

Broadening and displacement of end lines of caesium series by krypton. C. FÜCHTBAUER and H. J. REIMERS (*Z. Physik*, 1935, **95**, 1—5).—Displacement is towards the red, and from its limit the cross-section of Kr for slow electrons is calculated. A. B. D. C.

Stark effect for mercury. R. N. H. HASLAM (*Proc. Roy. Soc.*, 1935, **A**, **150**, 338—347).—The Stark effect for Hg has been examined over the range 2200—3000 Å., using a modified form of the Lo Surdo source. The displacements are in agreement with a simplified theory. L. L. B.

Spectral characteristics of electrically exploded mercury. H. P. KNAUSS and A. L. BRYAN (*Physical Rev.*, 1935, [ii], **47**, 842—844).—The spectrum of the region 2537—1950 Å., obtained by sending 300 amp. from a 150-volt generator through a small stream of Hg, gave continuous emission strong and clear enough for use in absorption experiments, and showed great broadening of many lines, due to strong electric fields of ions near the emitting atom, and a strong continuous background due to recombinations in which the kinetic energy plays a part. N. M. B.

Hyperfine structure of the mercury hydride bands. S. MROZOWSKI (*Bull. Acad. Polonaise*, 1935, **A**, 24—29; cf. *A.*, 1932, 104).—Observations on various HgH bands show each to have a no. of components. The intensity relations are different from those attributable to an isotope effect. A type of hyperfine structure occurs, analogous to that in line spectra. H. J. E.

Extreme infra-red spectrum of the sun. V. G. VAFLADI, S. S. KRIVICH, and G. V. POKROVSKI (*Nature*, 1935, **135**, 1035).—No radiation in the extreme infra-red has been detected from the sun. L. S. T.

Stark effect of hydrogen in first type stellar spectra. A. PANNEKOEK and S. VERWEY (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 479—489).—Mathematical. N. M. B.

Stark intensities in a canal-ray source at different pressures. R. L. THORNTON (*Proc. Roy. Soc.*, 1935, **A**, **150**, 259—266).—A new canal-ray tube is applied to the measurement of the relative intensities of the Stark components of H₂ and of the He group 2P—4Q. It is shown that the differences between Stark intensities observed by the canal-ray and Lo Surdo methods are mainly due to the great differences in gas pressures commonly selected. L. L. B.

Long and short spectral lines. S. DATTA and K. CHATTERJEE (*Indian J. Physics*, 1935, **9**, 357—368).—The long and short lines obtained in the arc spectrum when an image of the arc in the transverse position is thrown on the slit of a spectrocope have been examined for a Cu arc working at pressures ≥ 1 atm. A. J. M.

Magnetic and electric spectra in high frequency. V. K. ARKADIEV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **2**, 204—208). W. R. A.

Quantum theory of metallic reflexion. L. I. SCHIFF and L. H. THOMAS (*Physical Rev.*, 1935, [ii], **47**, 860—869).—The classical Drude theory, with Kronig's modifications, gives the electromagnetic field except within a transition layer over a few electron wave-lengths from the surface. In this layer the electric intensity perpendicular to the surface shows considerable fluctuations depending on the nature of the surface potential barrier. This fluctuating field can be used to correct the calc. surface photo-electric effect. N. M. B.

Electromagnetic fields due to variable electric charges and the intensities of spectrum lines according to the quantum theory. H. R. HULME (*Proc. Roy. Soc.*, 1935, **A**, **150**, 416—421).—Schott's treatment of the radiation emitted by an atom (*A.*, 1933, 206) is equiv. to the strict quantum-mechanical treatment, but the latter affords a simpler method of calculating the intensities. L. L. B.

Photometric measurements of X-ray reflexion. III. Atomic factors of sulphur and lead. P. DE LA CIERVA and J. PALACIOS (*Anal. Fís. Quím.*, 1934, **32**, 391—395).—The diagram for the scattering power of S exhibits undulations at vals. of $\sin \theta/\lambda$ between 0.2 and 0.4 which correspond with those predicted by Hartree but are more pronounced. The Pb diagram contains a horizontal portion at about 0.3, whereas the curve of Pauling and Sherman is continuous. The mean error of the measurements is $> 6\%$. H. F. G.

Effect of temperature on the scattering of X-rays by solids according to quantum mechanics. H. OTT (*Ann. Physik*, 1935, [v], **23**, 169—196).—Theoretical. A. J. M.

Deviations from the Sommerfeld formula for the K levels. M. I. KORSUNSKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **2**, 114—117).—A modification of Sommerfeld's equation yielding better vals. of the electronic charge is discussed. W. R. A.

K-Absorption edges of cobalt and its compounds. K. KOJIMA (*Mem. Coll. Sci. Kyoto*, 1935, **A**, **17**, 189—190).—Data for Co, Co(OH)₂, CoS, CoSiO₃, CoF₂, CoSO₄, CoCO₃, and Co₂O₃ are recorded. The bivalent compounds show a displacement in the direction of shorter λ . E. S. H.

Secondary cathode rays expelled from metals by molybdenum K α radiations. H. R. ROBINSON and C. J. B. CLEWS (*Proc. Roy. Soc.*, 1935, **A**, **149**, 587—595).—The energies of the electrons expelled by Mo K α_1 rays from Au, Pt, Ag, and Cu targets, using the magnetic spectrometer, are slightly $>$ those obtained by Kretschmar for the same elements. The results are discussed in relation to the abs. vals. of X-ray λ and the principal at. consts. L. L. B.

Influence of chemical combination on the K $\alpha_{1,2}$ doublet of silicon. N. G. JOHNSON (*Z. Physik*, 1935, **95**, 93—96).—O compounds show displacement of approx. 2.4 X, and K₂SiF₆ shows 3.8 X. A. B. D. C.

Spectroscopy of ultra-soft X-rays. IV. M. SIEGBAHN and T. MAGNUSSON (*Z. Physik*, 1935, 95, 133—157; cf. A., 1934, 232).—Measurements are given for the *L* series of elements between 27, Co, and 17, Cl. Displacement with chemical combination is recorded for NaCl, AlCl₃, KCl, RbCl, CsCl, and BaCl₂.
A. B. D. C.

Electronic energy bands of solid copper, nickel, cobalt, and iron. F. C. CHALKIN (*Nature*, 1935, 135, 998).—Measurements of the intensity of soft X-rays from Cu, Ni, Co, and Fe and the deduced distribution of electronic energy indicate that the electrons in these metals are not completely free and cannot normally occupy the whole of the space lattice of the crystal.
L. S. T.

Photo-effect with alkali metal films of atomic thickness on platinum. H. MAYER (*Physikal. Z.*, 1935, 36, 463—464).—With K on Pt, a max. photo-effect is obtained when the K film is unimol., but this is probably due to the presence of O₂. The secondary emission due to primary electrons of 50—1500 volts was also determined as a function of the thickness of the film. The curve was almost identical with that obtained for the photo-effect in its earlier stages, and showed no max.
A. J. M.

Mobility of sodium on tungsten. R. C. L. BOSWORTH (*Proc. Roy. Soc.*, 1935, A, 150, 58—76).—The mobility of Na on a W filament has been studied by a photo-electric method. A clean strip absorbs Na, but a portion of this reappears on the surface and evaporates when the strip is heated above 1300° abs. The capacity of the strip to absorb Na is limited, but when that limit has been attained, any excess of Na is stable on the surface, and if deposited as an active patch migrates over the surface at such a rate that the strip is approx. uniformly active after 1—2 hr. at 300° abs. or 5—10 sec. at 800° abs. The migration has an active energy of 0.25 volt, and the same energy is associated with the absorption process, from which it is concluded that the latter consists of migration into slip planes and intercryst. cracks.
L. L. B.

Influence of impurities in the core-metal on the thermionic emission from oxide-coated nickel. M. BENJAMIN (*Phil. Mag.*, 1935, [vii], 20, 1—24).—The effect of metallic impurities in Ni on the emission of BaO- and SrO-coated Ni filaments and on the crit. temp. of their emission is attributed to variation in the Ba metal content in the coating with the reducing power of the impurities. The phenomena are discussed with reference to modern theories of the mechanism of emission.
J. W. S.

Variation of the mobility of gaseous ions with temperature. I. Positive ions in their own gas. A. M. TYNDALL and A. F. PEARCE (*Proc. Roy. Soc.*, 1935, A, 149, 426—434).—The variation of mobility with temp. of the positive ions of He in He and of N in N₂ has been measured, over the range 20—480° abs. in He and 65—590° abs. in N₂. Expressing the results at normal density instead of at normal pressure, the mobility in He is found to be practically independent of temp. from 480° abs. to room temp., below which there is a marked decrease.

In N₂ the decrease of mobility with fall of temp. is continuous.
L. L. B.

Velocities of positive ions in the corona discharge. H. F. BOULIND (*Phil. Mag.*, 1935, [vii], 20, 68—75).—The velocities of positive ions in gases at low pressure can be measured accurately by the corona discharge method provided that X/p is < a certain val. The velocities are > anticipated from mobility measurements at higher pressures, indicating that the positive ions in the corona discharge are single particles and not clusters. Above the crit. val. of X/p the method is inaccurate, but results show that the velocity increases rapidly with X/p , this being attributed to increase in the mean free path of the ions. These observations confirm that positive ions may produce appreciable nos. of new ion pairs by collision with gas mols. (X =electric field strength.)
J. W. S.

Fifth Report of the Atomic Weights commission of the International Union for Chemistry. G. P. BAXTER, O. HONIGSCHMID, P. LEBEAU, and R. J. MEYER (*Ber.*, 1935, 68, [A], 73—84).—The only alteration is the substitution of 93.3 for 92.91 as at. wt. of Nb.
H. W.

Isotope regularities. A. CARRELLI (*Nuovo Cim.*, 1934, [ii], 11, 542—546; *Chem. Zentr.*, 1935, i, 657).—A discussion of nuclear structure.
H. J. E.

Volumetric determination of the at. wt. of terbium. J. K. MARSH (*J.C.S.*, 1935, 772—773).—The ratio Tb₂O₃ : 3C₂O₃ in the Tb material previously reported (cf. this vol., 180), determined by ignition of the oxalate and by titration with standard KMnO₄, gave the val. 158.9 for the at. wt. of Tb. N. M. B.

Relative frequency of isotopes of potassium and rubidium. H. BONDY, G. JOHANNSEN, and K. POPPER (*Z. Physik*, 1935, 95, 46—52).—Mass-spectrographic measurements give the relative abundance of K³⁹ : K⁴¹ as 16.2 : 1, and of Rb⁸⁵ : Rb⁸⁷ as 2.68 : 1.
A. B. D. C.

Isotope effect with copper hydride (CuH/CuD). T. HEIMER (*Naturwiss.*, 1935, 23, 372).—The band spectrum of CuD has been investigated and the nuclear vibration consts. have been calc. The isotope effect is considerable.
A. J. M.

Isotopes of platinum. B. FUCHS and H. KOPFERMANN (*Naturwiss.*, 1935, 23, 372).—Examination of the hyperfine structure of the Pt γ lines shows that all lines arising from the lowest state have a definite isotope displacement. Three isotopes, of masses 194, 195, and 196, occur, the abundance ratio being 5 : 8 : 8. The mechanical moment of Pt¹⁹⁵ is 1/2.
A. J. M.

Isotopic constitution of platinum and rhodium. A. J. DEMPSTER (*Nature*, 1935, 135, 993).—The analysis of Pt ions from a high-frequency spark (this vol., 677) shows isotopes 192, 194, 195, 196, and 198. The middle three form a triplet of approx. equal strength, whilst the heaviest is weaker and the lightest faint. Using as electrode an alloy of Pt containing 10% Rh direct comparison of the doubly-charged Pt ions with Rh¹⁰³ gave an at. wt. of 102.92 ± 0.03 for Rh.
L. S. T.

Isotopes of the radioactive elements and their disintegration. H. J. WALKER (Phil. Mag., 1935, [vii], 20, 25—32).—The absence of certain isotopes which would be expected for some elements is attributed to the β -radioactivity of these isotopes, leading to their disintegration. This theory is supported by the observed disintegration of the spontaneously radioactive elements. J. W. S.

The actinium problem. V. G. ELSER (Chem. Weekblad, 1935, 32, 343—344).—A review. The probable at. wt. is 231 ± 0.5 . S. C.

Tracks of α -particles and protons in photographic emulsions. H. J. TAYLOR (Proc. Roy. Soc., 1935, A, 150, 382—394).—A study has been made of the tracks of α -particles and protons in specially prepared photographic emulsions. Exposure of a plate to a neutron source gives rise to well-defined tracks due to the protons ejected by the neutrons in their passage through the gelatin of the emulsion. The experimental errors are discussed, and it is concluded that the method is unsuitable for determining the detailed distribution of neutron energies. L. L. B.

Specific ionisation of single α -particles. G. STETTER and W. JENTSCHKE (Physikal. Z., 1935, 36, 441—445).—A double ionisation chamber is used to determine the ionisation curve of single α -particles. The max. ionisation at n.t.p. occurs at a distance of 4.4 ± 0.3 mm. from the commencement of the curve. A. J. M.

Energies of α - and β -rays. H. A. WILSON (Proc. Roy. Soc., 1935, A, 150, 1—8).—Theoretical. Reasons are given for believing that α - and γ -ray energies, contrary to Gamow's view (A., 1930, 1339), involve electronic energies. The proposed modification in Gamow's theory, viz., that the observed α - and γ -rays have energies equal to a nuclear energy change plus or minus an energy change of the electronic system, is not necessarily in conflict with ideas based on quantum mechanics. L. L. B.

Rapid registration of small Hoffmann collisions. J. BEGGILD (Naturwiss., 1935, 23, 372).—The apparatus consists of an air ionisation chamber (effective vol. 35 litres, pressure 7 atm.), the ionisation current being compensated by a second chamber and a β -ray source. Differences in electrometer readings are registered photographically. A. J. M.

Wave-length of secondary γ -radiation accompanying anomalous absorption of hard γ -rays. K. TSU-TUNG (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 85—93).—In view of divergent theories, the absorption coeff. of the secondary γ -radiation associated with the anomalous absorption of Th-C'' γ -rays was determined for the scattering angle 120° for Al, Zn, Sb, and Pb, using a Geiger-Müller counter. λ deduced from the absorption coeff. is 25.4 X for Al and Zn; for Sb and Pb there appears, in addition, a harder component 13.8 X . The ratio of the no. of hard to soft component quanta is 1 : 23 for Sb and 1 : 9 for Pb. Results indicate that the Rayleigh scattering of Th-C'' γ -rays cannot be present appreciably; the component 25.4 X is attributed to positron and electron annihilation. The hard component is interpreted as continuous X-rays produced by scattered electrons and positrons. N. M. B.

Nuclear chemistry. S. FLUGGE and A. KREBS (Physikal. Z., 1935, 36, 466—480).—A summary of recent work on nuclear transformations, including artificial radioactivity. A. J. M.

Collisions of α -particles in deuterium. E. POLLARD and H. MARGENAU (Physical Rev., 1935, [ii], 47, 833—842).—Using three different but complementary methods, an investigation of the yields of deuterons emitted from D_2 under Po α -particle bombardment is reported and discussed. N. M. B.

Disintegration of the deuteron by impact. J. R. OPPENHEIMER (Physical Rev., 1935, [ii], 47, 845—846).—The probability and neutron yield of the disintegration of deuterons of energy $> 2 \times 10^6$ e.v. by impact with at. nuclei in passage through matter are calc. N. M. B.

Soft γ -radiation produced on disintegration of lithium by protons. A. ECKARDT, R. GEBAUER, and H. R. VON TRAUBENBERG (Z. Physik, 1935, 95, 210—214). A. B. D. C.

Excitation of the nitrogen nucleus to II -emission by polonium α -rays. H. STEGMANN (Z. Physik, 1935, 95, 72—83). A. B. D. C.

Nuclear transformations of beryllium and boron and the masses of the light elements. M. L. E. OLIPHANT, A. E. KEMPTON, and (LORD) RUTHERFORD (Proc. Roy. Soc., 1935, A, 150, 241—258).—It is not possible to interpret the results of experiments on the transformation of Be and B by protons and by ions of H^2 on the mass data at present available, but the assumption of a small error in the mass-spectrographic val. for the mass of He^4 brings all the data into agreement. Evidence is found of the existence of two new isotopes, Be^8 and Be^{10} . L. L. B.

Artificial radioactivity produced by neutron bombardment. II. E. AMALDI, O. D'AGOSTINO, E. FERMI, B. PONTECOEVO, F. RASETTI, and E. SEGRE (Proc. Roy. Soc., 1935, A, 149, 522—558).—The activation of several elements by neutron bombardment is increased by surrounding the source and activated substance by H_2O or paraffin wax; the suggested explanation is that the neutrons are slowed down by impacts with H nuclei, and that slow neutrons are more easily captured by some nuclei than fast ones. Some anomalously large absorption cross-sections for slow neutrons are observed, probably connected with the emission of γ -rays. Scattering experiments on slow neutrons, and the production of slow neutrons through the action of non-hydrogenated substances, are described. The results of a systematic investigation of the elements, both as regards the induced activities and the properties with respect to slow neutrons, are tabulated. L. L. B.

Absorption of slow neutrons. W. EHRENBURG and H. C. SHAN (Nature, 1935, 135, 993—994).—Under the experimental conditions described, slow neutrons are absorbed exponentially by Cd and Ag (see above). This suggests that either the active

neutrons are of approx. homogeneous speed, or in the region of their velocity the nuclear cross-section is practically independent of this velocity. L. S. T.

Transformation of aluminium by neutrons. H. KLARMANN (Z. Physik, 1935, 95, 221—226).—Protons of 9 cm. range and a small no. of α -particles are found. A. B. D. C.

Number and range of nuclear protons ejected from aluminium and nitrogen by α -rays. H. POSE (Z. Physik, 1935, 95, 84—92). A. B. D. C.

Artificial production of elements of an unknown radioactive family by irradiating thorium with neutrons. (MME.) I. CURIE, H. VON HALBAN, jun., and P. PREISWERK (Compt. rend., 1935, 200, 1841—1843).—Irradiation of Th with neutrons gave four radio-elements with half-life approx. 3.5 hr., and 25, 15, and 1 min. The first and third behave chemically as isotopes of Ac, and the second and fourth as isotopes of Th and Ra, respectively. The existence of the radioactive family ${}_{92}\text{Ac}^{237} \rightarrow {}_{90}\text{Ac}^{233} \rightarrow {}_{91}\text{Ac}^{233} \rightarrow {}_{92}\text{Ac}^{233} \xrightarrow{\alpha} {}_{90}\text{Ac}^{229} \xrightarrow{\alpha} {}_{88}\text{Ac}^{225}$ is suggested. H. J. E.

Artificial transformation of thorium by neutrons. Production of the missing $4n + 1$ radioactive series. O. HAHN and L. MEITNER (Naturwiss., 1935, 23, 320).—As a result of the bombardment of Th by neutrons, two different processes occur: (1) a non-reinforced process, to which the substance with half-life 1 min. discovered by Amaldi *et al.* (this vol., 910) belongs. This breaks down into a substance radiating β -rays, with half-life 11—12 min. (2) A reinforced process giving an element of half-life 30 min. These substances are isotopes of Th, and the changes are probably to be represented by

$$(1) {}_{90}\text{Th}^{232} + n \rightarrow {}_{88}\text{A}^{229} + \alpha \xrightarrow{1 \text{ min.}} {}_{89}\text{B}^{229} \xrightarrow{11 \text{ min.}} {}_{90}\text{C}^{229};$$

$$(2) {}_{90}\text{Th}^{232} + n \rightarrow {}_{90}\text{Th}^{233} \rightarrow {}_{91}\text{A}^{233}.$$

These series are of the new type $4n + 1$. A. J. M.

Artificial transformation of thorium by neutrons. E. FOYN, E. KARA-MICHAILOVA, and E. RONA (Naturwiss., 1935, 23, 391).—Th in aq. solution was bombarded with neutrons from Be + Rn, a method of chemical separation being employed to detect the products. After a series of separations with La (for Ac), Ba (for Ra), and Ta (for Pa) there was no increase in the natural β -ray emission of the sample. A. J. M.

Apparent effect of galactic rotation on the intensity of cosmic rays. A. H. COMPTON and I. A. GETTING (Physical Rev., 1935, [ii], 47, 817—821). N. M. B.

Diurnal variation of cosmic rays. J. CLAY and H. R. WOLTJER (Physica, 1935, 2, 582—584).—In equatorial regions there is no diurnal variation of cosmic rays $> 0.1\%$ of the total, and, therefore, no variation with sidereal time, confirming that cosmic rays are not due to novæ. M. S. B.

Transformations of cosmic radiation in matter. J. CLAY and P. H. CLAY (Physica, 1935, 2, 551—556).—No definite relation has been found between the primary cosmic corpuscular radiation

and the secondary radiation produced in Pb. The shower-producing radiations are probably photons. The absorption coeff. of the final corpuscular radiation in Pb is 4 cm.⁻¹ There appear to be two photon radiations between the primary and final corpuscular radiations. M. S. B.

Secondary effects of cosmic rays on the Hafelekar (2300 m. above sea level). J. A. PRIEBSCH (Z. Physik, 1935, 95, 102—114). A. B. D. C.

Application of liquid dielectrics to the study of ionisation "jumps" produced by cosmic radiation. C. BIAŁOBRZESKI and I. ADAMZEWSKI (Bull. Acad. Polonaise, 1935, A, 120—128).—Using 1 litre of C_6H_{14} in an ionisation chamber the frequency of ionisation jumps due to cosmic radiation reaches 37 in 13 hr., about 12% of the jumps being double or more complex. The advantages of liquid dielectric of low mobility are discussed. The surroundings have a considerable influence on the frequency of the jumps, presence of Al being particularly effective. J. W. S.

Theory of calcium chromosphere. M. KURIHARA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 51—58).—Mathematical. E. S. H.

Neutron-proton interaction. I. Binding energies of the hydrogen and helium isotopes. II. Scattering of neutrons by protons. E. FEENBERG (Physical Rev., 1935, [ii], 47, 850—856, 857—859).—Mathematical. N. M. B.

Mass defect in the heavy elements. M. I. KORSUNSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 112—114).—Light nuclei (up to Ca) are formed of groups of two protons and two neutrons. If each particle moves in the field of all the remaining particles the mass defect \propto the square of the no. of particles. The curve shows breaks at nuclei formed from an even no. of protons and neutrons. W. R. A.

General relation between the molecular spectrum and the electrons and electron orbits of the constituent atoms. H. DESLANDRES (Compt. rend., 1935, 200, 1997—2001; cf. this vol., 561).—A review and discussion of the correlation between electron arrangements in molecules and their Raman and infra-red spectra. H. J. E.

Electronic charge from de Broglie wavelengths of electrons. S. VON FRIESEN (Nature, 1935, 135, 1035).—A new method of calculating e from the electronic diffraction produced by a crystal of galena combines de Broglie's equation with the formula for the Rydberg const. Preliminary measurements give $e = (4.796 \pm 0.010) \times 10^{-10}$ e.s.u. L. S. T.

Effective cross-section of the neutrino. M. WOLFKE (Bull. Acad. Polonaise, 1935, A, 107—109).—From the no. of ions produced by neutrinos in an ionisation chamber, the max. possible effective cross-sectional area of the neutrino is 6.6×10^{-33} sq. cm., corresponding with a mean free path of 3.9×10^6 km. in ordinary air. J. W. S.

Detection of neutrinos. M. WOLFKE (Bull. Acad. Polonaise, 1935, A, 19—23).—It is shown theoretically that if a strong β -ray source (e.g., Ra-E)

be surrounded by sufficient Pb to absorb all primary β -rays and soft γ -rays, electrons produced by neutrinos should be detectable at the outer surface of the Pb with a counter or Wilson chamber. H. J. E.

Equation of the photon. G. PETIAU (Compt. rend., 1935, 200, 1829—1832).—Mathematical.

H. J. E.

Production of electron pairs and the theory of stellar structure. S. CHANDRASEKHAR and L. ROSENFELD (Nature, 1935, 135, 999).—Deviations from the gas laws may arise from the existence of a definite distribution of positrons and electrons in equilibrium with temp. radiation. L. S. T.

Ratio of the mass of the proton to that of the electron. H. ERTEL (Physikal. Z., 1935, 36, 464—465).—Mathematical. A. J. M.

Dependence of probability of the ionisation $H_2 \rightarrow H + H^+ + e$ + kinetic energy, on the orientation of the molecules with respect to the colliding electrons. N. SASAKI and T. NAKAO (Proc. Imp. Acad. Tokyo, 1935, 11, 138—140).—The probability of the above type of ionisation is found to depend on the mol. orientation. A. J. M.

Energy exchange between neon, argon, and mercury atoms and a solid wall. A. A. ZAITZEV and G. V. SPIVAK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 118—125).—Accommodation coeffs. for these gases on a metallic surface have been investigated, and the following vals. obtained: Ne 0.05, Ar 0.1, Hg 0.58. Substantial increase in these vals. is obtained by adding O_2 or CO_2 . W. R. A.

Statistical error in counting experiments. R. PEIERLS (Proc. Roy. Soc., 1935, A, 149, 467—486).—Mathematical. L. L. B.

Calculations of atomic wave functions. III. Results for beryllium, calcium, and mercury. D. R. HARTREE and W. HARTREE (Proc. Roy. Soc., 1935, A, 149, 210—231).—At. wave functions have been calc. by the method of the self-consistent field (A., 1928, 216) for the normal states of Be, Ca, and Hg, both neutral and doubly ionised. In the case of the neutral atoms, the perturbation of the core by the two valency electrons is not large for Be and Ca, but is considerable for Hg. The differences between the self-consistent field and the Thomas-Fermi field for neutral Hg are discussed. L. L. B.

Self-consistent field, with exchange, for beryllium. D. R. HARTREE and W. HARTREE (Proc. Roy. Soc., 1935, A, 150, 9—33).—Fock's equations for the self-consistent field of an atom, including exchange effect (Z. Physik, 1930, 62, 795), have been solved numerically for the normal state of neutral Be. The inclusion of the exchange terms has a small effect on the (1s) wave function, and a considerable effect on the (2s) wave function. L. L. B.

Annihilation radiation of positrons. H. A. BETHE (Proc. Roy. Soc., 1935, A, 150, 129—141).—Mathematical. A fast positron has a large probability of being annihilated during its motion, usually with emission of two quanta. The hard annihilation radiation is practically isotropic if emitted in substances

with high at. wt. and it is contended that it is identical with the hard component in the "scattered γ -rays" found by several authors. L. L. B.

Quantisation of the new field theory. II. M. BORN and L. INFELD (Proc. Roy. Soc., 1935, A, 150, 141—166; cf. *ibid.*, 1934, A, 147, 522).—Mathematical. A proof that the quantum mechanics of a particle can be derived from the new field theory. L. L. B.

Commutating co-ordinates in the new field theory. M. H. L. PRYCE (Proc. Roy. Soc., 1935, A, 150, 166—172).—Mathematical. A co-ordinate vector and an inner angular momentum which obey the simple commutation rules are defined. L. L. B.

Contributions to Born's new theory of the electromagnetic field. E. SCHRÖDINGER (Proc. Roy. Soc., 1935, A, 150, 465—477).—Mathematical. L. L. B.

Relativistic quantum mechanics. K. NIKOLSKY (Proc. Roy. Soc., 1935, A, 150, 411—415).—The connexion between Dirac's theory of electrons and the Eddington-Born-Infeld theory is obtained. L. L. B.

Relativistic basis of the quantum theory. III. H. T. FLINT (Proc. Roy. Soc., 1935, A, 150, 421—441).—Mathematical. Quantum phenomena are shown to correspond with geometrical conceptions which underlie those of the theory of relativity. L. L. B.

Infra-red photography and the spectroscopic determination of [chemical] constitution. R. MECKE (Angew. Chem., 1933, 48, 320—327).—A review of the application of observations on infra-red spectra to constitutional problems, with special reference to the C-H linking. H. J. E.

Filter for obtaining light at wave-length 560 mu. K. S. GIBSON (J. Res. Nat. Bur. Stand., 1935, 14, 545—552).—A combination of 4.55 mm. Corning 351, 5.82 mm. Corning didymium, 1.99 mm. Jena V.G. 3, and 1.94 mm. Jena B.G. 18 glass filters isolates and transmits light of 5600 Å. better than other filters. The characteristics of the filter are detailed. J. W. S.

Ozone in the Arctic night. E. TONSBERG and F. W. P. GOTZ (Naturwiss., 1935, 23, 354; cf. A., 1929, 419, 624, 1263).— O_3 absorption in mid-winter at Tromsø is not exceptionally large (cf. Dauvillier, A., 1934, 1326); max. val. occurs in spring. A. J. M.

Band spectrum of NH. R. W. LUNT, R. W. B. PEARSE, and E. C. W. SMITH (Nature, 1935, 136, 32).—The 2530 Å. band of NH and four weaker bands at 2730, 2835, 2885, and 2980, apparently due to NH^+ , have been observed in the spectrum of discharges through streaming NH_3 . L. S. T.

Ultra-violet absorption spectrum of ammonia. A. B. F. DUNCAN (Physical Rev., 1935, [ii], 47, 822—827).—Data for bands and intensities in the range 2300—850 Å. are tabulated. The bands down to 1665 Å. are diffuse through predissociation, and below this all are very sharp and show partly resolved rotational fine structure. Continuous absorption, as opposed to that due to pressure broadening, begins at approx. 1200 Å. and is so strong below 1150 Å. that no more bands could be measured accurately,

although sharp bands exist down to 1085 Å., leading to a val. of 11.3 volts for the first ionisation potential. Classification in four progressions is given.

N. M. B.

Absorption of light by carbon monoxide-hæmochromogens.—See this vol., 999.

Intensities of vibration rotation bands. (Miss) J. E. ROSENTHAL (Proc. Nat. Acad. Sci., 1935, 21, 281—285; cf. Dunham, A., 1929, 1126).—The exact expression for the probability of any transition $v' \leftarrow v''$ is derived by a simple method for the case of a Morse potential function between the nuclei. Explicit expressions for the ratio of the integrated absorption coeffs. and numerical vals. for HCl, HBr, and HF are given.

N. M. B.

Band spectra of ionised hydrogen halides. I. F. NORLING (Z. Physik, 1935, 95, 179—188).—A band spectrum between 3000 and 4000 Å. is ascribed to HBr⁺.

A. B. D. C.

Band spectrum of aluminium bromide. P. C. MAHANTY (Indian J. Physics, 1935, 9, 369—382; cf. this vol., 562).—The band spectrum of AlBr is excited in AlBr₃ vapour. The bands have sharp heads degraded towards the red. A classification is given. The isotopic displacements of the bands due to AlBr⁸¹, AlBr⁷⁹ are calc. and agree well with experiment. It is probable that the predissociation which sets in above $v'=3$ is due to a strong interaction with an unstable and strongly repelling Heitler-London level, thus preventing excitation of higher vibrational states.

A. J. M.

Interpretation of the spectra of the mono- and di-chlorides of tin. H. TRIVEDI (Indian J. Physics, 1935, 9, 331—345).—The absorption of SnCl₂ vapour was investigated between 6000 and 2000 Å. There are no bands, but three regions of continuous absorption starting at λ 4129, 3759, and 2883. There is optical dissociation of SnCl₂ into SnCl and Cl, both products existing in various states of excitation. Only faint fluorescence patches could be obtained after long exposure to 2535 Å. (Hg). The binding in both SnCl and SnCl₂ is ionic.

A. J. M.

Absorption spectrum of carbon disulphide. R. K. ASUNDI and R. SAMUEL (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 203—206).—The first predissociation limit of CS₂ is at 2965 Å., corresponding with decomp. into CS and S in the ³P states, respectively. The predissociation limit at 2160 Å. is interpreted as a decomp. into CS (ground ¹Σ) and S (excited ¹D).

J. G. A. G.

Far ultra-violet absorption spectra and ionisation potentials of the ethyl halides. W. C. PRICE (J. Chem. Physics, 1935, 3, 365—366).—The spectra of EtI, EtBr, and EtCl (1500—1700 Å.) are described. The extrapolated ionisation potentials are: EtI, 9.295 and 9.885 ± 0.005, EtBr, 10.24 and 10.56 ± 0.1. Results support the theory that the dipoles of Me and Et groups have a strong influence in reducing the ionisation potentials in adjacent linkings.

N. M. B.

Halochromism of ketones. II. L. C. ANDERSON and C. M. GOODING (J. Amer. Chem. Soc., 1935, 57, 999—1007; cf. A., 1933, 661).—Solutions of

COME₂, hexan-γ-one, cyclohexanone, dicyclohexyl ketone, cyclohexyl Ph ketone, CPh₂, Ph diphenyl ketone, and didiphenyl ketone in H₂SO₄ show increased light absorption in the region associated with the CO group. They retain their ketonic structure. Xanthone and fluorenone show a similar change and also possess new bands, which appear to be associated with the stabilisation of the quinonoid structure for these compounds. SnCl₄ produces the same changes as H₂SO₄ on the absorption of xanthone; the production of colour is not due to ether O. The colour of ketone chlorides and H₂SO₄ or SnCl₄ is different from that of ketones and resembles that of triarylcabinols and their salts. In such solutions the ketone chlorides probably exist in a quinonoid modification.

E. S. H.

Absorption spectrum of some organic vapours. C. M. B. RAO and R. SAMUEL (Current Sci., 1935, 3, 549).—Measurements are given to λ 1510 Å. for AcCl, AcBr, and CCl₃·COCl.

A. B. D. C.

Optical absorption of substituted benzenes. VI. Methylbenzenes and xylonitriles. H. CONRAD-BILLROTH (Z. physikal. Chem., 1935, B, 29, 170—177; cf. A., 1934, 715).—The absorption spectra of methylbenzenes accord with the calculation rule previously described, allowing for the *ortho*-error, and the variation of the intensity of the absorption max. from one compound to another is similar to what it is for the chlorobenzenes (A., 1932, 1188). Xylonitriles do not obey the rule, although those groups of bands which should have the same frequency lie close together.

R. C.

Ultra-violet absorption spectra of some organic compounds (acetylene, anthracene, phenanthrene). H. GORFERT (Z. wiss. Phot., 1935, 34, 156—173).—Anthracene (I) and phenanthrene (II) were heated to vaporise them. The diffuseness of the (I) spectrum is ascribed to pre-dissociation. The (II) spectrum is different, two sharp-edge systems appearing amongst diffuse bands. The data for C₂H₂ agree mainly with those of Kistiakowsky (A., 1931, 409), but are more detailed.

J. L.

Absorption of ultra-violet light by some organic substances. L. MARCHLEWSKI and J. SKULMOWSKI (Bull. Acad. Polonaise, 1935, A, 137—145).—Hydrocellulose (I) dissolved in NaOH shows no selective absorption initially, but an absorption band with max. at 3170 Å. gradually appears and shifts towards shorter λ , the max. after 22 hr. being at 2900 Å. The filtrates from the alkaline solutions after acidification with AcOH also show the development of an absorption band at 2600 Å. This change is also accompanied by increases in the Cu and I vals. of the cellulose. The extinction curve of (I) acetate in CHCl₃ solution is similar to that of cellulose acetate, whilst that of (I) benzoate shows a max. at 2758 Å. and a min. at 2622 Å. attributed to the C₆H₆ nucleus.

J. W. S.

Absorption spectra of mixed nitrogen-containing compounds and of their isomerides. T. UEMURA and Y. INAMURA (Bull. Chem. Soc. Japan, 1935, 10, 169—182).—The absorption spectra of the following compounds have been investigated: NPh:NPh; NPh:NMe; NPh:NEt; NPh:NPr;

NPh.NBu; NPh.N-CH₂Ph; (CH₃Ph.N)₂; NHPPh.N:CH₃; NHPPh.N:CHMe; NHPPh.N:CHEt; NHPPh.N:CHPr; NHPPh.N:CMc₂; NHPPh.N:CMoEt; NHPPh.N:CHPh; CH₂Ph.NH.N:CHPh; NPh.N-NHPh; NPhMe.N:N-NPhMe; (NHPPh)₂; CHPh.N:N:CHPh; NHPPh₂, and CHPh.NPh. When the N-containing radical is a strong chromophore, forming a conjugated double linking with the aromatic nucleus (e.g., NPh.NPh), two very strong absorption bands are obtained, the centres of which are independent of alkyls present. Hydrazones have only one absorption band, the position of which is almost independent of the alkyl group. The absorption is reduced by introduction of Ph into an alkyl. The effects of ·NH· and ·CH·N· groups are discussed. J. W. S.

Electronic spectra of polyatomic molecules. I. Saturated aldehydes. II. Acraldehyde. E. EASTWOOD and C. P. SNOW (Proc. Roy. Soc., 1935, A, 149, 434—446, 446—466).—I. The absorption spectra of the vapours of MeCHO, EtCHO, PrⁿCHO, PrⁱCHO, BuⁿCHO, C₆H₁₃·CHO, COMe₂, and COMeEt have been studied. The results of the vibrational analysis suggest that the electronic transition is effectively the same in all the mols. considered. The electronic structure of the ·CO group in these mols. is essentially similar to that of ·CO in CH₂O, both in the ground and upper states. The transition is not localised in the double linking.

II. The absorption spectrum of CH₂:CH·CHO (I) vapour has been measured under high dispersion. The frequencies of the upper state are 1270 and 500 cm.⁻¹, the latter being allotted to a vibration of the CH₂ about the C:C linking. This is supported by observations on the spectrum of CHMe:CH·CHO. The upper state of (I) is different in kind from that of the saturated aldehydes. Nine bands have been resolved into series of rotational lines; each series can be expressed by a single parabolic formula as though it were an isolated *R* branch. A possible explanation is suggested for the non-appearance of a related *P* branch, but not for the failure of the various formulæ to yield the same val. for the moment of inertia of the ground state. L. L. B.

Infra-red absorption spectrum of silane. W. B. STEWARD and H. H. NIELSEN (Physical Rev., 1935, [ii], 47, 828—832; cf. A., 1934, 1288).—In the range 13·0—1·0 μ data and partial resolution are given for bands at 11·0, 4·6, 3·17, 3·23, 5·5, and 2·3 μ, in decreasing order of intensity. Identifications by analogy with CH₄ are made. The calc. mol. moment of inertia gives *I*₀ = 8·9 × 10⁻⁴⁰ g.-cm.² N. M. B.

Infra-red absorption spectra of nitriles. F. K. BELL (J. Amer. Chem. Soc., 1935, 57, 1023—1025).—The infra-red absorption spectra of aceto-, *n*-butyro-, *n*-valero-, isohexo-, phenylaceto-, benzo-, α-naphtho-, and succino-nitriles have been examined between 1·0 and 12·0 μ. A characteristic, well-defined absorption band occurs at 4·4 μ in alkyl nitriles and at 4·5 μ in aryl nitriles. This band is traced to the CN linking. A region of characteristic absorption possibly occurs at 7·0 μ. E. S. H.

Light scattering and Raman effect. S. BHAGAVANTAM (Current Sci., 1935, 3, 526—531).—A summary.

Phenomenon of "wings" as a vibrational Raman effect: a correction. E. GROSS and M. VUKS (Nature, 1935, 135, 998; cf. this vol., 564).

L. S. T.

Raman spectrum of orthophosphoric acid. M. A. JEPPESEN and R. M. BELL (J. Chem. Physics, 1935, 3, 363; cf. Nisi, A., 1930, 662).—Data are given for the concn. range 50—10 mols.-%. A strong line, showing a frequency change with concn. of about 14 cm.⁻¹, appears at all concns. N. M. B.

Rotational Raman scattering in benzene at different temperatures. S. C. SIRKAR and B. B. MAITI (Indian J. Physics, 1935, 9, 323—330).—A re-investigation of the rotational Raman scattering of liquid C₆H₆ at 30° and 210° has been carried out to explain the discrepancy between the observed and calc. distribution of intensity in the rotational wing accompanying the Rayleigh line. The intensity of the wing is not a max. at the centre of the Rayleigh line, as previously reported, but is zero and attains a max. at 18 and 25 cm.⁻¹ from the centre at 30° and 210°, respectively. The intensity decreases and the wing extends up to 120 cm.⁻¹ at 30° and 100 cm.⁻¹ at 210°.

A. J. M.

Raman spectra of amides and anilides in the fused state. I. V. N. THATTE and M. S. JOGLEKAR (Phil. Mag., 1935, [vii], 19, 1116—1121).—Data for HCO·NH₂, NH₂Ac, NH₂Bz, CPh₂, CO(NH₂)₂, and NHPhAc are tabulated. N. M. B.

Raman spectra of decahydro- and tetrahydronaphthalene. S. K. MUKERJI (Phil. Mag., 1935, [vii], 19, 1079—1097).—Using solutions of quinine sulphate and *m*-C₆H₄(NO₂)₂ in C₆H₆ separately as light filters, 17 new lines for dekaline and 12 for tetraline were measured. Each gave three new anti-Stokes lines at 596, 494, 407, and 162, 265, 1433 cm.⁻¹, respectively. Corrections and extensions of assignments of weak frequencies previously reported (cf. Bonino, A., 1932, 7, 1076) are given. N. M. B.

Raman effect. XLII. Raman spectra of naphthalene and its mono-derivatives. H. GÖCKEL (Z. physikal. Chem., 1935, B, 29, 79—87; cf. this vol., 681).—The Raman spectra of C₁₀H₈ and C₁₀H₈-X (X=OH, Me, CN, SH, Cl, Br in 1- and 2-position and F in 1-position) and of some aliphatic bromides have been determined. R. C.

Raman spectrum of gaseous CD₄. A. DADIEU and W. ENGLER (Naturwiss., 1935, 23, 355).—CD₄ obtained from Al₄C₃ by the action of 99·2% D₂O, and subsequent purification, shows two Raman lines of frequency 2108 and 2141 cm.⁻¹ The first is stronger, intensity ratio 5 : 2. A. J. M.

Raman spectra of deuterobenzenes and the structure of benzene. W. R. ANGUS, C. R. BAILEY, J. L. GLEAVE, A. H. LECKIE, C. G. RAISIN, C. L. WILSON, and C. K. INGOLD (Nature, 1935, 135, 1033—1034).—Raman frequencies obtained for C₆D₆ and C₆H₅D are compared with those previously recorded (this vol., 806). The C₆D₆ frequencies are consistent with a *D_{6h}* symmetry for C₆H₆. L. S. T.

Phosphorescence process as revealed by the luminescence from solid nitrogen. L. VEGARD (Nature, 1935, 135, 1073).—The Vegard bands in the

afterglow of solid N are due to a recombination of N atoms produced from mols. dissociated by the bombarding rays. Phosphorescence and chemi-luminescence appear to be closely related. L. S. T.

Colour distribution in fluorite in relation to crystal structure. H. HABERLANDT and A. SCHIENER (Z. Krist., 1935, 90, 193—214).—Although great variations occur, there is usually an excess or a lack of colour in fluorite crystals in the diagonal planes. There are also colour regularities in zones parallel to (100) and in filaments perpendicular to (100). Microscopic colour periodicities about 1μ apart can be seen, corresponding with "mosaic" structure. The colour striations show many apparently homogeneous crystals as in reality an assemblage of smaller units. The presence of impurities is definitely associated with the colour variations.

B. W. R.

Electron conduction and colour centres in fluorspar. E. MOLLWO (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1934, [ii], 1, 79—89; Chem. Zentr., 1935, i, 670—671).—The absorption spectrum of fluorspar, coloured either electrically or thermally, shows max. at 3750, 5200 Å., the separation of the max. improving with cooling. The colour is due to excess of the cation metal, which can be detected by changes in λ , and by direct analysis. A blue coloration was observed in SrCl_2 , colloidal particles being formed on cooling to room temp.

H. J. E.

Colour centres of alkali halide crystals. R. W. POHL (Kolloid-Z., 1935, 71, 257—261).—A summary of published work.

E. S. H.

Measurement of number of colour centres in crystals. E. MOLLWO and W. ROOS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1934, [ii], 1, 107—113; Chem. Zentr., 1935, i, 525).—A discussion.

H. J. E.

Impurities and electrically excited phosphorescence of thin Al_2O_3 layers. H. BETZ (Z. Physik, 1935, 95, 189—197).—An electrolytically formed oxide layer on Al shows phosphorescence in a field of 10^7 volts per cm. The presence of Cr, Cu, Fe, or Mg leaves the intensity of phosphorescence unchanged; Zn decreases it, whilst Mn increases it to an extent dependent on the voltage of formation of the layer.

A. B. D. C.

Influence of unequal distribution of phosphorescence centres on Lenard phosphors. V. V. ANTONOV-ROMANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 105—111).—Theoretical.

W. R. A.

Phosphorescence of calcite. V. LEVSHIN and M. ALENTZEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 54—57).—A spectroscopic investigation of phosphorescence excited by the 365 mμ Hg line in calcite, aragonite, and stalactites is described.

A. B. D. C.

Cathodic phosphorescence phenomena. M. SERVIGNE (Compt. rend., 1935, 200, 2015—2017).—Pptd. CaWO_4 gave feeble blue cathodic phosphorescence compared with natural scheelite. The effect in the pptd. material was much enhanced by heating for 10 min. at 800° and cooling quickly. The blue phosphorescence was intensified by addition of Ag

(optimum 0.1%). Addition of 1% of Sm and Er produced orange-red and green phosphorescences, respectively.

H. J. E.

Influence of potassium iodide concentration on the time of decay of the uranine fluorescent radiation. W. SZYMANOWSKI (Bull. Acad. Polonaise, 1935, A, 34—37).—Data are recorded. The applicability of Vavilov's theory is discussed (cf. A., 1929, 489).

H. J. E.

Variability of the fluorescence spectrum of a glycerol solution of tryptaflavine. MŁŁE. A. WRZESIŃSKA (Bull. Acad. Polonaise, 1935, A, 38—41).—A band in the fluorescence spectrum at approx. 5000 Å. has been shown by measurements at -180° to 100° to consist of two components, the max. of which vary in position and relative intensity with temp.

H. J. E.

Time decrement of light due to polarised fluorescence of dye solutions. A. JABŁOŃSKI (Z. Physik, 1935, 95, 53—65).—Perrin's theory of depolarisation is applied to time decrement of fluorescence; this does not generally follow the exponential law. Fluorometer measurements are discussed.

A. B. D. C.

Negative polarisation of the phosphorescence of adsorbed dye molecules. A. JABŁOŃSKI (Bull. Acad. Polonaise, 1935, A, 30—33; cf. A., 1934, 584).—Measurements of polarisation in the low-temp. phosphorescence spectrum of tryptaflavine adsorbed on Cellophane are recorded and discussed.

H. J. E.

Photomagnetism. D. M. BOSE and P. K. RAHA (Phil. Mag., 1935, [vii], 20, 145—166).— $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ crystals and solutions containing V^{+++} or V^{++} ions show an increase in magnetic susceptibility on absorption of radiation. The photo-magnetic effect of aq. solutions containing various paramagnetic ions follows the order $\text{Ni}^{++} > \text{Cr}^{+++} > \text{Co}^{++}$ and approx. \propto the quenching of the orbital moment of the ions in their ground states. Solutions containing Cr^{+++} or Ni^{++} in dil. HCl give very small photo-magnetic effects, probably owing to the presence of undissociated paramagnetic mols. in these solutions which absorb the light and in which the orbital moment is equally quenched in the initial and final states. Quant. relations between the light absorption and change in susceptibility are deduced for CrCl_3 solutions.

J. W. S.

Surface-force theory of rectification in ionic crystals. S. R. KHASTGIR (Indian J. Physics, 1935, 9, 347—355; cf. this vol., 282).

A. J. M.

Dielectric loss of liquid insulators. H. RIECHE (Z. Physik, 1935, 95, 158—178).—Dielectric loss and const. have been measured for transformer oil, PhNO_2 , and C_6H_6 in the frequency range of 50 to 150×10^6 hertz, and from -80° to 100° ; the results agree with Debye's dipole theory rather than Wagner's theory of inhomogeneity.

A. B. D. C.

Conductivity-temperature studies on paraffin waxes. W. JACKSON (Trans. Faraday Soc., 1935, 31, 827—835; A., 1934, 585).—Different samples of paraffin wax have a negative coeff. of electrical conductivity over a small temp. range 10 — 15° below their m.p. The behaviour is apparently due to a

change of cryst. form. The instantaneous absorption current passes through a max. with temp. F. L. U.

Mechanism of dielectric loss in paraffin wax solutions at high radio frequencies. W. JACKSON (Proc. Roy. Soc., 1935, A, 150, 197—220).—An attempt to correlate the dielectric properties of solid insulating materials with their chemical and physical constitution. The results of measurements of the variations of power loss and dielectric const. for solutions of cetyl palmitate (I) in a paraffin wax medium over the temp. range 0—80° and at frequencies of 1.80×10^5 — 1.42×10^7 cycles per sec. are discussed. The variation of power loss is in good quant. agreement with Debye's theory of dipole orientation. Experimental results point to the conclusion that only a portion of the polar (I) mol. oscillates in the alternating electric field. L. L. B.

Conductivity of anisotropic liquids. V. FREDERIKS, G. MICHAÏLOV, and D. BENESCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 208—212).—The dependence of conductivity on field strength has been investigated for *p*-azoxyanisole and PhCl. W. R. A.

Dipole moment and molecular properties. O. GRABOWSKY (Pharm. Ztg., 1935, 80, 643—646).—A summary.

Constancy of two dipole moments in the vapour state and their apparent variation in solution. C. P. SMYTH and K. B. McALPINE (J. Chem. Physics, 1935, 3, 347—350).—The validity of the solution method for determining dipole moment is considered with reference to possible variation of moment with temp. The moments of heptyl bromide and BuCl in the vapour state are 2.07 ± 0.05 and 2.04 ± 0.01 , respectively, showing the absence of appreciable increase in moment with increase in C chain length. Estimated moment vals. for the vapour state are: PrⁿBr and BuⁿBr, 2.04 ± 0.03 ; PrⁿI and BuⁿI, 1.93 ± 0.04 . N. M. B.

Dielectric constants of gases and vapours. II. M. KUBO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 65—73; cf. this vol., 567).—The electric moments and at. polarisation of PrⁿOH, BuⁿOH, and allyl alcohol have been calc. from the dielectric consts. of their vapours. W. R. A.

Moments and internal potential energies of two molecules containing movable dipoles. C. P. SMYTH and K. B. McALPINE (J. Amer. Chem. Soc., 1935, 57, 979—983).—The dielectric consts. of the vapours of trimethylene chloride and (CHCl₂)₂ have been determined. The calc. dipole moments (2.10×10^{-18} and 1.36×10^{-18}) do not vary over the temp range studied (374—485° abs. and 401—436° abs., respectively). E. S. H.

Dipole moments of ethyl- and phenyl-carbimides. J. R. PARTINGTON and E. G. COWLEY (Nature, 1935, 135, 1038).—Ethyl- and phenyl-carbimide in C₆H₆ at 20° give P_{29} 185 and 144 c.c., P_E 18.3 and 33.9 c.c., and 2.81 and $2.28D$, respectively. The results, like the Raman spectra, indicate that N:C:O in the carbimides is linear. L. S. T.

New formula for molecular polarisation and refraction. P. C. HENRIQUEZ (Rec. trav. chim., 1935, 54, 574—575).—The Clausius-Mosotti expression is regarded as invalid for liquids. From Fairbrother's results (this vol., 13) the mol. polarisation (P) of PhNO₂ in *p*-xylene is given by $P = (\epsilon - 1)(\epsilon + 4)M / \{ (8\epsilon + 7)d \}$. For 12 "non-associated" substances this relation holds well if ϵ is < 20 , and the concn. is < 30 mol.-%. For liquids of $\epsilon > 20$, $P = (\epsilon - 1)(\epsilon + 4)M / \{ (8\epsilon + 7 + (\epsilon - 1)^3 \times 1.7 \times 10^{-3})d \}$. Even for pure liquids the deviation is small, dipole moments calc. from data for pure liquids differing by $> 10\%$ from vals. calc. from data for dil. solution. For $\epsilon < 6$, $P = 0.60(\epsilon^3 - 1)M/d$, and the mol. refraction $= 0.60(n - 1)M/d$. R. S. B.

cis-Cinnamic acids. F. EISENLOHR and W. HASS (Z. physikal. Chem., 1935, 173, 249—264).—The forms of m.p. 42°, 58°, and 68° have in C₆H₆ solution the same dipole moment, 1.12×10^{-18} e.s.u. In solution in C₆H₆, Et₂O, and dioxan the forms of m.p. 68° and 42° have the normal mol. wt. The heat of combustion of the acid of m.p. 42° is 1042.7 kg.-cal. per mol. Each form with *trans*-cinnamic acid has the f.-p. diagram of a typical binary system with eutectic. It is suggested that the relation between the three forms is some special kind of rotation isomerism; it is certainly not polymorphism (cf. A., 1930, 471). R. C.

Molecular volume of water in sodium salts. A. ESCRIBANO and E. MOLES (Anal. Fis. Quím., 1934, 32, 494—508).—Na₂B₄O₇ yields hydrates with 10, 4, 3(?) , 2, and 1 H₂O, Na₂S₂O₃ with 5 and 2 H₂O, and Na₂S₄O₆ with 2 H₂O. Density determinations on all the hydrates yield the normal val. for the mol. vol. of the H₂O, except in the case of Na₂S₂O₃.2H₂O (10.3) and Na₂S₄O₆.2H₂O (9.6). H. F. G.

Refractive index of the alkaline chlorides at low concentrations. H. J. WALKER (Phil. Mag., 1935, [vii], 20, 32—44).—At concns. $< 0.0005N$ the refractive index of NaCl, KCl, and LiCl solutions varies linearly with concn., this being interpreted as evidence for complete dissociation below this concn. Between 0.0005 and 0.002N it varies linearly with $\sqrt{\text{concn.}}$, suggesting that undissociated mols. may be present in these solutions. J. W. S.

New determination of atomic refractions. I. L. J. N. VAN DER HULST (Rec. trav. chim., 1935, 54, 518—522).—The at. refractions (r) calc. by Eisenlohr (A., 1911, ii, 81) are criticised on the grounds of incorrect mathematical derivation. From the paraffin hydrocarbons and aliphatic nitriles the mol. refraction of CH, has been calc. as 4.640 at 20° for 589 mμ, whence r for C and H = 2.590 and 1.025, respectively. Using these vals. the mol. refractions of the paraffin hydrocarbons have been calc., and no "exaltation" appears with higher members, contrary to the results of Eisenlohr. R. S. B.

Molecular refraction, molecular volume, and b.p. in molecular lattices. W. KLEMM (J. pr. Chem., 1935, [ii], 143, 106—114).—The relation between the ratio mol. refraction/mol. vol. and the abs. b.p. of a no. of elements and compounds has been examined. It is a smooth curve for inert gas elements

which becomes displaced towards higher b.p. in the case of polyat. mols. without dipole moment. Hydrides of this class (CH_4 , PH_3 , HI) lie on the inert gas curve, indicating an inert gas electronic structure. The presence of a dipole moment displaces the relation in the direction of higher b.p. This effect is explained with reference to interat. and interionic forces. In homologous series of saturated hydrocarbons, alcohols, and carboxylic acids, it tends to a const. with increasing b.p. R. S.

Factors modifying the polarisation of liquids. F. R. GOSS (J.C.S., 1935, 727—731; cf. this vol., 683).—The previously assumed equality of the mol. anisotropy factors arising from the local asymmetry of the optical and the electrical polarisation field is established for CCl_4 . The "false" orientation polarisation of C_6H_6 , attributed to the presence of co-ordinate links, is measured for the temp. range 10—50°. Several expressions for mol. refraction are compared with reference to temp. independence. N. M. B.

Theory of optical activity. I. General theory of a system of coupled isotropic oscillators. II. Molecules with a binary axis of symmetry. M. BORN (Proc. Roy. Soc., 1935, A, 150, 84—97, 97—105).—I. A development of the theory of rotatory power given previously (A., 1915, ii, 659). The mol. is considered as a set of isotropic oscillators coupled by Coulomb forces, and the interaction is calc. by the perturbation method.

II. A mol. consisting of 2 equal pairs of oscillators perpendicular to each other and to their central line is considered. The theory gives an angle of rotation of the expected order of magnitude. L. L. B.

Electrical birefringence of liquid oxygen and nitrogen. R. GUILLIEN (Compt. rend., 1935, 200, 1840—1841).—Data for O (64.05—90.15° abs.) and N (63.29—77.40° abs.) are recorded for λ 5461 Å. The vals. \propto 1/abs. temp., confirming the absence of a permanent electrical moment in the mols. H. J. E.

Rule for calculating the formulæ of acids and bases. M. CARRANZA (Bol. Soc. Quim. Peru, 1935, 1, No. 3, 58—61).—Methods for calculating the formulæ of acids and bases derivable from any given element are deduced from the no. of electrons which can be given or received by the outer electron shell. E. L.

Transition from metallic to heteropolar linking. U. DEHLINGER (Z. Elektrochem., 1935, 41, 344—346).—Theoretical. An explanation of the fluorspar-lattice structure of AuAl_3 . F. L. U.

The I—I linking in diphenyliodonium iodide. W. V. MEDLIN (J. Amer. Chem. Soc., 1935, 57, 1026—1027).—X-Ray investigation shows that the distance between the I atoms is 3.55 Å., which is compatible with an ionic, but not a covalent, structure. E. S. H.

Linking of HCl. R. SAMUEL (Current Sci., 1935, 3, 549—550).—The covalent nature of this linking is affirmed. A. B. D. C.

Problem of valency. R. F. HUNTER and R. SAMUEL (Chem. and Ind., 1935, 635—637; cf. A.,

1934, 1058).—Difficulties arising in the translation of the theory of co-ordination into wave-mechanical terms are discussed. The limitations of the method of mol. orbitals are considered, and it is maintained that the method should be interpreted as giving, in higher approximations, a pair-bond theory of valency, with strong interaction of electrons within the pair, and weak interaction between adjacent pairs. New band spectroscopic evidence confirms the non-bonding power of the s^2 group. The relation between bond and Raman frequency is discussed. The only method of treating co-ordination by wave-mechanics is to use the method of mol. orbitals as a single electron bond theory. A. J. M.

Number of canonical structures of each degree of excitation for an unsaturated or aromatic hydrocarbon. G. W. WHELAND (J. Chem. Physics, 1935, 3, 356—361).—Results are calc. and illustrated for mols. consisting of a straight chain, a ring, several rings, and an unpaired electron, respectively. N. M. B.

Formation and stability of complex ammines. B. N. SEN (J. Gen. Chem. Russ., 1935, 5, 169—172).—Ammines are formed only by those elements for which the distance D of closest approach of the central atoms is > 2.48 Å. The dissociation temp. T of hexammines is given by $k = \log(TDV)^3$, where V is the ionisation potential. R. T.

Class of perturbations of molecular levels. G. H. DIEKE (Physical Rev., 1935, [ii], 47, 870—876).—The conditions under which perturbations can occur, when the perturbing force is caused by the rotation of the mol., are examined. N. M. B.

Formation of mercury molecules. F. L. ARNOT and J. C. MILLIGAN (Nature, 1935, 135, 999—1000).—Magnetic analysis of ions in Hg vapour at various pressures and voltages shows that diat. mol. ions result from electron impact. The mol. ions are formed by the union of two atoms one of which at least must be excited, a view which reconciles the non-existence of Hg mols. chemically with the band spectra evidence of their presence. L. S. T.

Moles of vibration of butane and pentane. "Free rotation" about carbon-carbon linkings and a new type of stereoisomerism. L. S. KASSEL (J. Chem. Physics, 1935, 3, 326—335).—Mathematical. Rotational investigation of a chain of four C atoms indicates two isomeric forms of C_4H_{10} with plane C skeletons, and a third form in which the two Et are rotating about the central C-C linking. Vibration frequencies for a five-C chain are calc. Results are in fair agreement with observed Raman and infra-red lines. N. M. B.

Spectrum of the normal frequencies of a polar crystal lattice. I. General theory. J. H. C. THOMPSON (Proc. Roy. Soc., 1935, A, 149, 487—505).—Mathematical. The dynamical theory of the vibrations of the particles in a polar crystal lattice is worked out. A determinantal frequency equation, for the determination of a typical set of points of the "frequency spectrum," is obtained in a form in which the coeffs. can be calc. L. L. B.

Characteristic vibrations of mechanical models of molecules. II. Four-mass systems. F. TRENKLER (Physikal. Z., 1935, 36, 423—432; cf. this vol., 432).—The form of vibrations and characteristic frequencies of mols. of the types COCl_2 , CO_3^{--} , *trans*- and *cis*-(CHCl)₂, $(\text{CN})_2$, and C_2H_2 have been investigated with mechanical models. The results are in agreement with theory except in the case of the slow deformation vibrations, for which models are inadequate. A. J. M.

Dynamics of molecular crystal lattices. III. Models of vibrating crystals. V. DEITZ and D. H. ANDREWS (J. Franklin Inst., 1935, 219, 703—715; cf. this vol., 811).—The frequencies of vibrating mols. have been studied by mechanical vibration of an appropriate model, and an extension of the method to a complete crystal lattice is described. Models of solid Ne and N_2 (both face-centred cubic) were constructed, containing 15 and 36 unit cells, respectively. Elastic bands represented the forces between each atom and its nearest neighbours, also its next-to-nearest neighbours; thus in Ne lattice each "atom" was acted on by eighteen "forces." The model was vibrated mechanically at increasing frequencies. The effect of introducing a heavy "isotope" was studied. B. W. R.

Thermochemistry and physical properties of bromides and hydrosulphides. C. D. WEST (J. Physical Chem., 1935, 39, 493—507).—The lattice energies of alkali bromides and hydrosulphides have been calc. and shown to be similar. The proton affinities of Br' and SH' differ by about 23 kg.-cal. Calc. free energy changes indicate that MSH (M —alkali metal) is increasingly stable as the at. no. of the cation increases, and that the hypothetical LiHS must be thermodynamically unstable. The calc. heats of reaction of M with MSH are in accordance with the observation that MSH is readily decomposed by M , in contrast to the behaviour of M towards MOH . Various thermochemical data for MSH have been calc. from lattice energies. Physical properties of corresponding covalent bromides and hydrosulphides have been compared. Some cyanides have been considered. M. S. B.

Energy constants of a gas in the region of dissociation. F. A. F. SCHMIDT (Forsch. Ingenieurwes., 1934, A, 5, 60—66; Chem. Zentr., 1935, i, 677).—Formulae are derived for the heat content of a dissociating gas mixture. Data for CO_2 , H_2O , and NH_3 are discussed. H. J. E.

Parachor. V. DESREUX (Bull. Soc. chim. Belg., 1935, 44, 249—287).—The surface tensions and densities of many halogen-substituted hydrocarbons have been determined and the parachors deduced. The increase in parachor obtained by substitution of H by halogen is not const. and is always < calc., the greatest effects being observed with F. The physical significance of the parachor is discussed, and it is concluded that the anomalies may be due to the compounds not being in strictly comparable states. J. W. S.

Optical reciprocal law applied to X-ray interference. M. VON LAUE (Naturwiss., 1935, 23, 373).

—The Maxwell reciprocal law may be applied to radiation proceeding from atoms in a wave field. The two possible cases of the radiation proceeding into and out of the crystal are considered. Similar considerations apply to electron diffraction.

A. J. M.

"Quadratic form" of inverted polar crystalline space-lattices. V. LINITZKI (Ukrain. Chem. J., 1935, 10, 22—26).—Mathematical. R. T.

Rate of polymorphic transformations. III. Influence of mechanical deformation on rate of transformation. E. COHEN, W. A. T. COHEN-DE MEESTER, and A. K. W. A. VAN LIESHOUT (Z. physikal. Chem., 1935, 173, 169—177; cf. this vol., 688).—The observations accord with the view that a nucleus in a polymorphic metal is to be regarded as a local strain in the lattice. R. C.

Vitreous state. G. HAGG (J. Chem. Physics, 1935, 3, 363—364).—A discussion of a paper by Zachariassen (cf. this vol., 572). N. M. B.

X-Ray investigations on the thermal expansion of solids. II. G. SHINODA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 27—30; cf. B., 1933, 672).—The following thermal expansion coeffs., parallel and perpendicular to the hexagonal axis, respectively, are recorded: Mg 23.8×10^{-6} , 23.5×10^{-6} ; Cd 50.0×10^{-6} , 17.9×10^{-6} ; Zr 2.5×10^{-6} , 14.3×10^{-6} ; Co 16.1×10^{-6} , 12.6×10^{-6} . E. S. H.

Determination of the thickness of the [oxide film] on the surface of metallic lead. S. SHIMADZU (Mem. Coll. Sci. Kyoto, 1934, A, 17, 79—84).—X-Ray examination shows that the film consists of tetragonal PbO and is 50—200 m μ thick. E. S. H.

Interpretation of Weissenberg photographs in relation to crystal symmetry. D. CROWFOOT (Z. Krist., 1935, 90, 215—236).—Detailed technique is described for interpreting Weissenberg photographs to give the point-group symmetry of the crystal. Charts are reproduced for a special camera size, and particular attention is given to triclinic and monoclinic (*a* or *c* axis) photographs. B. W. R.

Interference phenomena in two-dimensional crystals. F. LAVES and W. NIEUWENKAMP (Z. Krist., 1935, 90, 273—278).—A theoretical discussion of the X-ray diffraction to be expected from a two-dimensional lattice. B. W. R.

Two-dimensional over-structures. F. LAVES (Z. Krist., 1935, 90, 279—282).—Certain rotation photographs of maucherite, Ni_3As_2 , are interpreted as indicating the existence of a two-dimensional lattice. B. W. R.

Derivatives of ferric oxide ($\text{FeO} \cdot \text{OH}$, FeO_2Na , FeOCl): determination of their structures. S. GOLDSZTAUB (Bull. Soc. franç. Min., 1935, 58, 6—76).—X-Ray analysis of the natural hydrates of Fe_2O_3 gives, except in the case of turgite (I), diagrams corresponding with that of either goethite (II) or lepidocrocite (III). (I) gives the hæmatite diagram (cf. A., 1929, 988). Hence in nature there is only one hydrate of Fe_2O_3 , viz., $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which has two different cryst. structures, that of (II) or (III). Thermomagnetic analysis shows that on dehydration

(III) gives an unstable Fe_2O_3 which is strongly magnetic, and this has enabled small quantities of (III) to be detected in minerals giving only the X-ray diagram for (II). Larger crystals (2–3 mm.) of Na ferrite (IV) have been prepared by a modification of the method of van Bemmelen and Klobbie (A., 1893, ii, 169). The at. structure of (IV) is discussed (cf. A., 1933, 215). The X-ray diagram of the product of hydrolysis at room temp. is different from that of (II) or of (III).

Goethite from the Restormel mine at Lanlivery, Cornwall, has a 4.64, b 10.0, c 3.03 Å.; space-group $V^{10} bnm$. The crystal is built up from units of $\text{FeO}\cdot\text{OH}$ and the formula should be written $\text{FeO}\cdot\text{OH}$, since there are no H_2O groups in the cryst. structure. Infra-red absorption spectra confirm this by showing only the presence of OH (A., 1933, 13). On dehydration (II) gives, without change of cryst. form, a stable Fe_2O_3 which is composed of an assemblage of crystallites of hæmatite oriented at 180° to each other.

By heating a mixture of FeCl_3 and Fe_2O_3 at 350° in a sealed tube for 2–3 weeks larger crystals (d 3.55) of FeOCl are formed. They readily show perfect parallel cleavage and are flexible but not elastic. Their at. structure is discussed (cf. A., 1934, 351). On hydrolysis with warm H_2O , Cl' is replaced by OH', and (III) is formed without loss of external form or of transparency, indicating that the structure of (III) resembles that of FeOCl . X-Ray examination of (III) confirms this. As in the case of (II) the structural unit is $\text{FeO}\cdot\text{OH}$, but the at. arrangement is different.

Lepidocrocite from Siegen has a 3.87, b 12.4, c 3.06 Å., d 3.95, with 4Fe, 4O, and 4OH in the unit cell. The at. arrangement is discussed. Rapid dehydration gives a product with a Debye-Scherrer diagram similar to that of magnetite, whilst that from slow dehydration gives the hæmatite diagram. Both products are magnetic. L. S. T.

Growth of crystals. V. (Supplement.) T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 497–498).— Sn^{++} ions promote the growth of NaCl crystals in presence of > 0.004 mol. ion per 1 mol. NaCl. Large, clear cubes grow in its presence. W. R. A.

Growth of crystals. VII. Influence of cations in the solution on the crystal growth of potassium salts. T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 499–506).—Influence of cations on the crystal growth of KI, K_2SO_4 , KNO_3 , and KClO_3 was studied under the microscope. Except for KClO_3 , cations which promoted crystal growth were found and are discussed. W. R. A.

Lattice parameters of solid solutions in silver. W. HUME-ROTHERY (Nature, 1935, 135, 1038).—In dil. solid solutions of Cd, In, Sn, or Sb in Ag, alloys of the same equiv. composition (at.-% of solute element \times valency) have identical lattice parameters. The initial expansion of the Ag lattice produced by an atom of the above elements \propto the valency. The relation is of the same type as that found for the depression of the f.p. of Ag, and may indicate an effect

which \propto the repulsion between a solute and a solvent ion. L. S. T.

Effect of temperature on cathode-ray interference. H. KAKESITA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 31–35).—With a single crystal of FeS_2 , the interference max. are more diffused at 220° than at 25° . With Au foil at 28° , 150° , and 320° the intensity effect increases with the angle of reflexion and with rising temp. E. S. H.

Melting of metal crystals at their boundaries and a theory of recrystallisation of metals. U. YOSHIDA and K. KOYANAGI (Mem. Coll. Sci. Kyoto, 1935, A, 18, 9–16).—When heated to a temp. just below its normal m.p., a metal begins to melt at the crystal boundaries, which become grooved. This is probably due to more rapid evaporation at the crystal boundaries than elsewhere. A crystal also appears to melt more easily where it comes into contact with its melt, and when distorted. A theory of recrystallisation of metals is based on these facts. A. J. M.

Lattice distortion in nickel-iron. W. G. BURGERS (Nature, 1935, 135, 1037–1038).—X-Ray diffraction photographs of a Ni-Fe alloy (53 at.-% Fe) distorted by cold working show that compression and stretching change the shape and possibly the size of the unit cell. L. S. T.

Mechanism of the transition in ammonium salts at -40° . J. A. A. KETELAAR (Chem. Weekblad, 1935, 32, 349–350).—Differences observed in the X-ray diagrams of NH_4Br and NH_4I are due to change of oscillation in the NH_4 group into rotation. S. C.

Atomic distribution in red and black phosphorus and the crystal structure of black phosphorus. R. HULTGREN, N. S. GINGRICH, and B. E. WARREN (J. Chem. Physics, 1935, 3, 351–355).—Five samples of black P of widely varying age gave identical powder patterns. A sample prepared at room temp. and 35,000 atm. gave the diffuse rings of an “amorphous” X-ray pattern. Another sample, prepared at 300° and 8000 atm., is a new form of P, having the same density as black. At. distribution curves of cryst. and “amorphous” black and red P were practically identical, showing three neighbours of 2.28 Å. and about 12 at 3.6 Å. The structure of black P shows double layers; the cell is side-centred orthorhombic, a 3.31, b 4.38, c 10.50 Å.; 8 atoms per unit cell; $d_{\text{calc.}}$ 2.69, $d_{\text{obs.}}$ 2.70; space-group $V^{18} Bmab$. N. M. B.

Orientation of the crystallites in cast nickel and the changes produced by rolling and recrystallisation. G. TAMMANN and F. LAASS (Z. Metallk., 1935, 27, 86–88).—The crystal orientation in cast Ni and in recryst. rolled Ni sheet is similar to that of Al, in that octahedral planes lie against the cooling surfaces of the casting and in the rolling plane of the annealed sheet. A. R. P.

Molecular arrangement in amorphous antimony. J. A. PRINS (Chem. Weekblad, 1935, 32, 348–349).—Amorphous Sb prepared by electrolysis of SbCl_3 contains occluded SbCl_3 , which keeps the metal in a “dispersed” form. It can be produced in thin layers by distillation in a high vac., but thick layers ($< 1000 \mu$) crystallise immediately. The electron

diffraction pattern corresponds with an at. arrangement similar to that in *cryst. Sb*, of co-ordination no. 6.

S. C.

Crystalline structure of electrolytic white tin. H. HIRATA and Y. TANAKA (*Mem. Coll. Sci. Kyoto*, 1934, **A**, 17, 143—152).—X-Ray examination. Sn deposited from a solution of SnSO_4 , H_2SO_4 , and Na_2SO_4 consists of micro-crystals arranged with the normals to their (111) planes in a common direction, perpendicular to the direction of max. growth of the deposited Sn. Patterns corresponding with two crystals, with one of the (101) planes in common, were detected.

E. S. H.

Copper amalgam CuHg with the γ -brass structure. F. SCHOSZBERGER (*Z. physikal. Chem.*, 1935, **B**, 29, 65—78).—The cubic crystals have a 9.406 ± 0.004 Å. Hume-Rothery's rule does not hold. If it is attempted to assign to the Cu and Hg atoms a similar arrangement to that in $\gamma\text{-Cu}_5\text{Cd}_8$ there appear discrepancies between observed and calc. intensities which are present, although less pronounced, in the γ -structures of Cu-Zn and Cu-Cd.

R. C.

Structure of the intermetallic compound Au₂Pb. H. PERLITZ (*Acta Comm. Univ. Tartuensis*, 1934, 27, No. 11, 12 pp.; *Chem. Zentr.*, 1935, i, 783).—The lattice is face-centred cubic (a 7.91 Å.; 24 atoms in unit cell). Au_2Pb is related to MgCu_2 and KBi_2 .

H. J. E.

X-Ray examination of selenium crystals. K. TANAKA (*Mem. Coll. Sci. Kyoto*, 1934, **A**, 17, 59—78).—"Metallic" Se has a 4.360 Å. and c/a 1.138; 3 atoms in unit cell; growth occurs most prominently along the trigonal axis. Vitreous and amorphous Se give the same diffraction band and are transformed into the metallic form when annealed at suitable temp. The transition temp., about 74°, has been determined by X-ray examination and confirmed by determinations of d .

E. S. H.

Phosphides and arsenides with modified nickel arsenide structure. K. E. FYLKING (*Arkiv Kemi, Min., Geol.*, 1935, 11, **B**, No. 18, 6 pp.).—Mn, Fe, and Co phosphides and arsenides, prepared by heating the elements in equal mol. proportions for \leq a day at 610° (for P) or 730° (for As), have lattice structures closely related to that of NiAs, but the metal atoms form zig-zag chains instead of straight rows. MnAs differs less from NiAs than FeAs and CoAs. The lattice dimensions of these compounds and parameter vals. for MnP and FeAs are recorded.

J. W. S.

Crystal structure of magnetic ferric oxide, $\gamma\text{-Fe}_2\text{O}_3$. G. HÄGG (*Z. physikal. Chem.*, 1935, **B**, 29, 95—103).—If Fe_3O_4 is oxidised to $\gamma\text{-Fe}_2\text{O}_3$ at 300° without losing the spinel structure, the length of the edge of the unit cube of the lattice changes continuously from 8.380 for Fe_3O_4 to 8.322 Å. for Fe_2O_3 . The increase in O concn. during oxidation is caused by the appearance of unoccupied positions in the Fe atom lattice of the spinel phase; in $\gamma\text{-Fe}_2\text{O}_3$ one ninth of the original Fe atom positions are empty. Thewlis' lattice structure for $\gamma\text{-Fe}_2\text{O}_3$ (*A.*, 1932, 113) is rejected. The belief that $\gamma\text{-Fe}_2\text{O}_3$ can be reduced to Fe_3O_4 by heating at 250° in a vac. (*A.*, 1932, 29) is erroneous.

R. C.

Crystal structure of the aluminium halides. II. **Crystal structure of AlCl_3 .** J. A. A. KETELAAR (*Z. Krist.*, 1935, 90, 237—255).— AlCl_3 is monoclinic pseudohexagonal, a_0 5.91, b_0 10.24, c_0 6.16 Å., β 71° 21', space-group C_2^2 . The lattice is essentially of layer type, Al_2Cl_6 being the mol. unit. The structure found from detailed intensity measurement does not agree with previous results (cf. *A.*, 1930, 1503).

B. W. R.

Crystal structure of bismuth oxyhalides. F. A. BANNISTER [with M. H. HEY] (*Min. Mag.*, 1935, 24, 49—58).—Minute crystals of BiOCl , BiOBr , and BiOI were prepared by diffusion of solutions $\text{BiCl}_3 + \text{HCl}$ etc. into water. They are tetragonal with the same structure as mallockite, BiFCl (*A.*, 1934, 1197). The unit cell contains 2 mols. and has dimensions: for BiOCl , a 3.89, c 7.37 (d 7.717); BiOBr , a 3.92, c 8.11 (d 8.082); BiOI , a 4.01, c 9.14 (d 7.922). The minerals bismoclite (BiOCl) and daubreelite ($\text{BiO}[\text{OH}, \text{Cl}]$) have a 3.89, c 7.37, and a 3.85, c 7.40 Å., respectively.

L. J. S.

Crystal structure of some amines of the type $\text{M}(\text{NH}_3)_2\text{Cl}_2$. C. A. MACGILLAVRY (*Chem. Weekblad*, 1935, 32, 346—347).—Compounds like $\text{MX}_2 \cdot 2\text{NH}_3$ ($\text{M} = \text{Hg}, \text{Zn}, \text{Cd}$; $\text{X} = \text{Cl}, \text{Br}$) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are all of centred lattice type of halogens and NH_3 (unit cell $4 \times 4 \times 4$ Å.); $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ is peculiar in that its X-ray diagram is practically identical with that of Ag. The Cd compounds have a tetragonal twin structure, giving rhombic X-ray diagrams.

S. C.

X-Ray study of the caesium salts of certain 12-heteropoly acids. J. A. SANTOS (*Proc. Roy. Soc.*, 1935, **A**, 150, 309—322).—The structures of the Cs salts of 12-phospho-, 12-silico-, 12-boro-, and tungstic acids ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, $\text{H}_5\text{BW}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, and $\text{H}_6\text{W}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$) have been studied (cf. *A.*, 1934, 479, 1296). In each case, the Cs salts contained only 3 Cs atoms per mol., and all attempts to prepare salts with > 3 Cs atoms failed. The formulae deduced are: $\text{Cs}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $\text{Cs}_3\text{HSiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $\text{Cs}_3\text{H}_2\text{BW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, and $\text{Cs}_3\text{H}_3\text{W}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, where $n = 2$ or 0. Corresponding Rb and Tl salts have been prepared, and found to have similar structures.

L. L. B.

Planar structure of quadricovalent cupric compounds. E. G. COX and K. C. WEBSTER (*J.C.S.*, 1935, 731—733).—*Cu disalicylaldoxime* has been prepared, and analogy with previously reported compounds (cf. this vol., 684) suggests a planar structure. X-Ray investigation of the *cryst. Cu salts* of CH_2Ac_2 , CH_2BzAc , $\text{CH}_2(\text{COEt})_2$, and γ -chloroacetylacetone established their planar configuration by means of space-group considerations, cell dimensions, and optical properties.

N. M. B.

Crystal structures of magnesium-aluminium spinels with alumina in excess and of γ -alumina. G. HÄGG and G. SÖDERHOLM (*Z. physikal. Chem.*, 1935, **B**, 29, 88—94).—The d of these spinels indicate that the excess of O is caused by the appearance of unoccupied positions in the metal lattices, the ratio $\text{Al} : \text{Mg}$ increasing parallel with the excess of O. The edge of the unit cube of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ is 8.056 Å. The upper limit of Al_2O_3 in the stable solid solutions is

about 67 mol.-%, whilst the unstable limit is to be regarded as γ - Al_2O_3 . This latter crystallises in the spinel lattice, cube edge 7.843 Å., but one ninth of the metal atom positions are empty. R. C.

Non-silicates with cristobalite-like structure. T. F. W. BARTH (J. Chem. Physics, 1935, 3, 323—325).—The cristobalite type of structure is shown to occur in $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3$, and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$. N. M. B.

Crystal structure of the guanidonium halides. III. Structure of guanidonium bromide $\text{C}(\text{NH}_2)_3\text{Br}$. W. THEILACKER (Z. Krist., 1935, 90, 256—272).— $\text{C}(\text{NH}_2)_3\text{Br}$ is rhombic bipyramidal, a_0 6.77, b_0 8.64, c_0 8.30 Å.; 4 mols. in cell; space-group V_{16}^h . The double refraction of the substance is considered and a set of at. parameters is obtained; the guanidonium ions have their planes parallel to the a axis and mutually perpendicular. B. W. R.

X-Ray diffraction in some long-chain aliphatic liquids. J. A. PRINS and R. FONTEYNE (Physica, 1935, 2, 573—574).—The strongly polar mols., alcohols and aliphatic acids, show a more conspicuous "inner ring" than other normal long-chain aliphatic compounds. The spacing in the diffraction pattern of cork is 4.4 Å. and not 4.1 Å., as given previously (A., 1934, 948). M. S. B.

The odd-membered n -primary alcohols (the $\alpha \rightarrow \beta$ transition). T. MALKIN (J.C.S., 1935, 726).—The β -forms of the C_{15} , C_{17} , and C_{19} n -primary alcohols give two main side spacings (3.7 and 4.2 Å.), whereas the α -forms give only one (4.2 Å.). Further, the α -forms are uniaxial, the β -forms are biaxial. These results accord with the view of Wilson *et al.* (A., 1934, 720) that the $\alpha \rightarrow \beta$ change is due to a change from a vertical rotating (α) form to a vertical non-rotating (β) form. The conclusion of Phillips and Mumford (cf. this vol., 20) that the odd alcohols above C_{14} exist in a β -tilted form is not valid. H. G. M.

Molecular structure and crystal symmetry. Fine structure of triethyl 1:3:5-benzenetricarboxylate. E. HERTEL and E. DUMONT (Z. physikal. Chem., 1935, B, 29, 112—116).—The hexagonal unit cell has I_a 11.3, I_c 20.1 Å. and contains 6 mols. Some crystals have the space-group C_2^2 , others C_6^2 , the two species differing in the sense of the twist of the helicohexagynes determining the crystal structure. Although the symmetry of the mol. is C_1 its triangular shape is probably responsible for the mol. arrangement in the crystal. R. C.

Difference in X-ray diffraction patterns of some isomerides. Z. MURO (Mem. Coll. Sci. Kyoto, 1935, A, 18, 79—82).—X-Ray diffraction patterns of d - and l -pinene and α -limonene, and of isomerides of the mol. formula $\text{C}_{10}\text{H}_{16}$, $\text{C}_{10}\text{H}_{16}\text{O}$, $\text{C}_{10}\text{H}_{18}\text{O}$, $\text{C}_{10}\text{H}_{12}\text{O}_2$, and $\text{C}_{10}\text{H}_{10}\text{O}_2$ were examined. With optical isomerides there is no difference in the form of the pattern, nor in the val. of the distance (d) between the planes. With ordinary isomerides there is a diminution of d accompanied by an increase of diffuseness of the pattern on passing from the normal to the *iso*-compound. In all cases, rise of temp. results in diminution of d and increase of diffuseness. A. J. M.

Crystal structure of p -toluidine. J. WYART (Compt. rend., 1935, 200, 1862—1864).—The crystals are orthorhombic (a 5.98, b 9.05, c 23.3 Å.; 8 mols. in unit cell; space-group D_{2h}^{19}). The 6 atoms in the nucleus form a regular hexagon of side 1.40 Å. The NH_2 is 1.18 Å. from the C, the C-N linking making an angle of 15° with the plane of the nucleus. This angle for the C-Me linking is 16° , the C-Me distance being 1.48 Å. H. J. E.

Structure of benzoquinone. Quantitative X-ray investigation. J. M. ROBERTSON (Proc. Roy. Soc., 1935, A, 150, 106—128).—The crystal is monoclinic, space-group $P2_1/a$ with 2 centro-symmetrical mols. per unit cell. The planar mols. are nearly parallel and lie almost in the (201) plane. The ring is not a regular hexagon; the C-C distance is about 1.5 Å., C=C about 1.32 Å., and C=O about 1.14 Å. The internal ring angle between single C linkings is 109° , and between double and single linkings 125° . The min. intermol. distance between O atoms is 3.62 Å. between O and C 3.36 Å., and between C and C 3.44 Å. L. L. B.

X-Ray analysis of the structure of dibenzyl. II. Fourier analysis. J. M. ROBERTSON (Proc. Roy. Soc., 1935, A, 150, 348—362; cf. A., 1934, 1297).—The experimentally determined structure factors for three zones of reflexions have been subjected to a double Fourier analysis. The results indicate that the regular three-dimensional model must be slightly modified, the planes of the C_6 rings being apparently turned 13 – 16° out of the symmetrical position. The C_6 rings are regular plane hexagon structures. The distance between aromatic C atoms is 1.41 Å., between aromatic C and aliphatic CH_2 1.47 Å., between the two CH_2 groups 1.58 Å. The angle between the linkings of the CH_2 group is 109.2 – 112° . The min. intermol. distance between aromatic and aliphatic C atoms is 4.10 Å., between aromatic C atoms 3.68 Å. L. L. B.

X-Ray investigation of the crystal structure of m -azotoluene. M. PRASAD and P. H. DALAL (Indian J. Physics, 1935, 9, 319—321).— $a : b : c = 0.8581 : 1 : 0.5469$; 4 mols. in unit cell. A. J. M.

Unidimensional change of the crystal lattice in passing from veronal to dial. E. HERTEL (Z. physikal. Chem., 1935, B, 29, 117—120).—The monoclinic crystals of dial have I_a 14.5, I_b 7.1, I_c 21 Å., β 100° , 8 mols. in unit cell, translation group Γ'_m . The monoclinic pseudorhombic crystals of veronal have I_a 14.4, I_b 7.1, I_c 9.7 Å., β 90° , 4 mols. in unit cell, translation group Γ'_m . In the change from veronal to dial the lattice alters in one direction. R. C.

X-Ray crystallography of the toad poisons, bufagin and cinobufagin, and of strophanthidin. (MISS) D. CROWFOOT (Chem. and Ind., 1935, 568—569).—Data are recorded for bufagin, +EtOH (I), cinobufagin (II), and the A (III) and B (IV) forms of strophanthidin. These confirm the accepted formula for (I), if the b axis is the α optical direction (the reversal compared with the sterol group probably being due to the *tert*.-OH) and the EtOH of crystallisation lies between the ends of the mols. Data for (II) are inconclusive, but suggest a formula $\text{C}_{26}\text{H}_{34}\text{O}_6$.

Results for (III) cannot be interpreted owing to decomp., but for (IV) confirm the formula $C_{23}H_{30}O_6$, $+0.5H_2O$. R. S. C.

X-Ray study of the hydration and denaturation of proteins. W. T. ASTBURY and R. LOMAX (J.C.S., 1935, 846—851).—X-Ray photographs of ordinary and boiled egg-white, serum-albumin, pepsin, trypsin, zein, casein, tobacco-seed and squash-seed globulin, and edestin from hemp seed, both dry and after adsorption of H_2O or $EtOH$, show inner and outer rings associated, respectively, with side-chain and backbone spacing of polypeptide chains; where spacing changes occur, due to adsorption, the side-chain spacing increases most, and the backbone spacing is almost unchanged. Denaturation by heat results in a sharpening of the backbone reflexion and the appearance of at least one other outer ring indicating a development of a common structural scheme. Results, in general, point to a scheme of crystallites built of parallel, fully-extended polypeptide chains, between which are the principal cross-linkings. N. M. B.

X-Ray diffraction pattern of native cellulose. U. YOSHIDA and C. PARK (Mem. Coll. Sci. Kyoto, 1934, A, 17, 443—447).—The unit cell is monoclinic and contains 4 $C_6H_{10}O_5$ groups. E. S. H.

Application of X-rays in the investigation of cellulose and its derivatives, with special reference to reaction mechanism. K. HESS and C. TROGUS (Ergebn. tech. Röntgenk., 1934, 4, 21—68; Chem. Zentr., 1935, i, 707—708).—A lecture. H. N. R.

Structure of liquid and solid mercury studied by cathode-ray diffraction. III. Temperature effect. H. KAKESITA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 241—248; cf. this vol., 919).—The patterns of solid and liquid Hg show a face-centred rhombohedral structure. The rings for solid Hg are 10% > those for liquid Hg. E. S. H.

Preparation of thin single crystals of silver and their investigation with electron beams. L. ROYER (Ann. Physik, 1935, [v], 23, 16—17).—The orientation of Ag single crystals formed on a rock-salt base given by Lassen and Brück (this vol., 286) is questioned. The data there given do not agree with the fact that parallel planes in the two crystal lattices should possess approx. equal parameters. A. J. M.

Preparation of thin single crystals of silver and their investigation with electron beams. H. LASSEN and L. BRÜCK (Ann. Physik, 1935, [v], 23, 18—20).—The results of Royer (preceding abstract) are based on the deposition of crystals from solution, the conditions being therefore not comparable with those obtaining in the authors' previous work (this vol., 286). The orientation there described is re-affirmed. A. J. M.

Investigation of effect of oxygen on graphite at high temperatures by means of electron diffraction. H. BOERSCH and L. MEYER (Z. physikal. Chem., 1935, B, 29, 59—64).—Measurements with C filaments coated with graphite show that in the dissolution of O in graphite at high temp. the layer lattice stretches along the c axis like a concertina (cf. A., 1932, 816). R. C.

Heat effects in the transformations of cobalt. H. VON STEINWEHR and A. SCHULZE (Z. Metallk., 1935, 27, 90—92).—From measurements made on a 20-kg. cylinder of Co containing Cu 0.24, Fe 1.6, and C 0.007% the heat evolution in the α - β transformation, which extends from 380° to 420°, has been determined as 0.1 ± 0.03 g.-cal. per g. The magnetic change occurs in the range 1070—1125° with heat evolution of 1.2 g.-cal. per g. A. R. P.

Gyromagnetic effect of some ferromagnetic compounds. D. P. R. CHAUDHURI (Indian J. Physics, 1935, 9, 383—414).—The ratio of angular momentum to magnetic moment (g -ratio) of the elementary carriers of ferromagnetism has been determined by the resonance method for Fe_3O_4 , Fe_2O_3 , NiO , Fe_2O_3 , CuO , Fe_2O_3 , MnO , Fe_2O_3 , and $2ZnO \cdot 3Fe_2O_3$. g is in each case < 2, the theoretical val. for the spinning electron, and this is probably due to the fact that the l -moment (orbital moment) also enters into ferromagnetic phenomena. A. J. M.

Chemielectric Curie point effect analogous to magnetochemical. J. A. HEDVALL and R. W. PAULY (Z. physikal. Chem., 1935, B, 29, 225—230).—A Curie temp. of 22.0—22.3° is deduced for Na K tartrate from observations on the dissolution relations in $EtOH$, which change abruptly at this temp. (cf. this vol., 153). R. C.

Influence of mechanical vibrations on the subsequent manifestations of magnetic viscosity. A. V. MITKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 25—29).—The effect of mechanical vibration favours the hypothesis that magnetic viscosity is due to an unstable magnetic state rather than to eddy current effect. A. B. D. C.

Temperature variation of conical indentation hardness of metals. I. J. ENGL and G. HEIDTKAMP (Z. Physik, 1935, 95, 30—41).—The hardness of mono- and poly-cryst. Cu was determined to 1900° using cones of synthetic corundum crystals. A. B. D. C.

Young's modulus of aluminium rod composed of large crystal grains. M. SUGIHARA (Mem. Coll. Sci., Kyoto, 1935, 17, 389—396).—Young's modulus of Al rods composed of crystal grains of various sizes has been measured by elongation and by acoustical vibration methods. Whilst the limit of elasticity decreased with size of crystal grain, the modulus remained almost const. W. R. A.

Heat evolved in metallic transformations. III. Iron. H. VON STEINWEHR and A. SCHULZE (Physikal. Z., 1935, 36, 419—423; cf. A., 1934, 725; this vol., 704).—The heat evolved in the magnetic (A2) transformation of Fe (99.97%) is 4.8 ± 0.2 g.-cal. per g. It takes place over the range 710—790°. The heat evolved in the allotropic (A3) change is 6.2 ± 0.08 g.-cal. per g. A. J. M.

Twinning in α -iron. H. O'NEILL (Nature, 1935, 135, 1076—1077).—Attention is directed to prior reports of twinning in α -Fe (cf. this vol., 811). The greater ductility of mild steel tinplate when cold-rolled and annealed over that which has been hot-rolled and normalised may be due to the more highly

twinned structure probably produced by the former process.
L. S. T.

"Recovery" of metals and recrystallisation phenomena in aluminium single crystals. N. J. SELJAKOV and E. I. SOVZ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 125—133).—The "recovery" process produces in single crystals marked changes in the intensity distribution of certain spots on the X-ray plate accompanied with an enhanced definition of the spots. The deformation of the crystals is discussed.
W. R. A.

Rotational dispersion of sound in hydrogen. A. S. ROY and M. E. ROSE (Proc. Roy. Soc., 1935, A, 149, 511—522).—No variation of the velocity of sound in H_2 is found below frequencies of the order of 10^6 cycles per sec., as predicted by the classical kinetic theory of Jeans, and by the quantum treatment of the inelastic collision between two H_2 mols.
L. L. B.

Thermo-electric power of the alkali metals in the solid and liquid state, with respect to platinum. E. HEIBER (Ann. Physik, 1935, [v], 23, 111—136).—The thermo-electric power of Li, Na, K, Rb, and Cs was determined for the solid and liquid elements (Li, solid only). Li and Cs are thermo-electrically positive, the others negative, with respect to Pt. dE/dT shows a jump at the m.p. which is greatest for Cs and Rb, but is within the limit of experimental error for Na and Li.
A. J. M.

Effect of a magnetic field on thermal conductivity and viscosity of paramagnetic gases. M. VON LAUE (Ann. Physik, 1935, [v], 23, 1—15).—Theoretical. There is no simple connexion between the effect of a magnetic field on these properties of paramagnetic gases.
A. J. M.

Influence of an electric field on the thermal conductivity of a solid. G. GROETZINGER (Nature, 1935, 135, 1001).—After solidification in an electric field bees-wax permanently shows a greater thermal conductivity in the direction of the field. Application of an alternating field of 50 cycles produces no such effect.
L. S. T.

Thermal conductivity of polyatomic gases. Erratum. A. R. UBBELOHDE (J. Chem. Physics, 1935, 3, 362; cf. this vol., 691).—A correction.
N. M. B.

Direct influence of light on the electrical resistance of metals. A. ETZRODT (Physikal. Z., 1935, 36, 433—441).—The increase in resistance of metals on illumination, reported by Majorana (A., 1932, 898, 1189; 1933, 353, 584; 1934, 114, 555) and assumed to be due to a thermal effect and an inner photo-electric effect, was investigated. It is not possible completely to separate these effects by cooling and increasing the frequency of the incident radiation, but if the temp. coeff. of the resistance is zero, thermal effects should disappear. The effect of temp. on the sp. resistance of wires composed of single crystals of Bi, and of constantan, and the temp. for which temp. coeff. is zero were determined. Parallel determinations of resistance and the Majorana effect showed that the total effect completely disappeared at temp.

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at which the temp. coeff. is zero; the Majorana effect is thus a thermal effect.
A. J. M.

Electrical conductivity of mixed metallic phases at low temperatures (Cu-Pt alloys). H. J. SEEMANN (Z. Physik, 1935, 95, 97—101).—Sp. resistances were measured for Cu-Pt alloys of 70 and 75 at.-% Pt; that at room temp. decreases on tempering at 400—550° due to formation of an ordered cubic structure. Sp. resistance-temp. curves for the 75% alloy are similar to those for Cu_3Pt , but those for the 70% alloy show anomalies probably due to ferromagnetism.
A. B. D. C.

Magnetic properties and critical currents of superconducting alloys. G. N. RJABININ and L. V. SHUBNIKOV (Nature, 1935, 135, 581—582).—Pb-Tl and Pb-Bi alloys lose their superconductivity at low temp. when the magnetic field strength is above a certain val.
W. P. R.

Magnetic susceptibility of water and the influence of dissolved salts. B. CABRERA and H. FAHLENBRACH (Anal. Fis. Quím., 1934, 32, 525—537).—The magnetic susceptibility (χ) of H_2O above 100° is const. at 0.727×10^{-3} . The variation with temp. below 100° is discussed. The variation of χ for KI solutions is due to depolymerisation of the H_2O and to the deformation of the K^+ and I^- ions under the dipolar action of the H_2O (hydration effect).
J. W. S.

Diamagnetism of heavy water in the liquid and solid states. B. CABRERA and H. FAHLENBRACH (Anal. Fis. Quím., 1934, 32, 538—542).—The general magneto-thermal behaviour of heavy water ($> 99\% D_2O$) is similar to that of ordinary H_2O , but the mol. susceptibility, its temp. coeff., and its change with change of state differ in the two cases.
J. W. S.

Cobalt, nickel, and copper complexes of the amides and imides: magneto-chemical studies. L. CAMBI and E. TREMOLADA (Gazzetta, 1935, 65, 322—338).—The structure of many complex compounds of Co^{II} , Ni^{II} , and Cu^{II} containing amide and imide groups is discussed. Magnetic susceptibility data are recorded.
O. J. W.

Diamagnetism of primary alcohols and other organic compounds. B. CABRERA and H. FAHLENBRACH (Anal. Fis. Quím., 1934, 32, 543—566).—The magnetic susceptibilities (χ) of primary alcohols of $C_{16}H_{33}OH$, C_6H_{14} , C_6H_6 , $PhNO_2$, $AcOH$, *sec.*- $BuOH$, *o*-, *m*-, and *p*-cresol, $C_6H_4Me \cdot NO_2$, and *p*- $C_6H_4Cl \cdot OH$ have been measured at various temp. in a "Uviol" glass tube. Like H_2O , alcohols show an abrupt change of χ at the m.p., and on each side of the m.p. there is a temp. range over which χ varies considerably with temp. The change in χ at the m.p. is related to the electric moment of the mol. The results are discussed with reference to Pascal's additivity theory.
J. W. S.

Magnetic properties of the phenanthroline ferric complexes. G. H. WALDEN, L. P. HAMMETT, and A. GAINES, jun. (J. Chem. Physics, 1935, 3, 364).—The at. susceptibility of the Fe atom in the blue complex $Fe(C_{12}H_8N_2)_3^{+++}$ obtained only by oxidation of the Fe^{II} complex, and in the solid brown salt,

$[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$ obtained by direct interaction of Fe^{III} salts and phenanthroline, is 2446×10^{-6} and 826×10^{-6} , respectively. The low val., 1.4 Bohr magnetons, for the magnetic moment in the latter case is attributed to the existence in the single mol. grouping of two or more Fe atoms so oriented that their moments partly neutralise each other. N. M. B.

Determination of the difference of the principal susceptibilities of some rare-earth ethyl sulphates. R. A. FEREDAY and E. C. WIERSMA (*Physica*, 1935, 2, 575—581).—The differences between the two principal susceptibilities (χ) of the hexagonal crystals of the Et sulphates of Ce, Nd, Pr, and Er have been determined. For Ce, Nd, and Er, which have an odd no. of electrons in the ion, the higher val. of χ is along the principal axis and the difference increases rapidly as the temp. falls. Pr has an even no. of electrons in the ion and, at room temp., χ is still the higher along the principal axis. The difference diminishes with fall of temp., and equality is reached at 130° abs.; at lower temp. χ along the binary axis becomes the higher. M. S. B.

Magne-crystallic action. III. Organic crystals. K. S. KRISHNAN and S. BANERJEE (*Phil. Trans.*, 1935, A, 234, 265—298; cf. A., 1933, 340).—Using a new method of measuring magnetic anisotropies adaptable to crystals < 1 mg., the principal susceptibilities of 29 org. crystals are tabulated. Mol. orientations in the crystal lattice deduced from the magne-crystallic data agree, in general, with X-ray determinations. The principal susceptibilities of 28 individual mols. are tabulated. N. M. B.

Magnetic susceptibilities of very small crystals. K. S. KRISHNAN and S. BANERJEE (*Current Sci.*, 1935, 3, 548).—The susceptibility of crystals > 0.1 mg. can be determined from their behaviour in a mixture of dia- and para-magnetic solutions. A. B. D. C.

Magnetochemical investigations. XIV. Magnetic behaviour of some heavy metal compounds of the phthalocyanines. L. KLEMM and W. KLEMM (*J. pr. Chem.*, 1935, [ii], 143, 82—89; cf. this vol., 436).—The magnetic susceptibilities of Ni, Co, Fe, Cu, Zn, Mn, and Mg phthalocyanines have been determined and compared with vals. calc. for at. and ionic linkings. At. linkings can be identified in the case of the Ni, Co, and Fe compounds. The chemical stability of the Cu and Zn compounds indicates a similar structure. Specimens of the Mn and Mg compounds were not sufficiently pure to yield decisive magnetic data, but the replacement of the metal by treatment with H_2SO_4 indicates ionic linkings. R. S.

Rotational heat of ortho-deuterium. K. CLU-SIUS and E. BARTHOLOME (*Z. physikal. Chem.*, 1935, B, 29, 162—169; cf. this vol., 573).—An apparatus for the prep. of *o*- D_2 is described. The rotational heat at 35 — 106° abs. has been measured. R. C.

Specific heat of liquid helium. W. H. KEESOM and (Miss) A. P. KEESOM (*Physica*, 1935, 2, 557—569, and *Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 490).—Sp. heat measurements of He, including measurements under the saturated v.p., have been made (cf. A., 1933, 16). The large change in sp. heat at

the λ -point occurs abruptly or in a temp. interval probably $< 0.0002^\circ$. The absence of latent heat at λ -point is confirmed, but it is difficult to determine here the exact val. of the sp. heat jump; it is probably $>$ is shown by experiment. It is suggested that the λ -transition depends on the interaction between neighbouring atoms. The heat conductivity of He also appears to change abruptly at λ -point. M. S. B.

Atomic heat of nickel from 1.1° to 19.0° abs. W. H. KEESOM and C. W. CLARK (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 490—491, and *Physica*, 1935, 2, 513—520; cf. this vol., 574).—The at. heat $>$ the heat capacity due to the at. lattice as calc. from Debye's law, is $>$ the contribution due to the interaction energy of the ferromagnetism electrons, and is probably connected with the energy of the conduction electrons. N. M. B.

Exact measurement of the specific heats of solid substances at higher temperatures. XVIII. Use of Dewar vacuum vessels in the metal block calorimeter for the control of the cooling rate. F. M. JAEGER, R. FONTEYNE, and E. ROSENBOHM. **XIX. Specific heats of zinc, magnesium, and their binary alloy MgZn_2 .** T. J. POPPEMA and F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 502—509, 510—520).—XVIII. Difficulties arising from the use of Dewar vessels and precautions necessary for their elimination are discussed.

XIX. Sp. heat data are tabulated for Zn, 100 — 360° , Mg, 100 — 550° , and MgZn_2 , 100 — 500° . Mol. heats of MgZn_2 are in fair agreement with the additive law, but divergences increase with rise of temp. N. M. B.

Low-temperature specific heats. V. Heat capacity of tricalcium phosphate between 15° and 298° abs. J. C. SOUTHARD and R. T. MILNER (*J. Amer. Chem. Soc.*, 1935, 57, 983—984; cf. A., 1934, 135).—Data are recorded for the α and β forms of $\text{Ca}_3(\text{PO}_4)_2$. E. S. H.

Purification and physical properties of organic compounds. VI. Applications and limitations of the specific heat method as a "non-comparative criterion of purity." E. L. SKAU (*J. Physical Chem.*, 1935, 39, 541—544).—Although it is probable that a given compound is pure if the val. of $(C_p)_{\text{solid}}$ increases almost linearly with rise of temp., and is $>$ that of $(C_p)_{\text{liquid}}$ at the f.p. (cf. A., 1934, 836, 1085), both true and apparent exceptions exist. The former include all the cases of impure samples where the change from the liquid to the solid state takes place completely at const. temp., e.g., a eutectic mixture. The latter are the cases in which the change from the liquid to the solid state takes place over a temp. range which lies completely above the highest temp. for which sp. heat data have been determined. M. S. B.

Heat capacity and v.p. of solid and liquid nitrous oxide. Entropy from its band spectrum. R. W. BLUE and W. F. GIAUQUE (*J. Amer. Chem. Soc.*, 1935, 57, 991—997).—The heat capacity of N_2O has been determined between 14° abs. and the b.p. Data are m.p. 182.26° abs., b.p. 184.59° abs., heat of fusion 1563 g.-cal. per mol., heat of vaporisation at b.p. 3958 g.-cal. per mol., v.p. of solid (148.48 —

182.26° abs.) $\log_{10} P = -(1286/T) + 9.13061 - 0.0014038T$, v.p. of liquid (182.26—185.85° abs.) $\log_{10} P = -(893.56/T) + 6.72158$. The calc. mol. entropy of the gas at the b.p. is 47.36 ± 0.1 e.u., which is 1.14 units < the val. calc. from spectroscopic data. The mol. entropy of N_2O at 298.1° abs. and 1 atm., based on band spectra data, is 52.581 e.u. (without nuclear spin entropy), and the abs. entropy 56.947 e.u. E. S. H.

M.p. of calcium, strontium, and barium. F. HOFFMANN and A. SCHULZE (Physikal. Z., 1935, 36, 453—458).—Ca, Sr, and Ba have m.p. 851°, 771°, and 704° ($\pm 1^\circ$), respectively. A. J. M.

Speed of sublimation and condensation. K. F. HERZFELD (J. Chem. Physics, 1935, 3, 319—323).—For the system crystal-saturated vapour, the equilibrium pressure is changed, in the case of atoms, if the electron wt. in the gaseous state differs from that in the solid state; hence for true metals the speed of sublimation is probably increased, and for non-metals a reflexion coeff. exists. For mols. the equilibrium pressure is higher than for atoms, resulting probably in an increased speed of sublimation. N. M. B.

Dissociation energy of the carbon monoxide molecule and the sublimation heat of carbon.

(A) P. GOLDFINGER and W. LASAREFF. (B) B. ROSEN (Nature, 1935, 135, 1077).—(A) The energy of dissociation of CO into normal atoms calc. from thermochemical and spectroscopic data is 11 ± 0.1 v.e. This gives 167 kg.-cal. for the sublimation heat of C.

(B) Schmid and Gero's results (this vol., 555) may provide an independent check of the above val.

L. S. T.

Thermal expansion of mono- and poly-crystalline antimony. P. HIDNERT (J. Res. Nat. Bur. Stand., 1935, 14, 523—544).—The average coeff. of linear expansion of monocryst. Sb at 0—100° is 17.2×10^{-6} along the trigonal axis and 8.0×10^{-6} at right angles to this axis. The linear expansion of polycryst. Sb indicates that there is no polymorphic transition between 20° and 560°, and differences observed for different samples are attributed to variations in the average orientation of the crystals. J. W. S.

Difference in vapour pressure between ortho and para forms of hydrogen isotopes. K. CLUSIUS (Z. physikal. Chem., 1935, B, 29, 159—161).—The v.p. of *o*- and *p*-D₂ at 20.38° are 262 and 247 mm., whilst those of *p*- and *o*-H₂ at 17.13° abs. are 262.0 and 247.1 mm., respectively. It is concluded that in the one-quantum rotational state there is superimposed on the dispersion effect, which is solely responsible for mol. attraction in the zero-quantum state, the interaction of rigid rotating multipoles. Thus the difference in v. p. between *o*- and *p*-forms is primarily due to the quadrupole moment of the mol. R. C.

Thermodynamic properties of hydrogen and deuterium. H. C. UREY (Angew. Chem., 1935, 48, 315—320).—Nobel lecture. A review and discussion of data. H. J. E.

Vapour pressure and condensation of radon at low temperatures. L. WERTENSTEIN (Proc.

Roy. Soc., 1935, A, 150, 395—410).—Results of measurements of the v.p. of radon at low temp. indicate that the condensation of Rn under usual conditions is not an equilibrium between gas and solid, but is a secondary effect, due to the presence of condensible impurities such as Hg, H₂O vapour, etc. L. L. B.

Law of Thomson and Gibbs : vapour pressure of small particles. M. VOLMER (Ann. Physik, 1935, [v], 23, 44—46, 49—50).—The method employed by Kossel in deducing the energetics of surfaces (this vol., 161) is criticised. A. J. M.

[Law of Thomson and Gibbs : vapour pressure of small particles.] W. KOSSEL (Ann. Physik, 1935, [v], 23, 47—48, 50).—A reply to the above. A. J. M.

(A) "Near" and "far" action in the thermodynamic equation of state. (B) Principle of the "dominant action" in the thermodynamic equation of state. W. JACYNA (Bull. Acad. Polonaise, 1935, A, 4—13, 14—19; cf. A., 1934, 1300).—Theoretical. H. J. E.

ψ_0 -value according to the new equation of state. W. JACYNA (Z. Physik, 1935, 95, 252).—This is calc. to be 273.22°. A. B. D. C.

Properties of real gases according to the thermodynamic equation of state. V. Compressibility of helium below the critical state in the range 4.34—2.59° abs. VI. Critical region of helium. W. JACYNA (Z. Physik, 1935, 95, 246—251, 253—261; cf. A., 1934, 1300).—The crit. coeff. for He is 3.18, and the crit. vol. 0.0151 cu. m. per kg. A. B. D. C.

Measurement of absolute viscosity coefficient by the pendulum viscosimeter method. B. V. ILIN and V. N. IVANOV (Kolloid-Z., 1935, 71, 265—267).—Vals. of η for a no. of liquids are in satisfactory agreement with those obtained with the Ostwald viscosimeter. E. S. H.

Temperature coefficient of viscosity of inorganic acid chlorides. G. P. LUTSCHINSKY (Z. anorg. Chem., 1935, 223, 210—212).— η for $POCl_3$ and $SbCl_3$ varies with temp. according to Batschinsky's formula, $\eta = C/(v - \omega)$, where v = sp. vol., and C and ω are consts. C and ω/M (M = mol. wt.) increase regularly with the at. wt. of the central atom in the chlorides of Si, P, and S, and decrease with rise of at. wt. within one group of the periodic table. J. S. A.

Viscosity measurements on alicyclic ketones and alcohols [and their acetates]. W. HUCKEL and H. W. WUNSCH (J. pr. Chem., 1935, [ii], 142, 225—231).—Data for 24 compounds over a range of temp. are given. D. R. D.

Critical state. V. Viscosity in critical state. E. SCHROER and G. BECKER (Z. physikal. Chem., 1935, 173, 178—197).—A falling-sphere viscosimeter is described permitting determination of the relative viscosity of small amounts of gas or liquid at high pressures and temp. with a precision of 0.5—1% (cf. A., 1934, 750). Measurements have been made with Et_2O in the crit. region and above at 184.5—235° under pressures, p , of 25—75 kg. per sq. cm. The

dynamic viscosity (η)- p isotherms resemble d - p isotherms, but intersect when the gas is still liquid, so that even before liquefaction the mechanism of viscosity is predominantly that of liquid viscosity, rather than of gaseous viscosity. The kinematic viscosity (ν)- p isotherms in the gaseous region fall rapidly with rising p , whilst those of liquid Et_2O run parallel to the p axis. η depends on temp. and p , although to a much smaller extent than on d ; the higher is d the larger is the (negative) temp. coeff. Measurements with CO_2 at 20° at pressures up to 101 kg. per sq. cm. give ν - p isotherms for the liquid which, unlike those of Phillips (A., 1912, ii, 832), are parallel to the p axis. R. C.

Influence of an electric field on the viscosity of liquids. S. DOBINSKI (Bull. Acad. Polonaise, 1935, A, 42—52).—The effect of an electric field on η , observed by various authors, is shown by measurements on 13 liquids (*e.g.*, CHCl_3 , PhNO_2 , C_6H_6) to be due to ionic impurities. It disappears with progressive purification, and is observed only in polar solvents. Impurities increase η in aliphatic and decrease η in aromatic solvents. H. J. E.

Inner friction of gases in a magnetic field. H. SACK (Helv. phys. Acta, 1934, 7, 639—641; Chem. Zentr., 1935, i, 675).—Data are recorded for O_2 , N_2 , and their mixtures. H. J. E.

Structure of intermetallic compounds of beryllium with copper, nickel, and iron. L. MISCH (Z. physikal. Chem., 1935, B, 29, 42—58; cf. this vol., S16).—The system Cu-Be shows the compounds CuBe and CuBe_3 , the latter being stable only in presence of excess of Be. CuBe_2 has the cubic face-centred lattice of MgCu_2 , with 24 atoms in the unit cell. The compounds NiBe, cubic body-centred, and $\text{Ni}_5\text{Be}_{21}$, apparently with a deformed γ -brass structure, are reported (cf. B., 1929, 724; A., 1929, 996). R. C.

Crystal structure and crystalline configuration of the normal and modified Si-Al alloys. H. KORÔ (Mem. Coll. Sci. Kyoto, 1935, A, 18, 17—33).—The modification of Si-Al alloys by the addition of Na and substances of similar properties has been investigated. Examination of the micro-structures of the normal and modified alloys shows that Na, K, and Li are very effective as modifying agents, the next most effective being Mg and Ca. The theory that modification is brought about by volatile elements is disproved by the fact that P, S, Se, Te, and As give no appreciable effect. Bi and Sb, which are immiscible with both Si and Al, produce no modification. Hence the ternary constituents theory which attributes modification to the separation of the agent from the Si-Al alloy on cooling cannot be correct. Thermal analysis of the normal and modified alloys indicates that supercooling is more marked with the former than the latter. X-Ray examination of the alloys shows that the actual cryst. structure does not always agree with that deduced from photomicrographs. Although Na and Li both modify Si-Al alloys, X-ray analysis shows that Na is not miscible with Si and Al, but that Li forms solid solutions and compounds with these elements. A. J. M.

Systematic studies in combination. LXIV. Combining power of platinum and phosphorus. W. BILTZ, F. WEIBKE, and E. MAY [with K. MEISEL] (Z. anorg. Chem., 1935, 223, 129—143).—The phase diagram confirms the existence of PtP_2 . There is also a *subphosphide*, Pt_{20}P_7 . Its existence is confirmed by X-ray examination and it is the compound responsible for the destruction of Pt apparatus by heating in contact with P compounds, since the eutectic mixture of Pt with Pt_{20}P_7 , containing 3.8 at.-% P, melts at 588° . M. S. B.

Crystallisation of binary eutectic systems. E. RAUB (Z. Metallk., 1935, 27, 77—83).—The grain structure of a cast eutectic alloy resembles that of a pure metal, the type and size of the grains being determined chiefly by those of the predominating constituent, other conditions being equal. The structure has little effect on the mechanical properties when there are great differences between the workability of the constituents, but has a determining effect when both constituents have similar mechanical properties, the eutectic in this case behaving like a pure metal and the distribution of the phases having little effect on the properties. In cold-working and recrystallisation on annealing the structure is deformed and re-formed in a similar manner to that of a metal and solid solution alloys, the recrystallisation grains being formed about the predominating constituent in such a way that the annealed sheet shows characteristic anisotropic phenomena which are ascribed to the setting up of an ordered recrystallisation position of that constituent. These phenomena are illustrated by photomicrographs and tables showing the properties of the Ag-Cu eutectic after various thermal and mechanical treatments. A. R. P.

Constitution of magnesium-zinc-silicon alloys rich in magnesium. E. ELCHARDUS and P. LAFITTE (Compt. rend., 1935, 200, 1938—1940; cf. A., 1934, 22).—The unstable compound Mg_4Si (m.p. 932°) forms a labile system (Mg - MgZn_2 - Mg_4Si) which gives a ternary eutectic (m.p. 314° ; Mg 51.85, Zn 47.7, Si 0.45%). In the binary system Mg-Si, Mg_4Si forms a eutectic (m.p. 575° ; 2.7% Si). H. J. E.

Iron-nickel-copper alloys of high initial permeability. O. VON AUWERS and H. NEUMANN (Wiss. Veroff. Siemens-Werken, 1935, 14, 93—108).—Examination has shown a zone of high initial magnetic permeability comprised by the region Ni 80, Fe 20% to Ni 40, Cu 50, Fe 10%. Over the greater part of this region the sign of magnetostriction is reversed. E. S. H.

System cobalt-iron-titanium. W. KOSTER and W. GELLER (Arch. Eisenhüttenw., 1934—1935, 8, 471—472).—The system up to 22% Ti has been examined by micrographic and pptn.-hardening methods. The two compounds Co_3Ti and Fe_3Ti form a continuous series of solid solutions (I) and the solubility of these compounds in the α - and γ -Fe-Co phases decreases with fall in temp. to a val. corresponding with 2% Ti at room temp. The eutectic equilibrium liquid $\alpha + \text{Fe}_3\text{Ti}$ in the Fe-Ti system and the peritectic reaction liquid $\alpha + \gamma$ in the Fe-Co system are displaced to lower temp. by the addition

of Co and Ti, respectively, and merge at 1150° into a plane of 4-phase equilibrium: liquid + α -solid solution (I) -solid solution. From this plane as the temp. falls there extends a field of 3-phase equilibrium: liquid $\rightleftharpoons \gamma + (I)$, which terminates in the Co-Ti eutectic. A. R. P.

Equilibrium diagram for quaternary alloys. V. FISCHER (Z. Metallk., 1935, 27, 88—89).—A method of representing the equilibria on a plane orthogonal co-ordinate system is illustrated graphically with reference to the Mn-Cu-Fe-Ni system. A. R. P.

Viscosity of mixtures of hexane and nitrobenzene in the neighbourhood of the critical point of dissolution. (MLLE.) Z. SZAFRAŃSKA (Bull. Acad. Polonaise, 1935, A, 110—119; cf. Drapier, A., 1911, ii, 968).—Anomalies in the viscosity-concn. curves for C₆H₁₄-PhNO₂ mixtures are observed only in concn. regions where opalescence is observed. The irregularities observed by Drapier are attributed to turbulent motion. J. W. S.

Internal friction of fused metals and alloys. VI. Internal friction of Pb, Cd, Zn, Ag, Sn, K, Na; structure viscosity of amalgams. K. GERING and F. SAUERWALD (Z. anorg. Chem., 1935, 223, 204—208).—A pressure viscosimeter for determining η for molten metals is described. The dependence of η on pressure in the case of amalgams at low pressure (Köhler, A., 1933, 895) has been confirmed, and also observed in pure Hg at very low pressures. In the case of amalgams the effect is explained by the existence of small crystals in suspension, whilst the effect in Hg is due to the large role played by surface tension and similar phenomena when the pressure is very low. M. S. B.

Calorimetric analysis of a binary mixture. R. N. M. A. MALOTAUX (Chem. Weekblad, 1932, 32, 348; cf. A., 1933, 465; 1934, 951; B., 1934, 354). S. C.

Magnetic measurements on molecular compounds in solution with a modified form of Decker's balance. S. S. BHATNAGAR, M. B. NEVGI, and G. TULI (Indian J. Physics, 1935, 9, 311—317).—The stability of mol. compounds in solution has been investigated by determining the diamagnetic susceptibility (χ) of the picrates of anthracene, C₁₀H₈, 1-C₁₀H₇-Me, and phenanthrene in the solid state and in solution in C₆H₆. In the latter case, χ does not vary appreciably with concn., but is < the val. for the solid substances, being nearer that given by the mixture law, thus indicating dissociation in solution. A. J. M.

Simultaneous formation of double and triple complexes in dipole association. I. SAKURADA (Z. physikal. Chem., 1935, B, 29, 104—111; cf. A., 1934, 475).—Assuming that in dipole association dipole-free double and triple complexes are formed simultaneously and that the mass law is valid, a method of calculating the equilibrium const. of the two kinds of association from dielectric data is described. The formation of such complexes in various binary mixtures is deduced. From the temp. coeff. of the association const. the heat of association

is calc. Hertel and Dumont's criticism (this vol., 430) is discussed. R. C.

Calculation of molar polarisation of solutes at infinite dilution with Hedestrand's formula. M. M. OTTO (J. Amer. Chem. Soc., 1935, 57, 1147).—The formula is applicable even to certain substances for which the dielectric const. and d are not linear functions of concn. E. S. H.

Relation between molecular polarisation in solution and the dielectric constant of the solvent. R. J. W. LE FÈVRE (J.C.S., 1935, 773—776).—Vals. of d^{25} and of the dielectric const., ϵ , at 25° for NH₂Ph, NHPMe, NPhMe₂, quinoline, isoquinoline, and C₂H₅N are recorded. The expression ${}_0P_1/{}_0P_2 = K(\epsilon_2 + 2)/(\epsilon_1 + 2)$, in which ${}_0P_1$ and ${}_0P_2$ are the orientation polarisations of a solute mol. in two media of dielectric const. ϵ_1 and ϵ_2 respectively, has been applied to: (a) pairs of solutions, (b) solutions and the corresponding solutes in the vapour states, and (c) solutions and the (liquid) solutes in bulk. In case (a), published data for polar and non-polar solvents afford vals. of K between 0.92 and 1.09 (cf. this vol., 240), in case (b), K lies between 1.17 and 1.36, and in case (c), K is generally between 1 and 1.7, but H₂O and EtOH afford vals. between 3.3 and 4.3. The theoretical basis of the expression is discussed and leads to $K=1$. J. G. A. G.

Conductivity and density in the system fused KCl-MgCl₂. S. KARPATSCHEV, A. STROMBERG, and O. POLTORATZKAJA (J. Gen. Chem. Russ., 1935, 5, 189—196).—The relations indicate the compound 2KCl.MgCl₂. R. T.

Vapour pressures and activities of completely and incompletely miscible binary and ternary alloys with one and two volatile components. K. JELLINEK and H. A. WANNOW (Z. Elektrochem., 1935, 41, 346—362; cf. this vol., 168).—V.p. for the following liquid alloys have been measured and the activities of the respective volatile components calc.: Sn-Zn, Sn-Cd, Sb-Zn, Pb-Zn, Cd-Zn, Sn-Sb-Zn, Sn-Pb-Zn, Sn-Cd-Zn. F. L. U.

Distillation of azeotropic mixtures. W. SWIENTOSLAWSKI (J. Chim. phys., 1935, 32, 293—299).—The b.p. of a mixture of two binary homoazeotropes, AC and BC , e.g., C₆H₆-EtOH and PhMe-EtOH, is always < that of the azeotropic agent C , and lies between the b.p. of AC and BC . With insufficient C , the proportion of AC and BC distilling depends on $[C]$ as well as on $[A]$ and $[B]$. The difference between the b.p. of the homoazeotropes is < that between the b.p. of A and B . Small quantities of C₆H₆ and PhMe can be removed from xylene by distilling with the appropriate quantity of MeOH. A method has been devised for determining whether four substances forming two ternary azeotropes also form a quaternary azeotrope. A mixture of the ternary azeotropes C₆H₆-EtOH-H₂O (I), b.p. 64.676°, and PhMe-EtOH-H₂O behaves as a binary mixture of two chemical individuals. The mixture of azeotropes (I) and C₆H₆-PrⁿOH-H₂O, b.p. 66.141°, does not form a quaternary azeotrope although it shows a positive deviation from Raoult's law. The degree

of dehydration achieved by azeotropic agents depends on the nature of the substances involved.

J. G. A. G.

Polymorphism in FeS-S solid solutions. I. Thermal study. H. S. ROBERTS (J. Amer. Chem. Soc., 1935, 57, 1034—1038).—The solid solutions extending from FeS to approx. $\text{FeS}_{1.14}$ appear in 6 different forms between room temp. and 575°. A reversible transformation occurs between 315° and 318°, and there is evidence that the form *b*, stable just above 318°, is not the form *a*, which is synthesised at 550—575°. In the compound FeS the form *c*, stable just below 315°, is transformed between 144° and 139° into a form *d*, which appears to be the stable form of all the solid solutions at room temp. This transformation temp. falls with increasing S content. From FeS to approx. $\text{FeS}_{1.05}$ the transformation is between *d* and *c*; at the latter point an intermediate form *e* appears, and beyond approx. $\text{FeS}_{1.07}$ the transformation is between *d* and *f*. The transformation temp. *c* \rightarrow *e* and *e* \rightarrow *f* are raised by increasing S content, reaching the limit of solid solution a few degrees below the *b* \rightarrow *c* transformation.

E. S. H.

(A) Position of the region of non-miscibility of binary systems in the surface tension-concentration diagrams. (B) Physico-chemical nature of binary liquid mixtures at the lower critical temperature. R. V. MERTZLIN (J. Gen. Chem. Russ., 1935, 5, 155—160, 161—163).—(A) The anomaly at the upper crit. temp. is ascribed to increase in the activity of capillary-active solutes with falling temp., in conjunction with a low temp. coeff. of solubility.

(B) Systems at the lower crit. temp. are of the irrational type; the principle of corresponding states is applicable to them.

R. T.

Influence of a current of hot water on air and radon dissolved in cold water. M. GESLIN (Compt. rend., 1935, 200, 2204—2206).—Dissolved gases are partly extracted from cold H_2O by the passage of a stream of hot H_2O containing CO_2 .

H. J. E.

Anomalous diffusion in true solution. H. FREUNDLICH and D. KRÜGER (Trans. Faraday Soc., 1935, 31, 906—913).—Concn. gradients may cause diffusion of uniformly distributed substance, owing to mutual change in solubility of the solutes. A thin layer of liquid on the border of the solution may therefore become less dense than the solution above it and lead to convection currents which disturb normal diffusion. It is found that diffusion anomalies disappear when the upper layer is sufficiently lighter than the lower.

J. W. S.

Variation of the permeability of palladium to hydrogen just below 200°. V. LOMBARD and C. EICHNER (Compt. rend., 1935, 200, 1846—1848; cf. A., 1934, 1302).—A rapid increase in permeability is observed at approx. 180°.

H. J. E.

Nitrates of lanthanum, and their solubilities in water. J. N. FRIEND (J.C.S., 1935, 824—826).— $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ exists in two forms, and the transition point is 43° approx. Solubilities have been determined between 0° and the m.p. of the β -form, 65.4°.

J. G. A. G.

Solubility of sodium bromide in acetone. L. E. SWEARINGEN and R. T. FLORENCE (J. Physical Chem., 1935, 39, 701—707).—The solubility of NaBr in COMe_2 is markedly increased by the presence of LiClO_4 or $\text{Ca}(\text{ClO}_4)_2$, and is much > that predicted by the interionic attraction theory of Debye and Huckel.

F. L. U.

Titration of *p*-hydroxybenzoic acid. A. OSOL and M. KILPATRICK (J. Amer. Chem. Soc., 1935, 57, 1053).—Revised vals. for the solubility of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ are given (A., 1934, 29), based on an improved method of titration.

E. S. H.

Solubility of gold in ferric sulphate and its geological applications. R. L. MILNER (Proc. Nova Scotian Inst. Sci., 1934, 18, 267—271).—Au is slightly sol. in $\text{Fe}_2(\text{SO}_4)_3$ solution and readily sol. in the presence of H_2SO_4 .

C. W. G.

Solubility of lead in mercury. H. E. THOMPSON, jun. (J. Physical Chem., 1935, 39, 655—664).—The solubility of Pb in Hg has been determined over the range 20—70°. The at. fraction of Pb in the saturated solution at T° abs. is given by $0.5893 - 0.004115T + 0.000007354T^2$.

F. L. U.

Solubility of sodium in aluminium. E. SCHEUER (Z. Metallk., 1935, 27, 83—85).—The solubility of Na in Al (Si 0.1, Fe 0.2%) rises linearly from 0.10 to 0.12% between 700° and 800°, whereas that in silumin rises from 0.08% at 600° to 0.13% at 750°, then decreases to 0.11% at 800°. In the 5% Mg-Al alloy it is 0.17% at 700° and 0.21% at 800°, and in the 8% Cu-Al alloy 0.15% at 700° and 0.18% at 800°. The presence of Fe and Si has no effect on the solubility. In the solid alloys the Na appears as a new phase; no evidence of solid solubility of Na in Al could be obtained.

A. R. P.

Solubility of potassium fluorotantalate in aqueous hydrogen fluoride. A. V. BABAIEVA and T. A. ARTSCHAKOVA (J. Gen. Chem. Russ., 1935, 5, 220—223).—The solubility of K_2TaF_7 increases with increasing [HF], to a greater extent at higher than at lower temp.

R. T.

Solubility of sucrose and lime in their concentrated solution at 30°. K. SUZUKI (J. Soc. Chem. Ind. Japan, 1935, 38, 177—178B).—Data are given for the solubility of sucrose + CaO in H_2O , and in presence of Na phosphate.

J. S. A.

(A) Solubility of sodium sulphate in aqueous ammonium carbonate at 32.5°. (B) Mutual system $\text{Na}_2\text{SO}_4\text{--NH}_4\text{HCO}_3\text{--H}_2\text{O}$ at low temperatures. A. P. BELOPOLSKI (J. Appl. Chem. Russ., 1935, 8, 193—194, 195—211).—(A) [with V. V. URUSOV]. The solid phase is Na_2SO_4 at $[(\text{NH}_4)_2\text{CO}_3] < 33.6$ g. per 100 g. of H_2O .

(B) [with S. J. SCHPUNT]. Equilibrium data at -5° and -10° are recorded.

R. T.

Mutual solubility of aluminium, sodium, potassium, and iron nitrates in water in presence of nitric acid. I. A. J. SASLAVSKY, J. L. ETTINGER, and E. A. ESEROVA (Z. anorg. Chem., 1935, 223, 277—287).—Isotherms in the system $\text{Al}(\text{NO}_3)_3\text{--KNO}_3\text{--NaNO}_3\text{--H}_2\text{O}$ and its partial ternary systems have been studied at 0°, 20°, 40°, and 60°.

Solid phases are KNO_3 , NaNO_3 , and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, with no formation of double compounds or mixed crystals. J. S. A.

Relation between separate and common solubility of the components of a ternary system. E. I. AKUMOV (J. Gen. Chem. Russ., 1935, 5, 131—142).—Relationships between the solubility of the individual components of a ternary system, separately and together, have been derived. R. T.

(A) Theory of L_p [solubility product]. (B) Influence of hydrolysis on solubility. N. A. TANANAEV (J. Appl. Chem. Russ., 1935, 8, 346—351, 352—355).—(A) For any sparingly sol. salt, $M_m A_n$, $L_i = (L_p/m^n n^n)^{1/(m+n)}$, where L_i is the ionic solubility, and L_p the product of the concns. of the ions.

(B) The concn. of M' in solutions of the sparingly sol. salt MA is given by $[M'] = \sqrt{[L_i/(1-\alpha)]}$, where α is the fraction of salt hydrolysed. R. T.

Influence of salt or acid hydrophilic colloids on the solubility of sparingly soluble acids and bases. II. Gelatin. H. BRINTZINGER and A. SCHALL (Kolloid-Z., 1935, 71, 302—307; cf. A., 1934, 1066).—The influence of gelatin (I) and acid on the solubility of salicylic, benzoic, and anthranilic acids, *o*-, *m*-, and *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, and strychnine has been determined. In all cases an increase of solubility is observed; this is traced to the presence of CO_2H and NH_2 in the mol. of (I). The different results obtained with gum arabic are explained by the absence of NH_2 . E. S. H.

Solubility of sparingly soluble substances in colloid solutions. H. BRINTZINGER and A. SCHALL (Kolloid-Z., 1935, 71, 300—302).—A discussion of the factors involved. E. S. H.

Distribution of (A) phenylacetic acid between two contiguous liquid phases, (B) chloroacetic acids between water and halides of saturated hydrocarbons, (C) malonic and ethylenelactic acid between water and saturated monobasic aliphatic alcohols. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1935, 5, 60—62, 63—68, 69—72).—(A) [with A. BEKTUROV]. Data are given for $\text{CH}_2\text{Ph} \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$, $-\text{PhMe}$, $-\text{PhNO}_2$, and $-\text{iso-C}_5\text{H}_{11} \cdot \text{OH}$, at 25° .

(B) [with F. S. KULIKOV]. Data are given for $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$ - and $\text{CHCl}_2 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O} \cdot \text{CCl}_4$, $-\text{EtBr}$, and $-\text{MeI}$, and for $\text{CCl}_3 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O} \cdot \text{MeI}$, at 25° .

(C) [with A. BEKTUROV]. Data are recorded for $\text{CH}_2(\text{CO}_2\text{H})_2 \cdot \text{H}_2\text{O} \cdot \text{Bu}^\text{t}\text{OH}$, $-n$ - and $-\text{iso-C}_5\text{H}_{11} \cdot \text{OH}$, and for ethylenelactic acid $-\text{H}_2\text{O} \cdot \text{iso-C}_5\text{H}_{11} \cdot \text{OH}$, at 25° . R. T.

Passage of helium through compact solids. (LORD) RAYLEIGH (Nature, 1935, 135, 993).—He passes through vitreous B_2O_3 but not vitreous borax at room temp. Single crystals of various substances are impervious to He at room temp. The provisional positive result reported for a crystal of beryl (this vol., 159) is withdrawn. L. S. T.

Adsorption. A. GANGULI (Kolloid-Z., 1935, 71, 275—279).—A discussion of published work. E. S. H.

Adsorption of alkali metals on metal surfaces. IV. Adsorption of atoms next to ions. V. In-

fluence of temperature on the normal photo-electric effect. J. H. DE BOER and C. F. VEENEMANS (Physica, 1935, 2, 521—528, 539).—IV (cf. A., 1934, 1066; this vol., 27). The metal is adsorbed as ions only until a certain val. of the covering fraction θ is reached. Above this val. adsorption takes place in the form of atoms. The arrangement of adsorbed atoms is such that photo-electric emission is diminished. At still higher vals. of θ the emission is increased, hence the at. dipoles are reversed in the later stages. The possible position of the atoms in relation to the ions, and the direction and magnitude of the dipoles are discussed. A more exact calculation is made of the val. of θ at which at. adsorption sets in for Cs on W.

V. At low vals. of θ for adsorbed ions photo-electric emission increases exponentially with θ in white light. At higher vals., for adsorbed atoms, emission increases more slowly and reaches a max. Rise of temp. increases the dipole moment of adsorbed ions and diminishes the induced dipole of adsorbed atoms; the emission changes in the corresponding direction in each case. This is demonstrated by the behaviour of Na on W. The effect is reproducible, but in the first heating a surface migration effect is observed. M. S. B.

Adsorption of vapours of ketones and esters by activated charcoal. J. N. PEARCE and A. C. HANSON (J. Physical Chem., 1935, 39, 679—691; cf. A., 1934, 593).—The adsorption of vapours of three ketones and four esters by activated C, measured at several temp. between 0° and 182° , conforms to Langmuir's equation for adsorption at plane surfaces for pressures > 200 mm. For both series of compounds the amount of vapour adsorbed at pressures > 0.8 mm. increases with increase of the b.p. or of the van der Waals const. a . At higher pressures the order is reversed. Dipole moment is without influence. F. L. U.

Essential structural discontinuities in certain adsorbed films. J. K. ROBERTS (Nature, 1935, 135, 1037).—The adsorption of diat. gas mols. on solid surfaces is discussed. The adsorbed films are not continuous: certain single atoms remain bare and may show catalytic activity. Confirmatory experimental evidence of these views in the case of O_2 on W has been obtained. L. S. T.

Alteration of the adsorption of dyes on nickel wires on transition of the wire from the hard to the soft state. G. TAMMANN (Z. anorg. Chem., 1935, 223, 222—224).—A rapid decrease in the adsorptive power of Ni wires for dyes (cf. A., 1934, 956) occurs over the same temp. range (500 — 600°) as the recovery of cold-worked Ni, the magnetic crit. temp., and the first perceptible recrystallisation, with which the effect is correlated. J. S. A.

Surface behaviour of zeolites. V. R. DAMERELL and R. CADLE (J. Physical Chem., 1935, 39, 693—694; cf. A., 1932, 680).—Experiments on the dehydration of scolecite and analcite indicate that H_2O is lost only from the surface portions of the zeolite lattice. F. L. U.

Active oxides. XC. Enhanced sorptive power of nascent zinc chromite. J. HAMPEL (Z. anorg. Chem., 1935, 223, 297—304).—The sorptive power towards Congo-red, acid fuchsin, and eosin of equimol. mixtures of ZnO and Cr₂O₃, heated at different temp., is much > that of either component, and passes through a max. in the neighbourhood of the max. in catalytic properties and magnetic susceptibility. The low sorptive power of cryst. ZnCr₂O₄ increases at high temp., probably due to volatilisation of ZnO from the surface. J. S. A.

Liberation of bromine and iodine from adsorption on active charcoal. V. A. PIANKOV (J. Appl. Chem. Russ., 1935, 8, 238—245).—Active C may adsorb 40% of its wt. of I from EtOH, and 65% from aq. solution. Most of the I is recovered by heating at 300°, but the last traces are obtainable only by burning the C. The desorption curves present certain differences according to whether the I was adsorbed from aq. or EtOH solution. C adsorbs ~ 25% of its wt. of Br from aq. solutions; 50—60% is liberated at 100°, and the remainder at 400°. HBr behaves similarly to Br in the above respects. R. T.

Heat of adsorption of vapours from a current of air by active charcoal at 24°. P. K. MIGAL (J. Gen. Chem. Russ., 1935, 5, 197—210).—The heat (*q*)—time curves, after a short induction period, are rectilinear for MeCl, CHCl₃, CCl₄, MeI, CS₂, and MeOH corresponding with $q = kcv(t - t_0)$, where *c* is the concn. of vapour, *v* its rate of flow, and *t*₀ is the time at the end of the induction period. R. T.

Porosity of charcoal. A. KING (Trans. Faraday Soc., 1935, 31, 935—937).—It is suggested that the porosity of a charcoal depends partly on the extent of inhibition of crystal growth during its prep., and that charcoals (e.g., sugar) which evolve only small amounts of gas after they are solidified are less porous and less active than wood charcoals where transformation occurs in the solid state throughout. Molasses charcoal is much more active than sugar charcoal, in accord with this theory. Activation of charcoal probably consists essentially in the removal by oxidation of hydrocarbons from the surface, yielding free valencies, as well as increasing the surface area of the charcoal. J. W. S.

Sorption of propyl and butyl alcohols by silica gel. A. FOSTER (Proc. Roy. Soc., 1935, A, 150, 77—83).—The isothermals for the adsorption of PrⁿOH, PrⁱOH, and BuⁿOH by SiO₂ gel at 25° are similar to those for MeOH and EtOH (A., 1934, 1169). A small hysteresis area is found just before saturation, the extent of which shows little variation. The relative pressure at which the hysteresis occurs diminishes from MeOH to BuOH, but the capillary radius calc. from these pressures by means of the Kelvin equation remains const. at about 15 Å. L. L. B.

Spectro-photometric study of the adsorption of copper in ammoniacal solutions by precipitated ferric hydroxide. (MME.) L. S. MATHIEU-LEVY (Compt. rend., 1935, 200, 1934—1936; cf. this vol., 819).—Data are recorded for the variation of the extinction coeff. with [NH₃] and with the Cu adsorbed.

Cu is adsorbed both as [Cu(NH₃)₄]⁺⁺ and as colloidal Cu(OH)₂. H. J. E.

Change in the capacity for [ionic] exchange of colloidal clay. II. A. L. S. BAR and H. J. C. TENDELOO (Rec. trav. chim., 1935, 54, 566—569; cf. this vol., 32).—The capacity for ionic exchange of 4 colloidal clays agrees with the formula of Verwey, $dy/d \log c = \text{const.}$, where *y* = adsorbed OH' and *c* = [OH']. The precise mechanism of the exchange is uncertain. R. S. B.

Heat of wetting. I. Influence of adsorbed ions. A. DUMANSKI and M. TSCHAPEK (Kolloid-Z., 1935, 71, 279—282).—The influence of adsorbed Fe⁺⁺⁺, Ca⁺⁺, Mg⁺⁺, NH₄⁺, K⁺, Na⁺, and H⁺ on the heat of wetting of activated C, SiO₂ gel, and permutite by H₂O has been determined. Part of the apparent heat of wetting is due to heat of hydration of the ions. The ratio of heat of hydration to heat of wetting is the greater, the more hydrophobic is the adsorbent. The influence of a given cation on heat of wetting varies with the adsorbent. E. S. H.

Determination of surface of powders in the light of heat of wetting; apparatus for determination of heat of wetting of polished metal surfaces by oil. H. HERBST (Kolloid-Z., 1935, 71, 282—290).—Sources of error in the determination of the surface of a powdered metal by means of adsorption measurements are pointed out. Such errors invalidate measurements of heat of wetting of metal powders by oil as a guide to lubricating efficiency. An apparatus for the direct determination of heat of wetting, using a polished metal surface of known area, is described. E. S. H.

Wetting power of metals of low m.p. for metals of high m.p. G. TAMMANN and A. RUHENBECK (Z. anorg. Chem., 1935, 223, 192—196).—It is shown that, of two metals miscible in the solid state, the more easily fusible one in the molten state will wet the other (solid) metal at temp. above that at which a change of structure takes place in the latter. This is illustrated by the behaviour of Sn, Pb, and Bi towards electrolytic Fe, Ni, W, Mo, Ta, and Cu, and also of Ag towards electrolytic Fe. Wetting by a fused drop is usually preceded by dome formation (cf. A., 1930, 1365). M. S. B.

Surface tensions and partial vapour pressures of aqueous aniline solutions. J. C. SPEAKMAN (J.C.S., 1935, 776—779).—The data refer to 0—0.356*M* solutions at 20°, and correspond with an area per mol. of 23.4 (±0.3) sq. Å. This is consistent with the formation of a unimol. film composed entirely of NH₂Ph mols. at the surface. J. G. A. G.

Surface tension of system sulphuric acid-water. L. SABININA and L. TERPUGOV (Z. physikal. Chem., 1935, 173, 237—241).—Measurements have been made at 10—50°. The temp. coeff. of the surface tension is a min. and the deviation from additivity at all temp. reaches a max. at H₂SO₄.2H₂O. There is no indication of the existence of any other compound. R. C.

Dimensions of the sodium palmitate molecule from a study of surface tensions in dilute aqueous solutions. E. R. WASHBURN and G. W. BERRY

(J. Amer. Chem. Soc., 1935, **57**, 975—977).—The equilibrium surface tension—concn. curve for aq. Na palmitate has been determined by the capillary-rise method. The dimensions of the Na palmitate mol. calc. from the min. of this curve are 23×10^{-8} cm. \times 62×10^{-8} cm. \times 3.7×10^{-8} cm. E. S. H.

Films built by depositing successive uni-molecular layers on a solid surface. K. B. BLODGETT (J. Amer. Chem. Soc., 1935, **57**, 1007—1021).—The building of films of palmitic, stearic, and arachidic acids and their Ca, Mg, Sr, Ba, Pb, and Zn soaps on surfaces of glass, Cr, Ni, brass, steel, cast Fe, Ag, and Pt, by transferring unimol. layers from a H_2O surface, is described. Two different types of layers of Ca stearate were observed, depending on the p_H and temp. of the H_2O from which the films were transferred. Films built in steps of odd-numbered layers showed interference colours when viewed in white light; a single layer could be seen on polished Cr by means of polarised light. The thickness of step-films was measured by the interference of reflected monochromatic light; n was determined from the polarising angle, measured by a new method. The results show the thickness to be slightly $>$ the long spacings of the corresponding fatty acids as determined by the X-ray method. The m.p. of Ba stearate films show that those taken from H_2O of p_H 8.5 probably consist of neutral stearate, whilst those taken from H_2O of p_H 6.9 are acid stearate.

E. S. H.

Theory of flotation. I. W. WARK (Z. physikal. Chem., 1935, **173**, 265—283).—Polemical against Ostwald (A., 1934, 958).

R. C.

Dielectric potentials at the solution-air interface. B. KAMIENSKI (Bull. Acad. Polonaise, 1935, A, 129—136).—A dynamical jet method is described, particularly suitable for measuring the dielectric potentials at the solution-air interface of solutions of very active substances. The potential for 0.01M-quinine hydrochloride changes from 0.055 volt at p_H 2.2 to 0.464 volt at p_H 7, the curve showing inflexions at p_H 4.15, 5.6, and 6.8. 0.001M-Quinine hydrochloride has a potential of 0.175 volt at the p_H of blood.

J. W. S.

Arrangement for studying the conditions within diffusion layers. T. TEORELL (Science, 1935, **81**, 491).—Experiments with a "multi-membrane" arrangement of Cellophane or collodion sheets show that the relation of the ionic concns. is qualitatively, at least, in accord with the Planck-Plettig predictions. The method has also been applied to diffusion systems associated with chemical reaction.

L. S. T.

Metal membranes. N. V. KULTASHEV and F. A. SANTALOV (Z. anorg. Chem., 1935, **223**, 177—184).—Cu membranes have been prepared by heating a Cu-Zn alloy until the Zn has volatilised. Such membranes are permeable to Cl^- , SO_4^{2-} , and $CO(NH_2)_2$, but not to glucose. The permeability is greatly increased by the action of 25% aq. HNO_3 . H_2O can be forced through at a pressure of 1 atm. For cells in which the electrode solutions were separated by a Cu membrane, evidence of the existence of a

membrane potential could be obtained. A Ag membrane, similarly prepared, showed similar properties. Having a larger pore vol. it was permeable to glucose also, but not to methylene-blue.

M. S. B.

Condition of substances dissociated in concentrated sulphuric acid. C. R. DE ROBLES and E. MOLES (Anal. Fis. Quim., 1934, **32**, 474—493).—The cryoscopic const. of H_2SO_4 , m.p. 10.52° , determined by measurements with solutions of $PhNO_2$, picric acid, $CCl_3 \cdot CO_2H$, and trinitrotoluene, is 65.4. $HClO_4$ yields normal results. When an excess of SO_3 is present I forms a compound I_2SO_3 . HNO_3 yields HSO_4NO , H_2O and O, the observed mol. wt. being 23. With S_2Cl_2 low vals. (105) are obtained, and decomp. occurs. Tetralite (2:4:6-trinitrophenylmethylnitroamine) forms a salt which yields 3 ions.

H. F. G.

Association of water and deuterium oxide in dioxan solution. R. P. BELL and J. H. WOLFENDEN (J.C.S., 1935, 822—824).—The f.p. of 0.1—1.8M- H_2O , $-D_2O$, and $-PhCl$ in dioxan show that H_2O and D_2O depart considerably from the laws of ideal solutions. The vals. of the osmotic coeffs. are consistent with Fuoss' treatment of dipole interaction (A., 1934, 728), and the assumption of a small difference of effective radius due to difference of zero-point energy accounts for the association factor for D_2O being approx. 3% $>$ for H_2O at the same mol. concn.

J. G. A. G.

F.-p. depression and constitution. W. HUCKEL, K. KUMETAT, and H. SEVERIN (Annalen, 1935, **518**, 184—203).—Determination of the cryoscopic const. of cyclohexane (I), C_6H_6 , $C_2H_4Br_2$, and $CHBr_3$ for a variety of solutes shows that it often deviates considerably from the theoretical val. and also frequently varies with concn. Such variation is not observed (with any one solute) in all solvents, and the above anomalies are due mainly to the formation of solid solutions and different partition vals. between the liquid and solid phases. In (I) the *trans*-forms of dicyclic ring systems give higher vals. for cryoscopic const. than do the *cis*-forms, but *trans*-decahydronaphthalene gives an almost normal (const.) val. The implications of these results are discussed, so-called "association" anomalies being due frequently not to dipole association but to solid solution formation. Abnormal vals. of cryoscopic const. may also arise from vol. changes on dissolution.

J. W. B.

Molecular arrangement and X-ray diffraction in ionic solutions. Errata. J. A. PRINS (J. Chem. Physics, 1935, **3**, 362; cf. this vol., 443).—A correction.

N. M. B.

X-Ray evidence on the ionic arrangement in thorium nitrate solutions. J. A. PRINS and R. FONTEYNE (Physica, 1935, **2**, 570—572).—Measurements have been made of the diffraction halo of aq. $Th(NO_3)_4$ of different concn. The results may be accounted for by assuming that each Th^{4+} is heavily hydrated so as to form a close-packed arrangement, NO_3^- finding a place somewhere between.

M. S. B.

Variation with concentration of equivalent refraction of some salts and acids in aqueous solu-

tion. R. LUHDEMANN (Z. physikal. Chem., 1935, B, 29, 133—149).—The variation of apparent equiv. refraction, R , with concn., c , in g.-equiv. per 1000 g. H_2O has been examined at 25° at concns. from N to saturation at 10° . For HI R falls with rising c more rapidly than for any strong electrolyte hitherto examined. With HCO_2Na R is const. for $c=1-2.5$. For HIO_3 and $LiIO_3$ R is a max. at concns. of ~ 7 and 2.75 , respectively. With HNO_3 the equiv. dispersion in the visible falls rapidly with increasing c .

R. C.

Non-additivity of equivalent refraction of strong electrolytes at large concentrations. K. FAJANS and R. LUHDEMANN (Z. physikal. Chem., 1935, B, 29, 150—157).—Extrapolation to zero concn. of available data for the rate of change with concn. of the apparent equiv. refraction, R , at concns. above 1.5 g.-equiv. per 1000 g. of H_2O has shown for 29 electrolytes additivity of R at zero concn., thus justifying the extrapolation. Examples are, however, given showing that in general R and its variation with concn. are not additive at higher concns.

R. C.

What is a colloid? J. W. MCBAIN (Nature, 1935, 135, 1033).—Association is regarded as the characteristic factor in the colloidal state. The case of long-chain mols. is discussed. In concns. $> 0.1N$ association is predominant in the simple sulphonic acids and is responsible for an increase in conductivity, f.p. lowering, and e.m.f. with concn.

L. S. T.

Preparation of colloidal metals. A. M. THOMAS and E. B. WEDMORE (Nature, 1935, 135, 1001).—A method for the prep. of colloidal suspensions of liquid metals and alloys in semi-conducting media is described.

L. S. T.

Preparation of colloid solutions by the silent electrical discharge. III. S. MIYAMOTO (Kolloid-Z., 1935, 71, 297—300; cf. A., 1934, 841, 1305).—Sols of Se and Te in H_2O and EtOH, and hydrosols of MnO_2 have been prepared by the action of the silent electric discharge. The stability of the sols and the influence of protective colloids have been studied.

E. S. H.

Validity of Rayleigh's formula for colloid systems. L. V. SMIRNOV (Kolloid-Z., 1935, 71, 261—265).—For white, non-metallic colloid systems the power to which λ is raised in the Rayleigh formula falls from 3.8 to 1.3 as the radius of particle is increased from 60 to 200 $m\mu$.

E. S. H.

Cryolysis, diffusion, and particle size. I. Experiments with sodium oleate, ovalbumin, and polyacrylic acid. F. E. M. LANGE and F. F. NORD (Biochem. Z., 1935, 278, 173—190; cf. A., 1931, 389).—The changes produced by freezing (to -79° or lower) and subsequent thawing in the rates of diffusion of these substances (in biological concns.) indicate that, with high concns., the state of aggregation is increased by freezing, whilst with low concns. it is decreased. A partial explanation is thus provided of the behaviour of colloidal materials (enzymes, soil).

W. MCC.

Structure of the gelatinous ortho-ferric hydroxide obtained by oxidising ferrous carbonate. A. KRAUSE and L. SKORUPSKA (Rocz. Chem., 1935,

15, 114—121).—The gel obtained by adding H_2O_2 to an aq. suspension of freshly pptd. $FeCO_3$ is probably $Fe(OH)_2 \cdot O \cdot [FeO \cdot OH]_4 \cdot FeO$.

R. T.

Changes in the refractive index of mixed alumina and silica gels under the influence of water and alkali. J. H. HELLMERS and R. KOHLER (Z. Pflanz. DÜNG., 1935, 39, 38—44; cf. B., 1934, 1074).—A microscopically uniform mixture of Al_2O_3 (I) and SiO_2 (II) gels is obtained by shaking the two components in $N-NaOH$. The n of the product varies with the composition of the mixture and with the proportion of adsorbed Na. No evidence was obtained of the formation of compounds of (I) and (II) on mixing Na silicate with $AlCl_3$ solution. The n of naturally occurring compounds of similar composition is discussed.

A. G. P.

Combination of iodine with starch. S. V. NEDZVETSKI (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1561—1569).—On adding I in KI to starch solution η remains const. up to a definite % of I and then rises rapidly. The point of change depends on the ratio starch/I and not on the concns. of the components. The stability of starch iodide towards electrolytic coagulants falls rapidly as soon as η increases. After coagulation the I is entirely retained by the starch. It is inferred that combination is at first "chemical," and is followed by adsorption of I.

R. S. B.

Viscosity and plasticity of disperse systems. V. Plastic-viscous properties of peat. M. P. VOLAROVITSCH, N. N. KULAKOV, and A. N. ROMANSKI (Kolloid-Z., 1935, 71, 267—274; cf. this vol., 701).—A capillary viscosimeter for use with systems composed of peat and H_2O is described. Determinations of plasticity const., flow resistance, and η have been made, and their dependence on the H_2O content of the system has been investigated. Bingham's theory of plastic streaming is applicable.

E. S. H.

Ionic exchange in relation to stability of colloidal systems. H. JENNY and R. F. REITEMEIER (J. Physical Chem., 1935, 39, 593—604; cf. A., 1932, 992).—For Putnam clays the ζ -potential is the higher, the smaller are the adsorbed cations, when the latter are of the rare gas type and of equal valency. The extent of the ionic exchange occurring when clays stabilised by different types of ions are brought in contact with various electrolytes, and its relation to the coagulation val. of the latter, are discussed.

F. L. U.

Lyophilic colloids. VII. Fractionation of agar and physico-chemical properties of the fractions. S. M. LIEPATOV and A. A. MOROSOV (Kolloid-Z., 1935, 71, 317—324; cf. this vol., 701).—Agar has been fractionated by progressive dialysis. The ash content, p_H , osmotic pressure, swelling, solubility, and heats of swelling and hydration of the fractions have been determined. The fractions differ in degree of association; the more highly associated fractions contain less Ca^{++} . The heat of chemical hydration of agar is $>$ that of gelatin, cellulose, or starch, although the heat of total solvation is less.

E. S. H.

Influence of hydrophilic colloids on structure formation in ferric hydroxide sols. G. FUCHS

(Kolloid-Z., 1935, 71, 307—316).—Viscosity-pressure curves show that albumin causes coagulation structure formation in $\text{Fe}(\text{OH})_3$ sols, which is followed after a time by spontaneous peptisation. The former is due to the fixing of Fe^{+++} by the albumin, thus involving desorption of the stabilising ions. The subsequent peptisation is due to the formation of NH_2 -acids from the albumin. Independent experiments show that α -alanine destroys the $\text{Fe}(\text{OH})_3$ structures. Starch causes similar structure formation in $\text{Fe}(\text{OH})_3$ sols, through the binding of H^+ in the intermicellar liquid.

E. S. H.

Action of electrolytes on hydrophobic colloids. H. R. KRUYT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 464—470).—The distinction between potential- and non-potential-determining ions is discussed and illustrated by data for the flocculation of negatively-charged AgI sol, flocculated by $\text{Al}(\text{NO}_3)_3$ and K_2SO_4 . The antagonistic effect of the K_2SO_4 causes a high concn. of the Al ion, the activity of which, however, decreases along the flocculation curve.

N. M. B.

Thixotropy, influenced by the orientation of anisometric particles in sols and suspensions. H. FREUNDLICH and F. JULIUSBURGER (Trans. Faraday Soc., 1935, 31, 920—921).—Thixotropic sols (e.g., V_2O_5 sol) or suspensions (e.g., $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}$) containing anisometric particles solidify in a few sec. when the particles are oriented by gentle movement, whereas up to 1 hr. is required for spontaneous solidification. The term "rheopexy" is suggested for the phenomenon.

J. W. S.

Refractive index of hydrosols of pectin substances. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1935, 5, 185—188).

R. T.

Physical chemistry of proteins in non-aqueous and mixed solvents. II. Electrochemical properties of protein solutions in glacial organic acids. D. M. GREENBERG and C. E. LARSON (J. Physical Chem., 1935, 39, 665—677; cf. A., 1930, 1118).—Casein, edestin, gelatin, and deaminised gelatin do not increase the electrical conductivity of anhyd. lactic acid, and the increase of that of AcOH is too small to permit the assumption of salt formation. The large increase observed with HCO_2H is due to formation of protein formates, the conductivities and transport nos. of which have been measured. The solvent action of the three acids is not primarily dependent on their ability to form charged protein ions.

F. L. U.

Isoelectric point of isinglass. H. FREUNDLICH and P. S. GORDON (Trans. Faraday Soc., 1935, 31, 915—919).—The isoelectric point of isinglass (I) in aq. solution, as measured by the cataphoretic velocity of quartz particles coated with (I) in buffer solutions, is p_H 5.9. The sedimentation vol. of quartz particles in buffer solutions containing (I) is a max. at p_H 5.8—6.0, but the abs. vol. is dependent on the presence of air, decreasing to half on evacuation. This decrease is only about 10% in absence of (I). The vol. of the sediment formed in a vac. increases only slightly on shaking with air. Similar results were obtained with gelatin, ovalbumin, and haemoglobin.

J. W. S.

Polysaccharoprotein sols. S. J. VON PRZYLECKI, H. ANDRZEJEWSKI, and E. MYSTKOWSKI (Kolloid-Z., 1935, 71, 325—333).—Measurements of turbidity and η have been made for solutions of several proteins, polysaccharides, and their mixtures. Departures from additivity on mixing several of the pairs are noted. These observations are discussed in relation to the mode of combination of the components.

E. S. H.

Rhythmic reactions in silicic acid gels. F. TABOURY and G. JAUNEAU (Bull. Soc. chim., 1935, [v], 2, 971—982).—The period of gelatinisation of SiO_2 by the addition of HNO_3 or H_2CrO_4 to Na_2SiO_3 increases with the dilution and becomes a min. with increasing [neutral salt]. The rate of penetration of CuSO_4 into gels containing K_2CrO_4 , and the formation of CuCrO_4 rings has been studied in relation to the $[\text{K}_2\text{CrO}_4]$ and [neutral salt]. Rhythmic pptn. of Ag_2CrO_4 , which has been similarly studied, is favoured by an impurity (e.g., NaBr) which produces a ppt. more insol. than Ag_2CrO_4 . The distances of successive rings from the origin are in agreement with the equations previously applied (A., 1932, 225).

R. S.

Electrokinetics. XIV. Critical comparison of electrophoresis, streaming potential, and electro-osmosis. H. B. BULL (J. Physical Chem., 1935, 39, 577—583; cf. A., 1934, 143).—The three methods give the same val. for the ζ -potential of surfaces covered with gelatin or ovalbumin, but not for surfaces of quartz or cellulose. A cell for electrophoresis is described.

F. L. U.

Comparison of electrophoretic, electro-osmotic, and stream potential isoelectric points at glass and gelatin surfaces. B. MONAGHAN, H. L. WHITE, and F. URBAN (J. Physical Chem., 1935, 39, 585—591).—The isoelectric concns. of Th^{+++} , Fe^{+++} , and Al^{+++} for Pyrex glass given by electro-osmosis and electrophoresis are several times $>$ those given by streaming potential measurements. All three methods give the same isoelectric $[\text{H}^+]$ for gelatin. It is inferred that only the diffuse component of the double layer is moved by hydrostatic forces, whilst both the diffuse and the outer Helmholtz layers move in an electric field.

F. L. U.

Influence of electrolyte concentration on the ratio of electro-osmotic to electrophoretic mobilities. H. L. WHITE, B. MONAGHAN, and F. URBAN (J. Physical Chem., 1935, 39, 611—622; cf. preceding abstract).—The ratio (R) of electro-osmotic velocity to the electrophoretic velocity of glass and of gelatin-covered particles of 1—3 μ diam. is > 3 in distilled H_2O , but decreases with increasing $[\text{KCl}]$ to 1 for concns. 10^{-3} — $10^{-2}M$ and higher. The causes are discussed.

F. L. U.

Electrical charges of activated carbons. H. L. OLIN, J. D. LYKINS, and W. F. MUNRO (Ind. Eng. Chem., 1935, 27, 690—693).—Cataphoretic velocities have been measured for Brownian particles of various types of activated C suspended in solutions of p_H 1.5—12.0. At each p_H val. many results are averaged and the resulting curves show two isoelectric points for each sample. There is a remarkable similarity between relative adsorptive capacities and drift

velocities, especially with high p_H vals. For this reason the method offers promise of usefulness in evaluating adsorptive C. I.

Derivation of thermodynamical relations for a simple system. A. N. SHAW (Phil. Trans., 1935, A, 234, 299—328).—A new procedure is developed whereby thermodynamic relations for a system which requires only three related variables for its description may be rapidly deduced. Compact tables are given which contain data for a great variety of transformations and illustrations of the use of the tables are provided by transformations connected with the theory of perfect gases, radiation in an enclosure, and saturated vapour. R. S. B.

Parachor and entropy of metallic elements. B. N. SEN (J. Chim. phys., 1935, 32, 300—302; cf. A., 1934, 719).—A formula is deduced whereby vals. for the entropy of metals calc. from the parachors are, in general, in good agreement with accepted vals. J. G. A. G.

Ethane-ethylene-hydrogen equilibrium. H. A. SMITH and W. E. VAUGHAN (J. Chem. Physics, 1935, 3, 341—343).—A statistical calculation of the equilibrium consts. over the temp. range 400—700° gives vals. < experiment by the factor 2. The discrepancy probably lies in the calc. entropy of free rotation in C_2H_4 . N. M. B.

Interpretation of reaction between allylthiocarbimide and piperidine. W. HEROLD (Z. physikal. Chem., 1935, B, 29, 121—126).—The equilibrium const. has been derived from Kremann and Riebl's absorption data (A., 1933, 885) and shows reaction to go almost to completion. The results suggest that the product of reaction is a substituted thiocarbamide. R. C.

Dissociation constants of some polybasic acids. W. R. MAXWELL and J. R. PARTINGTON (Trans. Faraday Soc., 1935, 31, 922—935).—The dissociation consts. of $C_6(CO_2H)_6$, $C_6H(CO_2H)_5$, 1:2:3- $C_6H_3(CO_2H)_3$, *o*- and *m*- $C_6H_4(CO_2H)_2$, and $BzOH$ are in the ratio 500:250:25:15:3:1, indicating the tendency of one CO_2H to promote ionisation of another and the effect of inter-group distance. The tendency of an ionised CO_2H to hinder ionisation of a further CO_2H is shown by the fact that dissociation consts. of the last CO_2H of the above compounds are in the ratio 10:35:120:500:2500:6000. J. W. S.

Hydrolysis of the aluminium benzenesulphonates. V. ČUPR and B. SLIVA (Publ. Fac. Sci. Univ. Masaryk, 1935, No. 200, 3—13; cf. A., 1931, 910).—The p_H of 0.01—0.5*N* solutions of $(PhSO_3)_3Al \cdot 9H_2O$, *p*-($OH \cdot C_6H_4 \cdot SO_3$) $_2Al \cdot 9H_2O$, $Al_2(SO_4)_3$, and $AlCl_3$ during hydrolysis is $-0.54 \log [Al^{+++}] + 2.65$. The following salts have been prepared from $Al_2(SO_4)_3$ and the appropriate Ba salts: *p*-($C_6H_4Me \cdot SO_3$) $_2Al \cdot 9H_2O$; *p*-($C_6H_4Cl \cdot SO_3$) $_2Al \cdot 9H_2O$; *p*-($C_6H_4Br \cdot SO_3$) $_2Al \cdot 9H_2O$; 2:1:4-($NO_2 \cdot C_6H_3Me \cdot SO_3$) $_3Al \cdot 12H_2O$; 3:6:1-($NO_2 \cdot C_6H_3Cl \cdot SO_3$) $_3Al \cdot 9H_2O$; *m*-($NO_2 \cdot C_6H_4 \cdot SO_3$) $_3Al \cdot 9H_2O$. F. R. G.

Nature of the ceric sulphates. E. G. JONES and F. G. SOPER (J.C.S., 1935, 802—805).— $Ce(SO_4)_2$ and $Ce(SO_4)_2 \cdot 4H_2O$ coexist in contact with a solution con-

taining 57—62% of SO_3 . $Ce(SO_4)_2$ forms metastable solutions in H_2O , which, on mixing with conc. H_2SO_4 , give two salts, $H_4Ce(SO_4)_4$ (English red) and $H_2Ce(SO_4)_3$ (orange), which gradually change to $Ce(SO_4)_2$. There is no evidence of migration of Ce to the cathode in solutions 0.5—20*N* with respect to H_2SO_4 and 0.01—0.13*M* with respect to $Ce(SO_4)_2$, either alone or with added K, Na, and Li sulphates. The coloured Ce ions migrate to the anode. In *N*- H_2SO_4 , the Ce is present chiefly as $H_3Ce(OH)(SO_4)_3$, and the colour of the solution decreases rapidly in <0.4*N*- H_2SO_4 . This is probably correlated with hydrolysis of the sulphato-cerate anion and the ultimate pptn. of the basic salt $HCe(OH)_3SO_4$. J. G. A. G.

Cryoscopy of mixtures of nitrogen peroxide and bromine. A. PERRET and R. PERROT (Compt. rend., 1935, 200, 2166—2168).—The f.-p. curve given affords no evidence for the existence of $NO_2 \cdot Br$. H. J. E.

Equilibrium in the system $Be(NO_3)_2-HNO_3-H_2O$. A. V. NOVOSSELOVA and N. D. NAGORSKAJA (Bull. Soc. chim., 1935, [v], 2, 967—971).—The solubility of $Be(NO_3)_2$ in aq. HNO_3 at 0° and 20° has been determined. Hydrates with 4, 3, 2, and 1 H_2O have been identified. The last three give metastable forms. R. S.

System water-sodium pentaborate. A. P. ROLLET and P. CHUNG-MING (Bull. Soc. chim., 1935, [v], 2, 982—985).—The solubility of $Na_2O \cdot 5B_2O_3$ in H_2O has been determined. There is an ice-salt eutecticat -1.7° and the transition $Na_2O \cdot 5B_2O_3 \cdot 10H_2O \rightarrow Na_2O \cdot 5B_2O_3 \cdot 2H_2O$ occurs at 100° . R. S.

System water-sodium pentaborate-sodium chloride. P. CHUNG-MING (Bull. Soc. chim., 1935, [v], 2, 985—993; cf. preceding abstract).—The saturated solution is in equilibrium with the solid phases $NaCl$, $Na_2O \cdot 5B_2O_3 \cdot 10H_2O$ (I), and $Na_2O \cdot 5B_2O_3 \cdot 2H_2O$ at $55^\circ \pm 3^\circ$, and with $NaCl$, $NaCl \cdot 2H_2O$, and (I) at -1.3° . (I) is metastable above 55° . There is a ternary eutectic ice- $NaCl \cdot 2H_2O$ -(I) at -22.7° . A saturated solution of $NaCl$ and $Na_2O \cdot 5B_2O_3$ deposits only pentaborate on cooling between 100° and -1.3° . R. S.

Vapour pressure and dehydration of unstable salt hydrates. Sodium perborate. T. I. TAYLOR and G. G. TAYLOR (Ind. Eng. Chem., 1935, 27, 672—680).—Commercial Na perborate (I) is represented by $NaBO_3 \cdot 4H_2O$ or more correctly $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$. The H_2O v.p. of a mixture of (I) with $NaBO_2 \cdot H_2O_2$ at temp. up to 50° is given by $\log 12.19 - 3286/T$. Rate of dehydration at a given temp. is governed by (1) rate of nucleus formation, (2) rate of linear propagation of interface, (3) size and shape of reactant particles, (4) rate of removal of H_2O vapour. In dehydration at atm. pressure the rate of removal of H_2O is the controlling factor until about 70% of the H_2O is removed. On heating to 90° the available O in (I) increases from 10% to 16%, but at higher temp. diminishes rapidly with O evolution. The solubility rises continually with heating. C. I.

Ammines of thorium bromide. R. C. YOUNG (J. Amer. Chem. Soc., 1935, 57, 997—999).—The

system has been studied by the tensimetric method at 0° and 25°. The equilibrium $\text{ThBr}_4 \cdot 20\text{NH}_3$, $\text{ThBr}_4 \cdot 14\text{NH}_3 + 6\text{NH}_3$ has been established. The decomp. pressures of the amines have been measured. E. S. H.

Thermal analysis of binary systems of antipyrine and resorcinol with certain organic compounds.—See this vol., 971.

Thermal equilibrium in ternary systems. IV. Antipyrine-phenacetin-salol. Thermal equilibrium in the system β -naphthol- β -naphthylamine.—See this vol., 970.

Equilibria in the system $\text{NiCl}_2\text{-H}_2\text{O-HCl}$. A. V. BABAEVA and T. A. ARTSCHAKOVA (J. Gen. Chem. Russ., 1935, 5, 216—219).—The solid phase at 20°, for $[\text{HCl}]$ from 0 to 21.2%, is $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (I) at higher $[\text{HCl}]$; at 80° only (I) is formed. R. T.

Equilibria in the system $\text{Na}_2\text{O-HF-H}_2\text{O}$. N. D. NAGORSKAJA and A. V. NOVOSELOVA (J. Gen. Chem. Russ., 1935, 5, 182—184).—The solubility of NaF falls rapidly with rising $[\text{NaOH}]$; the relations show little change between 0° and 94°. R. T.

System $\text{Na}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$. J. T. DOBINS and J. A. ADDLESTON (J. Physical Chem., 1935, 39, 637—642; cf. A., 1932, 341).—Isotherms for 0°, 30°, and 42° are given. Na alum is formed as a solid phase at 30° and 42°, but not at 0°. F. L. U.

System $\text{CaO-SiO}_2\text{-H}_2\text{O}$. R. NACKEN and R. MOSEBACH (Z. anorg. Chem., 1935, 223, 161—173).— Ca_2SiO_5 is gradually decomposed by H_2O forming successively, with increasing quantities of H_2O , $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, and $\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$. No appreciable dissolution of SiO_2 is indicated. Marked variation in solubility of CaO with fineness of division was observed. The most probable val. for the solubility at 20° is 1.2100 g. per litre. By grinding in contact with H_2O a supersaturation of 23% may be obtained. M. S. B.

Felspar system and the weathering of felspar to kaolin. M. HOLLENWEGER and H. RUMPELT (Z. techn. Physik, 1934, 15, 318—323; Chem. Zentr., 1935, i, 539).—M.-p. data are recorded for the system $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$. The free alkali formed on heating felspar samples for 24 hr. at 80° with H_2O is correlated with the equilibrium diagram. Weathering is discussed. H. J. E.

Ternary systems water, allyl alcohol, and salts at 25°. P. M. GINNINGS and M. DEES (J. Amer. Chem. Soc., 1935, 57, 1038—1040).—Data for systems of H_2O and allyl alcohol (I) with $(\text{NH}_4)_2\text{HPO}_4$, $\text{Na}_2\text{S}_2\text{O}_3$, MgSO_4 , NaNO_3 , K_2CO_3 , NaCl , SrCl_2 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and CdSO_4 , respectively, are recorded. (I) is more difficult to salt out than Pr^oOH or Pr^sOH . E. S. H.

System aniline-formic acid-water. J. R. POUND and A. M. WILSON (J. Physical Chem., 1935, 39, 709—719).—Equilibria at 15° have been determined. The only solid phase is aniline formate (I). The transformation of the liquid mixtures and of solid crystals of (I) into formanilide has been studied. F. L. U.

System alkali oxide- $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$. III. Action of CO_2 and K_2CO_3 on potassium di- and tetra-silicate. C. KROGER and E. FINGAS (Z. anorg. Chem., 1935, 223, 257—276).—Equilibria on the SiO_2 -rich side of the $\text{K}_2\text{O-CO}_2\text{-SiO}_2$ system have been investigated between 200° and 900° by measurement of the equilibrium pressure of CO_2 . The phase-rule diagram (cf. A., 1933, 916) is completed by the equilibria in the system $\text{K}_2\text{Si}_4\text{O}_9 + \text{K}_2\text{CO}_3 = \text{CO}_2 + \text{mixed crystals of K}_2\text{CO}_3 \text{ with K}_2\text{Si}_2\text{O}_5$. Heats of formation of K_2SiO_3 , $\text{K}_2\text{Si}_2\text{O}_5$, and $\text{K}_2\text{Si}_4\text{O}_9$ are calc. from the tensimetric data. J. S. A.

Heats of dilution and heats of vaporisation of $\text{D}_2\text{O-H}_2\text{O}$ mixtures. E. DOEHLEMAN and E. LANGE (Z. physikal. Chem., 1935, 173, 295—312; cf. A., 1934, 1071).—There is no heat effect on mixing CO_2 and $\text{CO}(\text{CD}_3)_2$. The integral heat of dilution on mixing H_2O and D_2O is considerable and increases linearly with the D content of the mixture. The partial mol. heats of dilution of H_2O and D_2O and the partial mol. heats of vaporisation have been calc. All these data agree with the assumption that the cause of the heat of mixing is not van der Waals forces, but $\text{H}_2\text{O} + \text{D}_2\text{O} \rightarrow 2\text{HDO} - 32 \text{ g.-cal.}$ If the heat of this reaction in the gaseous state is -156 g.-cal. the van der Waals part of the partial mol. heat of evaporation of HDO is not the mean of the corresponding vals. for D_2O and H_2O . If it is the mean, the heat of the above reaction must be the same in both gaseous and liquid states. The mol. heats of vaporisation of the solution have been calc. R. C.

Heat of dissolution of magnesium oxide in nitric acid, and of zinc oxide and silver oxide in hydrofluoric acid as dependent on the concentration of acid. Specific heat of hydrofluoric acid solutions. A. PRANSCHKE and H. E. SCHWIETE (Z. anorg. Chem., 1935, 223, 225—233).—The heats of dissolution of MgO in 2N-, 4N-, 5N-, and 9N- HNO_3 , and of ZnO and Ag_2O in 5N-, 10N-, 18N-, and 23N- HF , at 18° have been measured, and the sp. heat of aq. HF (9.8—40.7%) at 18° has been determined. J. S. A.

Salt effect in concentrated solutions. Change in the heat of dissolution of potassium chloride by other electrolytes. C. DRUCKER (Arkiv Kemi, Min., Geol., 1935, 11, A, No. 18, 27 pp.).—The effect of HCl , HNO_3 , H_2SO_4 , LiCl , NaCl , KCl , NH_4Cl , KI , MgCl_2 , CaCl_2 , BaCl_2 , CdCl_2 , LiNO_3 , NaNO_3 , KNO_3 , NH_4NO_3 , $\text{Be}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, NaOAc , KOAc , Na_2SO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and MgSO_4 on the heat of dissolution of KCl has been investigated. The greatest decrease occurs in presence of NO_3' and SO_4'' , and much less decrease with Cl' and especially OAc' . In general, bivalent cations have a greater effect than univalent cations. J. W. S.

Thermodynamics of system sulphur dioxide-water. W. A. ROTH (Z. physikal. Chem., 1935, 173, 313—318).—The heat of dissolution of SO_2 in H_2O consists of heat of dissolution without hydration (=heat of condensation), heat of hydration, and heats of first and second dissociation. Since the second dissociation is negligible, if hydration is complete the heat of dissociation should be a linear

function of the degree of first dissociation. From the deviation from linearity observed at higher concns. the hydration const. has been calc., permitting the derivation of a formula for heat of dissolution valid for solutions containing 37.5—7500 mols. of H_2O per mol. of SO_2 with an average error of 0.3%. Component parts of the heat of dissolution derived by the reaction isochore (this vol., 25) are less trustworthy than the calorimetric vals. R. C.

Thermochemistry of ammonium arsenates. A. DE PASSILLÉ (Compt. rend., 1935, 200, 1852—1854).—Data for heats of neutralisation of H_3AsO_4 by aq. NH_3 and for heats of dissolution of the products at 15° are recorded, and vals. for the heats of formation of $\text{NH}_4\text{H}_2\text{AsO}_4$, $(\text{NH}_4)_2\text{HAsO}_4$, $(\text{NH}_4)_3\text{AsO}_4$, and $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ are calc. H. J. E.

Electrical conductivity of extremely dilute solutions. M. HŁASKO and A. SALIT (Bull. Acad. Polonaise, 1935, A, 189—200).—A method is developed for the measurement to $\pm 2\%$ of the electrical conductivity of solutions of concn. down to $10^{-7}N$, and for the direct determination of the limiting mol. conductivity of strong electrolytes. The Kohlrausch extrapolation formula is applicable to the calculation of the limiting mol. conductivity of both strong and weak electrolytes. Data are given for solutions of KOH , H_2SO_4 , AcOH , and NH_3 . J. W. S.

Conductivity of alkali hydroxides in very dilute aqueous solutions. M. HŁASKO and A. SALITOWNA (Rocz. Chem., 1935, 15, 153—162).—Direct measurements show that λ_∞ is attained at the following concns.: LiOH $2 \times 10^{-6}N$, NaOH $4 \times 10^{-6}N$, KOH $5 \times 10^{-6}N$, RbOH $8 \times 10^{-6}N$, CsOH $10^{-5}N$; these results differ by 0.2% from those calc. from Kohlrausch's formula. The transport nos. of the ions are K^+ 74.7, Li^+ 40.0, Na^+ 50.9, Rb^+ 77.6, and Cs^+ 78.4. R. T.

A.c. and d.c. surface conductivity measurements in Pyrex slits. F. URBAN, S. FELDMAN, and H. L. WHITE (J. Physical Chem., 1935, 39, 605—609; cf. A., 1932, 699).—The surface conductivities of dil. aq. KCl in slits formed by cracking Pyrex flasks agree with those previously found for capillaries. There is thus no difference in the surface conductivities of fused and fractured glass. The apparent sp. conductivity is lower with d.c. than with a.c.; this is due to membrane potentials. F. L. U.

Electrolysis of solid alloys. W. JOST and R. LINKE (Z. physikal. Chem., 1935, B, 29, 127—132).—When a current is passed through a glowing wire of a Au-Pd alloy Au accumulates at the anode and Pd at the cathode end. The transport no. of Pd at 900° is $\sim 10^{-11}$ (cf. this vol., 158). R. C.

Electrochemical investigation of solid cadmium-antimony alloys. A. ÖLANDER (Z. physikal. Chem., 1935, 173, 284—294).—Electrode potentials of alloys in contact with molten mixtures of NaOAc , KOAc , and Cd(OAc)_2 at 240—290° have been measured. The stable intermediate phase CdSb exhibits a region of homogeneity extending from 50.0 to 50.5 at.-% Cd . The degree of disorder of the

lattice of this compound is calc. to be 0.00005 at 250°, but must rise continuously with the temp. R. C.

Diffusion potentials. II. V. ČUPR (Publ. Fac. Sci. Univ. Masaryk, 1934, No. 197, 1—14; cf. A., 1934, 149).—Theoretical. Planck's equation satisfies the relation formerly deduced when (a) the solutions in contact have the same concn. and cation (anion), or cations (anions) of the same mobility, (b) the solutions contain the same electrolyte in different concns., or (c) the diffusion potential between both solutions is zero. E. S. H.

Current-producing processes in concentration gradients in solid electrolytes. W. SCHOTTKY (Wiss. Veroff. Siemens-Werken, 1935, 14, 1—19).—Theoretical. The conditions under which an e.m.f. is produced by concn. differences in solid solutions, such as Na in NaCl etc., are discussed. E. S. H.

Electrometric studies of the precipitation of hydroxides. XIII. Constitution of aqueous solutions of silver oxide in ammonia, mono-, di-, and tri-methylamine and -ethylamine, pyridine, and ethylenediamine; dissociation constants of amines. H. T. S. BRITTON and W. G. WILLIAMS (J.C.S., 1935, 796—801).—The dissociation consts., K , of the amines determined potentiometrically at 18° are of the same order as recorded vals. K_b and K_{b_1} of $(\text{CH}_2\text{NH}_2)_2$ are 1.14×10^{-4} and 1.13×10^{-7} , respectively. The solubilities were determined at 15° in 0.04—3.1*N*-aq. solutions of the bases, and from the e.m.f. of the cell $\text{Ag}|\text{complex solution}|\text{sat. KNO}_3|\text{N-calomel}$, the instability consts. $[\text{Ag}^+][\text{B}]/[\text{AgB}_2^+]$ were calc. These vals. show that the order of the co-ordinating tendencies of amines (except NH_2Ph) with respect to Ag is primary > sec. > tert. Electrometric and conductometric titrations show the presence of bases, $\text{Ag(B)}_2\text{OH}$, similar in strength to NaOH . The strength of these complex bases is independent of the strength of the NH_3 base in the complex cation. J. G. A. G.

Polarographic studies with the dropping mercury cathode. XLVII. Passivation of small mercury anodes. V. MAJER (Coll. Czech. Chem. Comm., 1935, 7, 215—227).—In the polarographic investigation of aq. solutions of KCl and of KBr with small anodes, new passivity phenomena have been observed, which are due to the formation of anodic films of Hg_2Cl_2 and Hg_2Br_2 , respectively. These surface films of thickness $146 \pm 20 \text{ \AA}$. act like a resistance of 10^6 — 10^7 ohms. The theory of the passivation of small Hg anodes is discussed. O. J. W.

Polarographic studies with the dropping mercury electrode. II. Absolute determination of reduction and depolarisation potentials. J. HEYROVSKY and D. ILKOVIC (Coll. Czech. Chem. Comm., 1935, 7, 198—214).—In analytical applications of the polarographic method some uncertainty occurs in fixing the position of the characteristic bend in the current-potential curve. This uncertainty is eliminated and a const. val. of the electrode potential obtained by taking the potential at the point where the current is equal to half the limiting current (diffusion current). This potential is charac-

teristic of the electrolytic process and is independent of the concn. of the solution, sensitivity of galvanometer, rate of dropping of Hg, scale of co-ordinates, and height of diffusion current. O. J. W.

Intensity of the diffusion current in relation to the size and period of renewal of the cathode surface. G. SEMERANO (*Gazzetta*, 1935, 65, 289—298).—The dependence of the intensity of the diffusion current on the size of the dropping Hg cathode and on the rate of dropping has been studied for the deposition of Cd and of Ba. With increasing size of drops or rate of dropping the waves of the diffusion current are increased in height and the deposition potentials of the metallic ions become more positive. The thickness of the diffusion layer around the cathode is calc. to be 36—65 μ . The weight of the Hg drops is probably const. Means for increasing the precision of the polarographic method are described. O. J. W.

Reduction of deoxybenzoin and of benzoin at the dropping Hg cathode. G. SEMERANO (*Gazzetta*, 1935, 65, 273—288).—The reduction potentials of deoxybenzoin and of benzoin dissolved in 0.1*N*. NH_4Cl in 50% EtOH are -1.129 and -1.061 volts, respectively (referred to *N*-calomel cell). From the form of the polarisation curve and the displacement of the reduction potential with concn. of reducible substance and of H^+ , it is concluded that the reduction process is univalent and leads to the corresponding pinacols. A method is proposed for determining the constitution of isomeric benzoin. The solubility of benzoin in H_2O is 1.75×10^{-4} mol. per litre. O. J. W.

Simultaneous discharge of hydrogen ion and metal ions from solutions of complex cyanides. O. ESSIN, A. BALABAJ, and A. MATANZEV (*Z. physikal. Chem.*, 1935, 173, 216—222).—The equation previously derived (this vol., 450) has been confirmed by measurements of the simultaneous discharge of H^+ and Zn^{++} from solutions of $\text{K}_2\text{Zn}(\text{CN})_4$ and published data for the simultaneous discharge of H^+ and metal ions from solutions of other complex cyanides. The results permit calculation of γ coeffs. of Volmer's equation (A., 1930, 1376) for several ions. R. C.

Influence of light on the anodic polarisation of tungsten. J. P. E. DUCLAUX (*Compt. rend.*, 1935, 200, 1838—1840).—Ultra-violet light produces depolarisation of a W electrode, polarised in conc. aq. H_2SO_4 , the increase in current depending on the applied voltage. The max. sensitivity is at 3650 Å. The effect of light falls to approx. 10% of its initial val. after 24—48 hr. H. J. E.

Anodic behaviour of alcohols in alkaline solutions. S. KOIDZUMI (*Mem. Coll. Sci. Kyoto*, 1934, A, 17, 329—379).—Current-potential curves for anodes of Pt, Pd, Au, Rh, Ag, Ni, Cu, Ir, and C in solutions containing H_2O , NaOH, and MeOH or EtOH have been determined and the products of electrolysis analysed. The evolution of H_2 and hydrocarbons has been observed at the anode; the mechanism is discussed on the basis of the electronic theory, assuming adsorption and splitting of org. ions at the anode. Periodic variations of c.d. and p.d., accompanied by

the intermittent formation of a yellow film (possibly an aldehyde resin), were observed under certain conditions. E. S. H.

Kinetics of exothermic reactions. III. Role of the walls in chain reactions. N. N. SEMENOV (*Acta Physicochim. U.R.S.S.*, 1934, 1, 525—534).—There is a large class of gas reactions which are at the same time homogeneous and heterogeneous. They are particularly sensitive to the state of the surface, on which not only chain breaking, but also branching, occurs. The oxidation of hydrocarbons, which is a reaction of this class, is discussed. O. J. W.

Theory of termolecular reactions. H. GERSHINOWITZ and H. EYRING (*J. Amer. Chem. Soc.*, 1935, 57, 985—991).—Theoretical. Assuming that the rate of termol. homogeneous gas reactions is determined by the concn. of an activated complex of the three mols. involved, in which the individual mols. cannot rotate, the calc. rates for the reactions of NO with O_2 , Cl_2 , and Br are in good agreement with experiment. The negative temp. dependence of the NO- O_2 reaction follows from the theory. E. S. H.

Attempt to follow the course of a reaction by potentiometric measurements. J. A. REUTER-SKJOLD (*Svensk Kem. Tidskr.*, 1935, 47, 121—141).—A potentiometric method using glass electrodes for following the cleavage of $(\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ in alkaline solution is described. Correction formulæ are derived. The method is specially applicable in solutions with low $[\text{OH}^-]$. M. S.

Ignition of hydrogen and oxygen by electric sparks in different reaction vessels. M. MIYANISHI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, 27, 52—58).—The lower crit. ignition pressures p_c of $2\text{H}_2 + \text{O}_2$ for different igniting currents in vessels of glass, quartz, and Al are given. p_c was lowest in the glass vessel, in which the pressure decrease was > theoretical. This is accounted for by the interaction of reaction chains with the Na of the glass, which can be detected in the flame spectrum. The no. of such chains $\propto p_c^2$. R. S.

Critical phenomena in the oxidation and self-inflammation of hydrocarbons. A. EGERTON and A. R. UBBELOHDE (*Nature*, 1935, 135, 997—998). L. S. T.

Initial stages of combustion of hydrocarbon fuels. K. I. IVANOV and V. K. SAVINOVA (*J. Appl. Chem. Russ.*, 1935, 8, 64—92).—The products of heating mixtures of air and PhMe, methylcyclohexane (I), and *n*-heptane at 250—650° have been identified and determined. PhMe ignites at 633°, after an initial stage (> 590°) of production of aldehydes (chiefly CH_2O), alcohols, and acids; peroxides are not formed. The ignition temp. falls with increasing relative concn. of PhMe in the mixture. Production of 1- and 2-C oxy-compounds commences at 315°, is at a max. at 350—450°, and falls from 450° to the ignition point (530°), with corresponding increase in CO and CO_2 production. In the case of *n*- C_6H_{14} , the initial stage of oxidation commences at 252°, passes through a max. at 370°, and falls with approach to the flash point (515—580°); per-

oxide (including H_2O_2 and $\text{OH}\cdot\text{CH}_2\text{O}_2\text{R}$) formation varies similarly. The peroxides decompose at 110–115°, with formation of ketones, aldehydes, alcohols, acids, CO, and CO_2 ; the view is expressed that the initial stage consists chiefly in the formation and thermal decomp. of the peroxides. R. T.

Induction period in the oxidation of propane. W. P. MUNRO (J. Amer. Chem. Soc., 1935, 57, 1053–1054).—The effect of composition and total pressure on the lowest temp. of reaction and on the temp. coeff. has been investigated. The mechanism is discussed. E. S. H.

Relative rates of combination of light and heavy hydrogen with ethylene. R. N. PEASE and A. WHEELER (J. Amer. Chem. Soc., 1935, 57, 1144–1145).—The ratio of the rates for H_2 and D_2 , using a Cu catalyst, is 1.59 at 0° and 1.04 at 306°; in the homogeneous reaction the ratio is 2.10 at 524° and 2.0 at 560°. The influence of exchange is being investigated. E. S. H.

Chain process in the reaction between SO_2 and O_3 . I. Oxidation of aqueous SO_2 by ozone. S. S. VASILIEV, M. V. FROLOV, L. I. KASHTANOV, and T. L. KASTORSKAJA (J. Gen. Chem. Russ., 1935, 5, 149–154).—The no. of mols. of SO_2 oxidised per mol. of O_3 rises from 1 to 5 as the $[\text{SO}_2]$ rises from 0.02 to 0.5N. An optimum $[\text{O}_3]$ in the gas exists for each $[\text{SO}_2]$ in the solution; the most efficient oxidation (13 mols. of SO_2 per mol. of O_3) was obtained with 0.067% O_3 and 0.1N- H_2SO_3 . The results point to inductance of the reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ by the reaction $3\text{SO}_2 + \text{O}_3 \rightarrow 3\text{SO}_3$. R. T.

Homogeneous unimolecular decomposition of gaseous alkyl nitrites. III. Decomposition of *n*-propyl nitrite. E. W. R. STEACIE and G. T. SHAW (J. Chem. Physics, 1935, 3, 344–347; cf. A., 1934, 347).—The thermal decomp. is homogeneous and of the first order in the temp. range 170–210°. The reaction is $\text{PrONO} = \text{NO} + 0.5\text{EtCHO} + 0.5\text{PrOH}$. The reaction rate is given by $k = 2.75 \times 10^{14} e^{-37,650/RT}$ sec.⁻¹. Comparison shows that $k_{\text{Et.Pr}} = 1 : 1.95 : 4.07$; the increased rate for higher members of the series is probably due to participation of extra vibrational degrees of freedom. N. M. B.

Relation between explosiveness and chemical structure. V. PLETZ (J. Gen. Chem. Russ., 1935, 5, 173–178).—8 groups of explosives are distinguished, containing “explosophores” ($\cdot\text{NO}_2$, $\cdot\text{ONO}_2$, $\cdot\text{N}:\text{N}^+$, $\cdot\text{NCl}_2$, $\text{C}:\text{N}^+$, etc.) and “auxexplos.” R. T.

Explosion of ethyl azide. H. C. CAMPBELL and O. K. RICE (J. Amer. Chem. Soc., 1935, 57, 1044–1050).—The pressure limit for explosion has been determined as a function of temp. The crit. pressure is raised by decreasing the size of the reaction vessel, and by the addition of He; addition of CO_2 has no effect. The Semenov theory is in satisfactory agreement with the data. The reaction is compared with the explosion of azomethane. E. S. H.

Mechanism of additions to double linkings. I. Thermochemistry and kinetics of a diene synthesis. A. WASSERMANN (J.C.S., 1935, 828–839).—The heats of the 1:4-addition of benzoquinone (I) to cyclopentadiene (II) and of the hypothetical

1:2-addition have been calc. Both reactions are exothermic and there is no thermodynamic reason for the preferential 1:4-addition. The kinetics of the (I)–(II) reaction have been investigated. A second-order association is involved, which is relatively insensitive to catalysts, light, or a magnetic field. The activation energy in EtOH or in C_6H_6 is 13–14 kg.-cal. The dipole-induction energy for different mutual orientations of the two reacting mols. has been calc. For orientations which might lead to 1:4-addition the induction energy is > for those suitable for 1:2-addition. Heats of combustion are recorded. O. J. W.

Benzoin reaction. I. Reaction between pure benzaldehyde and pure potassium cyanide. D. R. NADKARNI, S. M. MEHTA, and T. S. WHEELER (J. Physical Chem., 1935, 39, 727–739).—Pure dry PhCHO and KCN yield benzoin at 100° and, more slowly, at 30°, provided that a certain min. quantity of KCN is used. A rapid homogeneous autocatalytic reaction and a slow heterogeneous reaction occur simultaneously. The results are treated mathematically and the mechanism of the reaction is discussed. F. L. U.

Rate of hydrolysis of chlorine. E. A. SCHILOV and G. V. KUPINSKAJA (Compt. rend. Acad. Sci., U.R.S.S., 1935, 2, 222–224).—Electrical conductivities of Cl_2 solutions show that Cl_2 is hydrolysed rapidly at 0°. W. R. A.

Rate of absorption of carbon dioxide. Effect of concentration and viscosity of normal carbonate solutions. L. B. HITCHCOCK and H. M. CADOT (Ind. Eng. Chem., 1935, 27, 728–732).—The initial rate of absorption of pure CO_2 by stirred solutions of Na_2CO_3 and K_2CO_3 follows an equation of the type $dV/dt = K(C_i + C_b)^{1/2}$, where C_i , C_b are interfacial and main-body concns. Max. occur at 1.5N for Na_2CO_3 and 2.9N for K_2CO_3 , after which increasing viscosity (η) causes a decrease. Consts. obtained experimentally are about 10% lower for Na_2CO_3 than for K_2CO_3 . Except at very low concns. the rate of absorption is only a fraction of that with NaOH or KOH, but it is much > with pure H_2O . Very discordant statements on these matters in the lit. are due to varying absorption conditions. The rate measured by the authors is not the true initial rate, but the “steady initial rate” attained in > 1 sec.

Ester hydrolysis in pure water. W. POETHKE (Ber., 1935, 68, [B], 1031–1037).—In pure H_2O the rate of hydrolysis of $\text{HCO}_2\text{Et} \propto [\text{H}^+]$. Addition of HCO_2Na retards the change. Hydrolysis of EtOAc in pure H_2O is not appreciable until after some days, its incidence appearing to depend on unidentified impurities. CO_2 hastens the incidence, but is without further effect. The absence of non-catalysed change is further established by the stability of H_2O in pure EtOAc. H. W.

Influence of temperature on the velocity of ionic reactions. II. A. VON KISS and R. KUKAI (Z. anorg. Chem., 1935, 223, 149–160; cf. A., 1934, 603).—The velocity of the reaction between OH^- and the acetylglucollate ion has been measured at 5–45° without addition of salt and also in aq. NaCl, NaNO_3 ,

NaClO_3 , Na_2SO_4 , KCl , KNO_3 , K_2SO_4 , BaCl_2 , and $\text{Ba}(\text{NO}_3)_2$ of different concn. The Bronsted-Debye-Hückel relation is followed throughout the temp. range in presence of Na^+ for ionic strength 0.0014–0.03, and, under the same conditions, the van 't Hoff temp. coeff. is independent of the ionic strength. The coeff. is lowered by Li^+ and raised by Ca^{++} ; addition of neutral salts in dil. solution depresses it, but when the salts are more conc. their action is sp. It decreases also with rise of temp., and for the Bronsted kinetic activity coeff. is approx. 1. In N-NaNO_3 the relation between $\log k$ and the salt concn. is linear. For const. salt concn. $\log k \propto 1/T$. Without addition of neutral salt the activation energy of the reaction for the whole temp. range is 12,660 g.-cal. in presence of K^+ and Na^+ . Ca^{++} gives a val. 8.6% higher. Addition of neutral salts lowers the activation energy in dil. solution. In conc. solutions the action is sp. In general, activation energy diminishes with rise of temp. The effect of neutral salts on the collision no. is $>$ on the activation energy, but there is no simple connexion between the two.

M. S. B.

Kinetics of keto-enol transformations. I. P. KRIVOBABKO and I. A. SCHTSCHERBAKOV (Ukrain. Chem. J., 1935, 10, 1–3).—The kinetics of the reaction $\text{COPhMe} \rightleftharpoons \text{OH} \cdot \text{CPh} \cdot \text{CH}_2$ are conveniently studied cryoscopically, by measuring the f.p. of the products obtained when a freshly-distilled sample of COPhMe is maintained at 20° and 25° for 0–168 hr. The temp. coeff. is 2.48, and the heat of activation is 31,496 g.-cal.

R. T.

Reaction kinetics of sulphonation by sulphuric acid containing water.—See this vol., 863.

Relative rates of formation of some organo-magnesium and -lithium compounds. H. GILMAN, E. A. ZOELLNER, J. B. DICKEY, and W. M. SELBY (J. Amer. Chem. Soc., 1935, 57, 1061–1063).—Formation of simple Mg alkyl bromides is more rapid than that of the simple aryl compounds. The rate of formation of MgBu^nHal increases in the order $\text{Hal} = \text{Cl} < \text{I} < \text{Br}$, of MgRBr ($\text{R} = n\text{-alkyl}$) as the chain length decreases, and in the order $\text{Bu}^\beta < \text{CH}_2\text{Pr}^\beta < \text{Bu}^\alpha$ and $\beta < \alpha$. $\text{C}_{10}\text{H}_7 <$ other aryl groups. *o*-, *m*-, and *p*-Tolyl compounds are equally readily formed. The rate of formation of LiR follows in general the reactivity of the RHal , but complications may be caused by a Wurtz reaction with excessively active compounds. Li aryl compounds are formed in lower yields than are the alkyl compounds. In general, Li compounds are more rapidly formed than are Mg compounds, although the final yield may be lower.

R. S. C.

Removal of hydrogen and acid radicals from organic compounds by means of bases. I. Removal of hydrogen chloride from aldchloroimines by sodium hydroxide. Rates of reaction in alcoholic solution. C. R. HAUSER, J. W. LE MAISTRE, and A. E. RAINSFORD (J. Amer. Chem. Soc., 1935, 57, 1056–1059).—The rate of loss of HCl from aldchloroimines is bimol., being \propto the amount of base and also affected by the strength of the base. It bears no relation to the temp. of instantaneous decomp., but is roughly parallel to the k of the corre-

sponding acid, except for *o*-compounds, where steric factors may interfere. Reaction thus probably proceeds by removal of H^+ by the base and subsequent ejection of Cl^- . k is determined for 17 aldchloroimines in 92.5% EtOH , for 4 in dioxan at 0° , and for 5 in 92.5% EtOH at 35° . Heats of activation for the last-mentioned 5 compounds are calc.

R. S. C.

Kinetics of polymorphic transformation of quartz. A. H. SCHTSCHUKAREV, N. S. KASJAN, and V. D. TZIGLER (Ukrain. Chem. J., 1935, 10, 35–43).—The velocity coeffs. of the reaction of transformation of quartz into cristobalite correspond equally well with a uni- and bi-molecular reaction. The reaction is catalysed by a no. of “mineralisers” (CaO , Fe_2O_3 , MnO_2 , NaCl).

R. T.

Corrosion of zinc in water in presence of oxidising agents. I. F. KROCHMAL (Rocz. Chem., 1935, 15, 122–135).—Corrosion of Zn immersed in H_2O saturated with O_2 varies with the cryst. structure of the samples; reproducible results are obtained more readily with coarsely than with finely cryst. samples.

R. T.

Reaction in ethylene-hydrogen mixtures induced by oxygen. R. N. PEASE and A. WHEELER (J. Amer. Chem. Soc., 1935, 57, 1147).—Small amounts of O_2 cause greatly increased initial reaction rates in the homogeneous reaction at 538° .

E. S. H.

Iodine ion catalysis of deuterium peroxide. E. ABEL, O. REDLICH, and W. STRICKS (Monatsh., 1935, 65, 380–385; cf. A., 1934, 1075).—The velocity of decomp., k , of H_2O_2 in 60–90% D_2O solution in presence of I^- was measured interferometrically at 25° and 8.3° . k for $\text{H}_2\text{O}_2 > k$ (HDO_2) $> k$ (D_2O_2), but the energies of activation are identical in spite of the difference of zero point energy. An explanation is advanced.

J. S. A.

Action of arsenic acid and arsenates on hydrogen peroxide. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1935, [vi], 21, 454–460).— H_3AsO_4 , unlike H_3PO_4 , accelerates the decomp. of aq. H_2O_2 . NaH_2AsO_4 has a similar action to H_3AsO_4 ; decomp. by Na_2HAsO_4 is not as great as that caused by Na_2HPO_4 . Decomp. is more rapid with increasing concn. of As compound. The formation of per-arsenates was not observed.

E. W. W.

Oxidation of sulphites. E. SERNAGIOTTO DE CASAVECCHIA (Chim. e l'Ind., 1935, 17, 220–223).—Experiments on the oxidation of sulphites, with and without the presence of catalysts, are described. The oxidation by O_2 follows the mass-action law.

O. J. W.

Catalytic action of silver ions on the velocity of oxidation of acetone by persulphates. E. BEKIER and S. W. KIJOWSKI (Rocz. Chem., 1935, 15, 136–152).—The process consists of the slow reaction $\text{S}_2\text{O}_8^{--} + \text{Ag}^+ \rightarrow 2\text{SO}_4^{\cdot-} + \text{Ag}^{++}$, and of the instantaneous one $\text{COMe}_2 + 4\text{Ag}^{++} + 3\text{H}_2\text{O} \rightarrow \text{OAc}^+ + 4\text{Ag}^+ + 9\text{H}^+ + \text{CO}_2$. The reaction is within wide limits $\propto [\text{Ag}^+]$ and $[\text{S}_2\text{O}_8^{--}]$, but not $\propto [\text{COMe}_2]$; the velocity coeff. is expressed by the Brönsted-Debye-Hückel equation.

R. T.

Specificity of iron as a catalyst for the reaction between hydrogen peroxide and pyrogallol. A. WASSERMANN (J.C.S., 1935, 826—828).—The reaction between H_2O_2 and pyrogallol as catalysed by FeCl_3 has been followed spectrophotometrically under various conditions. The FeCl_3 is about 3000 times as effective as a catalyst for this reaction as for the decomp. of H_2O_2 . The main product of the reaction is a brownish dye, the max. colour being developed after 8—10 min. The dependence of the dye formation on $[\text{H}^+]$ and $[\text{H}_2\text{O}_2]$ and on the temp. has been investigated. O. J. W.

Specificity of enzyme catalysis. A. E. BRAUNSTEIN (Acta Physicochim. U.R.S.S., 1934, 1, 535—550).—A general survey. O. J. W.

Adsorption and catalysis. J. E. NYROP (J. Physical Chem., 1935, 39, 643—653; cf. A., 1932, 553).—Theoretical. The influence of ionisation potential on adsorption and catalysis by metals is discussed. F. L. U.

Formation of acetone from acetaldehyde and water.—See this vol., 963.

Role of adsorbed atoms in heterogeneous catalysis. S. ROGINSKI (Acta Physicochim. U.R.S.S., 1934, 1, 473—482).—The adsorption of mol. and at. H at various metallic and non-metallic surfaces is discussed. The assumption that in catalytic hydrogenation H_2 is split up into H atoms in the adsorption stage appears to be unnecessary. O. J. W.

Ageing of thin layers of catalysts. D. DOBITSCHIN and A. V. FROST (Acta Physicochim. U.R.S.S., 1934, 1, 503—510).—The gradual decrease in the catalytic activity of thin Pd layers for the hydrogenation of C_2H_4 is accompanied by a sintering process in which the Pd crystals increase in size from $< 40 \text{ \AA}$. to $250\text{--}1000 \text{ \AA}$. With increase in size of the crystals there is no appreciable change in the amount of H_2 that can be adsorbed by a given surface, but the rates of adsorption and of desorption of the H_2 are decreased. The sintering process is retarded by H_2 and other gases, but is accelerated by rise in temp. O. J. W.

Variable activity of catalytic surfaces. H. S. TAYLOR (Acta Physicochim. U.R.S.S., 1934, 1, 397—406).—Evidence for the non-uniformity of catalytic surfaces and the theory of activated adsorption are discussed. O. J. W.

Mechanism of adsorption catalysis. S. ROGINSKI (Acta Physicochim. U.R.S.S., 1934, 1, 651—684).—A general discussion of surface reactions (energy exchanges, activation energies, kinetics). O. J. W.

Heterogeneous catalysis. I. Activated adsorption of hydrogen by carbon. R. KLAR (Z. Elektrochem., 1935, 41, 457—458).—A criticism of recent work (cf. this vol., 696). E. S. H.

Activated adsorption of hydrogen on charcoal and its influence on the catalytic activity of charcoal. R. BURSTEIN and P. KASHTANOV (Acta Physicochim. U.R.S.S., 1934, 1, 465—472).—The rate of *ortho-para*- H_2 conversion on charcoal "poisoned" by activated adsorption of H at temp.

of 300° , 500° , and 700° is considerably decreased. The conversion at high temp. does not take place through an intermediate stage of activated adsorption, and the above-mentioned decrease in the rate is not due to a change in the van der Waals adsorption. The H atoms formed in the activated adsorption process are so tightly bound by the charcoal surface that they do not hydrogenate adsorbed C_2H_4 . O. J. W.

Catalysts for destructive hydrogenation. II. Kinetics of the hydrogenation of aromatic hydrocarbons on MoS_2 . L. ALTMANN and M. NEMTZOV (Acta Physicochim. U.R.S.S., 1934, 1, 429—448; cf. A., 1934, 609).—The hydrogenation of PhMe on MoS_2 at high pressures and temp. $> 460^\circ$ is of the first order with respect to H_2 and of zero order with respect to PhMe. For pressures of H_2 of 50—250 atm., $\log k = 6.87 + \log (P_{\text{H}_2} \times 273/T) - 5058/T$, where K = quantity of PhMe hydrogenated per min. for 1 kg. of MoS_2 . The apparent activation energy at $400\text{--}460^\circ$ is 23—100 g.-cal. The advantages of non-metallic catalysts for destructive hydrogenation are indicated. The velocity of hydrogenation for different hydrocarbons at 420° increases in the order $\text{C}_3\text{H}_6 < \text{C}_6\text{H}_3\text{Me}_3 < \text{C}_6\text{H}_4\text{Me}_2 < \text{PhMe} < \text{C}_{10}\text{H}_8$. O. J. W.

Mechanism of catalytic hydrogenation. O. SCHMIDT (Ber., 1935, 68, [B], 1098—1107).—In the hydrogenation of C_2H_4 in presence of Rb, Cs, Ca, Sr, or Ba, activation of H occurs through H^- at the surface, whereas in presence of Cr, Mn, Re, Fe, Co, Ni, Cu, Pd, or Pt it takes place through H^+ within the metal, in the metallic solution as a typically electrolytic process for which the energy of solvation of H^+ can be determined. The processes in this metallic solution depend on the heat of solvation of H^+ , the work of recession, and the ease of transition, $\text{R}^{++} \rightleftharpoons \text{R}^+$. The electrolytic dissociation process within the metal has no relationship to the nature of the surface or the presence of edges or points. The conceptions of "outer" and "inner" surfaces are here inapplicable by reason of the wide differences of the external and internal forces. Both H^- and H^+ can pass into H, for which the heat of solvation and, particularly, the differences in the heat of solvation at the outer surface and in the interior, are appreciably smaller. It depends on individual conditions whether hydrogenation occurs at the place where H ions are formed or where H atoms are produced.

In the reduction of PhNO_2 at Ag, Au, Pb, or Cu the primary action is the formation of PhNO^+ or PhN^+ and metallic oxide which is reduced by H. The mechanism of the change PhNO^+ or $\text{PhN}^+ \rightarrow \text{NH}_2\text{Ph}$ is unknown. A similar initial stage is probably found in the conversion of CO_2 or CO into CH_4 in presence of Ni or Co. H. W.

Dehydrogenation of succinic acid by charcoal. Model of the mode of reaction of succinodihydrase. B. TAMAMUSHI and H. UMEZAWA (Acta Phytochim., 1935, 8, 221—230).—The transformation of $(\text{CH}_2\text{CO}_2\text{H})_2$ (I) into fumaric acid (II) by O_2 or methylene-blue (III) is accelerated by animal charcoal or carboraffin, the ash and Fe in which appear responsible for the change. The reversibility of the change, $(\text{I}) + (\text{III}) \rightleftharpoons (\text{II}) + \text{leucomethylene-blue}$ is

established by the Thunberg-Quastel method, although equilibrium is only slowly attained and its position greatly displaced in the direction of oxidation. Charcoal behaves like an enfeebled succinodehydrase. The restrictive action of KCN, amyl alcohol, and $\text{O:C}_6\text{H}_4\text{:O}$ is similar in the model and biological reactions.

H. W.

Finely-divided metals [as catalysts and adsorbents] and a method for their preparation. E. G. INSLEY (J. Physical Chem., 1935, 33, 623—636).—A method of preparing finely-divided Cu, Co, Ni, and Fe from their amalgams is described. The adsorptive capacity for H_2 , C_2H_4 , and C_2H_6 , and the ability to promote hydrogenation of C_2H_4 shown by specimens prepared from amalgams are comparable with those shown by the same metals prepared by reduction of their oxides by H_2 at a low temp. The adsorption of H_2 by Ni between -80° and 150° has been measured.

F. L. U.

Reactivity of gaseous nickel carbonyl. S. S. URAZOWSKI and N. A. JAKIMKIN (Ukrain. Chem. J., 1935, 10, 44—50).—The reactions $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ and $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ are more powerfully catalysed by $\text{Ni}(\text{CO})_4$ at its decomp. temp. (150°) than by other Ni catalysts. The reaction $\text{CO} + \text{CH}_4 \rightarrow \text{MeCHO}$ is not catalysed by $\text{Ni}(\text{CO})_4$.

R. T.

Role of rhodium in increasing the resistance of platinum gauze. I. E. ADADUROV (Ukrain. Chem. J., 1935, 10, 106—117).—Corrosion of Pt used as catalyst in the reaction $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$ is associated with adsorption of H_2 , followed by its entrance into the space lattice. In general, metals with an edge-centred cubic lattice for which $a > 3.903 \text{ \AA}$. absorb H_2 , whilst those with $a < 4.070 \text{ \AA}$. do not. Abolition of absorption of H_2 without loss of catalytic power can be effected by using alloys of Pt with Rh or Ag, but not with Au.

R. T.

Preparation of platinum oxide catalyst from spent material. E. L. BALDESCHWIELER and L. A. MIKESKA (J. Amer. Chem. Soc., 1935, 57, 977—978).—A satisfactory Pt hydrogenation catalyst can be prepared from spent material by a modification of Wichers' purification method (A., 1921, ii, 648).

E. S. H.

Influence of the solvent on the velocity of decomposition of hydrogen peroxide by means of platinum. II. T. S. GLIKMAN (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1593—1598).—The velocity of decomp., v , of H_2O_2 in $\text{H}_2\text{O}-\text{COME}_2$ by platinised Pt is given by $v = 1/(k_1 + k_2c)$, where k_1 and k_2 are consts. and c = concn. of H_2O , vals. of v being observed under comparable conditions. v is negligible with 10—15% of H_2O and then increases with c . The reaction differs from that in $\text{H}_2\text{O}-\text{Et}_2\text{O}$ in the absence of a max. val. of v , and in the smaller influence of changes in c on v . Rotating the Pt plate does not influence v .

R. S. B.

Catalytic action of platinum and manganese dioxide on benzoyl peroxide and perbenzoic acid. F. I. BERESOVSKAJA and O. SEMICHATOVA (Bull. Acad. Sci. U.R.S.S., 1934, 7, 1583—1592).—Platinised and spongy Pt catalyse the decomp. of Bz_2O_2 and BzO_2H in Et_2O , but MnO_2 has no action on Bz_2O_2 and

is less effective than Pt with BzO_2H . It follows that reaction with Bz_2O_2 does not proceed by way of BzO_2H produced from Bz_2O_2 by hydrolysis, since no reaction occurs with MnO_2 and Bz_2O_2 even in presence of a little H_2O . The inability of MnO_2 to decompose Bz_2O_2 is discussed.

R. S. B.

Velocity of oxidation of ammonia at a platinum gauze. V. I. ATROSCHTSCHENKO (J. Appl. Chem. Russ., 1935, 8, 25—34).—Formulae connecting the time of contact with the Pt surface, temp., pressure, concn. of NH_3 , etc. are derived.

R. T.

Surface reactions at very low pressures. I. Platinum-chlorine. B. Reactions at the surface of the finely-divided metal. C. NOGAREDA (Anal. Fis. Quím., 1934, 32, 396—431).—Sublimed Pt at 0° adsorbs a unimol. layer of Cl_2 , which is stable up to 150° . When the film, at 0° , is brought in contact with Cl_2 activated by contact with Pt at temp. $> 200^\circ$, reaction occurs with formation of PtCl_4 , in accordance with the equation $-dp/dt = ap(p_0 - p)^n$, where p_0 is the initial pressure (0.02 mm.), and n varies between 0 and 1 according to the area of the film and its degree of saturation. The activation energy is 14—15 kg.-cal. The reaction does not progress beyond the surface layer. If the PtCl_4 film is reduced at 400° , the product requires an activation energy of about 18 kg.-cal., and the adsorptive power is about one half that of the sublimed Pt.

H. F. G.

Surface reactions at very low pressures. II. Platinum-bromine. C. NOGAREDA (Anal. Fis. Quím., 1934, 32, 567—589).— Br_2 mols. are dissociated by a Pt wire at $950-1250^\circ$, the energy of activation being 43,000 g.-cal. per mol. of dissociated Br. The results are in accord with a limiting adsorption mechanism. Above 1200° Br atoms attack the Pt yielding PtBr_2 and PtBr_4 , which condense on the walls of the vessel. A sublimed layer of Pt adsorbs a limiting unimol. Br_2 film at 0° , stable to 150° , but a wall coated with Pt and maintained at 0° is attacked superficially by Br. mols. when a wire in the reaction vessel is heated to 250° and yields a surface film of PtBr_4 which protects against further attack. The energy of activation of the reaction with sublimed Pt at $250-500^\circ$ is 14,000—16,000 g.-cal. Reduced Pt possesses about half the adsorptive power and reactivity of the same surface of a sublimed layer. The behaviour with such layers is attributed to a sintering of the sublimed Pt.

J. W. S.

Contact sulphuric acid manufacture. IV. Platinum catalyst on magnesium sulphate.—See B., 1935, 589.

Mechanism of the catalytic oxidation of CO on MnO_2 . J. ZELDOVITSCH (Acta Physicochim. U.R.S.S., 1934, 1, 449—464).—The adsorption of CO, of O_2 , and of CO_2 on finely-divided MnO_2 has been studied. All three gases show an instantaneous mol. adsorption, which for CO and O_2 is appreciable only below 0° . The heats of adsorption for this stage are 2600, 2300, and 5500 g.-cal. per mol. for CO, O_2 , and CO_2 , respectively. With CO there is a further slow activated or chemical adsorption, and for this stage the heat of adsorption agrees with the heat of

the reaction: $\text{MnO}_2 + \text{CO} = \text{MnO} + \text{CO}_2 + 41,000 \text{ g.-cal.}$ The heat of activation for the adsorption of CO on MnO_2 is 8000 g.-cal. The mechanism of the oxidation reaction is discussed. O. J. W.

Catalytic oxidation of carbon monoxide on manganese dioxide. S. ROGINSKI and J. ZELDOVITSCH (*Acta Physicochim. U.R.S.S.*, 1934, 1, 554—594; cf. preceding abstract).—More detailed data are given regarding the mol. adsorption of O_2 , CO, and CO_2 on MnO_2 , and of the activated adsorption of O_2 and CO. O. J. W.

Mechanism of catalytic oxidation of carbon monoxide. II. S. ROGINSKI and J. ZELDOVITSCH (*Acta Physicochim. U.R.S.S.*, 1934, 1, 595—610; cf. preceding abstracts).—The kinetics of the activated adsorption of CO on MnO_2 are described in more detail. The CO may be oxidised either by MnO_2 or by gaseous O_2 and both mechanisms are discussed. O. J. W.

Action of chlorine on [a mixture of coal and] titanium dioxide. A. V. PAMFILOV, A. S. CHUDJAKOV, and E. G. STANDEL (*J. pr. Chem.*, 1935, [ii], 142, 232—236).—The action proceeds most rapidly at 400—420°, using MnO_2 as catalyst. Approx. 80% of the Cl_2 is converted into TiCl_4 and 15% into COCl_2 . D. R. D.

Catalysts for oxidation of ammonia to oxides of nitrogen.—See B., 1935, 590.

Alumina as catalyst of hydrocyanic acid formation [from carbon monoxide and ammonia].—See B., 1935, 589.

Zinc oxide-chromium oxide catalysts for methyl alcohol synthesis.—See B., 1935, 583.

Catalytic oxidation of ethyl alcohol.—See B., 1935, 584.

Influence of crystalline addenda on the decomposition temperature of carbonates. B. SREBROW (*Kolloid-Z.*, 1935, 71, 293—297).—The decomp. temp. of MnCO_3 , NiCO_3 , CoCO_3 , ZnCO_3 , CdCO_3 , and PbCO_3 are lowered by addition of the oxides of Mn, Fe, Co, Ni, Mg, etc. The observations are similar to those of Balarev and Lukova (*A.*, 1930, 1110) for the decomp. of CaCO_3 . E. S. H.

Comparison of the polymerising and adsorptive powers of silicates. J. M. SLOBODIN (*J. Appl. Chem. Russ.*, 1935, 8, 35—43).— SiO_2 gel and silicates (floridin, kaolin, and various clays) activated at < 200° or at > 600° do not catalyse polymerisation of isobutylene. The adsorptive properties of the silicates are unaffected by temp. > 650°. R. T.

Electrolytic reduction of oxygen to hydrogen peroxide. E. MULLER and K. MEHLHORN (*Z. anorg. Chem.*, 1935, 223, 199—203).—An apparatus for the electrolytic reduction of O_2 to H_2O_2 is described. A 3% solution of H_2O_2 was obtained with a 50% efficiency. M. S. B.

Anodic behaviour of tin in electrolysis in sodium stannate solution. G. HANSEL [with A. GREVEL] (*Z. Elektrochem.*, 1935, 41, 314—321).—Measurements of the anode potential of Sn during electrolysis of Na stannate solutions are recorded.

The c.d., temp., [Na stannate], and [NaOH] were varied. A compact and satisfactory cathode deposit is obtained when a film of SnO_2 is preformed on the anode, and when the latter dissolves directly as Sn^{++++} . Procedure for realising these conditions is described. F. L. U.

Electrolysis of aqueous solutions of ammonium chloride. F. JIRSA (*Z. Elektrochem.*, 1935, 41, 321—330).—Over a wide range of concn. and of c.d. the end-product in the anolyte is NH_4Cl_2 , formed by the action of Cl_2 on the NH_4Cl produced at first. The order of increasing efficiency of the anode material is graphite < Fe_3O_4 < Pt. Solutions containing NH_3 give a lower yield. Very little NH_4Cl_2 is formed unless a diaphragm is used. NCl_3 is produced only in conc. solutions at 35—40° and at low c.d., when the liquid is unstirred. F. L. U.

Titanium alum. J. MEYER and H. MEISSNER (*J. pr. Chem.*, 1935, [ii], 143, 70—81).—The prep. and electrolytic reduction of $\text{Ti}(\text{SO}_4)_2$ are described. A Hg or Pb cathode gives the best result. Pt catalyses the change $\text{Ti}^{+++} \rightarrow \text{Ti}^{++++}$. The influence of different $[\text{H}_2\text{SO}_4]$ on the stability of $\text{Ti}_2(\text{SO}_4)_3$ has been studied. Autoxidation occurs when $[\text{H}_2\text{SO}_4]$ is small. $\text{CsTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ has been prepared by addition of aq. $\text{Ti}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$ to aq. Cs_2SO_4 in an atm. of CO_2 . Pure $\text{RbTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ could not be obtained, and attempts to prepare K Ti, NH_4 Ti, and Tl Ti alums (I) failed. It is suggested that in stable alums the ratio M'/M^{+++} lies between 2 and 3, whereas in (I) M'/M^{+++} is < 2. R. S.

Anode effect in the electrolysis of melts. II. H. VON WARTENBURG and G. WEHNER (*Z. Elektrochem.*, 1935, 41, 448—450; cf. A., 1926, 912; 1928, 371).—The anode effect previously described is not electrical in origin, but is due to alteration of the interfacial tension at the electrode-melt boundary by the presence of oxide. E. S. H.

Preparation of cerium by electrolysis of its fused salts. S. I. SKLJARENKO and J. P. VIRSKI (*J. Appl. Chem. Russ.*, 1935, 8, 44—48).—Ce is obtained by a modification of Billy and Trombe's method (A., 1933, 1253). R. T.

Electrochemical preparation of aluminium oxide from aqueous aluminium sulphate. V. PLOTNIKOV, D. ZOSIMOVITSCH, O. KUDRA, and I. PODORVAN (*Mem. Inst. Chem. All-Ukrain. Acad. Sci.*, 1935, 1, 251—267).— $\text{Al}(\text{OH})_3$ containing 2% of SO_3 is obtained in 108% yield (on current) by electrolysis of 10% aq. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ containing 1% of $(\text{NH}_4)_2\text{SO}_4$ (150 min.; 30°; 0.5 amp., 5.5 volts), when the vol. of anolyte is 6 times that of the cathode. The final $[\text{H}_2\text{SO}_4]$ of the anolyte is raised to 23% by interposing two diaphragms between the electrodes. R. T.

Electrochemical study of the system $\text{AlBr}_3\text{—KBr}$ in ethyl bromide. V. A. PLOTNIKOV and S. I. JAKUBSON (*J. Gen. Chem. Russ.*, 1935, 5, 224—226).—Cryst. Al is deposited at the cathode, and Br is liberated at the anode; the decomp. potential is 2.02 volts. R. T.

Effect of chemical reactions on the cathode and anode in an arc discharge. A. VON ENGEL (*Naturwiss.*, 1935, 23, 305—306).—The calculation

of the temp. of a metal anode in an arc discharge is outlined. The effect of chemical reaction between the anode and the gas in which the arc is struck on the heat-resistance of the anode is discussed.

A. J. M.

Heterogeneous chemical reactions in the silent electric discharge. XIII. Reactions between hydrogen and solid inorganic compounds. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1935, 10, 199—204).— H_2SeO_3 yields Se; H_2SeO_4 yields H_2SeO_3 and Se; $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$ yields Na_2SeO_3 and Se; H_2TeO_3 yields Te; Na_2TeO_3 yields Te and NaOH; $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ yields Te and H_2TeO_3 ; $\text{K}_2\text{S}_2\text{O}_3$ yields K_2SO_3 , H_2S , and S; Ag_2CO_3 yields Ag and CO_2 ; $\text{LiClO}_3 \cdot 0.5\text{H}_2\text{O}$ yields LiCl; and NaBrO₃ yields NaBr.

J. W. S.

Catalytic influence of mercury vapour on the cracking of methane by the glow discharge. N. I. KOBOZEV, S. S. VASILIEV, and E. E. GALBRAITH (Compt. rend. Acad. Sci. U.S.S.R., 1935, 2, 235—243).—With electrodes of Al, Cu, Zn, Pb, or Fe about 1.5% of CH_4 is transformed by the glow discharge into ethylenic and acetylenic compounds. Under the same conditions but with Hg electrodes the conversion is 5.2%, increased to 14% by use of intermediate Hg electrodes or by warming the latter. Dissolution of Na in the Hg annihilates the change. The effect is ascribed to activation of the Hg vapour from which the energy is transferred to the CH_4 mols.

H. W.

Photochemical effect of nitrogen dioxide on the combination of hydrogen and oxygen. M. MIYANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 47—51).— H_2O is produced when the mixture $2\text{H}_2 + \text{O}_2 + \text{NO}_2$ is illuminated with monochromatic light in the region 2000—4000 Å. R. S.

Decomposition of hydrogen peroxide by the irradiation of its aqueous solution with X-rays. H. FRICKE (J. Chem. Physics, 1935, 3, 364—365).—The reaction is $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$; no detectable H_2 is formed. For the concn. range 0.0001—0.1 mols. per litre and X-ray intensities 3—15r per sec., the no. of mols. decomposed per unit dosage $\propto \sqrt{(\text{concn.}/\text{X-ray intensity})}$. The temp. coeff. rises with temp. Data are compared with results for the decomp. of H_2O_2 by light, and indicate that the primary process is the activation of H_2O mols. followed by the transfer of energy to the H_2O_2 .

N. M. B.

Photosynthesis of hydrogen chloride. J. C. POTTS and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1935, 57, 1027—1032).—Experiments over the range 140—300° abs. show that at room temp. the rate law of Bodenstein and Unger (A., 1931, 319) is valid, save for a small correction for an inhibiting action by the HCl formed. At temp. below 172° abs. the rate depends on the $\sqrt{(\text{light absorbed})}$. The temp. coeff. of the reaction has been determined at room temp. and at lower temp.

E. S. H.

Photochemical reactions of adsorbed iodine molecules. A. TERENIN (Acta Physicochim. U.R.S.S., 1934, 1, 407—428).—The discoloration by the action of light of a layer of I_2 adsorbed on TlI is attributed to the photodissociation of the adsorbed

I_2 mols. The liberated I atoms are then bound by Tl^+ ions. The max. discoloration is produced by light of about 5600 Å. The presence of adsorbed H_2 or O_2 mols. on the surface causes marked shifts of the active wave-lengths, but N_2 has no effect. This is ascribed to photochemical reactions between adsorbed I_2 and H_2 or O_2 , with the formation of HI and of I oxide, respectively. The absorption spectrum and potential energy diagram of I_2 in the adsorbed state are discussed.

O. J. W.

Oxidation of the nitrite to the nitrate ion by the irradiation of its aqueous solutions with X-rays. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 365).—The amount of NO_2^- oxidised is independent of the concn. and of the p_{H} . The transformation is due to H_2O mols. activated by X-rays, according to $\text{NO}_2^- + (\text{H}_2\text{O})_{\text{act.}} = \text{NO}_3^- + \text{H}_2$.

N. M. B.

Mercury-photosensitised polymerisation of acetylene and acetylene- d_2 . J. C. JUNGERS and H. S. TAYLOR (J. Chem. Physics, 1935, 3, 338—340).—The rate of reaction is 30% greater with C_2H_2 than with C_2D_2 for the pressure range 0.1—4 cm. At low pressures the rate \propto pressure, but in the range 0.7—4 cm. is independent of the pressure and is determined by the intensity of the absorbed resonance radiation. The quantum yield is approx. 6.5 for C_2H_2 and 5 for C_2D_2 < the yield for C_2H_2 at the same temp. in the photochemical reaction.

N. M. B.

Discoloration of silver iodide by aqueous ammonia. W. LANGE (Z. anorg. Chem., 1935, 223, 174—176).—By treatment with 5.34—30.7% aq. NH_3 , AgI forms a white compound $\text{AgI} \cdot 0.5\text{NH}_3$. It turns deep violet on exposure to light, evolves NH_3 on keeping, and has the same composition as the ammine obtained by the action of gaseous NH_3 on AgI.

M. S. B.

Action of aqueous solutions on photographic latent images of varying ages. C. JAUSERAN (Compt. rend., 1935, 200, 2076—2078).—Data are recorded for changes in density of the image with varying times between exposure and development. Immersion in H_2O , aq. Na_2CO_3 , aq. Na_2SO_3 , or a desensitising solution between exposure and development arrests development of the latent image if the time is not too long.

H. J. E.

Density surface of [a solid diagram representing] the Villard effect. III. H. ARENS (Z. wiss. Phot., 1935, 34, 125—135; cf. A., 1934, 374).—The density surfaces have been determined, and are illustrated, for a fine-grain and a large-grain unsensitised normal emulsion. The results produced by pre-exposure to X-rays, followed by various white light exposures, are compared with the theoretical "additive" results. At low intensities of the white light the actual densities, with the fine-grain emulsion, are > the additive figure, whereas at high intensities they are lower; the positions of the solarisations are also abnormal.

J. L.

Polymerisation of deuterio-acetylene by alpha-rays. S. C. LIND, J. C. JUNGERS, and C. H. SCHIFFLETT (J. Amer. Chem. Soc., 1935, 57, 1032—1034).—The no. of mols. polymerised per ion pair is the same for C_2H_2 and C_2D_2 .

E. S. H.

Chemical action produced by alpha-particles : combination of deuterium and oxygen. S. C. LIND and C. H. SCHIFFLETT (J. Amer. Chem. Soc., 1935, 57, 1051—1052).—The rate of combination of O_2 with D_2 is 25—30% < with H_2 . E. S. H.

Increase of chemical reactivity during phase changes in solid substances. J. A. HEDVALL (Z. Elektrochem., 1935, 41, 445—448).—Mainly a discussion of published work (cf. this vol., 589). E. S. H.

Recombination of hydrogen atoms in presence of hydrogen chloride. W. H. RODEBUSH and M. L. SPEALMAN (J. Amer. Chem. Soc., 1935, 57, 1040—1043).—The recombination appears to be due to the reaction $H + HCl = H_2 + Cl$ (i) followed by the rapid reaction $H + Cl = HCl$ (ii). (i) probably takes place in the gas phase and on the walls, whilst (ii) occurs on the walls only. E. S. H.

Concentration of the heavier isotope in carbohydrates. T. TITANI and M. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 205; cf. this vol., 458).— H_2O obtained by combustion of cane- and of beet-sugar is respectively 7.4 and 6.5 p.p.m. heavier than normal H_2O . H_2O from the combustion of substances consisting principally of glucose, lactose, starch, dextrin, galactose, mannose, or cellulose averages 6 p.p.m. heavier than normal H_2O . J. W. S.

Stability of hydrogen peroxide solution.—See B., 1935, 628.

Action of water on anhydrous sodium metaphosphates. A. BOULLE (Compt. rend., 1935, 200, 1403—1405; cf. this vol., 571, 591).—Action of H_2O on metaphosphate A' yields a solution of trimetaphosphate A (I) and a residue of an insol. product (metaphosphate B_1) which has X-ray structure identical with that of metaphosphate B (II), but passes slowly into colloidal solution, whereas (II) slowly yields a solution of (I). Evaporation of aq. (I), after boiling under reflux for several days, yields NaH_2PO_4 . A solution of metaphosphate C redeposits the same amorphous form. J. W. S.

Purification and preservation of sodium and potassium in the silvery state. I. I. PRUNDEANU (Bul. Chim. Soc. Romane, 1934, 37, 141—142).—The metal is melted under pure light petroleum, stirred to remove surface crusts and produce bright globules, cooled, and transferred to melted paraffin wax for preservation. A. R. P.

Silver-mercuric complex. J. BOUGAULT and E. CATTELAINE (Bull. Soc. chim., 1935, [v], 2, 996—1000).—The prep., properties, and analysis of $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$ are described. It loses $2H_2O$ above 100° . CN' was determined by oxidation to CNO' with $KMnO_4$ and the N liberated as NH_3 by H_2SO_4 , whilst the NO_3' was obtained as NH_3 by reduction with Devarda's alloy. R. S.

Active oxides. LXXXV. Intermediate steps in the transformation of a mixture of magnesium oxide and chromic oxide into magnesium chromite. T. MEYER and G. F. HUTTIG [with O. HNEVKOVSKY and H. KITTEL] (Z. Elektrochem., 1935, 41, 429—435; cf. this vol., 440).—Measurements

of d , the catalytic influence on the decomp. of N_2O , and magnetic susceptibility, and X-ray examination confirm the existence of active, intermediate states. E. S. H.

Formation of hydrogen carbonates in the system $CaCO_3-H_2O-CO_2-K_2SO_4$. A. P. BUNTIN and M. M. BIKOV (J. Appl. Chem. Russ., 1935, 8, 19—24).—The formation of H carbonates in the system $CaCO_3-H_2O-CO_2$ is augmented by adding K_2SO_4 , as a result of the reaction $Ca(HCO_3)_2 + K_2SO_4 \rightarrow 2KHCO_3 + CaSO_4$, which shifts the equilibrium of the reaction $CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$. R. T.

Preparation of phosphorescent zinc sulphide. N. Z. ANDREEV (J. Appl. Chem. Russ., 1935, 8, 49—51).—ZnS is pptd. from aq. $ZnSO_4$ containing KOAc and AcOH, at 75° , the suspension is boiled, an equal vol. of cold 1.5% NaCl is added, the ppt. is collected, dried, and heated at 900° with traces of $CaCl_2$, $BaCl_2$, $MgCl_2$, Na_2WO_4 , and In (or Cs, Rb, Os, Tl, U, or Th). R. T.

Reactions in the solid state at high temperatures. XII. W. JANDER and K. F. WEITENDORF (Z. Elektrochem., 1935, 41, 435—444; cf. A., 1934, 741).—The reaction between ZnO and Cr_2O_3 has been studied by measurements of the sp. vol., catalytic effect on the decomp. of CH_4 , solubility in HCl and H_2SO_4 , sorption of methylene-blue and fuchsin, electrical conductivity, and X-ray structure. The existence of intermediate stages before the formation of $ZnCr_2O_4$ has been established. E. S. H.

Complex compounds of 2:4:6-triamino-toluene. F. HEIN and F. WAGNER (Ber., 1935, 68, [B], 1116—1122).—By treatment of the requisite salt with a slight excess of 2:4:6- $C_6H_2Me(NH_2)_3$ (=R) in absence of H_2O the following complex salts are obtained: $CdI_2 \cdot R \cdot 0.5COMe_2$; $ZnCl_2 \cdot 2R$; $CdBr_2 \cdot 2\frac{1}{2}R \cdot 0.5COMe_2$; $HgCl_2 \cdot R \cdot 0.25COMe_2$; $2ZnCl_2 \cdot 2\frac{1}{2}R \cdot 2COMe_2$; $SbCl_3 \cdot 2\frac{1}{2}R \cdot 0.5EtOH$; $SbCl_3 \cdot 2\frac{1}{2}R \cdot \frac{1}{3}CHCl_3$; $3HgCl_2 \cdot 3\frac{1}{2}R$; $CoCl_2 \cdot 5R \cdot COMe_2$; $FeCl_2 \cdot FeCl_3 \cdot 5\frac{1}{2}R \cdot 2COMe_2$; $2[(CrCl_2OEt)_3 \cdot CrCl(OEt)_2 \cdot 2COMe_2] \cdot 5R$. The presence of fractions of a mol. of base is simply explained by the assumption that all three NH_2 groups of an individual mol. are involved in the complex union. H. W.

Dry purification of mercury. ZIENER (Glas u. App., 1934, 15, 187—189; Chem. Zentr., 1935, i, 540).—The Hg is treated in a 1—1.5-litre flask first at room temp. and then at $100—105^\circ$ with an airstream. Hg vapour is subsequently removed from the cooled air stream by active C containing I. H. J. E.

Behaviour of mercuric cyanide towards bases. F. REIFF, P. POHLS, and W. OVERBECK (Z. anorg. Chem., 1935, 223, 113—120).— $Hg(CN)_2$ dissolves in conc. aq. KOH; transport measurements indicate the existence of a complex anion containing Hg and confirm Hofmann's formula for the hydroxy-salt $[Hg(CN)_2OH]K \cdot H_2O$. The free acid is not present in aq. $Hg(CN)_2$ and there is no salt formation with insol. or slightly sol. metal hydroxides or with aq. NH_3 . Salts of NMe_4OH , C_5H_5N , and dioxan, corresponding with the K salt, have been prepared. Transport measurements also show that $CN \cdot Hg \cdot OH$ is not a hydroxy-salt of the composition $[Hg(CN)_2(OH)_2]Hg$,

but it forms the ions $(\text{HgCN})^+$ and OH^- . The formation of the compound $[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]\text{HgCN}$ with Reinecke's salt confirms the existence of the complex cation. M. S. B.

Preparation, analysis, and qualitative study of $\text{HgSO}_4 \cdot 2\text{HgS}$. G. L. CHABORSKI and E. POTAMIAN (Bul. Chim. Soc. Romane, 1934, 37, 153—164).—Digestion of HgS with conc. H_2SO_4 at 145° affords white $\text{HgSO}_4 \cdot 2\text{HgS}$ after washing and drying at 130° . Alkalis extract the SO_4^{2-} , halogen acids convert it into yellow compounds which redden on heating, and BaCl_2 gives a mixture of HgS and BaSO_4 . Methods of analysis are described.

A. R. P.

Complex compounds of mercuric cyanide. R. UZEL (Coll. Czech. Chem. Comm., 1935, 7, 159—182).—The prep. of compounds $\text{M}(\text{NH}_3)_4[\text{Hg}(\text{CN})_2\text{X}]_2$ ($\text{M}=\text{Cu, Zn, Cd, Ni}$, and $\text{X}=\text{Br, I, CNS, N}_3$), of $\text{Cu en}_2[\text{Hg}(\text{CN})_2\text{X}]_2$, and of $\text{Men}_3[\text{Hg}(\text{CN})_2\text{I}_2]$ ($\text{M}=\text{Zn, Cd, Ni}$) is described. The formation of the sparingly sol. salts of the last type is characteristic of iodides. Zn can be determined gravimetrically as $\text{Zn}(\text{NH}_3)_4[\text{Hg}(\text{CN})_2\text{I}]_2$.

O. J. W.

Thermal decomposition of aluminium nitrate. A. A. JAKOVKIN, S. S. MARKOV, and E. A. KREMLEVA (J. Appl. Chem. Russ., 1935, 8, 212—220).—The non-fusible salt, $\text{Al}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$, crystallises from aq. basic Al nitrate (I) at 140° ; the salt $3\text{Al}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ is obtained by heating (I) in a current of air at 200° , or in presence of HNO_3 vapours at 225° . (I), when heated, evolves H_2O and HNO_3 vapours in the proportion 6:1 at $< 225^\circ$, and chiefly the latter at higher temp. At 318° decomp. is complete after 6 hr., the residue corresponding with $\text{AlO}(\text{OH})$, and containing 15% of H_2O , whilst at 340° it contains 9.41% H_2O and 1.29% of N_2O_5 .

R. T.

Surface chemistry of tin. A. KUTZELNIGG (Z. Elektrochem., 1935, 41, 450—453).—Sn containing Sb is coloured black by aq. FeCl_3 ; a residue is obtained after dissolution in conc. HCl . 0.1% Sb in Sn can be detected by this method. The presence of 0.01% Sb accelerates the dissolution of Sn in hot, conc. HCl , whilst Bi retards it. Sn is readily dissolved by alcoholic I. Evidence for the existence of an oxide film on Sn is adduced.

E. S. H.

Decomposition of tin dioxide, insoluble sulphates, and the corresponding minerals. G. L. CHABORSKI and D. PIRTEA (Bul. Chim. Soc. Romane, 1934, 37, 129—132).— SnO_2 is reduced to Sn and PbSO_4 to PbS by heating in NH_3 at $700\text{--}800^\circ$. CaSO_4 , SrSO_4 , and BaSO_4 may be similarly reduced to the corresponding sulphides at $> 1000^\circ$, the ease of reduction decreasing in the order given.

A. R. P.

Chemical reactions with active nitrogen (formation of mercurous nitride, gallium nitride, and reactions with amalgams). E. TIEDE and H. G. KNOBLAUCH (Ber., 1935, 68, [B], 1149—1154).— Hg^{I} nitride is produced by the action of active N on cold, well-agitated Hg. Unless special precautions are taken, the trace of O necessary for activation of N gives rise to O_3 , causing production of HgO . Molten Ga also yields a nitride which differs from Ga_3N_2 , since

it is attacked by H_2O and loses N at $150^\circ/1$ atm. Amalgams of K, Na, Pb, Zn, Sn, or Cd (1%) yield exclusively nitride, only the Hg entering into reaction. With Na-Hg (85% = Na) production of azide in addition to nitride is observed. Li-Hg with mol. or active N gives only nitride. K-Na (5:1) gives azide and nitride.

H. W.

Red ammonium chloride. F. PAVELKA (Kolloid-Z., 1935, 71, 291—292).—The red crystals of NH_4Cl , obtained by crystallisation of solutions containing NH_4Cl and FeCl_3 , contain FeCl_3 , which is taken up in accordance with the adsorption isotherm. The colour varies more with the size of the crystals than with the FeCl_3 content.

E. S. H.

Mechanism of the action of liquid ammonia on phosphorus pentachloride. H. MOUREU and P. ROCQUET (Compt. rend., 1935, 200, 1407—1410; cf. A., 1934, 158).—Action of excess of liquid NH_3 on PCl_5 in a vac. yields a product with a dissociation pressure at 0° of 1036 mm., equal to that of $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$. After the removal of this NH_3 the pressure falls to 300 mm. From the vols. of NH_3 removed under the two conditions it is concluded that the primary reaction is $\text{PCl}_5 + 10\text{NH}_3 = 5\text{NH}_4\text{Cl} + \text{P}(\text{NH}_2)_5$, and that below 300 mm. at 0° the $\text{P}(\text{NH}_2)_5$ decomposes irreversibly yielding PN_3H_4 , which polymerises as produced and at 400° and 0.1 mm. yields PN_2H .

J. W. S.

Hydrogen diarsenide: As_2H_2 . E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1020—1024).—The prep. and properties of As_2H_2 are described and the rate of decomp. has been investigated. Decomp. is complete after 15 days' exposure to the air in the dark.

R. S.

Precipitation of protoactinium with titanium. (Mlle.) H. ZAVIZZIANO (Compt. rend., 1935, 200, 1843—1845).—Pa is pptd. almost quantitatively with Ti by hydrolysis of slightly acid $\text{Ti}(\text{SO}_4)_2$ solution. Details are given for the separation of Pa from a mineral by this method.

H. J. E.

Technical extraction of protoactinium.—See B., 1935, 590.

Complexity of the reaction between ozone and potassium iodide. J. GUERON and M. PRETTE (Compt. rend., 1935, 200, 2084—2086).—Action of O_3 on aq. KI, buffered to p_H 7, forms I and KIO_3 , the latter liberating equiv. I on acidification before titrating with $\text{Na}_2\text{S}_2\text{O}_3$. When 5% ozonised O_2 is passed into conc. aq. KI through a sintered glass plate, only KIO_3 is formed.

H. J. E.

[Formula of] hydrofluoric acid. H. MULLER (Compt. rend., 1935, 200, 2080—2082; cf. A., 1932, 691; this vol., 824).—From the lowering of the eutectic temp. for the ice- KNO_3 system, the formula is HF and not H_2F_2 . With KF, HF, the complex ion HF_2^- is formed in conc. solution. Cornec's method (A., 1913, ii, 840) was applied in studying the neutralisation of HF by KOH.

H. J. E.

Origin of polyhalides and polysulphides. M. M. PLATONOV (Ukrain. Chem. J., 1935, 10, 51—56).—Poly-halides and -sulphides are represented as anhydrides in which O is replaced by S or by X_2 .

R. T.

Oxides of manganese. Structure of mixed crystals. P. DUBOIS (Diss., Paris, 1935).—All methods of prep. yield the same form of MnO , identical with manganosite. Mn_3O_4 , prepared by thermal decomp. of Mn^{II} salts, has a crystal structure identical with that of hausmannite. $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, identical in structure with manganite, can be obtained by oxidation of MnSO_4 with H_2O_2 in alkaline solution. At 300° in air it yields MnO_2 and in a vac. $\alpha\text{-Mn}_2\text{O}_3$, which is converted into the normal form, $\beta\text{-Mn}_2\text{O}_3$, at 600° . $\beta\text{-Mn}_2\text{O}_3$ has the same structure as braunite. Thermal decomp. of $\text{Mn}(\text{NO}_3)_2$ or oxidation of $\alpha\text{-Mn}_2\text{O}_3$ in warm air yields the anhyd. $\beta\text{-MnO}_2$, identical with pyrolusite. It decomposes at $550\text{--}600^\circ$, yielding $\beta\text{-Mn}_2\text{O}_3$. The spontaneous decomp. of HMnO_4 , and reduction of KMnO_4 by MnSO_4 or H_2O_2 , yield highly hydrated $\alpha\text{-MnO}_2$, which is always associated with $\alpha\text{-Mn}_2\text{O}_3$ or $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and which loses H_2O progressively up to 500° and O_2 between 250° . No individual hydrate could be identified. At 500° it gives impure $\beta\text{-MnO}_2$. Thermal decomp. of Mn^{II} salts gives a mixture of $\beta\text{-MnO}_2$ and $\alpha\text{-Mn}_2\text{O}_3$. On addition of KMnO_4 to MnSO_4 under certain conditions a product is obtained of composition $\text{MnO}_{1.87}$, of distinct crystal structure similar to that of the product of decomp. of $\alpha\text{-MnO}_2$ in a sealed tube at 400° , suggesting the existence of an oxide between Mn_2O_3 and MnO_2 . Other products intermediate in composition are mixtures or adsorption complexes. The irreversibility of the reaction $4\text{MnO}_2 = 2\text{Mn}_2\text{O}_3 + \text{O}_2$ above 500° is attributed to transition into the β -forms which are non-reactive.

J. W. S.

New complex compound. N. A. TANANAEV (Ukrain. Chem. J., 1935, 10, 19—21).—A reddish-brown ppt. of $\text{Mn}(\text{AgHgC}_2\text{O}_4)_3$ (I) is obtained when an acid solution of Mn, Ag, and Hg nitrates is added to aq. $\text{H}_2\text{C}_2\text{O}_4$. (I) yields Mn^{++} , Hg^{++} , AgCl , and Hg-Ag with HCl , and Mn^{++} , MnO_3^{--} , Hg^{++} , $\text{Ag}(\text{NH}_3)_2^+$, and Hg-Ag with aq. NH_3 .

R. T.

Double salts of rhenium trichloride with rubidium and caesium chloride. W. GEILMANN and W. WRIGGE (Z. anorg. Chem., 1935, 223, 144—148).—The prep. of the insol. salts RbReCl_4 and CsReCl_4 , formed in the microchemical detection of Re, is described. Their composition (cf. Noddack, A., 1934, 44) has been confirmed. They are decomposed by heat into M_2ReCl_6 , Re, and ReCl_3 . K forms a sol. salt of corresponding formula.

M. S. B.

Amorphous and crystallised hydrated oxides and oxides. XXI. $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, goethite or needle ironstone, and the conversion of $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ into $\alpha\text{-Fe}_2\text{O}_3$. A. KRAUSE (Z. Elektrochem., 1935, 41, 337—339; cf. A., 1934, 1083).—The name goethite should be retained for $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ whether natural or artificial. Needle ironstone is also suitable for the former, but not for the latter. When goethite prepared from orthoferriic hydroxide (I) is heated at 300° it becomes almost completely sol. in $1.4N\text{-H}_2\text{SO}_4$. Further heating either of this product or of (I) at 800° greatly reduces the solubility. It is inferred that a sol. amorphous product is formed as an intermediate stage in the conversion of $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ into $\alpha\text{-Fe}_2\text{O}_3$.

F. L. U.

$[\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}]$, goethite or needle ironstone, and the conversion of $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ into $\alpha\text{-Fe}_2\text{O}_3$.] R. FRICKE (Z. Elektrochem., 1935, 41, 340; cf. A., 1934, 1083, and preceding abstract).—X-Ray examination of partly converted $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ indicates, not a mixture of amorphous and cryst. oxide, but a broken lattice with normal distance between the lattice planes.

F. L. U.

Complex iron thiocyanates with pyridine. O. BINDER and P. SPACU (Compt. rend., 1935, 200, 1405—1407).— $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_3(\text{CNS})_3]$ (I) and the black and yellow forms of $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2]$ (II) all have characteristic X-ray spectra. It is suggested that the yellow form of (II) is the *trans*- and the black form the *cis*-modification. Rosenheim's salt (A., 1932, 1009) is a mixture of (I) and small quantities of (II).

J. W. S.

Cobalto-complexes. J. V. DUBSKY (Z. anorg. Chem., 1935, 223, 197—198).—The action of piperazine on CoCl_2 affords a blue cryst. compound which is not a tetrahalogen salt, as previously supposed, but is $[\text{CoCl}_6]\text{H}_4\text{piperazine}$. The compound with piperazinodiethyleneamine is similar.

M. S. B.

Complex amines of fluoboric acid. G. SPACU and L. DRMA (Z. anorg. Chem., 1935, 223, 185—191).—The following cryst. compounds have been prepared: $[\text{Co en}_2]\text{BF}_4$, $[\text{Co en}_2(\text{NO}_2)_2]\text{BF}_4$, $[\text{Cd en}_3](\text{BF}_4)_2$, $[\text{Ni en}_3](\text{BF}_4)_2$, $[\text{Hg en}_2](\text{BF}_4)_2$, $[\text{Zn en}_3](\text{BF}_4)_2$, $[\text{Mn en}_3](\text{BF}_4)_2$, $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_4](\text{BF}_4)_2$, $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$, $[\text{Hg}(\text{C}_5\text{H}_5\text{N})_2](\text{BF}_4)_2$, $[\text{Co}(\text{C}_5\text{H}_5\text{N})_4](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$, $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$, $[\text{Mn}(\text{C}_5\text{H}_5\text{N})_2](\text{BF}_4)_2$, $[\text{Cd bzd}_3](\text{BF}_4)_3$, $[\text{en}=(\text{CH}_2\text{NH}_2)_2]$; $\text{bzd}=(\text{C}_6\text{H}_4\text{NH}_2)_2$. All but the last are sol. in H_2O .

M. S. B.

Triethylenediaminecobaltic salts with mixed anions. K. HOEHNE (J. pr. Chem., 1935, [ii], 143, 90—93).—The following compounds have been prepared: $[\text{Co en}_3]\text{Cl}_3$, $\text{CoCl}_2 \cdot \text{H}_2\text{O}$, green crystals; $[\text{Co en}_3]\text{NO}_2\text{Cl}_2$, $\text{CoCl}_2 \cdot \text{H}_2\text{O}$, reddish grey-brown plates, which give the dihydrate on exposure to the atm.; $[\text{Co en}_3]\text{NO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, reddish-yellow crystals. R. S.

Rhodium hydroxopentammines. B. E. DIXON (J.C.S., 1935, 779—781).—Rh forms the complex salts $[\text{Rh}(\text{NH}_3)_5\text{OH}]\text{Br}_2 \cdot \text{H}_2\text{O}$, $[\text{Rh}(\text{NH}_3)_5\text{OH}](\text{NO}_3)_2$, and $[\text{Rh}(\text{NH}_3)_5\text{OH}]\text{SO}_4 \cdot 2\text{H}_2\text{O}$, which strongly resemble the corresponding Ir compounds (cf. A., 1934, 267). They resemble the pentammine rather than the hexammine type in their behaviour towards sp. ammine reagents.

O. J. W.

Trichlorides of iridium^{III}-aquo-dipyridines. M. DELÉPINE (Compt. rend., 1935, 200, 1373—1375).—On heating an aq. solution of *cis*-pyridino- $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4]\text{M}$ (M=metal) at 130° for 1 hr. considerable decomp. occurs into the compound $[\text{Ir}(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ (I). *trans*- $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4]\text{M}$ gives the compounds $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_3]$ and $[\text{Ir}(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_3] \cdot \text{H}_2\text{O}$ (II), forming an orange-red aq. solution. (I) and (II) dissolve easily in NH_3 . NaOH and KOH solutions containing excess of alkali deposit salts of $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{OH})\text{Cl}_3]\text{H}$, but addition of acid reproduces the original complexes. On dehydration at $140\text{--}145^\circ$, (I) and (II) lose their H_2O of crystallisation and composition and are no longer sol.

in alkali. They combine with AgNO_3 in neutral or alkaline solution to form the sparingly sol. compounds $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2(\text{OH})\text{Cl}_3]_2\text{HAg}$, and in acid solution to form the compounds $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_3\text{NO}_3]\text{Ag}\cdot\text{H}_2\text{O}$, of which the product from (I) loses its H_2O on drying at $105\text{--}110^\circ$. The product from (II), on treatment with KCl , yields (II) and KNO_3 . (II) on oxidation with HCl-HNO_3 gives $\text{Ir}^{\text{IV}}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$, which on reduction regenerates $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4]\text{C}_5\text{H}_5\text{NH}$.

J. W. S.

Constitution of the heteropoly-acids. G. ELSTNER (Angew. Chem., 1935, 48, 343—347).—A review.

E. S. H.

Identification of artificial radioactive elements produced by neutron bombardment, and their application in chemistry as indicators. O. ERBACHER and K. PHILIPP (Angew. Chem., 1935, 48, 409—414).—Chemical and physical methods of identifying artificial radioactive elements are summarised.

A. J. M.

Rapid spectroscopic determination of metals. II. Comparator for the intensity of spectrum lines. A. P. SNESSAREV, N. N. ROSANOV, and P. J. ASSOSKOV (J. pr. Chem., 1935, [ii], 142, 237—242).—The background is illuminated by means of a separate source, the intensity of which is varied until the line becomes invisible. Data with NaF and BaCl_2 indicate that the concn. of metal can be determined to within a few %.

D. R. D.

Quantitative flame spectrum analysis. F. WAIBEL (Wiss. Veröff. Siemens-Werken, 1935, 14, 32—40).—The applications are discussed and technique is recommended. Two solution sprays are described.

E. S. H.

Microchemical spectral analysis in the high-frequency spark. A. SCHLEICHER and N. BRECHTBERGEN (Z. anal. Chem., 1935, 101, 321—338).—The spectra are excited by a high-frequency Tesla discharge between a Cu , Ag , or Au wire and a tilted glass plate carrying the specimen, and resting on the lower (plate) electrode. The ppt., or 1—2 microdrops of the solution under analysis, is applied to a 1-cm. filter, which is then embedded in a thin layer of hot agar-gelatin jelly (electrodialysed until spectrally pure). For detection of constituents of glass (Na , K , Si) Au foil is interposed between the specimen and the glass plate. Spectra are taken progressively during the ashing of the gelatin carrier. For complete qual. analysis, a group separation is made into (I) oxides insol. in HCl (Si , Ta , W , Ti , + AgCl); (II) metals pptd. by H_2S ; (III) metals pptd. by aq. NH_3 or by $(\text{NH}_4)_2\text{CO}_3$; (IV) remaining elements. Ppts. are best purified by electrodialysis before sparking.

J. S. A.

Sampling analyses and sample size.—See B., 1935, 609.

Recent development of colorimetric technique and allied processes of measurement. A. THIEL (Ber., 1935, 68, [B], 1015—1023).—A lecture.

H. W.

Personal error in colorimetry. R. A. HOUSTOUN and A. J. YOUNGER (Phil. Mag., 1935, [vii], 19, 1107—1115).—A discussion, based on statistical data, of anomalies in visual observations.

N. M. B.

Conductometry. W. BOTTGER and J. PIEPER (Z. Elektrochem., 1935, 41, 453—457).—Polemical (cf. this vol., 598).

E. S. H.

Conductometry. G. JANDER, J. HARMS, and K. F. JAHR (Z. Elektrochem., 1935, 41, 457).—A reply (cf. preceding abstract).

E. S. H.

p_{H} determination (indicator papers). K. HOLL (Chem. Fabr., 1935, 8, 218—219).—Colorimetric p_{H} determination may be carried out by a drop method on indicator papers covering the full p_{H} range. The method is advantageous for viscous or turbid solutions.

J. S. A.

Use of brilliant-yellow and Poirrier-blue C_4B as indicators of p_{H} . M. B. DE LA ROCHE (Bull. Soc. chim., 1935, [v], 2, 1148—1151).—With brilliant-yellow (I) the limit of transmission on the red side occurs at 7500 \AA . for all vals. of p_{H} , but on the violet side at $5025\text{--}5800\text{ \AA}$. for p_{H} 4.5—13. p_{H} may be determined by the transmission limit of (I) in the violet, or by the use of a series of standard papers, the colour changes being: p_{H} 3.5—6 citron-yellow, 6.2—6.8 Cd-yellow, 7—8 orange-yellow, 8.2—9.5 appearance of carmine, 9.7—10.1 carmine-orange, 10.4—13 carmine. With blue C_4B (II) the transmission spectrum occurs at $4100\text{--}5150\text{ \AA}$. for $p_{\text{H}} < 10$. At p_{H} 10.4 (p_{H} of dil. Na_3PO_4) the absorption increases considerably, and a feeble red band is transmitted at $6000\text{--}7500\text{ \AA}$., becoming intense at p_{H} 13. (II) may be used for titration of H_3PO_4 , the neutral point being given by the appearance in a spectroscope of the red band, but visual observation is inexact.

R. S. B.

Volumetric determination of free acid in solutions of iron salts.—See B., 1935, 628.

Extraction method for the determination of acids and its application to p -hydroxybenzoic acid. V. K. LAMER and J. GREENSPAN (J. Amer. Chem. Soc., 1935, 57, 969—973).—The principle of the procedure is to determine an acid (HA) in aq. solution by adding a measured, excess vol. of standard alkali, and determine the excess alkali by adding a measured, excess vol. of a second acid (HE), extracting the excess of HE with a solvent in which HA is insol., and subsequently determining the extracted excess of HE by the usual methods.

E. S. H.

Spectrographic determination of minor chemical constituents in water supplies.—See B., 1935, 608.

Rapid potentiometric determination of minute quantities of chlorides. S. V. BRUEVITSCH and F. E. VARFOLOMEIEVA (J. Appl. Chem. Russ., 1935, 8, 366—373).—0.5 mg. of Cl per litre can be determined by electro-titration (AgCl electrode), with a max. error of 4%, and 2.5 mg. with a max. error of 1.2%. The method is applicable to direct Cl determination in natural waters.

R. T.

Theory of potentiometric precipitation titrations using electrodes of the second kind. A. RINGBOM (Z. physikal. Chem., 1935, 173, 198—206).—Expressions for the concn. of the pptg. ion at the equiv. point and the turning point of the potential curve have been derived. The concn. and excess or

deficiency of this ion at the latter point when the two solid phases are binary or ternary electrolytes are tabulated for various solubility products. R. C.

Potentiometric titrations with electrodes of the second kind. A. RINGBOM (Z. physikal. Chem., 1935, 173, 207—215).—The titration of IO_3^- with $\text{Pb}(\text{NO}_3)_2$, using a $\text{K}_3\text{Fe}(\text{CN})_6$ - $\text{Pb}_2\text{Fe}(\text{CN})_6$ electrode, and of Ca^{++} with $\text{Na}_2\text{C}_2\text{O}_4$, using a $\text{Ag-Ag}_2\text{C}_2\text{O}_4$ electrode, are described and the results compared with the theory (cf. preceding abstract). The former titration is of little practical significance, whilst the second is practicable, but not very exact, at not too high dilutions and salt content. R. C.

Rapid determination of hydrogen sulphide in gaseous mixtures. P. WOOG, R. SIGWALT, and J. DE SAINT-MARS (Bull. Soc. chim., 1935, [v], 2, 1214—1216).—Paper dipped in aq. $\text{Pb}(\text{OAc})_2$ containing glycerol is pressed between filter-paper and placed in a tube which is evacuated and opened in the gaseous sample. Colorimetric examination of the stain permits the determination of as little as 1 in 80,000. R. S. B.

Nephelometric determination of sulphur dioxide in air. I. I. PLETNIK, A. V. VELITSCHKOVSKI, and I. O. FRIDMAN (Ukrain. Chem. J., 1935, 10, 7—14).—30 litres of air are bubbled through 50 c.c. of 0.1N-NaOH, 2 c.c. of 25% HCl and 5 c.c. of 0.1N- KMnO_4 are added, the solution is decolorised with 5% NaNO_2 , BaCl_2 is added, and SO_4^{--} is determined nephelometrically. 0.1 mg. of SO_2 can be determined with a mean error of 10—15%. R. T.

Determination of small quantities of sulphur dioxide and hydrogen sulphide. L. E. KARLSON (Ukrain. Chem. J., 1934, 9, 312—316).—Gorodetzki's method, consisting in leaving a known vol. of air containing SO_2 or H_2S in contact with aq. NH_3 containing H_2O_2 , and determining $(\text{NH}_4)_2\text{SO}_4$ after 24 hr., is untrustworthy when < 0.5 mg. of SO_2 is present; satisfactory results are obtained when the bottle is paraffin-coated, and when the solution, after evaporation, is heated for 15 min. at 100° , and not 135° , as suggested by Gorodetzki. Gurevitsch's method, depending on oxidation with aq. KClO_3 and determination of SO_4^{--} colorimetrically (as PbCrO_4), gives high results; substitution, in the case of SO_2 of aq. NH_3 , and in that of H_2S of ammoniacal H_2O_2 , for aq. KClO_3 gives good results. R. T.

Use of lead nitrate for precipitation-titration of anions. I. Potentiometric titrations. II. Hydrolytic precipitation titrations. A. RINGBOM (Acta Acad. Aboensis, 1934, 8, No. 5, 142 pp.; Chem. Zentr., 1935, i, 754—755).—I. SO_4^{--} , WO_4^{--} , MoO_4^{--} , and SO_3^{--} at $p_H > 6$ may be titrated potentiometrically with $\text{Pb}(\text{NO}_3)_2$ using a $\text{K}_3\text{Fe}(\text{CN})_6$ - $\text{Pb}_2\text{Fe}(\text{CN})_6$ electrode. CO_3^{--} , HCO_3^- , and $\text{C}_2\text{O}_4^{--}$ may be determined in hot solution, or by back titration.

II. $\text{Pb}(\text{NO}_3)_2$ may be titrated in dil. solution with Na_2CO_3 , using phenol-red (I) as indicator. The following anions may be determined similarly: $\text{C}_2\text{O}_4^{--}$ at p_H 8, with (I); SO_4^{--} at p_H 9, with bromocresol-purple (II); CrO_4^{--} at p_H 9, with (II); WO_4^{--} with (II) or bromothymol-blue; MoO_4^{--} , with (I).

"Depolarimetry" by thermo-electricity. J. GUZMAN and A. RANCAÑO (Anal. Fis. Quím., 1934, 32, 590—601).—A modified form of dead-stop end-point electrometric titration which employs a single Cu-constantan thermocouple heated by a Bunsen burner, and uses a small titration vessel mechanically stirred, is described. The method has been applied to the determination of $\text{Na}_2\text{S}_2\text{O}_3$ with I, CuSO_4 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , $\text{Ce}(\text{SO}_4)_2$, and ZnCl_2 and KIO_3 of Fe^{II} salts with $\text{K}_2\text{Cr}_2\text{O}_7$, and of KMnO_4 with $\text{H}_2\text{C}_2\text{O}_4$. J. W. S.

Separation of selenium from cadmium, lead, bismuth, antimony, molybdenum, tungsten, and vanadium. V. HOVORKA (Coll. Czech. Chem. Comm., 1935, 7, 182—197).—The determination of Se in a solution of H_2SeO_3 by reduction with N_2H_4 has been studied. In presence of the above metals a direct separation of Se by this method is possible only under certain conditions, which depend on the particular metals present. O. J. W.

Measurement of small volumes of nitrogen obtained by micro-Dumas method. H. C. GULL (Analyst, 1935, 60, 401—403).—The vol. of N_2 is calc. from the wt. of H_2O displaced from a flask of special construction. E. C. S.

Physiological arsenic and the use of the Kjeldahl flask in its detection. W. DECKERT (Z. anal. Chem., 1935, 101, 338—339).—Dissolution of As from the glass of the flask (cf. this vol., 554) is appreciable only on the first occasion a flask is used.

Physiological arsenic and the use of the Kjeldahl flask in its detection. G. LOCKEMANN (Z. anal. Chem., 1935, 101, 340—341).—A reply to Deckert (see preceding abstract). J. S. A.

Detection of nitrate ions. P. G. POPOV (Ukrain. Chem. J., 1934, 9, 310—311).—1 c.c. of solution and 1 c.c. of saturated aq. $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$ are stratified on conc. H_2SO_4 , when a violet-red ring indicates < 0.025 mg. of KNO_3 . Other oxidising agents do not interfere. R. T.

Potentiometric determination of hypophosphoric acid in presence of phosphoric acid and phosphorous acid. W. GRUNDMANN and R. HELLMICH (J. pr. Chem., 1935, [ii], 143, 100—105).—The determination of H_2PO_3 as Ag salt is unsatisfactory in presence of H_3PO_4 . H_2PO_3 can be determined in presence of H_3PO_4 and H_3PO_3 by potentiometric titration of a NaOAc -buffered solution with AgNO_3 , using a AgI indicator electrode. Cl^- , Br^- , I^- , CN^- , and CNS^- can be separately determined in presence of H_2PO_3 . R. S.

Colorimetric determination of arsenic. D. B. JOCHELSON (Ukrain. Chem. J., 1934, 9, 344—347).— Na_2S is added to the acid solution, the As_2S_3 is washed and dissolved in 2% aq. NH_3 , aq. AgNO_3 is added to the solution, and the brown coloration is compared with that given by standard As solution under the same conditions. The method is rapid and accurate, and may be applied to the determination of As in concns. of $< 0.0001\%$, in presence of organic substances. R. I.

Volumetric determination of minimal amounts of arsenic. J. H. KŘEPELKA and B. RAKUSAN (Lékár., 1934, 14, 290—301; Chem. Zentr., 1935, i, 757).—AsH₃ is passed through 0.1N-I and the excess titrated back. J. S. A.

Boric acid-alcohol flame reaction. W. STAHL (Z. anal. Chem., 1935, 101, 342—347; cf. A., 1931, 587).—The optimum amount of H₂SO₄ is 3 c.c. in 15 c.c. of MeOH. For detection of small amounts of B, the substance is mixed in a Rosenbladt apparatus with 0.5 c.c. of fresh MeOH+H₂SO₄, and kept for 15 min. The tube is warmed to 65°, and a current of air passed through it into a non-luminous gas flame. 0.00076 mg. of B may be detected. J. S. A.

Rapid determination of small amounts of boron through the intensity of the flame coloration. W. STAHL (Z. anal. Chem., 1935, 101, 348—356; cf. A., 1931, 587).—Equal currents of air are passed simultaneously through an unknown and a standard B solution in apparatus of identical dimensions into non-luminous gas flames, and the flame colorations compared. The concn. of the standard solution is varied to give the same intensity of flame coloration. Suitable apparatus is described. J. S. A.

Photo-colorimetric determination of silicic acid in presence of phosphoric acid. M. CERNÝ (Chem. Obzor, 1934, 9, 121—122, 138—140; Chem. Zentr., 1935, i, 600).—SiO₂ is converted by HCl+ (NH₄)₂MoO₄ into silicomolybdate, which is reduced with Na₂S₂O₄ and examined in a colorimeter. Interference by P₂O₅ is inhibited by addition of KMnO₄ and then NH₄ citrate. J. S. A.

Organic carbon in sea-water. L. ESPIL (Bull. Soc. chim., 1935, [v], 2, 1007—1012).—A method for the determination of org. C in sea-water is described. The org. C, which is partly due to the dissolution of marine algæ, is greatest in coastal waters, and is subject to seasonal variation. R. S.

Determination of carbon monoxide with various cuprous chloride solutions.—See B., 1935, 509.

Gas-analytical methods for determination of carbon suboxide in presence of carbon dioxide, carbon monoxide, and oxygen. A. KLEMENC, R. WECHSBERG, and G. WAGNER (Monatsh., 1935, 65, 405—410).—Mixtures of C₃O₂+CO₂ are treated with H₂O, and the CO₂ is pumped off. The CH₂(CO₂H)₂ formed is titrated with 0.01N-Ba(OH)₂, and CO₂ is determined nephelometrically (or in larger amounts by titration) with Ba(OH)₂. C₃O₂ and CO₂ are separated from CO and O₂ by condensation at -180°. O₂ is absorbed by P, and C₃O₂ and CO₂ in the non-volatile portion are determined as above. Very small amounts of CO, are better determined manometrically by pumping off at -40°. When recovery of C₃O₂ is desired, CO₂ may be fractionally pumped off from solid (but not liquid) mixtures at -125° to -130°. A suitable semi-micro gas analysis apparatus for 1 c.c. of gas is described. J. S. A.

Determination of traces of cyanides in water.—See B., 1935, 656.

Determination of small concentrations. IX. Hydrogen cyanide. E. M. JOFINOVA-GOLDFEIN and S. S. GURVITZ. X. Microalkalimetry. S. L. KAGAN (J. Gen. Chem. Russ., 1935, 5, 34—38, 179—181).—IX. The methods of Kolthoff (A., 1918, ii, 138), Smith (A., 1929, 686), and Anderson (A., 1916, ii, 585) serve for determining < 0.003 mg. of HCN.

X. The most uniform results in the microtitration of aq. Ba(OH)₂ are given by 0.01—0.02N-HCl.

R. T.

Determination of anions with benzdine. Oxalates and selenates. A. DEL CAMPO and F. SIERRA (Anal. Fis. Quím., 1934, 32, 451—473).—The solubility of benzdine (I) salts increases with decrease of *p*_H, whilst the salts have a marked power of adsorption. Means of obviating errors arising from these factors have been studied. The best reagent for determination of oxalate contains 2.7 g. of (I) and 130 c.c. of 0.1N-HCl per litre; the sample should contain 0.1—0.15 g. of oxalate, and 150—200 c.c. of reagent should be employed. With a more conc. reagent [0.5% (I)], and under the conditions described, selenate may be determined to within 1%; the error of published methods is 5—6%.

H. F. G.

Determination of potassium in oilfield water.—See B., 1935, 608.

Characterisation of metallic ions by micro-chemical tests with picric acid. C. FRANGOPOL (Bul. Chim. Soc. Romane, 1934, 37, 259—261).—Addition of 1% picric acid to salts of Na, K, NH₄, Be, Ag, Ba, Ca, Fe⁺⁺⁺, Mg, Mn, and Pb on a microscope slides affords characteristic crystals of the picrates: K, NH₄, and Pb triclinic prisms, Ba slender prisms with an inclined base, Ca stout triclinic prisms, Mg and Mn Y-shaped crystals, Ag sheaves of fine needles, Al aborescent growths, Na radiating clusters of fine needles. A. R. P.

Determination of sodium in potassium salts by the uranyl acetate method.—See B., 1935, 627.

Electro-analysis of silver with three electrodes. J. GUZMAN and L. QUINTERO (Anal. Fis. Quím., 1934, 32, 602—610; cf. A., 1916, ii, 114).—The Pt cathodes normally used in the Guzman method have been replaced successfully by Ag wire nets, Ag foil, and in some cases by Ag-plated brass, and the Pt anodes by stainless steel for acid solutions and by Fe (in some cases passified) for alkaline solutions. Data are given for solutions containing (NH₄)₂SO₄ and NH₃, (NH₄)₂SO₄ and NaOH, KCN and NaOH, NH₄OAc and AcOH in presence of EtOH, and HNO₃ and EtOH. The process is also applied to the large-scale determination of Ag. J. W. S.

Detection of barium, strontium, and calcium present together. N. A. TANANAIEV (Ukrain. Chem. J., 1935, 10, 15—18).—10 drops of saturated aq. K₄Fe(CN)₆ are added to 1 drop of the solution, the mixture is evaporated to dryness, and the residue warmed with 40 drops of H₂O, when an opalescent solution is obtained in presence of < 0.07 mg. Ca; Mg interferes, Ba and Sr do not. Sr is detected by adding HNO₃ to the solution, evaporating to dryness,

and warming, when $\text{Sr}(\text{NO}_3)_2$, sputtering into the flame, gives a red coloration. Ba is detected as BaCrO_4 . R. T.

Enrichment process for the detection of small quantities of chemical constituents in minerals. H. ROSE and R. BÖSE (*Naturwiss.*, 1935, 23, 354—355).—For the detection of small quantities of substances in beryl and other minerals the arc method of Mannkopff and Peters (*A.*, 1931, 991) is used. For the detection of small quantities of volatile substances, the mineral is heated in vac. to 1200° in a quartz tube open at one side. Ring-like deposits of metals are formed on the cooler parts of the tubes, which can be separated by cutting the tube. The deposits are separately dissolved, and the solutions examined by the spark spectrum. Elements not indicated by the arc method can thus be detected. A. J. M.

Reaction for cadmium. P. G. POPOV (*Ukrain. Chem. J.*, 1934, 9, 307—309).—1 c.c. of solution is heated with 0.5 g. of NH_4Br and 1.5 c.c. of conc. H_2SO_4 to evolution of SO_3 , H_2O is added to 8 c.c., 0.5 g. of Fe powder is added, the suspension is filtered after 30 sec., an equal vol. of H_3PO_4 added to the filtrate, and H_2S is passed, when a yellow ppt. is obtained with ≤ 0.9 mg. of Cd. Other metals do not interfere. R. T.

Determination of small amounts of lead. K. SEELKOPF and H. TAEGER (*Z. ges. exp. Med.*, 1933, 94, 539—548; *Chem. Zentr.*, 1935, i, 757).—The electrolytic method of Schmidt does not give quant. results. A colorimetric method using dithizone is described. J. S. A.

Determination of small amounts of lead. P. SCHMIDT, F. WEYRAUCH, A. NECKE, and H. MÜLLER (*Z. ges. exp. Med.*, 1934, 94, 1—6; *Chem. Zentr.*, 1935, i, 757).—A reply to Seelkopf and Taeger (cf. preceding abstract). J. S. A.

Application of diphenylcarbazone to determination of metals. E. S. VASSERMAN and I. B. SUPRUKOVITSCH (*Ukrain. Chem. J.*, 1934, 9, 330—340).—Many cations are quantitatively pptd. as complexes (I) insol. in H_2O , but sol. in org. solvents; the application of such solutions to the colorimetric determination of the metals gives untrustworthy results. Pb, Hg, and Zn may be determined gravimetrically as (I). R. T.

Determination of traces of thallium in presence of other metals. A. L. HADDOCK (*Analyst*, 1935, 60, 394—399).—Tl, together with Pb and Bi, is separated from other metals by extraction with dithizone in CHCl_3 , and determined in the form of TlCl_3 by liberation of I from KI. 0.005—0.200 mg. of Tl may be determined in presence of 1 g. of many metals and their salts, but 0.5 mg. of Bi and Pb or 0.1 g. of Hg, Ni, and Zn interfere. E. C. S.

Alkaloidal reagents. VII. Detection of thallium. J. C. MUNCH and J. C. WARD (*J. Amer. Pharm. Assoc.*, 1935, 24, 351—358).—Numerous pptn. reactions for the detection of Tl have been tested and their sensitivities recorded. M. T.

Sensitive detection of metals with "thionalid" [thioglycol- β -naphthylamide]. II. R. BERG and

W. ROEBLING (*Angew. Chem.*, 1935, 48, 430—432).—"Thionalid" gives ppts. with the following metals in EtOH or AcOH solution (limiting dilution $\times 10^6$ given in parentheses) Cu (10), Ag (5), Au (2.5), Hg (15), Sn (12.5), As (100), Sb (40), Bi (10), Pt (10), Pd (10). In alkaline tartrate solution the series is Cu (2), Au (0.2), Hg (1), Cd (2.5), Tl (10); Ag is reduced, Mn gives MnO_2 , and Fe^{++} is not sensitive. In tartrate solution containing KCN, it is Au (0.2), Tl (10), Sn (0.25), Pb (10), Sb (2), Bi (2.5) and in presence of NaOH-KCN it is reduced to Tl (10), Hg, Pb, Bi (not sensitive), which allows the reagent to be used for the detection of very small amounts of Tl (details given). S. C.

Fractional reaction for mercury. M. SCHTSCHIGOL (*J. Appl. Chem. Russ.*, 1935, 8, 158—159).—An equal vol. of 10% KI is added to the solution, followed by 30% aq. KOH, and the mixture is heated and filtered. 1 ml. of glycerol and 2—3 ml. of aq. NaOH are added to the filtrate, and the mixture is boiled for several min., when a black ppt. of Hg forms, or, in presence of very small amounts of Hg, the liquid darkens. ≤ 0.35 — 3.25 mg. of Hg can be detected in presence of other ions. R. T.

Volumetric determination of mercury. M. SCHTSCHIGOL (*J. Appl. Chem. Russ.*, 1935, 8, 160—164).—0.2—0.4 g. of substance is dissolved in H_2O , 20—30 ml. of 30% aq. NaOH and 5—10 ml. of glycerol are added, the mixture is boiled for 5 min., diluted to 100 ml., and filtered. The washed ppt. (Hg) is dissolved in 10—15 ml. of HNO_3 , the solution is diluted, oxides of N are removed by KMnO_4 , excess of which is removed by FeSO_4 , and Hg is titrated with 0.1N- NH_4CNS . The reactions involved are: $\text{HgX}_2 + 2\text{NaOH} \rightarrow \text{HgO} + 2\text{NaX}$; $\text{HgO} + \text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{OH})_2 \rightarrow \text{Hg} + \text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$. R. T.

Fractional detection of mercury. (A) N. A. TANANAEV. (B) N. A. TANANAEV and N. V. JUNITZKAJA (*J. Appl. Chem. Russ.*, 1935, 8, 356—358, 359—360).—(A) Br is added to 1—2 ml. of neutral solution to appearance of a yellow coloration, the solution is boiled and added to 5 ml. of a solution of 10 g. of KI in 100 ml. of 10% NaOH, the mixture is boiled and filtered, and SnCl_2 added to the filtrate, when a black ppt. indicates Hg ($\leq 0.001N$ in absence of other cations, and $\leq 0.005N$ in their presence).

(B) Wet Ag_2S is added to a few ml. of the neutral solution, the suspension is heated for 10—20 sec., allowed to settle, and the sediment is treated with boiling 50% HNO_3 , when HgS , if present, remains undissolved. Other cations do not interfere. R. T.

Rapid determination of mercury. F. I. TRISCHIN (*Ukrain. Chem. J.*, 1934, 9, 341—343).—Ag, KI, NaOH, and Br- H_2O are added to the solution, which is shaken, Na_2S is added, and the filtrate is made acid with HCl, when a black ppt. indicates the presence of Hg. Other cations do not interfere. R. T.

Volumetric determination of mercuric chloride with lead sulphide.—See B., 1935, 628.

Separation of rare earths. P. W. SELWOOD (*J. Amer. Chem. Soc.*, 1935, 57, 1145).—Separation of

Eu is facilitated by co-pptn. with BaSO_4 , which is then washed repeatedly with hot, conc. HNO_3 . Partial separation of Nd and Sm is effected by treating the anhyd. chlorides with H_2 at 700° , and treating the product with H_2O . E. S. H.

Precipitation of aluminium with ammonium hydrogen carbonate. T. KOZU (Mem. Coll. Sci. Kyoto, 1934, A, 17, 17—26).—The pptn. is quant.; procedure for the determination of Al is given. The ppt. is $4\text{Al}(\text{OH})\text{CO}_3 \cdot 6\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$, which is fairly stable in a solution at p_{H} 7.6 and has a solubility in H_2O of 0.00242 g. per 1000 c.c. at 20° . E. S. H.

Colour reaction between manganese and formaldoxime. E. KAHANE (Ann. Chim. Analyt., 1935, [iii], 17, 175—178; cf. A., 1932, 491).—The reaction is sensitive, is positive whatever the state of oxidation of Mn, and is suitable for colorimetry. Fe, which interferes, is removed with $\text{Zn}(\text{OH})_2$. E. C. S.

Determination of cobalt as a new complex compound. A. TAURINS (Z. anal. Chem., 1935, 101, 357—359).—Co is pptd. by an excess of 10% aq. K_2HgI_4 from strongly ammoniacal solution as $[\text{Co}(\text{NH}_3)_6][\text{HgI}_3]_2$ (I). The ppt. is washed with EtOH and Et_2O , and dried at room temp. (I) is decomposed by H_2O , and must be pptd. in a CO_2 atm. to avoid oxidation. J. S. A.

Quantitative separation of nickel and cobalt. E. RAYMOND (Compt. rend., 1935, 200, 1850—1852).—To the solution of Ni and Co salts is added excess of 20% $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ and then excess of aq. NaOH. Both metals form complex salts, that of Ni being decomposed quantitatively by boiling, with pptn. of $\text{Ni}(\text{OH})_2$. The ppt. is washed with 0.01N-NaOH, dissolved in H_2SO_4 , and Ni determined electrolytically. The filtrate containing Co is neutralised with H_2SO_4 , excess of $\text{CO}(\text{NH}_2)_2$ is added, and the Co determined electrolytically. Fe must be absent. The method may be used in qual. analysis. H. J. E.

Detection and determination of nickel by means of dimethylglyoxime in presence of copper. J. RANEDO (Anal. Fís. Quím., 1934, 32, 611—613).—Ni can be determined in presence of Cu by means of dimethylglyoxime (I) if excess of $\text{Na}_2\text{S}_2\text{O}_4$ is added before addition of (I). The method is particularly applicable to the analysis of Ni-Cu alloys. J. W. S.

Rapid determination of tungsten. C. RAJCHIN-SCHTEIN and N. KOROBOV (J. Appl. Chem. Russ., 1935, 8, 154—157).— WO_4^{2-} is determined by titration with standard aq. $\text{Pb}(\text{OAc})_2$, with diamine-scarlet 6BS as adsorption indicator. The method is also applicable to the determination of Pb. R. T.

Iodometric determination of titanium, uranium, molybdenum, and vanadium in presence of iron by the method of liquid amalgams. G. N. PANTSCHENKO (J. Appl. Chem. Russ., 1935, 8, 361—365).— Ti^{IV} , U^{VI} , Mo^{VI} , and V^{V} are reduced by Zn-Hg in HCl and H_2SO_4 to Ti^{III} , U^{III} , Mo^{II} , and V^{II} , and the solution is titrated with 0.1N-I. The method is suitable for determination of these elements in presence of Fe, as Fe^{II} is not oxidised by I. R. T.

Organic compounds as analytical reagents.
III. Pyrocatechol as reagent for the identification of titanium. N. R. PIKE, J. B. FICKLEN, and I. L. NEWELL (Ber., 1935, 68, [B], 1023—1026).—The pyrocatechol test is not sp. for Ti and can scarcely be used for the detection of the latter when unknown substances are present. Its sensitiveness (1 in 5×10^6) makes it very serviceable for the identification of Ti which has been separated by a standard process. H. W.

Sources of errors in the assaying of gold and platinum.—See B., 1935, 595.

Separation of metals of the platinum group by hydrogen under pressure. V. V. IPATIEV and V. G. TRONEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 29—35).—Separation of metals in the Pt group from binary mixtures depends on the oxidation-reduction potentials of the components. Pd is separated from a mixture of PdCl_2 and CuCl_2 , leaving the CuCl_2 unchanged; replacement of the CuCl_2 by FeCl_3 gives reduction of the FeCl_3 before deposition of the Pd-black. A mixture of PdCl_2 and H_2PtCl_6 gives reduction of Pt^{IV} to Pt^{II} , separation of Pd, and finally Pt-black from Pt^{II} ; by adjustment of this mixture rapid separation of Pd from Pt may be effected. Similar methods may be applied to Ir and Rh. A. B. D. C.

High-temperature hydrogen furnace. J. A. V. FAIRBROTHER (J. Sci. Instr., 1935, 12, 200—201).—The furnace consists of concentric SiO_2 tubes, the inner one being wound with W or Mo wire. A temp. of 1300° may be maintained for many hrs., and may be raised if the inner tube is of Al_2O_3 . C. W. G.

Production of high temperatures. A. N. SISIOV (Ukrain. Chem. J., 1934, 9, 405—409).—Temp. of 2000° can be obtained using a laboratory furnace in which the resistance consists of tubes of refractory material (Al_2O_3 , Fe_3O_4 , etc.) coated with graphite. The material is practically non-conductive at lower temp., but its resistance falls rapidly at $>500^\circ$. The furnace is economical (12,000 volts, 0.03 amp.), and can be used in an oxidising atm. R. T.

Laboratory furnace working at 1550° . K. KUMANIN (J. Appl. Chem. Russ., 1935, 8, 177—183).—An electrically heated oven is described. R. T.

Union calorimeter. Optimum volume of gas. W. C. MOSS (J. Sci. Instr., 1935, 12, 188—191).—Graphs of optimum vol. of gas against calorific val. are given. C. W. G.

Exact measurement of isotherms. J. J. M. VAN SANTEN (Comm. Kamerlingh Onnes Lab., 1934, No. 227, 1—10; Chem. Zentr., 1935, i, 677).—The calibration of a closed manometer, the construction of an electric thermostat, and the measurement of the expansion coeff. of glass are described. H. J. E.

Recording microphotometer. N. B. BHATT and S. K. K. JATKAR (J. Sci. Instr., 1935, 12, 185—188).—A photo-electric cell, a bridge amplifier, and a directly coupled recording camera are used. C. W. G.

Magnesium oxychloride for photometer screens and test plates. J. S. PRESTON (J. Sci.

Instr., 1935, 12, 197—198).—MgO is added to an equal wt. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in the min. quantity of H_2O , to the consistency of plaster. The cement is translucent in thicknesses of a few mm. and does not shrink or expand appreciably on setting.

C. W. G.

Measuring the optical constants of small crystals. R. G. WOOD and S. H. AYLIFFE (J. Sci. Instr., 1935, 12, 194—196).—A single-circle goniometer is mounted on a microscope stage with its axis of rotation horizontal. The crystal is immersed in a very shallow cell and the interference figure observed through the microscope.

C. W. G.

Method of taking stereoscopic radio-micrographs. U. YOSHIDA and H. TANAKA (Mem. Coll. Sci. Kyoto, 1934, A, 17, 401—404).—X-Ray apparatus, provided with two separate targets, is described.

E. S. H.

Photo-electric cell in the study of phosphorescence. W. H. BYLER and A. C. KRUEGER (J. Physical Chem., 1935, 39, 695—699).—The use of a photo-electric cell for the measurement of luminous intensity of phosphorescence is recommended in preference to the usual photometric method.

F. L. U.

Valve voltmeter. H. POLLATSCHEK (Z. Elektrochem., 1935, 41, 340—344).—The instrument described works without zero drift, with a grid current of $< 10^{-11}$ amp., and is accurate to ± 1 mv.

F. L. U.

Measurements with the glass electrode. G. KILDE (Dansk Tidsskr. Farm., 1935, 9, 129—152).—Chiefly a summary of the theory and use of the glass electrode. Data are given for the deviation of this from the H electrode at p_{H} 2—9. Above p_{H} 9, the glass electrode does not behave reproducibly, but is dependent on the presence of neutral salts. Its resistance increases greatly in alkaline solutions containing Na, owing to the transport of Na^+ through the glass.

J. S. A.

Moving mercury cathode apparatus. B. S. EVANS (Analyst, 1935, 60, 389—393).—The cathode consists of a thread of Hg issuing from a jet. The Hg is kept in continuous circulation by means of an air-lift, and the metal dissolved in it is partly removed by washing before again issuing from the jet.

E. C. S.

Measurements of dielectric constants. P. C. HENRIQUEZ (Physica, 1935, 2, 434—437).—A precision variable condenser and a small liquid condenser suitable for use in determination of the dielectric consts. of liquids are described. The vol. of liquid required is 0.5 c.c.

J. W. S.

General system of bimetallic electrodes for potentiometric analysis. I. A. ATANASTU and A. K. VELCULESCU (Bul. Chim. Soc. Romane, 1934, 37, 165—172).—The electrode system Pt—Ni can be used advantageously in all potentiometric titrations, in which it behaves as a completely polarised system; the potential jump at the end-point is usually $>$ with the Pt— Hg_2Cl_2 system. Examples of its use in the titration of Pb^{2+} with $\text{K}_4\text{Fe}(\text{CN})_6$, benzidine with KNO_3 , and 8-hydroxyquinoline with KBrO_3 are given.

A. R. P.

Micro-burette with a changeable tip. J. KHOURI (J. Pharm. Chim., 1935, [viii], 21, 607).

M. T.

Apparatus for determination of carbon dioxide. M. H. HEY (Min. Mag., 1935, 24, 76—83).—An apparatus for the absorption of CO_2 in $\text{Ba}(\text{OH})_2$ solution, and the filtration and washing of the BaCO_3 with exclusion of atm. CO_2 is described.

L. J. S.

Automatic device for recording drop numbers in interfacial tension measurements. C. W. GIBBY and C. C. ADDISON (J. Sci. Instr., 1935, 12, 198—199).—Rising drops of the lighter liquid strike a vane on a balanced arm and actuate a relay which is coupled directly to the escapement of a clock. The dial is altered to read directly in drops.

C. W. G.

Lead jointing of metals. H. G. JONES, G. E. ROWLAND, and A. WILLIAMS (J. Sci. Instr., 1935, 12, 201).—Pb is cast around the joint in a cardboard mould.

C. W. G.

Measurement of thickness of thin transparent crystalline plates. K. S. SUNDARARAJAN (Phil. Mag., 1935, [vii], 19, 1076—1079).—For measurements with plates of small area ($> 1.0 \times 0.5$ mm.) a modified form of Darbyshire's method is described (cf. Proc. Physical Soc., 1934, 46, 626). Results for chrysene are given.

N. M. B.

Vacuum filter for drop analysis. L. KULBERG (J. Appl. Chem. Russ., 1935, 8, 387—388).

R. T.

Silver absorber for gaseous halogen compounds. A. D. PELSCH (J. Appl. Chem. Russ., 1935, 8, 184—185).—AgCl is reduced with Zn, the powder is washed, dried, and heated at the sintering point of AgCl, when Ag is obtained in grains. The product is a satisfactory absorbent of Cl compounds formed during microanalytical combustions.

R. T.

Micropyknometric method for the determination of the specific gravities of minerals. F. V. SYROMYATNIKOV (Amer. Min., 1935, 20, 364—370).

L. S. T.

Acoustic interferometer for a wide temperature range. H. L. ANDREWS (Rev. Sci. Instr., 1935, [ii], 6, 167—168).—The Pierce acoustic interferometer is modified to measure velocities at a frequency of 4 megacycles from -63° to 150° to about 2%.

C. W. G.

Improved absolute manometer for pressures from 0.001 micron to one atmosphere. E. B. BAKER and H. A. BOLTZ (Rev. Sci. Instr., 1935, [ii], 6, 173—174).—Two McLeod gauges with bulbs of different sizes are connected together.

C. W. G.

Liebig condenser [modification]. H. SCHANZ (Chem.-Ztg., 1935, 59, 458).—A Liebig condenser having two right-angle bends 10—15 cm. apart between the inlet end and the condenser jacket is described. Increased turbulence of the vapours causes more efficient condensation and fewer fractures occur.

G. M.

Linear mineralogical arithmetic. A. L. PARSONS (Amer. Min., 1935, 20, 388—392).—A graphic

method of determining mol. proportions and the calculation of mineral percentages is illustrated.

L. S. T.

History of chemical catalysis. A. PASSAGEZ (Bull. Soc. chim., 1935, [v], 2, 1000—1002).—The dis-

covery of the catalysis of org. reactions has been erroneously attributed to Kirchoff (1811). C_2H_4 was prepared by Bondt, Deimann, Van Troostwyck, and Lauwerenburg (1795) by passing EtOH or Et_2O over Al_2O_3 etc. R. S.

Geochemistry.

Composition of air from the stratosphere. A. LEPAPE and G. COLANGE (Compt. rend., 1935, 200, 1871—1873).—Analytical data (O_2 , N_2 , total rare gases) are recorded for samples from altitudes up to 16.8 km. The proportions are the same as in ordinary air, indicating complete mixing. He was detected spectroscopically. H. J. E.

Water vapour and carbon dioxide in the air of the stratosphere. A. LEPAPE and G. COLANGE (Compt. rend., 1935, 200, 2108—2110; cf. preceding abstract).—The quantities of H_2O vapour found were many times $>$ the saturation pressure at -50° , the approx. stratosphere temp. The CO_2 was also abnormally high. H. J. E.

Origin of combined nitrogen in the atmosphere. Analysis of tropical rain and its importance in agriculture. A. RAM (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 147—158).—The mean $\text{NH}_3\text{-N}$ (I) and $\text{NO}_3'\text{-N}$ (II) in freshly collected rain-water at Allahabad is 0.469 and 0.881 mg. per litre, respectively. The NH_3 is derived chiefly from the soil and the decomp. of org. matter. There is no correlation between the incidence of thunderstorms and the (II) in the atm., and these oxides are possibly produced by photochemical oxidation of NH_3 and N_2 . In general, the (II) and the ratio (II)/(I) in the tropics are $>$ in other regions. J. G. A. G.

Partition coefficient of radon between gases and water from springs. M. GESLIN (Compt. rend., 1935, 200, 1423—1425).—The partition coeff. of Rn between H_2O and air at various temp. is compared with the ratio of the radioactivities of the H_2O and natural gases. The relatively high amounts found in the gases of hotter springs are attributed to the liberation of gas from cooler water on meeting hotter water. In cooler springs the dissolved gases liberated are $<$ the amounts corresponding with equilibrium. J. W. S.

Ionic ratios in sea-water. L. ESPIL (Bull. Soc. chim., 1935, [v], 2, 1012—1015).—The concns. of common anions and cations in the water of the Arcachon basin have been determined and compared with the vals. for ocean water. The variations are attributed to the presence of marine organisms. R. S.

Concentration of D_2O in natural ice. E. BARONI and A. FINK (Monatsh., 1935, 65, 386—390).—The concn. of D_2O in high-altitude ice from Alpine glaciers and ice caves was derived from pycnometric determination of d . All samples deviated from the normal $[\text{D}_2\text{O}]$, most showing an increase of 50—100%. J. S. A.

Heavy water in Czechoslovakian mineral waters. J. Z. SCHNEIDER and J. SLEZÁK (Chem.

Obzor, 1934, 9, 160—161; Chem. Zentr., 1935, i, 510).—No enrichment in D_2O was detected in 4 springs. H. J. E.

Isotopic composition of rain-water and snow. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 206).—During a rainfall the H_2O was initially slightly heavier than normal H_2O , and subsequently slightly lighter. This may be due to fractional condensation or vaporisation. H_2O from melted snow is 0.5—3.3 p.p.m. lighter than normal H_2O . This is attributed to the action of gravity on atm. H_2O . J. W. S.

Radioactivity of spring water from Hot Springs, Arkansas. H. SCHLUNDT (Amer. J. Sci., 1935, [v], 30, 45—50).—Radioactivity varies for the water and tufa of different springs. The mixed water contains 0.46 millimicrogram of Rn, corresponding with 0.46×10^{-9} g. Ra, whilst the amount of Ra found is only 1.38×10^{-12} g. per litre. L. J. S.

Isothermic evaporation at 25° of Lake Kutschuk water, with determination of the vapour pressure in relation to the concentration. M. N. JAKIMOV and E. I. KUMINOVA (J. Appl. Chem. Russ., 1935, 8, 221—226).—The v.p. and composition of the summer and the winter brines, at various concns., have been determined. The solid phases are NaCl and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ in winter, and NaCl , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and astrakhanite in summer brine. The mother-liquors contain 2.3—3 kg. of Br per cu.m., and may be used for the prep. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, for the cement industry, and for Br production. R. T.

Hydrogeology of the springs of the Ilmen district and of Lake Turgoyak (South Urals). M. O. KLER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 52—54).—Conditions at the Lake are not favourable for radioactivity. Rare-earth elements and U compounds give the springs high activity, but the deposits are unlikely to be of industrial val. A. B. D. C.

Radioactivity of the springs of the Ilmen district and of Lake Turgoyak (South Urals). P. R. BORODIN and M. G. GADD (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 47—51).—The highest radioactivity was shown by a spring located in the Ilmen mineralogical preserve. A. B. D. C.

Size of crystals. C. FRONDEL (Amer. Min., 1935, 20, 469—473).—Factors which influence the size of crystals are discussed. Large crystals of numerous minerals with their localities are cited. L. S. T.

Rational classification of silicates. A. J. MIKEI (Ukrain. Chem. J., 1934, 9, 472—474).—A classification is proposed. R. T.

Dilatometric study of natural silicates. I. J. MIKEI and I. A. BRODSKA (Ukrain. Chem. J., 1935,

10, 66—75).—The temp.-vol. diagrams of serpentine, tremolite, pelicanite, chloropal, and obsidian have been constructed. R. T.

Celadonite from Koktebel (Crimea). S. D. TSCHEVERIKOV and A. F. FIOLETOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 269—272).— V_2O_5 is reported in the celadonite which otherwise closely approximates to the composition of celadonite from Beskid. W. R. A.

Greenalite. F. JOLLIFFE (Amer. Min., 1935, 20, 405—425).—The typical greenalite (I) from the Mesabi iron range, Minnesota, is a green hydrated Fe^{II} silicate, probably $3FeO \cdot 4SiO_2 \cdot 2H_2O$, occurring in rounded granules, d 2.85—3.15, n_x 1.686 ± 0.001 , n_D 1.674 ± 0.001 , n_c 1.670 ± 0.002 , which are moderately magnetic. On heating, it loses H_2O readily and becomes black in colour and strongly magnetic. (I) is probably a definite mineral varying only slightly in composition and properties because of its colloidal origin. It has probably been deposited as a ppt. from H_2O which received Fe and SiO_2 directly from igneous sources. Alteration yields (i) Fe oxides and hydroxides by the action of surface waters, (ii) an aggregate of minute green crystals associated with small, opaque green masses (metagreenalite) by crystallisation, (iii) a light-coloured fibrous mineral, a hydrated metasilicate of Fe^{II} , Fe^{III} , and Mg, by the action of Mg-bearing H_2O not of surface origin, and (iv) an intergrowth of magnetite and amphiboles in the neighbourhood of heated igneous bodies. The greenalite rock has SiO_2 49.43, Fe_2O_3 8.16, FeO 30.52, MgO 4.77, CaO 0.18, MnO 0.17, $H_2O + 6.24$, H_2O —0.51, CO_2 0.43, and Cl, S, SO_3 trace, total 100.41%. L. S. T.

Crystallography of herderite from Topsham, Maine. G. M. YATSEVITCH (Amer. Min., 1935, 20, 426—437).—Novelties exhibited by crystals of herderite (I), $CaBe(OH,F)PO_4$, are described. (I) is abundant in this locality and is attached to quartz, cleavelandite, lepidolite, topaz, and sericite. The crystallography of the species is revised and referred to new parameters, $a:b:c=0.6307:1:1.2822$, β $90^\circ 6'$. L. S. T.

Dickite from Pennsylvania. A. P. HONESS and F. J. WILLIAMS (Amer. Min., 1935, 20, 462—466).—Dickite has been discovered in two new localities, at the Pine Knot Colliery, Schuylkill Co., and at Natalie, Pennsylvania. Optical, chemical, and X-ray data are summarised. L. S. T.

U-Galena and uraninite in Bedford, New York, cyrtolite. P. F. KERR (Amer. Min., 1935, 20, 443—450).—An unusual occurrence of galena (I) in the Bedford cyrtolite (II) which contains Pb 0.33 and S 0.05% is described. (I) must be made up essentially of Pb isotopes derived from U and is named "U-galena." Radiograms of (II) show a lack of uniformity in the distribution of the strongly radioactive areas. Microscopic and X-ray data indicate that much of the U is present as finely-divided uraninite (III) scattered throughout (II). The uneven distribution of (III) makes it doubtful that different specimens of (II) would give the same U content, and this may affect age determinations of the mineral. L. S. T.

Origin of cyanite. J. L. STUCKEY (Econ. Geol., 1935, 30, 444—450).—The cyanite deposits of N. Carolina appear to have been formed by metasomatic replacement by hot solutions given off by the quartz veins, pegmatite dykes, and their parent magmas. L. S. T.

Structure of the schonites. A. GARRIDO and E. MOLES (Anal. Fis. Quim., 1934, 32, 432—445).—The dehydration of compounds of the type $M^{II}SO_4 \cdot M^I SO_4 \cdot 6H_2O$, where M^{II} and M^I are respectively Zn and K, Cu and K, Mn and NH_4 , Fe and NH_4 , and Mn and K, has been studied. Dihydrates, but no tetra- or penta-hydrates, are formed in each case (except that of the Mn salts, which yield mono- and tri-hydrates), whilst when K is present a hemihydrate is also formed. Corresponding hydrates have approx. the same v.p. There is no evidence that 1 mol. of H_2O is associated with the anions and 5 mols. with the cations. The results accord with Werner's formula for schonites, viz., $[M^{II}(H_2O)_6]SO_4 \cdot SO_4 M^I$. H. F. G.

Petrology of Barnavave, Carlingford, Irish Free State. I. The junction hybrids. S. R. NOCKOLDS (Geol. Mag., 1935, 72, 289—315).—The basic hybrids and xenoliths, and the contaminated granites are described. Reciprocal reaction is discussed on the basis of the chemical analyses given, and the mineral transformations which have occurred are discussed. L. S. T.

Origin of basic xenoliths in plutonic rocks, with special reference to their grain-size. G. A. JOPLIN (Geol. Mag., 1935, 72, 227—234).—The formation of a fine-grained xenolith from a coarse- or medium-grained basic plutonic rock is discussed. Grain-size may be reduced (i) if the temp. of the invading magma be sufficient, by the formation of a granoblastic structure, (ii) by the development of highly poikilitic crystals of hornblende or biotite and their final disruption, and (iii) by the formation of granular masses of pyroxene or by criss-cross flakes of biotite during hybridisation. L. S. T.

Petrography of the Blea Wyke Series. R. H. RASTALL and J. E. HEMINGWAY (Geol. Mag., 1935, 72, 125—138). L. S. T.

Diorite-limestone reaction at Ben Bullen, New South Wales. G. A. JOPLIN (Geol. Mag., 1935, 72, 97—116).—Diorite tongues invading limestone are shown to have given rise to a series of contaminated rocks in which definite mineral assemblages are recognised. The petrography of the parent rocks and the contaminated zones are discussed and chemical analyses are given. The mineralogical changes brought about by assimilation of CaO are illustrated. A reciprocal reaction is shown to have occurred. Concn. is concluded to be the most important factor in contamination, and assimilation has occurred at a low temp. in presence of abundant volatiles, of which H_2O is the most important. L. S. T.

Structural relations of southern Appalachian zinc deposits. L. W. CURRIER (Econ. Geol., 1935, 30, 260—286).—The general geology of the various districts is described. The Zn deposits were accumulated in breccias of tectonic origin by ascending hypogene solutions. L. S. T.

Primary silver mineralisation at Sabinal, Chihuahua, Mexico. P. KRIEGER (Econ. Geol., 1935, 30, 242—259).—Mineralisation in the Florencia-Magda vein is described. Barite, SiO_2 , calcite, and siderite are abundant gangue minerals of the vein, and some fluorite and Fe oxide are present. Ag occurs chiefly as masses of nodular grains intimately associated with Co and Ni arsenides. The presence and mode of occurrence of the arsenides provide strong evidence for the primary origin of the Ag, which is supported by the galena, sphalerite, barite, calcite, and small amounts of chalcopyrite and tetrahedrite with which the Ag is also associated. Pyrargyrite and polybasite occur most abundantly along the contact of the vein material and the wall rock, and argentite forms fine intergrowths with many of the metallic minerals. The mineralisation in the Florencia-Magda vein is of a low-temp., epithermal character and the apparent source of mineralising solutions is an alaskite intrusive. Some supergene mineralisation has also occurred, and wires and plates of Ag of such origin are occasionally found.

L. S. T.

Revision of structure and stratigraphy of the Aspen district, Colorado, and its bearing on the ore deposits. J. W. VANDERWILT (Econ. Geol., 1935, 30, 223—241).—The general geology, structure, breccia, dolomitisation, and silicification are discussed.

L. S. T.

High-temperature mineral associations at shallow to moderate depths. A. F. BUDDINGTON (Econ. Geol., 1935, 30, 205—222).—Mineral associations formed at 300—500° and at depths >2000—3000 ft. are termed xenothermal, and the xenothermal deposits of Pt, magnetite (martite)-apatite-pyroxene, cassiterite and cassiterite-wolframite, molybdenite-orthoclase-quartz, scheelite, tourmaline-cherty quartz or jasperoid, and tourmaline-chalcopyrite of different localities are discussed.

L. S.

Differentiation in traps and ore deposition. T. M. BRODERICK and C. D. HOHL (Econ. Geol., 1935, 30, 301—312).—Differentiation in Keweenaw lava flows of the Michigan Cu district has been investigated. The Cu and S contents of twelve basaltic rocks, three quartz porphyries, and three phases of the Mt. Bohemia gabbro are recorded. The average Cu content selected for the Keweenaw traps is 0.01%, and the Cu is mainly in the form of Cu Fe sulphides. The distribution of the Cu, volatile transfer of elements, and ore deposition are discussed. The ascending magmatic H_2O theory best explains the occurrence of Cu in the Michigan deposits.

L. S. T.

Dumortierite-andalusite mineralisation at Oreana, Nevada. P. F. KERR and P. JENNEY (Econ. Geol., 1935, 30, 287—300).—Considerable quantities of andalusite (I) are associated with the dumortierite (II). Quartz (III), albite, and sericite also occur, together with minor amounts of titanite, rutile, leucoxene, zircon, magnetite, limonite, tourmaline, biotite, and vein carbonate in various parts of the mineralised zone. The history of the deposit appears to be (i) deposition of a series of rhyolitic and trachytic tuffs with intercalated flows, (ii) intrusion of an adjacent igneous mass accompanied by

shearing, devitrification and alteration of the tuff series, (iii) invasion of volcanics by quartz-albite end-stage material from the igneous source, accompanied or followed by a concn. of (I) and (III) along restricted zones in the tuffs, and (iv) hydrothermal mineralisation involving replacement of (I) by (II), resulting in the formation in three stages of coarse euhedral crystals of blue (I), matted lavender or pink masses, and fibrous veins or isolated crystals.

L. S. T.

Marginal and contact phenomena of the Dor-back granite. F. WALKER and C. F. DAVIDSON (Geol. Mag., 1935, 72, 49—63).

L. S. T.

"Limonite" of molybdenite derivation. R. BLANCHARD and P. F. BOSWELL (Econ. Geol., 1935, 30, 313—319).—When massive, molybdenite (I) normally oxidises to molybdic ochre, but when disseminated, Mo compounds frequently undergo complete leaching yielding an indigenous limonite (II) which, on account of its colour and frequent occurrence in Cu areas, may be confused with that of chalcocite origin. Two (II) products of (I) derivation, foliated boxwork and granular structure, have been identified, and serve as a means of differentiation from limonite of Cu derivation. (II) of (I) derivation occurs at many places in the South-western States, Mexico, and Australia.

L. S. T.

Comparison of three Scottish magmas. S. ELDER (Geol. Mag., 1935, 72, 80—85).—The percentages of $\text{FeO} + \text{Fe}_2\text{O}_3$, MgO , CaO , and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ are each plotted against those of SiO_2 for the Devonian, Carboniferous, and Tertiary igneous rocks of Scotland. The curves show the calc-alkali character of the Devonian and Tertiary as compared with the Carboniferous magma, and indicate a magnesian tendency in the Devonian and a ferriferous in the Tertiary magma.

L. S. T.

Spectrographic examination of smoky and ordinary quartz from Rincon, California. T. G. KENNARD (Amer. Min., 1935, 20, 392—399).—The colourless and the pale smoky quartz samples contain more Li than the dark smoky quartz. Al, V, Ti, Ca, and Mg are also present, but there is no significant difference in content between the various samples examined.

L. S. T.

Sericite of unusual composition. D. B. MEYER (Amer. Min., 1935, 20, 384—388).—Sericite (I) from Pilot Knob, Iron-ton, Missouri, SiO_2 47.30, Al_2O_3 36.31, Fe_2O_3 2.17, Na_2O 5.27, K_2O 2.70, H_2O 5.80, total 99.55%, has d 2.69 and μ 1.580 \pm 0.003. The dehydration curve of (I) is so distinctive that it should be used in determinations of the mineral. There is a slight loss of H_2O between 85° and 450° and between 600° and 1080° and a rapid loss at 450—600°. A mixture of albite and orthoclase may have been the original source of the mineral.

L. S. T.

Minerals of the White Raven Mine, Ward, Colorado. E. E. WAHLSTROM (Amer. Min., 1935, 20, 377—383).—The occurrence and origin of these minerals are described. Horn quartz, massive galena with small amounts of pyrite and sphalerite, manganese siderite, and native wire Ag, formed probably in this order, occur in important amounts

in the ore shoots of the Pb-Ag vein. Secondary minerals are calcite, and hydrated Fe and Mn oxides.

L. S. T.

Adamite from Gold Hill, Tooele Co., Utah. L. W. STAPLES (Amer. Min., 1935, 20, 371—376).—This adamite occurs as individual pale yellow crystals and as colourless rosettes; $a : b : c = 0.9742 : 1 : 0.7095$; $n_a 1.711 \pm 0.003$, $n_b 1.732 \pm 0.003$, $n_y 1.756 \pm 0.003$.

L. S. T.

Topaz from Devil's Head, Colorado. M. A. PEACOCK [with A. MONTGOMERY and E. OVER, jun.] (Amer. Min., 1935, 20, 354—363).—Topaz crystals of unusual size and regular development and smaller crystals of unusually distorted habits are described. The topaz is associated with quartz, microcline, albite, muscovite, fluorite, and cassiterite in pegmatite.

L. S. T.

Distribution of the heavy minerals in the clays of Middlesex County, New Jersey. A. C. HAWKINS (Amer. Min., 1935, 20, 334—353).—The residues obtained by elutriation of Cretaceous clays have been studied in detail. The percentages of ilmenite, tourmaline, and zircon have been used for the correlation of the clay beds. Total org. C has also been determined. The areal distribution of the heavy minerals and C has been plotted. Ilmenite is plentiful and rutile scarce.

L. S. T.

Tetradymite from Inyo Mountains, California. R. W. WEBB (Amer. Min., 1935, 20, 399—400).—Tetradymite occurs as numerous brilliant tabular crystals embedded in bismutite in a brecciated quartz vein in the quartz monzonite of the Inyo Mountains. A trace of S, but no Se, is present.

L. S. T.

Plasticity of crystals of sylvine. E. W. ZEHNOWITZER (Nature, 1935, 135, 1076).—Crystals of sylvine (I) become plastic after treatment with H_2O . At $700-780^\circ$, (I) possesses considerable plasticity. Crystals removed from their mother-liquor and wiped with filter-paper are at first very plastic, but become fragile on keeping in air for a few hr. The plasticity of crystals of (I) when formed from a melt or a solution may explain the frequent occurrence of bent and twisted crystals.

L. S. T.

Amphibolites from Zlatibor (West Serbia). S. PAYLOVITCH (Compt. rend., 1935, 200, 2094—2096).—Analytical data are recorded and discussed.

H. J. E.

Recrystallisation of diorites and quartzite diorites in the Manson plateau (Puy-de-Dôme) under the influence of granitic contact metamorphism. J. JUNG (Compt. rend., 1935, 200, 2091—2093).—A review and discussion of the minerals of the region.

H. J. E.

Petrographical study of Zlatibor peridotites (W. Serbia). S. PAYLOVITCH (Compt. rend., 1935, 200, 1864—1866).—Petrographical and analytical data are recorded.

H. J. E.

Hydroclastic elements of the Czeremosz district. H. TOKARSKI (Bull. Acad. Polonaise, 1935, A, 79—84).—Petrographical and analytical data for a no. of specimens are recorded and discussed.

H. J. E.

Mylonites from the San Andreas fault zone. A. C. WALTERS and C. D. CAMPBELL (Amer. J. Sci.,

1935, [v], 29, 473—503).—Description of crushed rocks from California are given. Analysis of an ultramylonite suggests that the original rock was an arkose.

L. J. S.

Role of kyanite in the "hornfels zone" of the Carn Chuinneag granite (Ross-shire). C. E. TILLEY (Min. Mag., 1935, 24, 92—97).—The hornfelses in the metamorphic zone surrounding the granite contain almandine (FeO 32.40, MnO 0.72%), and kyanite. The latter occurs as replacements of chiasolite and cordierite, as fine needles associated with biotite, and as larger crystals in quartz-kyanite veinlets. Kyanite is typically a stress mineral, and its occurrence as a transient mineral phase in the formation of cryst. schists is unusual.

L. J. S.

Chondrodite in the Glenelg limestone, Inverness-shire. H. H. READ and I. S. DOUBLE (Min. Mag., 1935, 24, 84—89).—Small grains of chondrodite (previously mistaken for fosterite) occur in the cryst. limestone, usually forming rims around crystals of fosterite. It has probably been formed by the introduction of F-bearing solutions.

L. J. S.

Ankerites from the Northumberland coal-field. L. HAWKES and J. A. SMYTHE (Min. Mag., 1935, 24, 65—75).—Several analyses, with determinations of d and n , are given of ankerite and calcite occurring as veinlets in the coal. The ankerites are members of an isomorphous series consisting of dolomite $MgCO_3$, $CaCO_3$ and ferrodolomite $FeCO_3$, $CaCO_3$, with small amounts of mangandolomite $MnCO_3$, $CaCO_3$, and they may hold up to 20% $CaCO_3$ in solid solution. $n(\omega)$ for $FeCO_3$, $CaCO_3$ is deduced as 1.765. The calcite is of later deposition.

L. J. S.

Two new bismuth minerals from South Africa. E. D. MOUNTAIN (Min. Mag., 1935, 24, 59—64).—Bismoclite was found as a pale grey nodule with Bi ores in pegmatite at Steinkopf in Namaqualand. Analysis corresponds closely with $BiOCl$; d 7.36. It differs from daubreelite ($BiO[OH, Cl]$) from Bolivia in containing more Cl (13%). Bokspitite from pegmatite at Bokspit in Gordonia is pale yellow to greyish-brown and massive. Analysis corresponds with $6PbO, Bi_2O_3, 3CO_2$; d 7.29.

L. J. S.

Chironomide tufa. J. WALLNER (Bot. Arch., 1935, 37, 128—134).—The tufa result from an association of $CaCO_3$ -depositing fresh-water algae and incrustated larva tubes of *Chironomidae*.

A. G. P.

Differentiation of Hawaiian lavas. H. A. POWERS (Amer. J. Sci., 1935, [v], 30, 57—71).—A field study of the crystallisation of basalt suggests conditions other than those obtained in the laboratory.

L. J. S.

Occurrence of petroleum, natural gas, iodised and sulphurated waters in South Bavaria. K. A. WEITHOFER (Petroleum, 1935, 31, No. 22, 1—8; No. 27, 5—8).—A survey is given of recorded observations of the occurrence of the above products.

C. C.

Radioactivity of Kuznietzk basin coals. E. S. BURKSER, V. V. KONDOGURI, N. P. KAPUSTIN, and P. P. POTAPOV (Ukrain. Chem. J., 1934, 9, 441—445).—The mean Ra content of 20 samples is $0.5 \times 10^{-12}\%$, and of Th $0.17 \times 10^{-3}\%$, as compared with $28 \times 10^{-12}\%$

and $0.37 \times 10^{-3}\%$ for Donetz basin coals. It is concluded that concn. of radioactive substances is not involved in the growth of plants. R. T.

Classification of coals. M. C. STOPES (Nature, 1935, 136, 33).—A reply to criticism (this vol., 843). L. S. T.

Organic Chemistry.

Internal energy relationships of organic compounds. VII. Laws of coupling of paired and unpaired *B* electrons. O. SCHMIDT (Ber., 1935, 68, [B], 1026—1028; cf. this vol., 480).—The double linking rule is qualitatively deduced from the course of the potential curve between paired *B* electrons and *A* electrons. Considerations of unpaired *B* electrons lead directly to Criegee's rule that when 2 atoms or groups in the $\alpha\delta$ position in a mol. are removed the remainder becomes ruptured between the β and γ atoms. H. W.

Catalytic influence of mercury vapour on the cracking of methane by the glow discharge.—See this vol., 943.

Straight-chain- and the many-membered CH_2 ring-molecule. A. MÜLLER (Nature, 1935, 135, 994).—At low-temp. X-ray data show that the vols. occupied by a CH_2 group in $n\text{-C}_{12}\text{H}_{26}$ and in the corresponding cyclohydrocarbon are identical. As the temp. rises the CH_2 in the straight-chain compound occupies more space than that of the ring compound, probably owing to its greater mobility. L. S. T.

Mechanism of catalytic hydrogenation.—See this vol., 940.

Action of hydrogen peroxide on olefines. A. P. BARCHASCH (J. Gen. Chem. Russ., 1935, 5, 254—255).— H_2O_2 does not react with C_2H_4 and amylene at room temp. In presence of FeSO_4 amylene and H_2O_2 yielded a mixture of products, amongst which COMe_2 , CO_2 , HCO_2H , and AcOH were identified; aldehydes, homologues of COMe_2 , EtCO_2H , and glycols were absent. R. T.

Absorption of ethylene by solid cuprous chloride. H. TROPSCH and W. J. MATTON (J. Amer. Chem. Soc., 1935, 57, 1102—1103).— CuCl_2 absorbs 1 mol. of C_2H_4 at 60—62 atm. The dissociation pressure at 0°, 16.8°, 30°, and 40° is 2.14, 5.95, 11.7, and 19.49 atm., respectively. The rate of absorption is increased by previous use of the CuCl_2 or addition of < 10% of infusorial earth or a little H_2O . No polymerisation occurs at 100—200°/65—80 atm. C_3H_6 is not absorbed, but $\text{C}_3\text{H}_6\text{--C}_2\text{H}_4$ mixtures cannot be quantitatively separated by CuCl_2 . Aq. CuCl_2 does not absorb C_2H_4 . R. S. C.

Isomerisation of allene hydrocarbons by silicates. II. Isomerisation of $\Delta^{\alpha\beta}$ -butadiene in presence of floridin. J. M. SLOBODIN (J. Gen. Chem. Russ., 1935, 5, 48—52).—The light hydrocarbon fraction obtained when CHMe:C:CH_2 (I) is passed over floridin at 245° contains (I) 96.6, Cet-CH 3.4%, divinyl traces; at 330° the corresponding yields are 75.5, 3.9, and 20.6%. The % of (I) converted into polymerides [the dimerides of (I) and (II) are absent] is 22 and 25. (I) is conveniently prepared from crotyl alcohol (a by-product of the synthetic

rubber industry) by conversion into $\text{CHMeBr-CHBr-CH}_2\text{Br}$, from which HBr is eliminated (KOH at 120°) to yield CHMeBr-CBr:CH_2 , and this gives (I) when boiled with Zn in EtOH . R. T.

Raman effect and organic chemistry. *cis-trans*-Isomerism of ethylenic compounds CHMe:CHR . Classification of the radicals *R*. (MLLE.) B. GREDY (Bull. Soc. chim., 1935, [v], 2, 1029—1037).—The Raman spectra of the following substances are given: *cis*- CHR:CHMe [*R* = Et, Pr, Bu^a (I), $n\text{-C}_5\text{H}_{11}$, $n\text{-C}_6\text{H}_{13}$, Ph (II)], *cis*- δ -cyclopentyl- Δ^{β} -butene, b.p. 156—158°, *cis*- ζ -cyclohexyl- Δ^{β} -hexene, *trans*-crotyl chloride (III), *trans*- δ -methyl- Δ^{β} -pentene, and the *trans*-isomerides of (I) and (II). The *cis*-compounds were prepared by hydrogenation (colloidal Pd) of the corresponding acetylenic compounds (cf. A., 1928, 28; 1930, 79). Some were converted into mixtures (IV) of the *cis*- and *trans*-isomerides by successive treatment with Br and Zn, or by the dehydration of the appropriate alcohol. The Raman spectra of (IV) have also been examined. The frequency (near 1600 cm^{-1}) characteristic of the ethylenic linking is higher for the *trans*- than for the corresponding *cis*-compounds (cf. A., 1932, 897). Radicals *R* are classified according to their effect on this line. A close parallelism exists between this classification and that based on the compounds CHR:CH_2 (cf. A., 1932, 676). (III) and MgPrBr do not give Δ^{β} -heptene. H. G. M.

Raman effect and organic chemistry. Tri-substituted ethylenes. (MLLE.) B. GREDY (Bull. Soc. chim., 1935, [v], 2, 1038—1044).—The Raman spectra of the following compounds have been measured: γ -methyl- Δ^{β} -nonene, b.p. 64.5—65°/14 mm., CMeBr:CHMe , CHMe:CMc-CHO , CHet:CMc-CHO , CHMe:Cet-CHO , β -methyl- Δ^{β} -octene, b.p. 145—146°, n_D^{25} 1.4240, and $\text{CHMe:CBr-CH}_2\text{Br}$. Only one line (near 1600 cm^{-1}) characteristic of the ethylenic linking has been observed. The classification of *R* and *R'* in CHMe:CRR' according to their effect on this line resembles that for the compounds CHMe:CHR (see preceding abstract). The effects on this line of conjugation (cf. A., 1932, 897) and of changes in the relative positions of Me, *R*, and *R'* in CHMe:CRR' are discussed. α -Methoxy- β -methyl-*n*-octane, b.p. 76°/16 mm., and HBr afford β -methyl-*n*-octyl bromide, b.p. 92°/16 mm., which with quinoline gives a mixture of β -methyl- Δ^{α} - and Δ^{β} -octene. Dehydration of γ -methylnonan- γ -ol, b.p. 91°/13 mm. (prepared by the Grignard reaction from Me hexyl ketone), affords mainly $\text{C}_5\text{H}_{11}\text{:CH:CMcEt}$. H. G. M.

New trimeric compound of acetylene. Acetylenyldivinyl. A. L. KLEBANSKI, C. A. DRANITZINA, and I. M. DOBROMILSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 229—236).— $\Delta^{\alpha\gamma\epsilon}$ -Hexadieneinene

(acetylenyldivinyl), b.p. 32°/100 mm. (Cu derivative), is isolated from the products of the polymerisation of C_2H_2 in presence of $CuCl-NH_4Cl-H_2O$. It is very sensitive towards air, yields (?) β -chloro- $\Delta^{2,4}$ -hexatriene with HCl, gives a ketone (semicarbazone) with dil. H_2SO_4 , and slowly affords non-cryst. substances with $p-C_6H_4Me-SH$. H. W.

Reaction for differentiating chloroform and carbon tetrachloride. J. ROZEBOOM (Pharm. Weekblad, 1935, 72, 689).—1 c.c. (free from EtOH) containing a crystal of I is treated with papaverine hydrochloride (10 mg.) or other alkaloid salt insol. in $CHCl_3$ but sol. in CCl_4 . The violet colour disappears in $CHCl_3$ but not in CCl_4 . S. C.

Differentiation of chloroform and carbon tetrachloride. N. SCHOORL (Pharm. Weekblad, 1935, 72, 751).— $CHCl_3$ reduces boiling Fehling's solution. CCl_4 gives $COCl_2$ and Cl_2 (detected with starch-KI) when one drop is heated in a loosely corked test-tube (flameless combustion). The tests are sp. S. C.

Reactions of bromo- and dibromo-olefines. G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 1088—1090).— α -Dibromo-olefines do not react with hot aq. Na_2CO_3 , anhyd. C_5H_5N , or NH_2Ph . $Me-[CH_2]_4-CH:CHBr_2$ and $NaOEt-EtOH$ give a 70% yield of heptinene and some AcOH. $CHMe:CHBr_2$ and $NaEtS$ give Et_2S_2 and $CMe-CH$. $CHMe:CHBr$, $Me-[CH_2]_5-CH:CHBr$, $CHMe:CHBr$, and $Me-[CH_2]_5-CH:CHBr_2$ with Na in liquid NH_3 give acetylenes and olefines, the ratio of these products formed being 0.012, 0.45, 0.71, and 1.8, respectively; the Br_2 -compounds give also some polymeric compounds. By addition of Cl_2 or Br in CCl_4 at -5° are obtained $\alpha\beta$ -dichloro- α -bromo-, b.p. 154.5°, $\alpha\beta$ -dichloro- $\alpha\alpha$ -dibromo-, b.p. 84°/16 mm., and $\alpha\alpha\alpha\beta$ -tetrabromo-propane (I), b.p. 122°/15 mm. $CHMe:CHBr_2$ does not react with O_2 in EtOH or NH_2Ph , but when homogeneous or in hydrocarbon solvents (best dry) affords $CHMeBr-COBr$, and, by partial hydrolysis and reaction of the liberated HBr, some (I). CH_2N_2 , $NOCl$, CH_2Ph-SH , and H_2-Pt do not react.

R. S. C.

o-Nitro-, m-nitro-, and 3:5-dinitro-phenylcarbimides as reagents for alcohols. F. HÖRKE (Rec. trav. chim., 1935, 54, 505—517).—The carbimide and alcohol are heated in light petroleum. Reaction occurs readily except with benzoin derivatives. *m*-Nitro- and 3:5-dinitro-phenylcarbimides fulfil all conditions required for a reagent for identification of alcohols. The following are described. *m*-Nitrophenylcarbimates: Pr^a , m.p. 76°; Bu^a , m.p. 51°; *n*-amyl, m.p. 62°; *n*-hexyl, m.p. 52°; *n*-heptyl, m.p. 57°; *n*-octyl, m.p. 63°; *n*-nonyl, m.p. 66°; *n*-decyl, m.p. 67°; *n*-undecyl, m.p. 56°; *n*-dodecyl, m.p. 76°; *cetyl*, m.p. 78°; *n*-octadecyl, m.p. 77°; Pr^b , m.p. 91°; Bu^b , m.p. 62°; Bu^v , m.p. 95°; *sec*-butyl, m.p. 86°; *benzyl*, m.p. 118°; β -phenylethyl, m.p. 80°; γ -phenyl-*n*-propyl, m.p. 57°; *benzoin*, m.p. 112°; *allyl*, m.p. 51°; *cholesteryl*, m.p. 184°. *o*-Nitrophenylcarbimates: Pr^a , m.p. 15°; Bu^a , m.p. -10° and $+7^\circ$; *n*-hexyl, m.p. 33°; *n*-heptyl, m.p. 17°; *n*-octyl, m.p. 44°; *n*-nonyl, m.p. 34°; *n*-decyl, m.p. 52°; *n*-undecyl, m.p. 37°; *n*-dodecyl, m.p. 60°; *cetyl*, m.p.

64°; *sec*-butyl, m.p. 26°; Bu^v , m.p. 90°; *benzyl*, m.p. 65°; β -phenylethyl, m.p. 58°; *benzoin*, m.p. 161°; *allyl*, m.p. 20°; *cholesteryl*, m.p. 169°. 3:5-Dinitrophenylcarbimates: Pr^a , m.p. 97°; Bu^a , m.p. 70°; *n*-amyl, m.p. 58°; *n*-hexyl, m.p. 75°; *n*-heptyl, m.p. 61°; *n*-octyl, m.p. 69°; *n*-nonyl, m.p. 66°; *n*-decyl, m.p. 70°; *n*-undecyl, m.p. 62°; *n*-dodecyl, m.p. 81°; *cetyl*, m.p. 86°; *n*-octadecyl, m.p. 88°; Pr^b , m.p. 112°; Bu^b , m.p. 119°; *sec*-butyl, m.p. 120°; Bu^v , m.p. 166° (decomp.); *benzyl*, m.p. 181°; β -phenylethyl, m.p. 139°; γ -phenyl-*n*-propyl, m.p. 71°; *benzoin*, m.p. 220° (decomp.); *allyl*, m.p. 114°; *cholesteryl*, m.p. 198°. *n*-Dodecyl phenylcarbimate, m.p. 74°. *p*-Nitrophenylcarbimates: β -phenylethyl, m.p. 135°; γ -phenyl-*n*-propyl, m.p. 104°; *allyl*, m.p. 108°. P. G. C.

Odd-membered *n*-primary alcohols. ($\alpha \rightarrow \beta$ -transition).—See this vol., 921.

Catalytic dehydration of butyl alcohol by alumina. I. Isomerisation of butenes. II. Determination and preparation of butenes. C. MATIGNON, H. MOUREU, and M. DODÉ (Bull. Soc. chim., 1935, [v], 2, 1169—1181, 1181—1187).—I. Bu^vOH and pure Al_2O_3 (from the sulphate or nitrate) at 380° gives Δ^a -*n*-butene, but presence of a trace of acid, e.g., $SO_4^{''}$, causes complete or partial isomerisation to Δ^b -*n*-butene, increased slightly by previous heating of the Al_2O_3 to 450° or by details of its prep. which could not be precisely defined. Al_2O_3 prepared from the carbonate is less liable to cause isomerisation.

II. Details are given for the prep. (above method) of pure Δ^a - or Δ^b -*n*-butene; the proportions of each in a mixture may be determined either by the b.p. curve of the mixed dibromides or by transformation thereof into the diacetates, hydrolysis to the glycols, oxidation of the $\beta\gamma$ -glycol in the mixture to Ac_2 , and determination of the Ac_2 by NH_4OH . R. S. C.

Action of calcium hypochlorite on organic compounds with hydroxyl and carbonyl groups.

I. Calcium hypochlorite and the higher primary alcohols. J. SUKNEVITSCH and A. TSCHILINGARJAN (Ber., 1935, 68, [B], 1210—1216).—The hypothesis that $EtOCl$ is the primary product in the action of OCl' on EtOH is strengthened by the observation that much less $CHCl_3$ is formed by the action of $NaOCl$ on EtOH in presence of Na oleate, undecenoate, or cinnamate than in control experiments. The presence of OEt and Cl in the fatty acid layer establishes the addition to oleic acid. $CHPh:CH-CO_2Na$ in absence of EtOH is oxidised to $BzOH$, whereas $CHPh:CHCl$ is produced in its presence. The following schemes: $MeCHO \rightleftharpoons CH^+CH-OH \rightarrow (+EtOCl) CH_2Cl-CH(OH)OEt$ etc. and $CH_2:CH-OH \rightarrow CH_2:CH-OCl \rightarrow CH_2Cl-CHO$ $CHCl:CH-OH$ are suggested, the former being regarded as the more probable, since $EtCHO$ and Pr^bCHO do not give $CHCl_3$, but only the corresponding acids, and $MeOH$ yields only HCO_2H , CO_2 , and $MeOCl$. If reaction between one of these aldehydes and $Ca(OCl)_2$ takes place in presence of $MeOH$, $CHCl_3$ is formed in good yield: $Pr^bCHO \rightleftharpoons CMe_2:CH-OH \rightarrow (+MeOCl) CMe_2Cl-CH(OH)OMe \rightarrow CMe_2Cl-CHO \rightarrow CMe_2Cl-CO_2H$. Salts of CMe_2Cl-CO_2H and $CH_2Cl-CH(OH)OEt$ readily afford $CHCl_3$, whereas $CH_2Cl-CH(OEt)_2$ does not. The yield of $CHCl_3$

from MeCHO and $\text{Ca}(\text{OCl})_2$ is increased by the presence of EtOH; the impossibility of isolation of intermediates is probably due to the fact that $\text{CH}_2\text{Cl}\cdot\text{CHO}$ is more readily enolised than MeCHO. $\text{CCl}_3\cdot\text{CHO}$ is readily oxidised by $\text{Ca}(\text{OCl})_2$ to $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and CaCO_3 formed during the usual prep. of CHCl_3 is due to the decomp. of $(\text{CCl}_3\cdot\text{CO}_2)_2\text{Ca}$ as well as to the oxidation of $(\text{HCO}_2)_2\text{Ca}$. Higher alcohols $\text{R}\cdot\text{CH}_2\cdot\text{OH}$ react thus: $\text{CH}_2\text{R}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{CH}_2\text{R}\cdot\text{CHO} \rightarrow \text{CRCl}\cdot\text{CHO} \rightarrow \text{CRCl}_2\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{CO}\cdot\text{CO}_2\text{H}$. Thus Pr^nOH affords AcCO_2H and thence by oxidation or enolisation AcOH , CO_2 , $\text{H}_2\text{C}_2\text{O}_4$, and CHCl_3 . Bu^nOH gives EtCO_2H and CO_2 with little CHCl_3 . Alcohols $\text{CHRR}'\cdot\text{CH}_2\cdot\text{OH}$ react: $\text{CHRR}'\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{CHRR}'\cdot\text{CHO} \rightarrow \text{CClRR}'\cdot\text{CHO} \rightarrow \text{CClRR}'\cdot\text{CO}_2\text{H} \rightarrow \text{OH}\cdot\text{CRR}'\cdot\text{CO}_2\text{H} \rightarrow \text{CORR}' + \text{CO}_2 + \text{H}_2\text{O}$, and therefore yield the same products as obtained from the ketone CORR' with, in addition, the acid produced by direct oxidation. Thus Bu^nOH yields $\text{Pr}^n\text{CO}_2\text{H}$, AcOH , CO_2 , and CHCl_3 , whilst COMe_2 gives AcOH and CHCl_3 . $\text{CHMeEt}\cdot\text{OH}$ affords $\text{CHMeEt}\cdot\text{CO}_2\text{H}$, EtCO_2H , AcOH (very little), CO_2 , and CHCl_3 ; the same products, except $\text{CHMeEt}\cdot\text{CO}_2\text{H}$, are derived from COMeEt . Aldehydes, in which all H atoms attached to C united with CHO are replaced, are oxidised by OCl' to acids ($\text{CCl}_3\cdot\text{CHO}$; Bu^nCHO). *sec.*-Alcohols are transformed by $\text{Ca}(\text{OCl})_2$ into ketones, whereas *tert.*-alcohols yield only small amounts of the corresponding alkyl hypochlorite. The lengthening of the C chain of a primary alcohol is accompanied by an increase in the amount of acid with the same no. of C atoms; this is ascribed to increasing difficulty of enolisation of the corresponding aldehyde.

H. W.

Preparation of glycerol trichlorohydrin from propylene chloride. A. L. KLEBANSKI and A. S. VOLKENSCHTEIN (J. Appl. Chem. Russ., 1935, 8, 106—116).— $\text{CHMeCl}\cdot\text{CH}_2\text{Cl}$ (I) is obtained in 80% yield from Cl_2 and $\text{CHMe}\cdot\text{CH}_2$; the further chlorination of (I) to $\text{CHCl}(\text{CH}_2\text{Cl})_2$ (II), in presence or absence of catalysts, yields a mixture of products, chiefly $\text{CHMeCl}\cdot\text{CHCl}_2$, with very small yields of (II). (I), when heated with CaCl_2 , BaCl_2 , CaO , $\text{Ca}(\text{OH})_2$, MgO , or soda-lime, affords α -chloropropene and allene, but no allyl chloride. The synthesis of glycerol from (I) is not commercially realisable.

R. T.

Existence of carbon monoxide acetals. II. F. ADICKES and P. P. PECKELHOFF (Ber., 1935, 68, [B], 1138—1140).—If, in accordance with Scheibler, the ppt. obtained by the action of HCO_2Et on CNaPh_3 contains $\text{ONa}\cdot\text{C}\cdot\text{OEt}$ in addition to HCO_2Na addition of anhyd. EtOH must produce NaOEt and HCO_2Et and the amount of HCO_2H in the filtrate must exceed that due to the solubility of HCO_2Na . Since this is not the case, the existence of $\text{ONa}\cdot\text{C}\cdot\text{OEt}$ is denied. The only possible cause of formation of HCO_2Na appears to be in fission of HCO_2Et by CNaPh_3 into C_2H_4 and HCO_2Na .

H. W.

Rotational contribution of chromophoric groups in compounds of analogous structure. W. KUHN and H. BILLER (Z. physikal. Chem., 1935, B, 29, 1—41).—The validity of the vicinal rule (A., 1933, 211) has been examined. The optical absorp-

tion, rotatory dispersion, and circular dichroism of the nitrites of methyl-*n*-hexyl-, methylcyclohexyl-, and phenylmethyl-carbinol show that ring closure at the *n*-hexyl group and the replacement of hexyl by Ph are to be regarded as small chemical changes in the sense of the vicinal rule. With rotatory dispersion and circular dichroism the absorption region is divided into discrete bands, which are absent or only faintly indicated in optical absorption. The replacement of cyclohexyl by Ph in hexahydromandelic acid is a small change, whilst the replacement of CO_2Et in $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ by CN or Me is a large change. Replacement by Me of the H attached to the asymmetric C of $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ is a large change in relation to the rotational contribution of the Ph absorption band, but only a small change for the contributions of the other substituents. This leads to the formulation of the rule that if a chemical change occurs in a mol., then of absorption bands with chromophoric centres equidistant from the point of change strong bands undergo less change in their active properties than weaker bands. The rule is valid even when there are large chemical changes lying outside the scope of the vicinal rule. Both rules are related to physical considerations.

R. C.

Thermal analysis of binary mixtures of organic nitrates. III. T. URBANSKI (Rocz. Chem., 1935, 15, 191—197).—The m.-p. diagrams do not suggest formation of compounds in the systems mannitol hexanitrate (I)—camphor; pentaerythritol tetranitrate—phthalide, $-\text{NHPh}\cdot\text{CO}_2\text{Et}$, and $-\text{dinitrodimethylloxamide}$; erythritol tetranitrate (II)—1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$, —1:3:5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$, $-\text{CO}(\text{NPhEt})_2$. 1:2-Compounds are found in the systems (I)—*m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, transition point 58.1° , and (II)—trinitroanisole, m.p. 61.6° .

R. T.

Mannitol-dimolybdic acid. (MME.) Z. SOUBAREV-CHATELAIN (Compt. rend., 1935, 200, 1942—1944).—The conclusions of Honnelaitre (A., 1925, i, 509) have been confirmed by the isolation of the substance $\text{C}_6\text{H}_{14}\text{O}_6\cdot\text{H}_2\text{Mo}_2\text{O}_7\cdot\text{H}_2\text{O}$ (I) by cooling an aq. solution of $\text{H}_2\text{Mo}_2\text{O}_7$ and mannitol (1:1). (I) loses $1\text{H}_2\text{O}$ above 120° giving a product freely sol. in H_2O . (I) gives no coloration with $\text{K}_4\text{Fe}(\text{CN})_6$, and with AgNO_3 gives a yellow ppt. only after some time or when the solution is heated.

H. G. M.

Simple alkaneseleninic acids. H. J. BACKER and W. VAN DAM (Rec. trav. chim., 1935, 54, 531—538).—Simple alkaneseleninic acids (I) are obtained by oxidation of dialkyl diselenides with the theoretical quantity of dil. HNO_3 . They are weaker than the corresponding carboxylic acids (dissociation consts. are given) and form mol. compounds (II) with strong acids. The m.p. of (I) and (II) show the same regularities. *Me*₂ diselenide, b.p. $155\text{—}157^\circ$, $57^\circ/21\text{ mm.}$, and *Me*₂Se, b.p. 58° , are obtained from *Me*₂SO₄ and *K*₂Se₂. *Pr*₂ diselenide, b.p. $103\text{—}104^\circ/15\text{ mm.}$, from *Pr*⁺Br and *K*₂Se₂, and *Bu*₂ diselenide, b.p. $129\text{—}130^\circ/13\text{ mm.}$, are described. *Methaneseleninic acid* (III), m.p. 134° (decomp.) (*Pb* and *Ba* salts), *ethaneseleninic acid* (IV), *n*-*propaneseleninic acid* (V), m.p. 75° (*Pb* and *Ba* salts), and *n*-*butaneseleninic acid* (VI), m.p. 68° (*Pb* salt), are described.

The following *mol. compounds* were obtained. Of (III): *hydrochloride*, decomp. 100°; *nitrate*, m.p. 103° (decomp.); *sulphate*, m.p. 130° (decomp.); *methanesulphonate*, m.p. 142°; *ethanesulphonate*, m.p. 105°; *benzenesulphonate*, m.p. 150° (decomp.); *methionate*. Of (IV): *hydrochloride*, m.p. 106° (decomp.; contracts at 103°); *nitrate*, m.p. 73°; *sulphate*, m.p. 98°; *methanesulphonate*, m.p. 115°; *ethanesulphonate*, m.p. 86°; *benzenesulphonate*, m.p. 130° (decomp.); *methionate*, m.p. 113°. Of (V): *hydrochloride*, decomp. 101—102°; *nitrate*, m.p. 101°; *sulphate*, m.p. 119°; *methanesulphonate*, m.p. 122°; *ethanesulphonate*, m.p. 103°; *benzenesulphonate*, m.p. 136° (decomp.); *methionate*, m.p. 115°. Of (VI): *hydrochloride*, decomp. 99°; *nitrate*, m.p. 96°; *sulphate*, m.p. 117°; *methanesulphonate*, m.p. 99°; *ethanesulphonate*, m.p. 98°; *benzenesulphonate*, m.p. 121°; *methionate*, m.p. 111°.

P. G. C.

Ester hydrolysis in pure water.—See this vol., 938.

Highly unsaturated acids in sardine oil. II. Constitution of hiragonic acid, $C_{16}H_{26}O_2$. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 192—199).—Oxidation of Me hiragonate with $KMnO_4$ gives AcOH, $(CH_2 \cdot CO_2H)_2$, and Me H adipate, whilst ozonolysis affords also MeCHO, $CHO \cdot [CH_2]_4 \cdot CO_2Me$, $CHO \cdot [CH_2]_2 \cdot CO_2H$, and $(\cdot CH \cdot CHO)_2$. Hiragonic acid is Δ^{w} -hexadecatrienoic acid.

F. R. S.

Preparation of pure elaidic acid and the elaidin reaction. C. LUTENBERG (Fettchem. Umschau, 1935, 42, 89—91).—The yield of elaidic acid (I) obtained by the Holde and Rietz-Rankoff method (cf. B., 1924, 264; A., 1931, 1271) depends on the time and temp. of the reaction and on the mount of $NaNO_2$ used. (I), prepared by a modified method (details given) from the "liquid" fatty acids separated from arachis oil fatty acids by Twitchell's method and recryst. from Et_2O and EtOH, had m.p. 44.4—44.6°, I val. 89.95, SCN val. 89, mol. wt. 278, and contained 0.5% of saturated acids. HCN is demonstrable in the volatile products of the elaidinisation reaction.

E. L.

New stereoisomeride of elæostearic acid in pomegranate seed oil. Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 182—185b).—*Punicic acid* (I), m.p. 43.5—44°, has been obtained from the oil extracted by Et_2O from pomegranate seeds. When dissolved in light petroleum and kept during a week under CO_2 (but not H_2) (I) is converted into β -elæostearic acid (II), m.p. 70.5—71°. (I) with Br in light petroleum affords a tetrabromide, m.p. 113.5—114°, identical with that obtained from (II). (I) is regarded as a stereoisomeride of (II) of the structure, $Me \cdot [CH_2]_3 \cdot [CH:CH]_3 \cdot [CH_2]_3 \cdot CO_2H$. This has been confirmed by ozonolysis of (I) and its Me ester.

H. G. M.

Another new stereoisomeride of elæostearic acid in the seed oil of karasu-uri, *Trichosanthes cucumeroides*. Y. TOMAYA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 185—187b).—*Trichosaninic acid* (I), m.p. 35—35.5°, has been isolated from the seed oil of karasu-uri. In petroleum under CO_2 or with a trace of I it passes readily into its iso-

meride, β -elæostearic acid (II). (I) with Br in light petroleum affords a tetrabromide, m.p. 113—113.5°, identical with that obtained from (II). H. G. M.

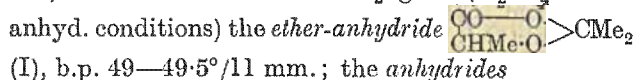
Synthetic fats. I. Preparation of trinonadecylin. D. W. WOOLLEY and R. B. SANDIN (J. Amer. Chem. Soc., 1935, 57, 1078—1079).—*Trinonadecylin*, α -, m.p. 66.5—67°, β -, m.p. 70.5°, and γ - (a glass), m.p. 60°, forms, is prepared. A form of $Me \cdot [CH_2]_{17} \cdot CN$ (modified prep. and hydrolysis) has m.p. 34—34.5°.

R. S. C.

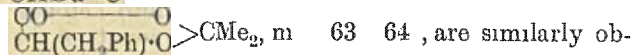
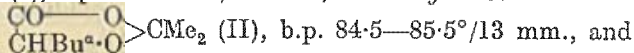
Anodic reactions during the electrolysis of α -hydroxy-acids. E. TOMMILA (Suomen Kem., 1935, 8, B, 25; cf. A., 1934, 739).—Electrolysis of lactic acid in 5*N*-NaOH (conditions described) gives at the anode a mixture of O_2 , CO, H_2 , CH_4 , C_2H_6 , AcOH, HCO_2H , MeCHO, and CO_2 . The reaction mechanisms are described.

J. L. D.

Acetone [isopropylidene] compounds of α -hydroxy-acids and their Raman spectra. H. OEDA (Bull. Chem. Soc. Japan, 1935, 10, 187—192).—Lactic acid and $COMe_2$ give $(H_2SO_4$ under anhyd. conditions) the ether-anhydride



(I), b.p. 49—49.5°/11 mm.; the anhydrides



tained. The Raman spectra of (I) and (II) correspond with those of a 5-membered saturated ring. F. R. S.

Kinetic studies of the cyclisation problem, with regard to the preparation of lactones with musk and amber odours. M. STOLL and A. ROUVE (Rev. Marques Parfums. Savonn., 1934, 12, 328—334; Chem. Zentr., 1935, i, 810).—The influence of the catalyst on the lactonisation of ω -OH-acids is limited, since the frequency of cyclising collisions is independent of the catalyst. ξ -Hydroxypentadecic acid is best lactonised by means of $PhSO_3H$ in C_6H_6 . Higher lactones, such as "exaltolide" (94% yield by the above process), are valuable in perfumery.

H. N. R.

Pyrolysis. II. Pyrolysis of derivatives of α -acetoxyisobutyric acid, and related substances. R. BURNS, D. T. JONES, and P. D. RITCHIE (J.C.S., 1935, 714—717; cf. this vol., 607).—*Me α -acetoxyisobutyrate*, b.p. 76—77°/18 mm. [obtained from Me α -hydroxyisobutyrate (I)], affords on pyrolysis AcOH and Me α -methylacrylate (II). Similarly β -methoxyethyl α -acetoxyisobutyrate, b.p. 105°/12 mm. [obtained from acetone cyanohydrin (III)], β -methoxyethyl alcohol, and H_2SO_4 , followed by acetylation], affords AcOH and β -methoxyethyl α -methylacrylate, b.p. 88—89°/20 mm.; and β -phenoxyethyl α -acetoxyisobutyrate, b.p. 166°/4 mm. (obtained similarly through β -phenoxyethyl α -hydroxyisobutyrate, b.p. 156—157°/5 mm.), affords β -phenoxyethyl α -methylacrylate, b.p. 138°/7 mm. The polymerisation of the methylacrylic esters is described.

(III) with Ac_2O and AcCl (or H_2SO_4) gives α -acetoxyisobutyronitrile (IV), but with $HClO_4$ as catalyst (IV) and *N*-acetyl- α -acetoxyisobutyramide (V), m.p. 81—82°, b.p. 120—130°/13 mm., are formed.

On pyrolysis (IV) gives α -methylacrylonitrile (VI) and some COMe_2 and HCN (the proportion of these two products increases with rise in temp.), whilst (V) gives AcOH and (VI). *Me* α -benzoyloxyisobutyrate, b.p. $156^\circ/19$ mm., is pyrolysed to (II) and BzOH , whilst *Me* α -chloroisobutyrate, b.p. $133\text{--}135^\circ/760$ mm., gives some HCl and (II). On pyrolysis (III) gives COMe_2 and HCN , and (I) gives some COMe_2 and (II). H. G. M.

Preparation of oxalic acid from sodium formate. V. M. SEMENOV, A. J. SCHAGALOV, and P. I. ASTRACHANTZEV (J. Appl. Chem. Russ., 1935, 8, 99—105).—The method of Merz and Weitz (A., 1881, 18) gives 83%, and that of Koepp (A., 1906, i, 4) 95%, yields. The latter method is studied in detail. R. T.

Reaction between sodium sulphate and oxalic acid. K. TANEMURA and S. MIYOSHI (J. Soc. Chem. Ind. Japan, 1935, 38, 188b).— $\text{H}_2\text{C}_2\text{O}_4$ reacts with conc. aq. Na_2SO_4 solutions containing H_2SO_4 , giving $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as solid phase. MgSO_4 or $(\text{NH}_4)_2\text{SO}_4$ remains in solution, but ZnSO_4 interferes. J. S. A.

Condensation of aldehydes with malonic acid in presence of organic bases. III. Condensation of salicylaldehyde with ethyl malonate. P. N. KURIEN, C. J. PETER, and K. C. PANDYA (Proc. Indian Acad. Sci., 1935, 1, A, 775—779).—Using $\text{C}_5\text{H}_5\text{N}$ as catalyst, the max. yield (55%) of Et coumarincarboxylate is secured when equimol. proportions of $\text{CH}_2(\text{CO}_2\text{Et})_2$ and *o*-OH- $\text{C}_6\text{H}_4\cdot\text{CHO}$ are treated with 0.15 mol. of $\text{C}_5\text{H}_5\text{N}$ at 100° for 18 hr. and then kept at room temp. for 3 days. Quinoline, isoquinoline, lutidine, α -naphthaquinoline, and quinaldine are somewhat less efficient, whereas cinchonidine (0.14 mol.) gives equally good results. H. W.

Reactivity of alkylmalonic esters. M. GRUNFELD (Bull. Soc. chim., 1935, [v], 2, 994—996).—The velocity of reaction between $\text{CR}'\text{R}''(\text{CO}_2\text{Et})_2$ (I) ($\text{R}'\text{R}''=\text{H}_2$, PrH , Pr_2 , BuH , and Bu_2) and *n*-octylamine in EtOH under seal at 100° has been studied. The reactivity of (I) decreases as its absorption in the ultra-violet diminishes (cf. A., 1930, 452; 1932, 365). H. G. M.

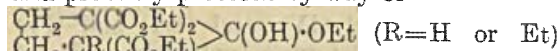
Structure of glutaryl chloride. S. G. P. PLANT and (Miss) M. E. TOMLINSON (J.C.S., 1935, 856).—Both forms of glutaryl chloride (I) are involved in its interaction with AlCl_3 and anisole, since a mixture of $\alpha\gamma$ -dianisoylpropane, m.p. 99° , and $\delta\delta$ -di-*p*-anisylvalerolactone, m.p. $111\text{--}113^\circ$, is obtained. Similarly, (I) with AlCl_3 and phenetole gives a mixture of $\alpha\gamma$ -diphenetoylpropane, m.p. 133° , and $\delta\delta$ -di-*p*-phenetoylvalerolactone, m.p. 82° . Glutaric anhydride and AlCl_3 with anisole gives γ -anisoylbutyric acid, m.p. 137° , and with phenetole γ -phenetoylbutyric acid, m.p. 114° , is obtained. P. G. C.

New reaction of tartaric acid. M. PESEZ (J. Pharm. Chim., 1935, [viii], 21, 542—546).—Addition of 0.1 c.c. of a solution containing 2 g. of resorcinol (I) and 10 g. of KBr in 100 c.c. of $\text{H}_2\text{O} + 1$ c.c. of H_2SO_4 to 0.1 c.c. of a tartrate solution in 2 c.c. of H_2SO_4 (*d* 1.84) and warming to 100° (2—5 min.) affords an intense blue colour, changed to currant-red by addition of 1 c.c. of H_2O , and giving a fugitive violet coloration

when neutralised. The reaction is sp. for tartaric acid (sensitivity 0.1 mg.) and for (I) (other phenols give different colours), is unaffected by BrO_3' , NO_2' , or Fe''' , but is negative in presence of OCl' , ClO_3' , NO_3' , MnO_4'' (all eliminated by Zn-Cu couple), I' , IO_3' , or CrO_4'' . $\text{CCl}_3\cdot\text{CHO}$ gives the same blue colour, but is easily removed by previous alkaline hydrolysis. J. W. B.

Complex formation between manganese or aluminium with tartaric acid in alkaline medium. S. P. GOVEL and B. L. VAISHYA (J. Indian Chem. Soc., 1935, 12, 193—196; cf. A., 1934, 615).—From polarimetric and potentiometric measurements of solutions of K tartrate (I), alkali, and MnCl_2 or $\text{Al}_2(\text{SO}_4)_3$ it is inferred that complexes containing Mn and (I) in the mol. ratio 1 : 1, and Al and (I) in the ratio 2 : 3 (cf. A., 1933, 240), are formed. H. G. M.

Cyclisation of $\alpha\beta$ -ethanedimalonic esters by sodium ethoxide. E. R. MEINCKE, R. F. B. COX, and S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1133—1135).— $(\text{CH}_2\text{Br})_2$ and Et_2 magnesiomalonate give $[\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2]_2$ and Et_4 1 : 1 : 4 : 4-cyclohexanetetra-carboxylate, b.p. $195\text{--}207^\circ/15$ mm., m.p. $76\text{--}77^\circ$ [giving the acid, m.p. $249\text{--}250^\circ$ (decomp.)], and thence hexahydroterephthalic acid, m.p. $172\text{--}173^\circ$. The former ester with NaOEt , first at $85^\circ/760$ mm. and then at $120^\circ/200$ mm., gives Et_2 cyclopentanone-2 : 5-dicarboxylate (31%), Et cyclopentanone-2-carboxylate (15%), Et_2CO_3 , and a trace of EtOH. Et_4 *n*-hexane- $\alpha\delta\delta$ -tetracarboxylate [from NaOEt , $\text{CH}_2(\text{CO}_2\text{Et})_2$, and $(\text{CO}_2\text{Et})_2\text{CET}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$], b.p. $192\text{--}195^\circ/8$ mm., with NaOEt at 115° gives 74.3% of Et_2 2-ethylcyclopentanone-2 : 5-dicarboxylate, m.p. $147\text{--}154^\circ/8$ mm. (hydrolysed to 2-ethylcyclopentanone), Et_2CO_3 , and a little EtOH. Et_4 *n*-octane- $\gamma\gamma\zeta\zeta$ -tetracarboxylate is largely unchanged by NaOEt even at 250° (gives a little Et_2CO_3 and EtOH). Cyclisation, therefore, requires presence of an α -H and probably proceeds by way of



subsequent elimination of CO_2Et and the ketal OEt to form Et_2CO_3 . R. S. C.

The two β -sulphoacrylic acids. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 54, 523—530).— $(\text{NH}_4)_2\text{SO}_3$ converts *cis*- β -chloroacrylic acid into *trans*- β -sulphoacrylic acid (I), also obtained from propiolic acid. The *Ba*, *K*, *Tl*, and NH_3Ph , m.p. $117\text{--}118^\circ$ (decomp.), salts are described. Similarly, *trans*- β -chloroacrylic acid affords *cis*- β -sulphoacrylic acid (II) ($+1\text{H}_2\text{O}$), m.p. $82\text{--}84^\circ$, ($+2\text{H}_2\text{O}$) m.p. about $87\text{--}88^\circ$ (*Ba* and NH_3Ph , decomp. $155\text{--}158^\circ$ after becoming discoloured at $120\text{--}130^\circ$, salts). Hydrogenation of (I) or (II) gives β -sulphopropionic acid. P. G. C.

β -Sulphocrotonic acid. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 54, 551—560).—The action of HSO_3' on salts of α -bromo- (I), α -bromois- (II), β -chloro-, or β -chlorois- crotonic acid gives the same β -sulphocrotonic acid (III), m.p. $94\text{--}95^\circ$ [*Ba*, *K*, and NH_3Ph , m.p. $191\text{--}192^\circ$ (decomp.)], salts], hydrogenated to β -sulphobutyric acid, which can be resolved into its optical antipodes by

brucine. Treatment of (III) with the requisite halogen affords α -bromo- β -sulphocrotonic acid (*Ba* and *quinine*, m.p. 157—158°, salts) and α -chloro- β -sulphocrotonic acid [*quinine* salt, m.p. 176° (decomp.)]. (I) or (II) yield *Et* α -bromocrotonate, b.p. 192°/760 mm., when esterified with EtOH and H₂SO₄ or when their Ag salts are treated with EtI. P. G. C.

$\beta\beta$ -Disulphoglutaric acid. J. M. VAN DER ZANDEN (Rec. trav. chim., 1935, 54, 561—565).— $\beta\beta$ -Disulphoglutaric acid, m.p. 162° (decomp.), has been obtained from H sulphite and sulphoglutaconic acid, β -chloroglutaconic acid, or glutinic acid. The *Ba*, *K*, *Pb*, *Tl*, *Sr*, *Ca*, *Ag*, *tri-aniline*, and *di*- and *tri-strychnine* salts are described. The Na salts from either of the strychnine salts were optically inactive. P. G. C.

Disproportionation reaction of diselenides.

A. FREDGA (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 46, 1—6).—An aq. solution of $\alpha\alpha$ -diselenodipropionic acid (I) with Ag₂SO₄ and H₂SO₄, Ag₂O and NaOH, or AgCl and NaOH (but not Ag metal) undergoes disproportionation and affords a mixture of AgSe·CHMe·CO₂H and AgSe·CHMe·CO₂Ag, whilst the solution contains α -seleninopropionic acid. Hg salts and (I) give a complex white ppt. It is possible that the following equilibrium obtains: 2(SeR)₂ + 2H₂O \rightleftharpoons 3R·SeH + R·SeO₂H (R = ·CHMe·CO₂H); the equilibrium lies to the left, but on the addition of a Ag salt, one of the products is removed as an insol. Ag salt. An alternative mechanism involving oxidation of (I) by Ag⁺ is not, however, excluded. H. G. M.

Configurative relationship between optically active selenodipropionic acid and α -thiodipropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 43, 1—6).—Se(CHMe·CO₂H)₂, m.p. 147°, has been resolved into its optical *antipodes* (I), m.p. 124°, [α]_D +234.5°, and (II) [α]_D -235° in 0.4*N*-HCl. The fusion diagrams of (I) and (II), (I) and (+)-thiodipropionic acid (III), (I) and (-)-thiodipropionic acid (IV), and (III) and (IV) are given. (I) and (III) form a continuous series of mixed crystals, whilst (I) and (IV) form a 1:1 mol. compound [optically active racemate (cf. A., 1921, ii, 598)]. It is concluded that (I) and (III) have the same configuration. The respective S and Se acids are regarded as isomorphous. H. G. M.

Interaction of diselenodicarboxylic acids with mercury. A. FREDGA (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 44, 1—4).—The compound Hg(Se·CH₂·CO₂H)₂ (I), decomp. 120°, or its alkali salts, is obtained when a solution of (Se·CH₂·CO₂H)₂ (II) (A., 1929, 1285), or its alkali salts, respectively, is shaken with Hg. Hg(S·CH₂·CO₂H)₂ could not be prepared in a similar way. (I) suspended in dil. H₂SO₄ may be titrated: Hg(Se·CH₂·CO₂H)₂ + 2I⁻ + 2KI = (Se·CH₂·CO₂H)₂ + K₂HgI₄. Homologues of (II) also react readily with Hg. Neutralised solutions of (II) dissolve Cu (but not Ag) and the resulting *Cu* compound is pptd. by addition of H₂SO₄ as an amorphous yellow ppt. The Hg in (I) is not pptd. by alkali or KI, or by H₂S except after a long time. The salts of (I) give a black ppt. with (NH₄)₂S. (I) is sol. in aq. KCN and is reprecipitated unchanged by the

addition of HCl. The *alkali*, *Pb*, *Ba*, *Ca*, *Sr*, *Mn*, *Zn*, *Cu*, *Cr*, *Ag*, *Fe*^{II}, *Te*^{III}, *Ni*, *Co*, *Bi*, and *Hg* salts are described. H. G. M.

Schiff colour reaction of aldehydes. P. RUMPF (Ann. Chim., 1935, [xi], 3, 327—442).—An historical account of the application and theory of the Schiff colour reaction is given. Reagents other than fuchsin, H₂O, and SO₂ fail to give the colour, whilst O does not enter into the reaction. The influence of different concns. of SO₂, aldehydes, etc. has been studied spectrographically. The reaction is not due to fuchsin or Schiff's bases, and is produced only by the combined action of SO₂ and a substance containing free CHO on aq. fuchsin. Aldoses liberate fuchsin. The absorption max. (5600—5850 Å.) is sp. for a given aldehyde only under strictly defined conditions. In buffer experiments, reaction is independent of the type of buffer used and is governed only by the *p*_H. The spectrographic data indicate that the no. of acid substituents in the NH₂ groups of the coloured complex (I) is variable. The rate of formation of (I), determined by a photo-electric cell, is initially $\propto t^2$ and approx. $\propto [\text{SO}_3]^{1/2}$, but decreases with increasing [H⁺]. Electrometric titrations with the glass electrode indicate the formation of strong monobasic acids in solutions containing SO₂ and aldehydes, but the titration curve of H₂SeO₃ is unaffected. Compounds of the type NHR·SO₃H could not be detected in dil. solutions of amines and SO₂. Addition of an aldehyde to SO₃^{II} solutions of aromatic amines produces strong complex acids containing one mol. of each constituent. Dissociation consts. of NH₂-derivatives of C₆H₆ and CHPh₃ indicate that (I) is a carbonium ion (II), basicity being conferred on the central C by the *p*-NH₂ groups. The decolorisation of various CHPh₃ dyes has been studied. The concn. of colourless -NH₃⁺ relative to coloured (II) $\propto [\text{H}^+]^n$, where *n* is the no. of *p*-NH₃⁺ groups. In the Schiff reagent, the H₂SO₃ may combine further with (II) itself. It is suggested that (I) consists of a univalent (II) containing a variable no. of ionisable CHR·SO₃H substituents in the NH₂ groups. R. S.

Separation of formaldehyde from hexamethylenetetramine at different hydrogen-ion concentrations and constant temperature. E. PHILIPPI and J. LOBERING (Biochem. Z., 1935, 277, 365—375).—The kinetics of the breakdown of (CH₂)₆N₄ into CH₂O and NH₃ in various buffer solutions of different *p*_H are investigated and a series of curves and velocity coeffs. summarise the results. P. W. C.

Limits of aldol condensation of acetaldehyde. E. A. SCHILOV (J. Appl. Chem. Russ., 1935, 8, 93—98).—Aldol and MeCHO afford a readily dissociable additive compound, CHMe< $\begin{array}{c} \text{O} \text{---} \text{CHMe} \\ \text{CH}_2 \cdot \text{CH}(\text{OH}) \end{array}$ >O, to the formation of which is ascribed the spurious equilibrium found in the aldol condensation. R. T.

Constitution of aldols. M. BACKES (Compt. rend., 1935, 200, 1669—1671; cf. A., 1933, 1050).—Acetaldo (I) in H₂O or aq. HCl (but not in C₅H₅N) shows a strong absorption band at 2800 Å., characteristic of CO⁺, which shows that the cyclic structure for (I) is favoured in non-aq. solutions. The ring is

opened easily by many aldehydic reagents, but its presence explains the thermal decomp. of (I) mainly to give 2 mols. of MeCHO, and not predominantly an unsaturated aldehyde. Propion-, iso- and *n*-butan-, and heptan-aldol, when heated, also decompose to give 30–60% of saturated and some unsaturated aldehyde, also polymerides. In presence of H₂O, the open-chain decomp. occurs almost exclusively. J. L. D.

Action of organomagnesium halides on $\alpha\beta$ -unsaturated aldehydes. P. G. STEVENS (J. Amer. Chem. Soc., 1935, 57, 1112–1117).—Only traces of 1:4-addition of MgRCl to CHMe:CH:CHO (I) occur when R=Ph, Et, Pr^a, allyl, or Pr^b, but considerable amounts (> 20%) when R=Bu^v or *tert*-amyl. MgBu^vBr gives 11% of 1:4-addition. MgBu^vCl gives also a substance, C₁₆H₃₀O, b.p. 96.3–97.9°/1 mm., unstable, and ? $\alpha\alpha$ -dimethyl-8-($\alpha'\beta'\beta'$ -trimethylpropyl)- Δ^8 -octene- γ -diol (II), m.p. 128–129°, probably formed thus: (I) + MgBu^vBr \rightarrow



CHO:CH:EtBu^v:CH(OMgCl):CH:CHMe \rightarrow (+ MgBu^vCl; + H₂O) (II). The content of 1:4-addition may thus be considerably > estimated for MgBu^vCl and also for Mg *tert*-amyl chloride (which gives substances, b.p. 84–89°/3 mm. and 120–121°/2 mm., respectively) and MgPr^bCl, which all give > 34% of complex products. Mesityl oxide and MgBu^vCl give no 1:4-addition, but this occurs to the extent of 41.4 and 54% with CHMe:CH:COMe and MgEtCl and MgBu^vCl, respectively. The results are inexplicable. The following are described. $\beta\gamma\gamma$ -Trimethylvaleraldehyde, b.p. 56–57°/19 mm. (semicarbazone, m.p. 166°), oxidised by Ag₂O to the acid, b.p. 124–124.5°/19 mm. (amide, m.p. 163–164°), which yields (P, Br, MeOH) *Me* α -bromo- $\beta\gamma\gamma$ -trimethylvalerate, b.p. 90.5–91°/8 mm., converted by NPhEt₂ at 190–200° into *Me* $\beta\gamma\gamma$ -trimethyl- Δ^2 -pentenoate, b.p. 184–186°/765 mm., which with O₃ in AcOH affords CHO:CO₂Me and COMeBu^v. $\alpha\alpha$ -Dimethyl- Δ^8 -hexen- γ -ol, b.p. 75–76°/36 mm., the *H* phthalate of which with strychnine affords the *d*-form, $[\alpha]_D^{25} +15^\circ$. $\beta\gamma\gamma$ -Trimethylhexaldehyde semicarbazone, m.p. 172°. β -Methyl- and $\beta\gamma$ -dimethyl-valeraldehyde semicarbazones, m.p. 128–129° and 136–137°, respectively. α -Phenyl- Δ^8 -buten- α -ol, b.p. 91–92°/0.5 mm., m.p. 33–35°. $\delta\epsilon\epsilon$ -Trimethylhexan- β -one, b.p. 72°/20 mm. [semicarbazone, m.p. 200–201° (decomp.)]. $\alpha\alpha\beta\epsilon$ -Tetramethyl- Δ^8 - γ -ol, b.p. 66.5–68°/11 mm., 178–180°/760 mm. (unchanged), dehydrated by I to a? hexadiene, b.p. 146–153°. R. S. C.

Hydrogenation of a mixture of two α -ethylenic aldehydes. General method of synthesis of glycols, OH:CHR:CHR':OH. J. WIEMANN (Bull. Soc. chim., 1935, [v], 2, 1209–1214).—Reduction of a mixture of two $\alpha\beta$ -unsaturated aldehydes by a Zn–Cu couple gives most mixed glycol if the rate of reduction of the two aldehydes is similar and if the nature of the aldehydes is diverse. Reduction proceeds by formation of :CHR:OH and coupling of two such residues. It leads to both stereoisomerides. Citral, which alone gives an oxide, C₂₀H₃₀O, b.p. 181–182°/9 mm., with CH₂:CH:CHO (I) or CHMe:CH:CHO (II) in aq. EtOH gives the products previously described (this vol.,

608) as formed in AcOH. A mixture of (I) and (II) gives Griner's [CH₂:CH:CH(OH):]₂ (III), Charon's [CHMe:CH:CH(OH):]₂ (IV), and a mixture of isomeric $\gamma\delta$ -dihydroxy- $\Delta^{\alpha\epsilon}$ -heptadienes, b.p. 111°/12 mm., hydrogenated (colloidal Pd) to heptane- $\gamma\delta$ -diol, b.p. 109°/15 mm., m.p. 103–104° (lit., 98–99°). (I) (4 mols.) and furfuraldehyde (V) (3 mols.) give (III) (15%) and a mixture of 2- $\alpha\beta$ -dihydroxy- Δ^v -butenylfurans (40%), b.p. 115–116°/3 mm. (stereoisomeric phenylurethanes, m.p. 189° and 116–118°, respectively). (II) and (V) yield (IV) (10%) and mixed 2- $\alpha\beta$ -dihydroxy- Δ^v -pentenylfurans [stereoisomeric phenylurethanes, m.p. 222–223° (block) and 220°, respectively]. (I) and PhCHO give stereoisomeric α -phenyl- Δ^v -butene- $\alpha\beta$ -diols (cf. this vol., 750). R. S. C.

Successive reactions in heterogenous catalysis.

III. Mechanism of the formation of acetone from acetaldehyde and water. M. J. KAGAN, I. A. SOBOLEV, and G. D. LUBARSKI (Ber., 1935, 68, [B], 1140–1146).—When the vapours of anhyd. EtOH or MeCHO are passed over Cu, Cu+Cr₂O₃, ZnO, or ZnO+Cr₂O₃ at 300–350° ester is produced in definite amount. If the reactants are previously mixed with steam the content of ester decreases, whilst that of AcOH increases. At temp. > 400° COMe₂ is obtained in place of AcOH. The intermediate production of EtOAc in the prep. of COMe₂ from MeCHO and H₂O is therefore regarded as established. At 300–600° MeCHO yields CO and CH₄; formation of H and keten is not observed. Anhyd. EtOAc is converted at 400° in presence of ZnO+Cr₂O₃ into COMe₂, EtOH, C₂H₄, and CO₂. Anhyd. EtOH similarly affords COMe₂ through decomp. of the intermediate EtOAc. Aq. EtOAc at 450° also affords COMe₂, but the process involves hydrolysis of the ester. H. W.

Influence of hydrogen sulphite solutions on mono- and di-hydroxyacetone at raised temperature. G. MENZINSKY (Ber., 1935, 68, [B], 1154–1159).—Acetol is partly resinified and partly oxidised to HCO₂H and AcOH when heated with aq. NaHSO₃ at 130°. Since it is little affected when heated with H₂O or H₂SO₄ the change is not due to H⁺, but is a sp. action of NaHSO₃. Under similar conditions CO(CH₂:OH)₂ affords HCO₂H and OH:CH₂:CO₂H. H. W.

Hydrazone and osazone reactions. E. G. R. ARDAGH and F. C. RUTHERFORD (J. Amer. Chem. Soc., 1935, 57, 1085–1088; cf. A., 1932, 377).—The formation of *d*-glucose-, fructose-, and *d*-galactose-phenylhydrazone is very slow in unbuffered solutions, increases tenfold as the buffer concn. rises to 0.3*M*, is much greater with PO₄^{'''} than with OAc' buffers, and rises with change of *p*_H from 7.5 to 4.0. The reaction is bimol. (cf. lit.). Osazone formation is similar. Only that portion of the NHPh:NH₂ present as salt reacts (cf. lit.). R. S. C.

Transformation of glucose into galactose and gulose by simple optical inversion. J. W. H. OLDHAM and G. J. ROBERTSON (J.C.S., 1935, 685–689).—The following experiments support the view (cf. A., 1934, 871) that anhydro-formation is the necessary precursor of the inversion of glucose into gulose and galactose (this vol., 329). Diisopropylideneglucose 3-*p*-toluenesulphonate affords diisopropyl-

ideneglucose, m.p. 107—108°, on boiling with KOH-EtOH. 6-Triphenylmethyl-2:3-dimethyl- α -methylglucoside 4-*p*-toluenesulphonate, m.p. 146—147°, $[\alpha]_D^{20} +66.3^\circ$ in CHCl_3 , is hydrolysed by NaOMe to (I), and after removal of CPh_3 is hydrolysed (NaOMe-MeOH- H_2O) to 2:3-dimethyl- α -methylglucoside and a trace of an unsaturated substance (probably a derivative of glucose). 6-Triphenylmethyl- α -methylglucoside 2:3-dibenzoate 4-*p*-toluenesulphonate, m.p. 163—164°, $[\alpha]_D^{20} +66.3^\circ$ in CHCl_3 , is converted by NaOH, H_2O , and COMe_2 , and then Ac_2O and $\text{C}_5\text{H}_5\text{N}$, into an amorphous compound considered to be 6-triphenylmethyl-3:4-anhydro- α -methylgalactoside 2-acetate. This with HCl and COMe_2 gives a mixture containing isopropylidene- α -methylglucoside acetate (II), m.p. 176—178°, $[\alpha]_D^{20} +76.8^\circ$ in CHCl_3 , and isopropylidene- α -methylgalactoside acetate (III), m.p. 101—102°, $[\alpha]_D^{20} +127.3^\circ$ in CHCl_3 . (II) is deacetylated to isopropylidene- α -methylglucoside (IV), m.p. 132—133°, $[\alpha]_D^{20} +88.5^\circ$ in CHCl_3 , hydrolysed by 0.02*N*- H_2SO_4 to the free sugar. (IV) with 0.002*N*- H_2SO_4 affords α -methylglucoside, m.p. 77—79°, $[\alpha]_D^{20} +109.7^\circ$ in H_2O . (III) is deacetylated to isopropylidene- α -methylgalactoside, m.p. 102—104° (cf. this vol., 329), $[\alpha]_D^{20} +147.9^\circ$ in CHCl_3 , $+168.6^\circ$ in H_2O , hydrolysed (dil. AcOH) to α -methylgalactoside. Further 4:6-benzylidene- α -methylglucoside 3-benzoate 2-*p*-toluenesulphonate affords on alkaline hydrolysis a 4:6-benzylidene-2:3-anhydro- α -methylhexoside, converted by NaOMe into a methyl-4:6-benzylidene- α -methylhexoside, which is not a derivative of glucose.

H. G. M.

Walden inversion in the sugar group. I. Fission of 3:4-anhydro- β -methylhexoside. A. MÜLLER (Ber., 1935, 68, [B], 1094—1097).—Treatment of the anhydro- β -methylhexoside (I) (obtained by hydrolysis of β -methylglucoside triacetate 4-*p*-toluenesulphonate (A., 1930, 1411; 1934, 513) with *N*- H_2SO_4 leads to a non-cryst. mixture of sugars from which *d*-glucosazone and *d*-gulosazone are isolated. (I) is either an anhydroglucoside or, if Walden inversion occurs during elimination of *p*- $\text{C}_6\text{H}_4\text{MeSO}_2$, an anhydrogalactoside. The balance of evidence favours the latter supposition, since the product does not appear to contain the oxide ring in the *trans* position, as it is stable towards boiling Ac_2O . The formation of galactosazone could not be established. The presence of gulose among the products of hydrolysis confirms the 3:4-position of the ring and its (*ll*)-*cis* configuration.

H. W.

Reagent for eliminating interference due to calcium in volumetric Fehling's titration for invert sugar. J. G. N. GASKIN (Analyst, 1935, 60, 318—319).— Ca^{++} is rendered inert by addition of Na hexametaphosphate (Calgon).

E. C. S.

Additive compounds of the carbohydrates. II. Potassium hydroxide-sucrose. E. G. V. PERCIVAL (J.C.S., 1935, 648—653; cf. A., 1934, 1092).—Sucrose (I) (or its octa-acetate), EtOH, and KOH afford the compound (II), $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{KOH}$, which with dry Me_2SO_4 yields much (I) and a trimethylsucrose, acetylated to a penta-acetate which is hydrolysed to 6-methylglucopyranose and 1:6-dimethylfructofuranose. In (II), therefore, one KOH is associated

(by co-ordination) with each of the three primary alcohol groups of (I). H. G. M.

Disaccharides in "hydrol." G. H. COLEMAN, (Miss) M. A. BUCHANAN, and P. T. PAUL (J. Amer. Chem. Soc., 1935, 57, 1119—1121).—Methylation (Me_2SO_4 -NaOH and Ag_2O -MeI) of the non-fermentable portion of "hydrol" (I) (the residue from the commercial hydrolysis of maize-starch) gives 20% of heptamethyl-8-methylgentiobioside and 80% of an oily octamethyldisaccharide, $[\alpha]_D^{20} +80^\circ$ in EtOH, hydrolysed to 2:3:4-trimethyl- and 2:3:4:6-tetramethyl-glucose. (I) may, therefore, contain 6- α -glucosidoglucose.

R. S. C.

Polysaccharides. IX. Hydrolysis of "xyloglucuronide" and the isolation of the new disaccharide "barium xyloglucuronate." K. NISHIDA and H. HASHIMA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 66—69).—Hydrolysis of xyloglucuronide yields xylose, glucuronic acid, and xyloglucuronic acid isolated and purified as the Ba salt $\text{C}_{22}\text{H}_{34}\text{O}_{22}\text{Ba}$, decomp. 180°, $[\alpha]_D^{20} +54.8^\circ$ in H_2O . No other hexoses or pentoses could be detected.

J. N. A.

Emulsin. XXI. Influence of substitution in the benzene nucleus of phenol- β -*d*-glucosides on their ease of fission with enzymes. B. HELFERICH, H. E. SCHEIBER, R. STREECK, and F. VORSATZ (Annalen, 1935, 518, 211—225).—With aq. EtOH-KCN *o*-bromo-*o*- and -*p*-cresol- β -*d*-glucoside tetra-acetate afford, respectively, the Ac_4 derivative, m.p. 143—145°, $[\alpha]_D^{20} -15.17^\circ$ in CHCl_3 , of *o*-(I), m.p. 170—175° (corr.), $[\alpha]_D^{20} -66.6^\circ$ in H_2O (deacetylation by NH_3 -MeOH), and *p*-cyanomethylphenol- β -*d*-glucoside (II), m.p. 159.5—161.5° (corr.), $[\alpha]_D^{20} -71.4^\circ$ in H_2O (Ac_4 derivative, m.p. 134—136°, $[\alpha]_D^{20} -19^\circ$ in CHCl_3). Hydrolysis of (I) and (II) with 2*N*-NaOH affords, respectively, *o*- (only as its Na salt, decomp. above 207°, $[\alpha]_D^{20} -52^\circ$ in H_2O) and *p*-carboxymethylphenol- β -*d*-glucoside, m.p. 190—193° (corr.), $[\alpha]_D^{20} -63^\circ$ in H_2O {Na salt, $[\alpha]_D^{20} -54.9^\circ$ in H_2O ; Me ester, sinters 106°, m.p. 121—124° (corr.)}. By heating the appropriate phenol with β -glucose penta-acetate and a dehydrating agent (ZnCl_2 , *p*- $\text{C}_6\text{H}_4\text{MeSO}_3\text{H}$) at 100°, or with tetra-acetylglucosidyl bromide and NaOH-aq. COMe_2 , and subsequent deacetylation are obtained 2:4-dimethylphenol-, m.p. 181—183.5° (corr.), $[\alpha]_D^{20} -65^\circ$ in H_2O (Ac_4 derivative, m.p. 171—173°, $[\alpha]_D^{20} -24^\circ$ in CHCl_3), *o*-, m.p. 157—158° (corr.), $[\alpha]_D^{20} -65^\circ$ in H_2O [Ac_4 derivative, m.p. 152—154° (corr.), $[\alpha]_D^{20} -28^\circ$ in CHCl_3], and *p*-ethylphenol-, m.p. 164—166° (corr.), $[\alpha]_D^{20} -65.4^\circ$ in H_2O [Ac_4 derivative, m.p. 146—147° (corr.) $[\alpha]_D^{20} -16^\circ$ in CHCl_3]; *o*-hydroxyacetophenone-, m.p. 152—154° (corr.), $[\alpha]_D^{20} -66.5^\circ$ in H_2O ; protocatechualdehyde-, m.p. 172—174°, $[\alpha]_D^{20} -93^\circ$ in H_2O (Glaser *et al.*, A., 1923, i, 820, give m.p. 73—74°, $[\alpha]_D^{20} -36.2^\circ$ in H_2O) [Ac_4 derivative, m.p. 180° (corr.), $[\alpha]_D^{20} -53^\circ$ in EtOH] (glucose residue is in the 4-position, since methylation gives the vanillin compound); iso-vanillin-, m.p. 174—175° (corr.), $[\alpha]_D^{20} -108.4^\circ$ in H_2O [Ac_4 derivative, m.p. 141—142° (corr.), $[\alpha]_D^{20} -28^\circ$ in CHCl_3]; 3-hydroxy-4-ethoxyphenol-, m.p. 169.5° (corr.), $[\alpha]_D^{20} -90^\circ$ in H_2O buffered to p_H 5.0 [Ac_4 derivative, m.p. 164° (corr.), $[\alpha]_D^{20} -33^\circ$ in

CHCl_3], β -D-glucoside; *protocatechualdehyde*- β -D-glucoside, m.p. 202–203° (corr.), $[\alpha]_D^{20}$ –109.4° in H_2O [Ac_8 derivative, dimorphous, m.p. 180° (corr.) and 168.5°, $[\alpha]_D^{20}$ –72° in CHCl_3], *o-cresol*- α -D-, + H_2O and anhyd., polymorphous, m.p. varies between 75° and 121°, $[\alpha]_D^{20}$ +188° in H_2O (Ac_4 derivative, m.p. 86–88.5°, $[\alpha]_D^{20}$ +173° in CHCl_3), and *vanillin*- β -D-galactoside, m.p. 203–205° (corr.), $[\alpha]_D^{20}$ –65° in H_2O [Ac_4 derivative, m.p. 126–127° (corr.), $[\alpha]_D^{20}$ –28° in CHCl_3], are similarly prepared. Ease of fission of the above with emulsin at $p\text{H}$ 5.0 does not run parallel to HCl-hydrolysis. Fission is promoted by *o*-Me or -Et (Me = Et), and retarded by *p*-Me or -Et. Unlike NH_2 a *p*- CO_2H (or CO_2Et) has no retarding action. The most effective substituents for accelerating fission are $\text{CH}_2\text{CN} < \text{COMe} < \text{CHO}$. Parallel results are obtained with β -D-glucosides and β -D-galactosides. J. W. B.

Hydrolysis and oxidation of salicoside.—See this vol., 1042.

Amyloses. Corn α -amylose and retrograded β -amylose. T. C. TAYLOR and S. G. MORRIS (J. Amer. Chem. Soc., 1935, 57, 1070–1072).—When a 3% clear dispersion of maize β -amylose (I) (the sol. portion of the whole starch) is frozen, then warmed to room temp., and finally boiled for 10 min., retrograded β -amylose (II) remains insol. Prolonged boiling of (II) in H_2O gives some material in solution indistinguishable from (I). (II) is readily dissolved by cold 2.5% NaOH and is not pptd. by cold dil. HCl. α -Amylose (III) (the portion of the whole starch originally insol.) is also dissolved by 2.5% NaOH, but is pptd. nearly quantitatively by HCl. Mixtures of (III) and (II) may be thus determined. The repptd. (III) contains the same amount (4.8%) of combined fatty acid as did the original (III). (III) is thus different from (II), and maize contains very little, if any, (II). (I) consists probably of single chains of glucose units, hydrated in solution, which are converted by freezing into partly dehydrated "bundles" of these chains. R. S. C.

Sakurada's publications [on cellulose]. H. STAUDINGER (Ber., 1935, 68, [B], 1234–1238).—Mainly a refutation of criticisms of the author's work. H. W.

Highly-polymerised compounds. CXIII. Cellulose in Schweitzer's reagent. H. STAUDINGER and B. RITZENTHALER [with, in part, S. KAUTZ] (Ber., 1935, 68, [B], 1225–1233).—When, under usual conditions, various types of cellulose are dissolved in Schweitzer's reagent and pptd. from the solution, the properties of the ppts. differ from those of the original material. If air and light are completely excluded during dissolution and pptn. is effected by dil. AcOH or in completely neutral Na K tartrate solution, the properties of the original and repptd. materials are identical. Since, however, the apparent mean degree of polymerisation of ramie cellulose decreases from 1300 to about 900 and then remains const., this is true only for cellulose mols. of mean degree of polymerisation about 900. Since cellulose thus behaves like a substance of low mol. wt., there is no reason to doubt its macro-mol. structure. H. W.

Osmometric investigations of dilute solutions of polymeric carbohydrates. VIII. State of technical cellulose acetate (cellit) in solution. M. ULMANN (Ber., 1935, 68, [B], 1217–1224; cf. this vol., 231).—The solution relationships of the highly viscous fraction I of technical cellit are more complicated than those of fractions II and III (*loc. cit.*). The observed mol. wts. are not integral multiples of $(\text{C}_6)_2$, vals. intermediate between $(\text{C}_6)_2$, $(\text{C}_6)_4$, $(\text{C}_6)_8$, $(\text{C}_6)_{16}$, and $(\text{C}_6)_{32}$ being obtained. Further dilution of the solution after reaching approx. the $(\text{C}_6)_2$ stage causes appearance of mols. $(\text{C}_6)_8$. The magnitude of the change in osmotic pressure during the transitions of the different types of mol. is explained by the hypothesis that the fraction contains two components one of which undergoes stepwise degradation on dilution, whereas the mols. of the other component remain stable. The most probable ratio of the two types is 1 : 1. H. W.

Compounds of high mol. wt. IV. Mol. wts. of esters of cellulose with higher aliphatic acids. A. NOWAKOWSKI (Rocz. Chem., 1935, 15, 234–248).—The HOI, cryoscopic, and viscosimetric methods of determining the mol. wt. of esters of cellulose with EtCO_2H , PrCO_2H , and $\text{C}_5\text{H}_{11}\text{CO}_2\text{H}$ yield comparable results. R. T.

Interaction of amines with heavy water. P. GOLDFINGER and V. LASAREV (Compt. rend., 1935, 200, 1671–1673).—The hydrochlorides of NH_2Me and NHMe_2 react with D_2O in H_2O at room temp., the N functioning as ter- (cf. A., 1933, 1020; this vol., 563) and not quinque-valent as in the form CH_2NH_3 which is present only in minute amounts. NaOAc reacts with D_2O after 6 months (cf. A., 1934, 497).

J. L. D.

Quaternary ammonium salts from bromo-propyldialkylamines. V. Conversion of cyclic ammonium salts into linear polymerides. C. F. GIBBS and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1137–1139; cf. A., 1934, 515).—When $\text{Br}[\text{CH}_2]_3\text{NMe}_2$ is kept in much EtOH at room temp. for 40 hr., it gives NN-dimethyltrimethyleneammonium bromide, cryst., which at room temp. (2 weeks) or 200° (3 min.) gives the linear polymeride, decomp. 240–250°, probably owing to dissociation to the Br-amine. Cyclic salts with radicals other than Me do not thus polymerise. The following are described. NN-Diisobutyl-, b.p. 149–150°/5 mm. (platinichloride, m.p. 119–120°), -isoamyl-, b.p. 159–160°/5 mm., -allyl-, b.p. 129–130°/5 mm., and -benzyl- γ -phenoxypropyl-amine, b.p. 215–217°/2 mm. (hydrobromide, m.p. 163–164°) NN-di-ethyl-, b.p. 165–167°/1 mm., and -n-butyl- γ -phenoxydecylamine, b.p. 171–173°/0.5 mm.; diisoamyl- γ -bromopropylamine, b.p. 109–111°/3 mm. (platinichloride, m.p. 159–160°); diisoamyl-trimethyleneammonium bromide, m.p. 71–73°. Other γ -OPh-bases were not cleaved by HI. R. S. C.

Synthesis of *d*-arginine anhydride and *d*-lysine anhydride and their ring fission by pepsin. Y. TAZAWA (Acta Phytochim., 1935, 8, 331–336).—Treatment of arginine Me ester dihydrochloride with MeOH-NH₃ at 30° gives *d*-arginine anhydride tetrahydrochloride (I), decomp. 240°, $[\alpha]_D^{20}$ +6.28°, which is stable towards boiling H_2O , whereas the corresponding

base undergoes auto-hydrolysis due to its proper alkalinity. *d*-Lysine anhydride dihydrochloride (II), decomp. 225°, $[\alpha]_D +8.25^\circ$, is obtained similarly. (I) and (II) are smoothly hydrolysed by pepsin, but are indifferent towards trypsin and papain. H. W.

Combination of certain fatty acids with lysine, arginine, and salmine. T. H. JUKES and C. L. A. SCHMIDT (J. Biol. Chem., 1935, 110, 9—16).—The p_K of 10 straight-chain fatty acids in EtOH-H₂O mixtures were determined and vals. of p_K between 4.9 and 5.0 were deduced for them all in H₂O. Lysine and arginine combine with lauric and oleic acids in 72% EtOH giving salts hydrolysed to < 1%. Salmine combines with HCl, octoic and lauric acids. Lysine and arginine laurate and stearate, arginine and lysine erucate were prepared. p_K salmine is 11.1 in H₂O and 12.3 in 72% EtOH. H. D.

Canavanine. J. M. GULLAND and C. J. O. R. MORRIS (J.C.S., 1935, 763—766).—The structure $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (cf. Kitawaga, A., 1930, 121) is established for canavanine by its conversion by chloramine-*T* into a mixture of (CHO), and tartronic semialdehyde (isolated as *p*-nitrophenylhydrazones), and by hot conc. HBr into a mixture of α -amino- γ -butyrolactone hydrobromide (I), NH₃, and guanidine. (I) and HBr gave optically inactive γ -bromo- α -aminobutyric acid hydrobromide, m.p. 164°, also obtained from synthetic α -aminobutyrolactone. P. G. C.

Djenkolic acid, a new amino-acid containing sulphur. A. G. VAN VEEN and A. J. HYMAN (Rec. trav. chim., 1935, 54, 493—501).—*Djenkolic acid*, $\text{CH}_2[\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}]_2$ (I), decomp. 300—350°, $[\alpha]_D -25^\circ$ in 1% HCl, is obtained in 1.6% yield from the djenkol bean (*Pithecolobium lobatum*). It gives a B_{22} derivative (+1H₂O), m.p. 85° (decomp.), hydrochloride, m.p. 250°, unstable *Et*₂ ester hydrochloride, m.p. 60°, and dihydantoin derivative, $\text{C}_9\text{H}_{12}\text{O}_4\text{N}_4\text{S}_2$, m.p. 200°. (I) yields CH₂O when treated with H₂SO₄ and is hydrolysed by conc. H₂SO₄ to S, SO₂, NH₃, and cystine. P. G. C.

Preparation of carbamide from carbon dioxide and ammonia. III. M. TOKUOKA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 41—44).—Thermodynamical considerations and experimental data show that the optimal temp. for the prep. of $\text{CO}(\text{NH}_2)_2$ from $\text{NH}_2\cdot\text{CO}_2\text{NH}_4$ or $\text{CO}_2 + \text{NH}_3$ is > the m.p. of $\text{NH}_2\cdot\text{CO}_2\text{NH}_4$, but > 19°. A catalyst is unnecessary but up to 2% of H₂O causes acceleration. The presence of a little EtOH is immaterial. 35% conversion can be obtained in 30 min. E. A. H. R.

Hydrogen cyanide. V. Reactions of imino-formylcarbylamine. L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1935, 674—679).—Imino-formylcarbylamine (I) is hydrolysed in cold H₂O to HCO_2NH_4 (cf. A., 1896, i, 71). (I) with AgNO_3 in H₂O gives an indefinite compound probably owing to the hydrolysis of (I), but with AgNO_3 in EtOH the compound $2\text{AgNO}_3\cdot 5\text{HCN}$ is formed. (I) with HgCl_2 in Et₂O affords the compound $\text{HgCl}_2\cdot 3\text{HCN}$, converted by HCl into the compound $2\text{HgCl}_2\cdot 3(2\text{HCN}\cdot\text{HCl})$. (I) and AlCl_3 afford $\text{AlCl}_3\cdot 2\text{HCN}$ (II), m.p. 125°, identical with the compound obtained from AlCl_3 and HCN (A.,

1932, 132). (I) is not formed when (II) is heated alone or with quinoline. AlCl_3 and $\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{CHCl}$ (III) [from (I) and HCl] give the compound $\text{AlCl}_3\cdot 2\text{HCN}\cdot\text{HCl}$ (IV), m.p. 80°, identical with that obtained from (II) and HCl at 80°, and by the decomp. of the compound $\text{AlCl}_3\cdot 2\text{HCN}\cdot 3\text{HCl}$ (V), m.p. 62°, prepared by the action of AlCl_3 on the sesquihydrochloride (VI) of HCN. (IV) at 100° yields (III), and with PhMe and AlCl_3 affords $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$, also obtained together with tolyl-hydrylamine (VII) by heating (V) with PhMe. (V) with PhMe and AlCl_3 at 50—55° affords only (VII). (I) heated with 2 mols. of a primary aromatic amine (NH_2Ph , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, α - and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, but not o - and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, 3 : 1 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$, or $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$) affords the corresponding *NN'*-diarylformamidine obtained by Dains (A., 1902, i, 602) from these amines and (VI) or (III). This supports the view that the first step in the latter reactions is the removal by the base of HCl from (VI) or (III) with the formation of (I), which then reacts with the amine. NHPhMe and (III) [or (VI) but not (I)] at 100° afford *N*-phenyl-*N*-methylformamidine hydrochloride, m.p. 192°, which with H₂O at 100° gives form-methylanilide, m.p. 8—10°, b.p. 244—245° (lit. b.p. 243—244°), and with 4*N*-NaOH gives NHPhMe . (III) and EtOH (dry) yield $\text{CH}(\text{OEt})_3$ and formamidine hydrochloride, m.p. 81°, and these products were also obtained from (I), HCl, and EtOH. They are also obtained (Claisen *et al.*, Ber., 1883, 16, 309) together with EtCl from EtOH and (VI), which must therefore readily decompose into (III) and HCl. H. G. M.

Saturation pressure of mustard oils and sulphides. H. BAUER and K. BURSCHKIES (Ber., 1935, 68, [B], 1238—1243).—In connexion with the physiological activities of vapours measurements are recorded of v.p. and temp. of PhNCS , MeNCS , Et_2S , $(\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2)_2\text{S}$, Bu^nS , Bu^sS , *du*soamyl sulphide, thiodiglycol, and $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$. H. W.

Magnesium methoxides. (MLLE.) M. L. QUINET (Bull. Soc. chim., 1935, [v], 2, 1201—1205).—Mg reacts smoothly with MeOH in presence of a little $\text{Mg}(\text{OMe})_2$, to give at -20° a compound, $\text{Mg}(\text{OMe})_2\cdot 4\text{MeOH}$ (I), at 20° a compound, $\text{Mg}(\text{OMe})_2\cdot 2\text{MeOH}$, and at 66° MgCO_3 and other decomp. products. (I) in air gives (II) and over H₂SO₄, more rapidly in vac. or at 110° , a compound $3\text{Mg}(\text{OMe})_2\cdot \text{MgCO}_3\cdot \text{H}_2$, and C_2H_6 . (I) in moist air at room temp. gives $\text{Mg}(\text{OH})_2\cdot 4\text{MgCO}_3$, and a solution of (I) in MeOH, faintly alkaline to phenolphthalein, is unchanged by CO₂, but with a few drops of H₂O gives a gel. (I) with *N*-H₂SO₄ or *N*-HCl gives first this gel and then the Mg salt. MgCl_2 gives a ppt., $x\text{MgCl}_2\cdot y\text{Mg}(\text{OMe})_2\cdot z\text{MeOH}$. R. S. C.

Interchange of heavy atoms in organo-metallic compounds. I. NORVICK (Nature, 1935, 135, 1038—1039; cf. this vol., 851).—Bi amyl dichloride and MgEtBr yield BiEt_3 and tri-*n*-amyl- and diethyl-*n*-amyl-bismuthine, indicating some looseness of linking between the Bi and the alkyl residues.

L. S. T.
Organic compounds of tin. M. LESBRE (Bull. Soc. chim., 1935, [v], 2, 1189—1201).—Mainly a comparison of known org. compounds of Sn with those of

C, Pb, Ge, etc. If SnCl_2 (1 mol.) is added to 10% aq. NaOH (7 mols.), the NaHSnO_2 formed decomposes at $>20^\circ$ to Sn and $\text{Na}_2[\text{Sn}(\text{OH})_6]$, but at $<20^\circ$ with RBr or RI (less well with RCl) gives *alkyl-* or *aryl-stannonic acids*, RSnO_2H , in which $\text{R}=\text{Ph}$, CH_2Ph , allyl, $\alpha\text{-C}_{10}\text{H}_7$, $\text{CH}_2\text{Br}\cdot\text{CH}_2$, CHCl_2 , and CH_2Ac , which give *hydrates*, $+\text{H}_2\text{O}$, *Na*, and *K* salts, a *basic salt*, $\text{RSnO}_2\text{Ag}\cdot\text{Ag}_2\text{O}$, and *complex acids*, $[\text{RSnCl}_5]\text{H}_2$ and $[\text{RSnBr}_4]\text{H}_2$ [K_2 , $(\text{C}_5\text{H}_6\text{N}_4\text{H})_2$, and $(\text{NH}_4)_2$, decomp. $>200^\circ$, salts], and decompose, when heated, partly into SnO and ROH , and partly into SnO_2 and RH , but, if $\text{R}=\text{aryl}$, some SnR_4 and H_2O are also obtained.

R. S. C.

Metallo-organic compounds of tin. S. N. NAUMOV and Z. M. MANULKIN (J. Gen. Chem. Russ., 1935, 5, 281—287).— SnMe_4 is obtained in 85% yield by boiling an Et_3O solution of MgMeI with SnCl_4 for 5 hr., distilling off the Et_2O , and heating the residue at $120\text{--}140^\circ$ for 8 hr. SnMe_4 and I in Et_2O yield SnMe_3I , which with MgEtBr in Et_2O affords SnMe_3Et ; this, in turn, is converted into SnMe_2EtI , SnMe_2EtPr , and SnMeEtPrI , separation of which into its optical antipodes was unsuccessful.

R. T.

Synthesis of mixed dihalogen derivatives of compounds of tin with aliphatic radicals. K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1935, 5, 211—215).—The reactions $\text{SnR}_4+\text{SnX}_4\rightarrow 2\text{R}_2\text{SnX}_2$ ($\text{R}=\text{Me}$, Et , Pr ; $\text{X}=\text{Cl}$, Br) take place with considerable heat evolution. The following reactions are described: $\text{SnMeBr}_3+\text{SnMe}_4\rightarrow 3\text{SnMe}_2\text{Br}_2$; $\text{SnEt}_3\text{X}+\text{SnX}_4\rightarrow 3\text{SnEt}_2\text{X}$; $\text{SnMe}_3\text{Br}+\text{SnMeBr}_3\rightarrow 2\text{SnMe}_2\text{Br}_2$.

R. T.

Preparation of mercury diisobutyl. A. MÜLLER (J. Amer. Chem. Soc., 1935, 57, 1142—1143).— HgBu^i_2 , b.p. $85^\circ/11\text{ mm.}$, is prepared in 27% yield from Bu^iBr and 0.5—1% Na-Hg in EtOAc .

R. S. C.

Hexadeutero benzene. I. G. R. CLEMO and A. McQUILLEN (J.C.S., 1935, 851—855).—Apparatus and conditions are described for optimum conversion of C_2H_2 into C_6H_6 over a Te catalyst, and the method is applied to the conversion of C_2D_2 into *hexadeutero benzene* (I), b.p. 82.5° , m.p. -1.0° . Nitration of (I) using HNO_3 and H_2SO_4 gave a $(\text{NO}_2)_6$ -compound, m.p. 89° not lowered when mixed with $m\text{-C}_6\text{H}_3(\text{NO}_2)_2$. Nitration using DNO_3 and D_2SO_4 gave *m-dinitrohexadeutero benzene*, m.p. 78° , mixed m.p. with $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ 87° .

P. G. C.

Function of sulphuric acid in nitration. D. I. JAMES (J.C.S., 1935, 785—787).—The conclusions of Hetherington *et al.* (A., 1933, 267) concerning the effect of H_2SO_4 on mononitration of PhNO_2 and $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ are extended to nitration of 1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$. Up to a point, represented approx. by 95° and an excess of 4 mols. of H_2SO_4 beyond that required to form the monohydrate, the action of the excess of H_2SO_4 is sufficiently explained by its promoting the miscibility of the reagents. Beyond this point, rise of temp. and increase of H_2SO_4 concn. diminish the amount of HNO_3 available for nitration.

P. G. C.

Dealkylation of aromatic hydrocarbons. Reversibility of the Friedel-Crafts reaction. N. N.

ORLOV and L. S. SOLODAR (J. Appl. Chem. Russ., 1935, 8, 117—127).— PhMe is obtained in 25% yield from xylene and AlCl_3 (4%) at the b.p., by a continuous process. No advantage is gained by passing HCl during the process, in disagreement with Dougherty's view as to the mechanism of the Friedel-Crafts reaction (A., 1929, 421).

R. T.

Condensation of alcohols with aromatic hydrocarbons in presence of anhydrous aluminium chloride. I. Condensation of *tert.*-aliphatic alcohols with benzene and toluene. I. TZUKKERVANIK (J. Gen. Chem. Russ., 1935, 5, 117—120).—*tert.*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ and AlCl_3 yield CMe_2CHMe and *tert.*- $\text{C}_5\text{H}_{11}\text{Cl}$, whilst Bu^iOH affords only Bu^iCl ; in presence of C_6H_6 or PhMe a Friedel-Crafts reaction takes place, to give $\text{C}_5\text{H}_{11}\text{Ph}$, b.p. $189\text{--}191^\circ$, and *m-amylltoluene*, b.p. $208\text{--}210^\circ$, and PhBu^i or $m\text{-C}_6\text{H}_4\text{MeBu}^i$.

R. T.

Constitution and reactivity. IX. Sulphonation of benzylidene chloride and benzotrichloride. K. LAUER (J. pr. Chem., 1935, [ii], 142, 252—257).— CPhCl_3 treated with gaseous SO_3 yields almost exclusively *m*-sulphobenzoyl acid. Similar treatment of CH_2PhCl and CHPhCl_2 gives unsatisfactory results. CHPhCl_2 and $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ at 35° yield mixed sulphobenzylidene chlorides, which with CaCO_3 form sulphobenzaldehydes, oxidised to a product which is mainly *p*-sulphobenzoyl acid.

E. W. W.

Sulphonation of mesitylene. H. J. BACKER (Rec. trav. chim., 1935, 54, 544—551).—Mesitylene is converted by ClSO_3H into the 2:4-disulphonyl chloride, m.p. $123.5\text{--}124^\circ$, which with oleum at 105° (16 hr.) gives *mesitylenetrisulphonic acid* (*Ba* and NH_4 salts). The following derivatives and salts of mesitylenedisulphonic acid are described: *di-strychnine*, *Ba*, *K*, and *Tl* salts; *Ph*₂ ester, m.p. $110\text{--}111^\circ$; *di-amide*, m.p. 240° ; *di-methylamide* (I), m.p. $171\text{--}171.5^\circ$; *di-methylnitrosoamide*, m.p. 183° ; *di-dimethylamide*, m.p. $137.5\text{--}138^\circ$; *di-tert.-butyl amide*, m.p. 223° (decomp.); *di-anilide*, m.p. $150\text{--}151^\circ$; *di-o-toluidide*, m.p. 178° . *Nitromesitylenedisulphomethylnitroamide*, $\text{NO}_2\cdot\text{C}_6\text{Me}_3(\text{SO}_2\cdot\text{NMe}\cdot\text{NO}_2)_2$ [from (I) and HNO_3 at -10°], m.p. 181° (explodes).

P. G. C.

Structure of tolan. A. WEISSBERGER (J.C.S., 1935, 855—856; cf. A., 1933, 339).—Catalytic hydrogenation of tolan (I) gives a 99.3% yield of $(\text{CH}_2\text{Ph})_2$, m.p. $52.5\text{--}53.2^\circ$; since rearrangement under these conditions is unlikely and CHPh_2Me is liquid at room temp., it is considered that (I) is $\text{CPh}:\text{CPh}$ not CPh_2C (Smyth *et al.*, A., 1931, 669; Berger, this vol., 431).

P. G. C.

Highly arylated aromatic compounds. V. W. DILTNEY, W. SCHOMMER, W. HOSCHEN, and H. DIERICH (Ber., 1935, 68, [B], 1159—1162; cf. this vol., 213).—Gradual addition of diphenyldiacetylene to 2:3:4:5-tetraphenyl- $\Delta^{2:4}$ -cyclopentadien-1-one (I) at $240\text{--}250^\circ$ yields CO and 2:3:4:5:6-pentaphenyltolan, m.p. 258° , which slowly decolorises Br and is oxidised by CrO_3 in AcOH to 2:3:4:5:6-pentaphenylbenzil, m.p. $276\text{--}277^\circ$. Replacement of acetylenes by olefines in the above reaction does not affect the elimination of CO , but the additional H causes

reduction of (I). Nevertheless, (I) and $(\cdot\text{CH}_2\text{CH}_2)_2$ at 260—290° afford 2 : 3 : 4 : 5 : 2' : 3' : 4' : 5'-octaphenyl-diphenyl, m.p. 318—319°, which does not add Br, whilst (I) and cyclohexene at 280° slowly yield 5 : 6 : 7 : 8-tetraphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 271—272°. (I) and CPh·CBr at 160° give bromopentaphenylbenzene, m.p. 281—282°. Pentaphenylpyridine, m.p. 241—242° (perchlorate, m.p. 299°), is slowly produced when a mixture of (I) and PhCN is boiled, but is best obtained in a sealed tube at 275—300°. 2 : 3 : 4 : 5-Tetraphenylthiophene, m.p. 184—185°, is obtained from (I) and S at 270—350°.

H. W.

Experimental demonstration of the allene asymmetry. P. MATTLAND and W. H. MILLS (Nature, 1935, 135, 994).—van 't Hoff's prediction that unsymmetrically substituted allenes would show enantiomorphism has been verified. With the usual dehydrating agents $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-*n*-naphthylalyl alcohol is converted into *r*-diphenyldi-*l*-naphthylallene, m.p. 242—244°. If dehydration is effected with *d*- or *l*-camphorsulphonic acid in C_6H_6 an optically active product is obtained from which *d*-, m.p. 158—159°, $[\alpha]_{5461}^{20} +437^\circ$, and *l*-, $[\alpha]_{5461}^{20} -438^\circ$, -diphenyldi-*l*-naphthylallene are isolated.

L. S. T.

Bromo-derivatives of naphthalene. J. SALKIND and Z. STETZURO (J. Gen. Chem. Russ., 1935, 5, 94—99).—1 : 4- $\text{C}_{10}\text{H}_6\text{Br}_2$, and Br in CS_2 at 0° afford $\text{C}_{10}\text{H}_6\text{Br}_2\text{Br}_4$ (I) and 1 : 4 : 6- $\text{C}_{10}\text{H}_5\text{Br}_3$ (II); at 80° the chief product is 1 : 4 : 6 : $x : x : \text{C}_{10}\text{H}_3\text{Br}_5$, m.p. 179—183°. (I) in C_6H_6 and NaOEt (at the b.p.) yield 1 : 4 : 6 : 7- and 1 : 2(3?) : 4 : 6- $\text{C}_{10}\text{H}_4\text{Br}_4$, m.p. 116—120°, both of which afford (II) when reduced (Zn in AcOH). 2 : 6- $\text{C}_{10}\text{H}_6\text{Br}_2$ and Br in CHCl_3 (in presence of Fe) give a mixture of 2 : 6 : $x : x : \text{C}_{10}\text{H}_5\text{Br}_3$, m.p. 171—173°, and 2 : 6 : $x : x : \text{C}_{10}\text{H}_4\text{Br}_4$, m.p. 100—101°. Bromination of 1 : 2 : 6- $\text{C}_{10}\text{H}_5\text{Br}_3$ affords $\text{C}_{10}\text{H}_3\text{Br}_5$, m.p. 274—279°. (I) and Mg in Et_2O give MgBr_2 and $\text{C}_{10}\text{H}_6(\text{MgBr})_2$.

R. T.

Action of selenium on compounds containing angular methyl groups. G. R. CLEMO and H. G. DICKENSON (J.C.S., 1935, 735—738).—An attempt to obtain simple examples of the structural changes which occur when, e.g., sterols are dehydrogenated with Se (cf. A., 1933, 610). 9-Methyldecahydronaphthalene (A., 1931, 1302), 8-methylhydrindane, b.p. 159—160°/760 mm. [from 2-acetyl-1-methyl- Δ^1 -cyclopentene and $\text{CHNa}(\text{CO}_2\text{Et})_2$, followed by hydrolysis and reduction], and 2-carboxy-1-methylcyclohexane-1-acetic acid were not attacked by Se, Pt, S, S+Se, or SeO_2 . 1 : 1 : 6-Trimethyltetrahydronaphthalene gave 1 : 6- $\text{C}_{10}\text{H}_6\text{Me}_2$. The Cl_2 -compound, b.p. 150—155°/13 mm., from 2 : 4-diketo-9-methyldecahydronaphthalene and PCl_5 was converted by Se (280—300°; 60 hr.) into 1- $\text{C}_{10}\text{H}_7\text{Me}$; migration of the Me may have resulted from the action of the PCl_5 or Se. 2 : 4-Diketo-8-methylhydrindane, b.p. 143°/0.3 mm., m.p. 91—92°, was converted by PCl_5 into a Cl_2 -compound, b.p. 109—110°/12 mm., which gave a small quantity of non-picrate-forming oil when heated with Se.

P. G. C.

Anthracene-9 : 10-disulphonic acid. C. MARSCHALK and N. OUROUSSOV (Bull. Soc. chim., 1935,

[v], 2, 1216—1218).—9 : 10-Dichloroanthracene and 5% aq. Na_2SO_3 in PhOH at 170—180° give Na_2 anthracene-9 : 10-disulphonate, cryst., readily hydrolysed by acid to anthracene and very readily oxidised to anthraquinone.

R. S. C.

Synthesis of carcinogenic 1 : 2-benzpyrene. A. WINTERSTEIN, H. VETTER, and K. SCHÖN (Ber., 1935, 68, [B], 1079—1085).—Improvements in Cook's method of preparing 1 : 2-benzpyrene from $(\cdot\text{CH}_2\text{CO})_2\text{O}$ and pyrene (I) (A., 1934, 601) coupled with chromatographic purification at two stages of the operations increase the yield of the hydrocarbon to 35—40%. (I) and methylsuccinic anhydride afford γ -pyrenoyl- α (or β)-methylpropionic acid, m.p. 204—205° (corr.; Berl), whence γ -1-pyrenyl- α (or β)-methylbutyric acid, m.p. 176° (corr.; Berl), transformed by SnCl_4 into 4'-keto-2'(3')-methyl-1' : 2' : 3' : 4'-tetrahydro-1 : 2-benzpyrene, m.p. 176—177° (corr.; Berl). The ketone is converted by Se into 2'(3')-methyl-1 : 2-benzpyrene, m.p. 143—144° (corr.; Berl).

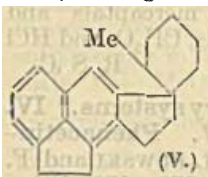
H. W.

Syntheses of polycyclic compounds related to the sterols. IV. Identification of 3'-methyl-1 : 2-cyclopentenophenanthrene and its preparation from cholesterol. D. J. C. GAMBLE, G. A. R. KON, and B. SAUNDERS (J.C.S., 1935, 644—646; cf. this vol., 741).—When carefully purified, 3'-methyl-1 : 2-cyclopentenophenanthrene (I) (A., 1934, 238) is identical with the hydrocarbon $\text{C}_{18}\text{H}_{16}$ (II) prepared by the method of Bergmann *et al.*, (A., 1933, 1154). The $\text{C}_6\text{H}_3(\text{NO}_2)_3$ (III) and $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ compounds and the styphnate (IV) of (I) and (II), respectively, have the same m.p., but the picrate of (I) melts 1° < that of (II). They are not fluorescent in daylight, but show a violet fluorescence in ultra-violet light. A hydrocarbon of identical properties was isolated from the dehydrogenation product of cholesterol, except that the picrate melted 4° too low. This is due to the presence of a second form (this vol., 286). (III) and (IV) (*ibid.*, 741), but not the picrate, are suitable for the identification of the hydrocarbon.

H. G. M.

Synthesis of cholanthrene. J. W. COOK, G. A. D. HASLEWOOD, and (Mrs.) A. M. ROBINSON (J.C.S., 1935, 667—671).—1-Iodoacennaphthene (A., 1931, 81), Mg, Et_2O , EtBr, and $(\text{CH}_2)_2\text{O}$ afford β -1-acenaphthylethyl alcohol, m.p. 94—95°, b.p. 179—180°/0.3 mm. [3 : 5-dinitrobenzoate, m.p. 233—234.5°; chloride (I), m.p. 54—55°, b.p. 145—150°/0.1 mm.; bromide (II), m.p. 66°, b.p. 165°/0.4 mm.]. (II) heated with K dissolved in Et cyclohexanone-2-carboxylate and C_6H_6 affords Et 2-(β -1'-acenaphthylethyl)cyclohexanone-2-carboxylate (III), m.p. 76—77°, b.p. 210—220°/0.4 mm., hydrolysed (MeOH-KOH) to α -(β -1'-acenaphthylethyl)pimelic acid, m.p. 165°. (III) is cyclised by H_2SO_4 to Et hexahydrocholanthrenecarboxylate, m.p. 150° (solutions of this have an intense violet fluorescence), hydrolysed to the acid, m.p. 241—242° (with evolution of gas). This on heating with Pt-black at 295—305° during 1½ hr. yields cholanthrene, m.p. 170—171° (sublimes 170—190°/0.05 mm.) (picrate, m.p. 167—168°). This on oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7$ -AcOH) and subsequent decarboxylation yields 5-methyl-1 : 2-benzanthraquinone (A., 1934, 180). (I), Mg, Et_2O , and 2-methylcyclohexanone

afford 1-ethylacenaphthene, m.p. 30°, b.p. 120—125°/0.4 mm. (picrate, m.p. 102—102.5°), and an oil, b.p. 210/0.7 mm., which on heating with KHSO_4 gives 2-methyl-(β -1'-acenaphthylethyl)- Δ^1 -cyclohexene (IV), b.p. 182—185°/0.2—0.3 mm. (picrate, m.p. 107—108°); this on treatment with AlCl_3 gives a mixture which on purification had m.p. 178—182° (picrate, 157—158°) and gave the same product after treatment with Se at 320—330° for 32 hr. This is believed to be the spiran (V). The cyclisation of (IV) is therefore anomalous. 2-Methylcyclohexanone and β -1-naphthylethyl chloride, Mg, and Et_2O afford 2-methyl-1-(β -1'-naphthylethyl)-



cyclohexanol, b.p. 185—195°/0.5 mm. (3:5-dinitrobenzoate, m.p. 136°), dehydrated by KHSO_4 to 2-methyl-(β -1'-naphthylethyl)- Δ^1 -cyclohexene, b.p. 135°/0.1 mm. This is cyclised by AlCl_3 to the anticipated methyl-octahydrochrysene (VI), b.p. 145°/0.1 mm. (picrate, m.p. 105—106°), and a heavy oil. (VI) was dehydrogenated to chrysene by Se at 295—305°, but not by Pt-black. H. G. M.

Dissociable organic oxides. 1:1'-Diphenylrubene, $\text{C}_{30}\text{H}_{20}$; thermal decomposition of its photo-oxide, $\text{C}_{30}\text{H}_{20}\text{O}_2$. C. DUFRASSE and M. LOURY (Compt. rend., 1935, 200, 1673—1675; cf. A., 1931, 1151).—Hydrolysis of Et 1:1'-diphenylrubene-3:3'-dicarboxylate (cf. this vol., 213) gives 1:1'-diphenylrubene (I), m.p. 301—302°, and another product. The absorption spectrum of (I) resembles those of other rubenes, but is displaced towards the violet. Photo-oxidation of (I) affords an oxide, m.p. 234—235°, which is converted at 170°, without evolution of gas, into a resin; some rubene is also formed. J. L. D.

Boranilide. C. R. KINNEY and D. F. PONTZ (J. Amer. Chem. Soc., 1935, 57, 1128—1129).—Chaudhuri's directions (J.C.S., 1920, 117, 1081) for the prep. of boranilide give $(\text{NH}_2\text{Ph})_2\text{ZnCl}_2$; some of the reactions described for the product could not be duplicated, but BzCl gives NHBzPh and $\text{Br}-p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$. R. S. C.

Hydrolysis of substituted benzanilides. F. ASINGER (J. pr. Chem., 1935, [ii], 142, 291—300).—The times of half-hydrolysis by about 12.5% KOH - EtOH under reflux of benz-3:4:5-, m.p. 210°, and -2:4:6-tribromoanilide, m.p. 204°, 3:4:5-, m.p. 220°, and 2:4:6-tribromobenzanilide, m.p. 237°, and NHBzPh are 2, 215, 5, ∞ , and 16 hr., respectively, showing the effect of steric hindrance. The prep. of the necessary acids and bases and of 3:4:5- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NO}_2$ is modified. 3:4:5- $\text{C}_6\text{H}_2\text{Br}_3\text{Me}$ gives $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{CBr}_3$ at 200—220°, but 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\text{Me}$ at this temp. gives only 2:4:6-tribromobenzyl bromide, m.p. 75°, b.p. 202°/18 mm., the CBr_3 -compound being obtained at 250—260°. R. S. C.

Reaction between chloral hydrate and phenylhydrazine. I. C. TORRES and S. BROSA (Anal. Fis. Quim., 1934, 32, 509—518).— $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ with 2:4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ (I) in dil. H_2SO_4 yields 2:4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ (cf. Brady, A., 1931, 937) and chloroglyoxalbis-2:4-dinitrophenylhydrazones, decomp. 278° (Ac derivative, decomp.

228°), which with NaOAc and Ac_2O yields the Ac_3 derivative of (I), m.p. 207° (decomp.), also given by (I), NaOAc , and Ac_2O . F. R. G.

Interaction of ethylene oxide with *m*-phenylenediamine. J. O. GABEL and R. M. MATZKEVITSCH (Ukrain. Chem. J., 1935, 10, 4—6).— $(\text{CH}_2)_2\text{O}$ and $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (30°; 8 hr.) yield β -*p*-aminophenyl-aminocetyl alcohol, m.p. 52—53° [picrate, m.p. 106—108° (decomp.); benzoate]. R. T.

Complex compounds of 2:4:6-triamino-toluene.—See this vol., 944.

Reactions of diazotised *p*-sulphanilic acid and formation of an azoxybenzene. E. JUSTIN-MUELLER (Bull. Soc. chim., 1935, [v], 2, 1024—1028).—Diazotised $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (I) is adsorbed by wool fibres in an acid medium. In an alkaline medium a reddish-brown coloration appears both on the fibres and in the solution. This is due not to the presence of tyrosine in the fibres (cf. A., 1905, i, 75), but to the formation of azoxybenzene-*pp'*-disulphonic acid (II). This occurs in alkaline solutions of diazotised (I), and also, but more slowly, in an AcOH medium. (II) is readily split into (I) by $\text{Na}_2\text{S}_2\text{O}_4$. H. G. M.

Coloured local anaesthetics. J. H. GARDNER and L. JOSEPH (J. Amer. Chem. Soc., 1935, 57, 901).—Diazotised procaine (I) gives dyes with H-acid , $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $m\text{-C}_6\text{H}_4(\text{OH})_2$, decomp. 250°, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, m.p. 196.5°, $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, m.p. 216—219°, $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, m.p. 109—110°, and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 190° (decomp.). Bisazo-dyes are obtained from (I) and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2 + \alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, decomp. 250°, (I) and Me anthranilate + $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, decomp. 250°, and (I) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{procaine}$, m.p. 169—172°. The acid and OH-compounds have no anaesthetic action. R. S. C.

Preparation of a fat-soluble azo-dye. I. Dye from stearic acid. O. ROUTALA and A. ARHO (Suomen Kem., 1935, 8, B, 25—26).—Stearo- β -naphthylamide affords a (NO_2) $_1$ -derivative (45%), reduced to 3-aminostearo- β -naphthylamide (45%), the diazonium derivative of which couples with α - and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ to give dyes, the latter of which when diazotised couples again with $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$. These dyes are sol. in fats and fatty acids. J. L. D.

[Metallic salts of] diazoamino-compounds.

II. III. Unsaturated chromophores. I. A. MANGINI (Gazzetta, 1935, 65, 298—308, 308—317).—II. The following derivatives of diazoaminobenzene yield *Hg* and *Ag* salts which are (I) yellow, (II) red, or (III) orange (mixed) (cf. A., 1934, 68): *p*-bromo-, *Hg* (I and II or III) and *Ag* (II and III) salts; *o*-nitro- (new prep. from $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$), *Hg* (I, II, and III) and *Ag* (II) salts; 4-bromo-2'-nitro-, *Hg* (I and III) and *Ag* (II and III) salts; 4-bromo-3'-nitro-, *Hg* (I) and *Ag* (I, III, and unstable II) salts; 4-bromo-4'-nitro-, *Hg* (I, II, and III) and *Ag* (I, II, and III) salts. β -Naphthyl diazoaminobenzene yields *Hg* (I, II, and III) and *Ag* (II) salts. 4-Bromo-2'-nitrodiazoaminobenzene, m.p. 149—150°, is obtained from diazotised $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$.

III. The *Na* and *K* salts of *o*-nitro- and 4-bromo-2'-nitro- and -4'-nitro-, and the *K* salts of *m*-nitro- and

4-bromo-3'-nitro-diazoaminobenzene, are all intensely coloured. Since *m*-compounds are included, the coloration is not due to a quinonoid structure. It is suggested that the NO₂-group acts as a negative auxochrome, promoting a dipole structure in the diazoamino-system, and that the Na and K salts are formed with the latter, and are not nitronic.

E. W. W.

Action of aromatic hydroxysulphonic acids on hippuric acid. I. G. MACHEK (Monatsh., 1935, 65, 433—442).—The product from PhOH and hippuric acid (I) in presence of H₂SO₄ gives, not sulphophenylglycine, C₆H₅O₂NS + H₂O (A., 1885, 55, 1235), but a salt, *glycine phenylsulphonate*, C₆H₁₁O₆NS, new m.p. 185—186°, which is also obtained using glycine instead of (I). Similarly are obtained *glycine o*-, *m*-, and *p*-*cresolsulphonates*, m.p. 161—162°, 175—176°, and 180—181° (all corr.), respectively. The last gives a *Ag* salt. These substances all give a strong FeCl₃ reaction.

E. W. W.

Constitution and reactivity. XI. Oxidation of *o*- and *m*-dinitrobenzene. K. LAUER (J. pr. Chem., 1935, [ii], 142, 310—312).—*o*-C₆H₄(NO₂)₂ and 30% oleum at 120—134° give 12% of 2:3-dinitrophenol. *m*-C₆H₄(NO₂)₂ and 35% oleum at 140—150° give 2:4- (6 parts) and 2:6-dinitrophenol (1 part).

R. S. C.

Two optically active diastereomeric forms of α -phenylsulphoxypropionic acid. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 55, 1—5).—*d*- α -Phenylthiolpropionic acid (I), [α]_D²⁰ +123.0° in 0.03*N* aq. solution, with H₂O₂ in COMe, at 0° affords after 5 days two optically active phenylsulphoxypropionic acids *A*+, m.p. > 180° (depends on mode of heating), [α]_D²⁵ +190° in 0.01*N* aq. solution, and *B*-, m.p. 98.3—98.6°, [α]_D²⁵ -112° in 0.03*N* aq. solution. These are readily separated on account of their different solubilities in C₆H₆, and on further oxidation both give *d*- α -phenylsulphonylpropionic acid (II). This oxidation is accompanied by slight racemisation, although (I) is oxidised directly to (II) by KMnO₄ without any racemisation. The solubility of *A*+ and *B*- in H₂O at 15° and [α]_D²⁵ at various concns. are given.

H. G. M.

Thiophenols. II. Reaction between aromatic mercaptals and formaldehyde. W. H. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 1065—1068; cf. A., 1934, 69).—PhSH, excess of CH₂O, and HCl in AcOH at room temp. give CH₂(SPh)₂ (I), m.p. 36°, but after several months at room temp. or a few hr. when heated the product is a mixture of mono- to tetra-merides, double m.p. 140—145° and 245—250°. The appropriate aldehyde, thiophenol, and HCl in AcOH give *m*-nitrobenzaldehyde diphenyl- (III), m.p. 65.5°, and *di-p*-tolyl-mercaptal (III), m.p. 85.5°, *p*-tolualdehyde *di-p*-tolylmercaptal, m.p. 72°, *o*-nitrobenzaldehyde diphenylmercaptal, m.p. 101°, and 2-bromo-5-hydroxybenzaldehyde *di-p*-tolylmercaptal (IV), m.p. 97°. (II), (III), and (IV) with CH₂O and HCl in hot AcOH give products (V), m.p. (double) 192—195° and 250°, 180—181°, and 179°. (I), CHPh(SPh)₂, CHPh(S·C₆H₄·NO₂-*p*)₂, CHPh(S·C₆H₄·Me-*p*)₂, and CH₂(S·C₆H₄·Me-*p*)₂ give similar products (V), m.p. (double) 181—184° and 250°, (double) 192—195° and

250°, 183°, 183—184°, and 186°, respectively. CPh₂(SPh)₂ does not react. (V) appear to be formed by replacement of the aldehyde by CH₂O and to be (VI) or its substitution products; for the products with double m.p. condensation may have occurred in the *p*-position with formation of large rings. (V) are not formed from the formaldehyde mercaptals and HCl in AcOH or from the thiophenols, CH₂O, and HCl in AcOH. M.p. are corr.

R. S. C.

Thermal equilibrium in ternary systems. IV. Antipyrine-phenacetin-salol. V. Phenacetin-acetanilide-sulphonal. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1935, 15, 173—179, 184—190).—IV. The eutectic, m.p. 32.5°, contains antipyrine 13.5%, phenacetin 4%, and salol 82.5%.

V. The eutectic, m.p. 69.5°, contains phenacetin 22%, NHPhAc 44%, and sulphonal 34%. R. T.

Thermal equilibrium in the system β -naphthol- β -naphthylamine. K. HRYNAKOWSKI and M. SZMYTÓWNA (Rocz. Chem., 1935, 15, 180—183).—The m.p. diagram corresponds with Roozeboom's third type.

R. T.

Preparation of 1-alkyl- β -naphthols. K. DZIEWOŃSKI and C. DRAGAN (Rocz. Chem., 1935, 15, 198—201).— β -C₁₀H₇·OH, anhyd. NPhMe₂, and β -C₁₀H₇·ONa yield 1-methyl- β -naphthol (300°; 8 hr.) (*picrate*, m.p. 163—164°). The corresponding 1-*Et* compound, m.p. 105° (*benzoate*, m.p. 75°), is prepared analogously.

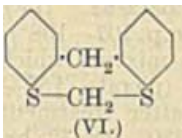
R. T.

Action of hydroxylamine on the hydrogen sulphite compounds of 1-nitroso- β -naphthol-6- and -7-sulphonic acids. S. V. BOGDANOV and I. I. LEVKOEY [with V. V. DURMASCHKINA] (J. Gen. Chem. Russ., 1935, 5, 18—27).—NaHSO₃ is added to an aq. suspension of Na 1-nitroso- β -naphthol-6-sulphonate (I) to complete dissolution of the latter, when HCl and NH₂OH·HCl (II) are added, to yield a ppt. of Na 2-nitroso- α -naphthol-4:6-disulphonate (III) (75% yield). (III) is also obtained by the action of HCl on the *dioxime* of 1:2-diketo-1:2:3:4-tetrahydronaphthalene-4:6-disulphonic acid, prepared from (I), NaHSO₃, and (II) in presence of NaOAc in neutral aq. solution, and converted by NaOH into the Na salt of the *dioxime* of 1:2-naphthaquinone-6-sulphonic acid, the *anhydride* of which is described. Under analogous conditions, the -7-sulphonic acid corresponding with (I) affords the -4:7-disulphonic acid analogue (IV) of (III). The constitutions of (III) and (IV) are established by comparing the products of reduction with the corresponding synthetically prepared aminonaphtholdisulphonic acids.

R. T.

Purification of benzonaphthol. G. A. KIRCHGOF and A. D. STEPANOV (Khim. Farm. Prom., 1934, No. 3, 16—17).—Washing with dil. alkali is followed by crystallisation from petroleum. CH. ABS. (r)

Purification of benzonaphthol. T. I. ZACHAROVA and F. PALEI (Khim. Farm. Prom., 1934, No. 3, 19—20).—Addition of PhCl to the reaction mixture hinders resin formation. The crude product meets pharmaceutical requirements. CH. ABS. (r)



Manufacture of monohydroxychrysene.—See B., 1935, 585.

Rearrangement of ψ -nitrosites of propenyl-phenyl ethers. Synthesis of β -nitro- α -alkoxy-phenylpropanols and their methyl ethers. V. BRUCKNER and E. VINKLER (J. pr. Chem., 1935, [ii], 142, 277—290).—The decomp. of propenylbenzene- ψ -nitrosites and β -nitro- α -acetoxypentenylbenzenes varies inexplicably with the nature of the substituents in the Ph nucleus. Asarone- ψ -nitrosite with hot MeOH gives 2:4:5-trimethoxy- $\alpha\beta$ -dioximinopropylbenzene peroxide, $\text{O} \begin{smallmatrix} \text{N:Car} \\ \text{O} \text{---} \text{N} \end{smallmatrix} \text{CMe}$, m.p. 155° (lit. 149°), and 2:4:5-trimethoxy- β -nitro- α -methoxypropylbenzene (I), m.p. 118°, also obtained with MeOH-HCl at 65°. Methylisoeugenol- ψ -nitrosite with hot MeOH gives β -nitro-3:4-dimethoxypropio-phenoneoxime, m.p. 91° (decomp.), and the (impure) glyoxime peroxide, but with HCl-MeOH at 70° affords 3:4-dimethoxy- β -nitro- α -methoxy-*n*-propylbenzene (II), m.p. 119°, also obtained from the corresponding α -OAc-compound (III) and HCl in MeOH or aq. MeOH. (III) and HCl-COMe₂ give, however, 3:4-dimethoxy- β -nitro- α -hydroxy-*n*-propylbenzene, m.p. 124—133° (decomp.), which is unchanged by HCl-MeOH and with AcCl-C₅H₅N re-forms (III). *iso*-Safrole- ψ -nitrosite with hot MeOH gives β -nitro-3:4-methylenedioxypropio-phenoneoxime, m.p. 122° (decomp.) (with alkali gives the glyoxime peroxide), and with HCl-MeOH affords 3:4-methylenedioxy- $\alpha\beta$ -dioximino-*n*-propylbenzene, m.p. 206—207° (decomp.), stable to alkali but hydrolysed by hot dil. H₂SO₄. 3:4-Methylenedioxy- β -nitro- α -acetox-*n*-propylbenzene is unchanged by 7% HCl-COMe₂, but with HCl-MeOH gives the α -OH-compound, an oil (decomposed when distilled), which is reduced electrolytically to 3:4-methylenedioxy- β -amino- α -hydroxy-*n*-propylbenzene hydrochloride, m.p. 195—196° (decomp.). (II) gives similarly electrolytically 3:4-dimethoxy- β -amino- α -methoxy-*n*-propylbenzene hydrochloride, m.p. 180°, but (I) affords 2:4:5-trimethoxy- β -hydroxy- α -amino- α -methoxy-*n*-propylbenzene, m.p. 128°.

R. S. C.

Thermal analysis of binary systems of antipyrine and resorcinol with certain organic compounds. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1935, 15, 163—172).—The m.p. diagrams of the systems antipyrine with *o*-, *m*-, and *p*-C₆H₄(OH)₂, salicylic and benzoic acids, and salipyrine, also of resorcinol with pyrocatechol, quinol, and phenacetin, indicate complete miscibility of the fused components. The existence of a no. of compounds previously described by other authors is confirmed. Resorcinol and phenacetin form a 3:2-compound, m.p. 76.5°.

R. T.

2:4:5-Trimethoxy-1-allylbenzene.—See this vol., 1041.

Stereochemistry of dicyclic ring systems. XI. Stereoisomerism of hexahydrohydrindenes and their derivatives. III. Hexahydrohydrindenes substituted in the five-membered ring. W. HUCKEL, M. SACHS, J. YANTSCHULEWITSCH, and F. NERDEL (Annalen, 1935, 518, 155—183; cf. A., 1927, 238).—Both *Et. cis*, b.p. 176°/21 mm., and

trans-cyclohexane-1-propionate-2-carboxylate, b.p. 164°/13 mm. [from the *cis*-, m.p. 103°, and *trans*- (I) -acid, which are prepared by catalytic reduction of *o*-CO₂H-C₆H₄-CH₂-CH₂-CO₂H], give with Na-EtOH, *Et* hexahydro- α -hydrindone-2-carboxylate, hydrolysed (KOH) to (I) and hexahydro- α -hydrindone, the *oxime*, m.p. 80°, of which is separated by crystallisation from ligroin (or by benzylation) into the *cis*-*oxime* (II), m.p. 100° (*Bz* derivative, m.p. 96°), and *trans*-*oxime* (III), m.p. 146° (*Bz* derivative, m.p. 153°) (ratio 10:1). Reduction (Na-EtOH) of (II) gives a mixture of two *cis*-amines, separated as the *Bz* derivative, m.p. 180°, and *Bz* derivative, m.p. 131°, of *cis*-hexahydro- α -hydrindylamine-I (*Ac* derivative, m.p. 126°) and -II: similar reduction of (III) gives only *trans*-hexahydro- α -hydrindylamine (*Ac* derivative, m.p. 110°) as its *Bz* derivative, m.p. 153°. Reduction (Adams) of α -hydrindone (improved prep.) affords first α -hydrindol, and finally a mixture of *cis*-hexahydro- α -hydrindols, separated (through various esters) into a *form*, m.p. 18° (*H phthalate*, m.p. 127°; *H succinate*, m.p. 63°; *p*-nitrobenzoate, m.p. 72°; phenylurethane, m.p. 115°) [oxidised to the ketone which gives only (II)], and a liquid *form* (*H phthalate*, m.p. 140°; *H succinate*, liquid; *p*-nitrobenzoate, m.p. 89°; phenylurethane, m.p. 100°). Similar reduction of β -hydrindone affords first β -hydrindol, m.p. 70° (*H phthalate*, m.p. 133—134°; *Ac* derivative, m.p. 32°; phenylurethane, m.p. 130°), and finally a mixture of *cis*-hexahydro- β -hydrindols, from which is isolated a pure *form*, m.p. 5°, b.p. 110°/12 mm. (cf. *loc. cit.*) (*p*-nitrobenzoate, m.p. 115°; *oxalate*, m.p. 94°). The other *form*, m.p. 10°, b.p. 108°/11 mm. (*H phthalate*, m.p. 103.5—105°; *H succinate*, m.p. 65.5°; phenylurethane, m.p. 102°), cannot be isolated pure from the mother-liquor, but is obtained by the action of HNO₂ on the amine (IV) below. Reduction (Na-EtOH) of *cis*-hexahydro- β -hydrindoxime affords a mixture of amines (IV), separated after benzylation into the *Bz* derivative, m.p. 144° (main product; also obtained by catalytic reduction), and the *Bz* derivative, m.p. 133° (dimorphous), of *cis*-hexahydro- β -hydrindylamine. Similar reduction of the *trans*- β -*oxime*, m.p. 161° (*Bz* derivative, m.p. 123°), gives *trans*-hexahydro- β -hydrindylamine (*Bz*, m.p. 140° and *Ac*, m.p. 94°, derivatives), converted by HNO₂ into (V) (below). Reduction (Skita or Na-EtOH) of *trans*-hexahydro- β -hydrindone affords only *trans*-hexahydro- β -hydrindol (V), m.p. 23°, b.p. 102°/11 mm. (*H phthalate*, m.p. 87°; *H succinate*, m.p. 58°; *oxalate*, m.p. 70°). Reduction (Adams) of β -hydrindoxime affords only *di*-(β -hydrindylamine, m.p. 102°. When heated with KHSO₄ at 180° (V) gives mainly *di*-(*trans*-hexahydro- β -hydrindyl) ether, m.p. 38°, and a little *trans*-hexahydrindene, b.p. 154—155° (oxidised by KOH-KMnO₄ to *trans*-cyclohexane-1-acetic-2-carboxylic acid). *dl*-*trans*-cyclohexane-1:2-diacetic acid is resolved (cinchonine and brucine salts) into the *d*-, [α]_D²⁵ +48.28°, and *l*-, [α]_D²⁵ -48.28° in EtOH, -acids, converted by Ac₂O at 250°, respectively, into *l*-, b.p. 92°/13 mm., [α]_D²⁵ -297.3° in EtOH [*oxime*, m.p. 160°, [α]_D²⁷ -97.74° in EtOH (*Bz* derivative, m.p. 130°, [α]_D²⁶ -60.50° in COMe₂)], and *d*-*trans*-hexahydro- β -hydrindone, b.p. 88°/11 mm., [α]_D²⁵ +297.4° in EtOH. *cis*-Hexahydrohydrindene, b.p. 166°/

760 mm., has a heat of combustion 1347.5 kg.-cal. per mol., the *trans*-compound, b.p. 159°/760 mm. (by Clemmensen reduction of *trans*-hexahydro- β -hydrindone), has 1345.7 kg.-cal. per mol. Comparisons with the various decalone derivatives are made. J. W. B.

Asymmetric reactions. IV. Causes of optical selectivity in reactions with optically active catalysts. R. WEGLER and A. RÜBER (Ber., 1935, 68, [B], 1055—1059; cf. A., 1934, 771).—The selectivity of the catalytic action of nicotine, benzylpipercoline, α -phenylethyl-dimethyl- or -methylpropylamine on the partial esterification of $\text{CHPhMe}\cdot\text{OH}$ by Ac_2O or the partial conversion of *r*-hydratropyl chloride into amide is very slight in comparison with that of brucine; a relationship between selectivity and constitution of catalyst is not obvious. In the presence of cinchonine (as Ac derivative) an ester-alcohol mixture is obtained with $\alpha_D +3.9^\circ$, whereas in that of the isomeric cinchonidine the product has $\alpha_D -2.2^\circ$. Apparently in the first case a predominating portion of the centres of asymmetry has a positive selective influence, whereas in the second instance the configurative alteration at two centres causes a more pronounced selectivity in the opposite sense. The possibility of obtaining catalysts of high selectivity by choice of isomerides obtained by accumulating asymmetric centres in a given compound is examined by converting camphor into the corresponding *N*-dimethylbornylamines, one of which gives an alcohol-ester mixture with $\alpha_D^{20} +1.6^\circ$, whereas the other affords a product with $\alpha_D^{20} +12.8^\circ$.

H. W.

Preparation of aromatic alcohols by the crossed Cannizzaro reaction with formaldehyde. D. DAVIDSON and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 905).—Aromatic aldehydes and CH_2O in hot MeOH give 85—90% yields of HCO_2H and the aromatic alcohol with 2—5% of aromatic acid. Anisyl, piperonyl, and veratryl alcohols are conveniently prepared thus.

R. S. C.

Sensitivity of β -amino- and β -hydroxylamino- α -alkoxyphenylpropyl alcohols to alkali. V. BRUCKNER [with A. KRÁMLI and E. VINKLER] (J. pr. Chem., 1935, [ii], 142, 301—309).—3 : 4-Dimethoxy- β -veratrylideneamino- α -hydroxy-*n*-propylbenzene (I), m.p. (+ H_2O) 151° after sintering at 90—100° or (anhyd.) 151° (sharp), is obtained (a) from 3 : 4-dimethoxy- β -acetamido- α -hydroxypropylbenzene and KOH-aq. MeOH at room temp. (several weeks), or from 3 : 4-dimethoxy- β -amino- α -hydroxypropylbenzene and (b) hot 10% H_2SO_4 or (c) veratraldehyde (II) and cold NaOH. 3 : 4-Methylenedioxy- β -piperonylideneamino- α -hydroxypropylbenzene (III), m.p. 119°, is obtained by methods (a) and (b). The nitron, m.p. 150—151°, corresponding with (I) is obtained from 3 : 4-dimethoxy- β -hydroxylamino- (IV) or β -*N*-acetylhydroxylamino- α -hydroxy-*n*-propylbenzene and 5% KOH-aq. MeOH (1 : 1) at room temp. (2—3 weeks) and from (III) and (II). The nitron, m.p. 179°, corresponding with (III) is similarly obtained. The reactions involved are: $\text{OH}\cdot\text{CHAr}\cdot\text{CHMe}\cdot\text{NRAc}$ ($\text{R}=\text{H}$ or OH) \rightarrow $\text{KOAc} + \text{OH}\cdot\text{CHAr}\cdot\text{CHMe}\cdot\text{NHR}$ (V) or \rightarrow $\text{NHAc} + \text{ArCHO}$; (V) \rightarrow $\text{NHAc} + \text{ArCHO}$; $\text{ArCHO} +$ (V) \rightarrow (I) and (III) or their nitrones. R. S. C.

Use of the ψ -nitrosites of propenylphenol ethers for the synthesis of β -hydroxylamino- and β -amino- α -arylpropanols. Wandering of acyl groups. Methylisoeugenol and isosafrole derivatives. V. BRUCKNER and (in part) V. KARDOS (Annalen, 1935, 518, 226—244).—Methylisoeugenol- ψ -nitrosite (improved prep. in 75% yield) is converted by Ac_2O -conc. H_2SO_4 into β -nitro- α -3 : 4-dimethoxyphenylpropyl acetate (I), m.p. 98°, hydrolysed (dil. KOH-EtOH) to $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$. Electrolytic reduction (conditions prescribed) of (I) affords (III) (below) and β -acetamido- α -3 : 4-dimethoxyphenylpropan- α -ol (II), m.p. 130—131° (additive compound with CHCl_3 and with C_6H_6), the structure of which is proved by its conversion by POCl_3 in boiling CHCl_3 into 6 : 7-dimethoxy-1 : 3-dimethylisoquinoline, m.p. 121.5°. The formation of (II) involves Ac migration from O to N. The reverse migration (N to O) also occurs since (II) with 4.66% MeOH-HCl affords the hydrochloride, m.p. 174—175° (decomp.), of β -amino- α -3 : 4-dimethoxyphenylpropyl acetate [reconverted by basification into (II)], and, by refluxing with 1% MeOH-HCl, is converted into the hydrochloride, m.p. 184° (decomp.), of β -amino- α -3 : 4-dimethoxyphenylpropan- α -ol (Bz derivative of Me ether, m.p. 121°). Under different conditions in the electrolytic reduction of (I) the main product is the N-Ac derivative (III), m.p. 176° (decomp.), of β -hydroxylamino- α -3 : 4-dimethoxyphenylpropan- α -ol (also formed by Ac migration from O to N), converted by N-MeOH-HCl at room temp. into the hydrochloride, m.p. 138°, of β -hydroxylamino- α -3 : 4-dimethoxyphenylpropyl acetate [converted by 40% CH_2O into the methylene nitron, m.p. 197° (decomp.)], reconverted into (III) by aq. Na_2CO_3 . Similar derivatives are prepared from isosafrole- ψ -nitrosite. This with Ac_2O - H_2SO_4 gives β -nitro- α -3 : 4-methylenedioxyphenylpropyl acetate (IV), m.p. 85°, hydrolysed to β -nitroisosafrole, reduced electrolytically to the hydrochloride, m.p. 188°, of β -amino- α -3 : 4-methylenedioxyphenylpropane. Electrolytic reduction of (IV) affords the N-Ac derivative (V), m.p. 162°, of β -hydroxylamino- α -3 : 4-methylenedioxyphenylpropan- α -ol [converted by HCl-MeOH into the hydrochloride, m.p. 159°, of β -hydroxylamino- α -3 : 4-methylenedioxyphenylpropyl acetate (methylene nitron, m.p. 218°), which is reconverted into (V) by NaOH], and β -acetamido- α -3 : 4-methylenedioxyphenylpropan- α -ol (VI), m.p. 124°, converted by MeOH-HCl into the hydrochloride, m.p. 176°, of the isomeric O-Ac derivative (reconverted by NaOH). (VI) with POCl_3 - CHCl_3 affords 6 : 7-methylenedioxy-1 : 3-dimethylisoquinoline, m.p. 147°. (VI) is hydrolysed (10% H_2SO_4) to the corresponding β - NH_2 -compound, m.p. 96.5° [hydrochloride, m.p. 195—196° (decomp.)].

J. W. B.

Amino-alcohols. X. Ring-substituted propadrines. W. H. HARTUNG, H. C. MUNCH, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1935, 57, 1091—1093; cf. A., 1933, 746).—Five ephedrine analogues are less useful than ephedrine. The relation of structure to pharmacological activity in this group is discussed. The following Et ketones are prepared: (a) from MgEtBr and the nitrile: *m*-tolyl (76.6%), b.p. 134—135°/30—33 mm. (semicarbazone, m.p. 172°); α - (68%), b.p. 166—169°/8 mm., and β - C_{10}H_7

(67%), b.p. 180—190°/8—10 mm., m.p. 56° (oxime, m.p. 133—133.5°; semicarbazone, m.p. 199°); (b) from EtCOCl: *p*-C₆H₄Cl (81%), b.p. 115°/3 mm.; *p*-C₆H₄Ph (90%), m.p. 102° (oxime, m.p. 162°). These give *oximino*-derivatives, m.p. 69.5—70°, 130°, 157°, 122—123° (gives the *dioxime*, m.p. 217° after decomp. from 208°), and 180° (*dioxime*, m.p. 235°), respectively. Hydrogenation (Pd-black; EtOH-HCl) then affords the *hydrochlorides*, m.p. 147°, 267° (uncorr.), 230—231°, 245°, and 228° (decomp.), respectively, of the corresponding β -amino- α -aryl-*n*-propyl alcohols. By analogy with ephedrine the following names are proposed: OH·CHPh·CHR·NH₂ alkadrine; OH·CHPh·CH₂·NH₂ ethadrine; OH·CHPh·CHMe·NH₂ propadrine, etc. R. S. C.

Phenanthrene series. VIII. Amino-alcohols derived from 1:2:3:4:5:6:7:8-octahydrophenanthrene. J. VAN DE KAMP and E. MOSETTIG (J. Amer. Chem. Soc., 1935, 57, 1107—1110; cf. A., 1934, 1104).— β -Amino- α -hydroxy-derivatives are made for pharmacological examination. 1:2:3:4:5:6:7:8-Octahydrophenanthrene (prep. by H₂-Raney Ni at 120°/1600—2100 lb.; 70—85% yield), b.p. 179—180°/20 mm., cryst., gives (Friedel-Crafts; -15°; CS₂) good yields of the 9-CO·CH₂Cl (I), -CO₂H (II), m.p. 241—242° (*Me* ester, m.p. 45°), -Ac (III), m.p. 58—59° (oxime, m.p. 158.5—159.5°; semicarbazone, m.p. 191.5—193°), and -COEt (IV) derivatives, m.p. 52.5—53° (oxime, m.p. 146—147°). (I) does not react smoothly with sec. bases. The position 9 of the substituent is proved by prep. of (II) by hydrogenation of phenanthrene-9-carboxylic acid. (III) and (IV) give *oximino*-derivatives, reduced by SnCl₂ to 9-glycyl- [hydrochloride, m.p. 232—234° (decomp. from 225°); picrate, m.p. 215—216° (decomp.)] and 9- α -amino-propionyl-1:2:3:4:5:6:7:8-octahydrophenanthrene [hydrochloride, m.p. 231—233° (decomp.); picrate, m.p. 181—182° (decomp.)], and with Br afford the 9-CO·CH₂Br, m.p. 55—56° (does not react with NH₂Me or NH₂Et), and 9-CO·CHBrMe derivative, an oil. These yield the following 1:2:3:4:5:6:7:8-octahydrophenanthrene derivatives by condensation with the appropriate base and/or hydrogenation (PtO₂; best in EtOH-HCl): 9-dimethylamino- [hydrochloride, m.p. 236—237.5° (decomp.) after sintering at 226°; picrate, m.p. 116—117°], -diethylamino- (perchlorate, m.p. 165—166°; picrate, m.p. 144.5—145.5°), and -piperidino-acetyl- (perchlorate, m.p. 220.5—222°; picrate, m.p. 116.5—117°); 9- α -dimethylamino- [perchlorate, m.p. 198.5—200°; picrate, m.p. 185—186° (decomp.) after sintering at 180°], -diethylamino- (perchlorate, m.p. 209—210°), -piperidino- (hydrochloride, m.p. 181—182°), -methylamino-, an oil [hydrochloride, m.p. 223—224.5°; picrate, m.p. 192—193° (decomp.) after sintering at 189°], and -ethylamino-propionyl-, an oil (hydrochloride, m.p. 226—228°; picrate, m.p. 163—164°); 9- β -amino-, m.p. 103—104° [hydrochloride, m.p. 253.5—254°; picrate, m.p. 208.5—209.5° (decomp.)], -dimethylamino-, m.p. 80—80.5° (hydrochloride, m.p. 217—218°; picrate, m.p. 193—194°), -diethylamino-, m.p. 72.5—73° (hydrochloride, m.p. 148—149°; picrate, m.p. 159—160°), and -piperidino- α -hydroxyethyl-, m.p. 86—86.5° (hydrochloride, m.p. 227—227.5°; picrate, m.p. 164.5—165.5°);

9- β -amino-, m.p. 164—165.5° [hydrochloride, m.p. 278—279°; picrate, m.p. 224—224.5° (decomp.) after sintering at 223°], -dimethylamino-, an oil (hydrochloride, m.p. 227—228°; picrate, m.p. 174—174.5°), -diethylamino-, an oil (hydrochloride, m.p. 210—211°), -piperidino-, m.p. 126.5—127.5° (hydrochloride, m.p. 235—236°), -methylamino-, m.p. 129.5—130° (hydrochloride, m.p. 218—219°; picrate, m.p. 179—180°), and -ethylamino- α -hydroxy-*n*-propyl-, m.p. 124.5—125° (hydrochloride, m.p. 118—119°). R. S. C.

Pinacol-pinacolone rearrangement. VII. Rearrangement of 9:10-diaryldihydrophenanthrenediols. W. E. BACHMANN and (Miss) J. H. CHU (J. Amer. Chem. Soc., 1935, 57, 1095—1098; cf. A., 1934, 1355).—Six 9:10-dihydroxy-9:10-dihydro-9:10-diarylphenanthrenes are prepared (a) from phenanthrenequinone by the Grignard reaction and (b) by Na-Hg reduction of 2:2-diacyldiphenyls (prep. from *o*-C₆H₄Br aryl ketones and Cu at 200—250°). In each case (a) and (b) give stereoisomeric pairs of compounds, both of which with I-AcOH lose H₂O to form the same 10-keto-9:9-diaryl compound, exclusively, which with KOH at 200—300° gives 2-diarylmethyl-diphenyl-2-carboxylic acids. The reverse of reaction (b) is effected by CrO₃-AcOH. The following are described. 9:10-Dihydroxy-9:10-dihydro-9:10-diarylphenanthrenes, m.p. referring to the products of reactions (a) and (b), respectively: phenetyl- (I), m.p. 140.5—141°, 155.5°, α -C₁₀H₇- (II), m.p. 263—264°, 204—204.5°, *p*-C₆H₄Ph- (III), m.p. 192—192.5°, 159—160°, *p*-C₆H₄Cl- (IV), m.p. 187—188°, 223°, *p*-C₆H₄F- (V), m.p. 180—181.5°, 210—211°, and *m*-C₆H₄Me- (VI), m.p. 148.5—149°, an oil. 9:9-Diarylphenanthr-9-ones: (I), m.p. 136—137°, (II), m.p. 258.5—259°, (III), m.p. 253—253.5°, (IV), m.p. 138—139°, (V), m.p. 170—170.5°, (VI), m.p. 197—198°. 2-Diarylmethyldiphenyl-2-carboxylic acids: (I), m.p. 97—98°, (II), m.p. 215°, (III), m.p. 197—198°, (IV), m.p. 205—206°, (V), m.p. 162°, (VI), m.p. 90°. *o*-C₆H₄Br *m*-tolyl, m.p. 54.4°, b.p. 180—181°/5 mm., *p*-C₆H₄·OEt, m.p. 81°, *p*-C₆H₄Ph, m.p. 90.5—91°, *p*-C₆H₄Cl, m.p. 49—49.5°, *p*-C₆H₄F, m.p. 49.5—50°, and α -C₁₀H₇-, m.p. 87°, ketones. 2:2'-Diacyldiphenyls: *m*-C₆H₄Me·CO, m.p. 105—106°, *p*-OEt·C₆H₄·CO, m.p. 137—138°, α -C₁₀H₇·CO, m.p. 200°, *p*-C₆H₄Ph·CO, m.p. 209.5—210°, *p*-C₆H₄Cl·CO, m.p. 139—140°, *p*-C₆H₄F·CO, m.p. 136.5—137.5°. R. S. C.

Heteropolarity. XXV. Constitution and colour. W. DILTHEY and R. WIZINGER (Ber., 1935, 68, [B], 1037—1040).—In reply to Hantzsch *et al.* (A., 1933, 1158) it is pointed out that the absorption spectra of aminated CHPh₃ dyes do not afford any experimental evidence of the new views of the action of auxochromes or of the presence of special conjugated systems. H. W.

Magenta series. I. Preparation and spectrography of the lower basic members. J. T. SCANLAN (J. Amer. Chem. Soc., 1935, 57, 887—892).—The following names are given: 4:4'-diaminofuchsonimonium chloride, magenta O; its 3-Me, 3:3'-Me₂, and 3:3':3''-Me₃ derivatives magenta I, II, and III, respectively [termed below (O), (I), (II), and (III), respectively]. The "old" (Couper) process (modified) gives these products in

a nearly pure form when the amines and nitro-compound are properly selected. The "new" (CH_2O) process gives anomalous results, as the 4:4'-diaminodiphenylmethane derivative apparently reacts by oxidation to the benzhydrol and fission to the aldehyde and hydrocarbon, thus providing only 1 Ph of the product. In accordance with this mechanism $\text{CH}_2(\text{C}_6\text{H}_4\text{NH}_2\text{-}p)_2$ (IV) with NH_2Ph , HCl , PhNO_2 , and FeCl_2 gives (0) and with $o\text{-C}_6\text{H}_4\text{MeNH}_2$ and $o\text{-C}_6\text{H}_4\text{MeNO}_2$ mainly (II), whilst the 3:3'-Me₂ derivative of (IV) with NH_2Ph and PhNO_2 gives mainly (I) and with $o\text{-C}_6\text{H}_4\text{MeNH}_2$ and $o\text{-C}_6\text{H}_4\text{MeNO}_2$ gives (III). (0), (I), (II), and (III) are characterised by absorption spectra.

R. S. C.

Surface films of sterols and their derivatives. N. K. ADAM, F. A. ASKEW, and J. F. DANIELLI (Biochem. J., 1935, 29, 1786—1801; cf. A., 1934, 1067).—Surface pressure and potential measurements of sterols and their derivatives confirm the generally accepted view of sterol constitution; differentiation between *epi* and normal configuration is sometimes possible. Sterols with OH at position 3 and with > one double linking stand practically vertical in the surface and occupy an area of 37—44 sq. Å. Tilting is produced by CO in the 3 and, to a great extent, CO or OH in the 6 or 7 position. Factors involved in tilting include H_2O -attraction and position in ring of the groups. *apo*Cholic acids form gaseous films with flat-lying mols.

F. O. H.

Synthesis of the carbon skeleton present in sterols etc. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 95—107).—Theoretically possible methods are outlined.

R. S. C.

Δ^3 -Tetrahydro-*p*-toluic acid. E. LEHMANN and W. PAASCHE (Ber., 1935, 68, [B], 1068—1072).—The product of the condensation of isoprene and acraldehyde is identified as Δ^3 -tetrahydro-*p*-tolualdehyde, since it is oxidised by CrO_3 in AcOH or by Ag_2O in 50% EtOH to Δ^3 -tetrahydro-*p*-toluic acid (I), m.p. 99°, also obtained from isoprene and acrylic acid and dehydrogenated by Se at 270° to *p*- $\text{C}_6\text{H}_4\text{MeCO}_2\text{H}$. (I) yields an *Et* ester, b.p. 105—108°/12 mm., and *chloride*, b.p. 90°/19 mm., which yields the *amide*, m.p. 182°, and *sec.-amide*, m.p. 203°. 4(3)-Hydroxy-3(4)-methylcyclohexanecarboxylactone, m.p. 69°, converted by boiling 15% NaOH into 4(3)-hydroxy-3(4)-methylcyclohexane-1-carboxylic acid, m.p. 156°, is obtained as by-product in the prep. of (I). Addition of Cl_2 to (I) in CCl_4 at 0° is accompanied by evolution of HCl and formation of 3-chloro- Δ^3 (4)-tetrahydro-*p*-toluic acid, m.p. 121°. Br and (I) in CCl_4 afford 3:4-dibromohexahydro-*p*-toluic acid, m.p. 108° (*Me*, b.p. 136—137°/4 mm., and *Et*, b.p. 128°/0.8 mm., esters), converted by $\text{CH}_3\text{BrCO}_2\text{Me}$ and Cu powder at 180° into *Me*, 2:2'-dimethyl- $\Delta^{1:1'2:2'}$ -octahydro-diphenyl-5:5'-dicarboxylate, b.p. 164—165°/1.5 mm. (corresponding acid, m.p. 227°).

H. W.

Derivatives of $\alpha\alpha$ -dibenzamidopropionic acid. B. H. NICOLET (J. Amer. Chem. Soc., 1935, 57, 1073).— AcCO_2H and NH_2Bz at 110—120°/20—30 mm. give $\alpha\alpha$ -dibenzamidopropionic acid, m.p. 181—186° (decomp.) [*Et* ester, m.p. 132—133°; *amide*, m.p. 212—213° (slight decomp.), stable to hot Ac_2O],

converted by hot AcOH into α -benzamidoacrylic acid, m.p. 137—138°, and by hot Ac_2O into the *azlactone*, m.p. 203—205°, which with glycine gives $\alpha\alpha$ -dibenzamidopropionylglycine, m.p. 197° (decomp.).

R. S. C.

Catalytic action of platinum and manganese dioxide on benzoyl peroxide and perbenzoic acid.—See this vol., 941.

Ring-systems with *para*-linkings. II. G. HELLER and R. EBELING (J. pr. Chem., 1935, [ii], 142, 274—276; cf. A., 1926, 286).—*p*-Nitrobenzhydrazide (modified prep.) gives *Et* acetoacetate-*p*-nitrobenzoylhydrazone, m.p. 115°, which at 170—175° yields *s*-di-*p*-nitrobenzoylhydrazine, m.p. 283°, reduced (Zn dust and HCl-AcOH) to the di-*p*-amino-compound, m.p. 303—304° (Ac_2 derivative, m.p. 335°), identical with the compound previously considered to be *p*-benzisopyrazolone.

R. S. C.

M.p. of sulphosalicylic acid. HORKHEIMER (Pharm. Ztg., 1935, 80, 660).—Sulphosalicylic acid (I) is usually stated to have m.p. 108—113°. If a finely-powdered sample is kept for 24 hr. over H_2SO_4 in a desiccator and the m.p. determined immediately it is opened, figures as high as 200° are obtained. Keeping for a few min. in the open allows sufficient H_2O to be absorbed to give results about 108—113°. The divergence is not due to loss of H_2O of crystallisation.

C. I.

Stereochemical studies. V. Optical isomerism of α -phenylsulphonylphenylacetic acids. W. PIECHULEK and J. SZUSZKO (Rocz. Chem., 1935, 15, 221—233).—Racemic $\text{SPh-CHPh-CO}_2\text{H}$ (I), m.p. 103—104°, and *brucine* yield a *salt* (II), $+\text{C}_6\text{H}_6$, m.p. 97° (decomp.), $[\alpha]_D^{20} +55^\circ$, from which the *d*-acid (III), m.p. 129—130°, $[\alpha]_D^{19} +216^\circ$, is regenerated; *cinchonidine* (IV) and *dl*-(I) yield a mixture of *d*- and *l*-salt (chiefly *d*-), from which pure (III) is obtained by hydrolysis and fractional crystallisation. The *salt* obtained from (III) and (IV) has m.p. 176—178° (decomp.), $[\alpha]_D^{20} +38.6^\circ$. The *acid* (V) regenerated from the mother-liquors from (II) has m.p. 129—130°, $[\alpha]_D^{20} -215.6^\circ$; a 1:1 mixture of (III) and (V) has m.p. 103—104°. (V) and *l*-menthylamine afford a *salt*, m.p. 157—158°, $[\alpha]_D^{20} -170.2^\circ$. (III) yields

$\text{PhSO-CHPh-CO}_2\text{H}$ (VI), m.p. 149—150°, $[\alpha]_D^{20} +419.4^\circ$, when treated with H_2O_2 in AcOH ; the filtrate contains $\text{PhSO-CHPh-CO}_2\text{H}$, m.p. 139° (decomp.), $[\alpha]_D^{20} +195^\circ$. The (—)_s, (—)_c, m.p. 148—149° (decomp.), $[\alpha]_D^{20} -420.4^\circ$, and (+)_s, (—)_c, m.p. 139° (decomp.), $[\alpha]_D^{20} -191.2^\circ$, acids are obtained analogously from (V). 1:1 Mixtures of the (—)_s, (—)_c, and (—)_s, (+)_c acids, and of the (+)_s, (—)_c and (+)_s, (+)_c acids have m.p. 135—137°, $[\alpha]_D^{20} \pm 116^\circ$. (III), on protracted treatment with H_2O_2 in AcOH , affords $\text{PhSO}_2\text{-CHPh-CO}_2\text{H}$, m.p. 180—187° (decomp.), $[\alpha]_D^{19} +107.6^\circ$ (both diminished on repeated crystallisation), which represents a mixture of unstable optical isomerides. The above findings for the diastereomerides of (VI) are in agreement with the principle of optical superposition. All vals. of $[\alpha]$ are in 1:1 EtOH-CHCl_3 .

R. T.

cis-Cinnamic acids.—See this vol., 916.

Modes of addition to conjugated unsaturated systems. VIII. Reduction of α -vinylcinnamic acid. C. K. INGOLD and M. A. T. ROGERS (J.C.S., 1935, 717—721).—Reduction of α -vinylcinnamic acid (I) by Na-Hg in alkaline and acid solution and by Al-Hg in neutral solution affords a mixture of α -benzylcrotonic acid (II) and varying amounts of a liquid product (III), b.p. 119—122°/2 mm., 174°/19 mm., shown, contrary to the conclusions of Kuhn *et al.* (A., 1932, 739), to be essentially β -phenyl- α -vinylpropionic acid, the theoretically expected product (A., 1929, 1270). This result was established by ozonolytic degradation by the methods of Burton and Ingold (A., 1929, 1270) and Fischer *et al.* (A., 1932, 1113). (III), however, is converted quantitatively into (II) by 2*N*-NaOH at 100° during 15 min., or at room temp. during a longer time. Et benzylmalonate with K in Et₂O and dibromoethylene afford Et benzyl- β -bromovinylmalonate, b.p. 130—140°/0.05—0.07 mm., reduced by Zn-EtOH to ethyl benzylvinylmalonate, b.p. 100—110°/0.14 mm. (cf. A., 1933, 51). This on hydrolysis by KOH-EtOH, NaOH-EtOH-H₂O, and HCl-AcOH gave only (II). Et α -vinylcinnamate, b.p. 106—108°/1 mm. [obtained from the Ag salt of (I) and EtI], affords on reduction (Al-Hg in moist ether) a H₂-derivative, b.p. 134—144°/13—14 mm. Reduction of α -styrylcinnamic acid by Na-Hg in EtOH-AcOH (cf. A., 1899, i, 614) and in NaOH-H₂O affords β -phenyl- α -styrylpropionic acid, unchanged when refluxed with 5*N* aq. NaOH during 2 hr.

The theory of Burton and Ingold is in agreement with all the known facts. It cannot, however, be applied to the reduction of β -phenylsorbic acid (A., 1933, 1159), as this case is too complicated (cf. A., 1929, 1270). Contrary to the views of Kuhn *et al.* (A., 1933, 1159), the theory readily accommodates the occurrence of pinacol-like reduction and the known effects of the purity of amalgams. Further, it can be linked to current views on over-potential.

H. G. M.

Synthesis of hydrogenated derivatives of phenanthrene and of phenanthrenic hydrocarbons. G. DARZENS and A. LEVY (Compt. rend., 1935, 200, 2187—2189).— α -C₁₀H₇·CH₂Cl (modified prep.) gives Et₂ 1-naphthylmethylmalonate, m.p. 32° (lit. an oil), and thence Et₂ 1-naphthylmethylallylmalonate (α -1-naphthyl- Δ^3 -pentene- $\beta\beta$ -dicarboxylate), m.p. 28°, b.p. 209°/2 mm., which yields the corresponding acid, an oil, decomp. at about 185—190° into α -1-naphthylmethyl- Δ^3 -pentenoic acid, m.p. 73.5°. With H₂SO₄-AcOH (1:1) at 50° this gives the lactone, m.p. 98°, and 1-methyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylic acid, m.p. 157°, converted by S at 265° into 1-methylphenanthrene. Yields are excellent.

R. S. C.

Synthesis of pinononic acid. P. C. GUHA and K. GANAPATHI (Current Sci., 1935, 3, 484—485).—trans-Norpinic acid (A., 1929, 445) with Ac₂O at 190—200° gives the *cis*-anhydride, which with NaOMe-MeOH (equimol. amount) affords Me H *cis*-norpinate; *cis*-norpinyl chloride with ZnMeI is converted into Me₂ pinononate, b.p. 130—135°/14 mm., hydrolysed to pinononic acid (cf. A., 1913, i, 495).

2-Iodo-3-hydroxybenzoic acid. T. A. HENRY and T. M. SHARP (J.C.S., 1935, 856—857).—The compound, m.p. 133° (J.C.S., 1922, 121, 1059, m.p. incorrectly given there as 233°), obtained by the oxidation of 2-iodo-3-hydroxybenzaldehyde (I) (cf. A., 1924, i, 738) in COMe₂ with KMnO₄ is impure (I). Oxidation of the Ac derivative of (I) in COMe₂ with KMnO₄ affords 2-iodo-3-acetoxybenzoic acid, m.p. 179—180° (corr.), from which the desired 2-iodo-3-hydroxybenzoic acid, m.p. 158—159° (corr.), is obtained by hydrolysis.

H. G. M.

Action of thionyl chloride on phenylglycollic acid. P. CARRE and D. LIBERMANN (Bull. Soc. chim., 1935, [v] 2, 1166—1168).—OH·CHPh·CO₂H (I) and SOCl₂ (1.2 mols.) in Et₂O at room temp. give CHPhCl·COCl and the sulphite anhydride,

$O \begin{array}{c} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{SO-O} \end{array} \text{CO}$, which decomposes at 29—30° into PhCHO, SO₂, and CO, or with H₂O or EtOH affords SO₂ and (I) or its Et ester, respectively. Explanations in the lit. are fallacious. CHPhCl, arises by reaction of PhCHO with excess of SOCl₂. OH·CPh₂·CO₂H and SOCl₂ (3 mols.) in CCl₄ at room temp. give an excellent yield of CPh₂Cl·CO₂H and a little COPh₂, probably formed from a sulphite anhydride (cf. lit.).

R. S. C.

Phenylpyruvic acid; product of its condensation with phenylacetonitrile. P. CORDIER (Compt. rend., 1935, 200, 1412—1413).—In EtOH-H₂O containing KOH or, preferably, K₂CO₃, CH₂Ph·CO·CO₂H and CH₂Ph·CN afford α -hydroxy- β -phenyl- α -cyano-benzylpropionic acid, slow decomp. > 160°, which decomposes into its components in presence of conc. alkali, and is transformed by AcOH at 100° into β -phenyl- α -benzylmaleic anhydride, m.p. 76°, converted by KOH and MeI into its Me₂ ester, m.p. 68°.

H. W.

Addition of mercaptans to ethylenic linkings.

B. H. NICOLET (J. Amer. Chem. Soc., 1935, 57, 1098—1099).— $\alpha\beta$ -Unsaturated ketones, in which the C:C linking is reactive, condense with mercaptans without addition of alkali. CHPh:CH·COPh (I) at 100° thus yields in 5 min. β -benzyl-, m.p. 71°, and *p*-tolyl-thiol- β -phenylpropiophenone, CHPh:CH·CO·CO₂H in 10 min. gives α -keto- γ -*p*-tolyl-, m.p. 97—98° (oxime, m.p. 160°), and -benzylthiol- γ -phenylbutyric acid, an oil (oxime, m.p. 95—97°). CHPh:CH·CO₂Me with (not without) a little piperidine gives (2 hr.) Me β -*p*-tolyl-, m.p. 59—60°, and -benzylthiol- γ -phenylpropionate, m.p. 119—120°. H₂S adds to such ketones in EtOH in presence of a little Na₂CO₃ and to (I) in neutral EtOH.

R. S. C.

Asymmetric syntheses. XII. Asymmetric synthesis of phenyl-*p*-tolylglycollic and *p*-tolylmethylglycollic acids. A. MCKENZIE and E. W. CHRISTIE (Biochem. Z., 1935, 277, 426—436).—The prep. is described of (–)-menthyl *p*-toluoylformate (I), C₁₉H₂₆O₃, an oil, b.p. 217—220°/11 mm., *n*_D²⁰ 1.5069, and of (–)-bornyl *p*-toluoylformate (II), C₁₉H₂₆O₃, an oil b.p. 215—217°/10 mm., 1.5195, and the mutarotation of these compounds examined. (I) with MgPhBr gave an acid, m.p. 128—130°, [α]_D²⁰ +1°. *d*-Phenyl-*p*-tolylglycollic acid, prepared by resolution with quinine of the *r*-acid, has [α]_D²⁰ +2.5° and

m.p. 125—127°, whereas the *r*-acid has m.p. 133—134°. (I) with MgMeI gave (–)*p*-tolylmethylglycollic acid, m.p. 139—142°, $[\alpha]_{D}^{20} -47^\circ$ in EtOH, which is practically optically pure, since the corresponding acid (by resolution with quinine of the *r*-acid) has m.p. 140—142°, $[\alpha]_{D}^{20} -51^\circ$. (II) with MgMeI gave *r-p*-tolyltrimethylethylene glycol, m.p. 79.5—80.5°, together with *r-p*-tolylmethylglycollic acid, m.p. 102—104°. P. W. C.

β-3-Hydroxycholic acid. F. REINDEL and K. NIEDERLÄNDER (Ber., 1935, 68, [B], 1243—1246).—Lithocholic, [α-3-hydroxycholic] acid (I) is oxidised by CrO₃ to dehydrolithocholic acid (II) [semicarbazone, m.p. 231—232° (decomp.)], which is hydrogenated (PtO₂) in acid solution to β-3-hydroxycholic acid (III), leaflets (+1H₂O) or anhyd needles, m.p. 176—177°, $[\alpha]_D^{20} +25.83^\circ$ in abs. EtOH [Me ester (III), m.p. 113—114.5°; Ac derivative, m.p. 183—185°]. The main product of the hydrogenation of (II) in alkaline medium is (I). (III) is partly isomerised to (I) by NaOEt at 180°. (III) and (IV) give ppts. with digitonin in 90% EtOH; these are more freely sol. than the digitonides of the sterols and do not appear in 95% EtOH. H. W.

Optical properties of some bile acids. B. JOSEPHSON (Biochem. J., 1935, 29, 1484—1489).—Sp. rotations and rotatory dispersions are given for cholic (I), deoxycholic (II), glycocholic, and taurocholic acids and their alkali salts. (I) and (II) have $[\alpha]_D^{20} +35.07^\circ$ and 55.56° in EtOH, respectively. For the other acids the rotation is dependent on the concn. of the solution. The alkali salts of all the acids showed increasing α_D with decreasing concn. J. N. A.

Constitution of caryophyllene. H. N. RYDON (Chem. and Ind., 1935, 557).—3:3-Dimethylcyclobutane-1:2-dicarboxylic and 3:3-dimethyl-Δ¹-cyclobutene-1:2-dicarboxylic acids, synthesised from β-dimethyladipic acid by the application of the method of Fuson and Kao (A., 1929, 794), show no depression of m.p. on admixture with racemic norcaryophyllenic and with dehydronorcaryophyllenic acids, respectively. The structures assigned to the latter acids (this vol., 351, 489) are thus confirmed. H. N. R.

Orientation in the benzene ring. Preparation of 5-chloro-β-resorcylic acid. R. B. SANDIN and R. A. McKEE (J. Amer. Chem. Soc., 1935, 57, 1077—1078).—5-Chloro-β-resorcylic acid, dimorphic, m.p. 224—225° (corr.) (after several months, 211—213°), best identified by the Ac derivative, m.p. 169° (corr.), is obtained from 4-chlororesorcinol and KHCO₃ or from β-resorcylic acid and SO₂Cl₂ or Cl₂ in AcOH (cf. lit.). R. S. C.

Homoamines and homoacids. P. L. JULIAN and B. M. STURGIS (J. Amer. Chem. Soc., 1935, 57, 1126—1128).—An improved prep. of rhodanine, m.p. 170°, renders practicable the large-scale prep. of arylacetonitriles and thence of aryl-ethylamines and -acetic acids from aromatic aldehydes. Veratrylidenerhodanine, m.p. 232°, with 15% NaOH at 100° gives α-thio-3:4-dimethoxyphenylacetic acid, CH₂R-CS-CO₂H, m.p. 179°, which with NH₂OH-EtOH affords 3:4-dimethoxyphenylpyruvic acid oxime, dehydrated by warm Ac₂O to veratryl cyanide. All

the yields are excellent. Piperonal and anisaldehyde give similar results. R. S. C.

Ketonic acid analogues with thyroxine. A. CANZANELLI, R. GUILD, and C. R. HARRINGTON (Biochem. J., 1935, 29, 1617—1619).—The synthesis of 3:5-di-iodo-4-(3':5'-di-iodo-4'-hydroxyphenoxy)-phenylpyruvic acid (I), the ketonic acid analogous with thyroxine, is described. The azlactone from acetyl glycine and 3:5-di-iodo-4-(4'-methoxyphenoxy)benzaldehyde, m.p. 227° (decomp.), on boiling with 30% KOH and saturating with SO₂, give 3:5-di-iodo-4-(4'-methoxyphenoxy)phenylpyruvic acid, m.p. 205° (decomp.), dark green FeCl₃ colour in EtOH solution, demethylated with HI-AcOH to 3:5-di-iodo-4-(4'-hydroxyphenoxy)phenylpyruvic acid, m.p. 156°, which with I-KI gave (I), m.p. 173°, intense reaction with HNO₂+NH₃. The ratio of the activities of thyroxine and of (I) on the metabolism of an adult female dog on const. maintenance diet was about 11:3. P. W. C.

Formation of unsymmetrical acid amides. B. H. NICOLET (J. Amer. Chem. Soc., 1935, 57, 1064—1065).—An *as*-acid anhydride, $\begin{matrix} X \cdot CO \\ Y \cdot CO \end{matrix} > O$, may react with NH₃ first by addition, to yield

CO₂H·Y·X·CO·NH₂. If the imide, $\begin{matrix} X \cdot CO \\ Y \cdot CO \end{matrix} > NH$, reacts with NaOH first by addition at the same CO, it will yield the isomeric amide, NH₂·CO·Y·X·CO₂H. This is true for *d*-camphoric anhydride [gives mainly α-amide (I)] and imide [gives very little (I)] and for the following cases. 3-Nitrophthalic anhydride and NH₂Ph at room temp. give 3-nitrophthal-2-anilic acid, m.p. (+0.5H₂O) 172°, (anhyd.) 154°, not identical with the 1-anilide, m.p. 181°, prepared from the phenylimide, which with NH₃ at 150° gives 3-nitrophthal-1-anilide-2-amide, m.p. 200—204° (decomp.). 3-Nitrophthalimide with NH₂Ph at 100° gives the 2-anilide-1-amide, m.p. 228—230°. R. S. C.

Dipole moment and structure of organic compounds. XIV. Direction of the electric moment of the N·C group. A. WEISSBERGER and R. SANGWALD (J.C.S., 1935, 855).—The moment of *p*-C₆H₄(CN)₂ is indistinguishable from zero. The CN group therefore shows axial symmetry about the direction of the bond of attachment to the benzene ring. 4:4'-Dicyanodiphenyl is not sufficiently sol. in C₆H₆ at 25° and in decalin at 70° to make a determination of the moment possible, but it is considered that the moment is zero and that the reported val. 1.1D (A., 1930, 399) is erroneous. H. G. M.

Modes of addition to conjugated unsaturated systems. VII. Addition of hydrogen cyanide and methyl malonate to methyl cinnamylidenemalonate. D. A. DUFF and C. K. INGOLD (J.C.S., 1934, 87—93).—Condensation of Et atropate with Et ethanetricarboxylate affords Et δ-phenyl-*n*-butane-αβδ-tetracarboxylate, b.p. 165°/0.03 mm., hydrolysed and decarboxylated to δ-phenyl-*n*-butane-αβδ-tricarboxylic acid, m.p. 210—212°. Et benzylmalonate (I) with Et fumarate yields Et δ-phenyl-*n*-butane-αβγγ-tetracarboxylate, b.p. 204—208°/0.09 mm., hydrolysed and decarboxylated to a δ-phenyl-*n*-butane-αβγ-tricarboxylic acid, m.p. 168°. (I) and Et bromosuccinate

yield *Et* δ -phenyl-*n*-butane- $\alpha\beta\gamma\gamma$ -tetracarboxylate, b.p. 184—186°/0.6 mm., hydrolysed and decarboxylated to a δ -phenyl-*n*-butane- $\alpha\beta\gamma$ -tricarboxylic acid, m.p. 187—190° (decomp.) (*Me*₃ ester, m.p. 60°; *Me*₂ ester, m.p. 112°; anhydro-acid, m.p. 114°), identical with that obtained by hydrolysis of the additive product (II) from HCN and *Me* cinnamylidenemalonate (III). (II) is therefore *Me* $\beta\gamma$ -dicyano- δ -phenyl-*n*-butane- $\alpha\alpha$ -dicarboxylate, and not the $\alpha\delta$ -dicyano-isomeride as supposed by Thiele and Meisenheimer (A., 1899, i, 603), initial $\alpha\beta$ -addition being followed by prototropic change and subsequent $\beta\gamma$ -addition. The additive product of $\text{CH}_2(\text{CO}_2\text{Me})_2$ (IV) and (III) is hydrolysed to β -phenyl-*isohexane*- $\alpha\alpha\epsilon$ -tricarboxylic acid, m.p. 140°, esterified and the *Me*₃ ester, b.p. 250°/0.2 mm., cyclised to the cyclic ketonic ester (V), m.p. 139°, described by Meerwein (A., 1908, i, 545), accompanied by a *stereoisomeride*, m.p. 64°, converted into (V) on keeping or on treatment with HCl-MeOH. (V), on hydrolysis, yields 3-phenylcyclohexanone-5-acetic acid, m.p. 118—119°, reduced (Clemmensen) to 3-phenylcyclohexane-1-acetic acid (VI), m.p. 52—54°. *Et* cyclopentanone-2-carboxylate, with CH_2PhCl in NaOEt-EtOH, affords *Et* α -benzyladipate, b.p. 208°/16 mm., hydrolysed to α -benzyladipic acid, m.p. 116—118°. With Ac_2O this yields 2-benzylcyclopentanone (VII), b.p. 144—146°/16 mm. (*semicarbazone*, m.p. 198—200°). (VII) condenses (piperidine) with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, yielding *Et* α -cyano-2-benzylcyclopentylidene-1-acetate, m.p. 81—83°, which cannot satisfactorily be hydrolysed; conc. H_2SO_4 affords *Et* 2-sulphobenzylcyclopentylidene-1-malonate, m.p. 120°. (VII), on reduction (Na-moist Et_2O), affords 2-benzylcyclopentanol, b.p. 154°/16 mm., converted by HBr-AcOH into 2-bromo-1-benzylcyclopentane, b.p. 150—155°/15 mm. This with $\text{CH}_2(\text{CO}_2\text{Et})_2$ affords *Et* 2-benzylcyclopentane-1-malonate, b.p. 142—150°/1 mm., hydrolysed to 2-benzylcyclopentanemalonic acid, m.p. 137°, which, when heated, yields 2-benzylcyclopentanecetic acid, m.p. 53—54°. 3-Phenylcyclohexanol, with HBr-AcOH, yields 3-bromo-1-phenylcyclohexane, b.p. 126°/0.5 mm., which, with $\text{CH}_2(\text{CO}_2\text{Et})_2$, affords *Et* 3-phenylcyclohexane-1-malonate, b.p. 160—165°/0.5 mm., hydrolysed to 3-phenylcyclohexane-1-malonic acid, m.p. 166°, decarboxylated to (VI), m.p. and mixed m.p. 52°. The structures assigned by Meerwein (*loc. cit.*) are thus confirmed. It is considered that, in the addition of (IV) to (III), both $\alpha\beta$ - and $\alpha\delta$ -additive products are formed, but only the latter can undergo further addition; hence, although it is thermodynamically the less stable, the excess of (IV) continuously displaces the equilibrium in its favour.

R

Michael reaction. I. Condensation of ethyl benzylmalonate with ethyl fumarate. H. N. RYDON (J.C.S., 1935, 420—425; cf. preceding abstract).—Condensation of *Et* bromosuccinate with *Et* benzylmalonate (I) affords *Et* δ -phenyl-*n*-butane- $\alpha\beta\gamma\gamma$ -tetracarboxylate (II), b.p. 203—209°/2.5 mm., which is hydrolysed and decarboxylated to a δ -phenyl-*n*-butane- $\alpha\beta\gamma$ -tricarboxylic acid (III), m.p. 190—191°. (II) does not contain H directly replaceable by Na, since attempted methylation in C_6H_6 affords only decomp. products yielding, on hydrolysis, a mixture containing benzylmethyilmalonic acid, identified by conversion

into β -phenyl- α -methylpropionamide, m.p. 106°. (II) is readily methylated in EtOH, yielding *Et* δ -phenyl- α -methyl-*n*-butane- $\alpha\alpha$ -trans- $\beta\gamma$ -tetracarboxylate (IV), b.p. 175—195°/1.5 mm., hydrolysed and decarboxylated to δ -phenyl- α -methyl- α -trans- $\beta\gamma$ -tricarboxylic acid (V), m.p. 181—183°. (I) with *Et* fumarate (VI) affords *Et* δ -phenyl-*n*-butane- $\alpha\alpha$ -trans- $\beta\gamma$ -tetracarboxylate (VII), b.p. 215—220°/1.5 mm., hydrolysed and decarboxylated to δ -phenyl-*n*-butane- α -trans- $\beta\gamma$ -tricarboxylic acid (VIII), m.p. 175°. (VII) differs from (II) in possessing a H directly replaceable by Na, since methylation proceeds readily in both C_6H_6 and EtOH, yielding (IV). (III) and (VIII) are stereoisomeric, since, when heated, both yield β -carboxy- α -benzylglutaric anhydride, m.p. 111—113°, reconverted into (VIII) by H_2O . It is concluded that the condensation of (I) with (VI) proceeds mainly in accordance with Thorpe's mechanism (J.C.S., 1900, 77, 923).

H. N. R.

Validity of Holden and Lapworth's theory of the mechanism of abnormal Michael additions. C. K. INGOLD and H. N. RYDON (J.C.S., 1935, 857—858).—The observations of Rydon (see above) on the addition of *Et* fumarate to *Et* sodiobenzylmalonate are accommodated to Holden and Lapworth's theory (A., 1931, 1272), and do not require Michael's hypothesis for their explanation. When the steric relations between the CO_2Et groups of $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I), required as an intermediate compound by Holden and Lapworth's theory, and the no. of Walden inversions which occur in the subsequent transformation of (I) and in the direct hydrolysis of (I) are considered, it is possible to account for the formation of a product which hydrolyses to a stereoisomeride of the compound, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained directly by hydrolysis of (I).

H. G. M.

Lichen substances. LII. Methanolysis of lichen depsides and synthesis of divaric acid. Y. ASAHINA and H. AKAGI. **LIII. Synthesis of hydroxydivaric acid and of sekikaic acid.** Y. ASAHINA and M. YASUE (Ber., 1935, 68, [B], 1130—1132, 1133—1137).—LII. Fission of depsides is conveniently effected by gentle warming with KOH-MeOH, the method being particularly suitable for those of the evernic acid type which afford free acids of the orsellinic variety and *Me* esters of the evernic acid class. Thus divaric acid affords divaric acid (I), m.p. 179° (decomp.) (*Me* ester, m.p. 78°), and *Me* divaricate, hydrolysed to divaric acid, m.p. 151°. Similar methanolysis of sekikaic, evernic, and lecanoric acids is recorded, whilst for gyrophoric, barbatic, and obtusatic acids a somewhat modified procedure is necessary.

[With T. WAKE.] Divarin is transformed by $\text{Zn}(\text{CN})_2$ and HCl in Et_2O followed by boiling H_2O into divarinaldehyde, which with ClCO_2Me and *N*-NaOH gives dicarbomethoxydivarinaldehyde. The latter substance is oxidised by KMnO_4 to dicarbomethoxydivaric acid, hydrolysed to (I), m.p. 179°.

LIII. 2-Aldehydo-1-propylpyrogallol 3:5-*Me*₂ ether (II) and NH_2Ph yield the corresponding *anil* (III), m.p. 86—87°, slowly converted by warm *MeI* into the *anil* of 2-aldehydo-1-propylpyrogallol 5-*Me* ether (IV),

m.p. 135—136° [hydrolysed by HCl to $\text{NH}_2\text{Ph}\cdot\text{HCl}$ and 2-aldehydo-1-propylpyrogallol 5-Me ether (V) (+0.5 H_2O), m.p. 98°, which re-forms (IV) with NH_2Ph], and 3-hydroxy-2:4-dimethoxy-6-propylbenzylidenaniline methiodide (VI), m.p. 163—165°, hydrolysed by dil. HCl to (II) and $\text{NHPhMe}\cdot\text{HCl}$. Loss of Me in the Freund-Becker reaction is therefore not due to MeI, but to a trace of HI. Treatment of (III) with $\text{NH}_2\text{Ph}\cdot\text{HI}$ in absence of MeI gives (IV) almost quantitatively, whilst (VI) yields (IV) when warmed with NH_2Ph . Addition of ClCO_2Et to (V) in $\text{C}_5\text{H}_5\text{N}$ at -15° affords 3:4-dicarbethoxy-2-aldehydo-1-propylpyrogallol 5-Me ether, m.p. 67—68°, oxidised by KMnO_4 in COMe_2 to hydroxydicarbethoxydivaricic acid, m.p. anhyd. 124—125°, m.p. (+1 H_2O), 128—129°, hydrolysed by N-NH_3 to hydroxydivaricic acid, m.p. 163—164°. Carbethoxydivaricic acid, m.p. 101°, from the acid and ClCO_2Et in $\text{C}_5\text{H}_5\text{N}$ at -15°, is transformed by SOCl_2 into the corresponding chloride, which is converted by successive treatments with (V) and ClCO_2Et in $\text{C}_5\text{H}_5\text{N}$ into dicarbethoxysekika-aldehyde, m.p. 136—137°; oxidation of the latter with KMnO_4 in COMe_2 at 40—50° leads to dicarbethoxysekikaic acid, m.p. 147—148° (decomp.), hydrolysed to sekikaic acid, m.p. 143—144°, identical with the natural product. H. W.

Benzoin reaction.—See this vol., 938.

Mixed magnesium alcoholates, and their molecular compounds. II. Molecular compounds formed from magnesium alcoholate iodides, aldehydes, and certain diketones. III. Existence of equilibrium systems in ethereal solutions of magnesium alcoholate iodides. V. M. TOLSTOPJATOV (J. Gen. Chem. Russ., 1935, 5, 73—82, 83—93).—II [with B. N. SVERDLOVA]. Cryst. 1:1 and 1:2 compounds are obtained from PhCHO or $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ and $\text{OR}\cdot\text{MgI}$ ($\text{R}=\text{Et}$, Bu^a , Bu^v) in Et_2O . $\text{OBu}^a\cdot\text{MgI}$ and $(\text{PhCO})_2$ (I) afford a 1:1 compound.

III [with A. T. RISKALTSCHUK]. $\text{OR}\cdot\text{MgI}$ ($\text{R}=\text{cetyl}$, α - and β -octyl, Bu^a , Pr) and COPh_2 in Et_2O afford the compound $\text{MgI}_2\cdot 3\text{COPh}_2$, whilst with (I) mol. compounds of the above type are formed. It is concluded that the equilibrium $2\text{OR}\cdot\text{MgI} \rightleftharpoons \text{Mg}(\text{OR})_2 + \text{MgI}_2$ exists in Et_2O . R. T.

Enamine form of Schiff's bases. R. WEGLER and A. RUZICKA (Ber., 1935, 68, [B], 1059—1062).—Treatment of *d*-valeraldehyde, α +10° to +11°, with $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, NH_2Ph , or $\text{NHPh}\cdot\text{NH}_2$ in well-cooled Et_2O and removal of the solvent at 20° after contact with much anhyd. Na_2SO_4 at >5° for 3 hr. gives Schiff's bases with α +4.30°, +5.4°, and +12.7°, respectively. These bases, and also those obtained with NH_3 , NH_2Me , or $\text{CHPhMe}\cdot\text{NH}_2$, are completely racemised in 10 hr. at 50°; the phenylhydrazone and semicarbazone, m.p. 105°, are exceptions. Racemisation is retarded greatly by the presence of a little free amine. The probability that racemisation is due to the transformation $\text{CHR}_2\cdot\text{CH}\cdot\text{N}\cdot\text{CHR}_2 \rightleftharpoons \text{CR}_2\cdot\text{CH}\cdot\text{NH}\cdot\text{CHR}_2$ is strengthened by the apparent non-existence of optically active Schiff's bases from optically active hydratropaldehyde. H. W.

New diene syntheses. E. LEHMANN and W. PAASCH (Ber., 1935, 68, [B], 1146—1149).—Acraldehyde (I) and α -phenylbutadiene at 100° afford 2-phenyl- Δ^3 -tetrahydrobenzaldehyde (II), b.p. 144°/12 mm. (additive compound with NaHSO_3), reduced by Zn-Hg and conc. HCl to 2-phenyl- Δ^3 -tetrahydrotoluene, b.p. 110—113°/12 mm., dehydrogenated by Se at 270—300° to *o*- $\text{C}_6\text{H}_4\text{PhMe}$, b.p. 255—258° (whence *o*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$, m.p. 112.5°), and oxidised by CrO_3 in AcOH to 2-phenyl- Δ^3 -tetrahydrobenzoic acid, m.p. 105°. Addition of (II) to acrylic acid gives 3-phenyl- Δ^4 -tetrahydrobenzoic acid, m.p. 122°. Addition of HCN to (II) in presence or absence of KCN does not appear to give the corresponding cyanohydrin, the sole isolable product being 2:2'-diphenyl- $\Delta^{3:3'}$ -octahydrobenzoin, m.p. 167°. (I) and β -2:4-dimethylphenylpentadiene at 100—110° afford 2:2':4'-dimethylphenyl-2-methyl- Δ^3 -tetrahydrobenzaldehyde, b.p. 179—181°/12 mm. (NaHSO_3 compound). Condensation of the aldehydes to phenanthrene derivatives could not be effected. H. W.

Studies in the synthesis of vitamin- . I. W. H. DAVIES, I. M. HEILBRON, W. E. JONES, and A. LOWE (J.C.S., 1935, 584—587).—Et β -hydroxy- δ -(2:2:6-trimethylcyclohexyl)- β -methylvalerate, obtained from tetrahydroionone and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (Reformatsky), is converted by PBr_3 in ligroin into the corresponding β -Br-ester, reduced (Zn-HCl-AcOH) to Et δ -(2:2:6-trimethylcyclohexyl)- β -methylvalerate. This is further reduced ($\text{Na-C}_5\text{H}_{11}\cdot\text{OH}$) to ϵ -(2:2:6-trimethylcyclohexyl)- γ -methyl-*n*-amyl alcohol, b.p. 136°/1.5 mm. (lit. b.p. 150—156°/7 mm.), which with PBr_3 in petroleum affords the bromide, b.p. 140—145°/4 mm. (cf. Karrer *et al.*, A., 1932, 852). This with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ in EtOH or C_6H_6 affords an unsaturated hydrocarbon $\text{C}_{15}\text{H}_{28}$, b.p. 112—115°/2 mm. [probably ϵ -(2:2:6-trimethylcyclohexyl)- γ -methyl- Δ^a -pentene]. β -Ionone, NaNH_2 in Et_2O , and C_2H_2 afford ϵ -(2:2:6-trimethylcyclohexenyl)- γ -methylpent-8-en- α -inen- γ -ol, b.p. 112—115°/3 mm. (cf. A., 1935, 492) (gives blue colour with SbCl_5 ; Ag salt), which could not be isomerised to α -aldehyde- δ -(2:2:6-trimethyl- Δ^6 -cyclohexenyl)- β -methyl- $\Delta^{a'}$ -butadiene (I), b.p. 92—93°/1.8 mm. (phenylsemicarbazone, m.p. 182—183°). This was obtained by dry distillation of the Ba salt of the corresponding α -carboxylic acid with $(\text{HCO}_2)_2\text{Ba}$, and was reduced by $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH to the alcohol, b.p. 99—100°/2 mm. (possesses no growth-promoting activity). (I) with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn in C_6H_6 affords Et β -hydroxy- ζ -(2:2:6-trimethyl- Δ^6 -cyclohexenyl)- δ -methyl- $\Delta^{a'}$ -hexadiene- α -carboxylate, b.p. 138—140°, which on hydrolysis and distillation of the Ba salt of the acid with $(\text{HCO}_2)_2\text{Ba}$ regenerates (I). (I) with COMe_2 and $\text{C}_5\text{H}_{11}\text{N}$ affords β -keto-*o*-hydroxy- θ -(2:2:6-trimethyl- Δ^6 -cyclohexenyl)- ζ -methyl- $\Delta^{a'}$ -octadiene, b.p. 104—105°/1.5 mm. (phenylsemicarbazone, m.p. 171—172°). H. G. M.

Jute-lignin. VI. Isolated lignin and lignin native in jute. P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 168—172).—Lignin, whether isolated or native in jute, contains no Ac groups and no alkoxy-groups other than OMe. From the OMe content of raw jute, delignified jute, and isolated (HCl) lignin

it is calc. that the theoretical OMe content of lignin is 18.37%, in agreement with the assumed mol. wt. 830 (cf. A., 1934, 1355; this vol., 214) and the presence of 5 OMe. During isolation by means of HCl lignin loses 1.96% OMe. The amounts of CO₂ obtained from jute, delignified jute, and lignin by boiling with 12% HCl have been determined. H. G. M.

Action of 2-chlorocyclopentanone on organo-magnesium halides. V. M. MITCHOVITCH (Compt. rend., 1935, 200, 1601—1603).—The reaction yields 2-alkyl- or -aryl-cyclopentanones, without change in the ring structure (cf. A., 1934, 654). In this way, 2-methyl-, -ethyl-, and -isopropyl-cyclopentanones are obtained, and 2-phenylcyclopentanone, m.p. 126—127° [oxime, m.p. 146°; semicarbazone, m.p. 228° (each decomp.)]. E. W. W.

cycloHexanone. C. L. WILSON (Chem. and Ind., 1935, 558).—The condensation of cyclohexanone with CH₂Br·CO₂Et is described in detail. H. N. R.

Synthesis of 2-methyldicyclo-[1 : 2 : 2]-heptan-3-one. G. KOMPPA (Ber., 1935, 68, [B], 1127—1129).—Reduction of santene ketone with Na and EtOH affords mainly 2-methyldicyclo-[1 : 2 : 3]-octan-4-ol (I), b.p. 97—99°/13 mm., accompanied by a stereoisomeride, C₉H₁₆O₂, m.p. 194—195°, of santene glycol which does not give a cryst. product with OBr' or a solid diphenylurethane. (I) is oxidised by HNO₃ (d 1.27) at 100° to α-methylhomonorcarnphoric acid, CH₂·CH(CHMe·CO₂H) > CH₂, m.p. 130—131° (Ca salt; dianilide, m.p. 241.5°), the Pb salt of which passes when heated into 2-methyldicyclo-[1 : 2 : 2]-heptan-3-one (6-methylnorcarnphor), b.p. 180—182°/761 mm. (semicarbazone, m.p. 184—185°). H. W.

Autoxidation of αβ-unsaturated ketones. VIII. Function of peroxides as intermediate products. W. TREIBS (Ber., 1935, 68, [B], 1049—1050).—The hypothesis that autoxidation of αβ-unsaturated ketones in alcoholic alkaline solution involves loss of H₂O₂ from the primary additive product of ketone and O₂ and transformation of unchanged ketone by H₂O₂ into the oxide is supported by the observation that 3 : 5-dimethyl-Δ²-cyclohexenone (I) is converted by H₂O₂ in presence of NH₃ into the substance (II), C₈H₁₂O₂·NH₃, m.p. 88° (decomp.). Both added O atoms of the peroxide can be titrated with KI. Treatment of (I) with (II) in EtOH yields the oxide, C₈H₁₂O₂, b.p. 212—214°. H. W.

Synthesis of Tiemann's irone. A. VERLEY (Bull. Soc. chim., 1935, [v], 2, 1205—1209).—Rhodinal and aq. HOCl give ζ-chloro-η-hydroxy-βη-dimethyloctaldehyde, which with COMe₂ and alkali affords 1-chloro-κ-hydroxy-ζκ-dimethyl-Δ⁷-undecen-β-one, dehydrated by H₂SO₄, H₃PO₄, H₂C₂O₄, or SiO₂ to 1-chloro-2 : 2 : 4-trimethyl-3-γ-keto-Δ⁶-butenylcyclohexane ("irone" hydrochloride), from which HCl is removed by KOH, NaNH₂, NR₃, etc., to give 1 : 1 : 1 : 3-trimethyl-2-γ-keto-Δ⁶-butenyl-Δ⁵-cyclohexene, b.p. 140°/12 mm., [α]_D -21° (phenylhydrazone), which possesses Tiemann's formula for irone and has high val. as a commercial perfume. R. S. C.

Synthesis of vitamin-A. I. Action of magnesium on a mixture of ionone and αδ-dibromo-

Δ⁶-butene. V. TETERIN and A. IVANOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 259—262).—The action of Mg and (·CH·CH₂Br)₂ or C₂H₄Br₂ on ionone causes reduction to the corresponding glycol ·CMe(OH)·CH·CH·C < $\begin{matrix} \text{CMe} \cdot \text{CH}_2 \\ \text{CMe} \cdot \text{CH}_2 \end{matrix}$ > CH₂)₂ which contains 2 OH (Zerevitinov) and absorbs 8 H (Pd-CaCO₃) giving a product oxidised to tetrahydroionone (semicarbazone, m.p. 163—165°). Divinyl is simultaneously produced. H. W.

α-Halogenated ketones. G. RICHARD (Compt. rend., 1935, 200, 1944—1946).—CHPhCl·COMe and powdered dry KOH in Et₂O afford CH₂Ph·COMe, Bz₂, and CH₂Ph·CH₂·CO₂H. Similarly Ph·[CH₂]₃·CO₂H is obtained from CH₂Ph·CHCl·COMe, and CHPh₂·CH₂·CO₂H from CPh₂Cl·COMe. These results are explained by tautomeric change of CHClR·COMe into CH₂R·CO·CH₂Cl, which with KOH is converted, probably through CH₂R·CH·CO, into CH₂R·CH₂·CO₂H (cf. A., 1934, 191). H. G. M.

Haloform reaction. XVI. Action of hypiodite on hindered ketones. R. JOHNSON and R. C. FUSON (J. Amer. Chem. Soc., 1935, 57, 919—920; cf. this vol., 751).—With a limited amount of NaOI acetomesitylene gives mesityl CH₂I ketone, m.p. 34.5—35.5°, but with an excess mesityl CHI₂ ketone, m.p. 98—99°. By use of an excess of NaOI are prepared di(di-iodoacetyl)mesitylene, m.p. 160° (decomp.), di-β-isoduroyl iodomethane, m.p. 191—192°, and 3-di-iodoacetyl-2 : 4 : 6-trimethylbenzoic acid, m.p. 132—133° (decomp.). No I₃-compounds could be prepared, nor could CHI₃ be obtained from these ketones. Pinacolone gives the mono- or di-iodo-compounds or CHI₃ according to the amount of NaOI used. These effects are steric. R. S. C.

Steric hindrance in α-diketones: mesitylbenzylglyoxal [αβ-diketo-γ-phenyl-α-mesitylpropane]. R. P. BARNES (J. Amer. Chem. Soc., 1935, 57, 937—940).—Mesityl styryl ketone (I) and 30% H₂O₂ in 6N-NaOH give the oxide (80% yield), b.p. 195°/8 mm., rearranged by hot aq. NaOH to αβ-diketo-γ-phenyl-α-mesitylpropane (II), m.p. 100°, shown by MgMeI to be 100% enolic when solid, but only 81—90% in various solvents (by Br). (II) is oxidised by Na₂O₂ to CH₂Ph·CO₂H and C₆H₂Me₃·CO₂H, and is, therefore, an α-diketone. It gives an O-allyl, m.p. 55°, b.p. 230°/30 mm. (unchanged), O-Me, m.p. 75°, b.p. 157°/2 mm., and O-CPh₃ ether, m.p. 195—198°, an O-Ac, m.p. 109°, and O-Bz derivative, m.p. 81°. It resists catalytic hydrogenation, but with SnCl₂ gives β-keto-α-phenyl-γ-mesitylpropane, m.p. 72°, the constitution of which is proved because the benzoate, m.p. 86°, of its oxime decomposes above the m.p., 85°, into BzOH and CH₂Ph·CN. (II) does not give a quinoxaline or dioxime, but yields a β-oxime, m.p. 88°, identical with the oximino-derivative obtained from nitrite and mesityl β-phenylethyl ketone, b.p. 163—165°/3 mm. [obtained by hydrogenation (PtO₂; EtOH) of (I)]. The configuration of the oxime is shown by decomp. of the benzoate, m.p. 95°, above the m.p. into BzOH, (II), and CH₂Ph·CN. (I) affords a semicarbazone, m.p. 227°, assumed by analogy to be a β-C-derivative. R. S. C.

Oxidation of benzophenoneoxime. K. VON AUWERS and H. WUNDERLING (Ber., 1935, 68, [B], 1072—1078; cf. A., 1933, 505; 1934, 654).—The blue compound (I) obtained by the oxidation of $\text{C}_6\text{H}_5\text{N}:\text{OH}$ with $\text{K}_3\text{Fe}(\text{CN})_6$, to which the structure $\text{C}_6\text{H}_5\text{N}:\text{O}$ — or $\text{C}_6\text{H}_5\text{N}:\text{O}$ has been tentatively ascribed, liberates from acidified HI 45—57% of the amount of I which would be expected if it evolves 1 O. Attempts to obtain additive products with C_6H_5 , CH_2N_2 , NO, or NO_2 failed. (I) is converted by cautious treatment with Zn dust and AcOH into $\text{C}_6\text{H}_5\text{N}:\text{OH}$. Reduction with H_2S immediately affords CSPH_2 , possibly through intermediate production of $\text{C}_6\text{H}_5\text{NH}$. Free halogens and halogen acids rapidly transform (I) into a mixture mainly of COPH_2 and the corresponding salts of $\text{C}_6\text{H}_5\text{NH}$ sometimes containing diphenylketazine oxide (II). COPH_2 and usually (II) are obtained by the action of I on $\text{C}_6\text{H}_5\text{N}:\text{ONa}$, but the formation of (I) is never observed. The oxidised product from the Na salt is further distinguished from (I) by its greater stability towards heat, but its behaviour towards acidified KI resembles that of (I). It appears therefore that an unstable blue and a stable colourless compound are formed during the oxidation of $\text{C}_6\text{H}_5\text{N}:\text{OH}$ with $\text{K}_3\text{Fe}(\text{CN})_6$. More or less deeply coloured products are obtained by the action of $\text{K}_3\text{Fe}(\text{CN})_6$ on *p*-methyl-, *o*-methyl-, and *p*-chloro-benzophenoneoxime, acetophenoneoxime, Ph Bu^v ketoxime, and $(\text{CH}_3\text{Ph})_2$ ketoxime. H. W.

Synthesis of naphthyl methyl ketone. Mechanism of the Friedel-Crafts reaction. S. M. RIVKIN (J. Gen. Chem. Russ., 1935, 5, 277—280).—A mixture of α - and β - $\text{C}_{10}\text{H}_7\text{COMe}$ is obtained in 90% yield from AcCl , C_{10}H_8 , and AlCl_3 in PhNO_2 at $>10^\circ$, and in 58% yield when benzene is substituted for PhNO_2 . R. T.

Phenanthrene derivatives. III. *o*-Toluoyle and β -methylnaphthoyle-phenanthrene. W. E. BACHMANN and L. H. PENCE (J. Amer. Chem. Soc., 1935, 57, 1130—1131; cf. this vol., 622).—Phenanthrene, $\text{o-C}_6\text{H}_4\text{MeCOCl}$, and AlCl_3 in PhNO_2 give 3- (24%), m.p. 89—90°, and 2-*o*-toluoylephenanthrene (3.4%), m.p. 115—116°, also obtained (Grignard and subsequent hydrolysis with conc. HCl at 200°; dil. HCl has no effect) in good yield from the cyanophenanthrenes and $\text{o-C}_6\text{H}_4\text{MeMgBr}$. Similar Grignard reactions give good yields of 9-*o*-toluoyle-, 3-, m.p. 148.5—149.5° (lit. 145—146°), 9-, m.p. 176—177° (lit. 170°), and 2-2'-methyl-1'-naphthoylephenanthrene, m.p. 184—185° (slow heating), or double m.p. (sudden heating) 168—170° and 184—185°.

R. S. C.

Planar configuration of diamagnetic nickel complexes. II. H. J. CAVELL and S. SUGDEN (J.C.S., 1935, 621—624; cf. A., 1932, 272).—Methyl-*n*-propylglyoxime, m.p. 175° (lit. m.p. 168°), affords a Ni derivative from which the α - (I), m.p. 165° (lit. m.p. 144° and 160°), and β -form (II), m.p. 133°, were obtained. Similarly methyl-*n*-butylglyoxime, m.p. 173°, prepared from Et *n*-butylacetoacetate through the intermediate oximinoketone, m.p. 60°, affords a Ni derivative, α - (III), m.p. 150°, β -form (IV), m.p.

86°. *p*- $\text{C}_6\text{H}_4\text{ClCOEt}$ was converted through its oximino-derivative, m.p. 119°, into *p*-chlorophenyl-methylglyoxime, m.p. 223°, the Ni derivative, m.p. 283°, of which is unsuitable for separation into isomerides. *p*-Chlorophenyl *n*-amyl ketone, m.p. 64°, b.p. 165°/20 mm., prepared from *n*-hexoyl chloride, C_6H_6 , and AlCl_3 , was converted through the oximino-derivative, m.p. 42°, into *p*-chlorophenyl-*n*-butylglyoxime, m.p. 206°, which gives a Ni derivative, α -form (V), m.p. 266°; indications of the existence of a lower-melting form were obtained. The α - and β -forms of these Ni derivatives are interconvertible by fusion; m.p. are therefore taken in a special way. The dipole moments of the Ni derivative were measured in C_6H_6 and are as follows (all in Debye units): (I) 1.4, (II) 1.5, (III) 1.3, (IV) 1.3, (V) 1.8, Ni benzyl-methylglyoxime, α - 1.3, β -form 1.6. The small effect of the C-Cl linkings in (V) on the observed moment strongly supports the view that the Ni glyoximes have a planar configuration (cf. Pauling, A., 1931, 670) and that the higher-melting forms have the *trans*-configuration.

Ni NN-*di-n*-propyldithiocarbamate, m.p. 135°, and Ni NN-*di-n*-butyldithiocarbamate, m.p. 91°, prepared from CS_2 , KOH, aq. NiCl_2 , and the corresponding dialkylamine, are diamagnetic, and on fusion and fractional crystallisation gave only one form. H. G. M.

α -Benzoylbutyrolactone, δ -keto- δ -phenyl-*n*-butyl alcohol, and δ -keto- δ -phenyl-*n*-butyl bromide. G. V. TSHELINCEV and E. D. OSETROVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 251—254).—The interaction of $(\text{CH}_2)_2\text{O}$ with $\text{CHNaBzCO}_2\text{Et}$ in EtOH gives α -benzoylbutyrolactone, b.p. 193—195°/8 mm., transformed by boiling 10% K_2CO_3 into δ -keto- δ -phenyl-*n*-butyl alcohol, b.p. 165—166°/10 mm., m.p. 32—33°, whence δ -keto- δ -phenyl-*n*-butyl bromide, m.p. 36°. H. W.

3-Methylindan-1 : 2-dione and its oxime; isocoumarin synthesis. G. HELLER [with R. EBELING] (Ber., 1935, 68, [B], 1085—1090; cf. von Braun *et al.*, A., 1913, i, 1363).—3-Methylindan-1 : 2-dioneoxime (I) and CH_2O in AcOH—conc. HCl gave the substance $\text{C}_{21}\text{H}_{19}\text{O}_5$, m.p. about 167° (slight decomp.) after softening at 160°, which like the simplest indandione does not immediately give a coloured solution in NaOH, showing thus that a preliminary transformation is necessary. (I) and NH_2OH in AcOH— H_2O give 3-methylindan-1 : 2-dionedioxiime, the alkaline solution of which does not become coloured until heated. Acetyl-3-methylindandione-2-oxime, m.p. 134—135° (decomp.), from (I) and Ac_2O (corresponding Bz derivative, m.p. 131—132°), is transformed by prolonged contact with 10% NaOH into *o*- α' -hydroxyethylphenylglyoxylic acid (II), m.p. 144°, and an amorphous substance, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}$, m.p. 173°. The formation of the blue colour is not due to salt formation, as in the case of isatin, but to absorption of O and transformation. (II) is converted by Ac_2O and NaOAc into 3 : 4-dimethylisocoumarin, m.p. 129°, transformed by conc. alkali into *o*- β -keto- α -methyl-*n*-propylbenzoic acid, m.p. 119°. (I) is transformed by NaOEt and EtI into methylindandione-oxime Et ether, m.p. 94°; the corresponding Me ether,

m.p. 138°, is too sensitive to alkali to be prepared in this manner or by Me_2SO_4 , but is obtained with CH_2N_2 . When treated with Zn dust and AcOH (I) gives a non-cryst. carmine-red Zn salt. Treatment of (I) with 10% NaOH and $\text{Na}_2\text{S}_2\text{O}_4$ followed by Ac_2O leads to 2-ketacetimido-1-hydroxy-3-methyldihydroindene, m.p. 127—128°. H. W.

Aldol condensation between aldehydes and β -keto-acids, and their importance in the biosynthesis of natural products. C. SCHÖPF and K. THIERFELDER (Annalen, 1935, 518, 127—155).—Optimum yields (in parentheses) of the condensation products of aldehydes and β -keto-acids are obtained in neutral solution, the yield decreasing in either acid or alkaline medium. Thus at p_{H} 7 PhCHO and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ (I) afford (90%) β -hydroxy- β -phenylethyl Me ketone (II), m.p. 38—39° (Kubota *et al.*, A., 1926, 520) (semicarbazone, m.p. 172°), converted by $\text{NHPh}\cdot\text{NH}_2$ not into its phenylhydrazone (*loc. cit.*) but into benzylideneacetonephenylhydrazone, m.p. 153—154°. The yield of (II) is reduced to 10% at p_{H} 1, and to 0 at p_{H} 13. Introduction of p -OH or OMe into the aldehyde greatly reduces the condensation yields with both (I) and (IV) (below). Thus (I) with anisaldehyde (III) gives only a trace of a compound which affords anisylideneacetone-semicarbazone, veratraldehyde affords (5%) β -hydroxy- β -3:4-dimethoxyphenyl Me ketone, m.p. 93—95°, but vanillin and COPhMe give no condensation products. Similar condensation of $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{H}$ (IV) with PhCHO (74%), (III) (8%), and MeCHO (27%) gives, respectively Ph β -hydroxy- β -phenylethyl ketone, m.p. 53—54° (semicarbazone, m.p. 180°), Ph β -hydroxy- β -p-methoxyphenylethyl ketone (as its semicarbazone, m.p. 183—184°), and Ph β -hydroxy- n -propyl ketone (as its semicarbazone, m.p. 153—154°, sinters 149°). Condensation of PhCHO with $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (in N_2) gives di-(β -hydroxy- β -phenylethyl) ketone, m.p. 163—165°, sinters 159°, and β -keto- δ -phenyl- Δ^7 - n -pentoic acid, m.p. 136—141° (decarboxylated to $\text{CHPh}\cdot\text{CHAc}$).

$\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ with PhCHO affords (42%), $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ gives (19%) p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, vanillin (V) and 3:4-(OH) $_2\text{C}_6\text{H}_4\cdot\text{CHO}$ give, respectively, 4-hydroxy-3-methoxy-, m.p. 145—147° [also from (V) and AcCO_2H], and 3:4-dihydroxy- + H_2O (yellow and red forms), sinters 196°, m.p. 202—204° (decomp.), -benzylidenepyruvic acid. The role of aldehyde- β -keto-acid condensations in biosynthesis is discussed, especially in relation to gingerol, alkaloids of angostura bark, and muscone. Such condensations probably play no important part in the biosynthesis of fatty acids.

Reduction of deoxybenzoin and benzoin.—See this vol., 937.

Compounds of α -benzoinoxime with bivalent metals. J. S. JENNINGS, E. SHARRATT, and W. WARDLAW (J.C.S., 1935, 818—822).—Cu benzoinoxime (I) [from aq. CuCl_2 and benzoinoxime (II) in EtOH (*cf.* A., 1923, n, 880)] with hot $\text{EtOH}\cdot\text{HCl}$ affords Cu benzoinoxime dichloride (III), $(\text{C}_{14}\text{H}_{13}\text{O}_2\text{N})\text{CuCl}_2\cdot\text{EtOH}$ (EtOH is lost on keeping),

sol. in EtOH and COMe_2 , but decomposed by H_2O into (I) and HCl . This confirms Feigl's structure $\text{CHPh}\cdot\text{O}\cdot\text{Cu}\cdot\text{NO}\cdot\text{CPh}$ for (I). (II) also forms compounds with Ni, Pd, and Pt (a ppt., but no pure compound, could be obtained with Co) [*cf.* A., 1923, ii, 880; "Organic Reagents for Metals" (1934)]. These compounds (structures given) exist in two forms which are interconvertible by means of solvents (*e.g.*, EtOH , CCl_4 , and CHCl_3). Their m.p. vary with the rate of heating. The second form of Ni dibenzoinoxime (IV) (obtained from the first by treatment with CCl_4) contains 1 mol. of CCl_4 of crystallisation lost on keeping or more readily at 90°. When (II) in EtOH is added to NiSO_4 and NH_4OAc in H_2O and the mixture heated at 40° during 1 hr., Ni dibenzoinoxime diacetate (V) is obtained (structure proposed). (VI) is also obtained from (IV) and AcOH . (II) functions as a chelate group in three ways: (a) with two principal valencies as in (I), (b) with one principal valency and one co-ordinate linking, (c) with two co-ordinate links as in (III) and (V). The Ni compounds of (II) are paramagnetic, but the corresponding Pd compounds are diamagnetic. The configurations of these compounds are discussed.

H. G. M.

Michael condensation. III. Addition of simple ketones. D. B. ANDREWS and R. CONNOR (J. Amer. Chem. Soc., 1935, 57, 895—898; *cf.* this vol., 215).—The reactivity of simple ketones with $\alpha\beta$ -unsaturated ketones is decreased by substitution in the reactive CH_2 , the effect of Et being > that of Me. $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$ with COPhMe gives 27% of bimol. and 56% of termol. product, with COPhEt $\alpha\gamma$ -dibenzoyl- β -phenylbutane, m.p. 102—103.5° (54%), and 27% of termol. compound, m.p. 231—235°, with COPhPr^a $\alpha\gamma$ -dibenzoyl- β -phenyl- n -pentane, m.p. 91—92° (corr.) (19%), and 58% of termol. compound, m.p. 219.3—219.6° (corr.), with COPhBu^a 5% of termol. compound, m.p. 308.2—308.7° (corr.), only [when catalysed, 30% of termol., much probably quadrimol., m.p. > 360°, and a trace of possibly bimol. compound, m.p. 139.6—139.9° (corr.)], with COEt_2 a mixture (giving as only pure product the termol. compound), and with COMeBu^a the termol., $\text{C}_{36}\text{H}_{38}\text{O}_3$, m.p. 244.6—246° (corr.), and no bimol. compound. $\text{CHPh}\cdot\text{CH}\cdot\text{COBu}^a$ with COPhMe gives α -benzoyl- γ -pivalyl- β -phenylpropane, m.p. 59—59.5° (39%), and with COPhMe the bimol. (25%) and termol. (51%) compounds, but does not react with COMeBu^a .

R. S. C.

Constitution of dehydroandrosterone. W. SCHOELLER, A. SERINI, and M. GEHRKE (Naturwiss., 1935, 23, 337).—Dehydroandrosterone has a *trans*-configuration. With digitonin it affords a sparingly sol. additive product, whereas androsterone does not. This difference in behaviour affords a simple means of separating the two substances, which are present in the urine of men in approx. equal amounts.

H. G. M.

Synthesis of dehydroandrosterone by the decomposition of γ -sitosterol from soya beans. R. V. OPPENAUER (Nature, 1935, 135, 1039).—Acetylated sitosterol from soya beans was chlorinated in the 5:6-position to protect the double linking, and

the side-chain removed by CrO_3 . The sparingly-sol. semicarbazone obtained from the dichlorinated and saponified reaction mixture gave, on hydrolysis, a hydroxyketone, m.p. 147—148° (corr.), chemically and physiologically identical with dehydroandrosterone (I) from urine [*oxime*, m.p. 190° (corr.); *benzoate*, m.p. 252—253° (corr.), $[\alpha] +13.5^\circ$ in EtOH]. (I) is therefore 3-hydroxy- $\Delta^{5,6}$ - α -etiocholonenol-(17).

L. S. T.

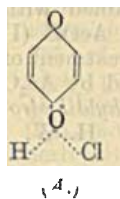
Derivatives of 2-methylcyclopentan-2-one and -ol. M. GODCHOT and M. MOUSSERON (Compt. rend., 1935, 200, 2189—2192).—2-Methylcyclopentanone with Cl_2 and CaCO_3 gives a mixture of *cis*- and *trans*-5-chloro-ketone (I), b.p. 87°/14 mm. and 98—99°/14 mm., with a little methylcyclopentenone. Both forms of (I) with hot H_2O give the same 1-methylcyclopentan-2-one-3-ol, b.p. 110°/14 mm., m.p. 100—101° (*phenylhydrazone*, m.p. 104—105°), and with hot quinoline 2-methyl- Δ^4 -cyclopentenone (II), b.p. 140° (*semicarbazone*, m.p. 175—176°). 3-Methylcyclopentenone gives a mixture of stereoisomeric 3-chloro-1-methylcyclopentan-2-ols, b.p. 69—70°/31 mm. and 101—102°/31 mm., converted by oxidation and heating with quinoline into (II). R. S. C.

Hydroxypolyketones. I. Alkylation of benzoylformoin. A. H. BLATT (J. Amer. Chem. Soc., 1935, 57, 1103—1107).—It is proved that benzoylformoin (I), $\text{OH}\cdot\text{CHBz}\cdot\text{COBz}$, with acid in EtOH gives the monoalkyl ether $\text{O} < \begin{array}{c} \text{CPh}=\text{C}\cdot\text{OR}' \\ \text{CPh(OR)CO} \end{array}$ (II; $\text{R}=\text{H}$), which has glucosidic properties and with $\text{NaOR}\cdot\text{RI}$ affords the dialkyl ether (II; $\text{R}=\text{alkyl}$), hydrolysed to the isomeric monoalkyl ether (III), $\text{OH}\cdot\text{CPh}\cdot\text{C(OR)COBz}$. (I) (modified prep.), m.p. 187° (decomp.), gives 2 mols. of BzOH with Na_2O_2 , is decomposed by conc. H_2SO_4 , cannot be methylated by CH_3N_3 or $\text{MeI}\cdot\text{NaOMe}$, but with $\text{HCl}\cdot\text{MeOH}$ gives the Me ether (II; $\text{R}=\text{Me}$, $\text{R}'=\text{H}$), m.p. 182°, which does not react with NH_2OH or $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, is decomposed by conc. H_2SO_4 owing to hydrolysis to (I), with $\text{HCl}\cdot\text{EtOH}$ gives the Et ether ($\text{R}=\text{Et}$) (from which it is re-formed by $\text{H}_2\text{SO}_4\cdot\text{MeOH}$), and with $\text{MeI}\cdot\text{NaOMe}$ affords the Me_2 ether (II; $\text{R}=\text{R}'=\text{Me}$) (4-keto-3:5-dimethoxy-2:5-diphenylfuran), m.p. 78—79°. This is unchanged by $\text{NHPh}\cdot\text{NH}_2$ or $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, gives with $\text{H}_2\text{SO}_4\cdot\text{EtOH}$ the Me Et ether (II; $\text{R}=\text{Et}$; $\text{R}'=\text{Me}$), and with hot NaOMe an 88% or with conc. H_2SO_4 a lower yield of the Me ether (III; $\text{R}=\text{Me}$) (α -hydroxy- β -methoxy- α -diphenyl- Δ^4 -butene- γ -dione), m.p. 126—127°, the structure of which is proved as follows. It is 85% enolic (Br titration), is also obtained from the Me Et ether by NaOMe , is reconverted into the Me_2 ether by $\text{HCl}\cdot\text{MeOH}$, and gives 2-phenyl-3-benzoylmethoxymethylquinoxaline, m.p. 131—132°, converted by MgPhBr into 2-phenyl-3- β -hydroxy- β -diphenyl- α -methoxyethylquinoxaline, m.p. 173—174°, which with CrO_3 affords COPh_2 and 3-phenylquinoxaline-2-carboxylic acid.

R. S. C.

Oxonium compounds. Acidic complexes of quinones and their chlorination and bromination. V. V. TSCHELINCEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 244—250).—Treatment of a solution of benzoquinone in cold conc. HCl with Cl_2

rapidly yields 2:3-dichloro- Δ^5 -cyclohexene-1:4-dione,



m.p. 147° (decomp.), converted by further action of Cl_2 into 2:3:5:6-tetrachlorocyclohexane-1:4-dione, m.p. 226° (decomp.). 2:3-Dibromo- Δ^5 -cyclohexene-1:4-dione, m.p. 170°, and 2:3:5:6-tetrabromocyclohexane-1:4-dione are obtained similarly. Thermochemical data and ketonic properties justify the structure A for compounds of quinones with HCl and invalidate Graebe's formulation of the former. H. W.

Influence of the $\text{R}\cdot\text{COO}-$ and $\text{R}-$ groups on the cationoid reactivity of the quinone nucleus. H. ERDTMAN and A. LEÓN (Anal. Fis. Quím., 1934, 32, 614—626; cf. A., 1934, 184).—The reactivities of mono- and di-alkyl- and -alkoxy-*p*-benzoquinones are in qual. agreement with the electronic theory of valency, but for more highly substituted quinones there is less agreement, probably owing to steric effects. Contrary to theory, hydroxy-*p*- and hydroxy-*m*-xyloquinones show about the same reactivity. *p*-Xyloquinone, on acetylation by Thiele's method, yields 2:3:5-triacetoxy-*p*-xylene, hydrolysed to 2:3:5-trihydroxy-*p*-xylene (I), m.p. 157—158°, and oxidised by FeCl_3 to hydroxy-*p*-xyloquinone (II), m.p. 145—146° after sublimation. (II) on acetylation gives 2:3:5:6-tetra-acetyl-*p*-xylene, m.p. 250—252°. 2:3:5-Trimethoxy-*p*-xylene, b.p. 143—145°/30 mm., from (I), with Br in CHCl_3 gives 6-bromo-2:3:5-trimethoxy-*p*-xylene (III), b.p. 175—180°/40 mm. (slight decomp.). Oxidation of (III) with HNO_3 yields 6-bromo-3-methoxy-*p*-xyloquinone, m.p. 81.5—82°. Acetylation of *m*-xyloquinone similarly yields triacetoxy-*m*-xylene, hydrolysed to 2:4:5-trihydroxy-*m*-xylene (IV), m.p. 119—121°, and oxidised by FeCl_3 to hydroxy-*m*-xyloquinone (V) (m.p. 103—104°), which on acetylation yields 2:4:5:6-tetra-acetoxy-*m*-xylene, m.p. 161°, hydrolysed to dihydroxy-*m*-xyloquinone, m.p. 168—169°. Methylation of (IV) gives 2:4:5-trimethoxy-*m*-xylene, which on oxidation with HNO_3 gives (V) and with Br in CHCl_3 yields 6-bromo-2:4:5-trimethoxy-*m*-xylene, b.p. 151—155°/23 mm., oxidised by HNO_3 to a bromomethoxy-*m*-xyloquinone, m.p. 74°. J. W. S.

Action of alkaline hydrogen peroxide on quinones and polyhydric phenols. E. WEITZ, H. SCHOBERT, and H. SEIBERT (Ber., 1935, 68, [B], 1163—1168).— α -Naphthaquinone is smoothly oxidised by H_2O_2 in alkaline solution to so-called diketotetrahydronaphthalene oxide, m.p. 136°, whilst β -naphthaquinone gives hydroxynaphthaquinone. Attempts to isolate a mono- or di-oxido-compound from benzoquinone were unsuccessful, but a vigorous action occurs when the alkali and H_2O_2 are used in large excess giving *as*-oxidoethylenedicarboxylic acid, from the Ba salt of which *r*-tartaric acid or chloromalic acid II is obtained by the action of dil. HNO_3 or HCl , respectively. Toluquinone is very rapidly oxidised, whereas chloranil is merely converted into chloranilic acid. Pyrocatechol gives the same products as quinol or benzoquinone. Resorcinol and quinol yield much CO_2 and non-investigated products. PhOH does not appear to react. Phenanthraquinone

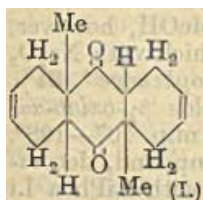
smoothly yields diphenic acid, whereas anthraquinone is not attacked.

H. W.

Preparation and hydrolysis of some α -hydroxy-anthraquinone glucosides. J. H. GARDNER, T. F. McDONNELL, and C. J. W. WIEGAND (J. Amer. Chem. Soc., 1935, 57, 1074—1076).—1-Hydroxyanthraquinone- β -D-glucoside (I), m.p. 232.2—232.8°, is obtained from the tetra-acetate, m.p. 212—212.5°, by KOH-EtOH. Acetobromo-D-arabinose, 1-hydroxyanthraquinone (II), and Ag₂O in quinoline give the triacetate, m.p. 189.2—189.4° (hydrolysed by cold K₂CO₃-EtOH), of 1-hydroxyanthraquinone- β -D-arabinoside (III), m.p. 203—203.5°. (I) and (III) are hydrolysed by KOH, HCl, or borax, with decreasing ease in the order given, to nearly pure (II), except that (III) and KOH give also an indefinite material probably formed by reduction of (II) by arabinose. These hydrolyses are not in accord for a glucosidic formula for barbaloin.

R. S. C.

Synthesis of hydroaromatic compounds with "angular" methyl groups. I. E. ADLER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 49, 1—5).—p-Xyloquinone when heated at 160—170° during 10 hr. with about 4 mols. of butadiene (in 20% C₆H₆ solution) affords 1 : 4 : 5 : 8 : 11 : 12 : 13 : 14-octahydro-



12 : 14-dimethylanthraquinone (I), m.p. 171°. A migration of the Me is excluded because the substance contains no OMe and because it is not oxidised to a quinone by atm. O₂ even in the presence of alkali at 100°. It is not acetylated by Ac₂O and C₅H₅N, yet fails to give an oxime, probably owing to steric hindrance. (I) heated with alkali gives a compound, m.p. 202°.

H. G. M.

Preparation of cyclic compounds [quinones from dienes].—See B., 1935, 621.

Manufacture of 1 : 2 : 2' : 1'-anthraquinono-anthraquinones.—See B., 1935, 585.

Preparation of picrotoxin. E. P. CLARK (J. Amer. Chem. Soc., 1935, 57, 1111).—The prep. (1.4% yield) of picrotoxin from *Anamirta cocculus* berries is modified. Optical data are given for this and for picrotin and picrotoxinin.

R. S. C.

X-Ray crystallography of bufagin, cinobufagin, and strophanthidin.—See this vol., 921.

Yellow pigment from yeast.—See this vol., 1027.

Carotenoid pigments of *Actinia equina*, *Aнемона sulcata*, *Actinoloba dianthus*, and *Tealia felina*.—See this vol., 1005.

New pigment with lycopene spectrum. L. ZECHMEISTER and L. VON CHOLNOKY (Naturwiss., 1935, 23, 407).—The polyene from *Solanum dulcamara* behaves like lycopene, and its absorption spectrum has max. at 547, 507, 474, and 444 m μ ; it is, however, distinguished by having m.p. 151° (corr.), depressed by adding lycopene.

E. W. W.

Constituents of roots of Ch'ai Hu.—See this vol., 905.

Syntheses in the vitamin-A field. J. SALKIND, S. ZONIS, and N. BLOCHIN (Compt. rend. Acad. Sci.

U.R.S.S., 1935, 2, 57—63).—Mg vinylacetylenyl bromide with β -ionone in N₂ gives γ -hydroxy- α -(2 : 2 : 6-trimethyl- $\Delta^{1:6}$ -cyclohexenyl)- γ -methyl- Δ^4 -heptadien- Δ^8 -inene, b.p. 135—145°/0.1 mm., which readily polymerises in air and is reduced (H₂-Pd; +10 H) to a compound (I), b.p. 125—129°/0.1 mm. (I) when oxidised (K₂Cr₂O₇-H₂SO₄) gives tetrahydroionone, trimethylcyclohexylacetic acid, and BuⁿOH. (I) has no curative action on xerophthalmia in rats.

J. L. D.

Isomerisation of linalool to geraniol. S. M. RIVKIN and E. A. MEERZON (J. Gen. Chem. Russ., 1935, 5, 274—276).—Geraniol is obtained in 14% yield from linalool and H₂O in presence of H₃BO₃ or ZnCl₂ (200°/19 atm.; 90 min.).

R. T.

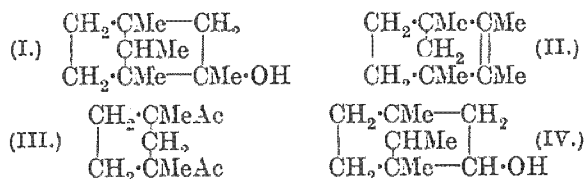
Recent progress in the chemistry of the terpenes. J. L. SIMONSEN (J.C.S., 1935, 781—785).—A lecture.

F. R. S.

Configuration of borneol and isoborneol. P. LIPP (Ber., 1935, 68, [B], 1029—1031).—The arguments of Asahina *et al.* (this vol., 625) are not regarded as decisive and it is doubtful whether the borneol-isoborneol problem can be solved by purely chemical methods.

H. W.

Tertiary 2 : 4-dimethylsantenol and 1 : 4-dimethylsantene. G. KOMPPA and G. A. NYMAN (Annalen, 1935, 518, 204—210).—4-Methylsantenone (this vol., 866) is converted by MgMeI into 2 : 4-dimethylsantenol (I), m.p. 55—58° (probably a mixture of stereoisomerides), dehydrated (KHSO₄ at 190—200°) with rearrangement to 1 : 4-dimethylsantene (II), b.p. 161—162°, converted by ozonolysis into the diketone (III), b.p. 108—115°/7 mm. (disemicarbazone, m.p. 235—236°), showing that the double linking is between two *tert*.-C. Hydration of (II) with AcOH-60% H₂SO₄ at 50—60° affords 4 : 6-dimethylsantenol (IV), b.p. 203—205° (Ac derivative, b.p. 97—98°/11.5 mm.), oxidised (CrO₃-AcOH) to the corresponding

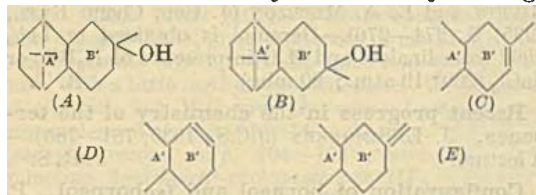


ketone, 4 : 6-dimethylsantenone, b.p. 202—205°/760 mm. (semicarbazone, m.p. 177.5—178.5°), further oxidised (KMnO₄-10% KOH) to cis-1 : 2 : 3 : 5-tetramethylcyclopentane-1 : 3-dicarboxylic acid, m.p. 191—192° (anhydride, m.p. 89—90°, by cold AcCl), which contains the same no. of C, thus proving the constitution of (IV).

J. W. B.

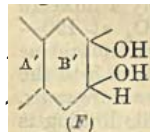
Elucidation of the constitution of certain sesquiterpenes by powerful oxidative degradation. I. Cedrene and cedrol. W. TREIBS (Ber., 1935, 68, [B], 1041—1049).—Cedrene (I) is unaffected by Pd- or Pt-asbestos at 300°, but passes in presence of Ni-pumice at 420—450° into *p*-cymene. The change of refraction in the apparently unaltered portion points to the intermediate formation of amylecymene, which loses the thermally unstable amylene. Repeated drastic oxidation of artificial (I) with KMnO₄ in COMe₂ readily yields the ketone C₁₄H₂₄O and diketone

$C_{15}H_{24}O_2$ obtained previously from natural (I); further oxidation of the salts thus obtained by $KMnO_4$ in H_2O affords much $CMe_2(CO_2H)_2$ and some $CO_2H\cdot CH_2\cdot CMe_2\cdot CO_2H$. The dicyclic system of (I) must therefore have the isopinane or camphane structure. Oxidation of the salts obtained from artificial (I) and $KMnO_4$ in $COMe_2$ with hot HNO_3 (d 1.4) leads to little $CMe_2(CO_2H)_2$, $(\cdot CH_2\cdot CO_2H)_2$, $CO_2H\cdot CHMe\cdot CMe_2\cdot CO_2H$, and a mixture of isomeric tricarboxylic acids, $C_9H_{14}O_6$, from which camphoric acid is obtained cryst. The dicyclic ring system



of (I) has the same structure as camphor, and cedrol (II) must have the structure A or B. Loss of H_2O during the conversion of (II) into (I) can occur in three directions. The constitution of cedrenedicarboxylic acid (III) proves that C is the predominant component of synthetic (I), whereas it is present in only small amount in natural (I).

Cedrene glycol (IV) is stable towards $KMnO_4$, but is readily oxidised by CrO_3 to a OH -ketone, $C_{15}H_{24}O_2$, b.p. 180—185°/17 mm., which is converted by more drastic oxidation into the ketonic acid, $C_{15}H_{24}O_3$, m.p. 82—83° (semicarbazone, m.p. 195°); since the latter can be degraded to (III) it is identical with the (non-cryst.) acid obtained by Semmler by ozonisation of natural (I). (IV) has the structure F. When treated with 30% H_2SO_4 it passes into the oxide, b.p. 148°/20 mm.



Contrary to Semmler, oxidation of (I) with $KMnO_4$ gives a mixture of acids, b.p. 200—230°/17 mm., from which a sparingly sol. semicarbazone, m.p. 240° (decomp.), is isolated. This when treated with $H_2C_2O_4$ yields a non-cryst. isoketo-acid transformed by $NaOBr$ into CBr_4 and isocedrenedicarboxylic acid, m.p. 210—211°. The acid is also obtained from (I) and HNO_3 (d 1.4) in boiling $AcOH$. It does not afford an anhydride. Since its Me_2 ester, b.p. 172°/17 mm., is converted by $MgMeI$ into a hydrocarbon, b.p. 150—160°/17 mm., the acid and Semmler's acid, m.p. 182°, must be *cis-trans*-isomerides. Artificial (I) is racemised by conc. H_2SO_4 with predominating production of an insol. stable and a sol., very readily autoxidised product. Natural (I) gives the same products in subsidiary amount, but 50% of it suffers polymerisation.

H. W.

Gossypol. L. SCHMID and S. MARGULIES (Monatsh., 1935, 65, 391—398).—Gossypol (formula $C_{30}H_{30}O_8$ confirmed) yields (Pd, H_2) hydrogossypol (I), $C_{30}H_{36}O_8$, decomp. 320° (evacuated tube), which forms no additive compound with $AcOH$, but which gives (C_5H_5N, Ac_2O) a Ac_6 derivative, decomp. 235°. $Zn-H_2$ distillation of (I) furnishes a substance (II), identified with synthetic β -isoamyl-naphthalene (III) [no picrate; the substance described as such (A., 1888, 1305; 1891, 730) is picric acid], with a sub-

stance containing O, m.p. 234—238°, b.p. 180°/12 mm. (II) or (III) with Br gives a substance, m.p. 70—72°, b.p. 135—140°/0.4 mm. (I) is oxidised by H_2O_2 - $NaOH$ to Pr^cCO_2H , with a substance, $C_{25}H_{30}O_{10}$ (?), decomp. about 170°, and a substance, b.p. 130°/12 mm.

E. W. W.

β -Oxanolols [$\beta\gamma$ -oxidopropan- α -ols]. E. P. KOHLER and C. L. BICKEL (J. Amer. Chem. Soc., 1935, 57, 1099—1101).—Cleavage of $\begin{matrix} CHR \\ | \\ O \end{matrix} > CH\cdot CR', \cdot OH$ into $CH_2R\cdot CHO$ and COR'_2 is dependent on replacement of the H of the OH by a metal, since org. Mg or Li compounds or Na in liquid NH_3 give metallic derivatives, which regenerate the oxide with acids, but, when heated, give the aldehyde and ketone. Re-

arrangement of the oxide to $OH\cdot CHR\cdot CH < \begin{matrix} CR' \\ | \\ O \end{matrix}$ is shown by the following reactions not to involve migration of R' or formation of a triol and to be an irreversible, catalytic reaction brought about by OH' or OMe' , since it is effected by alkali hydroxides or carbonates, BaO , $Mg(OEt)_2$, or $NMe_4\cdot OH$, but not by OAc' , NH_3 , C_5H_5N , or piperidine. $o-C_6H_4Cl\cdot CHO$ and $COPhMe$ in $NaOH$ -aq. $EtOH$ give β -hydroxy- β -o-chlorophenylpropionophenone, m.p. 80°, hydrolysed to the aldehyde and ketone by aq. $MeOH$ or heat, and stable to hot $AcOH$. In $NaOMe$ - $MeOH$, however, $o-C_6H_4Cl\cdot CH\cdot CH\cdot COPh$ is formed, which with Na_2O_2 gives $\alpha\beta$ -oxido- β -o-chlorophenylpropionophenone (84% yield), m.p. 73—74°; $MgPhBr$ yields $\beta\gamma$ -oxido- $\alpha\alpha$ -diphenyl- γ -o-chlorophenylpropan- α -ol, m.p. 107—108°, which with $MgEtBr$ gives a Mg compound, decomposed by keeping into $CPh_2Et\cdot OH$, with $LiPh$ a Li compound, reconverted immediately by acid into the original oxide, but after 30 min. boiling in Et_2O into $(C_6H_4Cl\cdot CHO)_x$ (also obtained with $COPh_2$ by Na in NH_3), and with bases affords $\beta\gamma$ -oxido- $\gamma\gamma$ -diphenyl- α -o-chlorophenylpropan- α -ol, m.p. 114—115°, the structure of which is proved by oxidation (CrO_3) to $COPh_2$ and $o-C_6H_4Cl\cdot CO_2H$, whilst autoxidation gives $o-C_6H_4Cl\cdot CHO$. α -Hydroxy- β -methoxy- β -phenylpropionophenone is obtained cryst., m.p. 47—48°. γ -Methoxy- $\alpha\alpha\gamma$ -triphenylpropane- $\alpha\beta$ -diol does not yield an oxide with bases.

R. S. C.

Extraction of furfuraldehyde from aqueous solutions. V. I. SHARKOV and I. BELJAEVSKI (Lesokhim. Prom., 1933, 2, No. 3, 15—19).—Salting-out effects are discussed. CH. ABS. (r)

Condensation of furan derivatives. IV. Nature of the coloured products of condensation of furfuraldehyde with acetone in aqueous sulphuric or hydrochloric acid, and the theory of reaction of alcohols and olefines with furfuraldehyde. V. Application of the furfurylidene test to the study of the process of condensation of acetone with formaldehyde. V. V. TSCHELINCEV (J. Gen. Chem. Russ., 1935, 5, 256—264, 265—273).—IV [with E. K. NIKITIN]. The compounds $C_4H_3O\cdot CH(CH_2\cdot COMe)_2$ (I), $C_4H_3O\cdot CH\cdot CH\cdot COMe$ (II), and $CO(CH\cdot CH\cdot C_4H_3O)_2$ (III) are obtained when $C_4H_3O\cdot CHO$ (IV) and $COMe_2$ are condensed in aq. HCl or H_2SO_4 . (I) does not afford a coloured product with acids, (II) gives an orange-red and (III) a violet-red coloration. (IV), when present in large

excess, undergoes polymerisation to yield a blue polymeride. The colorations obtained with fusel oil, pinene, and liquid olefins are due to the presence of COMe_2 in these products, or to its formation under the conditions of condensation.

V [with M. N. TILITSCHENKO]. CH_2O and COMe_2 react in presence of KOH in two ways: $\text{COMe}_2 + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{CH}(\text{OMe}) + \text{H}_2\text{O}$, and $2\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{MeOH}$. The latter reaction is favoured by higher $[\text{KOH}]$, and is catalysed by COMe_2 , and the HCO_2H produced neutralises the KOH , thereby creating conditions unfavourable for the aldol condensation.

R. T.

Orientation in the furan series. Hill's 3:5-dibromo-2-furoic acid. H. GILMAN, R. J. V. WAL, R. A. FRANZ, and E. V. BROWN (J. Amer. Chem. Soc., 1935, 57, 1146).—Hill's "3:5-dibromo-2-furoic acid" (A., 1886, 447) is really the 4:5- Br_2 -acid, because (a) replacement of the α -Br by H, reaction with KCN - CuCN , and subsequent hydrolysis gives furan-2:4-dicarboxylic acid, (b) decarboxylation, interaction with KCN , and hydrolysis affords the 2:3-dicarboxylic acid, and (c) the Et ester with MgPhBr gives α -bromo- $\delta\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadienol- γ -lactone, hydrolysed by 5% NaOH to CHPh_2COMe . Hill's structures for 5-chloro- and -bromo-3-sulpho- and 3:5-dichloro-furoic acid now need revision.

R. S. C.

Reactions of o-hydroxybenzylacetone. W. BAKER and J. WALKER (J.C.S., 1935, 646—648).— $\text{o-OH}\cdot\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{COCH}_3$ is reduced by $\text{H}_2/3$ atm. with Pd-SrCO_3 in MeOH to $\text{o-OH}\cdot\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{COCH}_3$ (I) in 80% yield, but with a PdCl_4 catalyst in EtOH to a mixture of (I) (NaOH -sol.) and 2-ethoxy-2-methylchroman (II), b.p. $105^\circ/11$ mm., $225^\circ/760$ mm., with some conversion into (III). The presence of (II) is due to HCl , since (I) is converted into (II) by EtOH -trace HCl at room temp. (II) is reconverted into (I) by hot dil. HCl . 2-Methoxy-2-methylchroman, b.p. $107^\circ/14$ mm., is similarly obtained. (I) dissolved in dry Et_2O over anhyd. Na_2SO_4 is slowly (2 weeks) converted (probably by way of 2-hydroxy-2-methylchroman) into 2-methylchromene (III), b.p. $95\text{--}97^\circ/10$ mm., also obtained by boiling (II) with Ac_2O . Reduction of (III) with H_2 - Pt-SiO_2 gel in AcOH gives 2-methylchroman, b.p. $100\text{--}102^\circ/11$ mm.; specimens of this compound previously described in the lit. are probably mixtures.

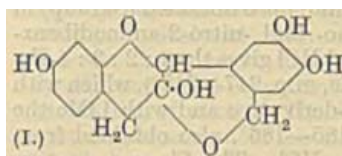
J. W. B.

Constitution of genistein. C. CHARAUX and J. RABATE (J. Pharm. Chim., 1935, [viii], 22, 32—33).—Genistein is an isoflavone, the formula $\text{C}_{15}\text{H}_{10}\text{O}_5$ of Baker and Robinson (A., 1929, 192) being correct. Sophoricoside is a β -glucoside of formula $\text{C}_{21}\text{H}_{20}\text{O}_{10}$.

H. G. R.

Leuco-anthocyanins and -anthocyanidins. I. Isolation of peltogynol and its molecular structure. (MRS.) G. M. ROBINSON and R. ROBINSON (J.C.S., 1935, 744—752).—Aq. extracts of the sawdust of *Peltogyne porphyrocardia* with EtOAc yield a leucoanthocyanidin, peltogynol (I), $\text{C}_{16}\text{H}_{14}\text{O}_6$, $[\alpha]_D^{20} +273^\circ$ in EtOAc (O-Ac , m.p. 173° , $[\alpha]_D^{20} +125^\circ$ in CHCl_3 , O-Bz , m.p. 244° , O-tetra-anisoyl , m.p. 218° , O-Me , m.p. 174° , $[\alpha]_D^{20} +264^\circ$ in CHCl_3 , and O-Me derivatives, m.p. 198° , $[\alpha]_D^{20} +254^\circ$ in CHCl_3 ; 2:4-

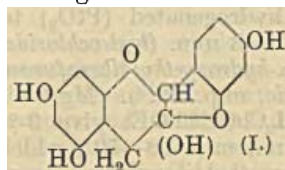
dinitrophenylhydrazone explodes 224°). Oxidation (HNO_3) of (I) gives styphnic acid, whilst the O-Me_3 compound yields 4:5-dinitroveratrole and with KMnO_4 affords *m*-hemipinic acid and *O-trimethylpeltogynic acid*, $\text{C}_{19}\text{H}_{18}\text{O}_7$ (?). Optical and X-ray crystallographic examination of (I) confirm the constitution assigned. The dihydroanthocyanidin state of oxidation is stabilised by the ketose group, and it is suggested that the corresponding structure will be found in other leucoantho-



cyanins and that the formation of the anthocyanidins from these precursors is actually the result of oxidation. *p*-Methoxysalicylaldehyde and ω -3:4-trimethoxyacetophenone (HCl) yield *O-tetramethylfisetinidin chloride*, which with CH_2O gives a solution closely resembling that of trimethylpeltogynidin salts.

F. R. S.

Constitution of cyanomaclurin. H. APPEL and R. ROBINSON (J.C.S., 1935, 752—755).—Cyanomaclurin (I) (Perkin, J.C.S., 1905, 87, 715) has $[\alpha]_D^{20} +215^\circ$ in EtOAc or $+192^\circ$ in H_2O , neither solution showing mutarotation. The supposed Ac_5 and Bz_4 derivatives are Ac_4 , $[\alpha]_D^{20} +95^\circ$ in EtOAc , and Bz_4 derivatives, respectively.



(I) forms *O-trimethylcyanomaclurin*, m.p. $73\text{--}85^\circ$ (Ac derivative), and is converted by Na_2CO_3 into morinidin chloride. Consideration of the reactions of (I) leads to the structure assigned.

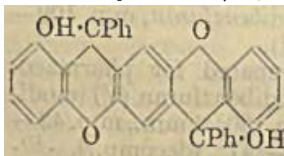
F. R. S.

Dibenzfuran [diphenylene oxide]. V. Dimetalation. H. GILMAN and R. V. YOUNG. VII. Amino derivatives. W. H. KIRKPATRICK and P. T. PARKER (J. Amer. Chem. Soc., 1935, 57, 1121—1123, 1123—1126; cf. this vol., 867).—V. Substitution of dibenzfuran by metals ("metalation") occurs in the 1 and 8 positions, showing the great effect of the O. Monometalation is best effected by LiBu^α or NaBu^α in Et_2O , and dimetalation by NaBu^α , but NaEt , PbEt_4 , or Na-K and $\text{MgBu}^\alpha\text{Cl}$ may also be used. Na 1-dibenzfuryl gives 1-methyl- (I) (45% yield) and 1-hydroxy-dibenzfuran (40%), m.p. 102° [Bz derivative, m.p. $91\text{--}92^\circ$; Me ether (II), m.p. 52° , b.p. $164\text{--}165^\circ/5$ mm.]. 1:8-Disubstituted dibenzfurans give 1:8-dimethyl- (90%), *di-iodo*- (19%), m.p. 160° , and *di-hydroxy*-dibenzfuran (III) (3%), m.p. 190° , and *dibenzfuran-1:8-dicarboxylic acid* (IV) (77%), m.p. 325° (Me_2 ester, m.p. $161\text{--}162^\circ$), and *disulphonic acid*, decomp. $183\text{--}185^\circ$, oxidised to the $(\text{SO}_3\text{H})_2$ -derivative, decomp. about 300° . (I) and (II) yield 1-methyl-8-carboxydibenzfuran-8-carboxylic acid, m.p. $238\text{--}240^\circ$ [Me ester, m.p. $80\text{--}81^\circ$; with KMnO_4 gives (IV)], and 1-hydroxy-8-methoxydibenzfuran, m.p. $109\text{--}110^\circ$, which with HI gives (III).

VI. NH_2 -derivatives are prepared for pharmacological examination. 2-Aminodibenzfuran (V) (modified prep.) yields the *N-Me*, b.p. $190^\circ/4$ mm., m.p. $48\text{--}49^\circ$ [*hydrochloride*, m.p. $245\text{--}247^\circ$ (decomp.)], *Et*- (*hydrochloride*, m.p. $>315^\circ$), *Pr*-, b.p. $203\text{--}205^\circ/1$

mm. (hydrochloride, m.p. 190°), $-Me_2$, b.p. 211—212°/4 mm., m.p. 96° (hydrochloride, m.p. 230—232°), and $-Et_2$, b.p. 205°/2—3 mm. [hydrochloride, m.p. 203—205° (decomp.)], derivatives, with $Br[CH_2]_5Br$ 2-piperidinodibenzfuran, m.p. 111° (hydrochloride, m.p. 258—260°), by a Skraup reaction pyrido-[3:2-b]- (VI), m.p. 167.5—168.5°, and -[2:3-c]-dibenzfuran, m.p. 112°, b.p. 209—210°/3 mm. [also obtained (Skraup) in poor yield from 3-bromo- and -nitro-2-aminodibenzfuran]. (VI) with Sn and HCl gives the 1:2:3:4- H_4 -derivative (hydrochloride, m.p. 247—248°), which with Me_2SO_4 gives the *N*-Me-derivative and with LiMe the 3-Me-compound, m.p. 185—186°, also obtained from (V) and CH_2O in conc. HCl. The Skraup reaction (As_2O_5) with 3-bromo-7-aminodibenzfuran affords a bromopyridodibenzfuran, m.p. 152°. 3-Aminodibenzfuran gives (Skraup) pyrido-[2:3-b]- and -[3:2-a]-dibenzfuran and two isomerides, m.p. 185—186° [hydrochloride, m.p. 307—310° (decomp.)] and 160.5—161.5° [hydrochloride, m.p. 296—298° (decomp.)], respectively. 3-Bromo- (from the Ac derivative and Br in Et_2O), m.p. 106—107°, and -chloro-acetyldibenzfuran (prep. by $CH_2ClCOCl$ in CS_2), b.p. 206—208°/1—2 mm., m.p. 109—110° (oxidised to the 3-carboxylic acid), give 3-diethylamino- (hydrochloride, m.p. 204—206°) and -piperidino-acetyldibenzfuran (hydrochloride, m.p. 270—271°), hydrogenated (PtO_2) to 3- β -diethylamino-, b.p. 220°/2—3 mm. (hydrochloride, m.p. 137°), and -piperidino- α -hydroxyethylidibenzfuran, m.p. 103—104° (hydrochloride, m.p. 242°). Mg 3-dibenzfuryl bromide and $CH_2ClCHClOEt$ give 3- β -chloro-, b.p. 204—206°/6 mm., m.p. 58—59°, which yields 3- β -piperidino- α -ethoxyethylidibenzfuran, m.p. 175°; epichlorohydrin yields similarly 3- γ -chloro-, b.p. 205—206°/2 mm., and -diethylamino- β -hydroxypropyldibenzfuran (hydrochloride, m.p. 145°); $(CH_2)_2O$ leads to 3- β -hydroxy-, m.p. 67—67.5°, -bromo-, b.p. 179—180°/2—3 mm., m.p. 62—62.5°, and -diethylamino-ethylidibenzfuran, b.p. 169—170°/2 mm. (hydrochloride, m.p. 192—193°). Li 1-dibenzfuryl and $(CH_3)_2O$ give 1- β -hydroxy-, m.p. 70—71°, b.p. 190—191°/4 mm., -bromo-, b.p. 163—165°/2 mm., m.p. 37—38°, and thence 1-diethylamino-ethylidibenzfuran (hydrochloride, m.p. 184—185°). 1-Hydroxydibenzfuran, $p-C_6H_4MeSO_3CH_2CH_2Cl$, and aq. NaOH give 1- β -chloro-, m.p. 64—65°, and thence 1- β -diethylamino- (hydrochloride, m.p. 128.5—129.5°) and -piperidino-ethoxydibenzfuran, b.p. 213°/2 mm. (hydrochloride, m.p. 210.5—212°). The 1-Li-derivative affords dibenzfuran-1-carboxyl chloride, m.p. 118°, which gives the amide, m.p. 181—182°, and thence 1-aminodibenzfuran, m.p. 84.5—85.5° (hydrochloride: Ac derivative, m.p. 172.5°), also obtained from the 1-OH-compound, $ZnCl_2$, and NH_4Cl at 275—280°. R. S. C.

Photochemical formation of diradicals. A. SCHONBERG (Annalen, 1935, 518, 299—302).—In part a priority claim (cf., *inter alia*, A., 1934, 643, 997).

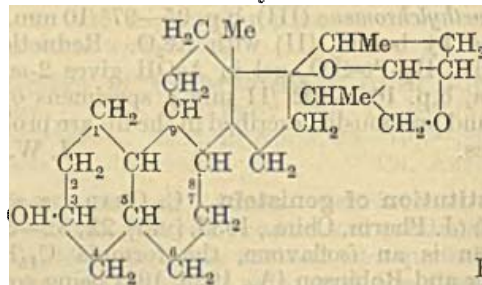


The compound formed by exposure of a chlorophyll solution to in presence of an acceptor (Gaffron, A., 1927, 1225) has a diradical character similar to that obtained with rubene (*loc. cit.*). Contrary to Liebermann *et al.* (A.,

1934, 531) the compound obtained by the action of HNO_3 on chromorufen is not a diradical peroxide, but a glycol (formula annexed). J. W. B.

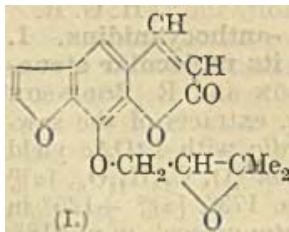
Synthesis of bergapten and its derivatives. I. Furocoumarins. J. N. RAY, S. S. SILOOJA, and V. R. VAID (J.C.S., 1935, 813—816).—7-Hydroxycoumarin with CH_2BrBz gives 7-phenacyloxycoumarin, m.p. 167° (with NaOEt forming 3'-phenyl-7:6-furocoumarin, m.p. 200°), and with CH_2ClAc yields 7-acetonyloxycoumarin, m.p. 167° (with NaOEt affording 3'-methyl-7:6-furocoumarin, m.p. 188°). β -Methylumbelliferone with CH_2ClAc forms 7-acetonyloxy-4-methylcoumarin, m.p. 157°, which with NaOEt gives 4:3'-dimethyl-7:6-furocoumarin, m.p. 220°. Acetylumbelliferone and $AlCl_3$ yield 7-hydroxy-8-acetylcoumarin, m.p. 167°, the oxime, m.p. 223°, of which with $POCl_3$ affords the isooxazole and 8-acetamido-7-hydroxycoumarin, m.p. 251°, hydrolysed to the amine, m.p. 278°. Pyrogallaldehyde and $CH_2(CO_2H)_2$ give daphnetin-3-carboxylic acid, m.p. 228°. Daphnetin and CH_2ClAc yield 8-hydroxy-7-acetonyloxycoumarin, m.p. 132—133°, methylated to the 8-OMe-compound, m.p. 81—82°, which with NaOEt forms 8-methoxy-3'-methyl-7:6-furocoumarin (+ H_2O), m.p. 155°. The furocoumarins described have the linear structure. F. R. S.

Neutral saponins. Conversion of digitogenin, gitogenin, and tigogenin into identical derivatives. R. TSCHESCHE (Ber., 1935, 68, [B], 1090—1094).—Digitogenic acid semicarbazone is reduced by NaOEt at 160—170° to gitogenic acid (I). Digitogenin (II) and gitogenin (III) therefore differ only because of the presence of a third OH in the second ring of the former. Oxidation of tigogenin (IV) with CrO_3 affords (I) and an acid, $C_{26}H_{35}O_8$, m.p. 218—220° (Me ester, m.p. 85—86°), previously obtained from (III). (IV) is therefore a $(OH)_1$ -compound with the same skeleton as (II) or (III). The annexed structure is suggested for (IV) whilst (III) is the 3:4-di- and (II) the 3:4:6-tri-hydroxy-compound of the same fundamental body.



H. W.

Natural coumarins. XV. Partial synthesis of imperatorin and preparation of oxyimperatorin. E. SPATH and H. HOLZEN (Ber., 1935, 68, [B], 1123—1125).—Treatment of xanthoxol as Na derivative with methyl- Δ^8 -butenyl bromide in Et_2O (not in MeOH) yields imperatorin, m.p. 101°, trans-



formed by BzO_2H in $CHCl_3$ into oxyimperatorin (I), m.p. 115—116°. H. W.

Thiacyclopentane 1 : 1-dioxides [tetramethylene sulphones]. H. J. BACKER and C. C. BOLT (Rec. trav. chim., 1935, 54, 538—544; cf. A., 1934, 662).—Catalytic hydrogenation of the unstable Δ^3 -thiacyclopentene 1 : 1-dioxide (butadiene sulphone) (I) gave the stable thiacyclopentane 1 : 1-dioxide (tetramethylene sulphone) (II). Rapidity of hydrogenation of substances of the type of (I) varies with structure. (II) has m.p. 20—21°, b.p. 149.5—150°/15 mm. (cf. A., 1917, i, 155). The following derivatives of (II) are described: 3-Me (m.p. 0—1°, b.p. 102—103°), from isoprene sulphone (cf. A., 1931, 1268); 3-Bu, m.p. 42—42.5°, b.p. 137—138°/2—3 mm.; 3-Ph, m.p. 96—97°, b.p. 220—221°/15 mm., 351—354°/760 mm.; 3-cyclohexyl (by hydrogenation of the 3-Ph compound), m.p. 62.5—63°, b.p. 202—204°/14 mm.; 3 : 4-Me₂, m.p. 50—51°, b.p. 136—137°/15 mm.; 2 : 3 : 4-Me₃, b.p. 117°/2 mm., 152—154°/14 mm. The decomp. temp. of many substances of types (I) and (II) are compared. P. G. C.

Manufacture of hydroxydiphenylene compounds and derivatives.—See B., 1935, 585.

Relative reactivities of certain 2- and 2 : 6-substituted piperidines. A. W. SINGER and S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1135—1137).—The rate of reaction of piperidine with Bu⁺Br at 150—155° is depressed by 2- or 2 : 6-substituents; Me is a more effective substituent than Ph, CH₂Ph, CH₂Ph·CH₂, or CO₂Et. *Et*, pyridine-, b.p. 188—188.5°/12 mm., m.p. 42—43°, and *piperidine-2 : 6-dicarboxylate*, b.p. 155—156°/11 mm., are described. 2 : 6-Di(phenylethyl)piperidine has b.p. 238—239°/11 mm. R. S. C.

Trichlorides of iridium^{III}-aquodipyridines.—See this vol., 946.

Complex iron thiocyanates with pyridine.—See this vol., 946.

Phenacylpyridinium compounds. F. KROLL-PFEIFFER and A. MÜLLER (Ber., 1935, 68, [B], 1169—1177).—*p*-Anisyl CBrMe₂ ketone is slowly converted by boiling C₅H₅N into *p*-methoxy- ω -*dimethylphenacylpyridinium bromide*, m.p. 171—172°, transformed by NaOH immediately followed by acid into *p*-OMe·C₆H₄·CO₂H and a little of the original salt and transformed in the usual manner into *p*-OMe·C₆H₄·CO₂H and the *N*-isopropylpyridinium salt (*picrate*, m.p. 193—194°). 2-Bromo-1-ketotetrahydronaphthalene smoothly yields 1-keto-2-tetrahydronaphthylpyridinium bromide (I) decomp. 216—218°, or, from MeOH with much Et₂O, a *product*, decomp. 246—248° (corresponding *picrate*, m.p. 187—188°). The action of alkali on (I) yields a substance, m.p. 75—80° (decomp.), which is certainly not the anhydro-base, reforms (I) when treated with acid or NH₄Cl, and is transformed by further treatment with alkali into γ -o-carboxyphenylpropylpyridinium chloride (II) [CO₂H·C₆H₄·[CH₂]₃·N⁺C₅H₅]⁺Cl⁻, m.p. 58—59° (corresponding *picrate*, m.p. 138—140°). When distilled in vac. (II) passes into the *lactone*, m.p. 54—56°, of *o*- γ -hydroxy-*n*-propylbenzoic acid, m.p. 70—71°, which is oxidised by KMnO₄ to β -o-carboxyphenylpropionic acid.

1-Ketotetrahydronaphthalene and 4 Br in CS₂
3 U

afford $\beta\beta$ -dibromo-1-ketotetrahydronaphthalene, m.p. 59—60°, transformed by NPhMe₂ into α -C₁₀H₇·OH and by C₅H₅N into 2-bromo- α -naphthol, m.p. 43—46°. The anhydro-base from 2-ethylthiol-5-methylphenacylpyridinium bromide and CS₂ in CHCl₃ yield the *substance*, C₁₆H₁₇·ONS, CS₂, m.p. 118—119° after softening, which is transformed by boiling AcOH into CS₂ and pyridinium salt and by conc. HCl or H₂SO₄ into readily hydrolysed salts of the base C₁₅H₁₁·ONS₂, decomp. 285° when rapidly heated, best obtained in addition to 2-ethylthiol-5-methylbenzoic acid by the action of alkali. The same base and the corresponding benzoic acid are also produced by the action of alkali on the CS₂ compounds, decomp. 117—119°, 2-methoxy-5-methylphenacylpyridinium bromide, or the corresponding 2-OEt-derivative. H. W.

Enol-betaines. I. F. KROHNKE (Ber., 1935, 68, [B], 1177—1195).—The intermediate products formed by the action of alkali or, preferably, alkali carbonate on acalkylpyridinium salts (I) and their analogues are regarded as enol-betaines (cf. A). Their intense colour is not due simply to the conjugated double linkings or the enol-betaine structure, but to co-ordinative unsaturation in conjunction with polarised double linking. The presence of the ethylenic linking is established by the occasional occurrence of *cis-trans* isomerism. The compounds react very readily with Bz₂O giving C·Bz compounds and easily afford additive compounds. They give very marked colour reactions with chloranil, bromanil, and 2 : 3-dichloro- α -naphthaquinone, whereas those with *p*-O·C₆H₄·O, toluquinone, and α -naphthaquinone are usually fugitive. Anthraquinone and its halogenated derivatives, o-quinones, and $\alpha\beta$ -diketones do not react, whilst 2-keto-1 : 1 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene behaves analogously to chloranil. Picryl chloride is a very sensitive reagent, followed by 1 : 2 : 4-C₆H₃Cl(NO₂)₂, C₆H₃(NO₂)₃, mono-, di-, and tri-nitrobenzaldehyde. Similar colour changes, usually occurring only with (I), are given by compounds ·CO·CRR'(Hal), in which at least R or R' is electronegative (e.g., CHBrPhBz, COPh·CHBr₂, CHBrBz₂, CBr₃·CHO, CCl₂Ph₂) or by compounds with accumulated negative groups (CCl₃·NO₂, CHBr₃, CHI₃, C₃HCl₇, CPh₃Cl). Non-cyclic NH₄ salts with an enolisable group and quaternary N give less intense colour reactions.

Phenacylpyridinium bromide and K₂CO₃ give the additive compound C₅₂H₄₅O₄N₄Br, m.p. 74° (decomp.). Phenacylpyridiniumenol-betaine and Bz₂O yield *dibenzoylmethylpyridiniumenol-betaine* (II) (cf. A), m.p. 220—222°, which does not immediately give the chloranil reaction and is transformed by 2*N*-HClO₄ into *dibenzoylmethylpyridinium perchlorate*, m.p. 149—150° after softening at 148°. (II) is also obtained from CHBrBz₂ and C₅H₅N. The *oxime*, m.p. 158—159°, of phenacylpyridinium perchlorate, the compound C₇₆H₆₁O₄N₄Br, m.p. 166° (decomp.), from *p*-phenylphenacylpyridinium bromide and K₂CO₃, and *acetonylpyridinium bromide*, m.p. 185°, are described. *p*-Bromophenacylpyridinium bromide, m.p. 235° (decomp.) (corresponding *perchlorate*, m.p. 241—242°), is transformed by K₂CO₃ into the corresponding

enol-betaine, m.p. 135—136° (decomp.), which yields *p*-bromophenacylpyridinium benzoate, m.p. 95—96° (decomp.), with BzOH in CHCl_3 and is converted by Bz_2O in CHCl_3 into *benzoyl-p*-bromobenzoylmethylpyridinium bromide, m.p. 219—220° (also + $2\text{H}_2\text{O}$), transformed by aq. HBr mainly into *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$. *m*-Nitrophenacylpyridinium perchlorate, m.p. 170—175°, and the corresponding *enol-betaine*, $\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}_2$, m.p. 145—147° (decomp.), are described. 3:4-Dichloro- ω -bromo-2-nitroacetophenone, m.p. 139.5—140°, affords 3:4-dichloro-2-nitrophenacylpyridinium bromide, m.p. 223° (decomp.), which yields two isomeric *enol-betaines*, orange-red leaflets, m.p. 160° (with transformation), and yellow needles, decomp. about 160°. ω -Acet-thienoylpyridinium bromide, m.p. 196—197°, is converted by *N*-NaOH into thiophen-2-carboxylic acid. The following compounds are described: phenacyl-3-nitropyridinium bromide, m.p. 210—220° (decomp.) [corresponding perchlorate, m.p. 198—199° (decomp.) after softening], and the *enol-betaine*, m.p. 147°; phenacyl-3-picolinium bromide, decomp. 225—230°; phenacyl-2-picolinium bromide, m.p. 214°, and dibenzoylmethyl-2-picolinium *enol-betaine*, m.p. 190.5°; *p*-bromophenacyl-2-picolinium bromide, m.p. 178°, and the *enol-betaine*, m.p. (indef.) 135° (decomp.); *p*-bromophenacyl-3-picolinium bromide, m.p. 244—245° (decomp.) after darkening [corresponding perchlorate, m.p. 223—227° (decomp.) after softening], and the *enol-betaine*, m.p. 130° after blackening at 80°; acetonylquinolinium bromide, m.p. 211, and the *enol-betaine*, m.p. 110° (decomp.); acetonylisoquinolinium bromide, m.p. 145°, and the *enol-betaine*, m.p. 100—103° (slight decomp.) (perchlorate, m.p. 149—150° after softening); phenacylquinolinium bromide, m.p. 212°, and the *enol-betaine*, m.p. 137—139°; *p*-bromophenacylquinolinium bromide and the *enol-betaine*, m.p. 125°; *p*-phenylphenacylquinolinium bromide, m.p. 228—229° (decomp.), and the *enol-betaine*, m.p. 155° (decomp.) after darkening at 60°; phenacylisoquinolinium bromide, m.p. 204—206° (corresponding perchlorate, m.p. 194—195° after softening at 193°), the *enol-betaine*, m.p. 192—193°, and dibenzoylmethylisoquinolinium *enol-betaine*, m.p. 251—252°; *p*-bromophenacylisoquinolinium bromide, m.p. 249° after softening and decomp., and the *enol-betaine*, m.p. 180°; *p*-phenylphenacylisoquinolinium bromide, m.p. 236°, and the *enol-betaine*, m.p. 203° (decomp.); desylpyridinium bromide, m.p. 157° (decomp.), which does not give reactions with chloranil or $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3$ in presence or absence of Na_2CO_3 , and the *enol-betaine*, m.p. 138° (also + $1\text{H}_2\text{O}$), which gradually loses $\text{C}_5\text{H}_5\text{N}$ when preserved; desylquinolinium bromide, m.p. 188° after softening at 183°; desylisoquinolinium bromide, m.p. 224—225°, and the hydrated *enol-betaine*; α -benzoyl- β -phenylthylpyridinium bromide, m.p. 192—193°, from $\text{CHBrBz}\cdot\text{CH}_2\text{Ph}$ and $\text{C}_5\text{H}_5\text{N}$, which gives a non-cryst. resin with K_2CO_3 and is transformed by KOH into BzOH and β -phenylethylpyridinium salt; 2-phenacylpyridine hydrobromide, m.p. 156—157° [corresponding perchlorate, m.p. 207° (decomp.)], and 2-phenacylpyridine methiodide, m.p. 190—191°, whence the anhydro-base (? *enol-betaine*), m.p. 122—123°, which is converted by 0.33*N*-NaOH into BzOH; phenacyltriphenylphosphonium bromide, m.p. 271—272° after softening at 270°, formed with triphenylphosphine

oxide, m.p. 154—155°, from PPh_3 and CH_2BrBz in CHCl_3 , which does not give the chloranil reaction and is stable towards 3*N*-NaOH at room temp.

H. W.

Condensation of α -carboxylic esters of the pyridine series. K. WINTERFELD and F. W. HOLSCHNEIDER (Arch. Pharm., 1935, 273, 305—315).—Et picolinate (I), pyrrolidone, and NaOEt in C_6H_6 give 3-picolinoylpyrrolid-2-one, m.p. 126—128°, b.p. 175°/0.5—1 mm. [HgCl_2 compound, m.p. 223° (decomp.)], which with hot conc. HCl yields 2-pyridyl γ -aminopropyl ketone (II) [dihydrochloride, + H_2O , m.p. 175° (decomp.); salt, $\text{B}_2\text{HCl}_2\cdot 2\text{HgCl}_2$, + H_2O , m.p. 194° (decomp.); aurichloride, m.p. 165—166° (decomp.); sulphophenylhydrazone dihydrochloride, m.p. 227° (decomp.); Bz derivative, m.p. 89—90° (HgCl_2 compound)]. (I) and $(\text{CH}_3\text{CO})_2\text{NMe}$ at 110—115° give similarly α -2-picolinoylsuccinimethylimide, m.p. 90—91° (picrate, m.p. 94—95°), converted by hydrolysis and esterification into Et γ -picolinoylpropionate, b.p. 162—163°/11 mm. (platinichloride, decomp. 177—178°; HgCl_2 compound, m.p. 87—88°); the hydrochloride of the corresponding acid yields by hydrogenation (PtO_2 -Pt-black) in EtOH γ -2-pyridylbutyrolactone, b.p. 155—157°/13 mm. (hydrochloride, m.p. 217—218°; aurichloride, m.p. 158—159°). (I) and γ -butyrolactone with Na or NaOEt (at 60—70°) in C_6H_6 afford α -picolinoylbutyrolactone, m.p. 50—51°, hydrolysed by HCl in poor yield to 2-pyridyl γ -hydroxypropyl ketone, an oil (platinichloride, sinters 85—86°, decomp. 134—135°; HgCl_2 compound, m.p. 151—152°). Et α -picolinoylacetate, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{OMe}$, and NaOEt give 2-pyridyl γ -methoxypropyl ketone, b.p. 115—117°/10 mm. (hydrochloride, decomp. 143—144°), and probably a little pyridyl Me ketone (hydrochloride, decomp. 215°). Et quinoline-2-carboxylate, *N*-methyl- α -pyrrolidone, and Na in C_6H_6 at 110° give 2-quinolyl 3-*N*-methylpyrrolid-2-onyl ketone, m.p. 109—111°, hydrolysed to 2-quinolyl γ -methylaminopropyl ketone hydrochloride, decomp. 155—156°. 2-Pyridyl γ -methylaminopropyl ketone and (II), but not the other products described above, have marked action on the uterus (isolated or *in situ*) of guinea-pigs at 1:100,000.

R. S. C.

Derivatives of β -2-pyridylpentan- β -ol. K. WINTERFELD and F. W. HOLSCHNEIDER (Arch. Pharm., 1935, 273, 315—319).—2-Acetylpyridine (modified prep.) and MgPr^+Br in Et_2O give β -2-pyridyl-*n*-pentan- β -ol (I), b.p. 102—103°/100 mm. [hydrobromide, m.p. 168°; Bz derivative (II), b.p. 174—175°], the hydrochloride, m.p. 180—181°, of which is hydrogenated (PtO_2) in EtOH to β -2-piperidyl-*n*-pentan- β -ol (III) (hydrochloride, m.p. 158—160°) giving with $\text{CH}_2\text{O}\cdot\text{HCO}_2\text{H}$ at 140—150° the *N*-Me derivative (IV), b.p. 113—114°/10 mm. (Bz derivative, b.p. 161—163°/? 10 mm.). (I) and PBr_3 at 100° give β -2-pyridyl- Δ^3 -*n*-pentene hydrobromide, m.p. 124—125°. (II) and (III) have slight, and (IV) large (25 mg. per kg. body-wt.), pressor action on cats. (IV) also paralyses smooth stomach muscle.

R. S. C.

Pyridyl-2-acetic acid and pyridyl-2:6-diacetic acid. M. P. OPARINA (Khim. Farm. Prom., 1934, No. 4, 12—15).—The oximes of the corresponding phen-

acyl compounds are converted into the anilides by the Beckmann transformation; these are then hydrolysed to the acids. CH. ABS. (r)

Condensation products of pyridine bases with benzaldehyde. M. P. OPARINA and B. SMIRNOV (Khim. Farm. Prom., 1934, No. 4, 15—16).—Condensation (ZnCl_2) of pyridine bases (b.p. 140—150°) with PhCHO yields a mixture containing distyrylpyridine and α - and β -stilbazoles. Oxidation affords 2:4- $\text{C}_5\text{H}_3\text{N}(\text{CO}_2\text{H})_2$, decarboxylated to the 4-carboxylic acid. CH. ABS. (r)

Substituted aromatic aldehydes in Hantzsch's pyridine condensation. IV. Derivatives of 3:4-dihydroxybenzaldehyde. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1935, 816—818; cf. A., 1932, 744).—The following compounds are obtained from the appropriate aldehydes by the method previously described (A., 1931, 1072) (% yields in parentheses): *Et* 4-(4'-hydroxy-3'-methoxyphenyl)- (I), m.p. 164° (74.1); *Et* 4-(2'-nitro-4'-hydroxy-3'-methoxyphenyl)-, m.p. 118° (71.9 and 57.6, yields are inconsistent owing to difficulty of isolation of product); *Et* 4-(3'-hydroxy-4'-methoxyphenyl)- (II), m.p. 165° (74.1 and 72.8); *Et* 4-(5'-nitro-3'-hydroxy-4'-methoxyphenyl)-, m.p. 185° (75.7) (+ *EtOH* of crystallisation, m.p. 185°); *Et* 4-(3':4'-dimethoxyphenyl)-, m.p. 144° (76.1 and 76.6) [identical with methylation products (Me_2SO_4 - NaOH) of (I) and (II)]; *Et* 4-(2'-nitro-3':4'-dimethoxyphenyl)-, m.p. 141.5° (74.2 and 77.0); *Et* 4-(5'-nitro-3':4'-dimethoxyphenyl)-, m.p. 154° (69.3 and 71.4); *Et* 4-(6'-nitro-3':4'-dimethoxyphenyl)-, m.p. 229° (68.7 and 67.3); *Et* 4-(3':4'-methylenedioxyphenyl)-, m.p. 132° (71.9 and 71.3); *Et* 4-(6'-chloro-3':4'-methylenedioxyphenyl)-, m.p. 139° (66.7 and 67.2); *Et* 4-(6'-bromo-3':4'-methylenedioxyphenyl)-, m.p. 169° (69.9 and 69.5); *Et* 4-(6'-nitro-3':4'-methylenedioxyphenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate (59.6 and 61.5) [+ *AcOH* of cryst., m.p. 144°; + *EtOH* of cryst., m.p. 101° (decomp.)]. Condensation with 2:6-dinitroisovanillin (III) yields only the NH_4 salt of (III), m.p. 190° (decomp.), reconverted into (III) by warm dil. HCl . The influence of substituents in the aldehyde on the yield of dihydropyridine is discussed. 5-Nitroisovanillin has m.p. 121° (lit., m.p. 113°). H. G. M.

Manufacture of pyridine compounds.—See B., 1935, 585.

Compounds of 8-hydroxyquinoline with alkali metals and zirconium. P. SUE and G. WETROFF (Bull. Soc. chim., 1935, [v], 2, 1002—1007).—The prep. and analysis of the Li, Na, K(+ KOH), and NH_4 (+ NH_3) salts of 8-hydroxyquinoline and the Zr salt, $\text{Zr}(\text{C}_8\text{H}_6\text{ON})_4$, and its *Br*-derivative, $\text{Zr}(\text{C}_8\text{H}_5\text{ONBr})_4$, are described. None of these salts is suitable for accurate determination of the metal it contains. H. G. M.

2-Methyl-4-quinolyldiazines. E. KOENIGS and (FRL.) M. VON LOESCH (J. pr. Chem., 1935, [ii], 143, 59—69).—Action of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (I) on 4-chloro-2-methylquinoline (II) at 150° gives a diamine (III), new m.p. 122°, incorrectly described by Marckwald and Chain (A., 1900, i, 521) as 2-methyl-4-quinolyldiazine (IV). (III) with HNO_3 yields a substance

(V), $\text{C}_{10}\text{H}_8\text{N}_4$, m.p. 126°, resolidifying at 240°, to melt again at 300°; (V) is converted by HCl into an isomeride, m.p. 342° (hydrochloride; Na salt, decomp. 230°). Similarly 4-chloro-6-methoxy-2-methylquinoline (VI) yields a diamine, $\text{C}_{11}\text{H}_{13}\text{ON}_3$, m.p. 100—103° [hydrochloride, decomp. 270°; picrate, m.p. 202° (decomp.)]; Cu salt], which with HNO_3 forms a substance, m.p. 186°, resolidifying at 240°, decomp. 305°, converted by HCl into an isomeride, m.p. 305°. 4-Chloro-6-ethoxy-2-methylquinoline (VII) gives a diamine, m.p. 116—117° [picrate, m.p. 200° (decomp.)]; Cu salt], which with HNO_3 forms a substance, $\text{C}_{12}\text{H}_{12}\text{ON}_4$, m.p. 212°, resolidifying, decomp. 270°, converted by HCl into an isomeride, decomp. 292° (hydrochloride, decomp. 265°). The action of (I) on (II) in *EtOH* on the water-bath gives the true 2-methyl-4-quinolyldiazine (IV), m.p. 200° (decomp.) [sulphate (VIII), m.p. 284—285°; hydrochloride, m.p. 306°; picrate, m.p. 204°; benzylidene derivative, m.p. 259° (all decomp.)], which with HNO_3 forms 2-methyl-4-quinolyldiazide, m.p. 78° (+ $2\text{H}_2\text{O}$) [picrate, m.p. 181° (decomp.)]. (VIII) is reduced (Zn , H_2SO_4) to 4-amino-2-methylquinoline. (VI) similarly gives 6-methoxy-2-methyl-4-quinolyldiazine, m.p. 208° [sulphate, m.p. 310°; picrate, m.p. 191° (both decomp.)], which forms 6-methoxy-2-methyl-4-quinolyldiazide, m.p. 106—107° (hydrochloride, decomp. 195°), and 4-amino-6-methoxy-2-methylquinoline, m.p. 211—213° [picrate, m.p. 250° (decomp.)]. (VII) gives 6-ethoxy-2-methyl-4-quinolyldiazine, m.p. 180° [sulphate, m.p. 276° (decomp.)]; hydrochloride, decomp. 300°; picrate, decomp. 193°], which forms 6-ethoxy-2-methyl-4-quinolyldiazide, m.p. 108° (picrate, decomp. 183°).

E. W. W.

Synthesis of quinolinic bases from hydroxymethylene derivatives of ketones. M. ROMET (Compt. rend., 1935, 200, 1676—1678; cf. A., 1887, 940).—The hydroxymethylene derivative of COEt_2 affords an anilide, which is converted by ZnCl_2 at 180° (or at 129° in *isoamyl* alcohol) into 3-methyl-2-ethyl- and 3-methyl-4-ethyl-quinoline, an oil. Similarly, the *p*-toluidide affords 3:6-dimethyl-2-ethyl-quinoline, m.p. 54° (picrate, m.p. 177°). The anilide and *p*-toluidide of the hydroxymethylene derivative of COMe_2 give quinaldine and 2:6-dimethylquinoline, respectively. The quinolines obtained indicate that the amine reacts with CO rather than CHO. COMeEt gives a mixture of two hydroxymethylene derivatives (cf. A., 1888, 671; 1916, i, 372) which give anilides, m.p. 129—130° and 96°, convertible into quinolines as above. J. L. D.

Derivatives of 8-aminoquinoline as antimalarials. IV. Compounds with long chains in position 8. O. J. MAGIDSON, O. S. MADAEVA, and M. V. RUBZOV (Arch. Pharm., 1935, 273, 320—333; cf. A., 1934, 417).—The ratio (*R*), for 6-methoxyquinolines with $\text{NMe}_2 \cdot [\text{CH}_2]_n \cdot \text{NH}$ in position 8 is greater if *n* is an odd than if it is an even no. up to *n*—9, max. occurring at *n*—3 and 9; higher homologues have very low *R*. κ -Bromodecyl acetate is less reactive than the λ -Br-ester. Periodicity is noticeable in the case of reaction of ω -bromoalkyl acetates with NHEt , and of ω -bromoalkyldiethylamines with 6-methoxyquinoline (I).

$\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$ and Na do not react in Et_2O , and in hot PhMe give PhOH , an unsaturated ether, and a little of a substance, m.p. $61\text{--}62^\circ$. With NaI in COMe_2 it gives the iodide, which with Na in Et_2O affords $\text{OPh}\cdot[\text{CH}_2]_6\cdot\text{OPh}$; with 60% HBr this yields the α -dibromide (II), also obtained from the glycol (modified prep.). (II) and KOAc in AcOH at 120° give ζ -bromohexyl acetate, b.p. $113\text{--}116^\circ/12\text{ mm.}$, converted by hot NHEt_2 into ζ -acetoxyhexyldiethylamine, b.p. $129\text{--}132^\circ/13\text{ mm.}$, whence the *Bramine* (III), an oil (readily cyclises; *hydrochloride*), is obtained by 60% HBr . (I) and (III) in EtOH at $110\text{--}115^\circ$ give 8- ζ -diethylamino-*n*-hexylamino-6-methoxyquinoline, b.p. $197\text{--}202^\circ/1\text{ mm.}$ [meconate, m.p. 102° (decomp.); *R* 13.3]. By similar reactions are obtained 8- η -diethylamino-*n*-heptyl-, b.p. $232\text{--}237^\circ/2.5\text{--}3\text{ mm.}$, *R* 33.3, 8- ι -diethylamino-*n*-nonyl-, b.p. $248\text{--}252^\circ/3\text{ mm.}$, *R* 40, 8- λ -, b.p. $246\text{--}247^\circ/2\text{ mm.}$, *R* 5, and 8- κ -diethylamino-*n*-undecyl-amino-6-methoxyquinoline, b.p. $238\text{--}240^\circ/1\text{--}2\text{ mm.}$, *R* 0. Prep. of the following is modified: heptane- $\alpha\eta$ -diol (from Et_2 pimelate), b.p. $160\text{--}167^\circ/24\text{ mm.}$, and -dibromide; nonane- $\alpha\iota$ -diol and -dibromide; Et_2 azelate; Et λ -bromoundecate; λ -hydroxyundecyldiethylamine, b.p. $168.5\text{--}169^\circ$; κ -bromoundecate acid. The following appear to be new: τ -bromoheptyl, b.p. $148\text{--}153^\circ/23\text{--}25\text{ mm.}$, and ι -bromononyl acetate, b.p. $144\text{--}152^\circ/9\text{ mm.}$; η -diethylaminohexyl alcohol, b.p. $146\text{--}148^\circ/17\text{ mm.}$, and bromide (*hydrobromide*, hygroscopic, m.p. $81\text{--}84^\circ$); $\alpha\tau$ -di(diethylamino)-heptane, b.p. $153\text{--}154^\circ/19\text{ mm.}$ (*hydrobromide*, m.p. 245°); ι -diethylaminononyl acetate, b.p. $155\text{--}157^\circ/9\text{ mm.}$, and bromide (*hydrobromide*); Et λ -, b.p. $183\text{--}184^\circ/11\text{--}12\text{ mm.}$, and κ -diethylaminoundecate, b.p. $184\text{--}186^\circ/14\text{ mm.}$ (*hydrochloride*, m.p. $87\text{--}88^\circ$); λ -diethylaminoundecyl chloride, b.p. $172\text{--}175^\circ/10\text{ mm.}$ (*hydrochloride*, m.p. $89\text{--}91^\circ$); κ -diethylaminoundecyl alcohol, b.p. $167^\circ/9\text{ mm.}$, and chloride (*hydrochloride*, m.p. $54\text{--}56^\circ$). R. S. C.

Preparation of possible antimalarial agents.—See this vol., 1017.

6-Methoxy-8-quinolyl ethyl ketone. I. T. STRUKOV (*Khim. Farm. Prom.*, 1934, No. 3, 13—14).—8-Cyano-6-methoxyquinoline (Sandmeyer; from 8-amino-6-methoxyquinoline) with MgEtI affords 6-methoxy-8-quinolyl *Et* ketone. CH. ABS. (r).

8-Amino-6-methoxyquinoline. I. T. STRUKOV (*Khim. Farm. Prom.*, 1934, No. 5, 19—21).—A technically applicable method of reduction of 8-nitro-6-methoxyquinoline is described. CH. ABS. (r).

Determination of 2-phenylquinoline-4-carboxylic acid in presence of salicylic and acetylsalicylic acids. A. CASTIGLIONI (*Annali Chim. Appl.*, 1935, 25, 240—242).—Unlike the other two acids named, 2-phenylquinoline-4-carboxylic acid (I) is pptd. by silicotungstic acid to form $12\text{WO}_3\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}\cdot 4\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2\cdot 2\text{H}_2\text{O}$, which, on calcination, gives silicotungstic anhydride; multiplication of the latter by 0.3604 gives (I). T. H. P.

Friedel and Crafts reaction in the carbazole series. S. G. P. PLANT, (MISS) K. M. ROGERS, and S. B. C. WILLIAMS (*J.C.S.*, 1935, 741—744).—In the Friedel-Crafts reaction, carbazole (I) is substituted

in the 3 and 6 positions, 3-substituted carbazoles in the 6 position, and 9-acylcarbazoles in the 2 position. (I) and AcBr yield 3:6-diacetylcarbazole (II), m.p. 232° (3:6:9- Ac_3 compound, m.p. 220° ; 9-*Me* compound, m.p. 192°). $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ and 4-bromo-3-nitroacetophenone give (Cu) 2-nitro-4:4'-diacetyldiphenylamine, m.p. 177° , which on reduction and addition of NaNO_2 forms 5:4'-diacetyl-1-phenylbenzotriazole, m.p. 224° ; 2-nitro-4-acetyl-4'-ethyldiphenylamine, m.p. 85° , and 5-acetyl-1-phenyl-4'-ethylbenzotriazole, m.p. 143° , are similarly prepared, but neither triazole could be converted into the carbazole. Reduction of (II) (Clemmensen) leads to 3:6-diethylcarbazole, m.p. 119° , also obtained by oxidising (S) 3:6-diethyl-1:2:3:4-tetrahydrocarbazole, m.p. $87\text{--}88^\circ$, prepared from the *p*-ethylphenylhydrazine of 4-ethylcyclohexanone (Fischer reaction). 3-Acetylcarbazole and BzCl afford 3-benzoyl-6-acetylcarbazole, m.p. 210° , also obtained from 3-benzoylcarbazole and AcCl . 9-Benzoylcarbazole with BzCl gives 2:9-dibenzoylcarbazole, m.p. $140\text{--}142^\circ$, and with AcCl forms the 2-benzoyl-9-acetyl compound, m.p. $136\text{--}137^\circ$, both substances being hydrolysed to 2-benzoylcarbazole, m.p. 163° . F. R. S.

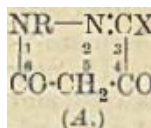
Manufacture of nitrogenous condensation products.—See B., 1935, 622.

Photochemical behaviour of pyridine, 2-benzylpyridine, papaverine, and some derivatives. A. MULLER and M. DORFMAN (*Monatsh.*, 1935, 65, 411—432; cf. this vol., 366).—The prep. of 2- (I) and of 4-benzylpyridine is improved, and their M_n determined. When (I) is exposed to light of λ 275 to $< 238\text{ m}\mu$, an aldehydic substance is formed. At λ 365—275 $\text{m}\mu$, the products are 2-benzoylpyridine (II) [*semicarbazone*, m.p. 184° (corr.)], with $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-2-pyridylethane (?), m.p. $220\text{--}221^\circ$. In O_2 -free H_2O vapour, $\text{C}_5\text{H}_5\text{N}$ and papaverine are unaffected by light; (I), (II), and papaveraldine darken. The effects of light of each λ from a Hg lamp on various substances are compared. The *semicarbazone*, m.p. 208° (corr.), of 4-benzoylpyridine is described. E. W. W.

Metabolism of monomethyltryptophans.—See this vol., 1015.

New derivatives of phenyldimethylaminopyrazolone. J. ERDOS and J. SURU, jun. (*Magyar Tars. Ért.*, 1934, 10, 424—429; *Chem. Zentr.*, 1935, i, 563).—The condensation of 4-aminoantipyrine with aldehydes to yield the following is described: *salicylidene*-, m.p. 198° ; *cinnamylidene*-, m.p. 157° , and *piperonylidene*-, m.p. 230° , -4-aminoantipyrine. H. N. R.

Ring-formation in heterocyclic compounds. A. SONN and (in part) W. LITTEN, H. LAURIEN, K. SCHUTZLER, and W. MEYER (*Annalen*, 1935, 518, 290—298).—The product obtained by interaction of PhN_2Cl with $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ (I) is 1-phenyl-4:6-diketo-1:4:5:6-tetrahydropyridazine-3-carboxylic acid (II) (A, R=Ph; X= CO_2H), m.p. $244\text{--}245^\circ$ [*Me* ester, m.p. 138° (converted by CH_2N_2 into its 6-*O-Me* ether, m.p. 154°); *anilide*, m.p. $177\text{--}178^\circ$], decarboxylated above its m.p. to 1-phenyl-4:6-diketo-1:4:5:6-tetrahydropyridazine (III), m.p. $221\text{--}222^\circ$.



Similar condensation with $\text{CO}_2\text{Et}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ affords 1-phenyl-5-ethyl-4:6-diketo-1:4:5:6-tetrahydropyridazine-3-carboxylic acid, m.p. 121—122°, and a similar constitution (A , $R=p\text{-C}_6\text{H}_4\cdot\text{NO}_2$, $X=\text{CO}_2\text{H}$) must be assigned to the anhydro-compound, m.p. 251°, obtained by similar condensation of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ with (I) and alkaline hydrolysis (Bülow *et al.*, A., 1901, i, 239). 4:5-Dibromo-1-phenyl-1:4:5:6-tetrahydropyridazin-6-one (IV) is converted by $\text{KOR}\cdot\text{ROH}$ into the corresponding 5-bromo-4-methoxy- and 5-bromo-4-ethoxy-, m.p. 135°, -derivatives, reduced to 4-ethoxy-1-phenyl-1:4:5:6-tetrahydropyridazin-6-one, m.p. 124—125°, also obtained by the action of $\text{EtBr}\cdot\text{NaOEt}$ on (III). Prolonged heating with dil. $\text{NaOH}\cdot\text{EtOH}$ converts (IV) into 5-bromo-1-phenyl-1:4:5:6-tetrahydropyridazine-4:6-dione, m.p. 270°. With the appropriate amine (IV) yields the corresponding 5-bromo-4-methyl-, m.p. 158—159°, -4-benzyl-, m.p. 203°, -4-diethyl-, m.p. 92—93°, -4-dimethyl- (V), m.p. 116°, -amino-1-phenyl-1:4:5:6-tetrahydropyridazin-6-one. The methiodide of (V) [by NMe_3 on (IV)] with Ag_2O affords a solution from which the picrate, decomp. $>280^\circ$, of $\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ is obtained. Condensation of the appropriate keto-ester with PhN_2Cl affords *Et benzeneazo-oxalodiethylacetoacetate*, m.p. 112—112.5°, and -diethylacetonedicarboxylate, m.p. 76—77°, the free acid, m.p. 150—151° (decomp.) (anhydride, m.p. 159—160°), of which, when kept, affords the phenylhydrazone, m.p. 78—79°, of $\text{CHEt}_2\cdot\text{CO}\cdot\text{CHO}$, and when heated in EtOH gives the phenylhydrazone, m.p. 68—69°, of $\text{CO}_2\text{H}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{CHO}$. The formation of such 5- and 6-membered heterocyclic rings is discussed, and it is suggested that the compounds obtained by condensation of Et formylsuccinate with $\text{NHPh}\cdot\text{NH}$, (Wislicenus *et al.*, A., 1909, i, 9) and N_2H_4 (von Rothenburg *et al.*, A., 1895, i, 302) have the structure

$$\text{NR}\cdot\text{CO}\cdot\text{N}=\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \quad (\text{R}=\text{Ph} \text{ and } \text{R}=\text{H}, \text{ respectively}).$$

J. W. B.

Pyrimidines. CXLVI. Synthesis of uracyl-5-methylamine. T. B. JOHNSON and (Miss) A. LITZINGER (J. Amer. Chem. Soc., 1935, 57, 1139—1140).—An aliphatic pyrimidine base, uracyl-5-methylamine, m.p. 295—300° (decomp.) [hydrochloride, m.p. 242—243° (decomp.); sulphate, m.p. 245—246° (decomp.)], is prepared from Et 2-ethylthiouracyl-5-acetate by way of the urethane, which is readily hydrolysed by H_2SO_4 or HCl .

R. S. C.

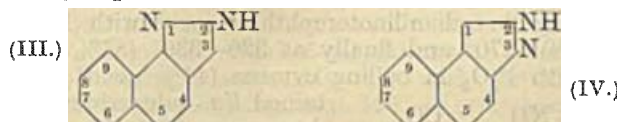
Indazoles. 2-p-Dimethylanilino-3-carbethoxyindazole. I. TANASESCU and E. TANASESCU (Bull. Soc. chim., 1935, [v], 2, 1016—1020).—Et o-nitrophenylacetate is not oxidised by nitrous vapours (cf. A., 1909, i, 925). When heated with $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, EtOH, and Na_2CO_3 (or Na_3PO_4 , but not $\text{C}_5\text{H}_5\text{N}$ and $\text{C}_5\text{H}_{11}\text{N}$) on a water-bath it affords 2-p-dimethylanilino-3-carbethoxyindazole 1-oxide, m.p. 212° (colour reactions with HCl and alcohols described), which on reduction ($\text{Zn}\cdot\text{EtOH}\cdot\text{H}_2\text{O}\cdot\text{CaCl}_2$) affords 2-p-dimethylanilino-3-carbethoxyindazole, m.p. 143° (hydrochloride, m.p. 197°), and with conc. HCl at the b.p. during 15 min. 2-p-dimethylanilino-3-chloroindazole 1-oxide, m.p. 167°, basic and readily sol. in mineral acids.

H. G. M.

Quinazolines. VII. Interaction of 2:4-dichloroquinazoline in alcohol with ammonia and methylamine. E. VOPICKA and N. A. LANGE (J. Amer. Chem. Soc., 1935, 57, 1068—1070; cf. A., 1933, 723).—2:4-Dichloroquinazoline and $\text{EtOH}\cdot\text{NH}_3$ or $\text{EtOH}\cdot\text{NH}_2\text{Me}$ at 150° give 2:4-diamino-, m.p. 259° [hydrochloride, m.p. 308°; sulphate, m.p. 330°; acetate, $+\text{H}_2\text{O}$, m.p. 208°; nitrate, m.p. 280°; oxalate, m.p. 274°; picrate, m.p. 304° (decomp.); Ac, derivative, m.p. 230°], and 2:4-dimethylamino-quinazoline, m.p. 120° (hydrochloride, m.p. 312°; picrate, m.p. 232°), respectively. M.p. are corr.

R. S. C.

Naphthindazoles. V. VESELY, A. MEDVEDEVA, and E. MULLER (Coll. Czech. Chem. Comm., 1935, 7, 228—238).—2:1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NO}_2$ in $(\text{CHCl}_2)_2$ with FeCl_3 and Cl_2 affords 8-chloro-1-nitro-2-methylnaphthalene, m.p. 114° [also obtained (Sandmeyer) from the corresponding 8- NH_2 -compound], and this, when dissolved in EtOH and slowly added to Fe in boiling $\text{AcOH}\cdot\text{H}_2\text{O}$, is reduced to the amine, m.p. 89° [Ac derivative (I), m.p. 214—215°]. When diazotised and poured into boiling EtOH, this amine affords some 9-chloro- α -naphthindazole (II), m.p. 159° (2-Ac derivative, m.p. 196°) (cf. A., 1891, 312), but no 8:2- $\text{C}_{10}\text{H}_6\text{ClMe}$ could be isolated. (II) was also obtained by treating (I) in Ac_2O with N_2O_3 , and boiling the resulting crude N-NO-derivative in C_6H_6 for 3 hr. (cf. A., 1908, i, 298). 4-Nitro-1-amino-2-methylnaphthalene in EtOH, when diazotised and



heated, affords 2:4- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NO}_2$ and 5-nitro- α -naphthindazole, m.p. 304—305° (2-Ac derivative, m.p. 196—197°). 6-Bromo- α -naphthindazole, m.p. 249—250° (cryst. from AcOH) and 202—204° (pptd. from EtOH solution by H_2O) (2-Ac derivative, m.p. 168°), is similarly obtained. 2:1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NHAc}$ in AcOH and N_2O_3 afford the N-NO-derivative, m.p. 82° (decomp.), converted by very cautious heating or, better, by boiling in C_6H_6 or PhMe into α -naphthindazole (III), m.p. 158° (picrate, m.p. 193°; Ac derivative, m.p. 108—109°). 1:2- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NHAc}$ is converted similarly into the N-NO-derivative, m.p. 91° (decomp.). This, when heated alone, or better in xylene, C_6H_6 , or benzene, affords β -naphthindazole (IV), m.p. 231° (picrate, m.p. 217—218°; Ac derivative, m.p. 116.5°; Ag salt).

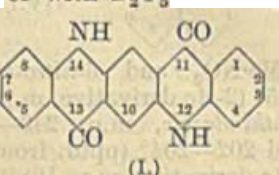
H. G. M.

Syntheses and molecular complexes in the phenazine series. II. G. R. CLEMO and H. McILWAIN (J.C.S., 1935, 738—741).—There are two types of mol. compound: (i) true phenazhydrins, formed between a phenazine and a 9:10-dihydrophenazine, green to purple, forming green dihydrochlorides, (ii) phenazine-primary or -sec. aromatic base complexes, orange-red, not giving hydrochlorides. Phenazine-N-methyldihydrophenazine dihydrochloride, m.p. 225° (decomp.), is prepared from its components. cycloHexane-1:2-dione, o- $\text{C}_6\text{H}_4(\text{NHMe})_2$, and HCl followed by NaOH give NN' -dimethyl-2:3:9:10-tetrahydrophenazine, m.p. 78°, whilst with $\text{NaOH}\cdot\text{AcOH}$, NN' -dimethyl-9:10-dihydrophenazine, m.p.

153°, is obtained [*phenazine-NN'-dimethyl-9:10-dihydrophenazine dihydrochloride*, m.p. 225—230° (decomp.)]. The following phenazine-base complexes have been prepared: *phenazine-o*-, m.p. 153°, -*m*-, m.p. 143°, and -*p*-phenylenediamine, m.p. 133°, and -*diphenylamine*, m.p. 57—58°. 1:2:3:4-Tetra- is reduced (Na-Hg) to 1:2:3:4:9:10:11:12-octa-hydrophenazine, m.p. 150°, neither compound forming a complex with phenazine. 2-Methyl-1:2:3:4-tetrahydrophenazine, b.p. 147°/0.1 mm., obtained from 1-methylcyclohexane-3:4-dione, *o*-C₆H₄(NH₂)₂, and NaOAc-AcOH, and 2-methyl-5:6:7:8-tetrahydrophenazine, m.p. 78°, obtained from 1:3:4-C₆H₃Me(NH₂)₂ and cyclohexane-1:2-dione, with I-AcOH give 2-methylphenazine, oxidised to phenazine-2-carboxylic acid. The nature of the complexes is discussed. F. R. S.

Neocyanine. F. M. HAMER (Chem. and Ind., 1935, 54, 640—641).—The evidence of absorption spectra indicates that the I atom is tautomerically shared between the N atoms of the carbocyanine chain rather than between the N atoms of the dicarbocyanine chain. H. W.

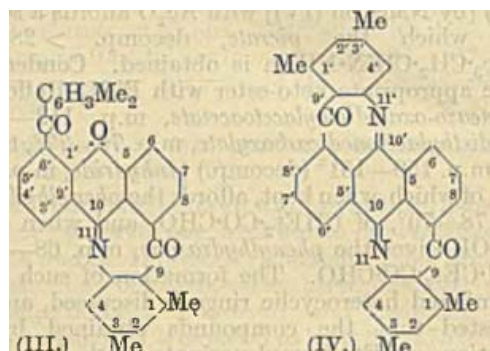
Rearrangement products of succinylsuccinic esters. VI. Formation of quinacridones from 2:5-diarylamino-terephthalic acids. H. LIEBERMANN [with H. KIRCHHOFF, W. GLIKSMAN, L. LOEWY, A. GRUHN, T. HAMMERICH, N. ANITSCHKOFF, and B. SCHULZE] (Annalen, 1935, 518, 245—259).—By heating 2:5-dianilinoterephthalic acid with H₃BO₃ at 260—270° and finally at 320—330° (87% yield) or with P₂O₅ in boiling cymene (44% yield) is obtained *ln*.-quinacridone (I), decomp. > 400° (Cl₁₀-derivative, m.p. 402°, by heating with SbCl₅-I). Similarly from the appropriate diarylamino-terephthalic acid (II) are prepared 4:8-, m.p. 347°, and 2:6-dimethyl-, m.p. 337°; 4:8-dimethoxy-, m.p. 318°; 1:2:5:6-dibenzo- (III) [together with a little 2-β-naphthylamino-7:8-benzacridone-3-carboxylic acid (IV) (Ba salt)], and 3:4:7:8-dibenzo-, m.p. 348° [dodecachlorodihydroxy-derivative, m.p. 410° (decomp.)], -quinacridone. Et 2:5-di-β-naphthylamino-terephthalate and Me₂SO₄ at 120—150° afford a little (III) and its 12:14-Me₂ derivative, m.p. > 400° (decomp.), and (IV). When warmed with conc. H₂SO₄ (III) gives its *disulphonic acid*. By heating the appropriate (II) with K₂CO₃, PhI, and Cu in C₅H₁₁OH at 195° are obtained 2:5-bisdiphenylamino-, m.p. 292° (decomp.) (Ag, Ba, Pb, and Cu^{II} salts), -phenyl-*o*-tolylamino-, m.p. 309° (NH₄ salt), -phenyl-*p*-tolylamino-, m.p. 287° (decomp.), -phenyl-β-, m.p. 296° (Ag and Ba salts), and -α-naphthylamino-, m.p. 320° (decomp.) (Ba salt), -terephthalic acid. These are converted by heating with BzCl into 12:14-diphenyl-, m.p. > 450°, 12:14-diphenyl-4:8-, m.p. 432°, and -2:6-dimethyl-, m.p. 420°, 12:14-diphenyl-2:6-dichloro-, 12:14-diphenyl-1:2:5:6- and -3:4:7:8-dibenzo-quinacridone. J. W. B.



and 2:6-dimethyl-, m.p. 337°; 4:8-dimethoxy-, m.p. 318°; 1:2:5:6-dibenzo- (III) [together with a little 2-β-naphthylamino-7:8-benzacridone-3-carboxylic acid (IV) (Ba salt)], and 3:4:7:8-dibenzo-, m.p. 348° [dodecachlorodihydroxy-derivative, m.p. 410° (decomp.)], -quinacridone. Et 2:5-di-β-naphthylamino-terephthalate and Me₂SO₄ at 120—150° afford a little (III) and its 12:14-Me₂ derivative, m.p. > 400° (decomp.), and (IV). When warmed with conc. H₂SO₄ (III) gives its *disulphonic acid*. By heating the appropriate (II) with K₂CO₃, PhI, and Cu in C₅H₁₁OH at 195° are obtained 2:5-bisdiphenylamino-, m.p. 292° (decomp.) (Ag, Ba, Pb, and Cu^{II} salts), -phenyl-*o*-tolylamino-, m.p. 309° (NH₄ salt), -phenyl-*p*-tolylamino-, m.p. 287° (decomp.), -phenyl-β-, m.p. 296° (Ag and Ba salts), and -α-naphthylamino-, m.p. 320° (decomp.) (Ba salt), -terephthalic acid. These are converted by heating with BzCl into 12:14-diphenyl-, m.p. > 450°, 12:14-diphenyl-4:8-, m.p. 432°, and -2:6-dimethyl-, m.p. 420°, 12:14-diphenyl-2:6-dichloro-, 12:14-diphenyl-1:2:5:6- and -3:4:7:8-dibenzo-quinacridone. J. W. B.

Morphanthridones. VI. Dehydration and cyclisation of 1:5-di-*m*-xyloylanthraquinone-mono- and -di-oxime to dimethyl-*m*-xyloylo-

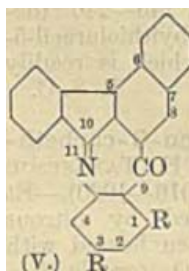
5:10-benzoylenemorphanthridone and tetramethyl-5:10-10':5'-dimorphanthridonylene. R. SCHOLL and J. DONAT. VII. Dehydration of 1-aroalloylallochrysoketoneoximes to 6:7-benz-5:10-phenylenemorphanthridones. R. SCHOLL and E. J. MULLER (Ber., 1935, 68, [B], 1062—1065, 1065—1068; cf. this vol., 869).—VI. 1:5-Di-*m*-xyloylanthracene is converted by HNO₃ (d 1.48) in boiling AcOH into 9-nitro-1:5-di-*m*-xyloylanthracene, m.p. 251—252° after softening, transformed by boiling KOH-MeOH into 1:5-di-*m*-xyloylanthraquinone-9-oxime (I), m.p. 219.5—220.5° (decomp.) after softening. (I) is preferably obtained by the action of NH₂OH on 1:5-di-*m*-xyloylanthraquinone in boiling EtOH and is separated from non-cryst. 1:5-di-*m*-xyloylanthraquinone-9:10-dioxime (II) by taking advantage of the solubility of the latter in aq. NaOH. (I) is transformed in boiling PhNO₂ containing HCl into 6'-*m*-xyloylo-5:10-benzoylene-1:3-dimethylmorphanthrid-9-one (III), m.p. 256.5—258°. Under similar



conditions (or in boiling AcOH) (II) passes more readily into 1:3:1':3'-tetramethyl-5:10-10':5'-dimorphanthrid-9:9'-onylene (IV), m.p. > 350°.

VII. Dehydrations analogous to those observed with 1-aroalloylanthraquinone-9-oximes and 1:5-diaroylanthraquinone-9:10-oximes are observed in the fluorenone series if anhyd. ZnCl₂ is used in place of the customary dehydrating agents, which yield only red to black amorphous resins.

1-*m*-Xyloylallochrysoketone is converted by NH₂OH, HCl and BaCO₃ in boiling EtOH into 1-*m*-xyloylallochrysoketone-9-oxime, decomp. 254—255° when rapidly heated (Na salt), converted by ZnCl₂ at 170—180° and then at 190° into 6:7-benz-5:10-phenylene-1:3-dimethylmorphanthridone (V; R=Me), m.p. 237°. allochrysoketone-1-carboxyl chloride, C₆H₆, and AlCl₃ at 60—70° afford 1-benzoylallochrysoketone, m.p. 220—222°, the oxime, decomp. about 250°, of which is transformed by ZnCl₂ into 6:7-benz-5:10-phenylene-morphanthridone (V; R=H), m.p. 227—228°.



H. W.

New mode of formation of hydantoin derivatives. Z. JERZMANOWSKA-SIENKIEWICZOWA (Rocz. Chem., 1935, 15, 202—208).—Et maleate or fumarate in EtOH and CO(NH₂)₂ in presence of NaOEt afford chiefly the *ureide*, decomp. at 273—274°, of hydantoin-5-acetic acid, together with the free acid (I) (Me

ester, m.p. 123°). Maleyl monoureide (II) affords *fumaryl monoureide* (III), decomp. at 262—264°, when heated with aq. HCl at 90°; the ureides yield respectively maleic and fumaric acids when hydrolysed with aq. KOH. (I) is obtained from (II) in 46%, and from (III) in 12% yield, by heating with MeOH-KOH; the reaction does not take place when EtOH is substituted for MeOH. *Fumaryl diureide*, decomp. at 285°, is obtained from fumaryl chloride and CO(NH₂)₂.

R. T.

3 : 4-Pyridino-7 : 8 : 9-triazoles. O. BREMER (Annalen, 1935, 518, 274—289).—Reduction (Na₂S₂O₄) of 3-nitro-4-aminopyridine (I) affords the 3 : 4-(NH₂)₂-compound (II), m.p. 215—216° (*dihydrochloride* + H₂O and anhyd., not melting at 280°), converted by HNO₂ into 3 : 4-pyridino-7 : 8 : 9-triazole + EtOH and solvent-free, m.p. 240° [*K* salt + 0.5H₂O; *hydrochloride*, m.p. 210° (decomp.)] (cf. this vol. 226 for nomenclature). With Br-AcOH-KOAc (I) gives its 5-*Br*-derivative, m.p. 181°, reduced to 5-bromo-3 : 4-di-aminopyridine, whence 5-bromo-3 : 4-pyridino-7 : 8 : 9-triazole (*K* salt + 4EtOH; *hydrochloride*) is obtained. (I) after reduction with SnCl₂-HCl (*d* 1.19) and treatment with Cl₂-H₂O gives the 6-*Cl*-derivative, m.p. 157—158°, of (II), converted into 6-chloro-3 : 4-pyridino-7 : 8 : 9-triazole, not melting at 280°. By condensation of 4-chloro-3-nitropyridine with the appropriate amine are obtained 3-nitro-4-methylamino-, m.p. 162—163°, -4-ethylamino-, m.p. 74° (5-*Br*-derivative, not pure; reduced to 3-amino-4-ethylamino-, m.p. 129—130°), -4-*n*-butylamino-, m.p. 47—48° (3-NH₂-compound, sinters 58°, m.p. 72—73°), -4-benzylamino-, m.p. 103° (3-NH₂-compound, m.p. 67—68°), -4-diethylaminoethylamino-, b.p. 166°/1 mm. (3-NH₂-compound, b.p. 181.5°/1 mm.), -4-β-hydroxyethylamino-, m.p. 144° (*hydrochloride*, m.p. 205—206°), -4-β-aminoethylamino-, unstable in air (*Ac* derivative, m.p. 176°; *dihydrochloride*, decomp. 265°), and (from 2-chloro-5-nitropyridine), 5-nitro-2-anilino-, m.p. 134° (*NO*-derivative, m.p. 112°), -pyridine. From these, by reduction (isolated products in parentheses above) and HNO₂ are obtained 9-methyl-, m.p. 120° [*picrate*, m.p. 178.5°; *hydrochloride*, m.p. 223° (decomp.)]; *methiodide*, m.p. 194—195°, 9-ethyl-, sinters 40°, m.p. 48°, b.p. 121.5°/1 mm. [*picrate*, m.p. 177°; *hydrochloride*, m.p. 183°; *methiodide*, m.p. 166—167°], 9-*n*-butyl-, b.p. 128°/1 mm. (*hydrochloride*, sinters 143°, m.p. 148°), 9-benzyl-, m.p. 124° (*hydrochloride*, m.p. 220°), 9-diethylaminoethyl-, b.p. 147°/1 mm., 9-β-hydroxyethyl-, m.p. 143—144° (converted by aq. EtOH-HCl into the 9-β-chloroethyl derivative, m.p. 110—111°, converted by 10% KOH-MeOH into the 9-vinyl compound, m.p. 93°), and 5-bromo-9-ethyl-, m.p. 119.5°, -3 : 4-pyridino-7 : 8 : 9-triazole. 4-Chloro-3-nitropyridine with C₂H₄(NH₂)₂·H₂O affords αβ-di-(3-nitro-4-pyridylamino)ethane, not melting at 270° (*dihydrochloride*), reduced (Na₂S₂O₄-COMe₂) to αβ-di-(3-amino-4-pyridylamino)ethane, decomp. 270°. 3-Nitro-4-pyridylhydrazine when heated with cyclohexanone in AcOH-EtOAc affords cyclohexanone-3-nitro-4-pyridylhydrazone, m.p. 91—92°. 2-Chloro-3-bromo-5-nitropyridine (PCl₅ on the 2-OH-compound) has m.p. 69.5°.

J. W. B.

Constitution and biological activity of flavins. R. KUHN and H. RUDY (Naturwiss., 1935, 23, 286).—

Synthetic and natural lactoflavin are readily esterified with H₃PO₄ by means of the glycerol extract from the small intestine of rats, whilst, under the same conditions, 6 : 7-dimethyl-9-*l*-araboflavin (this vol., 262, 760) is only slightly esterified, and 6 : 7 : 9-trimethylflavin remains unaffected. The extent of esterification runs parallel to the growth-promoting action of these substances. Enzymic esterification (this vol., 1035) therefore affords a new method for characterising flavins. It is expected that other factors apart from the redox potential and the ability to form an ester with H₃PO₄ are of importance in the relation between the chemical constitution and growth-promoting action of flavins.

H. G. M.

Synthesis of flavins. P. KARRER, H. SALOMON, K. SCHOPP, and F. BENZ (Naturwiss., 1935, 23, 355—356).—The lactoflavin isomeride, 6 : 7-dimethyl-9-*d*-1'-lyxitylisoalloxazine, m.p. 280—282°, [α]_D + 59.8° (± 5°) in 0.05*N*-NaOH (*Ac*₄ derivative, m.p. 225—226°), has been synthesised. Its properties confirm the identity of lactoflavin (vitamin-B₂) with the ribityl-flavin (cf. A., 1934, 1233; this vol., 359, 631).

F. O. H.

Porphyrins. XXXIV. Porphyrins with unsaturated side-chains. Interaction of diazomethane and ethyl diazoacetate and vinylpyrroles. H. FISCHER and C. E. STAFF (Z. physiol. Chem., 1935, 234, 97—126; cf. this vol., 362).—Sublimation of 5-carbethoxy-2 : 4-dimethylpyrrole-3-fumaric acid (I) (*Me* ester, m.p. 177°; *Me*₂ ester, m.p. 126°) at 190—200° in a vac. yields an acid, m.p. 237°, isomeric with 5-carbethoxy-2 : 4-dimethylpyrrole-3-acrylic acid (II). (I) with Pr^oOH and HCl gives the *Pr*^o ester, m.p. 126°, of (very probably) 5-carbethoxy-2 : 4-dimethylpyrrole-3-maleic acid and with Br in AcOH *o*-carbethoxy-2 : 4-dimethylpyrrole-3-maleic anhydride (III), m.p. 208° [corresponding acid loses H₂O at 175° to give (II); *Me* ester, m.p. 180°; *Me*₂ ester, m.p. 133°]. The *Me*₂ ester of (I) with Br yields the *Me*₂ ester, m.p. 140°, of 5-carbethoxy-4-methyl-2-bromomethylpyrrole-3-fumaric acid (IV), with SO₂Cl₂ the *Me*₂ ester, m.p. 138°, of 5-carbethoxy-4-methyl-2-chloromethylpyrrole-3-fumaric acid, with 2SO₂Cl₂ the *Me*₂ ester, m.p. 152°, of 5-carbethoxy-4-methyl-2-dichloromethylpyrrole-3-fumaric acid, and with 3SO₂Cl₂ a Cl₃-compound which with H₂O gives the *Me*₂ ester, m.p. 181° (*Me* ester, m.p. 143°), of 2-carboxy-5-carbethoxy-4-methylpyrrole-3-fumaric acid. (IV) with MeOH gives the *Me*₂ ester, m.p. 93°, of 5-carbethoxy-4-methyl-2-methoxymethylpyrrole-3-fumaric acid (V) and with NH₂Ph the *Me*₂ ester, m.p. 120°, of 5-carbethoxy-4-methyl-2-anilinomethylpyrrole-3-fumaric acid. Prolonged action (4 weeks) of CH₂N₂ on the *Me*₂ ester of (V) gives the *Me*₂ ester, m.p. 117—118° (decomp.), of 5-carbethoxy-4-methyl-2-methoxymethyl-3-dicarboxypyrazolinylpyrrole. Reduction of (V) with Na amalgam gives the *Me*₂ ester, m.p. 71°, of 5-carbethoxy-4-methyl-2-methoxymethylpyrrole-3-succinic acid (VI). The *Me*₂ ester of (IV) with H₂O at 100° for 1 hr. gives an oil and a cryst. substance, m.p. 132—135°. Alkaline hydrolysis of (I) gives 5-carboxy-2 : 4-dimethylpyrrole-3-fumaric acid, m.p. 188° (*Me*₂ ester, m.p. 127°). With NH₂Ph at 160—170° (I) gives *o*-carbethoxy-2 : 4-dimethylpyrrole-3-maleic anil (VII), m.p. 211°, 5-carbethoxy-2 : 4-di-

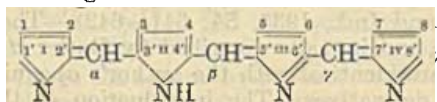
methylpyrrole-3-succinic acid (VIII) gives the corresponding *anil*, m.p. 187—188°, the Et₂ ester of 5-carbethoxy-2:4-dimethylpyrrole-3-methylmalonic acid gives the corresponding *anil*, m.p. 180°. Hydrolysis of (VII) gives 5-carboxy-2:4-dimethylpyrrole-3-maleic *anil*, which yields 5-carbomethoxy-2:4-dimethylpyrrole-3-maleic *anil*, m.p. 204°, with CH₂N₂. (VII) with 2Br gives 5-carbethoxy-2:4-dimethylpyrrole-3-N-phenylbromomaleic imide, m.p. 216°, and with 4Br 5-carbethoxy-4-methyl-2-bromomethylpyrrole-3-N-phenylbromomaleic imide, m.p. 221° (decomp.); this with MeOH gives 5-carbethoxy-4-methyl-2-methoxymethylpyrrole-3-N-phenylbromomaleic imide, m.p. 179°, and with aq. EtOH 5-carbethoxy-4-methyl-2-ethoxymethylpyrrole-3-N-phenylbromomaleic imide, m.p. 141°. The Me₂ ester of (VIII) with 1.05 mols. of Br gives the Me₂ ester, m.p. 123°, of 5-carbethoxy-4-methyl-2-bromomethylpyrrole-3-succinic acid (IX), which with MeOH gives the Me₂ ester of (VI). The Me₂ ester of (IX) with H₂O (1 hr.) loses CH₂O to give 5:5'-dicarbethoxy-4:4'-dimethyl-3:3'-tetramethyldisuccinyl-2:2'-pyrromethane (X), m.p. 170°. Hydrolysis of (X) with 8NaOH gives the Na₆ salt of 5:5'-dicarboxy-4:4'-dimethyl-3:3'-disuccinyl-2:2'-pyrromethane, which with HCO₂H and then HCl in MeOH gives the Me₃ ester, m.p. 317°, of 1:4:5:8-tetramethylporphyrin-2:3:6:7-tetrasuccinic acid (XI) (Fe salt, m.p. 228°). The Me₃ ester of (XI) with dil. HCl at 210° gives coproporphyrin II. After hydrolysis and oxidation with CrO₃ at >30° the Me₃ ester of (XI) gives carboxylated *haematic anhydride*, C₉H₆O₇, m.p. 173°; by oxidation at <0° carboxylated *haematic acid*, C₉H₆O₈N, m.p. 195° (decomp.), is obtained. The Me₂ ester of (VIII) with 2SO₂Cl₂ gives an α -dichloromethyl compound, which yields the Me₂ ester, m.p. 113° (*oxime*, m.p. 128°; *semicarbazone*, m.p. 179°), of 2-aldehydo-5-carbethoxy-4-methylpyrrole-3-succinic acid with MeOH and with 3 l mols. of SO₂Cl₂. The Me₂ ester of (VIII) gives a Cl-compound which, with MeOH, yields the Me₂ ester, m.p. 114°, of 2-carbomethoxy-5-carbethoxy-4-methylpyrrole-3-succinic acid. (I) with CH₂N₂ gives the Me₂ ester, m.p. 126°, of 5-carbethoxy-2:4-dimethylpyrrole-3-pyrazolinedicarboxylic acid; on the Me or Et ester of (II) the corresponding *pyrazolines*, m.p. 211° and 172—175°; on 5-carbethoxy-2:4-dimethyl-3-(ω -cyano- ω -carbethoxyvinyl)pyrrole (XII) (with loss of N) the corresponding cyclopropane derivative, m.p. 116°; on 5-carbethoxy-2:4-dimethyl-3-(ω -dicyanovinyl)pyrrole (XIII) 5-carbethoxy-2:4-dimethyl-3-(2:2'-dicyanocyclopropyl)pyrrole (XIV), m.p. 161°; on 2:4-dimethyl-3-(ω -cyano- ω -carbethoxyvinyl)pyrrole-3-carboxylic acid a substance, C₁₅H₁₈O₄N₂, m.p. 139°; on 2:4-dimethyl-3-(ω -dicyanovinyl)pyrrole the corresponding cyclopropane derivative, m.p. 160°; and on 2-carbomethoxy-5-carbethoxy-4-methyl-3-(ω -dicyanovinyl)pyrrole with addition of 2CH₂ a substance (XV), m.p. 123°. CHN₂·CO₂Et with (XII) and (XIII) gives, with loss of N, the cyclopropane derivatives, m.p. 124° and 149°; with the Me ester of (II) a *pyrazoline* derivative, m.p. 143° (decomp.); and with mesitylene an acid, C₁₁H₁₄O₂, m.p. 140° (ICHN₂·CO₂Et added). 5-Carbethoxy-2:4-dimethyl-3-carbomethoxypyrazolinylpyrrole on alkaline hydrolysis and decarboxylation gives 2:4-

dimethyl-3-carboxypyrazolinylpyrrole, m.p. 165° (decomp.), which with CrO₃ gives *pyrazoline-3:4-dicarboxylic acid*, m.p. 233° (decomp.). Me 5-carbethoxy-2:4-dimethylpyrrole-3- α - β -dibromoacrylate [from the Me ester of (II)] with CHNa(CO₂Et)₂ gives the Me ester, m.p. 159°, of 5-carbethoxy-2:4-dimethylpyrrole-3- β -bromoacrylic acid. (XIV) on alkaline hydrolysis loses HCN and gives a monocarboxylic acid, C₉H₁₁O₃N, m.p. 229° (decomp.) (Me ester, m.p. 145—148°), and with Br in MeOH it gives 2-carbomethoxy-5-carbethoxy-4-methyl-3-(2:2'-dicyanocyclopropyl)pyrrole, m.p. 128°. Hydrolysis of (XV) gives 3-propionyl-4-methylpyrrole-2:5-dicarboxylic acid, m.p. 203° (Me₂ ester, m.p. 48°). 2-Carbomethoxy-5-carbethoxy-3-(2-cyano-2'-carbethoxycyclopropyl)-4-methylpyrrole, m.p. 162°, is obtained from 5-carbethoxy-3-(2-cyano-2'-carbethoxycyclopropyl)-2:4-dimethylpyrrole by the action of Br and MeOH. 3-Acetyl-2:4-dimethylpyrrole-5-carboxylic acid [from 3-acetyl-5-carbethoxy-2:4-dimethylpyrrole (*oxime*, m.p. 195°)] with CH₂N₂ gives 3-acetyl-5-carbomethoxy-2:4-dimethylpyrrole, m.p. 159°. The *oxime* of 3-acetyl-2:4-dimethylpyrrole has m.p. 136°. W. McC.

Constitution of bile pigment. XIII. Constitution of bilirubin and its azo-dyes and the Gmelin reaction. H. FISCHER and H. W. HABERLAND (Z. physiol. Chem., 1935, 232, 236—258; cf. this vol., 632).—Catalytic hydrogenation (1 mol. of H₂) of bilirubin (I) gives 1':8'-dihydroxy-1:3:5:7-tetramethyl-8-ethyl-4:5-di-(β -carboxyethyl)-2-vinyldihydro-bilin (II), m.p. 315°. Total hydrogenation (3H₂) of (II) affords mesobilirubinogen, partial (H₂) yields mesobilirubin. With conc. HNO₃, (II) gives methyl-ethylmaleimide (< 50% of theory). Fusion of (II) with resorcinol yields mesoxanthobilirubin acid. Therefore in (I) the 8'-OH and the vinyl group in the pyrrole ring IV must have formed a dihydrofuran ring. The furan ring is opened by hydrogenation before the saturation of the vinyl group. With Br in CHCl₃, (I) gives tetrabromoglaucobilin hydrobromide (III), m.p. > 300° [Me ester (IV), sinters 160—168°; Zn salt]. Reduction of (III) with HI and subsequent oxidation with PbO₂ affords methylethylmaleimide. Reduction of (III) with Na-Hg and oxidation with CrO₃ yields a substance, m.p. 160—165°. Hydrogenation (Pd) of (IV) gives glaucobilin Me₂ ester. (III) is therefore diketo-1:3:6:7-tetramethyl-2:8-dibromoethyl-4:5-di-(β -carboxyethyl)bilin hydrobromide. The stages of the Gmelin reaction of (IV) are described and the mechanism is discussed. Mesobilirubin is oxidised by benzoquinone or PbO₂ to the green stage which isomerises to glaucobilin (blue-green or blue), also by PbO₂ to a higher stage of oxidation (blue) isomeric with the violet compound.

When coupled with PhN₂Cl mesobilirubin IX α -Me₂ ester hydrochloride gives a mixture (V), m.p. 184—185°, mesobilirubin XIII α -ester hydrochloride yields 5-hydroxy-5'-azobenzene-4:3'-dimethyl-3-ethyl-4'- β -carbomethoxyethylpyrromethene hydrochloride (VI), m.p. 196—197°. Mesobilirubin III α -ester hydrochloride gives 5-hydroxy-5'-azobenzene-3:3'-dimethyl-4-ethyl-4'- β -carbomethoxyethylpyrromethene hydrochloride (VII), m.p. 213°. (V) consists of (VI) and (VII). Copro-bilirubin Me₂ ester dihydrochloride affords 5-hydroxy-

5'-azobenzene-4:3'-dimethyl-3:4'-di-(β -carbomethoxyethyl)pyrromethene hydrochloride (VIII), m.p. 176°. "Analytical" Me neoxanthobilirubate gives (V). Me neo- and isoneo-xanthobilirubate give, respectively, (VI) and (VII). 5-Hydroxy-4:3'-dimethyl-3:4'-di-(β -carbomethoxyethyl)pyrromethene yields (VIII). The numbering of the C atoms of bilin is:



J. H. B.

Blood-pigment. XVII. Human hæmoglobins. XVIII. Globin and its hæmin-linking groups. XIX. Methæmoglobin and its compounds with hydrogen peroxide, cyanides, fluorides, and sulphides.—See this vol., 878.

Magnetic behaviour of heavy metal compounds of the phthalocyanines.—See this vol., 924.

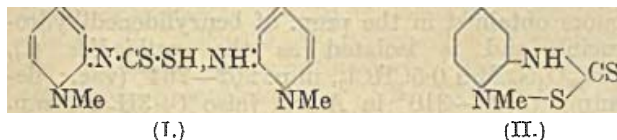
Synthesis of Δ^2 -oxazolines and Δ^2 -thiazolines from N-acyl- β -aminoethyl alcohols. H. WENKER (J. Amer. Chem. Soc., 1935, 57, 1079—1080).— $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (I) and the appropriate acid at 160—200° give the N-formyl (II), b.p. 191—193°/10 mm., -Ac, b.p. 195—196°/10 mm., -propionyl, b.p. 201—203°/10 mm., and -Bz, b.p. 230—231°/10 mm., derivatives. At 260—280° these afford 2-methyl-[picrate, m.p. 163° (lit. 159—160°)], -phenyl-, b.p. 246—248°, and -ethyl- Δ^2 -oxazoline, b.p. 124—125° (picrate, m.p. 154°), in 30, 22, and 35% yield, respectively. (II), however, gives CO and (I). With P_2S_5 Δ^2 -thiazoline and its 2-Me, -Et [picrate, m.p. 138° (lit. 135°)], and -Ph derivatives are formed.

R. S. C.

Chromate oxidation of o-toluenesulphonamide. I. G. ZILBERG (Khim. Farm. Prom., 1934, No. 4, 22—24).—The production of saccharin by this method is described; $\text{K}_2\text{Cr}_2\text{O}_7$ is superior to $\text{Na}_2\text{Cr}_2\text{O}_7$ for the purpose.

CH. ABS. (r)

Action of carbon disulphide on methylpyridone-imide. K. S. TOPITSCHJEV (Gazzetta, 1935, 65, 317—321).— CS_2 (1 mol.) reacts in EtOH with methylpyridoneimide (A., 1921, i, 450) (2 mols.) to form the salt (I), m.p. 160°, of the latter with its dithiocarbamic



(I.)

(II.)

acid. With CS_2 in excess, the product is N-methylpyridodithiodiazolone (II), m.p. 135°, b.p. 173°/3 mm., a substance of the "Hector's base" type. E. W. W.

Alkaloids of *Heliotropium lasiocarpum*. III. Hydroxyheliotridane. G. MENSCHIKOV (Ber., 1935, 68, [B], 1051—1054; cf. A., 1933, 727).—Catalytic hydrogenation (Adams) of heliotrine (I) leads to the absorption of 4 H with production of hydroxyheliotridane (II), $\text{C}_8\text{H}_{15}\text{ON}$, b.p. 126—128°/12 mm., m.p. 60—65°, $[\alpha]_D -14.5^\circ$ in H_2O [methiodide, m.p. 296°; picrate, m.p. 196° (decomp.) when rapidly heated], and heliotric acid. Reduction therefore occurs exclusively in the basic portion of (I) and is accompanied by reduc-

tion of the esterified OH, since similar treatment of heliotridine dibenzoate hydrochloride affords BzOH and non-cryst. hydroxyheliotridane benzoate. (II) is probably a *tert*.-alcohol, since it cannot be oxidised to a ketone or acid. It is transformed by conc. H_2SO_4 at 170—175° into the base (III), $\text{C}_8\text{H}_{13}\text{N}$, b.p. 165—166°, $[\alpha]_D -160^\circ$ [picrate, m.p. 222° (decomp.)], probably identical in structure with the product of the action of NaOEt on chloroheliotridane (which is therefore greatly racemised). Catalytic reduction of (III) gives a base, $\text{C}_8\text{H}_{15}\text{N}$, b.p. 167—168.5°, $[\alpha]_D -99.5^\circ$ (picrate, decomp. 236°), which is almost certainly heliotridane in an optically purer form than that described previously.

H. W.

[Simplification of Pictet's synthesis of nicotine.] E. SPATH and F. KUFFNER (Ber., 1935, 68, [B], 1125—1127; cf. this vol., 635).—An acknowledgment of the priority of Wibaut (this vol., 872).

H. W.

Amidation of alkaloids with sodium and potassium amides. Structures of chloroanabasine isomerides. M. I. KABATSCNIK and M. M. KATZNELSON (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 35—41; cf. A., 1934, 538).—The α -series of compounds of Menschikov *et al.* (A., 1934, 1014) is an α' -series. The authors re-state their previous conclusions.

J. L. D.

Vasicine. K. S. NARANG and J. N. RAY (Current Sci., 1935, 3, 552).—The picronolate of the reduction product of the compound B (this vol., 765) is identical with that of reduced vasicine. The structure of vasicine is probably that given by Morris *et al.* (*ibid.*, 873).

E. W. W.

Ergotocine. M. S. KHARASCH and R. R. LEGAULT (J. Amer. Chem. Soc., 1935, 57, 1140—1141; cf. this vol., 827).—Ergotocine, $\text{C}_{21}\text{H}_{27}\text{O}_3\text{N}_3$ (? H_{27} or H_{29}), m.p. 158—160° (decomp. from 155°), obtained by extraction of a solution of ergot at p_H 6.7—7.0 with CHCl_3 (not Et_2O , C_2HCl_3 , or C_6H_6), forms onium salts (oxalate, maleate, malonate, tartrate, and malate) with acids and also alkali salts, contains 3 active H, is hydrolysed by alkali to (?) lysergic acid and a basic fragment, and closely resembles its maleate, ergotocine, and ergotamine in absorption spectrum. Ergine has no oxytocic activity in doses up to 4 mg. given orally to human mothers.

R. S. C.

Ergobasine, a water-soluble alkaloid from the ergot of Seigle. A. STOLL and E. BURCKHARDT (Compt. rend., 1935, 200, 1680—1682).— CHCl_3 extracts ergobasine, $\text{C}_{19}\text{H}_{23}\text{O}_2\text{N}_3$ (I), decomp. at 162°, $[\alpha]_D +90^\circ$, from the H_2O -sol. portion of the alkaloids of ergot. (I) fluoresces in aq. solution, and is sensitive to light and O_2 . It gives the general reactions of alkaloids, and affords cryst. salts.

J. L. D.

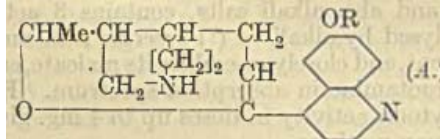
Preparation of ergometrine.—See this vol., 894.

Synthetic alkaloids from narcotine. E. V. SESHACHARYULU and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 159—168).—Condensation of cotarnine (from HNO_3 and narcotine) with substances containing reactive $\cdot\text{CH}_2$ in presence of Ac_2O yielded the anhydro-N-acetylcotarnine derivatives of hippuric acid, m.p. 235°, camphor, m.p. 188°, phenyl-

acetic acid, m.p. 193°, phenylacetone, m.p. 196°, Et cyanoacetate, m.p. 95°, Et malonate, m.p. 195°, Et oxaloacetate, m.p. 185°, Et acetoacetate, m.p. 192°, Et acetonedicarboxylate, m.p. 173°, Et succinosuccinate, m.p. 189°, thiohydantoin acetate, m.p. 227°, malonyl-carbamide acetate, m.p. 185°, deoxybenzoin, m.p. 169°, fluorene, m.p. 201°, acetylacetone, m.p. 193°, benzoyl-acetone, m.p. 199°, dimethyldihydroresorcinol, m.p. 187°, phthalide, m.p. 196°, acetophenone, m.p. 183°, 2:4-dinitrotoluene, m.p. 155°, benzylideneacetone, m.p. 203°, mesityl oxide, m.p. 194°, cinnamylideneacetone, m.p. 190°, piperonylideneacetone, m.p. 178°, furfurylideneacetone, m.p. 197°. Reactions of these substances with alkaloid reagents are described. F. O. H.

New alkaloid from the bark of *Holarrhena antidysenterica*. D. H. PEACOCK and J. C. CHOWDHURY (J.C.S., 1935, 734—735).—Lettocine, $C_{17}H_{25}O_2N$, m.p. 350—352° (methiodide, m.p. 235°), is isolated as the hydriodide, m.p. 256° (decomp.). The amount present is <0.1%; it appears to be a *tert*-base without OH. F. R. S.

Demethylation of quinidine. (MLLE.) R. LUDWICZAK and J. SUSZKO (Bull. Acad. Polonaise, 1935, A, 65—78, and Roczn. Chem., 1935, 15, 209—220; cf. A., 1933, 1312; 1934, 787).—Demethylation (60% H_2SO_4) of both quinidine and isoquinidine (I) yields cupreidine (II) and an isomeric phenolic base isocupreidine (III), m.p. 242—243°, $[\alpha]_D^{20}$ -7.0° in 96% EtOH [hydrochloride (+ H_2O), m.p. 236—237° (decomp.), $[\alpha]_D^{20}$ -35.0° in H_2O]; picrate, m.p. 204—205° (decomp.); methiodide (IV), m.p. 299—300° (decomp.), $[\alpha]_D^{20}$ -24.0° in H_2O ; dimethiodide, m.p. 212—213° (decomp.); Bz, m.p. 213—214° (decomp.) (+2HCl, EtOH, m.p. 201—207°), and *p*-toluenesulphonyl (+2HNO₃·0.5H₂O) derivative, m.p. 146—147° (decomp.); amine oxide (+ H_2O), m.p. 273—274°, which regenerates (I) on methylation with Me₂SO₄ or CH₂N₂ and is converted into (II) by 60% H_2SO_4 . (III) heated with 25% AcOH (100°; 20 hr.) yields isocupreidine (V), (A; R=H) [+0.5COMe₂,



m.p. 133° (decomp.), $[\alpha]_D^{20}$ +22.5° in 96% EtOH], also obtained by demethylation (15% HBr) of isoquinicine (A; R=Me) (cf. A., 1930, 97), formed together with *N*-methylisoquinicine by methylation with CH₂N₂ of (V). (IV) heated with NaOH (5 hr.) yields *N*-methylisocupreidine, previously named *apo-N*-methylisoquinicine (*loc. cit.*). F. R. G.

Cinchona alkaloids in pneumonia. III. *apocupreines (apoquinine)*. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1935, 57, 1083—1085; cf. this vol., 766).—“*apoQuinine*,” prepared from quinine by 25% HCl at 142—143° or by boiling 60% H_2SO_4 , is usually a mixture of α -. (I), m.p. 180—190° (decomp.), $[\alpha]$ -215° (hydrochloride, $[\alpha]$ -163°; dihydrochloride, $[\alpha]$ -223°; *H* sulphate, $[\alpha]_D$ -224°), and β -apocupreine, m.p. 180—190° (decomp.), $[\alpha]$ -194° (hydrochloride, $[\alpha]$ -145°; dihydrochloride, $[\alpha]$

-206°; *H* sulphate, $[\alpha]$ -208°), probably geometrical isomerides containing CHMe. Occasionally only one compound is obtained. (I) has pneumococidal effect *in vitro* at 1:300,000; both are very slightly toxic to mice and have high protective power. R. S. C.

apoQuinine. T. A. HENRY and W. SOLOMON (Chem. and Ind., 1935, 54, 641—642).—The α -*apo*-cupreine and its salts described by Butler *et al.* (see above) are identical with the author's *apoquinine* (I) and its derivatives. The introduction of the term *apocupreine* is deprecated. Butler's β -*apocupreine* is a mixture of (I) and a new alkaloid of low $[\alpha]$. H. W.

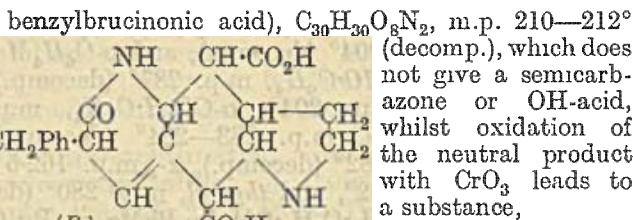
Synthesis of physostigmine (eserine). XI. Later phases of the synthetical investigations. F. E. KING and R. ROBINSON (J.C.S., 1935, 755—759).—Comparison and mixed m.p. of specimens of *dl*-noreserethole picrate and of *dl*-eserethole-*b* and its picrate, prepared by Hoshino and Kobayashi (cf. A., 1934, 667), show identity and the analytical figures for (I) as $C_{15}H_{22}ON_2$ are confirmed. De-ethylation of *l*-eserethole methiodide with HI, followed by addition of picric acid, gives *l*-eseroline methopicate, m.p. 193—195° (decomp.), in small yield. Eserethole methochloride is thermally decomposed to physostigmol Et ether, whilst the methofluoride is partly unchanged and partly converted into an unknown base (picrate, m.p. 197—198°; methopicate, m.p. 163—166°). F. R. S.

Constitution of corynanthine. C. R. SCHOLZ (Compt. rend., 1935, 200, 1624—1625).—The “ ψ -corynanthine,” obtained by treating corynanthine (I) with NaOH and re-esterifying (this vol., 365), is identical with the product from yohimbine (II) similarly treated [*i.e.*, is a Me yohimboate]. (I) and (II) are thus stereoisomeric; this is confirmed by preparing *apovohimbine* (J.C.S., 1923, 123, 1038) from both. E. W. W.

Strychnos alkaloids. LXXXVI. *iso*Benzylidenedihydrobrucine and the oxidation of 11-benzyl- and 11-nitroso-brucine. H. LEUCHS and H. BEYER (Ber., 1935, 68, [B], 1204—1210).—*iso*-Benzylidenedihydrobrucine is present in the mother-liquors obtained in the prep. of benzylidenedihydrobrucine and is isolated as the methiodide (I), $C_{30}H_{32}O_4N_2$ ·MeI·0.5CHCl₃, m.p. 262—264° (vac.; decomp.), $[\alpha]_D^{20}$ -310° in AcOH [also (+3H₂O), m.p. about 260° after softening at 180—200°, and (anhyd.), m.p. 190—195° (vac.), $[\alpha]_D^{20}$ -319.6° in AcOH, $[\alpha]_D^{20}$ -565°/d in CHCl₃]. In this and in the corresponding instance in the strychnine series the *p* position of the C₆H₅ nucleus of the alkaloid cannot therefore be



involved in the condensation. The production of a new ring (cf. A) is suggested. The condensation is induced by the reagents which cause the strychnine-isostrychnine isomerisation. (I) cannot be catalytically hydrogenated; it gives an Ac derivative, $C_{32}H_{34}O_5N_2$ ·MeI·0.5H₂O, m.p. 221—223° (vac.), $[\alpha]_D^{20}$ -288.5° in AcOH, which also resists oxidation. Treatment of benzylbrucine with KMnO₄ in COMe₂ gives an amorphous acid (.



11-Oximinobrucine when oxidised by CrO_3 in 3·6*N*- H_2SO_4 at 80—85° gives the NH_2 -acid, $C_{16}H_{20}O_6N_2$, m.p. > 360°, $[\alpha]_D^{20} +54\cdot3^\circ$ (diperchlorate), hydrogenated to the acid, $C_{16}H_{22}O_6N_2$. H. W.

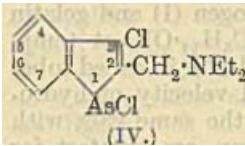
Use of liquid hydrogen chloride in preparation of dichloro-arsines. F. GOVAERT (Compt. rend., 1935, 200, 1603—1605).—Treatment of $NH(C_6H_5)_2AsR$ with HCl (cf. A., 1931, 1435) is difficult when $R=Bu^+$, since (I) decomposes at its m.p. Reaction in $C_{10}H_{12}$, Et_2O , or SO_2 was unsatisfactory, but in HCl at -85° to -90° was immediate. After evaporating off the HCl and dissolving in CCl_4 , 80% of $NHPh_2\cdot HCl$ and tert.-butyldichloroarsine, b.p. 61°/16 mm., with 20% of 10-chloro-5:10-dihydrophenarsazine, were obtained. E. W. W.

Reaction of phenylarsine with organic compounds of tin and lead. A. N. NESMEJANOV and R. C. FREIDLIN (J. Gen. Chem. Russ., 1935, 5, 53—59).— AsH_2Ph reacts with $HgPhCl$, $HgPh_2$, $PbPh_4$, $PbPh_2Cl_2$, and $PbPh_2I_2$ to yield $(AsPh)_2$, Hg or Pb , HCl , $PbCl_2$ or PbI_2 , and C_6H_6 . It does not react with $PbEt_4$, $SnEt_4$, $SnPh_2Et_2$, and $SnEt_2Cl_2$ at low temp.; at higher temp. the reaction $3AsH_2Ph \rightarrow AsPh_3 + 2As + H_2$ takes place, and the ppt. is a mixture of Pb or Sn with As . R. T.

Constitution of sulpharsphenamine. II. New interpretation. W. J. C. DYKE and H. KING (J.C.S., 1935, 805—813).—4-Nitro-2-aminophenol with Na formaldehyde H sulphite gives Na 5-nitro-2-hydroxyanilino-*N*-methylenesulphite (+2·5 or +1·5 H_2O), whilst in HCl with CH_2O and $NaHSO_3$, followed by $NaOH$, it forms Na_3 5-nitro-2-hydroxyanilino-*NN*-dimethylenesulphite (+2 H_2O , 1·5 $MeOH$), converted into the Na_2 salt (+3·5 H_2O). Similarly prepared are Na 4-nitro-2-hydroxyanilino-*N*- (+3 H_2O), Na_2 4-nitro-2-hydroxyanilino-*NN*- (+2·5 H_2O), Na_2 2-hydroxy-5-carbomethoxyanilino-*NN*-di- (+2 H_2O), Na 3-nitroanilino-*N*- (+2 H_2O), and Na_2 3-nitroanilino-*NN*-di-methylenesulphite (+1 $MeOH$). Examination by the Elvove oxidative method of S analysis has shown that part of the S is oxidised to sulphate and part remains as dithionate. Sulpharsphenamine is a Na salt of 3:3'-diamino-4:4'-dihydroxyarsenobenzene-*NNN'*-trimethylenesulphurous acid. When NH_2Ph , *o*-anisidine, *o*- and *p*- $NH_2\cdot C_6H_4\cdot OH$, 4-amino-2-hydroxyphenylarsinic acid, and arsphenamine are treated with CH_2O and $NaHSO_3$, the solutions show a deficiency of S by the Elvove method (cf. Newbery and Phillips, A., 1928, 311). F. R. S.

New arsindole ring closure. C. MANNICH (Arch. Pharm., 1935, 273, 275—284).—When heated with

$AsCl_3$ at 150—170° $CPh\cdot C\cdot CH_2\cdot NEt_2$ affords the hydrochloride, m.p. 118—119°, of γ -chloro- γ -phenyl- Δ^{β} -propenyldiethylamine, b.p. 155°/14 mm. (methiodide, m.p. 140—141°) {reduced to $CH_2Ph\cdot [CH_2]_2\cdot NEt_2$ (I), hydrolysed to $CH_2Bz\cdot CH_2\cdot NEt_2$ (II), and giving $BzCl$ by ozonolysis}, and the hydrochloride (III), m.p. 199°, of 1:3-dichloro-2-diethylamino-methylarsindole (IV) (corresponding 1-bromohydrobromide, decomp. 205°, 1-iodohydrobromide, decomp. 194—195°, and 1-hydroxyhydrochloride, m.p. 135°),



converted by aq. KCN into 3-chloro-1-cyano-2-diethylaminomethylarsindole, m.p. 65—66° (hydrochloride, m.p. 135°). (III) fused with $NaOH\cdot KOH$ at 250° gives $BzOH$, $AcOH$, and phenolic products, and oxidation with 60% HNO_3 gives *o*-arsinobenzoic acid, not melting at 330°, converted by HI into *o*- $AsI_2\cdot C_6H_4\cdot CO_2H$. With 38% HCl at 150° (III) gives $COPhMe$ and (II), and is reduced by $HI\cdot P$ to (I). Oxidation of (IV) with 30% $H_2O_2\cdot AcOH$ affords *o*-arsinophenylacetic acid, decomp. 184—185° (Me_1 ester, decomp. 176—177°) [reduced by $HI\cdot P$ to *o*-carboxymethylphenyldi-iodoarsine, m.p. 155—170° (decomp.)], and (from the mother-liquor) β -*o*-arsinophenylpropionic acid, decomp. 165—170°. J. W. B.

Arsenicals containing the furan nucleus. W. G. LOWE and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 1081—1083).—2-Chloromercurifuran (I) and $AsCl_3$, best in hot C_6H_6 , give furyldichloroarsine (II), lachrymatory and vesicant, unstable at room temp., rapidly resinified by heat at 10 mm. or by hot $AsCl_3$, and giving furan with hot H_2O , difurylchloroarsine (III), similar to (II) in properties, and trifurylarsine (IV), m.p. 35°, which is somewhat more stable. (II) and cold $H_2S\cdot EtOH$ give furylarsine sulphide, m.p. 125° (decomp.), sol. in warm *N*- $NaOH$ and giving furan when boiled therein. (III) gives tetrafulylarsine sulphide, an oil. (IV) with $HgCl_2$ in aq. $EtOH$ regenerates (I) and with I gives 2-iodofuran. 2:5-Dichloromercurifuran and $AsCl_3$ at room temp. give a solution, which with $I\cdot CCl_4$ gives 2:5-di-iodofuran, but with H_2O affords aliphatic compounds with I As . R. S. C.

Organic mercurials. M. C. HART and H. P. ANDERSEN (J. Amer. Chem. Soc., 1935, 57, 1059—1061).—The following are prepared. Hg^{II} mandelate, m.p. 183—184°; 4-acetoxy-, m.p. 187—188°, and -nitratomercuri-2-nitroanisole, m.p. 219—220°; acetoxymmercuri-*m*-cresol, m.p. 177°; 3:5-diacetoxymmercuri-4-hydroxybenzoic acid; diacetoxymmercuri-*p*-chlorophenol, -*amyl-m*-cresol, m.p. 190°, and -2-chloro-5-hydroxytoluene; phenylmercuric acetate, m.p. 149°, lactate, m.p. 155—157°, and basic nitrate (Hg 63·2%), m.p. 179—183°; *p*-tolylmercuric nitrate, m.p. 179—180°, acetate, m.p. 138—140°, and lactate. Bacteriostatic data for these and 6 similar Hg compounds are recorded. In general simple compounds are more effective than complex ones. The most effective is *o*-hydroxyphenylmercuric chloride, m.p. 150—151° (1:75,000 in 5 min. to *S. aureus*), which is also bactericidal at 1:1000. R. S. C.

Halide-mercuri-nitrocresols -See B., 1935, 655.

Synthesis of dipeptides.—See this vol., 1014.

cycloPeptides arising from blood-albumin.—See this vol., 999.

Alcoholic hydrolysis of caseinogen and gelatin.

A. A. CHRISTOMANOS (Biochem. Z., 1935, 277, 394—400).—The degradation of caseinogen (I) and gelatin (II) by MeOH, EtOH, and *iso*-C₂H₅·OH at temp. between the b.p. of the alcohol and 220° in sealed tubes is investigated. The degree and velocity of hydrolysis above 180° approximate to the same vals. with all the alcohols, but at lower temp. are greatest for MeOH. Part of the total N resulting is volatile [24% with (I) and only 2.2% with (II)]. From the hydrolysis products of (I) were obtained leucine anhydride and leucine-valine anhydride, and the presence of a tyrosine-tryptophan compound was indicated, whilst from (II) glycylalanine anhydride was obtained. P. W. C.

X-Ray study of hydration and denaturation of proteins.—See this vol., 922.

Mol. wt. of proteins. (MME.) A. ROCHE (Bull. Soc. Chim. biol., 1935, 17, 704—744).—A lecture.

Identification of organic compounds by the mixed m.p. G. LOCK and G. NOTTES (Ber., 1935, 68, [B], 1200—1204).—The mixed m.p. method for the identification of similarly constituted compounds, particularly of polyhalogenated derivatives with closely similar m.p., is valid only when distinct depression is observed, notably when the relative proportions of the components are greatly varied. It is not sufficient to use any accidental mixture; the substances in extreme ratios must also be employed. Functional derivatives of such compounds frequently have very similar m.p. and show analogous behaviour. The following compounds are incidentally described: 2:6-dichloro-4-bromo-3-ethoxybenzaldehyde, m.p. 66.5°, from the OH-aldehyde, NaHCO₃, and Et₂SO₄, its *anil*, m.p. 59°, *oxime*, m.p. 128.5°, *phenylhydrazone*, m.p. 122°, and 2:6-dichloro-4-bromo-3-ethoxybenzoic acid, m.p. 148° (corr.); 2-chloro-4:6-dibromo-3-ethoxybenzaldehyde, m.p. 81.5°, its *anil*, m.p. 63.5°, *oxime*, m.p. 152°, *phenylhydrazone*, m.p. 113.5°, and 2-chloro-4:6-dibromo-3-ethoxybenzoic acid, m.p. 167° (corr.). H. W.

Identification of linoleic and linolenic acids. T. G. GREEN and T. P. HILDITCH (Biochem. J., 1935, 29, 1552—1563).—The best method for characterising linoleic (I) and linolenic acid (II) is oxidation with alkaline KMnO₄ to the tetra- or hexa-hydroxystearic acid, but the yields are only 40% and 15—18%, respectively, from (I) and (II). (I) of seed fats is very probably confined to one geometrical form. The isomeric tetrahydroxystearic acids obtained from (I) with alkaline KMnO₄ and with AcO₂H bear no simple relationship to each other. J. N. A.

Azides. IV. *p*-Chlorobenzazide as a reagent for the identification of phenols. C. H. KAO, H. Y. FANG, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 109—112). *p*-C₆H₄Cl·CO·N₃ and the appropriate phenol in hot PhMe give the following *N*-*p*-chlorophenylurethanes: *Ph*, m.p. 150—152°, *o*-NO₂·C₆H₄, m.p. 280—281° (decomp.), 2:4:6-

C₆H₂(NO₂)₃, m.p. 285—286° (decomp.), *o*-, m.p. 162—163°, *m*-, m.p. 203—204° (decomp.), and *p*-C₆H₄Me, m.p. 188—190°, *o*-CHO·C₆H₄, m.p. 287° (decomp.), 2-aldehydo-*p*-tolyl, m.p. 294°, *o*-CO₂H·C₆H₄, m.p. 295°, 2-carboxy-*p*-tolyl, m.p. 283—284° (decomp.), *o*-CO₂Et·C₆H₄, m.p. 282° (decomp.), α -, m.p. 162.5°, and β -C₁₀H₇, m.p. 192°, and *thymyl*, m.p. 280° (decomp.). *o*- and *p*-NH₂·C₆H₄·OH in PhMe or Bu₂O give the *carbamides* (or, less probably, urethanes), m.p. 200° and 248—250° (decomp.). These derivatives may be used for identification of the phenols.

R. S. C.

Pyrocatechol as reagent for identification of titanium.—See this vol., 951.

Acidimetric titration of *p*-hydroxybenzoic acid alone and in presence of acetic acid. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1935, 57, 973—974).—*p*-OH·C₆H₄·CO₂H (I) can be determined as a monobasic acid by titrating to 6.8 with standard NaOH, using bromothymol-blue. The results are about 0.3% high. The sum of AcOH and (I) can be determined by titrating to *p*_H 6.95 with NaOH. Phenolphthalein is unsuitable as an indicator for (I).

E. S. H.

Extraction method for the determination of acids and its application to *p*-hydroxybenzoic acid.—See this vol., 947.

Micro-copper-pyridine reaction on organic acids. A. J. STEENHAUER (Pharm. Weekblad, 1935, 72, 667—669).—Characteristic, cryst. compounds are obtained when anisic, anthranilic, benzoic, fumaric, cinnamic, salicylic (I), and acetylsalicylic (II) acids are treated with aq. CuSO₄·C₅H₅N. The test is recommended for distinguishing (I) from (II).

S. C.

2:4-Dinitrophenylhydrazine as a quantitative reagent for carbonyl compounds. II. **Benzo-phenone and acetone.** G. W. PERKINS and M. W. EDWARDS (Amer. J. Pharm., 1935, 107, 208—211; cf. A., 1934, 425).—COPh₂ and COMe₂ are determined with an error of < 3%. Iddles and Jackson's determinations of PhCHO (cf. this vol., 101) are criticised.

J. L. D.

Highly sensitive reaction of indole and pyrrole. P. SACCARDI (Annali Chim. Appl., 1935, 25, 157—159).—The reaction of Au with pyrrole in HCl solution (cf. A., 1935, 355) detects 7.05×10⁻⁶ g. of Au in 10 c.c. By H₂S 8.1×10⁻⁴ g. of Au in 10 c.c. is detectable. The min. amount of pyrrole detectable is 6.87×10⁻⁵ g. in 10 c.c. Indole behaves similarly, 1.37×10⁻⁴ g. of Au or 4.9×10⁻⁵ g. of indole being detectable.

T. H. P.

Photometric determination of small amounts of pyrrole. F. FROMM (Mikrochem., 1935, 17, 141—154).—The solution, containing 0.1—90 mg. of pyrrole (I), is made alkaline, and (I) is extracted with Et₂O. The Et₂O is removed by dropping the solution into glacial AcOH at 40—50°, the solution being then diluted to 100 c.c. and heated at 100° for 10 min. with HCl+0.05% isatin, forming pyrrole-blue (II), which is determined photometrically with filtered light. 90—97% of (I) present is converted into (II). (I) in turbid or tarry solutions may be separated as the HgCl₂ compound (III) by addition of saturated aq.

HgCl₂. (III) is dissolved in 5% aq. NaCN, the solution being made up to 100 c.c. and treated as before. (I) may also be determined photometrically by condensation with *p*-NMe₂·C₆H₄·CHO. J. S. A.

Bromo-acidimetric determination of 8-hydroxyquinoline. A. CASTIGLIONI (Annali Chim. Appl., 1935, 25, 236—240).—The action of Br-H₂O on 8-hydroxyquinoline (I) solution yields the compound C₉H₄NBr₂·OBr, which readily loses, as HBr, the Br replacing the hydroxylic H. Thus, 1 mol. of I yields, in all, 3 HBr, and may thus be determined by titration of the resulting acidity with NaOH. T. H. P.

Colour reactions for pyrimidone. N. SCHOORL (Pharm. Weekblad, 1935, 72, 669—670).—0.1N-I solution is a more sensitive and more satisfactory reagent than K₂S₂O₈ in the colour test for pyrimidone (cf. this vol., 877). S. C.

Mercurimetric method for the determination of hydrastinine, hyoscyamine, scopolamine, eserine, and apiol. Reaction for identifying apiol. A. IONESCO-MATIU and C. POPESCO (Bull. Soc. Chim. biol., 1935, 17, 671—677).—The authors' method (A., 1934, 269) of determining substances pptd. by Hg^{II} is applied to the determination of hydrastinine, hyoscyamine, scopolamine, eserine, and apiol. Apiol may be identified by the red coloration produced on warming after addition of phosphomolybdic acid and H₂SO₄. A. L.

Reaction of Weydel and its application to the colorimetric micro-determination of caffeine. G. DENIGES (Bull. Soc. Chim. biol., 1935, 17, 657—666).—The reaction of Weydel for the colorimetric determination of purine derivatives is modified by the substitution of aq. Br as oxidising agent and aq. Hg(OAc)₂ or Zn(OAc)₂ for the NH₃. A. L.

Biochemistry.

Blood. C. C. STURGIS, R. ISAACS, S. M. GOLDHAMER, F. H. BETHELL, and G. E. FARRAR (Arch. Int. Med., 1935, 55, 1001—1081).—A review of recent literature on diseases affecting the condition of the blood. A. L.

Permeability of the erythrocyte to glycerol. A. K. PARPART and J. C. SHULL (J. Cell. Comp. Physiol., 1935, 6, 129—135).—Data for ox erythrocytes are given. A. G. P.

Solvent-water in the normal mammalian erythrocyte. A. K. PARPART and J. C. SHULL (J. Cell. Comp. Physiol., 1935, 6, 137—150).—Approx. 50 vol.-% of the cell-H₂O can act as solvent for glycerol or (CH₂·OH)₂. Urea probably dissolves in or reacts with other than aq. constituents of the cell. A. G. P.

Variation of the protein content of the red corpuscles after intake of food. G. PETRANYI and A. BLAZSÓ (Z. ges. exp. Med., 1934, 94, 689—695; Chem. Zentr., 1935, i, 741—742).—The increase of protein in the red corpuscles after ingestion of food does not originate from hæmoglobin. The corpuscles apparently play a part in protein transport. R. N. C.

Absorption of light by carbon monoxide-hæmochromogens. S. SCHÖNBERGER (Biochem. Z., 1935, 278, 428—436).—The max. on the curves for neutral and alkaline (Na₂CO₃) CO-hæmoglobin are at the same points, but the curve for the alkaline form is 4% higher than that for the neutral. The curves for CO-hæmochromogens (globin, albumin, NH₃) are identical (in the visible part of the spectrum) with that of neutral CO-hæmoglobin, but the curve for CO-hæm is not. W. McC.

Determination of bilirubin in blood by the diazo-method. E. G. GODFRIED (Biochem. J., 1935, 29, 1337—1339).—The modification by McNee and Keefer (Brit. Med. J., 1925, ii, 52) of Thannhauser and Andersen's method (A., 1922, ii, 671) is satisfactory for clinical purposes. F. O. H.

Method for making indefinite or invisible bloody finger-prints visible. M. WAGENAAR (Pharm. Weekblad, 1935, 72, 463—470).—The part is painted with a solution of benzidine (0.1 g.) and 3% H₂O₂ (3 c.c.) in EtOH (40 c.c.), when a permanent brown stain is obtained. S. C.

New hæmoglobinometer, the "Orthohæmometer." K. BÜRGER (Münch. med. Woch., 1934, 81, 1815—1816; Chem. Zentr., 1935, i, 603).—Dil. blood is treated with a little Na₂S₂O₄ and compared colorimetrically with a standard. The hæmoglobin content per erythrocyte averages 32.4 × 10⁻¹² g. in men and 30.2 × 10⁻¹² g. in women. A. G. P.

Properties of reptilian blood. II. The gila monster (*Heloderma suspectum*, Cope). H. T. EDWARDS and D. B. DILL. **III. The chuckwalla (*Sauromalus obesus*, Baird).** D. B. DILL, H. T. EDWARDS, A. V. BOCK, and J. H. TALBOTT (J. Cell. Comp. Physiol., 1935, 6, 21—35, 37—42).—II. Compared with human blood that of *H. suspectum* has a low hæmoglobin (I) content and the (I) has a relatively low buffer val. The O₂ dissociation curve at 20° resembles that of man at 37.5°. The effects of temp. and reaction on the combination of O₂ and CO₂ with blood are examined.

III. The blood of *S. obesus* resembles that of *H. suspectum* except in its response to temp. changes. A. G. P.

Adult blood after eleven years on egg and milk diet. J. HAMEL, M. CHAVAROT, and P. AUBRY (Compt. rend. Soc. Biol., 1935, 119, 864—866).—After feeding with egg and milk through the nose for 11 years the blood was normal. H. G. R.

Formation of cyclopeptides arising from blood-albumin by hydrolysis in the autoclave. V. S. SADIKOV, E. V. LINDQUIST-RISAKOVA, R. G. KRISTALLINSKAJA, V. N. MENSCHIKOVA, L. N. RUBEL, E. G. CHALEZKAJA, and A. G. PESSINA (Biochem. Z., 1935, 278, 60—70).—Hydrolysis of this protein by different methods (e.g., with 25% HCl for 36—72 hr., with 3% H₂SO₄ in the autoclave at 180° for 2 hr.,

with alkali, etc.) gives very different results. Autoclave hydrolysis with raised temp. for a shorter time enriches the yields of cyclic compounds, which must be regarded as the precursors of the NH_2 -acids, and lessens the degradation, *e.g.* of tryptophan. The greater part of the *cyclopeptides* is then separated by continuous extraction with Et_2O , CHCl_3 , and EtOAc . Tables summarise the total, amide-, NH_2 -, and humin-N, and the tyrosine, tryptophan, cystine, histidine, methionine, etc. contents of the various fractions and of the acid hydrolysis products of these fractions. P. W. C.

Spectroscopic determination of gum acacia in blood. Rate of disappearance in normal dogs. S. A. PEOPLES and N. M. PHATAK (Proc. Soc. Exp. Biol. Med., 1935, 32, 635—637).—Gum acacia (I) is determined in blood by Folin-Wu pptn., dilution of the filtrate, hydrolysis with H_2SO_4 , addition of bile salts, and spectroscopic examination in comparison with a standard solution. The intensity of the absorption band \propto the (I) content. (I) is eliminated very slowly from the blood-stream in normal dogs. R. N. C.

Diurnal variations in plasma-lipids. E. M. BOYD (J. Biol. Chem., 1935, 110, 61—70).—Free and ester cholesterol (I), phospholipins, and neutral fats in normal subjects at different times of the day showed only slight variations which could not be correlated with the intake of ordinary meals or sleep. The variation from one person to another was 2—3 times $>$ the average variation per person per day. The conditions for hydrolysis in the total (I) determination were standardised. H. D.

Blood-cholesterol and resistance to saponin in animals on liver diet. G. INGRASSIA (Riv. Patol. sper., 1934, 13, 459—468).—In dogs receiving raw liver daily, blood-cholesterol rose, but on continued liver administration returned to normal. The red blood-cells showed a greater resistance to the hæmolytic action of saponin. NUTR. ABS. (m)

Determination of cholic acids in blood. B. JOSEPHSON (Biochem. J., 1935, 29, 1519—1524).—Details are given for the determination of bile acids in blood. Practically no loss of acids occurs if the proteins are pptd. with EtOH containing $\text{Ba}(\text{OH})_2$. With concn. of acids $>$ 5 mg. per 100 c.c. the error is \geq 6—8%. J. N. A.

Determination of total fatty acids in blood. C. P. STEWART and E. B. HENDRY (Biochem. J., 1935, 29, 1677—1682).— EtOH-CHCl_3 and EtOH -light petroleum mixtures will extract the same amount of fatty acid from blood as do $\text{EtOH-Et}_2\text{O}$ mixtures. The yield of fatty acid is not increased by refluxing the blood with $\text{EtOH-Et}_2\text{O}$, but some oxidation occurs giving an increase in CO_2H groups. Refluxing does not increase the recovery of lipin-P. EtOH-NaOH and NaOEt are equally good as hydrolysing agents, and a single hydrolysis by the former will give the max. yield of fatty acids. The filtration method is compared with the method in which fatty acids are extracted by light petroleum. The sol. fatty acids in blood amount to $<$ 3% of the total. P W C

Presence of creatinine in blood. J. A. BEHRE and S. R. BENEDICT (J. Biol. Chem., 1935, 110, 245—248).—A criticism of the conclusion by Hayman *et al.* (this vol., 642) that creatinine is the chief chromogenic compound in blood-plasma. E. A. H. R.

Determination of blood-indole. P. MAZZOCCO (Compt. rend. Soc. Biol., 1935, 119, 879—881).—The method of Garcia-Blanco and Vidal (A., 1933, 1065) has been modified utilising Et_2O -extraction. H. G. R.

Diazo-value of blood. G. BARAC (Compt. rend. Soc. Biol., 1935, 119, 545—547).—There are only traces of monophenols in the blood, the diazo-val. being due principally to glyoxalines. H. G. R.

Spectrophotometric study of the diazo-reaction of the blood. A. LAMBRECHTS and G. BARAC (Compt. rend. Soc. Biol., 1935, 119, 547—549; cf. preceding abstract).—The absorption spectrum of the diazo-reaction of blood is nearly identical with that of the glyoxalines. H. G. R.

Specific carbohydrates of blood groups. II. K. FREUDENBERG and H. EICHEL (Annalen, 1935, 518, 97—102; cf. A., 1934, 795).—A detailed description is given of the isolation of the polysaccharide mixture (I) from the urine of individuals of the blood-group A. Hydrolysis of (I) by acids leads to the isolation of glucosamine. Inactivation of (I) by alkali is caused mainly by elimination of *N*-Ac, since acetylation of the inactive product (II) yields an inactive acetate, sol. in CHCl_3 , from which *O*-Ac can be removed without affecting the re-introduced *N*-Ac; the material so obtained has about the same activity as the original substance. Ketene, which in H_2O acetylates solely NH_2 , completely restores the activity of (I). (I) is not affected by amylases or diastases, but is partly degraded with complete loss of activity by snail enzyme, whereby *N*-acetylglucosamine (III) is obtained. The presence of a uronic acid (IV) in small amount is established. (I) therefore contains galactose (V) and (III), but it remains uncertain whether (IV) is a component of (I) or an admixture. Considerations of the N balance indicate the presence of a further N component probably with higher % N. (V) is also obtained by the acid hydrolysis of the material obtained from the urine of individuals of blood-group O. H. W.

Blood-sugar curves after intravenous injection of hypertonic glucose. N. FIESSINGER and A. BRON (Compt. rend. Soc. Biol., 1935, 119, 839—841).—In normal cases the curves for arterial and capillary blood are similar, showing an elevation of 0.4—0.75 g. after 10 min. In cirrhosis, the curve rises to 0.5—1.5 g. and the duration is prolonged for 1½ hr. In hepatic cedema, the val. for capillary blood rises to 1 g. and that for arterial to 1.5 g. H. G. R.

Mercury-cadmium deproteinisation and micro-iodometric determination of blood-sugar. C. DUMAZERT and M. BIERRY (Compt. rend. Soc. Biol., 1935, 119, 737—739).—Blood is deproteinised by an acid solution of $\text{Hg}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$. The sugar in the filtrate is oxidised with I in $\text{NaOH-Na}_2\text{HPO}_4$ solution at room temp., excess of I liberated with

H₂SO₄, the solution neutralised with Na₂B₄O₇, and I titrated with 0.005*N*-Na₂S₂O₃. The method gives results concordant with those obtained by the Hagedorn-Jensen method, and permits the micro-determination of the "true" blood-sugar. R. N. C.

Determination of fructose in blood. J. PATTERSON (Biochem. J., 1935, 29, 1398—1399).—The NHPh₂ method of Radt (A., 1928, 1151) for determination of fructose in aq. solution and in blood is slightly modified and used for determinations in the bloods of 2 normal and 3 pathological subjects, the results comparing closely with those obtained by the method of Scott (cf. this vol., 770). 100 ml. of blood contain about 1 mg. of fructose. P. W. C.

Blood-sugar of the fasting, gizzardectomised fowl (*Gallus domesticus*). W. H. BURROWS, J. C. FRITZ, and H. W. TITUS (J. Biol. Chem., 1935, 110, 39—41).—The peak in the blood-sugar curve of fowls occurring on the 4th day of fasting (A., 1934, 683) is not observed in gizzardectomised animals. H. D.

Blood-chemistry of birds after destruction of the comb or enucleation of the eyeballs. C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1935, 119, 630—632).—Blood-sugar rises in cockerels deprived of their combs, and in ducks deprived of their eyeballs. Blood-Ca and cholesterol fall, whilst K and the K/Ca ratio rise. R. N. C.

Fermentability of blood-sugar, especially of the bound sugar in diabetics. M. MORIMUNE (Mitt. med. Akad. Kioto, 1934, 12, 281—288).—No significant difference was found between the fermentability of both free and bound blood-sugar in diabetics as compared with normal individuals.

NUTR. ABS. (b)

Spontaneous variations in blood-sugar in normal and diabetic subjects. J. O. NUNEZ (Ann. Med., 1934, 36, 234—241).—Consecutive blood-sugar determinations at intervals of 5 min. show that there are spontaneous variations in the blood-sugar levels of both normal and diabetic subjects. These may be the result of instability of the autonomic nervous system.

NUTR. ABS. (b)

Glycolysis in blood. II. Glycolysis and distribution of phosphate compounds. S. MORGULIS and J. D. MUNSELL (Biochem. Z., 1935, 278, 89—100).—No quant. relationship could be detected between changes of the different blood-P fractions and the degree of glycolytic power. Under the action of arsenate, glycolysis is greatly increased in rabbit's but somewhat decreased in dog's blood (cf. A., 1932, 530, 1273), the readily hydrolysable esters increasing and the difficultly hydrolysable esters decreasing in strongly and showing a tendency to decrease in weakly glycolysing systems. P. W. C.

Determination of phosphorus in blood with the step photometer. S. A. SIWE (Biochem. Z., 1935, 278, 437—441; cf. Teorell, A., 1931, 662).—By means of a modification of the method of Fiske *et al.* (A., 1926, 443) the P content of 0.05—0.1 c.c. of blood-serum is determined with an error of $\pm 5\%$. The results agree well with those of Briggs (A., 1922, ii, 718). W. McC.

Colloidal calcium phosphate of blood and calcium partition in serum. D. M. GREENBERG, C. E. LARSON, and E. V. TUFTS (Proc. Soc. Exp. Biol. Med., 1935, 32, 647—650).—Results indicate that the colloidal salt is Ca₃(PO₄)₂, and that the equilibrium between protein-bound Ca and Ca⁺⁺ conforms to the law of mass action. R. N. C.

Determination of calcium in blood. S. A. SIWE (Biochem. Z., 1935, 278, 442—446).—The Ca content of 0.05—0.1 c.c. of blood-serum is determined by pptg. with (NH₄)₂C₂O₄, dissolving the ppt. in HNO₃, adding excess of 0.01*N*-KMnO₄, and titrating with 0.01*N*-Na₂S₂O₃ after addition of KI. The whole procedure is carried out in one tube, the apparatus of Linderström-Lang *et al.* (A., 1931, 1445) being used. The error is $\pm 3.6\%$. Alternatively, the ppt. of CaC₂O₄ is converted into CaCO₃ by heating at 550—600° [the temp. given by Nordbo (A., 1932, 531) is too low], dissolved in excess of 0.01*N*-HCl, and titrated with 0.01*N*-NaOH. The error is $\pm 3.5\%$.

W. McC.

Comparison of wet and dry ashing methods for determination of blood-iron. A. A. FABIAN, A. SACHS, and V. E. LEVINE (Proc. Soc. Exp. Biol. Med., 1935, 32, 662—664).—The dry method is recommended. The blood is dried, ashed at low red heat, and evaporated with HNO₃. Fe is dissolved out with HCl and separated from Cu (if necessary) by pptn. with aq. NH₃, Cu being determined by the McFarlane method. The Fe ppt. is dissolved in H₂SO₄, K₂S₂O₈ added, and the Fe determined colorimetrically with KCNS. R. N. C.

Mineral differences in blood composition according to sex, in *Cyprinus carpio*. E. A. PORA (Compt. rend. Soc. Biol., 1935, 119, 373—375).—Na and serum-Cl in the blood of the male are > in the female, whilst K, Ca, total protein, the alkaline reserve and the NaCl/total osmotic pressure ratio are less.

R. N. C.

Citric acid content of serum in rabbits with special reference to certain diets. H. LINDHOLM (Skand. Arch. Physiol., 1934, 70, 295—302).—The serum of rabbits fed on a mixed diet of grass, roots, oats, and barley contains 10 mg. of the acid per 100 ml. (6.3 mg. after 24 hr. starvation). When the diet contains no grass or other green food the val. is 6—8 mg., and this can be raised by adding green food.

NUTR. ABS. (m)

Selective accumulation of lipochrome. L. ZECHMEISTER, P. TUZSON, and E. ERNST (Nature, 1935, 135, 1039).—The blood-serum of the horse, after feeding on green food, contains no xanthophyll, but the carotene content is increased. Xanthophylls probably do not cross the wall of the gut, and selection appears to take place in the digestive organs.

L. S. T.

Globulin and albumin fractions of serum. VII. Tyrosine and cystine contents of protein fractions of fluids from sarcoma, carcinoma, and liver (in cirrhosis). B. LUSTIG and E. MANDLER (Biochem. Z., 1935, 278, 312—319; cf. A., 1931, 505; 1932, 960).—Colorimetric methods for determination (without hydrolysis and isolation) of NH₂-acids in proteins give only qual. vals. The tyrosine (I) con-

tent of the H_2O -sol. globulin fractions is $>$ that of the globulins sol. in aq. NaCl and much $>$ that of the globulins sol. in aq. Na_2CO_3 . All but one of the albumin fractions have similar (I) contents. The cystine (II) content of the albumin fractions is much $>$ that of the globulins. The H_2O -sol. euglobulins from carcinoma fluid contain more (II) than do the those from the other fluids. The globulins sol. in aq. NaCl and aq. Na_2CO_3 do not differ as regards (II) content. Albumin fractions from carcinoma and sarcoma fluids have (II) content $<$ that of corresponding fractions from the other fluid. The euglobulins sol. in aq. Na_2CO_3 when digested with pepsin and HCl yield a fraction, insol. in H_2O and rich in P and carbohydrate, which appears to yield xanthine bases on acid hydrolysis. W. McC.

Isolation of serum-vitellin. M. LASKOWSKI (Biochem. Z., 1935, 278, 345—348; cf. this vol., 374).—Plasma from laying hens acidified with HCl (p_{H} 5.0—5.5) is diluted tenfold with H_2O , pptd. material is dissolved in 5% aq. NaCl , and the solution is saturated with NaCl . After removal of pptd. impurities the vitellin (I) is pptd. by dilution (hundredfold) with H_2O . Dissolution in 5% aq. NaCl , saturation with NaCl , filtration, and dilution are repeated, and the ppt., after washing with Et_2O — EtOH , is successively extracted with EtOH (24 hr.) and Et_2O . (I) thus obtained is still impure (contains about 0.9% of protein-P). Plasma from cocks or non-laying hens yields no (I) when treated in this way. Possibly the (I) is identical with that of hens' eggs (cf. Calvery *et al.*, A., 1932, 294). W. McC.

Changes in blood-serum under the influence of heat. C. ACHARD and A. BOUTARIC (Compt. rend., 1935, 200, 1697—1700).—The smallest amount of adsorbent C which will restore the surface tension of horse blood-serum, diluted 1/500 with 0.85% NaCl , to that of the diluent is about 160 mg. per 15 c.c. This quantity diminishes regularly with increasing time and rise of temp. of heating, indicating that the no. of individual protein particles decreases. F. A. A.

Hæmolytic action of carbohydrates [? hydrocarbons]. L. P. BRIULLOVA (J. Physiol., U.S.S.R., 1934, 17, 389—391).—The presence of hydrocarbons, aliphatic or aromatic, stimulates hæmolysis by saponins. CH. ABS. (p)

[Relation between] time of coagulation and concentration of coagulant. A. FISCHER (Biochem. Z., 1935, 278, 320—325; cf. A., 1933, 522).—The rate of coagulation of blood-plasma \propto a power of the concn. of the coagulant and is calc. by means of a simple equation valid within limits much wider than those within which the equation previously given is applicable. W. McC.

Coagulating action of homologous organ-extracts. A. FISCHER (Biochem. Z., 1935, 278, 334—339).—As regards their power to coagulate autologous and homologous blood-plasma, extracts of organs of the hen form the series, lung $>$ muscle $>$ heart $>$ kidney $>$ spleen $>$ brain $>$ liver, this order being preserved at all ages of the hen from embryo onwards. As regards their relative content of heparin

the extracts form the series brain $>$ lung $>$ spleen $>$ liver. W. McC.

Stoicheiometric combination of heparin and coagulant. A. FISCHER and T. ASTRUP (Biochem. Z., 1935, 278, 326—333).—The proportions in which extracts of organs and blood-plasma (from hens) and heparin interact indicate that heparin and the substance which stimulates coagulation react in stoicheiometric proportions (1 mol. of each). The compound dissociates in solution. W. McC.

Coagulation of the blood as a chain reaction. A. FISCHER (Nature, 1935, 135, 1075).—An active principle of coagulation, which can be transferred indefinitely into new plasma without loss of activity, is described. It is formed during the clotting process of blood-plasma and increases and then disappears almost instantaneously at the moment of coagulation. The facts support the view that blood-coagulation is a chain reaction. L. S. T.

Combination of heparin with protein. A. FISCHER (Biochem. Z., 1935, 278, 133—160).—Heparin (I) combines with protein only on the acid side of, and in close proximity to, the isoelectric point, and is therefore always in the free condition in blood-plasma and in serum. Organ extracts which accelerate clotting of blood combine with (I), and the spontaneous changes (denaturation) in such extracts on keeping which result at first in an increase followed later by a decrease of clotting-acceleration power are accompanied by parallel changes in the extent of combination with (I). Protein combines with (I) only when it has been denatured, the liberated basic groups being utilised for the union. Addition of clotting-active lipins to protein results in denaturation and union with (I). Blood-clotting is regarded, therefore, as a special case of denaturation, and the inhibiting action with (I) depends on its great affinity for the basic groups of the active material of the organ extracts, these groups in absence of (I) reacting with the acid groups of the plasma-protein. P. W. C.

Possibility of a new quantitative technique of the Wassermann reaction, based on the nullifying action of the components of alexin. O. G. BIER (Compt. rend. Soc. Biol., 1935, 119, 758—760).—The use of the alexin fractions serves to differentiate sera where the Sordelli-Miravent technique breaks down. R. N. C.

Behaviour of the fractions of alexin in the Wassermann reaction. O. G. BIER (Compt. rend. Soc. Biol., 1935, 119, 756—758).—The serum-yeast fraction has the strongest nullifying action on the Wassermann reaction. R. N. C.

Behaviour of alexin in an electric field. P. GIRARD, M. LOURAU, and E. PITRES (Compt. rend. Soc. Biol., 1935, 119, 408—410).—Alexin in an electric field behaves like an ion on the isoelectric point of which is difficult to recognise on account of its sensitivity to p_{H} . Its mobility is $>$ that of hæmolysins or agglutinins, and is apparently the same as that of globulins, to which class alexin probably belongs. R. N. C.

Use of sera precipitated by *N*/300-hydrochloric acid in the fixation reaction for tuberculosis. R. WAHL and P. LAVAL (Compt. rend. Soc. Biol., 1935, 119, 389—390).—The sensitivity of the fixation reaction is not increased by previous pptn. of the sera with 0.003*N*-HCl. R. N. C.

Production of diphtheria toxin with high antigenic power. E. M. TAYLOR (Compt. rend. Soc. Biol., 1935, 119, 510—512).—The antigenic power of diphtheria toxin can be increased by peptic digestion. H. G. R.

Basal metabolism in rabbits and the Schwartzman phenomenon. G. EUSTATZIOU, I. POPESCO, and S. STAMATESCO (Compt. rend. Soc. Biol., 1935, 119, 619—621).—Basal metabolism increases similarly in rabbits injected subcutaneously with the toxic filtrate of *B. coli*, whether or not they show a positive Schwartzman phenomenon. The increase is parallel with the intensity of the local reaction, but not with the rise of temp. R. N. C.

Adsorption of purified diphtheric vaccines by aluminium hydroxide. S. SCHMIDT (Biochem. Z., 1935, 278, 257—262).—The extent to which purified, salt-free diphtheric vaccines are adsorbed by $\text{Al}(\text{OH})_3$ frequently varies with their N (protein) content. A high degree of adsorption increases the efficiency of the vaccine. W. McC.

Preparation of anti-vibrioseptic serum by suspension of the antigen in lanolin. M. WEINBERG and M. GUILLAUMIE (Compt. rend. Soc. Biol., 1935, 119, 719—721). R. N. C.

Antitoxic power of some metal-protein complexes obtained from anti-diphtheria and anti-tetanus sera. H. DIACONO (Compt. rend. Soc. Biol., 1935, 119, 801—804).—Diphtheria and tetanus antitoxins are pptd. unchanged by HgCl_2 or CuSO_4 and may be eluted from the complex with Na_2SO_3 . H. G. R.

Which component of the complement is lacking in the lymph of the peripheral vessels? S. FUNAOKA and T. SHIMAOKA (Proc. Imp. Acad. Tokyo, 1935, 11, 203—205).—The albumin, but not the globulin, fraction obtained by Liefmann's procedure from guinea-pig blood contains the complement necessary for hæmolyzing the corpuscles of goat blood. Lymph drawn from the popliteal sac has no hæmolytic action. J. L. D.

Spectrographical study of the biochemical reactions of nerves. B. MINZ and M. PAIC (Compt. rend. Soc. Biol., 1935, 119, 521—524).—On electrical excitation of a fragment of vagus nerve in Locke-Ringer solution, a substance having a characteristic absorption spectrum passes into the solution. H. G. R.

Crystal structure of the myofibrils. Metal-histology of animal fibres. F. WORSCHTIZ (Fortschr. Röntgenstrahlen, 1934, 50, 174—178; Chem. Zentr., 1935, i, 585).—The micelle structure of the myofibrils is not altered by drying. The X-ray diagram indicates a structure of a cryst. character, the lattice const. of which in the direction of the thread axis is $\sim 2 \text{ \AA}$. Interference is caused by the existence of a liquid-cryst. substance of the smectic type, which

originates probably from the sarcoplasm of the muscle threads or the intrafibrillary liquid. R. N. C.

Decomposition of animal substances while embedded in marine sediments. F. HECHT (Kali, 1934, 28, 209—215; Chem. Zentr., 1935, i, 652). H. J. E.

Isolated cell and tissue constituents. III. Separation of the thyroid into colloid, cells, and nuclei. M. BEHRENS (Z. physiol. Chem., 1935, 232, 263—269; cf. A., 1933, 1184).—Thyroid tissue after freezing, drying, and pulverising is separated into colloid, cells, and nuclei by taking advantage of their different densities in suitably chosen liquids. The colloid consists principally of thyroglobulin, but contains other proteins; it is sol. in cold H_2O and in AcOH on warming. Only a trace of cells is sol. in AcOH. Insulin was separated from pancreas by the same method. J. H. B.

Secretion of dyes by the kidney. R. HOBER (J. Cell. Comp. Physiol., 1935, 6, 117—128).—The tubules of the aglomerular kidney of the toadfish are permeable to certain diffusible acid dyes. The distribution of injected dyes is examined and compared with that in the frog. A. G. P.

Seasonal variations in the contents of water, organic and mineral substances of the muscle and liver of the frog. A. GRADINESCO and C. DEGAN (Bull. Soc. Chim. biol., 1935, 17, 751—763).—In the gastrocnemius muscle and the liver of the green frog the content of org. and mineral substances increases in summer and autumn and decreases in winter and spring. These losses are compensated for by corresponding increases in the H_2O content. The variations in the male are $>$ those in the female. A. L.

Nuclein metabolism. V. Constitution of nucleic acid. K. MAKINO (Z. physiol. Chem., 1935, 232, 229—235).—Depolymerisation of yeast-nucleic acid (I) by *N*-NaOH at room temp., which does not decompose the mononucleotides, liberates four acidic groups. Since thymonucleic acid (II) cannot be depolymerised chemically without destruction of the mononucleotides, it was hydrolysed by nuclease. Although dephosphorylation is approx. equal to depolymerisation, no increase in acidity occurs through dephosphorylation. Four acidic groups are again liberated. Thus (I) and (II) possess four ester linkings, and as both are tetrabasic they probably possess a similar ring structure. J. H. B.

Choline, acetylcholine, and carnitine content of muscle. E. STRACK, P. WORDEHOFF, E. NEUBAUER, and H. GEISSENDORFER (Z. physiol. Chem., 1935, 233, 189—203).—Neither choline (I) nor acetylcholine (II) was detected in the skeletal muscle of the ox and dog. (II) was also shown to be absent by the biological test. In the muscle free (I) is not produced on incubation at 37° . In the hydrolysed aq. extract of skeletal muscle, no (I) was obtained by Au pptn., although the muscle does not destroy added (I). The so-called (I) and (II) found by Kinoshita (A., 1910, ii, 631) and Bischoff *et al.* (A., 1932, 765) was probably carnitine (III). Ox-muscle contains 0.01—0.2% of (III) chloride. J. H. B.

Glycogen and total carbohydrate content of the human heart. H. BLUME (Beitr. path. Anat. allg. Pathol., 1934, 93, 20—35; Chem. Zentr., 1935, i, 433).—The glycogen (I) contents of the ventricle and septum of the normal human heart are equal. (I) in the infant heart is > in the adult. The heart contains 0.46—1.46% of carbohydrate, 70% of which is (I); a (I) content > 1.5% indicates hypertrophy. After death 90% of the (I) of the heart is converted into glucose in 9 hr., the remainder being unaltered; in infants the breakdown is slower. R. N. C.

Glycogen of the placenta. H. GUTHMANN and L. BÖHME (Arch. Gynakol., 1934, 158, 336—344).—At the 2nd month maternal portions of human placenta contained nearly twice as much glycogen (I) as foetal portions. By the 6th month this difference had disappeared. No evidence was obtained that (I) could pass as such from maternal to foetal tissues. If (I) transference does take place, hydrolysis and resynthesis must occur. NUTR. ABS. (b)

Quantity, distribution, and significance of placental glycogen in the different phases of pregnancy. Function of human and hæmo-choroidal placenta. B. SZENDI (Arch. Gynakol., 1934, 158, 409—425).—In rabbits the placental glycogen (I) increased rapidly from 0.3% on the 11th to 1.0% on the 17th day of gestation and thereafter fell to about 0.1% on the 30th day. In human pregnancy the placenta contained most (I) about the 2nd month (0.5%); by the 9th month < 0.1% of (I) was present. Hence the (I) in the placenta is part of the metabolic structure of the placental cell and is not connected with the carbohydrate metabolism of the embryo. NUTR. ABS. (b)

Fatty acids of pig liver. III. General analysis. E. IRVING and J. A. B. SMITH (Biochem. J., 1935, 29, 1358—1368; cf. A., 1934, 913, 1381).—Data from bromination and from oxidation and hydrogenation of fractionally distilled Me esters are given. The main saturated acids (approx. 36%) are palmitic (14%) and stearic (18.8%) and the unsaturated oleic (28%), C_{20} (20%), and C_{22} (7.5%). The C_{20} and C_{22} acids have probably 2—4 double linkings. F. O. H.

Relationships of liver-lipins. F. BREUSCH and R. SCALABRINO (Z. ges. exp. Med., 1934, 94, 569—578; Chem. Zentr., 1935, i, 737).—In man the proportion of lipochromes increases somewhat with age. Vals. were high in uræmia and hypertension, and subnormal in liver cirrhosis. The vitamin-A content decreased with age and, markedly, in uræmia and cirrhosis, but was high in diabetes. Free cholesterol varied but little. Cholesteryl esters increased in hypertension and in sclerosis. Phosphatides increased in uræmia and decreased in cirrhosis and hypertension. The total fat content was high in carcinoma and tuberculosis. With increasing total fat the I val. declined. A. G. P.

Polysaccharoproteins. V. State of glycogen in muscle. E. M. MYSTKOWSKI (Biochem. Z., 1935, 278, 240—245; cf. this vol., 882).—In muscle (rabbit, dog) there is equilibrium between the various forms (free, dissolved, protein-bound) of glycogen. Part of

it is bound to myosin, but probably none to myogen. The globulin-X also binds a small amount, and the stroma always contains some. The results of Willstätter *et al.* (A., 1934, 913) are confirmed.

W. McC.

Ammonia content and ammonia formation in muscle. XXII. I. Determination of adenosinetriphosphoric acid. II. Second ammonia-forming substance of muscle. J. K. PARNAS and C. LUTWAK-MANN (Biochem. Z., 1935, 278, 11—22).—A method for determination of adenosinetriphosphoric acid (I) is described with the help of which it is shown that muscle contains no adenylic acid. The sum of NH_3 -N and of the (I)- NH_2 -N of muscle increases during NH_3 formation by 2 mg. of N per 100 g., and it appears, therefore, that muscle contains in addition to (I) some other NH_3 -forming substance. P. W. C.

Constitution of adenosinetriphosphoric acid. K. MAKINO (Biochem. Z., 1935, 278, 161—163).—The readily hydrolysable H_3PO_4 groups are not attached to OH at C2 or C3 of ribose or to NH_2 of adenine. P. W. C.

Synthesis of asterubin. D. ACKERMANN (Z. physiol. Chem., 1935, 234, 208—211; cf. this vol., 771).—Aq. taurine (I) heated at 120° for 5 hr. with dimethylcyanamide gives asterubin in poor yield. The biological synthesis probably takes the form of a reaction between (I) and guanidine. W. McC.

Total nitrogen of the liver of frogs in summer and winter and during fasting and administration of nitrogen-rich diet. C. GAUTIER, J. RATELADE, and R. CASATI (Bull. Soc. Chim. biol., 1935, 17, 745—750).—The total N of the liver of frogs decreases considerably in summer and winter when the animals are fed on frog-muscle. A. L.

Structure of tooth-tartar (Calculus dentalis supragingivalis). H. PHILIPP (Z. physiol. Chem., 1933, 233, 209—214).—X-Ray diagrams of tooth-tartar indicate that the phosphate belongs to the apatite group and is, from its behaviour at 1000° [combination with adsorbed phosphate, yielding β - $Ca_3(PO_4)_2$], a hydroxyapatite. Owing to adsorbed phosphate it analyses approx. as $Ca_3(PO_4)_2$, but contains 0.28% of CO_2 . J. H. B.

Molybdenum content of sound and carious teeth. H. TER MEULEN (Chem. Weekblad, 1935, 32, 350).—Sound and carious human teeth contain 0.55 and 0.03—0.06 mg. Mo per kg., respectively. Ox and calves' teeth contain 0.21—0.34 mg. and the bones 0.04 mg. Mo per kg. S. C.

Chemistry of bone-salts. J. MAREK, O. WELL-MANN, and L. URBANYI (Z. physiol. Chem., 1935, 234, 165—175; cf. A., 1934, 1133; this vol., 234; Gabriel, A., 1894, ii, 21).—The bones of calves and cows, on boiling with H_2O , aq. KOH, aq. K_2CO_3 , glycerol (I), (I)+KOH, or aq. Na_2HPO_4 , are converted into material similar to $Ca_3(PO_4)_2$. Most of the combined CO_2 is present as $CaCO_3$. These and other facts indicate that the mineral part of the bones consists chiefly of $Ca_3(PO_4)_2$ and $CaCO_3$ with small amounts of $Mg_3(PO_4)_2$ and Ca alkali phosphate. Klement's conclusions are erroneous. W. McC.

Role of zinc in reproduction. Experiments with castrated silk-worms (*Bombyx mori*, L.). A. AKAO (Keijo J. Med., 1935, 6, 49—60).—The [Zn] in the ovaries and testes is similar, and the total quantity in the former is therefore greater (24 times). The Zn content of the blood of normal and castrated males and normal females is similar, but there is a sudden rise with ovariectomised females shortly before emergence from the cocoon. The [Zn] in the blood-cells is 4 times that in the plasma. K is not subject to a similar variation in the ovariectomised female.

P. G. M.

Composition of the fishes *Bothus macoticus*, Pall, and *Gobius melanostomus*, Pall. K. WYNOFF (Z. Unters. Lebensm., 1935, 69, 174—176).—The % of H₂O, protein, fat, and ash are given.

E. C. S.

Lipochromes of sea anemones. I. Carotenoid pigments of *Actinia equina*, *Anemonia sulcata*, *Actinoloba dianthus*, and *Tealia felina*. I. M. HEILBRON, H. JACKSON, and R. N. JONES (Biochem. J., 1935, 29, 1384—1387).—Hydrolysis of actin-erythrin (I) from *A. equina* (A., 1934, 676) yields a violet pigment, *violerythrin*, m.p. 191—192°, absorption spectrum max. at 625, 576, and 540 m μ in CS₂. The pigment of *A. sulcata* is mainly *sulcatoxanthin*, C₄₀H₅₂O₈ (?), ill-defined m.p. 125—130°, absorption max. at 516, 482, and 450 m μ in CS₂; the tentacles contain chlorophyll-*a* (Elmhirst and Sharpe, Biochem. J., 1920, 14, 48). *A. dianthus* yields a red acidic pigment, m.p. 195—197°, whilst *T. felina* contains two lipochrome esters, one possibly identical with (I) and the other (max. at 500 m μ in CS₂) giving an acidic pigment, m.p. 205—208°.

F. O. H.

Coalescence of fat particles. W. FRITZ (Milch. Forsch., 1934, 16, 476—484; Chem. Zentr., 1935, i, 813).—Chain formation of fat globules in milk exposed to an electric field is followed by coalescence if the temp. is raised to < 90°. The relationship between this phenomenon and the ionic layer surrounding the globules is discussed.

A. G. P.

Occurrence of an octadecadienoic acid in cow butter-fats. T. G. GREEN and T. P. HILDITCH (Biochem. J., 1935, 29, 1564—1575).—The mixture of unsaturated C₁₈ acids from cow butter-fat consists of oleic acid (75%), tri- or tetra-ethenoid C₁₈ acids (1.5%), and octadecadienoic acid (I) (23.5%). Oxidation of the octadecadienoic acids from butter-fat and ground-nut oil shows that they are structurally similar, but that (I) is a different geometrical isomeride of the Δ^9 -acid of seed-fats. It is concluded that the kind of (I) in butter-fat depends on the diet of the cow, and that linoleic acid when present in the glycerides of land animals is a product of assimilation and not of synthesis.

J. N. A.

Cause of low stability of vitamin-C in milk. J. E. JACOBSEN (Z. Unters. Lebensm., 1935, 69, 306—313).—Vitamin-C is determined in a serum prep. from milk by titration at p_H 2.5 with dichlorophenolindophenol. The extremely small amount of -C in milk is readily destroyed by mixing or by pouring from one vessel to another. -C is more resistant in fresh than in stored milk. Change from winter feeding to pasture caused no increase in % of

-C. It is calc. that the adult must consume 3 litres of the best milk *per diem* to satisfy completely his -C requirement.

E. C. S.

Cryoscopic measurements of Indian milk. P. S. MACMAHON and L. N. SRIVASTAVA (Analyst, 1935, 60, 307—309).—The mean f.-p. depressions of cow's and buffalo's milk were 0.551° and 0.562°, respectively.

E. C. S.

Magnesium content of the cerebrospinal fluid: relation to blood-magnesium. C. B. UDAONDO, M. SCHTEINGART, and R. GAIBROIS (Rev. Soc. Argent. Biol., 1933, 9, 321—324).—The Mg contents of spinal fluid and of serum were practically the same and were unchanged in chronic affections of the central nervous system.

CH. ABS. (p)

Van den Bergh reaction of bilirubin in xanthochromic cerebrospinal fluid. S. L. VAUGHAN and R. S. HUBBARD (Proc. Soc. Exp. Biol. Med., 1935, 32, 618—620).—The reaction occurs promptly when the protein (I) concn. is normal, or the bilirubin (II) concn. is high. It is increasingly delayed as (II) falls and (I) rises.

R. N. C.

Adenylic acid in the central nervous system. C. RIEBELING (Klin. Woch., 1934, 13, 1422—1424; Chem. Zentr., 1935, i, 744).—The mean NH₃ content of the cerebrospinal fluid is 0.07 mg. per 100 c.c. It increases considerably in epilepsy, the extra NH₃ probably originating in the brain. Brain-NH₃ increases rapidly after death through enzymic deamination of a parent substance, probably adenylic acid. NH₃ is high in the brains of patients who have died in convulsions.

R. N. C.

Acid secretion by the stomach. IV. Effect of alkalosis on the secretion of acid in the dog. Effect of the ionic environment in the blood. G. DELRUE and A. LACQUET (Arch. internat. Physiol., 1934, 39, 295—310).—The production of alkalosis in a dog by prolonged ingestion of NaHCO₃ altered neither the p_H nor the total acid content of the gastric juice secreted.

NUTR. ABS. (b)

Influence of the acid-base equilibrium on gastric secretion. N. F. MACLAGAN (J. Physiol., 1934, 83, 16—17p).—There was no correlation between the acidity of the gastric juice and the acid-base ratio of the blood. The induction of NH₄Cl acidosis had no influence on the acidity of gastric secretion in response to histamine or EtOH test meals.

NUTR. ABS. (b)

Spectrographic study of the gastric content in fasting men. I. L. KARCZAG and M. HANAK. **II.** L. KARCZAG (Biochem. Z., 1935, 278, 105—107, 108—111).—I. Normal gastric and duodenal juice and their ultrafiltrates possess a selective absorption in the ultra-violet, which is considerably modified by alkali and acid and is not accounted for by the content of protein, polypeptides, aromatic NH₂-acids, uric acid, etc.

II. The above properties of gastric juice closely resemble those of the vitamin-B complex.

P. W. C.

Gastro-intestinal p_H in rats. I. M. EASTMAN and E. G. MILLER, jun. (J. Biol. Chem., 1935, 110, 255—262).—Normal rats generally show an acid re-

action in the gastro-intestinal tract, with the p_H rising from the stomach to the ileocaecal valve, falling in the caecum, and again rising in the colon. Young rats have a higher alimentary p_H than adult rats. On a bread diet the contents of the colon tend to be more acid than in the caecum. The McCollum rachitogenic diet causes a slight but consistent rise in the intestinal p_H throughout, otherwise wide variations in diet have no significant effect. Local conditions of absorption, secretion, and bacterial action, rather than the p_H at higher levels, determine the p_H at a given level. E. A. H. R.

Gastro-intestinal studies. IV. The relation of p_H to the pepsin and rennin content of the gastric juice. O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (Amer. J. Digest. Dis. Nutrit., 1934, 1, 120—123).—The presence of pepsin and rennin in human gastric secretion after histamine stimulation is dependent on p_H . Pepsin and rennin were present when the p_H was ≤ 7 , but neither could be detected when the p_H was > 7 . The concn. of the enzymes, however, did not depend on the amount of acid secreted. When the acidity is determined by p_H methods or titration, stomach contents which show a p_H of 7 are considered to have an acidity, a condition in which there is an absence of free acid, pepsin, and rennin. NUTR. ABS. (b)

p_H of the duodenal contents in absence of bile. G. LOEWY (Compt. rend. Soc. Biol., 1935, 119, 382—384).—Deprivation of bile causes a rise of duodenal p_H , the increase at the pyloric end being $>$ at the jejunal end. R. N. C.

p_H of the duodenal contents in the absence of pancreatic juice. G. LOEWY (Compt. rend. Soc. Biol., 1935, 119, 490—491).—In the absence of pancreatic juice the stomach, duodenum, and jejunum of the dog have the same p_H . No inflammation of the mucous membrane of the duodenum or jejunum is observed. H. G. R.

Duodenal secretion and sugar metabolism. J. LA BARRE and P. HOUSSA (Compt. rend. Soc. Biol., 1935, 119, 538—540).—Sugar tolerance is decreased if secretion is removed by prolonged washing of the intestine with dil. HCl. H. G. R.

Elimination of dyes in gastric and pancreatic secretions. Mechanism of secretion of acid and base. R. C. INGRAHAM and M. B. VISSCHER (J. Gen. Physiol., 1935, 18, 695—716).—Following intravenous injection into dogs, dyes appearing in the gastric and pancreatic juice (invoked by histamine and secretin, respectively) ionise with the chromogen electro-positively and -negatively, respectively. An explanation of the phenomena based on polar adsorption at the membrane pores of the glands (*i.e.*, electrostatic filtration) agrees with the conception of the mechanism of the natural secretions. F. O. H.

Keratin digestion in the larvæ of the clothes moth. K. LINDERSTRÖM-LANG and F. DUSPIVA (Nature, 1935, 135, 1039—1040).—The secretion of the middle intestine of *Tineola biselliella* contains a powerful proteinase (I) (p_H optimum at 9.3) which is little sensitive to SH-compounds. The secretion contains a reducing agent of unknown nature, which

appears capable of reducing the S-S linkings in the hair. The reduction of the hair-keratin then opens the peptide chains to attack by (I). Digestion of sheep-wool by (I) using Na thioglycollate as reducing agent at p_H 10 resulted in rapid degradation of the wool with the formation of equiv. amounts of NH_2 and CO_2H . Pancreatic trypsin-kinase had no effect owing to inhibition by the SH-compounds.

L. S. T.

Formation of gall-stones. A. DE KUTHY (Bull. Soc. Chim. biol., 1935, 17, 774—779).—Since in the intact bile vesicle the ratio of the amount of bile salts (I) to that of cholesterol (II) remains const. during a stoppage and the solubility of (II) increases as the square of the concn. of (I), a stoppage does not lead to the pptn. of (II). Infections and metabolic disturbances, however, which cause a diminution of the concn. of (I) increase the tendency for (II) pptn.

A. L.

Constituents of human seminal plasma. M. W. GOLDBLATT (Biochem. J., 1935, 29, 1346—1357).—The concns. of constituents of the plasma (from centrifuging normal semen) have the following ratios to those of blood-plasma: Cl', cholesterol, 0.3—0.5; HCO_3' , 0.7—1.0; Ca, glucose, urea, 2.0—3.0; lactic acid, 5.0—6.0; acid-sol. P (inorg. 50, spermine-30, and undetermined 20%), 30. Proteins present include mucin, nucleoprotein, albumin, globulin, and proteoses (primary and occasionally secondary). Protamines, histones, and SH groups are absent. Glycolysis (demonstrable only if active sperm cells are present) is associated with a large increase in lactic acid, which, however, is insufficient to account for the loss in reducing power. Diastase and thrombo-kinase, but not protease, are present. F. O. H.

Action of monohalogenoacetic acids on the glycolysis and mobility of sperms. E. E. IVANOV (Biochem. Z., 1935, 278, 101—104).—The mobility of mammalian sperms can be retained in presence of either HCN or of the monohalogenoacetic acids even when the concn. of these reagents is sufficient to inhibit respiration or glycolysis, respectively.

P. W. C.

Urine analysis. N. S. KING and O. UVAROV (Vet. Rec., 1935, 15, 553—555).—Results are given for urine analysis in typical cases of illness in dogs.

R. N. C.

Application of the iodide-thiocyanate process in the determination of urinary sugar. E. TSCHIRCH and D. KRUGER (Pharm. Ztg., 1935, 80, 695—696).—Urinary sugar is determined rapidly and accurately by boiling with a known quantity of Fehling's solution, acidifying, removing excess of Cu^{++} with KI and KCNS, and titrating the liberated I with 0.1N- $Na_2S_2O_3$. The urine generally requires dilution.

R. N. C.

Excretion and determination of thiosulphate in urine. W. ZORKENDORFER (Biochem. Z., 1935, 278, 191—194; cf. Wollak, A., 1929, 1030).—0.1N-I is slowly added to urine (made just acid, if necessary, with AcOH) until interaction with $Na_2S_2O_3$ is slow, and large excess of I is added. After ≤ 15 min. aq. $Pb(OAc)_2$ is added, the mixture is filtered, and K_2SO_4 added until pptn. ceases. After several hr. the mix-

ture is filtered and KI, aq. starch, and a few drops of dil. H_2SO_4 are successively added to the filtrate (vol. 200 c.c.). If a blue colour develops it is destroyed with just sufficient 0.01% aq. NaHSO_3 . One drop of phenolphthalein solution, 5% aq. NH_3 (to rose-pink colour), and 5 c.c. of 10% aq. KCN are now successively added. After 15 min. 25 c.c. of dil. H_2SO_4 (1:3) are added and the liquid is titrated with 0.01N-I, more starch being added if necessary. The $\text{Na}_2\text{S}_2\text{O}_3$ thus determined is half of that originally present. For determination of $\text{Na}_2\text{S}_4\text{O}_6$ the procedure prior to addition of NH_3 and KCN is omitted. In rabbits and man the amount of $\text{Na}_2\text{S}_2\text{O}_3$ excreted increases with that administered (intravenous>subcutaneous>oral). $\text{Na}_2\text{S}_2\text{O}_3$ not so excreted is quantitatively removed in the urine as Na_2SO_4 . Injection of S causes no increase in $\text{Na}_2\text{S}_2\text{O}_3$ excretion.

W. McC.

Volatile amines of human urine. H. LOFFLER (Z. physiol. Chem., 1935, 232, 259—262).—The method of isolation and detection of the amines is described. NH_3 and NHMe_2 are the chief volatile bases of normal human urine; NMe_3 and NH_2Me occur in smaller amount.

J. H. B.

Thyrotropic substances in human urine. B. GIEDOSZ (Klin. Woch., 1934, 13, 1507; Chem. Zentr., 1935, i, 741).—Intravenous injection in rabbits of urine from healthy or sick individuals produces in some cases a thyrotropic effect, and in other cases an increase of colloids, due to folliculin-like substances.

R. N. C.

Effect of exercise on excretion of uric acid.
Effect of benzoic acid on uric acid elimination in liver diseases. A. J. QUICK (J. Biol. Chem., 1935, 110, 107—112; cf. A., 1932, 1277).—In man excretion of uric acid (I) is unaffected by mild, but is diminished by strenuous, exercise, the excretion of creatinine remaining unaffected and the lactic acid (II) of the blood increasing at the same time. Since administration of (II) diminishes excretion of (I), (I) retention may be due to over-production of (II). In liver diseases administration of BzOH causes prolonged (I) retention, but the degree of retention does not run parallel with the accompanying diminution in the rate of hippuric acid production. W. McC.

Dehydroandrosterone [in urine].—See this vol., 981.

Differentiation of chloride and bromide by the kidney. M. A. B. TOXOREUS (Arch. exp. Path. Pharm., 1935, 178, 416—419).—Determinations of Br^- and Cl^- in urine, blood, plasma, and serum after oral administration of aq. NaBr to rabbits and dogs fail to support the contention of Frey (A., 1932, 89) and of Møller (*ibid.*, 412, 639) that the kidney does not distinguish between Cl^- and Br^- (cf. A., 1930, 639).

F. O. H.

Protein-free urines giving a biuret-like reaction. E. G. GODFRIED (Biochem. J., 1935, 29, 1340—1345).—Fresh urine of healthy or diseased persons gives a rose or purplish-red colour with 1% aq. CuSO_4 and 5% aq. Na_2CO_3 , the reaction not being identical with the biuret test. The substance responsible is not a peptone or urobilin, but either a

pigment or associated substance of the urochrome group.

F. O. H.

Xanthurenic acid. II. L. MUSAJO. III. Origin of xanthurenic acid. L. MUSAJO and F. M. CHIANCONE (Atti R. Accad. Lincei, 1935, [vi], 21, 461—467, 468—470).—II. The urine of animals fed on fibrin contains, in the albino rat and the rabbit, xanthurenic acid (I), kynurenine (II), and kynurenic acid (III); in the dog, (III) and (II), without (I). The isolation of (II) is described.

III. Albino rats fed on a diet containing tryptophan (IV) or (II) excrete (I); those fed on gelatin do not, and those fed on (III) excrete only minute amounts of (I). It is concluded that (I) is produced in the animal from (IV) by way of (II), which gives either (I) or (III); (I) may be a hydroxykynurenic acid.

E. W. W.

Crystal structure data and calculus (urate) formation. F. WORSCHITZ and J. VON HERMAN (Fortschr. Röntgenstrahlen, 1934, 50, 305—307; Chem. Zentr., 1935, i, 585).—The structure of spherical calculi is that of a polycryst. aggregate, generally with orientation and inner strain along the radii.

R. N. C.

Porphyria metabolism. Spectroscopic determination of porphyrins. K. LAGEDER (Arch. Verdauungs-Krankh., 1934, 56, 237—256).—A spectroscopic method of porphyrin (I) determination is described. The normal rate of urinary excretion of (I) is 0.01—0.08 mg. per 24 hr. It is frequently very low in subjects on a meat-free diet. It is increased in cirrhosis of the liver, icterus, pulmonary tuberculosis with fever, sometimes in pernicious anaemia, but seldom or not at all in cancer of the stomach, hæmolytic jaundice, and Addison's disease. There is a correlation between abnormal skin pigmentation (e.g., in psychopathic states) and disturbance of (I) metabolism.

NUTR. ABS. (m)

Experimental acidosis. V. Acidosis and liver function. S. TATSUZAWA (Sei-i-kwai Med. J., 1933, 52, No. 10, 91—103).—Liver function in rabbits is disturbed in experimental acidosis.

CH. ABS. (p)

Relation between the respiration of the red corpuscles, glutathione, and the reticulocytes in secondary anæmias in the rabbit. G. LITARCZEK, S. BAICOIANO, and M. BALS (Compt. rend. Soc. Biol., 1935, 119, 764—768).—Corpuscular respiration or the reticulocyte content of the blood, but is not absolutely dependent on the blood-glutathione.

R. N. C.

Corpuscular respiration in secondary anæmias in the rabbit. G. LITARCZEK, S. BAICOIANO, and M. BALS (Compt. rend. Soc. Biol., 1935, 119, 761—763).—The increase of respiration of the blood of anæmic rabbits is a function of the red corpuscles alone.

R. N. C.

Treatment of hæmophilia: action of Congo-red. C. P. WALDORF and A. G. ALVAREZ (Semana méd., 1935, I, 6—11).—Among many substances examined, Congo-red, injected intravenously or intramuscularly, gave best results. CH. ABS. (p)

Mouse leucæmia. X. Metabolic differences between transmission lines of mouse lymphatic

leucæmia. J. VICTOR and M. R. WINTERSTEINER (Amer. J. Cancer, 1934, 22, 561—571).—Metabolic differences, as shown by O_2 consumption, aerobic and anaerobic glycolysis of lymph nodes, are exhibited between lines of transmissible leucæmia from the same organ and between those derived from different organs in the same case. CH. ABS. (p)

Blood-potassium after extirpation of the adrenal glands. C. I. URECHIA, G. BENETATO, and (MME.) RETEZEANU (Compt. rend. Soc. Biol., 1935, 119, 439—440).—Extirpation of both adrenals in the cat produces a marked rise of blood-K. Extirpation of one adrenal in the cat or dog produces a slight rise followed by a fall. R. N. C.

Calcification process of the aorta studied radiographically. F. WORSCHITZ and J. VON HERMAN (Fortschr. Röntgenstrahlen, 1934, 50, 307—309; Chem. Zentr., 1935, i, 585).—The X-ray picture of the sclerotic aorta is marked by additive Ca rings, whilst the interference of the fibres declines. The deposition of the sclerotising substance takes place intracellularly or intramurally according to the crystal structure, the deposited crystals not exceeding 10^{-6} cm. in size. The calcified centre appears as a homogeneous substance, showing no stratification of the crystals. R. N. C.

Carbohydrate tolerance in cancer patients and the effect thereon of X-radiation. F. H. L. TAYLOR and H. JACKSON, jun. (Amer. J. Cancer, 1934, 22, 536—547).—Lowered carbohydrate (I) tolerance in cancer results from malnutrition and cachexia. Irradiation has no effect on (I) metabolism. CH. ABS. (p)

Therapy of spontaneous mouse tumours: failure of additional inorganic compounds. M. C. MARSH (Amer. J. Cancer, 1934, 22, 572—577).—Injection of saturated aq. NaCl into epithelial tumours destroyed these. Other inorg. salts, oxides, hydroxides, I, and $CHCl_3$ had no effect. CH. ABS. (p)

Effect of radiation, lactate, and iodoacetic acid on tumours. W. R. FRANKS, M. M. SHAW, and W. H. DICKSON (Amer. J. Cancer, 1934, 22, 601—605).—Growth of tumours was not inhibited by injections of Na lactate and the efficiency of subsequent X-irradiation was unchanged. CH_2I-CO_2H slightly inhibited growth of tumours, and its effect was increased by previous irradiation. CH. ABS. (p)

Co-enzyme of glycolysis from tumours. III. H. KRAUT and R. W. NEFFLEN (Z. physiol. Chem., 1935, 232, 270—279; cf. A., 1933, 1202).—Co-enzyme T (I) from ox-brain is purified by adsorption on kaolin and elution with 0.001N-NaOH. The presence of $AcCO_2H$ cannot be detected. Further purification is attained by pptn. with 25% aq. HCl, (I) being an acid. It may also be pptd. as the Ba salt, which is then decomposed by H_2SO_4 . Purified (I) shows no loss of activity after 5 min. at 100° . J. H. B.

Enzymic efficiency in malignancy. I. Influence of growing Walker carcino-sarcoma on concentration of blood and tissue enzymes of the albino rat. B. SURE, M. C. KIK, and K. S. BUCHA-

NAN (Biochem. J., 1935, 29, 1508—1514).—Subcutaneous inoculation of Walker carcino-sarcoma No. 256 in the rat caused marked decreases in the serum-amylase, -esterase, and -trypsin, and small decreases in hepatic esterase, pancreatic amylase, and serum-phosphatase. H. D.

Chemical composition of normal and cataract crystalline lenses. M. PAGET, G. PARTURIER, and G. LEVIN (Compt. rend. Soc. Biol., 1935, 119, 581—583).—In the cryst. lens in senile cataract, cholesterol, Ca, and total S are increased, whilst Na and K are relatively decreased. R. N. C.

Carbohydrate metabolism in circulatory insufficiency. V. C. VASILENKO and M. L. JEVUCHOVA (J. Cycle med., 1933, 3, 319—330).—Of 52 cases of cardiac disease, 30% showed some variation of the blood-sugar (I) from normal (16% hypo- and 14% hyper-glycæmia), under-nourished patients always having a low (I). The curve of alimentary hyper-glycæmia in circulatory insufficiency showed a much slower rise, but eventually attained a higher level than in a normal subject. The (I) bore no stable relation to the sugar content of ascitic fluid or fluid from oedematous areas. NUTR. ABS. (b)

Effect of ingestion of minute quantities of cobalt by sheep affected with "Coast disease." E. W. LINES (J. Council. Sci. Ind. Res. Australia, 1935, 8, 117—119).—Diseased sheep improved rapidly after feeding 1 mg. of Co as $Co(NO_3)_2$ daily. Ironstone gravel produced no beneficial effect. A. G. P.

Metabolism of sulphur. XXII. Cystine content of hair and nails of cystinurics. H. B. LEWIS and L. FRAYSER (J. Biol. Chem., 1935, 105, 23—27).—The cystine content of the hair and nails of cystinurics was not different from normal. H. D.

Experimental "superabundance" diabetes in a normal dog. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1935, 119, 664—666).—The R.Q. rises steadily to a val. slightly > 1 in a normal dog receiving glucose (I) intravenously for 6 hr. at 1—9 g. per kg. per hr.; it remains at this steady max., independent of the rate of injection and the intensity of glycolysis, until the end of the injection, when it falls again to normal. The amount of (I) oxidised increases with rate of injection, the curve being a hyperbola until oxidised (I) reaches a max. when the rate is 6 g. per kg. per hr. The oxidation quotient of (I) increases with rate of injection, reaching 3.6 at 5 g. per kg. per hr. R. N. C.

Relation between the metabolism of carbohydrates, uric acid, and oxalic acid in diabetes. M. MAIO (Riv. Patol. sper., 1934, 13, 469—485).—The blood- $H_2C_2O_4$ (I) in diabetes was raised, but there was no relationship between the blood and urine vals. or between (I) and uric acid vals. There was, however, parallelism between blood- and urine-(I) and the glycæmic level, but not abs. proportionality. With dietary control, (I) fell somewhat, and with simultaneous insulin administration the fall was more pronounced, particularly for blood-(I). NUTR. ABS. (b)

Hypoglycæmia provoked in diabetics. A. BAUDOUIN, J. LEWIN, and E. AZERAD (Compt. rend. Soc.

Biol., 1935, 119, 686—688).—The blood-sugar curves of diabetics after injection of insulin fall into two groups, depending on whether or not the blood-sugar recovers after reaching its min. R. N. C.

Elimination of chlorine in skin diseases. J. R. PRAKKEN (Nederl. Tijdschr. Geneesk., 1934, 78, 3851).—Urinary elimination of Cl was moderately diminished in eczema and dermatitis exfoliativa, and very greatly in a case of pemphigus, the Cl and albumin contents of the blood-plasma being also lowered. NUTR. ABS. (m)

Guanidine, glucose, and calcium content of the blood in eclampsia. V. I. KRIEGER (Med. J. Austral., 1934, ii, 746—749).—Vals. for guanidine (I) are not markedly > in normal pregnant women (eclampsics: 0.21—0.54; mean, 0.39; normal: 0.27—0.39; mean, 0.34 mg. per 100 ml.). Hypoglycæmia is present in some cases, but, contrary to Minot and Cutler, there is no correlation of glucose and Ca with (I). NUTR. ABS. (m)

Role of the marrow in the production of hyperglycæmia following experimental "cerebral" embolism. H. HERMANN, F. JOURDAN, and P. CORNUT (Compt. rend. Soc. Biol., 1935, 119, 601—603).—The spinal marrow plays a part in the production of the hyperglycæmia provoked by experimental encephalomedullary embolism, this function being important in animals that have not been decapsulated, on account of the release of adrenaline by anæmic excitation of the spinal adrenaline-secreting centres. R. N. C.

Liberation of histamine-like substances in experimental cerebral embolism. J. TINEL, G. UNGAR, and A. GROSSIORD (Compt. rend. Soc. Biol., 1935, 119, 702—703).—Injection of lycopodium powder in the primitive carotid of the dog produces increased gastric secretion both in the injected animal and in another animal with which its circulation is crossed; the effect is thus due to histamine-like substances. R. N. C.

Carbohydrate metabolism in Graves' disease and goitre: effect of operative treatment. T. CHIBA (Tohoku J. Exp. Med., 1934, 23, 474—493).—The fasting blood-sugar was within normal physiological limits in 14 cases of Graves' disease and goitre. Carbohydrate tolerance, as measured by glucose "double loading," was impaired in proportion to the degree of toxicosis in Graves' disease, but was normal in simple goitre without thyrotoxicosis. Following thyroidectomy in Graves' disease, normal carbohydrate metabolism was either entirely or partly restored. NUTR. ABS. (b)

Iodine metabolism and the thyroxine content of nodular goitres. I. ABELIN and N. E. FINKELSTEIN (Schweiz. med. Woch., 1934, 64, 985—987).—Inorg. I in simple goitre was 19% of the total compared with the normal mean. 56% of all the glands were deficient in thyroxine-I (about 10% instead of the normal mean of 25%). Total I per g. was subnormal in all goitrous glands. I present in di-iodo-tyrosine (I) and I organically bound other than in thyroxine and (I) were also determined. NUTR. ABS. (m)

Iodine and thyroid hyperplasia. I. Iodine content of human skimmed milk from goitrous and non-goitrous regions. R. G. TURNER (Amer. J. Dis. Children, 1934, 48, 1209—1227).—The I content of milk from mothers in goitrous regions was > that from non-goitrous regions. The Ca and inorg. P of milk from the former were > those from the latter during the first 3—4 months of lactation, but subsequently became lower. CH. ABS. (p)

Fat tolerance in hyperthyroidism. O. E. HEPLER (Arch. Int. Med., 1935, 55, 979—996).—Administration of thyroid to dogs, after causing a slight decrease, resulted in a considerable increase in blood-fat (I), blood-cholesterol (II) remaining normal. During a rest period immediately following, (I) and (II) increased greatly, then during a second period of thyroid administration both decreased somewhat, although they were still > normal. During hyperthyroidism the metabolism of the body may be at a higher level, thus requiring the maintenance of the (I) and blood-sugar also at a higher level. A. L.

Iodine metabolism in hyperthyrosis. L. SCHEFFER (Klin. Woch., 1934, 13, 1570—1572; Chem. Zentr., 1935, i, 588).—I excretion is in equilibrium with I intake in hyperthyrosis; a considerable proportion of the I is excreted in the faeces, which normally contain only very small quantities. In Basedow's disease, where the excretion is > the intake, the principal excretory organ is the kidney. Hence urinary and faecal I determinations provide a means of distinguishing between hyperthyrosis and thyrotoxicosis. R. N. C.

Lipoidosis. S. J. THANNHAUSER (Klin. Woch., 1934, 13, 161—167; Chem. Zentr., 1935, i, 589—590).—A review. R. N. C.

Reaction of lipins in blood-leucocytes to fever and infection. E. M. BOYD (Surg. Gynecol. and Obstet., 1935, 60, 205—213).—The lipin content of leucocytes from persons recovering from fever was high; that from those who did not recover was low. CH. ABS. (p)

Influence of infection on tissue respiration. W. FREI and O. FROEBEL (Biochem. Z., 1935, 278, 1—10).—The O₂ utilisation of liver and kidney slices from guinea-pigs infected with fowl cholera, paratyphosis Gärtner, Rauschbrand's bacillus, etc. is > with slices of normal animals, but no relationship could be detected between respiration, clinical results, and body-temp. The respiration of slices from animals poisoned with the culture filtrates of these organisms and also of normal liver and kidney slices on addition of culture filtrates was increased. No essential difference was detected with aerobic and anaerobic organisms. P. W. C.

Treatment of cutaneous Streptococcus infections with intravenous cuprammonium sulphate. E. OTHAZ (Rev. assoc. med. Argent., 1934, 48, No. 336).—Injection with NaOBz or caffeine gave satisfactory results, but secondary effects were observed. CH. ABS. (p)

Hyperglycæmia and hypoglycæmia provoked in myxœdema. A. BAUDOUIN, E. AZERAD, and J. LEWIN (Compt. rend. Soc. Biol., 1935, 119, 688—

690).—Blood-sugar in two cases of myxœdema recovered after ingestion of glucose, but not after insulin (I). The so-called "hypoglycæmia troubles" appeared when hypoglycæmia due to (I) was relatively small, but not at higher vals., and hence are independent of the blood-sugar. R. N. C.

Blood-sugar in internal disease. F. W. LAPP and H. DIBOLD (Deut. Arch. klin. Med., 1934, 177, 40—47).—Variations in the fasting blood-sugar (I) were observed according to the time of day. In gastric, intestinal, and hepatic disease the fasting (I) averaged 70—110 mg. per 100 ml.; vals. were low in gastric and intestinal conditions and high in obesity. Under normal conditions fasting (I) shows a fall at noon: in duodenal ulceration, hyperchlorhydric gastritis, and intestinal conditions the noon and evening vals. were raised; in hypochlorhydric gastritis, achylia, and obesity these findings were reversed. The tolerance to glucose in the above conditions did not agree with the daily "profile" of the (I), being increased in the former and somewhat diminished in the latter group. Seasonal variations were detected in the fasting (I), the val. being max. during February to April and min. during the winter months. NUTR. ABS. (b)

Decrease in sodium chloride content of blood after vomiting. A. TORDAY (Orvosi Hetilap, 1934, 78, 959—961).—Ill effects of vomiting are caused not only by loss of fluid, but also by loss of Cl' . CH. ABS. (p)

Iron metabolism in infancy. Relation to nutritional anæmia. H. W. JOSEPHS (Bull. Johns Hopkins Hosp., 1934, 55, 259—272).—Infants up to 2 months old have a small negative Fe balance which subsequently changes to positive at approx. 6 mg. per month. Infection causes a negative Fe balance. An exclusive milk diet cannot cause severe anæmia in the absence of other factors disturbing Fe metabolism. CH. ABS. (p)

Thyroxine in infancy. J. C. PELLARANO and S. SCHERE (Semana méd., 1935, I, 133—143).—Thyroxine gave better results than thyroid extracts. CH. ABS. (p)

Elimination of the gonadotropic hormone of the anterior pituitary and of folliculin in mania, depression, and schizophrenia at puberty. W. OESTERREICHER (Wien. klin. Woch., 1934, 47, 1385—1388; Chem. Zentr., 1935, i, 586).—Folliculin elimination is considerably reduced in women with mania or depression, but in schizophrenia it is found only in hebephrenics. R. N. C.

Hyperglycæmia provoked in nephritics. F. RATHERY, P. DE TRAVERSE, and V. FARLEY (Compt. rend. Soc. Biol., 1935, 119, 386—389).—Hyperglycæmia after ingestion of glucose in nephritics is > in normal subjects, and more prolonged. There is no correlation between hyperglycæmia and glycosuria or increased blood-urea. R. N. C.

Ability of nephritic patients to deaminate and form urea from ingested glycine. E. KIRK (J. Clin. Invest., 1935, 14, 136—141).—Following ingestion of glycine, the increase in plasma- $\text{NH}_2\text{-N}$ was greater in uræmic than in normal cases. The

return to predigestive levels also occurred more slowly. The delayed conversion into urea in uræmic cases is due to the retardation of the deaminising function rather than of the urea-forming reaction.

CH. ABS. (p)

Causes of the brevity of the hyperglycæmic effect produced by section of the four depressors in the dog. J. MALMEJAC, E. DESANTI, and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 119, 731—733).—The brief hyperglycæmia following section of the depressors is due to increased secretion of adrenaline, which is rapidly corr. by increased insulin secretion. R. N. C.

Clinical significance of a very low concentration of urea in blood. A. E. OSTERBERG and N. M. KEITH (J. Lab. Clin. Med., 1934, 20, 141—144).—Low blood-urea vals. are associated with wasting diseases and with bilateral renal disease. In the latter, there may be increased excretion of urea by kidneys or a decreased production through disturbed N metabolism. CH. ABS. (p)

Salyrgan and ammonium chloride in cardiac œdema. I. HARRIS, E. L. RUBIN, and J. S. LAWRENCE (Acta med. Scand., 1934, 83, 23—40; Chem. Zentr., 1935, i, 745—746).—Salyrgan diuresis is associated with hydræmia which is probably related to the decreased cation concn. of the serum. NH_4Cl -diuresis is associated with a concn. of blood. Serum-cations are reduced by NH_4Cl with restricted, and remain normal with excessive, amounts of fluid. A. G. P.

Calcium and phosphorus metabolism in osteomalacia. III. Effects of varying levels and ratios of intake of calcium to phosphorus on their serum levels, paths of excretion, and balances. S. H. LIU, R. R. HANNON, S. K. CHOU, K. C. CHEN, H. I. CHU, and S. H. WANG (Chinese J. Physiol., 1935, 9, 101—117).—In healing osteomalacia, serum- and faecal $\text{Ca} \propto \text{Ca}$ intake. When $\text{Ca}:\text{P}$ is high serum- and urine-P are low and faecal Ca and urine- Ca increase. On lowering the ratio, urine- Ca tends to disappear and -P to increase. P retention depends on Ca and P intake, but excess Ca can be retained without an equiv. amount of P for bone formation. H. G. R.

Guanidine and parathyroid glands. J. A. SAUNDERS (Biochem. J., 1935, 29, 1597—1598).—Guanidine (I) is not isolated from the blood of parathyroidectomised cats and dogs in tetany, nor is (I), injected into the operated animals, excreted any less rapidly than normally. H. D.

Action of the diet-factor J on the development of pneumonia in guinea-pigs. H. VON EULER, H. SODER, and M. MALMBERG (Z. Hyg. Infektionskr., 1935, 116, 672—682).—Guinea-pigs inoculated with pneumococci while on a complete basal diet containing vitamin-A, -B, and -D develop fatal bronchopneumonia. This is not avoided by administration of ascorbic acid, but is prevented by daily doses of lemon, blackberry, or elderberry juice, which contain factor J. R. N. C.

Chemo- and sero-therapy of pneumococcal pneumonia in the mouse. F. NEUFELD and W. A.

COLLIER (Z. Hyg. Infektionskr., 1935, 117, 129—136).—At early stages the effect of Au and immune-serum combined is $>$ that of either alone. At later stages the combination is less effective, whilst the separate effects of Au and serum are increased.

R. N. C.

Changes in the distribution of fats in the cells of the corpus luteum of pseudo-gestation in rabbits. A. PERAUS (Compt. rend. Soc. Biol., 1935, 119, 771—772).—The distribution of fats in the corpus luteum in pseudo-pregnancy is the same as in pregnancy, but the activity of the corpus luteum is of short duration.

R. N. C.

Histidine secretion in pregnancy. B. BODÓ (Orvosi Hetilap, 1934, 78, 761—763).—A positive Kapeller-Adler reaction was obtained in pregnancy urines. Histidinuria is probably related to altered protein metabolism following disturbed liver functions in pregnancy.

CH. ABS. (p)

Renal rickets. H. A. SALVESEN (Acta med. Scand., 1934, 83, 485—500).—In a case of renal rickets (I) (boy aged 15 years) the urine had low sp. gr. Blood-urea (II) increased from 170 to 368 mg., serum-Ca (III) was 4.8—7 mg., and inorg. P 7 mg. per 100 ml., whilst plasma- CO_2 was 31.8 vols.-% and p_{H} 7.28. There was a reduction of 24 millimols. in total bases of the blood. Ca lactate and cod-liver oil by mouth produced a decrease in (II), an increase in (III), and temporary clinical improvement. (I) is due to Ca deficiency effected through phosphate retention. Parathyroid over-activity may be a factor.

NUTR. ABS. (m)

Rickets and spasmophilia. I, II, III. S. SIVE (Acta paediat., 1934, 17, 1—71, 157—183, 184—214).—There is frequently no alteration in the composition of cerebrospinal fluid in tetany. Manifest tetany may be present even with normal vals. for serum-Ca. It may occur in breast-fed infants when the breast-milk is low in Ca. The occurrence of rickets with low serum-Ca may be due to associated tetany.

NUTR. ABS. (m)

Thyroid in the pathogenesis of human rickets and tetany. Blood-iodine. A. NITSCHKE and H. DOERING (Acta paediat., 1933, 16, 473—479).—The blood of normal infants contained, on an average, 9.3×10^{-6} g. of I per 100 ml., but with rickets or tetany 2.9 and 2.8×10^{-6} g., respectively. The blood-I of such children after treatment with vitamin-D (I) rose from 2.4 to 8.8×10^{-6} g. Excess of (I) in rabbits caused a rise in blood-I well above normal. In rickets and tetany there was also a fall in basal metabolic rate. (I) may have an indirect, stimulating action on the thyroid.

NUTR. ABS. (b)

Production of calcæmia after intravenous injection of calcium gluconate in dogs with acute and chronic tetany. F. MATHIEU (Compt. rend. Soc. Biol., 1935, 119, 549—551).—After injection of Ca gluconate, calcæmia persists longer in latent than in acute tetany.

H. G. R.

Phosphorus retention and alkalosis in infantile tetany. N. MORRIS (Acta paediat., 1933, 16, 580—587).—Tetany, complicating rickets in children, may occur without excessive retention of P over Ca, and

excessive P retention may occur without signs of tetany. Alkalosis is not necessarily a concomitant of tetany or acidosis of active rickets. Acidosis induced by administration of NH_4Cl cures tetany probably by making available the body-store of Ca. No support is given to the view that tetany and rickets are due to disturbance in the acid-base balance of the body.

NUTR. ABS. (m)

Ammoniogenesis. Blood-ammonia in tetany from hyperventilation. G. POPOVICIU, G. BENETATO, and C. OPRISU (Compt. rend. Soc. Biol., 1935, 119, 443—444).—Blood- NH_3 increases in simple and adrenaline hyperventilation, but falls in that due to ergotamine. Acid-base equilibrium is shifted towards alkalosis, and blood-P falls.

R. N. C.

Non-protein-nitrogen content of serum and elimination of glycine during experimental tuberculosis. F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, 119, 513—515).—After infection, the non-protein-N increases rapidly and gradually returns to normal; after injection of glycine, it falls rapidly and slowly returns to normal.

H. G. R.

Effect of the tuberculin reaction on metabolism of residual nitrogen, and curve of elimination of glycine in normal, tuberculous, or BCG-inoculated rabbits. F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, 119, 727—730).—Residual N metabolism is unchanged by tuberculin in normal, slightly raised in BCG-inoculated, and considerably in tuberculous, rabbits.

R. N. C.

Blood-cholesterol in typhoid fever. H. SZPIDBAUM (Compt. rend. Soc. Biol., 1935, 119, 667—668).—The blood-cholesterol curve proceeds in the inverse sense to the temp. curve in typhoid fever.

R. N. C.

Effect of the gonadotropic hormone on blood-cholesterol and evolution of typhoid fever. H. SZPIDBAUM (Compt. rend. Soc. Biol., 1935, 119, 668—672).—Injection of the gonadotropic hormone of pregnancy urine in cases of typhoid fever produced increases in blood-cholesterol and falls of temp.

R. N. C.

Resistance of capillaries. II. Fall of capillary resistance in patients on gastro-intestinal diets, particularly ulcer diet, and its behaviour with vitamin-C. III. Improbability of avitaminosis-C as the ætiological factor in gastric ulcer. P. SCHULTZER (Acta med. Scand., 1934, 83, 544—554, 555—564; Chem. Zentr., 1935, i, 431; cf. A., 1934, 1389).—II. Capillary resistance falls in patients with gastric ulcer on a diet deficient in vitamin-C, and is restored to normal by -C.

III. The distribution of decreased capillary resistance in patients is apparently independent of the type of disease, which makes it improbable that -C deficiency is the ætiological factor in gastric ulcer.

R. N. C.

p_{H} of gastric juice in gastroduodenal ulceration. G. SELVAGGI (Policlin., 1934, 41, 674—684).—Before injection of histamine (1 mg.) the average p_{H} of the juice was about 1.75 in healthy persons and in persons with ulcers. After injection the vals. were about 2.6 and 1.12—2.67, respectively.

NUTR. ABS. (m)

Chemical and electrical properties of connective tissue. R. KELLER (Biochem. Z., 1935, 278, 447—453; cf. A., 1934, 1246).—The tissue is electro-negative. W. McC.

Distribution of electrolytes in a solution of albumin. L. AMBARD and C. DEVILLER (Compt. rend. Soc. Biol., 1935, 119, 575—576).—Distribution of Cl^- is not uniform, the concn. being max. in the intermicellary zone, and, in the micelles, inversely \propto their size. R. N. C.

Hofmeister's series and the grouping of ions. R. KELLER (Biochem. Z., 1935, 278, 454—459).—The diffusion of ions into and out of different parts of the animal organism and their ionic contents accord with the predominantly (biologically) electro-positive or -negative nature of the parts and suggest a classification of the ions similar to or identical with that of Hofmeister. Account must be taken of non-ionised electrolytes, however, and physiological concns. only considered. W. McC.

Relation of water and electrolytes to metabolism. H. A. DAVIS (Science, 1935, 81, 493—494).—The O_2 consumption of dogs is markedly increased by intravenous injection of isotonic solutions of 0.9% NaCl and 5% glucose solutions, the effect produced by glucose being the greater. The H_2O lost \propto the increase in O_2 consumption and metabolic rate. H_2O given by mouth increased the consumption only slightly and is retained longer than that given by vein. Repeated blood-letting lowered the metabolic rate and isotonic solutions were then retained for longer periods. The O_2 consumption of the body-tissues appears to be one of the fundamental factors concerned in H_2O regulation. L. S. T.

Effect of salt and sugar solutions on water exchange through the skin of frogs. B. B. RUBENSTEIN (J. Cell. Comp. Physiol., 1935, 6, 85—99).—Passage of H_2O through frog-skin may occur in both directions and is probably under nervous control. Mucus or slime covering the skin exerts an anti-osmotic effect which is abnormally high in relation to its osmotic activity. This effect corresponds with a "protective" action depending on some form of structural fixation of the protein on the cell surface. A. G. P.

Theory of permeability of thin films. J. F. DANIELLI and H. DAVSON (J. Cell. Comp. Physiol., 1935, 5, 495—508).—The permeability of living cells is explicable if the plasma membrane be assumed to consist of lipid matter. Such a membrane is capable of distinguishing mols. of different sizes and solubility characteristics and ions of different charge. Salt antagonism is also explained. A. G. P.

Permeability of living cells to heavy water. B. LUCKÉ and E. N. HARVEY (J. Cell. Comp. Physiol., 1935, 5, 473—482).—The rate of penetration of D_2O was the same as that of H_2O . High concns. of D_2O inhibited the development of fertilised cells. A. G. P.

Effect of temperature on osmotic equilibrium of living cells (unfertilised eggs of *Arbacia punctulata*). B. LUCKÉ (J. Cell. Comp. Physiol., 1935, 5,

465—471).—In the range 5.4—29.3° temp. had no effect on the osmotic equilibria. A. G. P.

Osmotic regulation in *Gunda ulva*. L. C. BEADLE (J. Exp. Biol., 1934, 11, 382—396).—*G. ulva* can live in any concn. of sea- H_2O down to 5%. Internal osmotic relationships are examined.

CH. ABS. (p)

Tension at the surface of mackerel-egg oil: nature of the cell surface. J. F. DANIELLI and E. N. HARVEY (J. Cell. Comp. Physiol., 1935, 5, 483—494).—The low interfacial tension between the aq. and the oily matter of the egg is attributable to the absorption of a globulin-like protein at the oil surface. The denaturation of egg-proteins at the oil- H_2O interface is examined and the nature of the cell surface is discussed. A. G. P.

Influence of variations of the cryoscopic depression of the external medium on that of the blood and urine of anodonts. M. FLORKIN (Bull. Acad. roy. Belg., 1935, [v], 21, 432—435).—Specimens of *Anodonta cygnea* were kept in fresh H_2O to which varying amounts of sea- H_2O were added. The blood and urine were always isotonic and became isotonic with all external media having a cryoscopic depression >0.1 . W. R. A.

Relative values of cations in antagonising the action of hydroxyl ions on the premembrane system of the eggs of five echinoids. A. R. MOORE (J. Cell. Comp. Physiol., 1935, 5, 433—440).—The crit. concns. of cations adequate to preserve the membrane-forming capacity of eggs were determined in solutions of urea isosmotic with sea- H_2O at p_{H} 8.0. Vals. for alkali metals were similar for an individual species, but differed with the species. The effectiveness (1/crit. concn.) of Mg, Sr, Ca, and Ba, as chlorides, increased in the order named, and was much $>$ that of the alkali metals, whilst that of cobaltamine salts increased with valency, bivalent compounds being more effective than alkaline earths. A. G. P.

Binuclear cells in tissue cultures. J. ZWEIBAUM and M. SZEJNMAN (Bull. Acad. Polonaise, 1935, B, 37—48).—The formation of binuclear cells in cultures of fowl embryo *in vitro* is favoured by low p_{H} , excess of CO_2 , O_2 insufficiency, evaporation, hypertonia or hypotonia of the medium, and a temp. of 34—36°. Prolonged cultivation in the same medium favours binuclear cell production by formation of acid metabolic products. R. N. C.

Inducing agent in embryonic development. F. G. FISCHER, E. WEHMEIER, H. LEHMANN, L. JUHLING, and K. HULTZSCH (Ber., 1935, 68, [B], 1196—1199).—Evidence is adduced in favour of the view that the inducing agent of unorganised materials may be an acid. Whether this is also the case with living agents is not established. H. W.

Linking of chemical changes in muscle. D. M. NEEDHAM and W. E. VAN HEYNINGEN (Nature, 1935, 135, 585—586).—Working with dialysed muscle extracts, it is shown that adenylic acid and creatine are essential intermediaries in the reaction by which muscle obtains its energy from the transformation of glycogen into lactic acid. W. P. R.

Permeability of the intestine *in vitro*. H. G. K. WESTENBRINK (Arch. néerl. Physiol., 1935, 20, 116—122).—The permeability to glucose of rat intestine immersed in Ringer's solution saturated with air at 37° increases with the time of immersion. The adaptation of glucose resorption through the intestinal walls in presence of carbohydrate in the food, observed *in vivo*, cannot be demonstrated *in vitro*, nor can the partial conversion of fructose into glucose during its passage through the walls. R. N. C.

Basal metabolism and prolonged exogenous hyperthermia. S. GELINEO (Compt. rend. Soc. Biol., 1935, 119, 645—647).—The basal metabolism of rats placed in high external temp. for long periods increases at the outset, but soon falls to normal, showing no further change throughout the period. R. N. C.

Metabolism in undernutrition. J. M. STRANG, H. B. McCLUGAGE, and M. A. BROWNLEE (Arch. Int. Med., 1935, 55, 958—978).—During the treatment of human undernutrition by administration of diets of high calorific val. only very slight changes in the basal metabolism were observed. The levels of N metabolism were within normal limits, and the digestive and absorptive capacities of the patients were adequate. A. L.

Effect of prolonged feeding with tomatoes. A. SCHEUNERT and M. SCHIEBLICH (Z. Unters. Lebensm., 1935, 69, 127—131; cf. Z. Krebsforsch., 1931, 34, 348, 362; 1932, 36, 128).—No harmful consequences resulted from feeding rats for 1 year on a diet containing 42% of raw or cooked tomatoes. E. C. S.

Nutrition of *Flabellula mira*, Schaeffer. N. E. RICE (J. Elisha Mitchell Sci. Soc., 1934, 50, 39—40).—*F. mira* reproduces in media containing 20—150% of the total salts in normal sea-H₂O, rarely in 20% sea-H₂O, and not in distilled H₂O, or in solutions isotonic with sea-H₂O containing single salts or combinations of salts lacking in NaCl. Reproduction is normal in solutions containing MgCl₂ and CaCl₂ in proportions occurring in sea-H₂O and less frequent in those containing NaCl and either MgCl₂ or CaCl₂. The rate of reproduction is correlated with osmotic concn., and to the ratio of uni- to bi-valent cations. In the range examined p_H had no influence. CH. ABS. (p)

Metabolism of the lung-fish. I. Fasting metabolism in active fish. H. W. SMITH [with N. FARANACCI and A. BREITWEISER] (J. Cell. Comp. Physiol., 1935, 6, 43—67).—From the beginning of fasting the O₂ consumption falls in a regular (approx. logarithmic) manner for at least 300 days, reaching a val. of 10—20% of that in the fully-fed condition. The decline in O₂ consumption is related to a change in the nutritional state rather than to the wt. of the fish. The latter decreases more slowly as fat and protein are consumed. A. G. P.

Changes in the body constituents during metamorphosis of *Bombyx mori*, L. Y. YONEZAWA and K. YAMAFUJI (Bul. Sci. Fak. Terkult. Kjusu, 1935, 6, 126—138).—A detailed account is given of the variation during the life-cycle of the insect of its carbohydrate, fat, total and protein-N, total and

org. phosphate, ash, and Fe contents. During the spinning of the cocoon most of the protein is excreted and fat and glycogen are stored for utilisation in the pupal stage. Variations in the nature of the fat and protein in the various stages of development are also described. E. A. H. R.

Respiration of fragments obtained by centrifuging the egg of the sea urchin, *Arbacia punctulata*. R. SHAPIRO (J. Cell. Comp. Physiol., 1935, 6, 101—116).—The unfertilised but nucleated half of the cell consumes O₂ at a rate similar to that of the whole, whereas the pigmented half containing most of the yolk and echinochrome but no nucleus shows much higher vals. On fertilisation the O₂ consumption of the nucleated half increases, but that of the pigmented half is unchanged. A. G. P.

Relative effects of increased carbon dioxide tensions and decreased oxygen tensions on the heart frequency of young trout. C. HAYWOOD, T. O. STEVENS, H. M. TEWINKEL, and M. SCHOTT (J. Cell. Comp. Physiol., 1935, 5, 509—518).—Increased CO₂ tension causes a rapid decline in heart frequency of trout. A lowered O₂ tension produces a similar effect after a preliminary lag period. Rates of recovery from these effects are examined. A. G. P.

Mechanism of [tissue] respiration. A. SZENT-GYORGYI (Nature, 1935, 135, 1040).—A reply to criticism (cf. this vol., 777). L. S. T.

Mechanism of the Pasteur effect. K. DIXON and E. HOLMES (Nature, 1935, 135, 995—996).—KCl produces increased O₂ uptake in brain-tissue with substrates other than glucose (I), e.g., fructose and lactate, which cannot form lactic acid (II) in N₂. The rate of disappearance of lactate is increased by K. KCl also causes aerobic glycolysis of mannose which can form (II) anaerobically. The co-existence of aerobic glycolysis and increased respiration with (I), and the slight action of O₂ on the glycolysis of normal cells, is probably due to a change in the permeability of the cell-membrane which limits the rate at which (I) can reach the cell-enzymes. Inhibition of the Pasteur effect consists of a removal of this limitation, and the increase in permeability results in increased rates of respiration and (II) formation. O₂ and Ca decrease this permeability. Rb and Cs have a similar effect to K in causing aerobic glycolysis. L. S. T.

Metabolism of normal and tumour tissues. XIII. Neutral salt effects. F. DICKENS and G. D. GREVILLE (Biochem. J., 1935, 29, 1468—1483).—Alkali chlorides when added in 0.1 M concn. to Ringer's solution increase the respiration of rat brain-tissue, the order of activity being Li, Na < Rb, Cs, K. KCl increases the glucose oxidation, but decreases the anaerobic glycolysis. The effects on the brain metabolism of leaving out, in turn, various cations of the solution are described. Neutral salt effects on brain metabolism are ascribed to changes in the colloidal state of the protoplasm, and the similarity between control of brain metabolism by changes in the medium, and the control of muscle contraction is pointed out. J. N. A.

Effect of high-protein diet on arterial pressure in cases of hypertony. I. HARRIS, C. N. ALFRED,

and A. G. H. ENGLISH (Lancet, 1935, i, 1327—1328).—When a high-protein diet does not raise the blood-pressure there is an increase of non-protein-N, and when it raises the blood-pressure conspicuously non-protein-N does not increase but may even fall. When the blood-pressure falls, non-protein-N increases.

L. S. T.

Amino-acid composition of important food-proteins. I. Theoretical. A. E. SCHARPENAK. II. Method of determining the amino-acid composition of proteins. III. Amino-acid composition of meat-proteins (beef). O. N. BALASCHOVA, V. V. LVOVA, E. M. SOLOVEEVA, and A. E. SCHARPENAK (J. Physiol. U.S.S.R., 1934, 17, 264—267, 268—276, 277—286; cf. this vol., 652).—II. Hydrolysed proteins were extracted with BuOH prior to fractionation.

III. Analytical data are given. Cystine vals. are low (1.2%). CH. ABS. (p)

Biological value of proteins and the digestibility of food constituents of mixed vegetarian diets containing processed wheat brans. S. WAN (Chinese J. Physiol., 1935, 9, 125—140).—15% of bran does not affect the biological val. or digestibility of the other constituents, the biological val. being increased slightly if processed bran is used. On reducing the protein to 10% both biological val. of the protein and digestibility of the fat and carbohydrate are increased, but digestibility of the ash and fibre is decreased. All bran diets gave fairly good growth, reproduction, and lactation.

H. G. R.

Metabolism of amino-acids. III. Deamination of amino-acids. H. A. KREBS (Biochem. J., 1935, 29, 1620—1644).—The enzymic system catalysing the deamination of the natural ("l-") NH_2 -acids is different from that catalysing the deamination of the non-natural "d"-acids, in that the former system is destroyed by drying, cannot be extracted, and is inhibited by octyl alcohol and 0.01M-KCN, whilst the latter is not destroyed by drying, is readily extracted from fresh or dried tissue by aq. solutions, and is not affected by octyl alcohol or KCN. The activity of the "d" and "l"- NH_2 -acid deaminases under varying conditions, and their occurrence in various tissues and animals, is investigated. The "l"- NH_2 -acid deaminase is active in ground tissue when suspended in a small vol. of fluid, but activity disappears on dilution, approx. \propto the extent of dilution. The cell respiration shows a similar sensitivity to dilution. The effect of dilution is explained on the assumption that a ternary collision plays a role in the reaction. The deamination of l- and d- NH_2 -acids in kidney slices is inhibited by substances which can be oxidised by kidney. If two different substances, each of which causes an increase in O_2 consumption, are added together to kidney or yeast, no summation of the effects on the O_2 uptake ensues, the substrates competing for the O_2 and displacing each other. The process of activation of O_2 is identical for all substrates which show no summation.

P. W. C.

Synthesis of dipeptides with an amino-group in a serine residue. E. ABDERHALDEN and A.

BAHN (Z. physiol. Chem., 1935, 234, 181—195; cf. A., 1933, 1063).—Advantage is taken of the fact that N-Bz derivatives of NH_2 -acids and peptides vary greatly in their resistance to acid hydrolysis (e.g., with 10% H_2SO_4 for 3 hr. at 70—80°) in the separation of the constituents of mixtures (e.g., of aspartic and glutamic acids) and in the synthesis of peptides containing a serine residue, this residue having the free NH_2 group. The peptides are identified by treatment with PhSO_2Cl and hydrolysis of the product to benzenesulphonylserine and the NH_2 -acid with which it was combined. dl-Leucyl-dl-serine treated with MeOH at 0° and then (3 days) with MeOH saturated with NH_3 gives the anhydride, m.p. 224°, which with 10% H_2SO_4 (4 days) yields dl-seryl-dl-leucine, m.p. 216° (benzenesulphonyl derivative). Similarly glycyl-dl-seryl anhydride, m.p. 218—220°, gives dl-serylglycine (benzenesulphonyl derivative). 1 mol. of serine reacts with dicarbobenzyloxytyrosyl chloride (I) to give di(dicarbobenzyloxytyrosyl)serine (II), m.p. 158—159°, $[\alpha]_D^{20} +22.5^\circ$ in 20% HCl [no (II) is produced if 2 mols. of serine are used], and dicarbobenzyloxytyrosylserine (III). (III) on reduction (H_2 -Pd) gives l-tyrosyl-d-serine, which yields the anhydride (IV), m.p. 253—255°, as before. dl-Seryl-l-tyrosine (dibenzenesulphonyl derivative) is obtained from (IV) by acid hydrolysis (alkaline hydrolysis gives tyrosylserine). (II) is rapidly hydrolysed by erepsin and less rapidly by trypsin. (III) on treatment with erepsin gives l-tyrosyl-d-serine, $[\alpha]_D^{20} +18^\circ$ in 20% HCl, but is not attacked by trypsin. The anhydride from l-tyrosyl-l-serine on acid hydrolysis gives l-seryl-l-tyrosine, m.p. 293—298°, $[\alpha]_D^{20} +27.5^\circ$ in 20% HCl. 2 mols. of (I) with 1 mol. of tyrosine give di(dicarbobenzyloxytyrosyl)tyrosine, reduced (H_2 -Pd) to dityrosyltyrosine (hydrochloride), which readily decomposes into tyrosine and tyrosyltyrosine.

W. McC.

Blood-arginine and growth. M. REISS, L. SCHWARZ, and F. FLEISCHMANN (Z. physiol. Chem., 1935, 234, 201—207).—100 c.c. of normal rabbit blood contain 5—7 mg. of free arginine (I). This amount is reduced to about half in pregnant rabbits (normal vals. restored *post partum*). Rabbits with carcinoma and rats with sarcoma have diminished amounts of (I) in their blood. In virgin rabbits (but not in those from which the ovaries have been removed) administration of the hormone of the anterior lobe of the pituitary causes decrease in blood-(I), but the normal vals. are then attained if the ovaries are removed. Intravenous injection of arginase activators (cysteine, glutathione, FeCl_2) causes decrease in blood-(I).

W. McC.

Adrenaline synthesis *in vitro* under physiological conditions. W. SCHULER and A. WIEDEMANN (Z. physiol. Chem., 1935, 233, 235—256).—Slices of the surviving adrenal of the guinea-pig can synthesise adrenaline (I) [or a substance reacting as (I)] from tyramine, but not from dihydroxyphenylalanine or phenylhydroxyethylamine. The (I) was determined by the Folin reaction using the spectrophotometer and in some cases was identified by the biological method (effect on blood-pressure). The adrenal medulla is active, but not the cortex. Tyramine is probably synthesised in another organ,

possibly the kidney. The synthesis is but little affected by the concn. of the substrate or the amount of tissue employed, but depends almost entirely on the synthetic power of the sample of tissue, which varies widely with different samples and is a vital function of the cell.

J. H. B.

Metabolism of monomethyltryptophans. W. G. GORDON and R. W. JACKSON (J. Biol. Chem., 1935, **110**, 151—164; cf. A., 1929, 1485; Matsuoka *et al.*, A., 1931, 513).—3-Indolyl-5-(1-methylhydantoyl)methane, m.p. 213—214° (obtained from the product of interaction of 3-indolealdehyde and 1-methylhydantoin by reduction with Na-Hg), when boiled with aq. Ba(OH)₂ gives α -methylamino- β -3-indolylpropionic acid (I), m.p. 297° (decomp.) [picrate, m.p. 186° (decomp.)]. Although 5- and 2-methyltryptophan cannot replace tryptophan (II) in the diet of rats, (I) stimulates their growth, although not so efficiently as does (II), when they are subsisting on a diet deficient in (II).

W. McC.

Organs which regulate indolæmia and indoxylæmia after injection of indole. B. A. HOUSSEY, V. DEULOFEU, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1935, **119**, 875—876).—Indole (I) is transformed into indoxyl (II) in the liver. Only one third of the (I) introduced into the circulation can be recovered as (II).

H. G. R.

Indoxylogenic substances in the organism. B. A. HOUSSEY, V. DEULOFEU, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1935, **119**, 877—879).—Substances which increase indoxylæmia when introduced into the blood are tabulated.

H. G. R.

Fate of nicotine in fresh liver. A. WENUSCH (Biochem. Z., 1935, **278**, 349—350).—In 24 hr. at 37° fresh minced pig-liver has no effect on nicotine, which is recovered unchanged.

W. McC.

Diffusion equilibria for the isolated frog's kidney. II. Urea. E. J. CONWAY and F. KANE (Biochem. J., 1935, **29**, 1446—1458).—Active isolated frogs' kidneys can concentrate urea from an external urea-Locke solution, whereas inactive kidneys (urea-cyanide-Locke) do not possess this power. Determination of urea in the frog's kidney by the xanthinohydrase and the urease methods gave identical results.

P. W. C.

Nitrogen catabolism in invertebrates. IV. Synthesis of uric acid in *Helix pomatia*. E. BALDWIN (Biochem. J., 1935, **29**, 1538—1546).—Surviving slices of the hepatopancreas of *H. pomatia* convert a mixture of urea and tartronic acid into uric acid. It is suggested that urea is synthesised in *H. pomatia* by means of the ornithine cycle, and then converted into uric acid probably by way of dialuric acid.

J. N. A.

Endogenous nitrogen metabolism of hypophysectomised rats. B. BRAIER and R. MOREA (Compt. rend. Soc. Biol., 1935, **119**, 881—882).—On a protein diet, urinary N does not vary, but the creatinine is < normal. On a protein-free diet, endogeneous protein catabolism is < normal.

H. G. R.

Cholesteryl esters as a mechanism of fat metabolism. H. PETERSILIE (J. Lab. Clin. Med.,

1934, **20**, 144—149).—Abnormal variations in the % of cholesteryl esters in blood, in cases of liver and kidney diseases, depend on conditions of diet and therapy, and are closely related to carbohydrate metabolism.

CH. ABS. (p)

Fate of vegetable sterols in the animal organism. II. H. DAM and U. STARUP (Biochem. Z., 1935, **278**, 342—344; cf. this vol., 113).—In the dog, intravenously injected vegetable sterol is excreted in the faeces. In the rat, the amount excreted is 82% of that injected. New-born rats of a mother receiving injections of the sterol excrete no sterol in the faeces.

W. McC.

Fat metabolism. B. FLASCHENTRAGER and K. BERNHARD (Naturwiss., 1935, **23**, 356).—Ingestion of Me decoate by dogs fed on a diet including coconut oil and butter is followed by the occurrence of sebatic (I) and suberic acids in the urine. Et, but not Me, dodecoate behaves similarly, but to a smaller extent, whilst Na decoate and cooking-fat yield (I). The bearing of the data on ω -oxidation is discussed (cf. A., 1934, 1027).

F. O. H.

Fat absorption. Its value as an index of function of the liver. M. SULLIVAN and J. A. B. FERSHTAND (Arch. Int. Med., 1935, **55**, 834—841).—Using the Rückert method, the average total serum-lipin of man in the fasting state was 0.576 c.c. per 100 c.c., which was not affected by body-wt. or fasting. The absorption curves, after ingestion of cotton-seed oil, were characteristic for diseases of the liver and for diabetes.

H. G. R.

Is it possible, in a balanced ration, to substitute for glycerides the corresponding fatty acids? B. LECOQ (Compt. rend., 1935, **200**, 1979—1980).—Oils (castor, olive, etc.) cannot be replaced by mixtures of glycerol and the fatty acids in a pigeon ration, without nutritional disturbance, even when yeast is supplied to provide vitamin-B.

A. G. P.

Comparative value of fat and carbohydrate in the utilisation of protein. E. F. TERROINE (Bull. Soc. Chim. biol., 1935, **17**, 690—692).—A criticism of the results of Maignon (this vol., 388).

A. L.

Comparative value of fat and carbohydrate in the utilisation of protein. F. MAIGNON (Bull. Soc. Chim. biol., 1935, **17**, 693—695).—A reply (cf. preceding abstract).

A. L.

Influence of lipin on the carbohydrate metabolism. I. Changes in the content of glucose and lactic acid in blood and of the latter in urine of rabbits caused by the injection of cholesterol and lecithin. N. HOSAKA (Japan. J. Exp. Med., 1934, **12**, 455—495).—Starvation of rabbits caused a decrease in the blood- and urinary lactic acid (I) and in the blood-sugar (II). Injection of cholesterol (III) during starvation caused the blood-(I) first to rise and then gradually to fall, and the urinary (I) and (II) to decrease. Injection of lecithin (IV) produced a fall in blood-(I), and an increase in the urinary (I) and (II). Injection of these lipins into rabbits which were being fed produced no changes. The results produced by injection of (III) and (IV) irradiated with X-rays or a quartz lamp were also investigated.

NUTR. ABS. (b)

Mutual displacement of glycogen and fat in liver cells. S. NAGAO (Tôhoku J. Exp. Med., 1934, 24, 555—564).—In rabbits on a normal diet, intravenous injection of fat caused a complete disappearance of liver- and muscle-glycogen. The fat content of the liver and, to a smaller extent, of the muscles was raised. Increased deposition of liver-glycogen following intravenous injection of glucose was accompanied by a decrease in liver-fat. With simultaneous administration of fat and glucose there was no significant change. NUTR. ABS. (b)

Law of mass action and specific dynamic action of carbohydrates. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1935, 119, 436—438).—The sp. dynamic heat increase in the dog on continuous injection of glucose \propto the rate of injection when this is small; it increases less rapidly than the rate, reaching a steady max. at 6 g. per kg. per hr. The ratio of the heat evolved by all the glucose assimilated to sp. dynamic heat increase is const. for the whole range of rates of assimilation. The sp. dynamic action of glucose is almost entirely of oxidative origin when the rate of injection is > 1 g. per kg. per hr. R. N. C.

Mechanism of alimentary hyperglycæmia. I. Blood-sugar after oral and intraduodenal glucose administration. II. Rate of absorption of glucose in the small intestine. III. Sugar content of blood in various vessels after intraduodenal glucose administration. F. MEYTHALER and H. SEEFISCH (Arch. exp. Path. Pharm., 1935, 178, 461—466, 467—469, 470—479).—I. Oral or intraduodenal administration of glucose to men and dogs is followed successively by an alimentary pre-hyperglycæmia (1—5 min. duration), pre-hypoglycæmia (1—5 min.), and hyperglycæmia (approx. 1 hr.) and finally a post-hyperglycæmic hypoglycæmia (approx. 1 hr.).

II. Glucose intraduodenally administered to narcotised (somnifen) dogs is rapidly absorbed. The portal vein blood-sugar (I) curve indicates that the absorption is related to the rhythmic function of the intestinal mucous membrane. The initiation of absorption is independent of the concn. of glucose, whilst its rapidity and extent are not related to the fasting val. of the (I).

III. Intraduodenal administration of glucose to dogs produces an immediate (within 1 min.) increase of the portal (I), the rate of absorption being independent of the nutrition of the animal. The portal (I) is $>$ that of the hepatic vein, whilst the difference between the latter and that of the inferior vena cava represents the peripherally retained sugar. The variations in (I) immediately following absorption are described and the mechanism involved is discussed. F. O. H.

Metabolism of galactose. I. Phosphorylation during galactose fermentation and its relation to the interconversion of the hexoses. G. A. GRANT (Biochem. J., 1935, 29, 1661—1676).—The sp. mechanism developed in certain yeasts during the process of adaptation on galactose (I) and required for fermentation of (I) is largely destroyed when the adapted yeast is treated with PhMe or

dried or used for the prep. of cell-free juice. During the fermentation of (I) by adapted yeast, chiefly 1 : 6-diphosphofructofuranose together with diglucose phosphate, trehalose monophosphate, and possibly smaller amounts of Robison's ester accumulate in solution, but no evidence was obtained of the production of a (I) phosphate and moreover synthetic (I) 6-phosphate was not readily fermented by this yeast. The polysaccharides synthesised by the adapted yeast when grown on (I) consist mainly of glucose and to a smaller extent of fructose and mannose. The mechanism of the transformation of (I) into the other hexoses is discussed. P. W. C.

Gastric and duodenal function in relation to sugar tolerance tests. M. PELLEGRINI (Atti R. Accad. Fisioer. Siena, 1934, 11, 478).—Changes in motor and secretory activity of the stomach are reflected in changes in the level of blood-sugar (I) after ingestion of sugar. Hypersecretion and hypermotility frequently give a curve showing an early max. concn. of (I), whilst hypo- and a-chlorhydria give a retarded rise in (I). The shape of the (I) curve is very variable in cases of gastric and duodenal ulcer. NUTR. ABS. (b)

Post-mortem glycogenolysis in rabbit liver. H. R. NOLTIE (Quart. J. Exp. Physiol., 1934, 24, 261—270).—The rate of glycogenolysis in rabbit liver incubated at 38° is not determined by the initial glycogen %. Although "free sugar" increases markedly, lactic acid rises but little, and the two together are always insufficient to account for the glycogen loss. The results are similar whether the glycogenolysis occurs in air or in N₂.

NUTR. ABS. (b)
Effect of prolonged muscular work on the metabolism of carbohydrates introduced at constant velocity into the circulation. M. WIERZUCHOWSKI, T. CHMIELEWSKI, A. GOSTYNSKA, and H. FISZEL (Compt. rend. Soc. Biol., 1935, 119, 433—435).—The rate of assimilation of glucose in the dog is increased by muscular work; maltose assimilation also increases proportionally with the rate of hydrolysis by blood-maltase. Assimilation of sucrose is slightly diminished, whilst that of fructose is unaffected. R. N. C.

Comparative determination of the rate of oxidation of alcohol in the organism by blood-alcohol curves and direct measurement. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 119, 568—571).—In the case of EtOH ingested or introduced intraperitoneally in rabbits, determination of the rate of oxidation by blood-EtOH curves is not trustworthy. Widmark's results for man are only approx. R. N. C.

Effect of the concentration of alcohol attained at the surface of the tissues on its rate of oxidation *in vivo*. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 119, 572—575).—In rats and mice the rate of oxidation of EtOH is independent of the blood-EtOH (I); in the guinea-pig, cock, and rabbit, it decreases with (I). R. N. C.

Transformation of natural *l*-phosphoglyceric acid by animal tissue. II. Conversion into

phosphopyruvic acid. H. K. BARRENSCHEEN, G. LORBER, and W. MEERAUS (Biochem. Z., 1935, 278, 386—395; cf. this vol., 521).—Since Hg^{II} salts convert phosphopyruvic acid (I) into AcCO_2H (II), (I) and (II) can be determined in presence of each other as dinitrophenylhydrazones. In fresh muscle extract and pulp and kidney pulp (rabbit) and in human erythrocytes the conversion of phosphoglyceric acid (III) into (I) rapidly (< 30 min.) reaches its max., but the conversion of (I) into (II) proceeds much more slowly. When $\text{HgCl}_2 + \text{HCl}$ are used to deproteinise, more H_3PO_4 is found than when $\text{CCl}_3\text{-CO}_2\text{H}$ is used, the excess corresponding with the amount of (II) produced from (I). Only part of the easily hydrolysed phosphate produced during transformation of (III) is accounted for by production of (I).

W. McC.

Production of phosphoric esters in the intestinal mucous membrane during resorption of sugars, glycerol, [and fat]. L. LASZT and H. SULLMANN (Biochem. Z., 1935, 278, 401—417; cf. this vol., 521).—The amount of acid-sol. org. phosphate in the rat intestine is greatly (about 100%) increased by administration of glucose, fructose, galactose, glycerol, and olive oil and increased to a smaller extent by that of sorbose. No increase follows administration of xylose, arabinose, or mannose. Most of the org. phosphate produced is easily hydrolysed. Hence the resorption of carbohydrates (and glycerol) and fats in the intestine is associated with phosphorylation.

W. McC.

Interference of hepatic fructolysis and adrenaline glycogenolysis in a normal dog at three states of assimilation. M. WIERZUCHOWSKI and F. SEKURACKI (Compt. rend. Soc. Biol., 1935, 119, 661—664).—Blood-lactic acid (I) in the normal dog on continuous injection of fructose reaches different levels according to the diet previously administered to the animal; (I) after protein $<$ after carbohydrate (II) $<$ after starvation. All three levels are raised proportionately by adrenaline (III). Urinary lactic acid also reaches similarly dependent levels, but the max. effect with (III) is obtained after the (II) diet. Glycogenolysis also plays a part in lactic acid increase.

R. N. C.

Significance of lactic acid in heart metabolism. A. RUHL (Klin. Woch., 1934, 13, 1529—1534; Chem. Zentr., 1935, i, 592—593).—The intact heart in a heart-lung prep. takes up lactic acid (I) from the coronary blood in normal conditions and partial O_2 deficiency, but liberates it in complete anoxæmia due to HCN . (I) is also consumed in $\text{CH}_2\text{I-CO}_2\text{H}$ poisoning. Glucose is taken up only in the hyperglycæmic state. Only 30% of the O_2 consumed is accounted for by oxidation of (I) and carbohydrates. In an insufficient heart an increase of (I) uptake corresponds with a decreased O_2 consumption.

R. N. C.

Effect of diet on ketogenesis. H. TRIMBACH (Arch. internat. Physiol., 1934, 39, 434—461).—An exclusive fat diet produces a greater ketonuria than does a strict carbohydrate diet in the rat and pig, but not in the dog. Proteins are not ketogenic. A diet of fat and carbohydrate reduces the ketonuria caused by an exclusive fat diet.

NUTR. ABS. (m)

Effect of the hydrogen carbonate ion on muscle metabolism. E. M. BERKOVICH (J. Physiol. U.S.S.R., 1934, 17, 383—388).—The lactic acid content of muscle is increased by CO_2 and HCO_3' , but not by CO_3'' .

CH. ABS. (p)

Distribution of potassium in cells and the changes taking place during stimulation. V. BUREAU (Arch. internat. Physiol., 1934, 39, 311—328).—The reagent used by Macallum to demonstrate the presence of K in tissues is hypertonic and toxic, so that the cells are stimulated and the distribution of K is changed before pptn. of the K can occur. The reagent was therefore modified to make it isotonic and to ensure rapid fixation of the tissues. Under such conditions, when the cell was at rest, the intracellular K was most abundant close to the cell-membrane and the nuclear membrane. K was also distributed uniformly, but in smaller concn., throughout the cytoplasm and nucleoplasm. In striped muscle, K was condensed on the cell-membrane and inside the anisotropic discs. There was no K in the isotropic discs. Stimulation of cells led to passage of K to the outside of the cell.

NUTR. ABS. (b)

Sodium and calcium requirements of the animal organism (*Drosophila*). D. L. RUBINSTEIN, V. LVOVA, and H. BURLAKOVA (Biochem. Z., 1935, 278, 418—427; cf. A., 1934, 1035).—*D. melanogaster* lives and reproduces normally when almost completely deprived of Na and Ca (95% and 99% removed) by propagation on a medium (purified yeast, salts, and glucose on SiO_2 gel) free from Na and Ca.

W. McC.

Metabolism of copper. E. J. COULSON, R. E. REMINGTON, and K. M. LYNCH (U.S. Dept. Commerce, Bur. Fisheries Invest. Rept., 1934, 23, 1—12).—Prolonged feeding of Cu (525 mg. per kg. of diet) in the form of "green" oysters or CuSO_4 had no toxic effect on rats. Oysters fed in conjunction with a high-Cu diet inhibited storage of Cu in the liver.

CH. ABS. (p)

Preparation of possible antimalarial agents. R. F. A. ALTMAN (Chem. Weekblad, 1935, 32, 345).—Derivatives of 6-methoxyquinoline with $\text{NH}\cdot[\text{CH}_2]_n\cdot\text{NEt}_2$ in position 8 show antigametocidal properties similar to those of "plasmoquin." Derivatives of quinine containing substituents in the sec-OH and $\cdot\text{CH}\cdot\text{CH}\cdot$ groups have no therapeutic activity.

S. C.

Derivatives of 8-aminoquinoline as antimalarials.—See this vol., 989.

Identity of the reducing substance in the urine of normal persons after the ingestion of amidopyrine. M. ENKLEWITZ (J. Pharm. Exp. Ther., 1935, 54, 100—104).—A reducing substance appearing in urine after the ingestion of amidopyrine (I) has been identified as the glycuronate of (I).

M. T.

Role of amidopyrine in the ætiology of granulocytopenia with special reference to its chemical structure. L. F. HERZ (J. Lab. Clin. Med., 1934, 20, 33—40).—Amidopyrine is a very frequent cause of granulocytopenia. Its toxicity is due to the imido-group and its action resembles that of $\text{NHPH}\cdot\text{NH}_2$.

CH. ABS. (p)

Reaction of the blood-vessels. I. Electrical stimulation. II. Influence of various medicaments on electrical excitation. III. Influence of various nerve or muscle poisons on electrical excitation. IV. Influence of paralysing drugs on electrical excitation. V. Influence of stimulative drugs on electrical excitation. Y. KOSUGE (*Acta Schol. Med. Kioto*, 1934, 17, 22—26, 27—29, 123—131, 132—136, 137—145).—I. The technique is described.

II. Codeine phosphate decreased electrical response. Theocin Na acetate in small concns. (to 0.01%) increased and in higher concns. decreased electrical stimulation.

III. Atropine, eserine, cocaine, and nicotine decreased and $\text{Ba}(\text{ClO}_3)_2$ increased response. Pilocarpine and adrenaline in low concns. had a positive and in large proportions a negative effect.

IV. Morphine, Na phenobarbital, urethane, dial, and chloral hydrate caused a decrease in response.

V. Increased response followed treatment with caffeine, NaOBz, diuretin, gadamin, digifolin, strophanthin, pituitrin, or EtOH. Strychnine had the opposite effect. CH. ABS. (p)

Action of pilocarpine group on alkali reserve and blood-sugar. A. M. PREOBRASHENSKI (*J. Physiol. U.S.S.R.* 1934, 17, 886—895).—Intravenous injection of pilocarpine alkaloids into dogs increases blood-sugar and lowers the alkali reserve. Eserine, pilocarpine, and arecoline were the most active in this respect. A. G. P.

Vasodilating action of quinine; cardiovascular effects of quinine phenylethylbarbiturate. H. BUSQUET and C. VISCHNIAC (*Compt. rend. Soc. Biol.*, 1935, 119, 503—506).—The contractions of the heart are increased and blood-pressure is lowered. H. G. R.

Absorption of drugs through oral mucosa. R. P. WALTON and C. F. LACEY (*J. Pharm. Exp. Ther.*, 1935, 54, 61—76).—The ratios of sublingual dosages to similarly effective subcutaneous dosages as determined on dogs are as follows: Na pentobarbital (I) 1:1; apomorphine (II) 2:1; strychnine 4:1; atropine (III) 8:1; morphine (IV) 10:1; dilaudid (V) 15:1; codeine, > 15:1. No distinct effect was produced by sublingual application of adrenaline (VI) and insulin, even in large doses. With alcoholic solutions there was an increase of absorption of (III). With men, results comparable with those produced in dogs were obtained for (I)—(VI). M. T.

Metabolic action of strophanthin on the warm-blooded heart. B. WEICKER (*Arch. exp. Path. Pharm.*, 1935, 178, 524—533).—With the perfused cat's heart, therapeutic doses of strophanthin do not affect the total acid-sol. PO_4 content, whilst toxic doses decrease phosphagen (I), adenylypyrophosphoric acid (II), and free adenylic acid (III). Stimulation of work output by the impaired heart may produce aerobic resynthesis of (I) followed by that of (II) and (III). Transient anaerobic increase in work output increases (I) practically to normal vals.; resyn-

thesis of (II) or (III) does not occur. The mechanism of the cardiac action of *Digitalis* preps. is discussed.

F. O. H.

Distribution of therapeutic substances in various parts of the central nervous system and their micro-determination in tissues. I. Scopolamine and atropine. F. VEIT and M. VOGT. II. Quinine and mezcaine. M. VOGT. III. apomorphine and bulbocapnine. IV. Strychnine. F. VEIT. V. Barbituric acid derivatives. VI. Chloral hydrate. M. VOGT (*Arch. exp. Path. Pharm.*, 1935, 178, 534—559, 560—576, 577—592, 593—602, 603—627, 628—638).—I. The determination of scopolamine (I) and atropine (II) ($< 10^{-4}$ and 10^{-1} mg., respectively) in brain-tissue (2 g.) is described. Administration to dogs and cats is followed by a transient period during which the greatest concn. occurs in the cell-rich parts of the nervous tissue; the distribution then becomes more equalised. Finally (I) and (II) disappear from the nervous tissue and appear in liver, kidney, and blood.

II. A micro-extraction method for quinine and mezcaine (β :3:4:5-trimethoxyphenylethylamine) in tissue is described. Following injection into animals their distribution in nervous and other tissues is similar to that of (I) and (II).

III. apomorphine and bulbocapnine (method of determination in tissues given) behave similarly to (I) and (II). The liver content attains vals. > those of the brain.

IV. The distribution of strychnine (method of determination in tissues given) in animals in which the tolerated dose is increased by Et_2O narcosis is similar to that of (I) and (II), marked preferential localisation occurring in certain parts of the nervous system. The content in liver and kidney is > that of brain and, to a greater extent, that of blood. Only traces occur in the cerebrospinal fluid.

V. The equalisation of distribution of dial and phanodorm in nervous tissue occurs more rapidly than that of veronal, the irregular distribution phase of which is detected with difficulty. The narcotic effect of each \propto the content in the brain. The content of liver or kidney is < that of the brain, whilst small amounts occur in the cerebrospinal fluid.

VI. The micro-determination of chloral hydrate by reduction to Cl' ($\text{Zn}-\text{AcOH}$) followed by Volhard titration is applied to nervous tissue. Following administration to cats or dogs, the content in nervous tissue rapidly attains a max. and then diminishes, during which period the distribution in various parts is irregular. Only traces appear in the cerebrospinal fluid. F. O. H.

Respiratory effects of morphine, codeine, and related substances. IV. Effect of α -monoacetylmorphine, monoacetyldihydromorphine, diacetylmorphine (heroin), and diacetyldihydromorphine on the rabbit. C. I. WRIGHT and F. A. BARBOUR (*J. Pharm. Exp. Ther.*, 1935, 54, 25—33).— α -Mono- and di-acetylmorphine have very nearly the same effect on the respiration of the rabbit. A dose of 0.03 mg. per kg. definitely decreases the respiratory rate, minute vol., and the response to CO_2

stimulation. The hydrogenated derivatives of acetylmorphines are much less effective as respiratory depressants. > 0.1 mg. of mono- or di-acetyldihydromorphine is required to decrease the minute vol. and to change significantly the response to CO₂ stimulation. Also the rate of O₂ consumption, the heart rate, and rectal temp. are more strongly affected by the above acetylmorphine compounds than by their hydrogenated derivatives. M. T.

Motor effects of morphine and some derivatives on Thierry fistulæ. R. P. WALTON and C. F. LACEY (J. Pharm. Exp. Ther., 1935, 54, 53—60).—The min. dilauid (I) dose producing a definite spastic effect is about 1/30 the min. dose of morphine (II) and 1/300 that of codeine (III). The abs. doses producing a 20-min. spastic period are respectively 0.01, 0.3, and 3.0 mg. per kg. body-wt. There is no indication of a connexion between the initial stimulating effect and the constipating effect of (I). It does not produce prolonged periods of spasticity to the same degree as (II) and (III). M. T.

Cardiostimulant effect of Japan camphor: *d-trans*-7-aldehydopcamphor as the true active substance.—See this vol., 865.

Diuresis following the administration of salyrgan; its effect on the specific gravity, the total nitrogen, and the colloid osmotic pressure of the plasma of normal and cedematous dogs. A. H. BRYAN, W. A. EVANS, jun., M. N. FULTON, and E. A. STEAD, jun. (Arch. Int. Med., 1935, 55, 735—744).—In normal dogs the effect of salyrgan was slight, but in cedematous dogs a prolonged diuresis was observed together with a rise in sp. gr., total N, and colloid osmotic pressure of the plasma, indicating a direct effect on the kidney. H. G. R.

Pharmacology of convolvine. J. K. NOLLE (Khim. Farm. Prom., 1934, No. 5, 39—46).—Convolvine (from *Convolvulus pseudocantabrica*), C₁₅H₂₁NO₂, m.p. 114—115°, is a strongly basic, optically inactive cryst. substance, the hydrochloride of which is anæsthetic. CH. ABS. (p)

Effect of some barbituric acid derivatives on the intestine of the cat. N. B. DREYER and C. O. HEBB (Proc. Nova Scotian Inst. Sci., 1933—1934, 18, 282—285).—Many barbiturates, even in massive doses, increase the tonus of cat intestine if respiration and the circulation are unimpaired. Section of the vagi or splanchnics has no effect. J. L. D.

Distribution of barbiturates in brain. T. KOPFANYI and J. M. DILLE (J. Pharm. Exp. Ther., 1935, 54, 84—86).—There is no sp. distribution of Narbarital nor any accumulation in the sleep centres after the administration of small hypnotic doses. The distribution in the different parts of the central nervous system is approx. the same after large and small doses, with the exception of cerebellum and medulla, the amount in these being somewhat < in the rest of the brain. M. T.

Antagonism between thyroxine and narcotics with regard to their structure. I. ZARDAY and P. WEINER (Orvosi Hetilap, 1934, 78, 682—684).—Antagonism is demonstrated between narcotics of the barbituric group and thyroxine. CH. ABS. (p)

Effect of specific substances of the body on blood-pressure in man. IV. Action of liver preparations (Campolon, Degewop, Hepatrat, and Hepatopson) administered intravenously. H. A. HEINSEN and H. J. WOLF (Klin. Woch., 1934, 13, 523—526; Chem. Zentr., 1935, i, 589).—Liver preps. provoke falls of blood-pressure, suggesting the presence of histamine-like substances or of Lange's "fourth substance." R. N. C.

Plants with cardiac action. R. JARETZKY (Arch. Pharm., 1935, 273, 334—348).—A lecture. *Adonis vernalis*, L., but not 4 other varieties or 2 related plants, contains (most in the stems) substances with cardiac action and yields *eranthin-A*, insol. in CHCl₃, and *-B*, CHCl₃-sol., which give some strophanthin colour reactions. *Gratiola officinalis*, L., yields *gratiotoxin*, which has great cardiac action. Purified gratiolin has m.p. 268—269° (decomp. from 255°) (cf. lit.). *Bavica volubilis*, Harv., bulbs, but not related plants, contain extremely active glucosides. R. S. C.

Assay of *Allium* preparations. U. HINTZELMANN (Arch. exp. Path. Pharm., 1935, 178, 480—485).—The survival period of mice poisoned by 0.2—0.3 c.c. daily of viganol is prolonged two- to three-fold by simultaneous administration of preps. from *A. ursinum*. The application of this phenomenon to the assay of *Allium* preps. is discussed. F. O. H.

Pharmacodynamic action and chemistry of secretin. G. ÅGREN (Skand. Arch. Physiol., 1934, 70, 10—87).—A method for preparing pure secretin in quantity is described. It can be prepared only from the mucosa of the small intestine. Injected intravenously, a concn. of 1:40 × 10⁶ in the blood of a urethanised cat is sufficient to cause pancreatic secretion. Administered subcutaneously, intramuscularly, or intraperitoneally it is rapidly destroyed and consequently without action on the pancreas. It is a true cholagogue, increases the flow of succus entericus, but does not affect gastric secretion or urine formation by the kidney. There is no action on blood-sugar level, on blood-pressure, or on the musculature of the gall-bladder or gut. The chemistry of the substance is discussed.

NUTR. ABS. (m)

Influence of vitamin-B₂ on hæmatopoiesis in experimental anæmia in the albino rat. M. I. SMITH and E. F. STOHLMAN (U.S. Publ. Health Repts., 1934, No. 49, 1569—1575).—Recovery of rats from NHPH-NH₂-induced anæmia is not materially affected by the absence of vitamin-B₂ from the diet.

CH. ABS. (p)

Biological action of 7-methyl-9-[*d*-1'-ribityl]-isoxalloxazine. P. KARRER, H. VON EULER, M. MALMBERG, and K. SCHOPP (Svensk Kem. Tidskr., 1935, 47, 153—154).—The compound exhibits vitamin-B₂ activity so that the Me in position 6 is not essential, but the min. dose for normal growth is probably about double that for the Me₂ derivative. W. O. K.

Phenanthrene derivatives. IV. Veratrine-like action on skeletal muscle. R. G. SMITH (J. Pharm. Exp. Ther., 1935, 54, 87—99).—The

veratrine-like effect could be obtained in cats, rabbits, and mice only with the Na phenanthrene-9-carboxylate (I). Other phenanthrene derivatives examined, e.g., salts of the 2- (II) and 3-carboxylic acids (III), yielded no comparable results. On direct and indirect stimulation with the sciatic nerve being cut and on direct stimulation in the curarised animals, there was a distinct muscular effect by (I) and to a smaller degree by four other 9-substitution products of phenanthrene, but not by (II) and (III). In frogs, this effect was replaced by a morphine-like picture when (I) was used.

Effect of trimethylenetetrazole on the heart. A. DE CHATEL (Orvosi Hetilap, 1934, 78, 813—814).—Relatively large doses restore normal rhythm in a heart poisoned by CHCl_3 . CH. ABS. (p)

Pharmacological action of phenaceturic acid. II. Y. TOZAWA (Folia Pharmacol. Japon., 1934, 19, No. 1, 90—101).—Diuretic effects are described.

CH. ABS. (p)

Effect of some isomeric sodium aminonaphthalenetrisulphonates on the structure of diphtheria toxin and antitoxin. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 119, 402—405).—Na naphthalenetrisulphonates permit the pptn. of globulins by citric acid at p_H 5, this effect being independent of the no. and positions of the SO_3H , and of the presence or absence of an NH_2 . Albumins are partly pptd. Complete pptn. of the active principles of diphtheria toxin (I) and antitoxin is permitted only by β -naphthylaminetrisulphonates (II). Pptn. with α -naphthylaminetrisulphonates is slow and incomplete, but is complete with Na 8-hydroxy- α -naphthylamine-3:6-disulphonate, which also ppts. peptones in acid solution. (II) do not affect the toxic and antigenic powers of (I). R. N. C.

Effect of histamine, adrenaline, and destruction of the spinal cord on the osmotic pressure of the blood in the skate. A. F. CHAISSON and M. H. F. FRIEDMAN (Proc. Nova Scotian Inst. Sci., 1933—1934, 18, 240—244).—Adrenaline subcutaneously has no effect on the blood-Cl' (I), blood concn., or the vol. of gastric secretion. Histamine lowers the first two (and later increases Cl'), but has no effect on the secretion. Destruction of the cord invokes a large and highly acid gastric secretion and lowers blood concn., probably a result of loss of urea. J. L. D.

Mobilisation of calcium by salts of pyrocatecholdisulphonic acid. O. RIESSER and L. KARBE (Arch. exp. Path. Pharm., 1935, 178, 455—460).—Oral or intramuscular administration of the Na salt increases the total and, to a greater extent, the ultrafilterable Ca of the blood. With daily administration, the effect rapidly diminishes, being approx. zero on the third day. This diminution, but less marked, also occurs with the Ca salt. The Ca content of brain and heart also slightly increases. The source of the mobilised Ca is unknown.

F. O. H.

Oral toxicity of *o-n*-alkylphenols to white rats. H. W. BROWN and P. D. RAMSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 592—594).—The toxicity decreases as the alkyl chain increases in length. The *o-n*-alkylphenols are less toxic than the corresponding

4-*n*-alkylresorcinols, but equally toxic with the corresponding 6-alkyl-*m*-cresols.

R. N. C.

Dinitrophenol. Blood, urine, and tissues of dogs on continued medication and after acute fatal poisoning. M. L. TAINTER, W. C. CUTTING, D. A. WOOD, and F. PROESCHER (Arch. Path., 1934, 18, 881—890).—Administration to healthy dogs of 5—10 mg. of 2:4-dinitrophenol per kg. of body-wt. daily for 27 weeks caused no change in wt., O_2 capacity of the blood, fragility of red cells, blood picture, or serum-bile pigment. Slight transient albuminuria occurred, but no increase in blood-urea. The animals remained healthy.

NUTR. ABS. (b)

Pharmacology of *l*-ascorbic acid. J. V. SUPNIEWSKI and J. HANO (Arch. exp. Path. Pharm., 1935, 178, 508—523).—Parenterally administered *l*-ascorbic acid (Na salt) rapidly disappears from the blood and appears in the urine, the vol. of which increases. In mammals a pressor action follows cardiac stimulation, whilst the respiration is first stimulated and then depressed. The sensitivity of mice to MeCN poisoning is diminished.

F. O. H.

Toxicity and hypoglycaemic effect of guanidine compounds. G. S. SAMUELSEN (J. Pharm. Exp. Ther., 1935, 54, 17—24).—Benzthiazolylguanidine (I) produces, in fairly large doses, a rise in the blood-sugar level in rabbits. Benzselenazolylguanidine (II) and α -*m*-tolyl-, α -diphenyl-, α -3:6-dimethylphenyl-, and α -*o*-tolyl-diguanide show, if any, only a slight effect on blood-sugar level, raising it in some cases, when lethal doses are used. In all cases except (I), there is a rise in blood-N. All preps., with the exception of (II), are more or less toxic, the order of toxicity increasing with the no. of Ph and Me groups.

M. T.

Gastric motility in experimental hyperaminocidanæmia. J. LA BARRE and P. DESTREE (Compt. rend. Soc. Biol., 1935, 119, 536—538).—Intravenous injection of glycine causes a hypermotility of the stomach.

H. G. R.

Action of monoiodoacetic acid on carbohydrate metabolism in rabbits. Y. NISHIDA (Mitt. med. Akad. Kyoto, 1934, 12, 1379—1380).—For 5 hr. after subcutaneous injection of the min. lethal dose of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ in rabbits there was a progressive increase in blood-sugar and -lactic acid and a decrease in the alkali reserve. In comparable muscles, frozen *in situ* with liquid CO_2 and removed at intervals, glycogen decreased slightly and lactic acid increased steadily. If both splanchnic nerves were cut all these changes were less marked.

NUTR. ABS. (b)

Chemical constitution and antitoxic activity (*in vitro*) of some organic molecules. L. VELLUZ (Bull. Soc. Chim. biol., 1935, 17, 838—847).—The antitoxic action of certain org. compounds for tetanus and diphtheria toxin is associated with the presence of the CO_2H . Substituted benzoic acids are active for tetanus and naphthenic and benzofuran derivatives are sp. for diphtheria. Phenolic and halogen groups, inactive alone, increase the antitoxic action when associated with CO_2H ; the free NH_2 , however, has an inhibiting action. The position of the sub-

stituents in active isomeric compounds has a marked effect on antitoxic action. A. L.

Poisoning by potassium borotartrate. P. O. SAGRERAS and L. TREPAT (Rev. Assoc. med. Argentín., 1932, 46, No. 318, 1670—1675). CH. ABS. (p)

Action of hypertonic solutions on the crystal structure of animal fibres. F. WORSCHITZ and J. VON HERMAN (Fortschr. Röntgenstrahlen, 1934, 50, 178—180; Chem. Zentr., 1935, i, 585).—The micelle structure of muscle fibres is destroyed irreversibly by hypertonic solutions of NaCl, homatropine, pilocarpine, urea, or AcOH, the extent of the change increasing with the concn. R. N. C.

Influence of a calcium diet on disturbances of the liver function. I. Calcium diet and bilirubin metabolism. II. Calcium diet and the metabolism of urobilin substances. Y. ASODA (Japan. J. Gastroenterol., 1934, 6, 51—55, 56—60).—I. After liver injury with CCl_4 the appearance of bilirubin (I) in the blood was less frequent, and injected (I) disappeared more rapidly in rabbits receiving Ca lactate.

II. The urobilin substances of blood, urine, and bile were unaffected by Ca feeding, but CCl_4 injury to the liver was somewhat less severe. CH. ABS. (p)

Influence of thyroid and pituitary glands on chloride distribution. M. A. B. TOXOPEUS (Arch. exp. Path. Pharm., 1935, 178, 412—415).—Following intravenous injection of aq. NaCl into dogs, the NaCl content of the skin, but not that of the muscle, increases. With simultaneous subcutaneous injection of thyroxine or posterior pituitary extract there is a relative displacement of NaCl from skin to muscle. F. O. H.

Penetration of therapeutic substances from the organism of the mother into the embryo. M. N. LEBEDEVA (Khim. Farm. Prom., 1934, No. 4, 44—45).—Arsphenamine, Sb, Bi, As, and germanin, following injection into pregnant animals, were found in \times traces in the embryo. CH. ABS. (p)

Inclusions in renal epithelial cells following the use of certain bismuth preparations. A. M. PAPPENHEIMER and E. H. MAECHLING (Amer. J. Path., 1934, 10, 577—588).—Globules occurring in nuclei and cytoplasm of the cells following intramuscular injection of various Bi preps. gave equivocal tests for Bi, were insol. in lipin solvents or in strong acids or alkalis, resisted tryptic digestion, gave no reaction for Ca or Fe, but stained as myelin.

CH. ABS. (p)

Pathological changes encountered in wild ducks. J. P. TORREY, F. THORPE, jun., and R. GRAHAM (Cornell Vegetarian, 1934, 24, 289—298).—Inclusion of Pb shot in the diet caused Pb poisoning in ducks.

CH. ABS. (p)

Lead compounds R232 and R237b used in experimental therapy of tumours and leucosis. C. KREBS and J. CLEMMESSEN (Z. Krebsforsch., 1934, 41, 260—266; Chem. Zentr., 1935, i, 437).—The compounds R232 and R237b (K and Na plumbodithiopyridinecarboxylates), dissolved in H_2O and stabilised at p_{H} 7.4 with glycine, show relatively low

toxicities to their high Pb contents, but are apparently without therapeutic effect on mouse carcinoma.

R. N. C.

Poisoning by thallium acetate. A. BUZZO and C. F. GANDOLFO (Rev. Assoc. med. Argentín., 1932, 46, No. 313, 97—99).—Toxic effects of TlOAc , used as a depilatory, were cured by hypertonic glucose, serum, insulin, and Na "hyposulphite."

CH. ABS. (p)

Growth of human fibroblasts in media containing silver. J. P. M. VOGELAAR and E. EHRLICHMAN (Amer. J. Cancer, 1934, 22, 555—560).—Fibroblasts from the thyroid grew normally in media containing 0.0028 mg. of Ag per c.c., but not in those having 0.04 mg. Activation of the proteolytic enzymes with certain [Ag] is indicated.

CH. ABS. (p)

Influence of metals on adrenaline hyperglycæmia in rabbits. H. SCHNETZ (Arch. exp. Path. Pharm., 1935, 178, 420—438).—Injection of simple or complex salts of Cu, Zn, Cd, Mn, Ni, Co, Fe^{II} , and Fe^{III} has no effect on the fasting blood-sugar of rabbits. The hyperglycæmia due to injection of 0.1 mg. of adrenaline per kg. of body-wt. is, however, considerably reduced by previous daily subcutaneous injection of the salts of the analogous metals Cu, Zn, and Cd, but not with those of Mn, Ni, Co, Fe^{II} , or Fe^{III} . Daily injection of 0.5—2.0 mg., but not of 0.2—0.1 mg., of Cu or Zn per kg. will produce the effect (cf. this vol., 410). F. O. H.

Influence of metallic couples on the growth *in vitro* of fibroblasts and osteoblasts. G. MENEGAUX and D. ODIETTE (Compt. rend. Soc. Biol., 1935, 119, 485—486).—The toxicity of a metal is not affected by the presence of another metal as a couple. H. G. R.

Action of metallic chlorides on tissue cultures. II. Hepatic, renal, and nerve tissue. J. VERNE and C. SANNIE (Bull. Soc. Chim. biol., 1935, 17, 678—689).—The toxicity of the alkali and alkaline-earth metals is small; that of the heavy metals is considerable and varies according to the nature of the metal. The fibroblasts of the liver, kidney, and nerve tissue, although more resistant than the functional cells, are more sensitive than those of the chicken-embryo heart. A. L.

Effect of physico-chemical changes in environment on embryo formation in the frog. J. W. CULBERTSON and H. V. WILSON (J. Elisha Mitchell Sci. Soc., 1934, 50, 50—51).—Exposure to low temp. or to dil. solutions of NaCl or LiCl disturbs the physiological organisation of the embryos of artificially inseminated frog eggs. CH. ABS. (p)

Preventive role of methæmoglobin-forming substances (sodium nitrite) in intoxication by fluorides. V. KARASSIK, V. ROCHKOV, and O. VINOGRADOVA (Compt. rend. Soc. Biol., 1935, 119, 807—809).—The mortality of white mice injected with NaF is decreased from 80 to 24% by previous injection of NaNO_2 . H. G. R.

Effects of fluorine on respiration, blood-pressure, coagulation, and blood-calcium and -phosphorus in the dog. D. A. GREENWOOD,

E. A. HEWITT, and V. E. NELSON (J. Amer. Vet. Med. Assoc., 1935, 39, 28—42).—Intravenous injection of NaF increased respiration and lowered blood-pressure. Oral administration (0.45—4.52 mg. of F as NaF per kg. body-wt.) did not affect the total Ca, acid-sol. inorg. P, hæmoglobin, or coagulation time of blood. Bones were unchanged, but teeth became mottled.
CH. ABS. (p)

Fluorine poisoning. A. SLAVIERO (Arch. Ist. Biochim. Ital., 1934, 6, 285—310; Chem. Zentr., 1935, i, 746).—Physiological effects on dogs are recorded.
A. G. P.

Fluorine toxicosis. M. C. SMITH (Amer. J. Publ. Health, 1935, 25, 696—702).—Drinking-H₂O containing < 1 p.p.m. of F will cause the permanent teeth of children to have faulty enamel, but if [F] is > 12 p.p.m. the first set also will be affected. The action is not directly in the mouth, but through the blood-stream on the organ producing the enamel. Later, this organ disappears, and the enamel of adults is unaffected, although the dentine which receives nutrient from the blood may be affected and result in a general weakening which does not show externally. The decalcification is not prevented by an increased Ca content of the diet or by a liberal intake of vitamin-D, e.g., from cod-liver oil. Since the level of human tolerance to F is so low, the growing use of insecticides containing it is to be deprecated.
C. J.

Pathologico-anatomical conditions in arsine poisoning. H. HILTERHAUS (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 70—79).—Conditions in two cases of AsH₃ poisoning are described, including hæmolytic action and methæmoglobin content.
R. N. C.

Determination of minimal concentrations of arsenic in expired air. A. PLESCHTIZER and A. A. PREOBRJENSKY (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 80—86).—The expired air of cases of As poisoning contains traces of As, which can be detected by Feigl's reaction, or by absorption with Br and NH₃ and cultivation in the solution of *P. brevicarule*, which forms AsHET.
R. N. C.

Toxic effects of sulphur on guinea-pigs and rabbits. G. B. LAWSON, K. T. REDFIELD, and O. D. BOYCE (J. Lab. Clin. Med., 1934, 20, 169—171).—Effects of ingestion and injection of S are examined.
CH. ABS. (p)

Action of sulphur-containing gases on the cocoons of *Bombyx mori*. L. I. HIRAIWA, K. YAMAFUJI, and Y. YONEZAWA (Bull. Sci. Fak. Terkult. Kjushu, 1935, 6, 119—125).—2 parts of SO₂ in 10,000 and 2 parts of H₂S in 100,000 interfere with the formation of the cocoon and affect the quality of the silk.
E. A. H. R.

Toxic gases. Adjuvant groups in organic halogen compounds. M. HANNE (Chim. et Ind., 1935, 33, 1317—1320).—The effect of modifying groups in the mol. on the toxic, vesicant, lachrymatory, and sternutatory properties of known org. Cl-compounds is discussed.
F. N. W.

Influence of carbon dioxide and ammonia on cocoon formation of *Bombyx mori*. L. K.

YAMAFUJI, Y. YONEZAWA, and I. HIRAIWA (Bull. Sci. Fak. Terkult. Kjushu, 1935, 6, 111—118).—CO₂, expired by the larvæ, and NH₃ (in very low concns.) have a damaging effect on the formation of the cocoon.
E. A. H. R.

Toxicity for sheep of aqueous solutions of hydrocyanic acid and the effectiveness of the nitrite-thiosulphate combination as a remedy. J. F. COUCH, A. B. CLAWSON, and H. BUNYEA (J. Washington Acad. Sci., 1935, 25, 272—276).—The min. lethal dose of HCN administered to sheep in a drench is 2.3 mg. per kg. Intraperitoneal administration of 15 c.c. of a solution containing 1 g. of NaNO₂ and 2 g. of Na₂S₂O₃ produced recovery in about 50% of cases with doses up to 4 times the min. lethal dose.
W. O. K.

Pathogenesis of silicotic tissue changes. I. Experimental production of silicotic welts by quartz and colloidal silicic acid. H. SIEGMUND.
II. Behaviour of quartz dust in silicotic tissue.
III. Nature of asbestosis particles. G. F. KOPPENHÖFER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 1—17, 18—37, 38—62).—I. Quartz particles injected into the blood-stream in rabbits are removed by the reticulo-endothelial cells, but are deposited in different tissues according to their size, where they produce characteristic changes. Colloidal H₂SiO₃ injected intravenously produces fibrosis in the liver.

II. The morphological changes produced in silicotic tissues by quartz particles are described.

III. The gelatinous shell of asbestosis particles in tissue sections is of inorg. origin, and contains Fe, Mg, and SiO₂.
R. N. C.

Atmospheric ozone and heliotherapy. R. LATARJET (Compt. rend. Soc. Biol., 1935, 119, 610—612).—The therapeutic effect of solar radiation is diminished considerably by O₃ in the atm.; it falls more rapidly than O₃ increases. The O₃ content is influenced by the height of the sun at noon.
R. N. C.

Physico-chemical effects of irradiation of crystalline ovalbumin solutions with α -particles. L. E. ARNOW (J. Biol. Chem., 1935, 110, 43—59).—Irradiation of ovalbumin (I) solutions by α -particles produced coagulation at the isoelectric point only; quantities of gas (chiefly H₂) were evolved; there was no change in the N content of the solution. The η , ultra-violet absorption, and coagulation temp. of the solution were raised at $p_{\text{H}} < 4.8$ and lowered at $p_{\text{H}} > 4.8$ by the irradiation. From the curves of gas evolution against Rn disintegration it is deduced that H₂ and O₂ are utilised by (I), the former process involving at least two reactions.
H. D.

Effect of light on the sensitivity of wheat seedlings to X-rays. L. C. CHESLEY (J. Cell. Comp. Physiol., 1935, 6, 69—84).—Seedlings sprouted in light were less sensitive to X-rays than were those sprouted in darkness, when compared on a fresh wt. or respiration basis. Linear growth was not protected by light. The influence of light decreased as irradiation was increased, and also tended to become less with time. Results are discussed in relation to the theory of the destruction of auxin by X-rays.
A. G. P.

Effects of radiations on biological systems. II. Immediate and subsequent effects of X-irradiation on respiration of *Drosophila* larvæ. R. HUSSEY and W. R. THOMPSON (J. Gen. Physiol., 1935, 18, 669—674; cf. A., 1932, 1150).—X-Irradiation of the larvæ produces an immediate decrease in the CO_2 respiration [which \propto the time of irradiation] and a latent effect persisting for several days. F. O. H.

Radium emanation and elimination of phosphorus by frog's muscle. O. V. HYKES and J. REĀBEK (Biochem. Z., 1935, 278, 123—132).—Rn increases PO_4 elimination to a greater extent than does rise of temp. of both resting muscle and of muscle undergoing nervous stimulation. Under the prolonged action of Rn, the PO_4 elimination is not linear, but is greatest for the first few min. Rn affects first the permeability, and may also affect the chemical processes occurring in muscle. P. W. C.

Photons in chemistry and biology. F. DANIELS (Science, 1935, 81, 523—528).—A lecture. L. S. T.

Action of electrolytes on electrical stimulation of skeletal muscle. I. CHAO (J. Cell. Comp. Physiol., 1935, 6, 1—19).—The immediate sensitising effect of Na salts was in the order $\text{Cl}' < \text{Br}' < \text{NO}_3' < \text{I}' < \text{SCN}'$. The action of NaSCN is characterised by a period of secondary depression which is probably related to the presence of CaCl_2 . KCl produces at first an increase followed by a decrease in response, the relative intensity of these effects increasing with concn. CaCl_2 at all concns. decreased contraction. Antagonism between the actions of Ca and K salts occurs within certain narrow ranges of concn. A. G. P.

Theory of diffusion in cell models. II. Solution of the steady state for three diffusing substances. L. G. LONGSWORTH (J. Gen. Physiol., 1935, 18, 627—642).—Theoretical considerations of diffusion in cell models (A., 1934, 107) have been extended to the simultaneous penetration of H_2O and two salts. Vals. thus calc. for the steady state agree with experimental data. F. O. H.

Elementary actions of mineral waters. P. TESTONI (Annali Chim. Appl., 1935, 25, 111—116).—Classification of a mineral water according to its elementary composition is insufficient to indicate its biological effects. T. H. P.

Dinner demonstration of threshold differences in taste and smell. A. F. BLAKESLEE (Science, 1935, 81, 504—507).—Results of a large-scale experiment are described. L. S. T.

Mechanism of enzyme actions. K. G. FALK (Science, 1935, 81, 471—475).—A discussion. L. S. T.

Catalytic causation of physiological phenomena. A. MITTASCH (Naturwiss., 1935, 23, 361—369).—A review of the characteristics of catalytic action and the types of bio-catalysts. The connexion between bio-catalysis and stimulation and instinctive reaction is considered. A. J. M.

Synthesis of synthetic enzymes. W. LANGENBECK (Bull. Soc. Chim. biol., 1935, 17, 627—636).—A resume. A. L.

Tissue-enzymes. F. MAIGNON (4me. Congr. Chim. biol., Paris, Nov., 1934).—Extracts of fresh organs of healthy animals (Lebedev's method) contain substances which restore functional activity in cases of insufficiency of liver, kidney, ovary, thyroid, etc. The extracts show marked specificity and have no effect on the healthy organism. In old dogs with hepatic or renal insufficiency, a single dose of 1 mg. maintains normal conditions (blood-urea etc.) for a week or more, and a second dose has a similar effect. NUTR. ABS. (b)

Ascorbic acid oxidase. H. TAUBER, I. S. KLEINER, and D. MISIKIND (J. Biol. Chem., 1935, 110, 211—218).—The isolation of an enzyme, from the pericarp of the Hubbard squash, which oxidises ascorbic acid (I) instantaneously and completely is described. Its kinetics are those of a single enzyme, and in this it differs considerably from Szent-Gyorgyi's hexoxidase (cf. A., 1931, 533). (I) is probably oxidised by the introduction of two OH at the double linking. The oxidation product of (I) can be reduced again by H_2S . No oxidation takes place in an atm. of N_2 . The enzyme shows activity only between p_{H} 4 and 7 (max. activity about p_{H} 5.6). It is more easily destroyed by excess of H' than of OH' ; it is stable to O_2 , CO , and to small concns. of KCN (0.005%). It is irreversibly inactivated by 0.01% KCN and by H_2S . Trypsin slowly inactivates it, so that it must either be a protein or have protein as an indispensable part. E. A. H. R.

Enzymic dehydrogenation of citric acid. T. WAGNER-JAUREGG and H. RAUEN (Z. physiol. Chem., 1935, 233, 215—222).—The rate of methylene-blue reduction by citric acid (I) in presence of phosphate extracts of various seeds and of frog muscle is accelerated by addition of co-enzyme (from horse erythrocytes) and yellow enzyme (from yeast). This holds with bean extracts for the substrates *l*-malic acid, EtOH, and hexosemonophosphoric acid. The degradation of (I) occurs in stages with the co-operation of two different co-enzymes, yellow enzyme only assisting at a later stage. Acetonedicarboxylic acid is not a stage, and is probably not the end-product of the dehydrogenation. J. H. B.

Synergistic action of milk- and muscle-oxidases. D. I. MACHT and H. F. BRYAN (J. Biol. Chem., 1935, 110, 101—105).—Methylene-blue is decolorised by juice or suspensions of muscle (rat, ox, chicken, rabbit, frog, gold-fish, pike) much more rapidly than by milk, but the times required for decolorisation are greatly reduced when small amounts (< 1 part in 60) of milk are added to the juice (or suspension) or small amounts of juice (or suspension) to the milk. W. McC.

Correlation of oxidation and phosphorylation in hæmolysed blood in presence of methylene-blue and pyocyanine. J. RUNNSTROM and L. MICHAELIS (J. Gen. Physiol., 1935, 18, 717—727).—Aerobic oxidation of glucose (I) or anaerobic glycolysis does not occur in hæmolysed blood (horse)-(I) systems. With blood-hexose phosphate in presence of methylene-blue (II), aerobic oxidation occurs, and is increased by cozymase (when phosphorylation occurs). Re-

placement of (II) by pyocyanine does not change the rate of oxidation, but phosphorylation occurs in absence of cozymase. Oxidation always occurs during phosphorylation, but not *vice versa*. $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ always inhibits phosphorylation, but only under certain conditions decreases oxidation; neither process is affected by CN' . F. O. H.

Yellow oxidation enzyme. H. THEORELL (Biochem. Z., 1935, 278, 263—290).—By treatment in the modified cataphoresis apparatus (see below) followed by pptn. with aq. $(\text{NH}_4)_2\text{SO}_4$ (67% at p_{H} 5.2) the enzyme, $[\alpha] -30^\circ$ in H_2O , mol. wt. 70,000—75,000, isoelectric point at p_{H} 5.25 \pm 0.03, is obtained pure and cryst. in about 60% yield. It exhibits absorption max. at 265, 380, and 465 $\text{m}\mu$ and min. at 240, 320, and 415 $\text{m}\mu$. The polysaccharide associated with (but not bound to) the enzyme acts as protective colloid. Enzyme reconstituted from the components after hydrolysis is as active as non-hydrolysed enzyme. Heating (to 75°) causes irreversible hydrolysis. The protein component, which is very labile and easily denatured, combines with hæmins to give hæmochromogens. The yellow component (flavin-phosphoric ester) is readily sol. in H_2O , but insol. in MeOH , COMe_2 , or CHCl_3 . When dry this component is stable in the dark. In aq. solution the Ca salt is more stable. Since the yellow component is only very slowly inactivated by blood-serum, it probably has a more powerful vitamin action than has lactoflavin. W. McC.

Cataphoresis apparatus for preparative purposes. H. THEORELL (Biochem. Z., 1935, 278, 291—297; cf. this vol., 188).—Materials (*e.g.*, yellow respiratory enzyme) which cannot otherwise be isolated can be purified in quantity in a modified form of the apparatus previously described. Conducting liquids (buffer solutions) and semi- or non-permeable membranes appropriate to the substances to be purified are required. W. McC.

Catalase in body-fluid of the silkworm. S. MATSUMURA (Bull. Sericult. Japan, 1935, 7, 5).—The body-fluid catalase activity in the male silkworm is $>$ in the female. It is strong soon after the 4th moult, but becomes weaker at maturity. It varies with race and strain, but is not related to blood colour. E. A. H. R.

Mechanism of increase in amylase activity during autolysis of barley powder. R. H. R. RAU (Proc. Indian Acad. Sci., 1935, 1, B, 686—692).—Amylase activity in barley powder increases during autolysis as a result of liberation of β -amylase. No amylokinase is formed. A. G. P.

Protective action in ultra-violet irradiation of amylase solutions. W. R. THOMPSON and R. THOMPSON (J. Gen. Physiol., 1935, 18, 675—680).—The protective action of dog's sera against the destruction of aq. pancreatic amylase preps. by ultra-violet irradiation is due to competitive absorption by the sera for inactivating radiations. F. O. H.

Rennin and the diastatic power of ungerminated grains. T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1935, 278, 112—122).—Rennin is able to increase the amylolytic power of various grains, the

effect being greatest in respect to the saccharifying power and only slight in respect to the dextrinifying and liquefying powers. With most grains the effect is as great as that with papain, whilst with oats and buckwheat it is even greater. The effect is not due to the traces of pepsin in rennin. Addition of CaCl_2 inhibits this increase of the active amount of amylase by rennin. P. W. C.

Inactivation of heparin in blood. A. SCHMITZ and L. KÜHL (Z. physiol. Chem., 1935, 234, 212—215).—The inactivation is almost complete in 3 hr. at 56° in blood-serum, and only a small part of the inactivating power remains after 18 hr. at room temp. in plasma (hen) or albumin or globulin solutions. W. McC.

Determination of the unit of heparin. A. SCHMITZ (Z. physiol. Chem., 1935, 234, 216—217; cf. A., 1932, 1054).—The procedure of Scott *et al.* (A., 1933, 1317) is untrustworthy. The concn. of heparin \propto the log of the coagulation time. Determinations must be made at 38° in 2—20 min. A "heparin unit" is 30 times that amount which increases the log of the coagulation time of hen plasma, under given conditions, by 0.1. W. McC.

Preparation of thrombin. A. C. ROBERTS (Proc. Soc. Exp. Biol. Med., 1935, 32, 606—608).—Fibrin from calves' blood, after being freed from hæmoglobin, is extracted for 24 hr. with Et_2O , and then with cold 8% NaCl . The NaCl extract is filtered, and excess of NaCl removed by dialysis against H_2O ; this is followed by further dialysis against a PO_4^{3-} buffer at p_{H} 7.38, and against H_2O . The solution is filtered, and thrombin obtained by evaporation at room temp.

Coagulation and inactivation of emulsin by heat. Influences of crystalloidal and of colloidal solutes. D. L. FOX and L. L. SORKNESS (Biochem. J., 1935, 29, 1532—1537).—Emulsin (I) in dil. aq. solution is inactivated by incubation for 0.5 hr. at a temp. $> 75^\circ$, but is not pptd. Fluorescein, Congo-red, and neutral-red lower the inactivation temp., as does a p_{H} val. of 1.97 or > 7.65 . Glucose raises it several degrees, whilst 0.5% lactose solution has no effect. Dil. acids and phosphates cause pptn. of (I). In the absence of H_2O , (I) can be heated to 150° without loss of activity. There is no direct relationship between heat-inactivation and heat-coagulation of (I). J. N. A.

Baicalinase, an enzyme causing fission of flavoneglucuronide. II. T. MIWA (Acta Phytochim., 1935, 8, 231—243).—Scutellarein (Ac_4 derivative, m.p. 237°) is identified among the products of the hydrolysis of scutellarin (I) by baicalinase (II). Fission of (I) and of baicalin by (II) is a reaction of the first order after 25% hydrolysis, proceeding most rapidly at p_{H} 5.7 and $50\text{--}60^\circ$. H. W.

[Properties of] highly purified cozymase. H. VON EULER, H. ALBERS, and F. SCHLENK (Z. physiol. Chem., 1935, 234, I—II).—Cryst. cozymase (possibly $\text{C}_{12}\text{H}_{19}\text{O}_4\text{N}_4\text{P}$) regenerated (in 80% yield) from the Cu^1 salt is much more active than the starting material and is almost free from S. No increase in activity is achieved by repeated conversion into the

salt and regeneration. The degree of activity attained is independent of that of starting material which has activity \leq a certain val. The purification is without effect on the co-enzyme activity towards EtOH dehydrogenase, but destroys the activator effect in the hexose phosphate dehydrogenation system if purified dehydrogenase solutions are used. W. McC.

Enzymes of *Bombyx mori*, L. X, XI. Gastric lipase. K. YAMAFUJI and Y. YONEZAWA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 14—16, 30—33).—X. The gastric lipase (I) of silkworms has its p_H and temp. optima at 9.8 and 40°, respectively. Heating at 70° for 1 hr. nearly destroys (I). Quinine and atoxyl have only a slight toxic effect. Its activity increases on starvation for 1 day, but decreases if starvation is prolonged. The (I) content of the male is $>$ that of the female, and increases during growth up to the 5th day, while the body-fat is built up, after which it decreases. There is no significant difference in the (I) content of different species of silkworm.

XI. A prep. of lipase from the gastric juice of silkworms is described and an account of its kinetics given. The pancreatic lipase of vertebrates and (I) have similar activators and inhibitors. E. A. H. R.

Castor-bean lipase. VIII. E. TAKAMIYA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 46—48).—Castor beans contain a lipase-activating substance the power of which is destroyed by autoxidation. E. A. H. R.

Determination of lipase in pancreas. L. VOGEL and P. LAEVERENZ (Z. physiol. Chem., 1935, 234, 176—180).—When the method of Willstatter *et al.* (A., 1923, i, 403) is applied to impure preps., the vols. of aq. CaCl_2 and albumin should be increased to 1.6 c.c., and 1.6 c.c. of 2% Na oleate solution should be added. W. McC.

Lipase activity of mammalian organs in the healthy and carcinomatous organism. S. EDLBACHER and M. NEBER (Z. physiol. Chem., 1935, 233, 265—275).—The lipase activity of brain extract is only about 0.02 of that of liver. Fission by lipase in the organs examined is the same in O_2 , air, and N_2 . The characteristic inhibition by atoxyl and quinine of human lipase is not shown by lipase from rat's liver and brain. Tumours and necrotic tissue show activity of the same order as brain. The lipase activity of organs of carcinomatous animals is much $<$ that of normal animals. J. H. B.

Extraction and preservation of α -lipase of blood-serum. Z. GRUZEWSKA and E. BERAUT (Compt. rend. Soc. Biol., 1935, 119, 699—700).—Dried serum is freed from fat with EtOH and Et_2O , and α -lipase extracted with pure or 87% glycerol. The extracts retain their hydrolysing power for long periods in the cold, and the active principles of the serum are unaltered. R. N. C.

Rachitogenic action of cereals. Calcium and phosphorus liberated by digestion of cereals *in vitro*, with or without sodium chloride. G. POPOVICIU, G. BENETATO, and R. OPREAN (Compt. rend. Soc. Biol., 1935, 119, 445—447).—Digestion of cereal flours *in vitro* by pancreatic enzymes and enterokinase at p_H 8.4 liberates small quantities of Ca and P. Addition of NaCl increases Ca liberation. R. N. C.

Occurrence of trypsin in the stomach. M. HIRVONEN (Skand. Arch. Physiol., 1934, 71, 16—17).—In most cases the contents of the fasting human stomach contained trypsin (I). After a test meal, (I) was also present; the more acid the gastric contents, the greater was the amount of (I). NUTR. ABS. (b)

Enzymic histochemistry. IX. Pepsin in gastric mucosa of pigs. X. Acid localisation in gastric mucosa of pigs. XI. Peptidase in gastric mucosa of pigs. K. LINDERSTRÖM-LANG and H. HOLTER. XII. Esterase in gastric and duodenal mucosa of pigs. D. GLICK. XIII. Enzyme distribution in the stomach of pigs as a function of histological structure. K. LINDERSTRÖM-LANG, H. HOLTER, and A. S. OHLSEN (Compt. rend. Trav. Lab. Carlsberg, 1935, 20, No. 11, 1—32, 33—41, 42—56, 57—65, 66—125).—Pepsin (I) is found mainly in the chief cells of the fundus, but is also found in the fundus, in the neck chief cells, and in the pylorus, cardia, and duodenum. (I) in the neck chief cells is not so easily extracted by glycerol as that in the fundus chief cells. In different layers of the fundus mucosa glycerol extracts very varying amounts of (I), and this may be in accord with the concept of a desmo- and a lyo-pepsin. HCl is found exclusively in the fundus, and, probably, in its parietal cells. Peptidase is found in the fundus and cardia only in the chief cells, in the pylorus also in the neck chief cells, and in the duodenum in the cylinder cells and Brunner cells. There is no typical localisation of esterase activity in definite regions or layers of the gastric mucosa. E. A. H. R.

Effect of mucin and mucinoids on peptic digestion. H. C. BRADLEY and M. HODGES (J. Lab. Clin. Med., 1934, 20, 165—169).—The digestion of caseinogen, native and coagulated fibrin, etc. is retarded by the presence of gastric mucin for 3—4 days, but subsequently normal amounts are digested. Chondroitin sulphate and vegetable mucinoids produce similar effects. CH. ABS. (p)

Adsorption of crystalline pepsin by denatured ovalbumin and silk-fibroin. P. S. YANG (Chinese J. Physiol., 1935, 9, 189—196).—Loss of activity of pepsin solution by adsorption on ovalbumin or silk-fibroin involves an equiv. loss of pepsin-protein. H. G. R.

Proteases of *Ficus carica*. G. DE VITO (Annali Chim. Appl., 1935, 25, 151—156).—As with papain and bromelin, the proteolytic action of these enzymes is greatly enhanced by HCN. T. H. P.

Thiol nature of papain. T. BERSIN (Biochem. Z., 1935, 278, 340—341).—The activation of papain by $\text{K}_3\text{Fe}(\text{CN})_6$ in presence of veronal is due to reduction of the $\text{K}_3\text{Fe}(\text{CN})_6$. Since the author's results have been confirmed by Hellermann *et al.* (A., 1934, 1402), Purr (this vol., 252), and Mirsky *et al.* (*ibid.*, 506), the criticisms of Maschmann *et al.* (*ibid.*, 897) are rejected. W. McC.

Nature of urease; fractional ultrafiltration. P. GRABAR and A. RIEGERT (Compt. rend., 1935, 200, 1795—1797).—The behaviour of cryst. urease (I) towards ultrafiltration resembles that of globulin; other (I) preps. were less homogeneous. Such smaller

particles as are produced by partial tryptic digestion of cryst. (I) have no (I) activity. F. A. A.

Arginase activation. L. WEIL (J. Biol. Chem., 1935, **110**, 201—209).—The cysteine-Fe⁺⁺ complex, unlike cysteine or Fe⁺⁺ alone, activates arginase (I) independently of the origin or purity of the enzyme prep. After depletion of Fe⁺⁺ by feeding with 2:2'-dipyridyl, addition of Fe⁺⁺ to liver-(I) preps. produces a strong activation. The liver-(I) of carcinomatous animals shows similar activation, but the amount is < in normal animals. E. A. H. R.

Glyoxalase. V. Enzymic nature of kidney antiglyoxalase. E. F. SCHROEDER, M. P. MUNRO, and L. WEIL (J. Biol. Chem., 1935, **110**, 181—200).—The action of kidney antiglyoxalase (I) is explained as an enzymic hydrolysis of glutathione (II) (the glyoxalase co-enzyme), probably into glycine and glutamylcysteine, p_H optimum 7. Pancreatic (I) is probably identical with pancreatic carboxypolypeptidase, as this hydrolyses reduced (II) slowly and oxidised (II) more rapidly. High concns. of *d*- and *l*-histidine have no effect on glyoxalase activity, so that the claim that the (I) action of a pancreas prep. is due to histidine is disproved. E. A. H. R.

Production and properties of dry glyoxalase. P. G. EFENDI, J. O. GIRŠAVIČIUS, and A. P. RIZHOVA (Biochem. Z., 1935, **278**, 246—251).—Liver (fresh or dried with COMe₂ and Et₂O) is extracted with H₂O, and 0.1*N*-NaOAc (p_H 4) is added; purified material is obtained from the filtrate, after neutralisation with aq. NaHCO₃, by repeated pptn. with COMe₂, drying, and re-extraction with H₂O or physiological aq. NaCl. Most or all of the glutathione is removed. The enzyme exhibits no special sensitivity towards EtOH. Dried preps. lose a great part of their activity within 1 month. W. McC.

Antiglyoxalase action of histidine. J. O. GIRŠAVIČIUS and A. P. RIZHOVA (Biochem. Z., 1935, **278**, 252—256; cf. this vol., 122, 476).—When the change of p_H caused by histidine (I) is prevented, the amounts of (I) required to inhibit the action of glyoxalase are > those required when there is no prevention. Inhibition is gradual when fresh liver extracts are used, but when dried preps. are used inhibition is independent of time. No competition for AcCHO occurs between (I) and glutathione. W. McC.

Enzymic hydrolysis of dihydroxyacetonephosphoric acid. H. COLLATZ (Biochem. Z., 1935, **278**, 364—371).—The views of Schaffner *et al.* (this vol., 661) notwithstanding, K dihydroxyacetonephosphate and (better) its NaHSO₃ compound are completely hydrolysed in a few days by taka-phosphatase to CO(CH₂·OH)₂ and H₃PO₄. W. McC.

Phosphatases. III. Mechanism of the inactivating action of sodium oxalate and phosphates on "alkaline" phosphatases of animal tissue. S. BELFANTI, A. CONTARDI, and A. ERCOLI (Biochem. J., 1935, **29**, 1491—1507; cf. this vol., 660).—The hydrolysis of β -glycerophosphate (I) in the presence of Na₂C₂O₄ by liver extracts at alkaline p_H is slow at first, then increases rapidly, and finally attains approx. the same rate as without Na₂C₂O₄.

Bone extracts do not show the phenomenon. By varying the concns. of enzyme and (I) it is shown that the inhibitory action of Na₂C₂O₄ ceases when a certain concn. of inorg. P is freed. Added inorg. P prevents the inhibition of both liver and bone extracts; Na₂C₂O₄ tends permanently to deactivate the latter. Pig's kidney extract behaves similarly to that of rabbit's liver. H. D.

Phosphatase in fractures. E. H. BOTTERELL and E. J. KING (Lancet, 1935, *i*, 1267—1270).—The phosphatase (I) content of callus and bone near healing fractures, produced experimentally in rabbits, is > that of normal bone. This increase appears to accompany the formation of hypertrophic cartilage cells, osteoblastic activity, and the formation of bone matrix. There is little indication of concomitant changes in the serum-(I) of man or rabbits during the repair of fractures. Introduction of (I) into the site of experimental fractures produces no change in the rate or apparent quality of the calcification of the bone matrix. L. S. T.

Degradation of α - and β -glycerophosphate by fresh yeast and by dissolved yeast-enzymes. W. SCHUCHARDT (Biochem. Z., 1935, **278**, 164—172).—Yeast-phosphatase can degrade at p_H 4 and 6 both α - and β -glycerophosphates, but the β -isomeride is more readily attacked than the α . With aq. suspensions of dried yeast at p_H 4 the β -form and at p_H 6 the α -form is the more readily attacked. With yeast maceration juice and with glycerol extracts of yeast before and after dialysis, the α -variety is more readily decomposed. P. W. C.

Fermentation enzymes. III. First phases of phosphorylation in alcoholic fermentation. A. SCHAFFNER, H. BERL, and E. BAUER (Z. physiol. Chem., 1935, **234**, 146—150; cf. this vol., 784).—Added hexosediphosphoric acid (I) has no catalytic effect in a purified enzyme system [the reaction ceasing when all (I) has been consumed], and (I) cannot be replaced by hexosemonophosphoric acid (II). The Neuberg and Robison esters yield dihydroxyacetonephosphoric acid when attacked by zymohehexase only after addition of yeast maceration juice which contains an enzyme (or component of an enzyme) capable of converting (II) into (I). The primary product of phosphorylation is a hexose mono-ester identical with or easily convertible into the Robison ester. W. McC.

Yellow pigment containing sulphur from yeast. R. KUHN, T. WAGNER-JAUREGG, F. W. VAN KLAVEREN, and H. VETTER (Z. physiol. Chem., 1935, **234**, 196—200).—Yeast, milk, sugar-beet, and similar materials contain at least 3 structurally different blue-fluorescent substances, the fluorescence of which is removed by reduction (*e.g.*, with Na₂S₂O₄) and restored by shaking with air. One of these is *thiochrome* (I) (20 mg. from 1200 kg. of yeast), C₁₂H₁₄ON₄S, m.p. 222° (decomp.), a H₂O-sol. base containing NMe; absorption max. 358 and 375 $m\mu$ (hydrochloride, max. 348 $m\mu$). The fluorescence of (I) in alkaline solution is irreversibly destroyed by sunlight. In yeast (I) is probably present entirely as a colourless, non-fluorescent chromogen possibly identical with vit-

amin- B_1 (II) (cf. Peters, this vol., 415). Me is quantitatively eliminated from (I) and (II) picrolonate during determination of NMe by the method of Slotta *et al.* (A., 1932, 291). W. McC.

Reproduction in yeast cultures. A. KLEM (Hvalrad. Skrift., 1933, No. 7, 55—91; Chem. Zentr., 1935, i, 734—735).—The rate of CO_2 production per single cell is examined. Relationships between the EtOH concn. and that of sugar in the culture liquid are determined. A. G. P.

Respiration of yeast. J. GJAJA and L. MARKOVIC (Compt. rend. Soc. Biol., 1935, 119, 639—641).—Variation of the concn. of yeast suspension in a medium containing EtOH or glucose, through vals. $>7\%$, scarcely affects the O_2 consumption, which, however, is increased by dilution to $<$ this val. In a mineral medium the variations of O_2 consumption are less marked; NaF suppresses it in a glucose or EtOH medium, but not in a mineral medium. Hence there are two types of respiration of yeast. R. N. C.

Action of 2 : 4-dinitrophenol on washed yeast. J. FIELD and A. W. MARTIN (Compt. rend. Soc. Biol., 1935, 119, 458—461).—Washing the yeast in distilled H_2O or PO_4''' buffer has no effect on the stimulation of respiration by 2 : 4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$. H. G. R.

Action of dinitrocresol on yeast fermentation and oxidation. M. E. KRAHL and G. H. A. CLOWES (J. Amer. Chem. Soc., 1935, 57, 1144).—4 : 6-Dinitro-*o*-cresol at optimum concn. ($10^{-5}M$) increases the rate of anaerobic CO_2 and EtOH production, to a smaller extent the (aerobic) consumption of O_2 , and the total amount of glucose consumed by yeast cells, but not the rate of growth of the cells. Higher concns. cause abnormally low activity. R. S. C.

Action of top yeast on levosin in solution and during the process of bread-making. R. GEORFROY (Bull. Soc. Chim. biol., 1935, 17, 848—851).—Free levosin (I) extracted from wheat flour is not fermented by top yeast. During the process of bread-making, however, the (I) in the flour is fermented, although much more slowly than sucrose and maltose. A. L.

Precipitinogenic properties of "radium" strains of *Zygosaccharomyces mandshuricus*. Saito. J. M. OLENOV (Bot. Arch., 1935, 37, 140—149).—New strains produced by repeated irradiation of cultures show successive changes in the serological reactions of their proteins. A. G. P.

Permeability of *Amoeba proteus* to water. S. O. MAST and C. FOWLER (J. Cell. Comp. Physiol., 1935, 16, 151—167).—Permeability data in Ringer's solution containing lactose are recorded. Permeability is not influenced by the thickness of the plasma-gel, but is probably regulated by the plasma-lemma. A. G. P.

Growth of *Chilomonas paramecium* in inorganic media. J. B. LOEFER and R. P. HALL (Science, 1935, 81, 486).—The strain used appeared incapable of synthesising protoplasm from NH_4 and other inorg. salts. L. S. T.

Auxogenic action of vitamin- B_1 on a micro-organism. W. H. SCHOPFER (Compt. rend., 1935,

200, 1965—1967).—The effects of a no. of cryst. preps. of vitamin- B_1 on the growth of *Phycomyces* are practically identical, and confirm the essential character of $-B_1$ for the synthesis of growth-substance by the organism. A. G. P.

Acid-producing power as a means of characterising strains of *Aspergillus niger*. G. VASSILIEV (Biochem. Z., 1935, 278, 226—234).—The production and accumulation of citric and gluconic acids by different strains of *A. niger* (on a medium containing sugar) is specifically influenced by 0.01% ZnSO_4 , which restricts these activities in some cases, but stimulates them in others. ZnSO_4 also affects the respiration of the mould and its power to consume sugar. W. McC.

Formation of intermediate products in the growth of *Aspergillus niger* as a function of the age of the mycelium. R. BONNET and R. JACQUOT (Compt. rend., 1935, 200, 1968—1970).—Formation of $\text{H}_2\text{C}_2\text{O}_4$ in cultures of *A. niger* increases with the age of the culture in media containing KNO_3 , but none is formed in those containing NH_4 salts. $\text{H}_2\text{C}_2\text{O}_4$ is an unutilisable by-product, and its production is related to the maintenance of an appropriate energy balance in the culture. Citric acid is formed from spores and is subsequently utilised during the growth of mycelium. In older cultures autolysis of mycelium results in a further accumulation of citric acid in the medium. A. G. P.

Can excess of a metal correct insufficiency of potassium in the development of *Aspergillus niger*? C. PONTILLON (Compt. rend. Soc. Biol., 1935, 119, 349—350).—K can be replaced by Na, Mg, or Ca, but Fe and Al inhibit germination of the spores. R. N. C.

Thermochemical investigations of the energy balance during the growth of fungi. A. YAMAMOTO and S. YAMAGATA (Acta Phytochim., 1935, 8, 245—254).—The formation of 1 g. of the substance $\text{C}_{409}\text{H}_{717}\text{O}_{233}\text{N}_{46}$ of *A. oryzae* from NH_3 and galactose is accompanied by evolution of 632.5 g.-cal. H. W.

Production of trimethylarsine by *Penicillium brevicaulis* (*Scopulariopsis brevicaulis*). F. CHALLENGER and C. HIGGINBOTTOM (Biochem. J., 1935, 29, 1757—1778).—Bread cultures of *P. brevicaulis* containing hydroxytrimethylarsonium nitrate (A., 1933, 266) or hydroxytri-*n*-propylarsine oxide (corresponding *picrate*) evolve AsMe_3 and AsPr_3 , respectively; no odour of NMe_3 is detected with $\text{NMe}_3\text{Cl}\cdot\text{OH}$ or NMe_3O . Na arsenate affords AsMe_3 but no gaseous product giving a ppt. with 2 : 4-dinitrophenylhydrazine. Neither Na nor Ca β -hydroxyethylarsinate yields AsMe_3 . Addition of propionates or butyrates to cultures (normal or grown with EtCO_2Na or PrCO_2Na as sole source of C) containing As_2O_3 yield always pure AsMe_3 , contrary to the theory of formation of methylarsinic acid from AcOH ; also arsinoacetic acid affords only traces of AsMe_3 (due to hydrolysis). With glycine or alanine, NH_3 but not betaine is formed in absence of As_2O_3 , whilst in presence of As_2O_3 the yield of AsMe_3 is \approx normal. Yields of AsMe_3 with fructose, xylose, glycerol, etc. as source of C and with addition of MeOH ,

EtOH, HCO_2Na , CH_2O , $(\text{CH}_2\text{O})_3$, $(\text{CH}_2)_6\text{N}_4$, or Na formaldehydesulphoxylate are tabulated. Reactions between choline chloride or betaine and arsenite, selenite, and tellurite indicate the possibility of elimination of Me from methylated bases. No active enzyme prep. could be isolated from the mould. The data indicate a reducing action by *P. brevicaulis* on As^V derivatives; reduction of $\text{OH}\cdot\text{CH}_2\cdot\text{PO}_3\text{H}_2$ to a volatile phosphine or MePO_3H_2 , however, could not be achieved. The bearing of the results on the mechanism of methylation by moulds is discussed.

F. O. H.

Biochemistry of micro-organisms. XLVI. *i*-Erythritol, a metabolic product of *Penicillium brevicompactum*, Dierckx, and *P. cyclopium*, Westling. A. E. OXFORD and H. RAISTRICK (Biochem. J., 1935, 29, 1599—1601).—*i*-Erythritol (I) is isolated in small yields together with mannitol from the mycelium and the metabolism solution of *P. brevicompactum* and *P. cyclopium* when grown on media containing glucose and tartaric acid, growth being stopped before all the sugar has disappeared. With *P. cyclopium* the presence of tartaric acid is not essential for its formation. (I) is present in the mycelium in the largest amounts in the earlier stages of growth, and may disappear from the mycelium before disappearing from the medium.

P. W. C.

Protein synthesis by the genus *Azotobacter*. R. A. GREENE (Soil Sci., 1935, 39, 327—336).—Proteins occurring in the organisms were principally globulins, glutelins, and albumins. Arginine and lysine were the chief NH_2 -acids; tyrosine, tryptophan, cystine, and histidine were found in smaller amounts. Approx. 40% of the total N occurred in the non-basic fraction. A S-containing substance (possibly glutathione) was also detected. A close similarity is shown between the composition of *A. vinelandii* and *A. agilis*, and between *A. chroococcum* and *A. Beijerinckii*.

A. G. P.

Formation of hydrogen from glucose and formic acid by "resting" *B. coli*. I. A. TASMAN and A. W. POT (Biochem. J., 1935, 29, 1749—1756).—Differentiation between the formation of mol. H_2 from glucose (by glucose hydrogenylase) and from HCO_2H (by formic hydrogenylase) by "resting" *B. coli* could not be confirmed (cf. A., 1930, 251; 1932, 880; 1933, 1333). Production of H_2 by growing and "resting" *B. coli* generally has HCO_2H , and in a few cases AcCO_2H , as an intermediary.

F. O. H.

Volume increase of bacteria from X-ray irradiation. T. J. DIERZ (Radiology, 1935, 24, 31—38).—The increased vol. per normal bacterium (*E. coli*) following irradiation comprises an increased protoplasmic vol. due to stimulation and additional swelling caused by H_2O absorbed from the medium.

CH. ABS. (p)

Chemistry of the diphtheria bacillus. Fractional extraction of the lipins; separation of the hapten fraction; presence of soap in the bacterial cell. M. A. MACHEBŒUF and H. CASAGNE (Compt. rend., 1935, 200, 1988—1990).—The hapten of the diphtheria bacillus closely resembles that of the tubercle bacillus. It occurs only in the P-rich fraction of the lipin sol. in COMe_2 . It is possibly free

and not in the form of an antigenic protein complex. The MeOH extract of the diphtheria bacillus contains appreciable amounts of Na palmitate.

A. G. P.

Purification of diphtheria toxoid. P. J. MOLONEY and M. D. ORR (Biochem. J., 1935, 29, 1525—1531).—The toxoid is pptd. from its crude solutions by FeCl_3 or COMe_2 , or by adsorption on FePO_4 . The yields (70—100%) and degrees of purification are the same for the three methods.

J. N. A.

Purification and concentration of diphtheria toxin and anatoxin with sodium β -naphthylamine-3 : 6 : 8-trisulphonate. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 119, 518—520).—The toxin or anatoxin can be pptd. with the Na salt and citric acid at p_H 4 and redissolved in physiological salt solution.

H. G. R.

Serological analysis of the different lipid fractions of BCG. E. CHARGAFF and W. SCHAEFER (Ann. Inst. Pasteur, 1935, 54, 708—714).—Only the phosphatide fraction of BCG shows antigenic activity *in vitro* and *in vivo*. It acts in a dose of 0.0003 mg.

M. T.

Fluorescence of phthiocol, the pigment of the human tubercle bacillus. C. DHERE (Compt. rend. Soc. Biol., 1935, 119, 780—782).—Phthiocol is not fluorescent in the usual org. solvents, but shows a violet fluorescence in ultra-violet light, after treatment in Et_2O solution with aq. Na_2SO_4 . The orange and red bands of the ultra-violet fluorescence spectrum of cultures of *B. tuberculosis* are not due to the presence of phthiocol.

H. G. R.

Methylene-blue reduction by *B. tuberculosis* R and S. T. GUTHE (Compt. rend. Soc. Biol., 1935, 119, 694—697).—Methylene-blue is reduced by avian and mammalian strains of *B. tuberculosis* R and S. Reduction is more rapid with the mammalian than with the avian strains of the S variety.

R. N. C.

Oxidation of amino-acids by resting *Bacillus proteus*. F. BERNHEIM, M. L. C. BERNHEIM, and M. D. WEBSTER (J. Biol. Chem., 1935, 110, 165—172).—At p_H 7.8 in presence of the resting bacillus, leucine, phenylalanine, and methionine are rapidly oxidised utilising 1 O per mol. Serine (I), alanine (II), and proline (III) utilise, respectively, 3, 4, and 7 O per mol. Tyrosine and tryptophan (IV), which utilise, respectively, 2 and 3 O, are oxidised more slowly. Glycine is completely oxidised to CO_2 , H_2O , and NH_3 , but valine (V), isoleucine (VI), hydroxyproline, and histidine are only very slowly oxidised. Except with (I) and (II), both forms of which are oxidised, only the naturally occurring optical isomerides are oxidised. In *dl*-mixtures non-natural isomerides of (V) and (VI) restrict the oxidation of the natural isomerides. The oxidations are completely inhibited by 0.005M-KCN. Except with (V) the extent of deamination corresponds with the O_2 uptake. Only (I)—(V) are decarboxylated. Methylene-blue, in the presence of the bacillus, is reduced by the acids at varying rates not correlated with the rates of O₂ uptake during oxidation.

W. McC.

Action of intestinal bacteria on aesculin-gelatin. L. JAME, R. CROSNIER, and F. MOREL (Compt. rend. Soc. Biol., 1935, 119, 849—850).—The blackening

effects on an aesculin-gelatin medium by various intestinal bacteria are tabulated. H. G. R.

Fermentation of sugars by the group [*Salmonella pullorum-gallinarum*]. G. PACHECO and C. RODRIGUES (Compt. rend. Soc. Biol., 1935, 119, 889—890).—The group can be identified by differential fermentation reactions. H. G. R.

Physiology of the respiration of bacteria. II. Intracellular indophenol reaction of bacteria. S. YAMAGUCHI (Acta Phytochim., 1935, 8, 263—284).—In normal cells respiration is due to the oxygenated cytochrome system, and in such cells the intracellular oxidation of the "Nadi" reagent in presence of indophenolase (I) is carried on by mol. O_2 transferred by this system. In considering poisoning, the effect on (I) and the system must be considered separately. The "Nadi" oxidation of *Micrococcus ochraceus* and 4 *Pseudomonas* type is either not restricted or accelerated by 90% CO , which does not hamper the O_2 respiration of these bacteria. The indophenol reaction occurs also without aid of the cytochrome oxidation. On the other hand, the indophenol reaction of *B. mycoides*, *B. xylinum*, *B. subtilis*, and *B. mesentericus vulgaris*, in which respiration is rendered possible by the cytochrome system, is hampered by CO , and the restriction is removed by irradiation, as is the case with respiration, so that the action of (I) is more or less dependent on the cytochrome- O . Indophenolase reaction is not observed with *Escherichia*, *Proteus*, and *Staphylococcus* types in which respiration is restricted by CO . The indophenol reaction of all bacteria examined is remarkably restricted by HCN ; "Nadi" oxidation of *M. ochraceus*, the O_2 respiration of which is resistant to HCN , is greatly hindered. Generally, HCN affects the indophenol reaction of bacteria at concn. so small that the respiration is unaltered. HCN exerts therefore a twofold action: the damaging of (I) and the restriction of cytochrome activity. No parallelism appears between the occurrence of cytochrome and (I) in bacteria. With the exceptions of *B. mycoides* and *B. abortus equi* (I) is not present in bacteria free from cytochrome- c . In all types of bacteria containing (I) the c -component of cytochrome is present, although in certain bases the "Nadi" reaction is not observed. H. W.

Bacterium tumefaciens, Smith and Townsend: biochemistry of two varieties of different pathogenicity. G. AMOUREUX (Ann. Inst. Pasteur, 1935, 54, 730—763).—The two species display some differences in their action on sugars, $AcCO_2H$, and peptone. They have similar actions on starch, L -aspartic acid, asparagine, and urea. The action of *B. tumefaciens* on substrates containing sucrose is probably due to the enzymic action of invertase. There are probably four enzymes in *B. tumefaciens*, viz., dextrinase, amylase, invertase, and urease, all being endocellular. No action on ovalbumin and gelatin and no coagulation of milk or gelification of pectin could be demonstrated. M. T.

Mechanism of the acetic acid fermentation. A. JANKE and S. KROPACSY (Biochem. Z., 1935, 278, 37—59).—The oxidation of $EtOH$ to $AcOH$ by resting cultures of *B. ascendens* is followed using the

authors' methods (see this vol., 1044). The further oxidation of $AcOH$ to CO_2 , supposed to take place with proliferating organisms, does not occur. Curves show the influence of p_H on the O_2 -utilisation curves. The dismutation process ceases as soon as a relatively small amount of acid has accumulated in the fermentation liquid. Very different p_H optima are obtained for the two dehydrogenation processes on the one hand and for the dismutation process on the other. With the same suspension of organisms, the O_2 utilisation for both dehydrogenation processes depends on the p_H and on the age of the culture. The velocity of the dismutation process in acid solution is so small that in the technical $AcOH$ process it can play no significant part. P. W. C.

Physiology of acetic bacteria. II. Oxidation of organic acids in presence of acetic bacteria. K. TANAKA (Acta Phytochim., 1935, 8, 285—313).— $AcOH$, $(-CH_2 \cdot CO_2H)_2$, $AcCO_2H$, malic (I) and fumaric acid (II) are degraded in presence of *B. aceti* with absorption of O_2 and evolution of CO_2 ; the quotients CO_2/O_2 are in harmony with the vals. calc. for complete oxidation to CO_2 and H_2O . HCO_2H , $EtCO_2H$, $H_2C_2O_4$, $OH \cdot CH_2 \cdot CO_2H$, glutaric, tartaric, and citric acids are unaffected. Max. activity of the bacteria is observed at p_H 5 with substrate concn. 0.03—0.1 M . If any two of the above acids are present simultaneously, a summation effect with respect to absorption of O_2 is never observed; the mechanism of degradation of the various acids is therefore closely similar. The oxidising power of the bacteria towards $AcOH$ and $(-CH_2 \cdot CO_2H)_2$ is most affected by rise in temp. and towards $AcCO_2H$ least. Aldehydease is far more stable than alcohol-dehydrase and the activities can be separated by this means. In the dehydrogenation of these acids the bacteria cannot utilise benzoquinone or methylene-blue as H acceptor. Addition of $PhMe$ greatly retards the dehydrogenation of acids; the activity of the bacteria towards (I) and (II) is restored by thorough washing, but towards other acids is mostly or completely lost. $CH_2I \cdot CO_2H$ at very low concn. restricts the absorption of O_2 . All aerobic oxidations except that of $AcCO_2H$ are greatly retarded by minute amounts of HCN . CO also restricts oxidation; prevention of this inhibition by light is somewhat indistinctly observed. The powerful inhibitory action of benzoquinone is irreversible. H. W.

Bacterial metabolism. I. Reduction of propionaldehyde and propionic acid by *Clostridium acetobutylicum*. K. C. BLANCHARD and J. MACDONALD (J. Biol. Chem., 1935, 110, 145—150). Since fermenting cultures of the bacteria convert $EtCHO$ and $EtCO_2H$ into Pr^aOH ($EtCO_2H$ first into $EtCHO$) without accompanying production of any other end-products (e.g., aldols or their transformation products) not normally produced by the bacteria in the fermentation of carbohydrates, it is improbable that intermediate production of aldol occurs during the production of Pr^aCO_2H and Bu^aOH from carbohydrates by these bacteria. W. McC.

Activator of the metabolism of *Bacterium propionicum*. P. CHAISE and C. FROMAGEOT (Bull. Soc. Chim. biol., 1935, 17, 874—892; cf. A., 1934,

330).—The accelerating action of potato extract on the growth of *B. propionicum* (I) on a boiled maize medium containing glucose is confirmed using a conc. prep. of potato extract made by treatment with $\text{Hg}(\text{OAc})_2$ in aq. Na_2CO_3 and H_2S . When lactic acid is substituted for glucose in the medium no activation occurs. Determinations of the amount of fermentation taking place with small quantities of (I) indicate that with glucose as substrate there is a threshold for the amount of (I) below which no growth takes place in the absence of the activator. By the action of the activator the threshold is lowered. With lactic acid as substrate the phenomenon is not so marked. A. L.

Behaviour of bacteria and infectious lysin in the ultra-violet spectrum. C. HALLAUER (Z. Hyg. Infektionskrankh., 1935, 117, 18—25).—Lysins agree approx. with the organisms that produce them with regard to resistance to ultra-violet radiations, formation of max. of sensitivity, and the spectral range of radio-sensitivity. R. N. C.

Ultrafiltration of the virus of vesicular stomatitis. J. H. BAUER and H. R. COX (Proc. Soc. Exp. Biol. Med., 1935, 32, 567—570).—The filtration end-point of the virus is independent of the source or serological type, and is approx. 140 m μ . R. N. C.

Formation of the Forssman antigen by a strain of *B. dysenteriae*, Shiga, in different nutrients. M. EISLER and A. HOWARD (Z. Hyg. Infektionskrankh., 1935, 117, 56—65).—The antigen is not produced when *B. dysenteriae*, Shiga, *L* is grown in media containing asparagine, leucine, and cystine as N source, and lactate, mannitol, and glycerol as C source. The agglutinability is fundamentally altered. If glycyl-glycine or -leucine is added, these effects do not occur. This behaviour is sp. for the *L* strain. R. N. C.

Paradoxical relation between ζ -potential and suspension stability in *S* and *R* variants of intestinal bacteria. E. W. JOFFE and S. MUDD (J. Gen. Physiol., 1935, 18, 599—613).—Determinations of electrokinetic potentials and suspension stability of 4 strains of non-flagellate intestinal bacteria indicate that the *S* (smooth) variants have ζ -potentials of approx. zero over a wide range of p_{H} and electrolyte concn., yet form stable suspensions by virtue of hydrophobic constituents. *R* (rough) variants have potentials varying with p_{H} and electrolyte concn. in the normal way, whilst the vals. of potential are crit. for suspension stability. F. O. H.

Physico-chemical difference in antibodies against *S* and *R* variants of a single bacterial strain. E. W. JOFFE (J. Gen. Physiol., 1935, 18, 615—625).—The antibodies against *R* and *S* variants of *B. typhosum*, when studied as deposits on maximally sensitised bacterial surface, differ in isoelectric point and ζ -potential. With increasing time of immunisation (rabbit), the isoelectric point moves to the alkaline side, but the agglutination titre does not change in a parallel manner. Rabbits immunised with single cell strains of *R* slowly develop antibodies for *S* and *vice versa*. F. O. H.

Bactericidal substances of human serum, particularly in fever. F. WULFF (Compt. rend. Soc. Biol., 1935, 119, 424—426).—Some properties of the anti-typhoid and anti-meningococcal substances of febrile serum are described. R. N. C.

Action of gastric juice on typhoid bacilli. K. TONOROVITCH (Compt. rend. Soc. Biol., 1935, 119, 638—639).—The resistance of the bacilli to gastric juice falls as total acidity increases. R. N. C.

Antagonistic action of sterile broth extract of *B. prodigiosus*. M. EISLER and I. JACOBSON (Z. Hyg. Infektionskrankh., 1935, 117, 76—91).—A thermostable substance that inhibits growth of diphtheria bacilli, gonococci, and certain other types is present in sterilised broth in which *B. prodigiosus* has been grown. Its action is associated with its adsorption on the bacilli and is $>$ that of pyocyanase. R. N. C.

Resistance to drugs and chemical tolerance of trypanosomes. E. SINGER and V. FISCHL (Z. Hyg. Infektionskrankh., 1935, 116, 683—687).—Strains of *T. nagana* exposed temporarily to non-trypanocidal atebirin or rivanol afterwards absorb considerably more of these drugs than untreated strains; hence chemical tolerance is fundamentally different from resistivity to drugs. Spontaneously resistant *T. lewisi* is not affected either positively or negatively by solu-salvarsan. R. N. C.

Chemotherapy of rat trypanosomiasis. V. FISCHL and E. SINGER (Z. Hyg. Infektionskrankh., 1935, 116, 652—659).—Many arsenicals and other substances, including normal and syphilitic human serum, were without therapeutic effect on rats infected with *T. lewisi*. Storage and activity were parallel only in the case of arsenicals, Au compounds being stored in considerable quantities in spite of their inactivity. R. N. C.

Antagonism of the actions of chemotherapeutic agents. II. A. HASSKÓ (Z. Hyg. Infektionskrankh., 1935, 116, 669—671).—Me- and Et-violet and pyocyanine reduce the absorptivity for trypanflavin of the flagellae of *T. nagana* in rats. Brilliant-green exerts the same effect through its high toxicity when injected intraperitoneally, but not subcutaneously. Trypan-red and -blue are both absorbed by trypanosomes, and reduce absorptivity to a min. There is no great difference between the dye contents of the parasites and the serum. R. N. C.

Mode of action of chemotherapeutic agents. I. A. HASSKÓ (Z. Hyg. Infektionskrankh., 1935, 116, 660—668).—Inoculation into normal mice of trypanosomes treated with trypanflavin or neosalvarsan (I) results in a retarded increase of trypanosomes; the retardation \propto the quantity, therapeutic index, and time of action of the drug, which affects the vitality of the flagellates. Their disappearance from the bloodstream inversely \propto the dye content. Parafuchsin has scarcely any effect on trypanosomes. (I) cannot be detected in them, the active agent being formed from (I) by the animal body. The therapeutic effect of tartar emetic is reduced by exclusion of reticulo-endothelial cells. R. N. C.

Action of alkaloids on pure cultures of *B. radicola*. G. MEZZADROLI and L. SGARZI (Atti R. Accad. Lincei, 1935, [vi], 21, 105—110).—With liquid cultures (containing glucose, K_2HPO_4 , and KNO_3) of *B. radicola*, caffeine increases growth in concns. of 0.005—0.025%, depresses it at 0.11%, and is toxic at 0.15%. Quinine and, to a greater extent, strychnine give corresponding lower vals. The effects are less marked in solid (agar) nutrients. F. O. H.

Effect of dyes on colonies of certain pathogenic fungi. III. J. W. WILLIAMS and L. GREEN (Proc. Soc. Exp. Biol. Med., 1935, 32, 625—628).—The effects of certain dyes on a no. of fungi are given. In general, growth is more profuse and more frequently coloured on acid than on basic dyes.

R. N. C.

Bactericidal and sterilising powers of aminobenzoic esters. A. MOREL, A. ROCHAIX, and H. DELABORDE (Compt. rend. Soc. Biol., 1935, 119, 612—615).—The bactericidal and sterilising powers of a no. of aminobenzoic esters on different organisms are given. They are < those of vegetable essences. They are not very different from those of the corresponding hydroxybenzoic esters. Sterilising power is not affected by the position of the NH_2 ; it is reduced by introduction of Me, but increased by Bu, in the NH_2 .

R. N. C.

Bactericidal and fungicidal action of homologous halogenophenol derivatives and its "quasi-specific" character. II. Derivatives of *o*-chlorophenol. Chlorine-free alkylphenol derivatives. E. KLARMAN, V. A. SHTERNOV, and L. W. GATES (J. Lab. Clin. Med., 1934, 20, 40—47; cf. A., 1934, 68).—Aliphatic and aromatic derivatives of *o*- $C_6H_4Cl \cdot OH$ (I) show similar relationships between mol. wt. and bactericidal and fungicidal properties, as do corresponding *p*-derivatives of *p*- $C_6H_4Cl \cdot OH$, although their action is less effective. Higher homologues of (I) and the *p*-alkyl derivatives of $PhOH$ (Cl-free) have a selective or "quasi-sp." action on Gram-positive organisms. The microbiological potency increases, and toxicity to animals decreases, with increasing mol. wt. of the substituting radical. Introduction of Cl into the nucleus of *p*-alkylphenols decreases their toxicity. CH. ABS. (*p*)

Stimulatory and inhibitory effects of silver and formaldehyde on bacterial growth: growth curves. W. OETTEL (Arch. Hyg. Bakt., 1934, 113, 71—91; Chem. Zentr., 1935, i, 424).—In sub-lethal concns. solutions of colloidal Ag and of CH_2O produce periodically alternating stimulatory and inhibitory effects on the growth of *B. coli* and of staphylococci. The nature and extent of these effects vary with the concn. of antiseptic applied.

A. G. P.

Sterilisation of hydatid sand by formolised and by iodised solutions. F. DEVE (Compt. rend. Soc. Biol., 1935, 119, 352—354).—Hydatid gravel is sterilised by 1% aq. CH_2O , by Lugol's I solution, whether freshly prepared or after 4 months' storage, and by 0.1% I in EtOH.

R. N. C.

Culture of micro-organisms on Cellophane membranes. T. R. BHASKARAN, M. SREENIVASAYA, and V. SUBRAHMANYAN (Current Sci., 1935, 3, 484).—

Cellophane, closely applied to the surface of a culture medium, permits the ready growth of bacteria, which are thereby obtained free from the solid constituents of the medium.

J. L. D.

Adrenal cortex and resorption of fat. F. VERZAR and L. LASZT (Biochem. Z., 1935, 278, 396—400; cf. this vol., 524).—In rats, the inability to resorb fats caused by extirpation of the adrenals is counteracted (up to 77% of administered olive oil resorbed) by subcutaneous injection of the hormone ("eucortone") of the adrenal cortex. Adrenaline and/or ascorbic acid have no such effect. The hormone acts by controlling phosphorylations.

W. McC.

Variations of blood-sugar in the course of continuous intravenous injection of adrenaline. J. MALMEJAC and V. DONNET (Compt. rend. Soc. Biol., 1935, 119, 734—736).—Continuous intravenous injection of adrenaline (I) at the rate of 0.05 mg. per kg. per hr. in dogs produces an increase of blood-sugar, which reaches its max. in $\frac{1}{2}$ hr., and then returns to normal. This fall is due to increased secretion of insulin and to suppression of (I) secretion.

R. N. C.

Blood-vessels, blood-pressure, and adrenaline. D. P. ORAHOVATS and T. GOTSER (Pflüger's Archiv, 1935, 235, 367—376).—Adrenaline (I) produces a vaso-dilatation of the intestinal blood-vessels in the dog more often than a vaso-constriction, whilst the effect on the vessels of the extremities varies. (I) injected into the mesenteric artery causes contraction of the blood-vessels. The effects are independent of the quantity of (I) injected, and are not affected by p_H changes, spinal or vagal section, atropine, asphyxia, or hyperventilation.

R. N. C.

Effect of adrenaline on the metabolism of isolated muscle. D. NACHMANSOHN, J. WAJZER, and R. LIPPMANN (Compt. rend., 1935, 200, 1981—1982).—The action of adrenaline on the energy metabolism of muscle consists only of a sp. acceleration of lactic acid production.

A. G. P.

Hypoglycæmia provoked by insulin before and after nephrectomy. E. GAUJOUX, M. RECORDIER, and M. ANDRAC (Compt. rend. Soc. Biol., 1935, 119, 745—746).—The max. fall in blood-sugar provoked by insulin in rabbits varies after nephrectomy; in some cases after double nephrectomy it is < after single nephrectomy. Blood-sugar remains low for a longer period in nephrectomised rabbits.

R. N. C.

Effect of the state of the kidney on the activity of insulin. E. GAUJOUX, M. RECORDIER, and M. ANDRAC (Compt. rend. Soc. Biol., 1935, 119, 747—748).—The max. fall of blood-sugar provoked by insulin is independent of blood-N.

R. N. C.

Can glycogen accumulate in the liver of a totally depancreatized dog under the influence of an insulin deprived of vagotonising action? L. HÉDON and A. LOUBATIERES (Compt. rend. Soc. Biol., 1935, 119, 358—360).—Vagotonin-free insulin provokes glycogen deposition similarly to the commercial product.

R. N. C.

Pituitary growth-hormone and glutathione concentration: does the hormone influence the

concentration concurrently with the stimulation of increase in weight? P. W. GREGORY and H. Goss (J. Exp. Zool., 1934, 69, 13—35).—The livers and muscles of rats killed after a period of growth induced by anterior pituitary injections show an increased content of I-reducing substances. This is not due to ascorbic acid, which remains the same as in controls. It is attributed to an increase of glutathione compounds during the induced growth.

NUTR. ABS. (b)

Effects of antuitrin-S and pituitary extract on the armadillo ovary. G. W. D. HAMLETT (Anat. Rec., 1935, 62, 201—207).—Human pregnancy urine extract and whole pituitary extract stimulate cystic and luteinised follicle production, and in some cases corpus luteum formation. The urine extract, but not the pituitary extract, causes resorption of the unimplanted blastocyst.

R. N. C.

Concentration of the antidiuretic factor of the anterior lobe of the pituitary. H. R. DOWNES and L. RICHARDS (J. Biol. Chem., 1935, 110, 81—90).—Dried pituitary gland is extracted with aq. AcOH and the antidiuretic factor is separated from the extract by dialysis; impurities are removed from the dialysate by pptn. with COMe_2 . Biological assays indicate that the treatment removes vasopressin, most of the oxytocin, thyrotropin, intermedin, and the gonad-stimulating hormone. The antidiuretic factor occurs chiefly in the posterior lobe and the pars intermedia.

H. D.

Effect of the thyrotropic hormone on carbohydrate metabolism. V. JONAS (Z. ges. exp. Med., 1934, 94, 495—503).—Repeated injection of thyrotropic hormone (I) had no effect on the fasting blood-sugar (II) of healthy subjects or patients with Graves' disease, but caused a higher and more prolonged curve after the ingestion of glucose, usually with glycosuria. In two cases of Graves' disease with disturbances of carbohydrate metabolism these became more marked. In a patient with myxoedema (II) rose and approached normal; the alteration in carbohydrate metabolism, which resembled that occurring in Graves' disease, generally occurred later than the increase in basal metabolism. In one patient with Graves' disease, who showed galactosuria after galactose, administration of (I) caused a higher and more prolonged (II) curve and a greater degree of galactosuria. The disturbances in carbohydrate metabolism occurring in Graves' disease are directly related to altered thyroid function.

NUTR. ABS. (m)

Seasonal changes in the thyroid gland of the thirteen-lined ground-squirrel (*Citellus tridecemlineatus*) with particular reference to its sexual cycle. M. ZALESKY (Anat. Rec., 1935, 62, 109—137).—Thyroid activity falls during hibernation, but can be stimulated to levels > the summer level by anterior pituitary extract. In the female the max. activity coincides with pregnancy and lactation. Activity is not affected by castration, sex hormones, or pregnancy urine extracts.

R. N. C.

Action of thyroid secretion on the variations of the chromic residual index of the blood-plasma. M. POLONOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 119,

585—586).—Thyroxine reduces the index in cases of diabetes and cancer when this is initially high, but does not affect it when it is initially normal or low.

R. N. C.

Diuresis of hyperthyroidism. A. S. DIX, J. M. ROGOFF, and B. O. BARNES (Proc. Soc. Exp. Biol. Med., 1935, 32, 616—618).—Thyroid administration produces diuresis in normal, but not in depancreatised, dogs, although it increases the metabolic rate in the latter.

R. N. C.

Gonadotropic hormones from various organs. S. SZARKA (Orvosi Hetilap, 1934, 78, 1009—1012).—Luteocrescin (I) differs in biological action from gonadotropic hormones from urine or anterior pituitary. The luteinising and ovary-stimulating effect of (I) is much > that of hormones from the named sources.

CH. ABS. (p)

Differential effect of some gonadotropic substances on development of cyclic sex characteristics in the English sparrow. E. WITSCHI and W. N. KECK (Proc. Soc. Exp. Biol. Med., 1935, 32, 598—603).—The hormone of the pituitary, but not that of pregnancy urine, accelerates the development of the sex glands.

R. N. C.

Colour reaction of the sex hormones and its application to colorimetric determination. W. ZIMMERMANN (Z. physiol. Chem., 1935, 233, 257—264).—Alkaline $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ gives a coloration with the $\text{CO}\cdot\text{CH}_2\cdot$ group. It detects androsterone, follicular hormone, luteosterone, and pregnandione in amounts of 0.01, 0.02, 0.05, and 0.025 mg., respectively, and may be used for the determination of these hormones.

J. H. B.

Constitution of equol. G. F. MARRIAN and D. BEALL (Biochem. J., 1935, 29, 1586—1588).—Equol (A., 1932, 1156) is isolated from the Et_2O -sol. phenolic fraction of the PhMe extract of urine of both pregnant and non-pregnant mares and stallions by crystallisation from CHCl_3 . The yields varied seasonally, becoming zero in winter. Mild KOH fusion yielded 2:4-(OH) $_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$, resorcinol (I), and a trihydric phenol which gave a Me_2 ether with CH_2N_2 . More vigorous fusion gave (I), $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $p\text{-C}_6\text{H}_4\text{Et}\cdot\text{OH}$. On the basis of these facts three formulæ are suggested for the constitution of equol: 7-hydroxy-2-, 7-hydroxy-3-(4'-hydroxyphenyl)-chroman, and 6-hydroxy-2-(4'-hydroxybenzyl)-coumaran.

H. D.

Presence of testicle hormones in the blood. L. PTASZEK (Soc. biol. Lwow, 1933, May 8th).—Resection of the vas deferens causes an increase in the male sexual hormone in blood.

CH. ABS. (p)

Male hormone. VI. Male hormone from boar testes. New crystalline male hormone. VII. Test of the male hormone by measurement of increase in weight of seminal vesicles of castrated rats. New rat unit. A. OGATA and S. HIRANO (J. Pharm. Soc. Japan, 1934, 54, 1010—1019).—VI. The cryst. hormone, m.p. 129—130°, is N-free and more active than other testicular preps. Its activity is not destroyed by boiling with KOH-EtOH.

VII. A new technique is described. CH. ABS. (p)

Quantitative studies on the response of the capon's comb to androsterone. A. W. GREENWOOD, J. S. S. BLYTH, and R. K. CALLOW (Biochem. J., 1935, 29, 1400—1413).—For the study of the response of the comb of the brown Leghorn capon to cryst. androsterone (I), groups of five kinds of similar initial comb-size and body-wt. are used and the technique of comb measurement is carefully standardised. Daily injections are made for 5 days and the response is measured in terms of increase of max. length + height of comb. The response \propto the log of the dose between the limits of 0.5 and 8 mg. The results, which imply a standard error of about $\pm 18\%$ in the determination of the dose, are considered in relation to the formulation of a technique for the assay of male hormone. The amount and nature of the solvent influence the response, the latter being the same for groups of birds of different ages (4 months to 6 years) and for both subcutaneous and intramuscular injection. As a precautionary measure, birds should not be used earlier than 12 months after castration. No relationship was detected between body-wt. and comb response. Birds should not be used for a new series of doses until 1 month after the previous doses. The activity of (I) is unaffected by heating the solution in arachis oil at 150° for 24 hr.

P. W. C.

Growth and maintenance of the fowl's comb by administration of androsterone. R. K. CALLOW and A. S. PARKES (Biochem. J., 1935, 29, 1414—1423).—Very rapid growth of the combs of capons with complete restoration to normal size in the course of a few weeks can be induced by injections of cryst. androsterone (I) in doses of the order of 2.5—5 mg. daily. The comb can be maintained at the normal level by daily doses of 1 mg. of (I). This requirement is not inconsistent with the view that secretion of (I) accounts for the whole androkinetic activity of the testes of the cock. Observations are made also on the restoration of the vas deferens. The comb of the Leghorn capon is several times more sensitive to (I) than is that of the Plymouth Rock capon. The comb of the hen is much less responsive than is that of the capon.

P. W. C.

Effect of androsterone and of male hormone concentrates on the accessory reproductive organs of castrated rats, mice, and guinea-pigs. R. K. CALLOW and R. DEANESLY (Biochem. J., 1935, 29, 1424—1445).—Androsterone (I) is injected into groups of adult rats for 14 days, beginning on the day of castration. 1 mg. daily maintained the growth and normal structure in the prostate of 140—160-g. rats, but > 2 mg. daily were required for maintenance of seminal vesicles. Larger rats receiving 3 mg. (I) had prostate larger than and seminal vesicles of normal size. With mice 1—2 mg. daily of (I) failed to maintain completely the seminal vesicles or the cranial lobes of the prostate. A comparison of different urine concentrates showed that in two urines the effect per capon unit on the accessory glands of rats is much the same as that produced per capon unit of cryst. (I), whilst in a third urine, the activity on rats was 3—4 times as great. The activity of the most effective urine concentrate can-

not be reproduced by combined administration of œstrone and (I), which gave results little if any better than (I) alone. Some urine concentrates may contain a male hormone other than (I) with much greater activity on the accessory glands of mammals.

P. W. C.

Crystalline male hormone from testes (testosterone), more active than androsterone prepared from urine or from cholesterol. K. DAVID, E. DINGEMANSE, J. FREUD, and E. LAQUEUR (Z. physiol. Chem., 1935, 233, 281—282).—A hormone from testis extract, *testosterone* (I), m.p. $154—154.5^\circ$, $[\alpha]_D^{25} +109^\circ$ in EtOH, has an activity of 1 capon unit in 10^{-5} g. An activator present in inactive testis extract or urine is necessary to enable (I) to exert its full growth-promoting power on the seminal vesicles of the infantile castrated rat.

J. H. B.

Androsterone. IV. Degradation of stigmasterol to isoandrosterone and androstenedione. Relationship between hormone of the corpus luteum, allopregnanolone, and androsterone. A. BUTENANDT and H. COBLER. **V. Androstenediol, a physiologically active reduction product of androsterone.** A. BUTENANDT and K. TSCHERNING (Z. physiol. Chem., 1935, 234, 218—223, 224—234).—IV. *alloPregnanolone* (1 g. from 17 g. of stigmasterol) with MeMgI gives a *carbinol* (I), $C_{27}H_{48}O$, m.p. $182—186^\circ$, which loses H_2O when heated with AcOH and Ac_2O , giving the *acetate* (II), m.p. 144° , of the unsaturated alcohol, $C_{22}H_{36}O$, and an *isomeride*, m.p. $111—112^\circ$. A second *isomeride*, m.p. $64.0—64.5^\circ$, is obtained from the mother-liquors of (I) by acetylation. Oxidation of (II) with O_3 gives the *acetate*, m.p. $96—97^\circ$, of *isoandrosterone* (III) (3-hydroxy α -allocholanone-17), which differs from androsterone (IV) only in the spatial position of the OH. (III), like (IV), yields androstenedione on oxidation with CrO_3 .

V. Reduction of (IV) with Na and Pr^+OH gives a mixture of which the chief constituent is androstenediol (V), m.p. 221° , $[\alpha]_D^{25} +12.6^\circ$ [diacetate (VI) m.p. $159—160^\circ$]. (V) and (VI), which are identical with the corresponding substances described by Ruzicka *et al.* (this vol., 346), are about three times as active as (IV), the effects of (VI) being more protracted and its max. effect being attained later.

W. McC.

Use of albino rats for assay of the male sex hormone. Y. WANG and H. WU (Chinese J. Physiol., 1935, 9, 149—163).—The rats are castrated at 4 weeks and given 2 daily injections at 8 weeks; 48 hr. later the preputial glands are dissected and weighed. 1 rat unit corresponds with a 50% increase in wt. over that of the control. The effect of the same amount of hormone in 2 daily injections is $>$ that of a single injection.

H. G. R.

Chemistry of œstrogenic substances. E. FRIEDMANN (Nature, 1935, 135, 622—623).—A discussion of the mol. structures which give rise to œstrogenic activity. It is claimed that benzylidene- and (to a greater extent) furfurylidene-pyruvic acid are active.

Chemistry of œstrogenic substances. J. W. COOK and E. C. DONDS (Nature, 1935, 135, 793,

959).—Friedmann's views (see above) are criticised. No oestrogenic activity of benzylidene- or furfurylidene-pyruvic acid or their Na salts could be detected when injected in amounts of 100 mg. per rat.

L. S. T.

Effect of progynon on regeneration of erythrocytes. T. MINOUCHI and H. SCHWALM (Klin. Woch., 1934, 13, 1565—1568; Chem. Zentr., 1935, i, 586).—Progynon (I) has only a slight effect on the red-cell count in normal or castrated female rabbits. After venesection in normal animals, (I) increases the reticulocyte count; the effect does not appear in castrated animals.

R. N. C.

Does folliculin provoke the interruption of gestation by arrest of the function of the corpus luteum? S. SKOWRON and A. PERAUS (Compt. rend. Soc. Biol., 1935, 119, 772—774).—The abortive action of folliculin in rabbits is not related to arrest and regression of the corpus luteum, and is not checked by progesterin.

R. N. C.

Action of ovarian hormone on lachrymal elimination of sodium chloride. D. MICHAEL and P. VANCEA (Compt. rend. Soc. Biol., 1935, 119, 447).—Lachrymal NaCl is increased by injection of ovarian hormone, reaching its max. 1 hr. after injection. The effect is the same in both sexes.

R. N. C.

Colorimetric determination of oestrin in the urine of non-pregnant women. G. F. MARRIAN and S. L. COHEN (Nature, 1935, 135, 1072).—The method described for pregnancy urine (A., 1934, 1269) is of little val. for the determination of the much smaller amounts of oestrin present in the urine of non-pregnant women.

L. S. T.

Hydrolysis of combined forms of oestrone and oestriol in human pregnancy urine. S. L. COHEN and G. F. MARRIAN (Biochem. J., 1935, 29, 1577—1585).—The optimum conditions for the hydrolysis of human pregnancy urine previous to the determination of oestrone (I) and oestriol (II) (A., 1934, 1269) are a $[H^+]$ such that the final $p_H < 1$, and autoclaving at 120° for 2 hr. Destruction of both (I) and (II) occurs on heating in alkaline or acid solution in presence of O_2 . Heating urine with alkali causes only about 50% hydrolysis; subsequent treatment with HCl completes the process.

H. D.

New agent produced from urine of pregnant women and its biological effects. J. BAUMANN (Orvosi Hetilap, 1934, 78, 1138—1141).—The new substance affects the ovaries of mature but not of infantile rats, and differs from the oestrus hormone and from gonadotropic agents.

CH. ABS. (p)

"Anti-hormones." T. MARTINS (Compt. rend. Soc. Biol., 1935, 119, 753—755).—Theoretical.

R. N. C.

Relations between hormones and vitamins. Mechanism of the action of the antirachitic vitamin in the organism with reference to the physio-pathology of the thymus. M. MESSINI and M. CORPO (Arch. Ist. Biochim. Ital., 1935, 8, 195—232).—The toxic action of vitamin-D (I) in thymectomised rabbits is $<$ in normal rabbits; blood-Ca is not increased, nor bone decalcification compensated by (I), and calcification of fractures is not

affected as in parathyroidectomised animals. (I) increases bone Ca and ash, but scarcely affects P, H_2O , and dry residue. The action of (I) on the normal calcification process is obstructed in thymectomised animals by the acid reaction, which prevents its catalysis of the formation of the $Ca_3(PO_4)_2$ -saline complex. A sp. thymus function, possibly hormonal, is hence probably involved in the regulation of the action of (I) on Ca.

R. N. C.

Role of vitamin-A in nutrition. M. B. RICHARDS (Brit. Med. J., 1935, 1, 99—102).—A review.

CH. ABS. (p)

Vitamin-A and cholesterol metabolism. J. A. COLAZZO, I. TORRES, and SANCHEZ-RODRIGUEZ (Klin. Woch., 1934, 13, 1678—1682; Chem. Zentr., 1935, i, 429).—The level of cholesterol in serum and organs of rats was considerably lowered in avitaminosis-A and increased (especially in the central nervous system) in hypervitaminosis-A.

A. G. P.

Effect of vitamin-A on the serum-cholesterol in man. F. LASCH (Klin. Woch., 1934, 13, 1534—1536; Chem. Zentr., 1935, i, 429).—Increased serum-cholesterol following administration of vitamin-A is primarily due to the increased proportion of cholesteryl esters.

A. G. P.

Influence exerted by the nervous system on the vitamin-A content of the blood. A. CHEVALIER, J. MALMEJAC, and Y. CHORON (Compt. rend. Soc. Biol., 1935, 119, 739—740).—Blood-vitamin-A is increased by excitation of the central ending of the pneumogastric, and of the peripheral ending of the splanchnic.

R. N. C.

Chemical composition of the white rat during the course of avitaminosis-A. L. EMERIQUE (Bull. Soc. Chim. biol., 1935, 17, 612—619).—The tissues of white rats undergoing progressive avitaminosis-A show first a deficiency in the protoplasmic constituents, then in the reserve fatty matter, and finally, when the avitaminosis has reached an advanced state, in the calcification of the bones. Under normal conditions there may therefore be an equilibrium between vitamin-A and -D.

A. L.

Discrepancy between biological assays and other methods of determining vitamin-A. I. R. S. MORGAN, J. R. EDISBURY, and R. A. MORTON (Biochem. J., 1935, 29, 1645—1660).—Biological assays for vitamin-A (I), Lovibond blue vals., and spectroscopic estimates of the % of (I) ($C_{20}H_{29}OH$) present are given for 22 oils and concentrates covering a range of potency of 530—1,290,000 international units per g., and the results are examined statistically. Accepting the characteristics of the rich Carr and Jewell concentrate as those of the pure (I), the assays are extrapolated to pure (I) and give vals. varying from 1.23 to 3.38 ($\times 10^6$) units per g. (mean 1.77) when calc. from the blue vals. and from 1.08 to 2.9 ($\times 10^6$) units per g. (mean 1.73) calc. from the spectroscopic estimates. This variation is $>$ can be accounted for by the known error of the assays. Generally the highest vals. are given by cod-liver oils of medicinal grade. Accepting the unit of (I) as the activity of 0.6×10^{-6} g. of β -carotene (II), it is calc. that if (II) is efficiently converted into (I) at the levels of dosage

used in the assays, the potency of pure (I) would be 1.56×10^6 units per g. Vals. < this might be accounted for by the presence of biologically inactive material showing selective absorption and chromogenic power, whilst vals. significantly higher suggest the existence of a biologically active material without selective absorption or chromogenic power, or with these characteristics much weaker than in (I).

P. W. C.

Modification of Sherman and Smith's vitamin-A-deficient ration for rats. H. C. HOU (Chinese J. Physiol., 1935, 9, 197—205).—By substituting soya-bean protein for casein, a shorter depletion period and a better wt. increase were observed. Substitution of potato- for corn-starch gave the shortest depletion period and the best wt. increase.

H. G. R.

Syntheses in the vitamin-A field.—See this vol., 978, 979, 983.

Effect of type of carbohydrate on vitamin-B synthesis in the digestive tract of the rat. N. B. GUERRANT, R. A. DUTCHER, and L. F. TOMEY (J. Biol. Chem., 1935, 110, 233—243).—The vitiating effect of coprophagy on vitamin-B (I) assay is most serious when the experimental diet contains dextrinised maize-starch (II) as the source of carbohydrate. Animals fed on such a diet have an unusually large caecum, which contains an enormous no. of live yeast cells and incompletely digested (II). It is suggested that under these conditions (I) is synthesised, and coprophagy enables animals fed on a (I)-free diet to maintain their normal growth curve. E. A. H. R.

Relationship between nutrition and the enzymic activity of the blood-serum. K. ARIMOTO (Sei-i-kwai Med. J., 1933, 52, No. 10, 103—107).—Feeding albino rats with excess of vitamin-B causes no appreciable increase in blood-amylase (I) unless excess of carbohydrate is also supplied, when (I) decreases.

CH. ABS. (p)

Vitamin-B₁ content of foods. A. Z. BAKER and M. D. WRIGHT (Biochem. J., 1935, 29, 1802—1807).—The trustworthiness of the cure of bradycardia as a method of determining vitamin-B₁ (A., 1934, 705) is confirmed. The contents (in international units) of various foods thus determined are tabulated.

F. O. H.

Crystalline vitamin-B₁. VII. **Relation to pathological states.** R. R. WILLIAMS, R. E. WATERMAN, and J. C. KERESZTESY (Science, 1935, 81, 535—536).—The antineuritic activity of the crystals towards human beri-beri has been confirmed. Rats fed on a vitamin-B₁-free diet show complete freedom from polyneuritis with only $1-2 \times 10^6$ g. of the crystals per day, but growth is slight. Marked insufficiency of B₁ may be possible without manifestations of polyneuritis.

L. S. T.

Tissue respiration in avitaminosis-B₁. H. G. K. WESTENBRINK (Arch. neerl. Physiol., 1935, 20, 175—176).—A reply to Abderhalden and Wertheimer (cf. this vol., 669)

R. N. C.

Crystalline vitamin-B₁. VIII. **Sulphite cleavage. II. Acidic product.** R. R. WILLIAMS, E. R. BUCHMAN, and A. E. RUEHLE (J. Amer. Chem.

Soc., 1935, 57, 1093—1095; cf. this vol., 668).—The "aminosulphonic acid" (I), $C_6H_5O_3N_3S$, obtained from vitamin-B₁, is probably a 6-aminopyrimidine. It chars slowly > 400°, melts > 440°, is sol. in dil. alkali or NH_3 , conc. HNO_3 , or H_2SO_4 (with which it does not react), has p_H 5.2 in saturated aq. solution, does not react with $p-SO_3H \cdot C_6H_4 \cdot N_2Cl$ (II), moist NaOH at 135°, NH_3 , or HCl at 100°, is pptd. by $AgNO_3$ at p_H 8.9 but not by phosphotungstic acid, gives much $SO_3^{''}$ with NaOH at 185° and $SO_4^{''}$ with H_2O at 200°, and with conc. HCl at 150° gives a 96% yield of a "hydroxysulphonic acid" (III), $C_6H_5O_4N_2S$, m.p. 360°, which gives no colour with $p-SO_3H \cdot C_6H_4 \cdot N_2Cl$, resists hydrolysis, and is probably a 6-hydroxypyrimidine. (I) and (III) resemble also the 2-substituted pyrimidines chemically, but differ therefrom in absorption spectra and in that 2-hydroxy-4:6-dimethylpyrimidine gives a strong colour with (II). The absorption spectra of 6-amino- and 6-hydroxy-2:4-dimethylpyrimidine resemble those of (I) and (III), respectively.

R. S. C.

Characteristics of avitaminosis in rats caused by lack of skin factors in the diet. H. VON EULER and M. MALMBERG (Biochem. Z., 1935, 278, 351—363).—Some of the symptoms (e.g., loss of hair and skin) of pellagra are caused by lack of lactoflavin (I) in the diet. At least partial cure (florid dermatitis cured) is achieved by administration of (I) with supplement (yeast juice). Basal diets containing in addition (I) and supplement lack components present in a normal mixed diet. Healthy skin can readily be distinguished histologically from skin of rats deprived of (I) even when external symptoms of pellagra are absent.

W. McC.

Determination of vitamin-B₂ by measurement of fluorescence. F. H. COHEN (Arch. neerl. Physiol., 1935, 20, 167—174).—The fluorescence of pure vitamin-B₂ (I) in aq. EtOH increases linearly with the concn. up to 10^{-6} g. per c.c.; at higher concns. the rate of increase slackens. Fluorescence falls with p_H ; it varies slightly with the solvent, max. occurring in C_5H_5N , and min. in H_2O , at the same concn. The adsorption of (I) on franconite and subsequent elution are quant. Plant extracts after irradiation show a residual fluorescence. Pure (I) added to the extracts cannot always be recovered quantitatively. The (I) content of carrot extracts is determined from the difference of intensities of fluorescence before and after exhaustive irradiation.

R. N. C.

Enzymic esterification of lactoflavin with phosphoric acid. H. RUDY (Naturwiss., 1935, 23, 286—287).—The glycerol extract of the enzyme of the small intestine of rats, in 0.01M- $PO_4^{'''}$ at p_H 7.2 and 37°, converts lactoflavin quantitatively into a phosphoric ester. The vitamin-B₂ phosphoric ester so obtained, like that obtained by means of $POCl_3$ (this vol., 545), gives readily sol. Ca and Ba salts. No esterification occurs when the phosphatase solution is deactivated by heating for a short time. It is probable that those flavins which cannot be esterified with H_3PO_4 in the animal body cannot show any growth-promoting action.

H. G. M.

Constitution and biological activity of flavins.—See this vol., 993.

Ascorbic acid of the adrenals and mortification. G. MOURIQUAND and A. COEUR (Compt. rend. Soc. Biol., 1935, **119**, 615—616).—The Giroud-Leblond AgNO_3 reaction is positive in normal guinea-pig adrenals 96 hr. after death. It remains negative after this time in scorbutic animals. R. N. C.

Histochemistry of adrenal gland. I. Distribution of vitamin-C. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1935, **110**, 1—7).—Ox adrenals were sectioned by the method of Linderström-Lang (A., 1934, 1260) and the vitamin-C (I) in the different sections was determined (this vol., 793); the (I) content is plotted against distance from the surface of the gland. The no. of cells per slice of tissue was counted and hence the quantity of (I) per cell was plotted as above. The highest peak in the curve occurs in the fascicular region. H. D.

Behaviour of *l*-ascorbic acid and chemically related compounds in the animal body. Antiscorbutic activity in relation to retention by the organism. S. S. ZILVA (Biochem. J., 1935, **29**, 1612—1616).—When the animal organism (guinea-pig) was exhausted of *l*-ascorbic acid and a variety of substances administered (e.g., *l*-arabo-, *l*-gluco-ascorbic acid, which are antiscorbutically active to different extents; *d*-ascorbic, *d*-gluco- and *d*-galactoscorbic acid, which are inactive) the degree of "fixation" by the tissues, especially by the adrenals, anterior lobe of pituitary, and intestine, appeared to vary directly with the degree of antiscorbutic activity, and the kidney excreted these compounds in amounts which varied inversely with the potency. P. W. C.

Effect of vitamin-C (ascorbic acid) on the growth of plants. S. VON HAUSEN (Suomen Kem., 1935, **8**, B, 27—28; cf. A., 1933, 757; 1934, 225).—Ascorbic acid (I) causes an increased development of plants grown in sterile cultures. (I) is stored by the plant. J. L. D.

Diphtheria toxin and vitamin-C. D. M. CARDOSO (Compt. rend. Soc. Biol., 1935, **119**, 749—750).—Diphtheria toxin destroys vitamin-C in the adrenals of guinea-pigs. R. N. C.

Action of different biological agents on vitamin-C. I. *Penicillium digitatum* (Pers.). Sacc. M. BIFANO and O. SERVAZZI (Arch. Ist. Biochim. Ital., 1935, **8**, 151—156).—The vitamin-C content of lemon-juice is not appreciably decreased by experimental infection of the lemons with *P. digitatum*. R. N. C.

Vitamin-C content of some Indian plant materials. M. DAMODARAN and M. SRINIVASAN (Current Sci., 1935, **3**, 553).—The ascorbic acid content of *Phyllanthus emblica*, L., *Moringa oleifera*, Lamk., *Sesbania grandiflora*, Pers., *Capsicum frutescens*, L., and *Anacardium occidentale*, L., is 1—4 mg. per g. of fresh material. Extracts from the first and last are stable, the former even for a week; the others undergo oxidation rapidly. After pptn. by Hg salts, or treatment with $\text{Pb}(\text{OAc})_2$ or $\text{CCl}_3\cdot\text{CO}_2\text{H}$, the extracts are readily autoxidisable: the presence of protective substance(s) in *P. emblica* and *A. occidentale* is there-

fore deduced. Ascorbic acid in *C. frutescens* reaches a max. at a certain stage of ripeness. E. W. W.

Interfering action of glutathione in the silver nitrate test for ascorbic acid. J. L. SVIRBELY (Biochem. J., 1935, **29**, 1547—1551).—The $\text{NH}_3\text{-AgNO}_3$ test for ascorbic acid (I) depends on the amounts of (I) and glutathione (II) present. If (II) is absent, the limit of sensitivity is 0.015 mg. of (I). Adrenaline, glycogen, lactose, gelatin, and starch do not interfere. With increasing amounts of (II) the test is less sensitive, and is not as definite as titration with dibromophenol-indophenol-blue. J. N. A.

Determination of vitamin-C in brain, cerebrospinal fluid, and serum. F. PLAUT, M. BULOW, and F. PRÜCKNER (Z. physiol. Chem., 1935, **234**, 131—145).—The determination of the ascorbic acid (I) contents of these materials by a spectrographic method described is frequently possible (often impossible with human blood-serum), and the results agree well with those obtained by titration. Complete removal of interfering substances is sometimes impossible and undesired oxidation of (I) cannot always be avoided. W. McC.

Vitamin-D content of vegetable oils. T. BERZACZY and K. RUPILIUS (Wien. klin. Woch., 1934, **47**, 1449—1450; Chem. Zentr., 1935, i, 431).—Crude olive oil, in contrast to the commercial oil, has antirachitic activity. The activity is dependent on the harvesting time, winter-gathered fruit supplying the most active oil. The activity is increased by ultraviolet irradiation, with or without addition of Fe^{++} . R. N. C.

Seasonal variations in the vitamin-D potency of pilchard oil. B. E. BAILEY (Pacific Biol. Sta. Nanaimo, Prog. Dept. 1934, No. 19, 5—6).—The vitamin-D potency of the oil probably \propto the oil content of the fish. CH. ABS. (p)

Calcium and phosphorus. X. Effect of variation of calcium, phosphorus, and vitamin-D in the diet on iron retention in rats. D. H. SHELLING and H. W. JOSEPHS. XI. Effect of prophylactic and curative doses of standardised viosterol on human tissues; necropsy report of thirteen cases showing no tissue damage. D. H. SHELLING and D. A. JACKSON (Bull. Johns Hopkins Hosp., 1934, **55**, 309—313, 313—334; cf. this vol., 409).—X. A high-Ca, low-P diet causes abnormally low hæmoglobin vals. in rats, whether viosterol (I) is given or not. Fe retention is similarly lowered and is $<$ that of animals fed on low-Fe milk. (I) increases Fe retention in rats receiving a high-P diet, but does not affect those on a high-Ca diet.

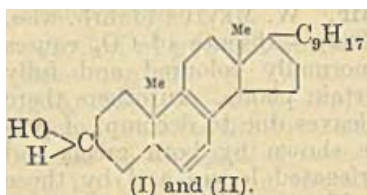
XI. Administration of (I) had no ill-effects on the soft tissues or skeletons of infants. CH. ABS. (p)

Calcifying factors in the diet of salamander larvæ. E. M. PATCH (Science, 1935, **81**, 494).—Salamander larvæ do not differ widely from higher animal forms in their responses to calcification factors in the diet. They should form a suitable means for the biological assay of calcifying agents. L. S. T.

Ring structure of calciferol. I. M. HEILBRON, K. M. SANANT, and F. S. SPRING (Nature, 1935, **135**, 1072).—With CrO_3 or KMnO_4 calciferol (I) and calci-

feryl acetate yield an oily aldehyde, $C_{21}H_{34}O$ (semicarbazone, m.p. 242°). A three-ring formula is suggested for (I) and the probable positions of the ethylenic linkings are indicated. L. S. T.

Vitamin-D and its thermal and photochemical reaction products. M. MÜLLER (Z. physiol. Chem., 1935, 233, 223—234).—Se dehydrogenation of the mol. compound isopyrovitamin (I)—pyrocalciferol (II) yields methylcyclopentenophenanthrene. Thus ring-closure on heating the vitamin (III) occurs at the same place as the photochemical fission. The acetate of (I) (dinibenzozate, m.p. $171-172^\circ$, $[\alpha]_D^{25} + 281^\circ$ in $CHCl_3$) with conc. HNO_3 affords 1 : 2 : 3 : 4 : 5- $C_6HMe(CO_2H)_4$ (IV) (isolated as the Me_4 ester), and condenses with maleic anhydride giving a product $C_{34}H_{48}O_5$, m.p. $203-204^\circ$. The H_2 uptake of the acetate is 3 mols. (II) (acetate, m.p. $81-82^\circ$, $[\alpha]_D^{25} + 403^\circ$ in $CHCl_3$) with HNO_3 also affords (IV). The acetate with maleic



anhydride gives a product, m.p. $161-162^\circ$, and takes up $2H_2$. These properties are expressed by the annexed constitution.

(I) and (II) probably differ only in

the steric arrangement of the substituents at C_5 and C_{10} .

Se or Pt dehydrogenation of suprasterol-I (V) or -II (VI) gave non-cryst. products. (V) absorbs (Pt) $3H_2$ (2 quickly), (VI) absorbs about $3.5H_2$ (oxalate $6.6H_2$). Ring-closure must have occurred in (V), but is doubtful in (VI). The constitution of the products derived from (III) is discussed. J. H. B.

Vitamin-E. I, II. Measurement of absorption band. S. UENO, Y. OTA, S. YOKOYAMA, and S. MATSUDA (J. Soc. Chem. Ind. Japan, 1935, 38, 190—192B, 192—195B).—I. From the unsaponifiable matter of rice oil a fraction, b.p. $200-250^\circ/1$ mm., has been obtained which closely resembles the vitamin-E fraction isolated from wheat-germ oil by Evans and Burr. Constituents of the unsaponifiable matter vary with the mode of manufacture of the oil.

II. The absorption spectra of rice oil and some of its components have been measured. The fraction of b.p. $200-250^\circ/1$ mm. has an absorption band at about $260 m\mu$ (cf. A., 1933, 987). H. G. M.

Rate of absorption of ammonium- and nitrate-nitrogen from culture solutions by ten-day-old tomato seedlings at two p_H levels. L. B. ARRINGTON and J. W. SHIVE (Soil. Sci., 1935, 39, 431—435; cf. B., 1934, 468, 776).—The rate of absorption of NO_3-N was much $>$ that of NH_4-N at p_H 4 and 7. Intake of NH_4-N at p_H 7 was $>$ that at p_H 4, whereas that of NO_3-N was somewhat higher at p_H 4. The influence of the reaction of the medium on N absorption was more marked in the case of NO_3-N than of NH_4-N . A. G. P.

Absorption of ions by living cells. H. LUNDEGÅRDH (Naturwiss., 1935, 23, 313—318).—The role of adsorption, hydration, dissociation, etc. in the absorption of ions by plant cells is discussed (cf. A., 1933, 874). A scheme is advanced depending on the p.d. existing between the sides of a cell membrane, a

negatively-charged colloid participating in the transport of cations, whilst the anions are primarily carried by positively-charged protoplasmic micelles, the complex being oxidatively (aerobic or anaerobic) decomposed to CO_2 and the acid corresponding with the anion. F. O. H.

Water relationships of tomato plants. I. W. SELMAN (Cheshunt Exp. Sta. Ann. Rept., 1934, 89—95).—The suction force of tomato leaf-cells increases during the day in summer, probably as the result of increased osmotic pressure of the cell contents. The phenomenon does not occur in winter. Loss of H_2O per unit leaf area by transpiration is highest in embryonic and least in fully expanded leaves. Differences in permeability of leaf cells to H_2O are indicated. Increases in leaf area during the night are closely correlated with the H_2O deficit of the cells. A. G. P.

Nutrient intake of plants from flowing and stationary nutrient solutions. II. E. UNGERER (Z. Pflanz. Düng., 1935, 39, 15—23; cf. this vol., 131).—The poorer growth of plants in dil. but flowing media as compared with that in conc. stationary media results from inability to take up sufficient K and N in the early stages of growth from solutions of low osmotic pressure. It is unlikely that plants can grow to maturity in nutrients as dil. as the soil solution.

Assimilation of inorganic nitrogenous salts, including sodium nitrite, by the grass plant. W. G. E. EGGLTON (Biochem. J., 1935, 29, 1389—1397).—The transformation of various forms of inorg. N applied to the soil into org. N in the plant is investigated, determinations of NH_4^- , pepsin-HCl-sol, true protein-, total, NH_3^- , NO_2^- , and NO_3^-N being carried out (the last three determinations also on the corresponding soil extracts). Inorg. N was detected in substantial amounts in the herbage only 2 hr. after application to the soil. In early spring, synthetic processes in the leaf are slow enough to permit accumulation of simple org. and inorg. compounds. This margin of partly elaborated N rapidly disappears, but at a diminished rate, when inorg. N salts are applied to the soil. NO_2^- occurs naturally in spring grass, and the amount is increased when the grass is treated with $(NH_4)_2SO_4$ or $NaNO_3$ at this time. Grass treated with $NaNO_2$ at the rate of 3 cwt. per acre shows no visible signs of distress, although some metabolic disturbances do occur. The possible significance of NO_2^- in the synthesis of protein is discussed and it is suggested that nitrites play a part in the "grass tetany" of cattle. P. W. C.

Absorption of nitrates by corn in the dark. P. L. GILE (Science, 1935, 81, 520—521).—Maize grown under alternating periods of light and dark assimilates NO_3^- as well in darkness as in light. Practically all the N needed can be taken up in complete darkness. L. S. T.

Nitrogenous nutrition of the flower. R. COMBES (Compt. rend., 1935, 200, 1970—1972; cf. this vol., 552).—The protein content of the calyx and corolla of *Lilium croceum* increases rapidly with growth until the flower begins to open, when vigorous proteolysis and translocation ensue. The protein content of

the androecium declines steadily from the "button" stage until full expansion. In the gynæcium protein increases throughout, but the major portion of the N leaving the perianth is translocated to the stem.

A. G. P.

Zinc and cadmium as stimulators of oxidation processes in certain plant-seed extracts. T. THUNBERG (Skand. Arch. Physiol., 1934, 69, 247—254; Chem. Zentr., 1935, i, 733).—Zn and Cd activate the decolorisation of redox indicators in plant extracts.

A. G. P.

Restoration of potassium effect by action currents. W. J. V. OSTERHOUT and S. E. HILL (J. Gen. Physiol., 1935, 18, 681—686).—Treatment of *Nitella* cells with distilled H₂O removes the ability to give p.d. (approx. 80 mv.) between 0.01M-KCl and NaCl ["K effect"]; this effect, however, is restored by action currents following application of a p.d. of 500 mv. It appears to be due to a substance or mixture, substance R.

F. O. H.

Mechanical restoration of irritability and of potassium effect. S. E. HILL and W. J. V. OSTERHOUT (J. Gen. Physiol., 1935, 18, 687—694).—The irritability and "K effect" of *Nitella* cells, lost on treatment with distilled H₂O, are restored by the mechanical forcing of sap (containing substance R) into the protoplasm (cf. preceding abstract).

F. O. H.

Photosynthetic behaviour of leaves with variations in temperature. B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 1, B, 736—753).—With normal atm. [CO₂] the assimilation of radish leaves increases with rise of temp. to a max. at 30°. Above this assimilation has the same initial rate as at 30°, but this declines with time. The hourly decrease in assimilation is very marked at 37°. Increased [CO₂] at 29° causes a higher rate of assimilation. Assimilation commences at < 12.6° and ceases at 47.4°.

A. G. P.

Effect of light on growth and differentiation in tomato seedlings, variety E.S.I. B. D. BOLAS and I. W. SELMAN (Cheshunt Exp. Sta. Ann. Rept., 1934, 86—89).—The curve representing the wt. per plant at the seventh leaf stage at different periods of the year closely resembles that for the total illumination per day or for day length, but is displaced several weeks forward. Although illumination ceases to limit assimilation after about April (greenhouse), it affects growth and leaf differentiation throughout the summer months.

A. G. P.

Reaction of the assimilatory system to alterations of light intensity. B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 1, B, 754—762).—The assimilation rate of radish leaves increases with light intensity up to 68,000 m.-candles under normal atm. conditions and up to somewhat higher vals. when [CO₂] is artificially increased. A time factor is apparent at 180,000 m.-candles. The depression in photosynthetic activity at high light intensities is related to a reversible inactivation of chloroplasts. The threshold val. for this activity is approx. 4000 m.-candles.

A. G. P.

Nature of the photoperiodic effect (induction), and the effect of length of day on the activity of [plant] oxidising enzymes. M. C. TSCHAILACHIAN

and V. A. ALEXANDROVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 161—166).—"Short-day" plants (millet) exhibited no "long-day" photoperiodic after-effects, and *vice versa*. Induction effects in millet and barley occurred when the causative factor accelerated the fruiting process and the development of the plants. The peroxidase (I) of millet was higher under long-day conditions, and that of barley (a "long-day" plant) under short-day conditions. Temporary (6-day) exposure of plants to an altered day period affected (I) in the direction in which the new photoperiod acted. In soya bean and *Phaseolus*, (I) was more active under short-day conditions when growth processes were retarded. Tomato leaves contained no (I). The catalase activity of plant leaves was practically unchanged throughout the experiment.

A. G. P.

Behaviour of illuminated [plant] leaves in carbon dioxide-free air. W. MEVIUS (Jahrb. wiss. Bot., 1935, 81, 327—382).—Absence of CO₂ causes rapid defoliation of normally coloured and fully turgid leaves in certain plants. In others there is a slow yellowing of leaves due to decomp. of proteins. The effects are shown by both green and colourless areas of variegated leaves and by those screened with tinfoil. Plants which normally bear anthocyanin pigments in leaves and stems cease to produce pigment in newly developing leaves, when deprived of CO₂. This effect is accentuated if the supply of NO₃ is maintained. The formation and destruction of these pigments are photosynthetic processes, and are closely related to the carbohydrate and N economy of the plants.

A. G. P.

Chlorophyll fluorescence and assimilation of carbonic acid. IV. Effect of oxygen on fluorescence in living leaves. H. KAUTSKY and A. HIRSCH (Biochem. Z., 1935, 278, 373—385; cf. this vol., 794).—The usual course of the fluorescence on irradiation of green leaves is a consequence of interaction between O₂ (bound in dissociable form to the chloroplast) and stimulated chlorophyll. Leaves irradiated in an atm. free from O₂ fluoresce from the beginning with max. unchanging intensity until liberated or added O₂ restores the normal behaviour.

W. McC.

Growth-stimulating substance in indigenous plants. II. Physiology. F. BOAS (Ber. deut. bot. Ges., 1935, 53, 495—511).—The presence is recorded of widely varying amounts of yeast growth-promoting substance in numerous plants and in cattle manure. Notably large amounts occur in mistletoe and in camomile. The proportion of this substance in *Phaseolus* varies with the λ of light to which the plant is exposed.

A. G. P.

Artificially induced root formation by means of growth-substance paste. F. LAIBACH and O. FISCHNICH (Ber. deut. bot. Ges., 1935, 53, 528—539).—The growth-promoting effects of the treatment of intact *Coleus* stems with β -indolylacetic acid paste are described.

A. G. P.

Inhibition of the action of growth-substance by parts of living plants. P. KORNMAN (Ber. deut. bot. Ges., 1935, 53, 523—527).—The activity

of agar block preps. of the growth-promoting substance of maize-gluten meal was counteracted by placing on the block tips of, or rings from, the base of the coleoptile of oats, but not the coleoptile tips of maize. Agar-oat flake preps. were not affected by oat tips; their activity was increased by maize tips but decreased by basal rings of oats. Maize tip-agar blocks were unactivated by oat tips. The presence of a growth-inhibiting substance in the older parts of a no. of plants is indicated. A. G. P.

Method for determining the callus-forming action of pastes containing growth-promoting substance. F. LAIBACH and O. FISCHNICH (Ber. deut. bot. Ges., 1935, 53, 469—477).—The activity of growth-promoting substance is determined by the rate of callus formation on decapitated epicotyls of *Vicia faba* in comparison with that of a standard prep. of β -indolylacetic acid (73×10^{-6} g. per g. of lanolin paste). A. G. P.

Action of growth-substance in parallelotropic plant organs. A. T. CZAJA (Ber. deut. bot. Ges., 1935, 53, 478—490).—Application of growth-substance parallel to the direction of the growth-substance stream in decapitated stems etc. causes lengthening but no thickening of the stem. Transverse applications cause thickening below the point of application. Cell elongation due to the growth-substance is unaccompanied by cell division. The latter occurs as a secondary effect of the disturbed polarity, following transverse treatment of stems with growth-substance. A. G. P.

Vitamins and growth-factors in plants. Growth-factor content of spores of *Phycomyces*. W. H. SCHOPFER (Ber. deut. bot. Ges., 1935, 53, 466—468).—The heterotrophic character (in respect of growth-factors) of *Phycomyces* is established. Spores contain enough growth-factors for germination, but external supplies of vitamin- B_1 or extracts of cultures on vitamin-containing media are necessary for further development. A. G. P.

Growth-hormone of plants. VII. Fate of growth-substance in the plant and nature of growth process. J. BONNER and K. V. THIMANN (J. Gen. Physiol., 1935, 18, 649—658; cf. A., 1934, 1272).—Removal of hormone-producing tips of *Avena* coleoptiles is followed by a decrease in growth (and hence in hormone) to approx. 50% in 2 hr. and then by a return to normal levels after 3 hr. Immediate increase in growth follows application of hormone-containing agar blocks. The hormone is inactivated in the plant to an extent either = or, when conditions are unfavourable for growth, > the proportionate amount of growth. Inactivation of the hormone, which appears to be irreversible, is not affected by HCN. The process of growth is discussed. F. O. H.

Growth-hormone and dwarf type of growth in maize. J. VAN OVERBEEK (Proc. Nat. Acad. Sci., 1935, 21, 292—299).—Auxin destruction, which may be due to oxidation-reduction changes, is greater in *nana* maize than in normal, and this causes the dwarf type of growth. Another growth-factor (cell-extension material) is present in coleoptiles of maize. M. S.

Auxins. A. J. H. SMIT (Chem. Weekblad, 1935, 32, 398—403).—A lecture.

Effect of oestrogenic substances on plants. IV. W. SCHOELLER and H. GOEBEL (Biochem. Z., 1935, 278, 298—311; cf. A., 1934, 1145).—Follicular hormone (cryst. but not quite pure) supplied in H_2O during early stages of growth to plants (primula, fuchsia, pink, chrysanthemum, violet, forget-me-not, cyclamen, tomato) growing in soil has a powerful general and sp. effect on the growth, the no. of blossoms and fruit being very greatly increased. The amount of hormone required for optimal effect varies from species to species of plant. W. McC.

Flower development and hormone action. R. HARDER and I. STORMER (Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl., VI, 1934, 1, 11—16; Chem. Zentr., 1935, i, 737).—Contrary to the results of Schoeller and Goebel (A., 1934, 1145), neither cryst. α -folliculin nor progynon affects the flowering of a no. of plants. A. G. P.

Growth and metabolism of plants with mineral salt nutrition. III. Sugar content of the press-juice of tobacco leaves in relationship to the mineral salt nutrition of plants. K. BONING and E. BONING-SEUBERT (Biochem. Z., 1935, 278, 71—88).—Increase of the mineral salts administered to the plant decreases, and decrease of salts increases, the sugar content of the leaf press-juice, the effect of the anions and cations being in the order $PO_4 < SO_4 < NO_3 < Cl$ and $Ca < Na < K$. Thus the more readily permeable ions have the largest decreasing effect on the leaf-sugar content, whilst the less permeable either have little effect on or may increase the sugar content. P. W. C.

Structure of cell-wall of coffee[-bean]. K. TAUFEL and H. THALER (Z. Unters. Lebensm., 1935, 69, 152—158).—A sample of coffee contained 52.6% of cell-wall (i.e., residue after extraction with Et_2O and H_2O), of which 47.0% consisted of the glucose fraction (mannan 15.3, xylan 1.8, cellulose 29.9%) and 5.6% of material rendered sol. by treatment with aq. ClO_2 (cf. A., 1931, 1101). E. C. S.

Influence of the pyrrole nucleus on the formation of chlorophyll. G. POLLACCI (Ber. deut. bot. Ges., 1935, 53, 540—542).—The growth of *Chlorella vulgaris* and other algæ is not injured if Mg is supplied in the form of Mg pyrrole-2-carboxylate (I). Replacement of (I) by $MgSO_4$ in Fe-free media results in new growth containing high leucoplast but no chloroplast contents. Re-addition of (I) causes normal green growth. The function of Fe in the cells is purely catalytic. It is probably concerned in the formation of the pyrrole compounds. A. G. P.

Leaf, flower, and fruit characters of the Santra orange (*Citrus nobilis* var. *deliciosa*). S. S. BHAT (Poona Agric. Coll. Mag., 1934, 26, 116—124).—Analytical data are given. CaC_2O_4 was deposited in leaves as cystoliths below the upper epidermis; it also occurred in leaves of *Citrus sinensis*, Swingle. CH. ABS. (p)

Distribution of constituents of the beech (*Fagus sylvatica*, L.). E. GAUMANN (Ber. deut.

bot. Ges., 1935, 53, 366—377).—The fat, protein, and carbohydrate contents of the various organs of the beech at different growth periods are examined.

A. G. P.

Chemical genetics of barley mutants. Chlorophyll and gramine contents of the mutants. H. VON EULER, H. HELSTROM, and N. LOFGREN (Z. physiol. Chem., 1935, 234, 151—164; cf. A., 1934, 1419).—The chlorophyll and gramine (I) contents of normal and chlorophyll-defective barley mutants are recorded. (I), $C_8H_6N \cdot CH_2 \cdot NMe_2$, which occurs chiefly in the roots (not in the coleoptile), on heating for 3 hr. at 80° with 0.1N-HCl gives a substance exhibiting max. absorption at 330 m μ and identical with "phenyl-X," the product of spontaneous transformation. The transformation probably consists in addition of H₂O to a pyrrole double linking. The product of transformation is accompanied by another substance having absorption max. at 270 m μ .

W. McC.

Identity of calycopterin and thapsin. W. KARRER and K. VENKATARAMAN (Nature, 1935, 135, 878).—The yellow colouring matter from the leaves of *Calycopteris floribunda*, Lamk (this vol., 246), and the thapsin obtained from a Spanish *Digitalis* (*ibid.*, 91) are identical. The name "calycopterin" should be retained for the flavone constituents of these two plants.

L. S. T.

Carotene and xanthophyll in pineapples. O. C. MAGISTAD (Plant Physiol., 1935, 10, 187—191).—The yellow colour in pineapples is due principally to carotene (I) (0.1—0.25 mg. per 100 g. of flesh) and xanthophyll (II). The ratio (I):(II) averages 8—13:1.

A. G. P.

Pigments of pink grapefruits, *Citrus grandis*, L., Osbeck. M. B. MATLACK (J. Biol. Chem., 1935, 110, 249—253).—The dried flesh of the Foster and the Marsh pink grapefruits was extracted with CS₂, and after a preliminary purification, the pigments were separated and isolated by the Tswett chromatographic method. The separated pigments were identified spectroscopically as lycopene (I) and β -carotene (II). (I) predominates in Foster and (II) in Marsh variety.

E. A. H. R.

Carotenoids. I. Carotenoids of *Diospyros* fruits. II. Carotenoids of *Arbutus* fruits. K. SCHON (Biochem. J., 1935, 29, 1779—1782, 1782—1785).—The fruits of *D. costata* and *A. unedo* contain α - and β -carotene, lycopene, cryptoxanthin, zeaxanthin, and violaxanthin (I). Approx. 80% of the total pigment of *A. unedo* is (I), m.p. 203° (corr.).

F. O. H.

[Chemistry of] algæ. I. Lipochromes of *Fucus vesiculosus*. I. M. HEILBRON and R. F. PHIPERS. II. Relationship between certain algal constituents. III. Isolation of lactoflavin. I. M. HEILBRON, E. G. PARRY, and R. F. PHIPERS (Biochem. J., 1935, 29, 1369—1375, 1376—1381, 1382—1383).—I. Dead material from *F. vesiculosus* (I) contains β -carotene (II) and zeaxanthin, whilst the living plant contains (II) and fucoxanthin (III) but no xanthophylls usually associated with higher plants. (III), $C_{40}H_{60}O_6$, m.p. 166—168° (uncorr.), $[\alpha]_D^{20}$ (cf. A., 1931, 733), which yields a

substance $C_{40}H_{78}O_2$, m.p. 63—64°, on complete hydrogenation under pressure, appears to be a dihydroxycapsorubin (this vol., 233).

II. Examination of the unsaponifiable fractions from *Cladophora sauteri*, *Nitella opaca*, *Oedogonium*, and *Rhododymenia palmata* indicates the lipins to be characteristic for each species and related to their habitat. All contain lutein, taraxanthin, (II), and small amounts of hentriacontane (A., 1934, 1347), whilst *C. sauteri* contains α -carotene. *N. opaca* and *Oedogonium* yield a *phytosterolin*, $C_{35}H_{66}O_6$, m.p. 283—285° (cf. A., 1934, 637).

III. Lactoflavin was isolated from aq. extracts of *C. sauteri* by direct adsorption and lumilactoflavin from irradiated alkaline extracts of (I).

F. O. H.

Occurrence of cytochrome in higher plants and algæ. E. YAKUSHIJI (Acta Phytochim., 1935, 8, 325—329).—Cytochrome is detected in the seeds of *Soja hispida*, the roots of *Raphanus macropoda*, *Brassica campestris*, in *Sagittaria trifolia*, apple, and in *Allium cepa*, in cabbage-leaves (after removal of chlorophyll by COMe₂) and in *Sargassum Thunbergii*, *S. piluliferum*, *S. serratifolium*, *Cystophyllum sisymbrioides*, *Endarachne Binghamiae*, *Myeloplucus cespitosus*, *Ishige Okamurai*, *Gelidium Amansii*, *Gymnogongrus flabelliformis*, *Porphyra tenera*, *Enteromorpha Linza*, and *Ulva* types.

H. W.

Chemistry of pigments of pepper. Red pigment in the perfection pimento (*Capsicum annuum*). W. L. BROWN (J. Biol. Chem., 1935, 110, 91—94; cf. Zechmeister *et al.*, A., 1934, 657).—The pigment is identical with the capsanthin of Hungarian paprika.

W. McC.

Saponins of *Chenopodium ambrosioides*, L. S. GREIFINGER (Wiad. farm., 1934, 61, 275—277, 289—291; Chem. Zentr., 1935, i, 746).—Saponins occur in largest amounts in roots (2.5%). The amount increases with age and is influenced by soil type and manuring. The pure saponin is amorphous, m.p. 196—200°, and has a mild hæmolytic action.

A. G. P.

Presence of saponins in tobacco; an accompanying substance. (FRL.) M. KOBEL and C. NEUBERG (J. pr. Chem., 1935, [ii], 143, 29—41).—Freshly plucked and chopped tobacco leaves heated to stop fermentation, and extracted with boiling EtOH, yield a product containing saponins. The hæmolytic action of various fractions (from aq. EtOH and/or Et₂O) is measured; it is arrested by cholesterol. Rutin is also present, with nicotine, and material hydrolysed to a product containing uronic acids and a sugar.

E. W. W.

Alkaloid content and activity of saprophytic ergot cultures. R. JARETZKY (Arch. Pharm., 1935, 273, 348—357).—Ergot grown on maltose-peptone-agar contains more alkaloids than if grown on other media, as shown by colorimetric determination by *p*-NMe₂·C₆H₄·CHO and by biological tests on the rabbit's isolated uterus.

R. S. C.

Protein of healthy potato tubers. H. KAHO (Biochem. Z., 1935, 278, 235—239).—The H₂O-sol. protein of potatoes is pptd. by salts only when their

concn. is high (6*N* to saturation). The degree of stimulation of heat-coagulation of the protein by anions and cations varies in accordance with the reversed lyotropic series, and provides a means of distinguishing between different sorts of potatoes. The protein occurs in potatoes combined with an acid (possibly $\text{H}_2\text{C}_2\text{O}_4$). W. McC.

Organic nitrogenous and non-nitrogenous compounds occurring in the Alaska pea. II. Isolation of pyrrolidonecarboxylic acid, tyrosine, and diamino-acids from the non-proteins thereof. S. L. JODIDI (J. Amer. Chem. Soc., 1935, 57, 1142; cf. B., 1934, 852).—An EtOH extract of defatted Alaska peas gives with $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ pyrrolidonecarboxylic acid. The peas yield arginine (0.7%) and give colour reactions for histidine and tyrosine. R. S. C.

Betaine in wheat bran. F. E. NOTTBOHM and F. MAYER (Z. Unters. Lebensm., 1935, 69, 289—300; cf. A., 1934, 571).—The aq. $\text{Mg}(\text{OH})_2$ extract of wheat bran consists largely of betaine (I), which constitutes 0.35% approx. of the bran. The composition and properties of phosphatide (II) from wheat bran and oats (cf. A., 1911, ii, 426) are described. Both contain (I), but it is present as an impurity, probably in combination with sugar. The P.-L. no. (cf. B., 1934, 425) of wheat-bran-(II)=3.44; that of seeds \propto the % of N in the fat-free material. E. C. S.

Presence of 2-hydroxy-5-methoxyacetophenone in extracts of rhizomes of *Primula acaulis*. A. GORIS and H. CANAL (Compt. rend., 1935, 200, 1990—1992).—The isolation and characterisation of the compound are described. A. G. P.

Resin of wheat straw. L. MARION (Canad. J. Res., 1935, 12, 554—563).— $\text{MeOH--C}_6\text{H}_6$ (1:1) extracts from wheat-straw lignin (4.72%) and a resin (1.5%), which contains free fatty acids [including palmitic (I), stearic (II), and lignoceric], glycerides [yielding (I), (II), linolenic and oleic acids], ceryl cerotate, m.p. 70°, much wax [containing a little P and yielding ceryl alcohol, sitosterol, m.p. 137°, (I), and cerotic acid], a sterol ester [giving a sterol, $\text{C}_{27}\text{H}_{46}\text{O}$ (Ac derivative, m.p. 134—135°)], a phytosterolin, $\text{C}_{33}\text{H}_{56}\text{O}_6$, m.p. 291—292° (Ac derivative, m.p. 157°; yields a sterol, m.p. 137°, and glucose) (cf. A., 1934, 1276), KNO_3 , and *D*-inositol. R. S. C.

2:4:5-Trimethoxy-1-allylbenzene. Asarone (allyl). B. S. RAO and K. S. SUBRAMANIAN (Current Sci., 1935, 3, 552).—The "asarone" obtained from calamus roots (A., 1934, 529), when treated with H_2SeO_3 and distilled from Na, is a liquid, b.p. 283°/685 mm., identified as 2:4:5-trimethoxy-1-allylbenzene, and named "asarone (allyl)." When heated with KOH, this gives ordinary asarone ["asarone (propenyl)"]. E. W. W.

Constituents of *Verbena officinalis*, L. I. Identity of verbenalin and cornin. B. REICHERT (Arch. Pharm., 1935, 273, 357—360).—Verbenalin from *V. officinalis* (A., 1908, i, 197) and cornin from *Cornus florida*, L. (A., 1928, 1137), are identical. R. S. C.

Composition of Bourdaine bark. III. Isolation of frangularoside and its hydrolysis

product frangularol. IV. Water-soluble complex purgative hydrolysed by rhamnodiastase. M. BRIDEL and C. CHARAUX (Bull. Soc. Chim. biol., 1935, 17, 780—792, 793—816).—III. The fresh bark, in contrast with the commercial product, gives on autolysis a rhamnoside, *frangularoside*, $\text{C}_{21}\text{H}_{34}\text{O}_9$, m.p. 234°. This on hydrolysis with aq. H_2SO_4 and HCO_2H yields *frangularol*, $\text{C}_{15}\text{H}_{14}\text{O}_5$, m.p. 301°, and rhamnose.

IV. The active principle of Bourdaine bark, extracted with 95% aq. EtOH and pptd. with COMe_2 , gives on hydrolysis with 5% aq. H_2SO_4 40% of emodol, 43% (2 mols.) of glucose, and 16% (1 mol.) of rhamnose. It is partly hydrolysed by rhamnodiastase with the formation of franguloside and glucose with small quantities of emodol and an unidentified anthraquinone derivative, m.p. 160°. It may consist of a compound of 1 mol. of franguloside with 2 mols. of glucose. A. L.

Sophoricoside, a heteroside of the fruits of *Sophora japonica*, L. C. CHARAUX and J. RABATÉ (J. Pharm. Chim., 1935, [viii], 21, 546—554).—From the boiling 80% EtOH extract of the pods of *S. japonica*, L., is isolated (1.5% yield) a β -glucoside *sophoricoside*, m.p. 297.5° (block), $[\alpha]_D^{20}$ —32.2° in $\text{C}_6\text{H}_5\text{N--10% H}_2\text{O}$, hydrolysed by boiling $\text{AcOH--6% H}_2\text{SO}_4$ or by emulsin to glucose and genistein, previously isolated from *Genista tinctoria* (Perkin et al., J.C.S., 1899, 75, 830; 1900, 77, 1310).

J. W. B.

Kuromamin, the colouring matter of "Kuro-mame." III. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1935, 11, 189—191; cf. A., 1934, 229).—Kuromamin is identical with cyanidin 3-mono-glucoside (cf. A., 1931, 1423). J. L. D.

Phytosterol and phytosterolin from the sweet potato. M. B. MATLACK (Science, 1935, 81, 536).—A phytosterol, consisting mainly of sitosterol, and a phytosterolin, sitosterol glucoside, have been isolated from *Ipomœa batatas*, Poir. L. S. T.

Production of sterols by plants. The "oily chloroplasts" described by Savelli in cacti. J. MANUEL (Compt. rend. Soc. Biol., 1935, 119, 480—482).—The properties of these chloroplasts from *Echinocereus procumbens* and *Cephalocereus senilis* are described. H. G. R.

Unsaturated acids of natural oils. II. Highly unsaturated acids of the kernels of *Parinarium laurinum*. E. H. FARMER and E. SUNDERLAND.

III. Highly unsaturated acid of the kernels of *P. macrophyllum*. W. B. BROWN and E. H. FARMER (J.C.S., 1935, 759—761, 761—763; cf. B., 1933, 476).—II. Kernels of *P. laurinum* gave 44% of fat (n_D^{25} 1.5565) on extraction with petroleum. 10 g. of fat gave with KOH-EtOH 2.5—3 g. of unsaturated acid, m.p. 83.5°, which is attacked by atm. O_2 ; with alkaline KMnO_4 it gave EtCO_2H and azelaic acid, and on Pt hydrogenation stearic acid. The structure $\text{Et}[\text{CH}:\text{CH}]_4[\text{CH}_2]_7\text{CO}_2\text{H}$ is ascribed.

III. Kernels of nuts of *P. macrophyllum* or *P. Senegalense* (Rosaceæ, tropical Africa) gave 70% of drying oil (4% on nuts). The unsaturated acid from the oil is shown to be α -elæostearic acid. The

unsaturated acid, m.p. 73°, described by Steger and van Loon (B., 1934, 369) may be β -elæostearic acid formed from β -elæostearin resulting from irradiation of α -elæostearin in the oil. P. G. C.

Biochemistry of the Salicaceæ. X. Leaf enzymes of *S. purpurea*. XI. Hydrolysis of salicoside by leaf enzyme preparation. XII. Oxidation of salicoside by leaf enzyme preparation. J. RABATE (Bull. Soc. Chim. biol., 1935, 17, 561—571, 572—601, 602—611).—X. Whereas the enzyme from the leaves of *S. purpurea* hydrolyses rapidly phenolic glucosides such as salicoside (I), piceoside (II), helicoside, chloropiceoside, and β -phenylglucoside, the hydrolysis of β -methylglucoside (III), benzylglucoside, amygdalin, and aucuboside proceeds slowly.

XI. Under the action of the enzyme prep. (IV) from the leaves of *S. purpurea*, the hydrolysis of (I) leads to the formation of some β -salicylglucoside. Starting with MeOH and glucose, no synthesis takes place with (IV), although with emulsin (V) there is considerable synthesis. When, however, the hydrolysis of (II) by (IV) is carried out in the presence of 3% MeOH, 57% of the glucose liberated is converted into (III) compared with 6% when (V) is used. Addition of (V) in this reaction does not prevent the synthesis, which can take place only if the glucose is liberated in the presence of the alcohol. The glucose when liberated is probably in an active form.

XII. The oxidation of saligenol is 3 times as rapid as, and is brought about with less CO₂ formation than, that of pyrocatechol (VI). It is believed therefore that the action of the oxidase responsible for the blackening of the leaves of *Salix* does not lead to the intermediate formation of (VI). A. L.

Alleged autohydrolysis of vegetable ivory. D. MELNICK and G. R. COWGILL (Biochem. J., 1935, 29, 1515—1518).—Paton's statement (A., 1924, i, 801) that a mannanase exists in *Phylelephas macrocarpa* is disproved by incubation experiments; failure to obtain reducing substances from the ivory after heating at 100° and washing is due to the removal of these substances by this treatment and not to the inactivation of an enzyme. A reducing substance is pptd. from an aq. extract of the ivory with AcOH which on hydrolysis is converted into mannose. Albumin and globulin fractions showing no enzymic activity are prepared. H. D.

Hemicelluloses extracted from mesquite wood after chlorination. L. SANDS and P. NUTTER (J. Biol. Chem., 1935, 110, 17—22).—Mesquite sawdust was extracted as before (A., 1933, 989), treated with Cl₂ and aq. NH₃, and the hemicelluloses (I) were removed by aq. NaOH. By successive extractions four fractions were obtained. The pentosan content increased as the delignification proceeded. Hydrolysis of (I) gave xylose in three fractions and glucose in one. No free uronic acid was found in the hydrolysates, 2 mols. of pentose being associated with the acid. H. D.

Analysis of carbohydrates of the cell-wall of plants. I. Relation between uronic anhydride content and furfuraldehyde. F. W. NORRIS and C. E. RESCH (Biochem. J., 1935, 29, 1590—1596).—The determination of the products of distillation of the

cell-wall with 12% HCl is investigated. The relation between uronic acid (I) concn. and the CO₂ produced by the decarboxylation method of Dixon (A., 1930, 453) in pure specimens of galacturonic, pectolic, and euxanthic acids is determined. Furfuraldehyde (II) is pptd. from the reaction products as the phloroglucose and weighed as such and the relation between (II) produced and (I) concn. is determined for the same acids. H. D.

Liberation of methyl sulphide by seaweed. P. HAAS (Biochem. J., 1935, 29, 1297—1299).—The identity of the gaseous odoriferous principle evolved by *Polysiphonia fastigiata* and *P. nigrescens* with MeSH has been confirmed. P. W. C.

Amount of hydrocyanic acid in blue couch grass (*Cynodon incompletus*, Nees). H. FINNEMORE and A. B. JAFFRAY (J. Council. Sci. Ind. Res. Australia, 1935, 8, 136—138).—The decrease in HCN content of the grass (determined after complete decomp. of glucoside by enzyme) during drying and subsequent storage was much < that in cases recorded by Seddon and King (A., 1930, 812). A. G. P.

Iodine content of tea. A. ITANO and Y. TUZI (Proc. Imp. Acad. Tokyo, 1935, 11, 141—143).—Japanese tea contains 0.45—1.20 $\times 10^{-6}$ g. of I per g. of dried leaves, of which 33—75% is extracted by hot H₂O. More I is contained in younger leaves. H. G. R.

Constituent of *Pertusaria dealbata*, Ach., Nyl. G. KOLLER and H. HAMBURG (Monatsh., 1935, 65, 375—379).—This lichen when extracted with Et₂O gives a substance C₁₉H₁₆O₁₁, decomp. 223° (in evacuated tube), which is considered to be thamnic acid (A., 1929, 818; 1932, 275), since it contains OMe, decomposes to form an atranol-like substance, with orcinol Me₁ ether, and is converted by MeOH into Me evernate and a resin, and by HCO₂H into thamnol, and since the acid C₁₀H₁₀O₆, m.p. 207°, which it gives on treatment with KHCO₃ and Na₂SO₃, is methylated to Me 3:5-dimethoxytoluene-1:4-dicarboxylate (A., 1929, 1460). E. W. W.

Chemical characteristics of fungi. G. REIF and G. BORRIES (Biochem. Z., 1935, 277, 329—336).—A table summarises the colours obtained when aq. extracts of the dried, finely powdered, Et₂O-extracted tissues of a variety of fungi were treated with m-NO₂-C₆H₄-CHO-H₂SO₄ reagent. P. W. C.

"Blackfellow's bread," the sclerotium of the fungus *Polyporus mylittæ*, Cke. and Mass. J. C. EARL and G. H. MCGREGOR (J. Proc. Roy. Soc. New South Wales, 1935, 68, 149—152).—The principal constituent of the sclerotium of *P. mylittæ* is closely allied to fibre cellulose, containing a polyfructosan (?) in admixture with the main polyglucosan constituent. Fats and proteins are absent. F. N. W.

Histological characteristics of plants grown in toxic concentrations of boron. I. E. WEBBER (J. Agric. Res., 1935, 50, 189—194).—Histological abnormalities in B-injured stems and leaves of prune, peach, and apricot are most marked in tissues in which accumulation of B is relatively large. No sp. reaction of the plant to B is observed. A. G. P.

Physiology of germination of sugar beet. E. W. SCHMIDT (Z. Wirts. Zuckerind., 1935, 85, 303—315).—Seedling injury, closely resembling in appearance that of mosaic virus, is produced by dil. solutions of HgCl_2 , TiSO_4 , KI, and Na_3AsO_3 , HgCl_2 being the most active in this respect. Solutions of KClO_3 caused general destruction of the chlorophyll apparatus of the leaves. Root injury by KClO_3 is intermediate in severity between that by Na_3AsO_3 and KI, and is < that by HgCl_2 and TiSO_4 . A. G. P.

Composition of mineral matter in wart-resistant and -susceptible varieties of potato. A. NEMEC (Phosphorsäure, 1934, 4, 352—357; Chem. Zentr., 1935, i, 812).—Resistant varieties have higher Mg and usually Mn contents, but less Ca, than susceptible kinds. The Mg:Ca ratio in the former varies from 2.4 to 4.4 and that in the latter from 1.5 to 3.2. Infected tubers and also the warts have a low ash content and the warts contain much Ca and SiO_2 and little Mg. A. G. P.

Diseases of potatoes. II. E. PFANKUCH and G. LINDAU (Biochem. Z., 1935, 277, 129—138).—Acceleration of oxido-reduction reactions appears to be the most important metabolic disturbance in diseased tubers, but this is not a const. change in the press juice. The phenolase activity is at first greater but the difference disappears after a time. The determination of phenolase activity is best carried out in a buffered solution of quinol-*isovitamin-C*. P. W. C.

Chemistry of white rots of wood. IV. Effect on wood substance of *Ustilina vulgaris*, Tul. W. G. CAMPBELL and J. WIERTELAK (Biochem. J., 1935, 29, 1318—1321).—*U. vulgaris* produces in lime (*Tilia vulgaris*, Hayne) wood a typical white rot, both the carbohydrates (cellulose etc.) and lignin being attacked and the alkali-solubility when calc. as % of sound wood decreasing steadily as decay proceeds. The organism also attacks beech wood (*Fagus sylvatica*, L.) but more slowly, the attack being conc. as before on the cellulose. The fungus has a pronounced detrimental effect on the mechanical properties of the wood. P. W. C.

Properties of the curly top virus [of sugar beet]. C. W. BENNETT (J. Agric. Res., 1935, 50, 211—241).—Isolation of the virus is described. Its resistance to ageing and to desiccation is influenced by the nature of the medium in which it is preserved. Acid media (p_H 2.9) caused rapid inactivation, but alkaline media (p_H 7.9) are not deleterious. Preps. in 75% EtOH or COMe_2 retain considerable activity after 56 days. The virus is notably resistant to CuSO_4 (1 in 200), HgCl_2 (1 in 50), CH_3O (1 in 100), and PhOH (1 in 25) but is inactivated by exposure to the expressed juice of beet or other plants. A. G. P.

Statistical aspect of the production of primary lesions by plant viruses. J. G. BALD (Nature, 1935, 135, 996). W. J. YOUNDEN (*ibid.*, 1075). L. S. T.

"Iron-stain" disease of potatoes. G. EHREKE (Biochem. Z., 1935, 278, 195—225).—As compared with the healthy parts of potatoes the brown ("iron-stained") parts have high salt and H_2O contents, reduced catalase and increased oxidase and per-

oxidase activity, increased O_2 consumption, increased fermenting power, usually decreased NH_2 -acid content, increased diastase activity, increased content of reducing substances (glutathione, ascorbic acid), and increased Fe and Mn contents. These characteristics are especially pronounced in the starch-free parts of the diseased tissue. W. McC.

Spectrochemistry of algæ. C. DHERE and A. RAFFY (Compt. rend. Soc. Biol., 1935, 119, 232—235; cf. A., 1931, 884).—The fluorescence spectra of *Ulva lactuca*, *Fucus serratus*, and the phycocyanin of *Aphanizomenon flos aquæ* have been examined using plates especially sensitive to infra-red. H. G. R.

Intake of fluorescent substances by living plant cells. H. DORING (Ber. deut. bot. Ges., 1935, 53, 415—437).—Applications of fluorescence microscopy are described and factors affecting the absorption of luminescent substances are examined. A. G. P.

Use of methylal for inclusions in paraffin. J. DUFRENOY (Compt. rend. Soc. Biol., 1935, 119, 375—376).—Methylal, being sol. in H_2O and paraffin, can be used as an intermediary in the replacement of H_2O in tissues by paraffin. R. N. C.

Reactions of dyes with cell-substances. I. Staining of isolated nuclear substances. II. Differential staining of nucleoprotein and mucin by thionine and similar dyes. E. G. KELLEY and E. G. MULLER, jun. III. Apparatus for the definition of colour in stained histological sections. E. G. KELLEY (J. Biol. Chem., 1935, 110, 113—118, 119—140, 141—144).—I. In histological staining (*e.g.*, of β -nucleohistone, α -nucleoprotein, nucleic acid, histone, metaprotein, thymus) the changes in colour produced by varying the p_H , type of dye, and type of fixative are adequately explained by supposing that salt formation occurs, but adsorption may also take place. With unmordanted hæmatoxylin the histological metachromasy appears to depend directly on $[\text{H}^+]$.

II. Dyes which, on dilution, exhibit a shift towards longer $\lambda\lambda$ in the position of max. absorption stain mucins and nucleoproteins differently, the mucins being coloured chiefly by the form of the dye which occurs in conc. solution, the nucleoproteins chiefly by that which occurs in dil. solution. The difference does not depend on $[\text{H}^+]$.

III. An instrument similar to the Nutting monochromatic colorimeter is described. W. McC.

Mechanism for controlled continuous flow of nutrient solutions. F. P. MEHRLICH (Plant Physiol., 1935, 10, 169—177).—Apparatus is described. A. G. P.

Determination of hydrogen exponent by means of the step-photometer. A. JANKE and F. SEKERA (Biochem. Z., 1935, 277, 452).—A correction of the author's paper (A., 1932, 471). The indicator, 2:4-dinitrophenol, is used in a concn. not of 0.01M but of 0.002M. P. W. C.

Use of quinhydrone and antimony electrodes for determining the p_H of solid culture media. P. E. TILFORD (Phytopath., 1935, 25, 362—367).—Suitable technique is described. In the p_H range 2.0—7.1 the quinhydrone electrode gave results in

closer agreement with colorimetric tests than did the Sb electrode. In alkaline ranges both electrodes recorded unduly low vals. The former is more generally satisfactory than colorimetric tests. A. G. P.

Spectroscopically pure γ -ferric oxide in colloidal aggregation as a biological indicator.—See this vol., 834.

Reagents for analysis of plant sections. E. STEINMETZ (Bull. Soc. bot. France, 1934, 81, 296—297; Chem. Zentr., 1935, i, 446).—A solution for the differential staining of cell constituents is described.

H. N. R.

Deproteinising agent. R. VLADESCO (Compt. rend. Soc. Biol., 1935, 119, 768—770).—Saturated solutions of CuSO_4 and $\text{K}_4\text{Fe}(\text{CN})_6$ together form a good general deproteinising agent through pptn. of $\text{Cu}_2\text{Fe}(\text{CN})_6$. It removes none of the normal determinable constituents from blood and milk, except uric acid.

R. N. C.

Destruction of organic matter in plant material by nitric and perchloric acids. J. E. GIESEKING, H. J. SNIDER, and C. A. GETZ (Ind. Eng. Chem. [Anal.], 1935, 7, 185—186).—Wet ashing with boiling HNO_3 — HClO_4 gives good recovery for Ca, Mg, K, and P. The analytical results are uniformly > after dry ashing procedures.

J. L. D.

Micro- and submicro-determination of methyl alcohol. Determination in blood and tissues. M. NICLOUX (Bull. Soc. Chim. biol., 1935, 17, 194—202).—The author's earlier method for determination of EtOH by complete oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ and determination of $\text{K}_2\text{Cr}_2\text{O}_7$ disappearing can be applied also to MeOH with the same degree of accuracy.

P. W. C.

Determination of ethyl alcohol and its oxidation products in biological substrates. A. JANKE and S. KROPACSY (Biochem. Z., 1935, 278, 30—36).—The oxidation is stopped by addition of Ag_2SO_4 , the EtOH + MeCHO determined by oxidation with CrO_3 — H_2SO_4 mixture, the MeCHO alone by a modified H sulphite method, and the AcOH by steam-distillation of the solution after acidification with H_3PO_4 and titration of the distillate.

P. W. C.

Determination of total cholesterol with digitonin. R. GORFINET (Compt. rend. Soc. Biol., 1935, 119, 330—331).—After saponification and acidification with HCl, cholesterol is pptd. with digitonin.

H. G. R.

Application to the colorimeter of the Schoenheimer and Sperry method for determination of total and free cholesterol. F. FITZ (J. Biol. Chem., 1935, 109, 525—527).—The Schoenheimer—Sperry determination of cholesterol (A., 1934, 1240) is adapted to the colorimeter; samples of serum extracts must contain > 0.05 mg. of cholesterol, and a fresh quantity of the standard solution must be used for each determination.

H. D.

Colorimetric determination of amino-acid function by triketohydrindene hydrate (ninhydrin). M. POLONOVSKI and F. MORENO-MARTIN (Compt. rend. Soc. Biol., 1935, 119, 583—585).—The blue compound of α - NH_2 -acids and ninhydrin is separated from photosensitising yellow substances

by extraction with CHCl_3 , followed by re-extraction from the CHCl_3 with 0.01N-NaOH, and can then be used for colorimetric determination.

R. N. C.

Simple modification of Nessler colorimetry for determination of total, residual, and polypeptide-nitrogen and of urea. E. HERZFELD (Mikrochem., 1935, 17, 155—164).—1 c.c. of serum is deproteinised at 100° with 20 c.c. of EtOH containing 5 drops of 1% aq. AcOH. EtOH is evaporated from the filtered liquid, H_2SO_4 is added, and the residue oxidised with H_2O_2 . The liquid is diluted, made alkaline, and Nessler solution + 5 c.c. of 1% gelatin added. Albumoses and peptones are similarly determined after degradation with pepsin. Urea is determined by deproteinising with AcOH and hydrolysing with urease.

J. S. A.

Composition of tissue-proteins. I. Determination of purines in tissues. S. GRAFF and A. MACULLA (J. Biol. Chem., 1935, 110, 71—80).—The composition of the tissue-proteins in relation to the anatomy and physiology of the cell is investigated. Purines (I) are determined in microtome slices of the frozen tissue by extraction with EtOH, EtOH— Et_2O (1 : 1), and COMe_2 . The extract is hydrolysed by a 10N- HCO_2H —N-HCl mixture, which does not destroy (I). (I) are pptd. with Cu_2O twice under controlled conditions, and after dissolving the Cu complex in H_2SO_4 and H_2O , total N is determined.

H. D.

Determination of carbon dioxide in culture solutions. L. B. ARRINGTON, C. H. WADLEIGH, and J. W. SHIVE (Soil. Sci., 1935, 39, 437—441).—Apparatus is described.

A. G. P.

Micro-volumetric determination of sodium in blood. S. RASEJA (Bull. Soc. Chim. biol., 1935, 17, 817—830).—The material is oxidised with HNO_3 and HClO_4 , PO_4^{3-} removed with CaO, and Na pptd. as $\text{NaMg}(\text{UO}_2)_3(\text{OAc})_6$. The ppt. is reduced with Zn—Hg for 3 hr. at 80°, and the U^{IV} titrated with aq. KMnO_4 . By this method Na in normal human blood-corpuses and plasma is 0.6954 and 3.3843 mg. per c.c., respectively, and the ratio Na : Cl of the plasma 1.097.

A. L.

Micro-determination of sodium. A. P. WEINBACH (J. Biol. Chem., 1935, 110, 95—99).—Na is determined (e.g., in 0.1 c.c. of serum, plasma, or whole blood) by a volumetric modification of the method of Barber *et al.* (A., 1932, 52).

W. McC.

Digesting biological materials for calcium and phosphorus analysis. H. W. GERRITZ (Ind. Eng. Chem. [Anal.], 1935, 7, 167—168).—Digests of biological materials with boiling HNO_3 —70% HClO_4 are suitable for the determination of elements which do not form insol. perchlorates.

J. L. D.

Microchemical detection of aluminium and its presence in the plant world. Y. YOSHII and T. JIMBO (Sci. Rep. Tohoku, 1932, [iv], 7, 65—77; Bied. Zentr., 1934, A, 5, 261).—Alizarin-S is used for detecting Al in plant materials. Marked accumulation of Al occurs in leaves of nearly all members of the affmilies, Symplocaceae, Diapensiaceae, Theaceae, Cytheaceae, Gleicheniaceae, and Lycopodiaceae.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1935.

General, Physical, and Inorganic Chemistry.

Excitation of some spectral lines of hydrogen by electron impact. A. A. KRUTHOF and L. S. ORNSTEIN (*Physica*, 1935, 2, 611—622).—The excitation functions of the singlet and triplet lines at 4634 and 4617 Å., respectively, and of the H_γ lines for direct excitation from mols., have been measured. Vals. for the probability of dissociation of H_2 for different electron velocities are recorded.

H. J. E.

Infra-red spectra of noble gases (10,500—13,000 Å.). W. F. MEGGERS (*J. Res. Nat. Bur. Stand.*, 1935, 14, 487—497).—The first spectra of He, Ne, Ar, Kr, and Xe excited by uncondensed discharges in Geissler tubes have been explored between 10,500 and 13,000 Å. using Eastman I-Z plates. Most of the new lines found represent combinations of already established spectral terms, and thus confirm the structural analyses. Two missing 2s terms are revealed for Xe and possibly one new f -type term each for Ne and for Ar.

A. R. P.

Absorption spectrum of metastable nitrogen molecules. A. A. FROST and O. OLDENBERG (*Physical Rev.*, 1935, [ii], 48, 66—68).—The use of special equipment and plates failed to reveal the existence of any absorption spectrum.

N. M. B.

Influence of the chemical medium on bands of the second positive group of nitrogen. M. DUFFIEUX (*Compt. rend.*, 1935, 201, 197—198).—A discussion of the cause of the intensity distribution in the phosphorescence spectrum observed on interrupting a discharge in NO_2 .

H. J. E.

Excitation of the Vegard-Kaplan bands by electronic bombardment of a mixture of argon and nitrogen. R. BERNARD (*Compt. rend.*, 1935, 200, 2074—2076).—Measurements are recorded.

H. J. E.

Effect of a magnetic field on the absorption bands of sulphur. J. GENARD (*Compt. rend.*, 1935, 200, 1926).—The absorption bands of S_2 between λ 2800 and 3300 Å. became more intense in a field of 25,500 gauss. There was no change in the rotational structure or in the predissociation. Bands between λ 3650 and 4000 Å., attributed to S_4 , were uninfluenced by the field.

H. J. E.

Intensity relations in chromium spectra. J. S. V. ALLEN and C. E. HESTHAL (*Physical Rev.*, 1935, [ii], 47, 926—931).—Measured relative intensities, tabulated for 4 multiplets of Cr I and 8 multiplets of Cr II, deviate in some cases from those calc. for Russell-Saunders coupling; the deviations accord

with independent observations for the Fe group, and may be due to perturbing energy levels. Two multiplets in the septet system of Cr II are corr. for excitation, the corresponding temp. of the Cr arc source being 4060° abs.

N. M. B.

Low terms in Mn V and Fe VI. I. S. BOWEN (*Physical Rev.*, 1935, [ii], 47, 924—925).—Classifications of about 50 additional lines in Mn V and 100 lines in Fe VI, including intercombination lines, arising from transitions between d^3 and $d^2 4p$ configurations, and term vals. deduced from them, are tabulated. Significant coincidences with lines in nebulae and novae are discussed.

N. M. B.

Spectra of exploded filaments in the far ultra-violet and Schumann regions. G. VAUDET and R. SERVANT (*Compt. rend.*, 1935, 201, 195—197).—Filaments of Fe, Cu, Al, and Zn were studied; spark lines were most prominent in the spectra.

H. J. E.

Arc spectrum of copper in the infra-red. C. C. KIESS (*J. Res. Nat. Bur. Stand.*, 1935, 14, 519—521).—In the infra-red range up to 12,000 Å. 30 new lines of Cu have been measured by the photographic method; all, except one, are accounted for as combinations between previously known terms of Cu I.

A. R. P.

Spectra of zinc, cadmium, and mercury in the extreme ultra-violet. L. BLOCH and E. BLOCH (*Compt. rend.*, 1935, 201, 137—139).—Data for Zn and Cd are recorded for the regions 478—425 and 550—500 Å., respectively. The spectra were excited in a high-frequency electrodeless discharge.

H. J. E.

Absorption band spectrum of selenium. T. E. NEVIN (*Phil. Mag.*, 1935, [vii], 20, 347—354).—A vibrational analysis for the heads due to $Se^{80}Se^{80}$ is given. There is probably a change in the law of force between the nuclei at the level $v'=20$. An isotope effect was found, and the calc. and observed positions of the isotope heads agree satisfactorily.

A. J. M.

Intensity distribution of spectral lines excited in molecular rays. R. MINKOWSKI and H. BRUCK (*Z. Physik*, 1935, 95, 274—283).—Lines excited by electron collision with mol. rays are much sharper than any others, and are more useful for determining excitation functions.

A. B. D. C.

Intensity distribution of the red cadmium line excited by electron collision with molecular rays. R. MINKOWSKI and H. BRUCK (*Z. Physik*,

1935, 95, 284—298).—This line is complex, due to isotope effects. A. B. D. C.

Regularities in the spectrum of iodine iv. S. G. KRISHNAMURTY (Current Sci., 1935, 3, 610—611).—The spectrum of a condensed discharge at various stages of excitation reveals the interval $6s^3P_1-^3P_2=8252.3\text{ cm}^{-1}$ together with all terms of the $6p$ configuration. L. S. T.

Ultra-violet fluorescence spectra of iodine vapour: McLennan bands. F. DUSCHINSKY and P. PRINGSHEIM (Physica, 1935, 2, 633—644; cf. this vol., 800).—Data are recorded for the variations of intensity of the bands with λ of the exciting light. H. J. E.

Hyperfine structure of europium. H. CASIMIR (Physica, 1935, 2, 719—723).—Schüler and Schmidt's observations (this vol., 804) are explained on the assumption that the nucleus has a quadrupole electrical moment. H. J. E.

Influence of an axial magnetic field on the discharge density in mercury vapour at low pressures. L. V. MIRLAS (J. Tech. Phys. U.S.S.R., 1934, 4, 1522—1534).—With a heated cathode a strong concn. of the electron beam was observed. CH. ABS. (e)

Characteristics of the Pb spectrum revealed by instantaneous spectrograms. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1935, 11, 171—173; cf. this vol., 676).—For different ionised states, spectral features depending on the position and shape of the electrodes and the oscillation of the discharge are discussed. N. M. B.

Interpretation of continuous absorption of hydrogen in stars of the first spectral types. D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1935, 200, 1730—1732).—A discussion. H. J. E.

Spectrum analysis of the hot carbon star, R Coronae Borealis. L. BERMAN (Astrophys. J., 1935, 81, 369—425).—From a detailed spectrum analysis the composition of the star's atm. is found to be C 69, H 27, N < 0.3, metals (chiefly Mg and Fe) 4%. A list of elements identified in the spectrum is given. L. S. T.

Absorption continuum due to quasi-molecules of calcium in dwarf stars of type M. B. LINDBLAD (Nature, 1935, 136, 67).—The presence of excited Ca mols. is inferred. L. S. T.

Chromospheric emission in the wings of H and K. A. D. THACKERAY (Astrophys. J., 1935, 81, 338—340).—Two lines due to Nd^+ and Ce^+ are identified. L. S. T.

Nebular spectrum of Nova Herculis. D. BELORIZKY (Compt. rend., 1935, 201, 191—193). H. J. E.

Red rays of oxygen in the spectrum of the night sky. J. CABANNES (Compt. rend., 1935, 200, 1905—1908).—Line sin in the spectrum of O I were observed ($^1S_0 \rightarrow ^3P_{0,1,2}$). In the luminous layer of the upper atm. O is in the at. state, and N in the mol. state. Intensity variations are discussed. H. J. E.

Structure of the electric arc. N. SZULC (Compt. rend., 1935, 201, 48—50; cf. A., 1934, 1051).—Spectroscopic observations are recorded for a C arc containing BaCl_2 and CaF_2 . Processes taking place in different parts of the arc are discussed. H. J. E.

True and apparent width of spectral lines. R. MINKOWSKI and H. BRÜCK (Z. Physik, 1935, 95, 299—301).—The true width is related to that observed with the Fabry-Perot interferometer. A. B. D. C.

Relative temperature and pressure of gases in an electric arc. G. RIGHINI (Physica, 1935, 2, 585—590).—Assuming the Boltzmann law to hold, vals. of temp. and pressure in different parts of the arc are calc. from intensity measurements of the (1,0) and (1,1) bands of the violet $^2\Sigma \rightarrow ^2\Sigma$ group of CN. Temp. of 3800—4800° abs. were observed. H. J. E.

Change of temperature with time in the alternating-current arc discharge. D. T. J. TER HORST, H. BRINKMAN, and L. S. ORNSTEIN (Physica, 1935, 2, 652—668).—Temp. measurements, based on intensity determinations for the violet CN band spectrum, are recorded as a function of phase for frequencies of 50—500 per sec. Ornstein and Brinkman's theory is supported (A., 1934, 1052). H. J. E.

Hyperfine structure formulæ for the configuration p^3s . M. F. CRAWFORD and L. A. WILLS (Physical Rev., 1935, [ii], 48, 69—72).—Mathematical. N. M. B.

X-Ray wave-lengths by the plane-grating vacuum spectrograph, and the structure of the K line of carbon. D. P. R. PETRIE (Proc. Physical Soc., 1935, 47, 626—643).—In the range 10—100 Å., experimental conditions do not justify the superior resolving power of a concave grating. A plane-grating spectrograph was designed for high-precision relative λ measurements; dispersion and resolving power are calc., and a no. of measurements relative to $\text{Cu } L\alpha_{12}$ (13.310 Å.) are reported. Microphotometer curves show that the C K line has two additional components of shorter λ . N. M. B.

Effect of chemical combination on the $K\beta_1$ lines of sulphur, chlorine, and potassium. J. VALASEK (Physical Rev., 1935, [ii], 47, 896—898).—Using a special form of target, the $K\beta_1$ lines in the spectrum of the secondary X-radiation from a series of alkali halides and some alkaline-earth sulphides were measured, and from the electron affinities of Cl^- and S^{2-} and the ionisation potentials of K^+ the vals. for the free ions are deduced by Pauling's theory. Results are compared with independent data and discrepancies are discussed. N. M. B.

Relative ionisation of gases measured with the $K\alpha$ line of copper. O. GAERTNER (Ann. Physik, 1935, [v], 23, 255—258).—Data are given for Ne, Ar, Kr, Xe, N_2 , O_2 , air, CO_2 , CH_4 , C_2H_4 , C_2H_2 , and C_3H_8 . W. R. A.

Intensity of polarised X-rays. W. H. GEORGE (Nature, 1935, 136, 180).—A single crystal of Cu cut parallel to the 311 planes forms a polariser for $\text{Cu } K\alpha$ radiation which is 100- to 1000-fold more efficient than the standard methods. L. S. T.

Absolute probability of K -electron ionisation of silver by cathode rays. J. C. CLARK (Physical Rev., 1935, [ii], 48, 30—42).—The Ross balanced foils method was used to separate the $K\alpha$ quanta from the thin Ag foil target radiation; the X-ray energy was absorbed in MeBr and SO_2 in a standard ionisation chamber, the ionisation currents were measured, the no. of quanta absorbed in the chamber was computed, and the no. of Ag K ionisations per bombarding electron was calc. The K -electron ionisation cross-section for Ag for 70-kv. electrons is $(4.80 \pm 0.43) \times 10^{-23}$ sq. cm. Results are compared with relative vals. (cf. Webster, A., 1933, 760) and with theory. N. M. B.

Shapes and wave-lengths of K series lines of elements Ti 22 to Ge 32. J. A. BEARDEN and C. H. SHAW (Physical Rev., 1935, [ii], 48, 18—30).—From measurements by double-crystal spectrometer of the widths at half-max. and the indices of asymmetry of the principal K -series lines, curves of width-at. no. and degree of asymmetry-at. no. are given. From measurements of the widths of certain satellites and of their intensities and displacements the diffraction angles of the peaks of the lines were determined and $\lambda\lambda$ calc. N. M. B.

Intermediate region [of the spectrum]; structure of the K -lines of the lightest elements. A. HAUTOT (Ann. Physique, 1935, [xi], 4, 5—87).—Vac. spectrographs are described for 10—1300 Å. with max. first-order dispersion of 1 Å. per cm. The K -lines of O, N, C, B, and Be have been photographed, and the $\lambda\lambda$ of their components and satellites measured. The mol. matrix of which the atom forms a part affects the lines by varying the no., relative intensity, or λ of the components; thus chemical linkings play a significant part in their emission. T. G. P.

Intensity of X-ray lines of gold. L. PINCHERLE (Physica, 1935, 2, 597—605).—Factors influencing the intensity of X-ray lines are discussed. Vals. in agreement with observation are calc. for the L line of Au. H. J. E.

Theories of ionisation. J. S. E. TOWNSEND (Phil. Mag., 1935, [vii], 20, 242—263).—The classical theory of Townsend, viz., that in which the ionisation of a gas is attributed to single collisions of electrons and positive ions with mols. of the gas, gives a satisfactory explanation of the principal phenomena of conduction by gases. The newer theories which assume the formation of metastable atoms are unnecessary, and fail to explain the properties of currents obtained in discharges under simple conditions, and of the uniform positive column in wide discharge tubes. A comparison of the classical and newer theories with regard to the conductivity of, and radiation from, He and A, and He-A mixtures shows that the newer theories do not explain why only He lines are obtained from the discharge through He, purified by ordinary methods, when the potential is the sparking potential. The mechanism of ionisation of impure He is considered, and it is shown that the classical theory explains adequately the large increase in conductivity when a small amount of A is added to He, whilst the theory of metastable atoms fails to

account for He lines becoming more prominent as the amount of impurity is reduced. A. J. M.

Ionisation potential of the nitrogen molecule. M. DE HEMPTINNE and J. SAVARD (Compt. rend., 1935, 200, 2147—2148).—Measurements by the method of electron impact gave potentials at 15.6, 21.2, and 23.1 volts. The energy of dissociation of N_2 is 6.72 volts. H. J. E.

Variation of mass of electrons in rapid cathode rays. M. NACKEN (Ann. Physik, 1935, [v], 23, 313—329).—The method of deflexion of cathode rays by electric and magnetic fields was used. Results agree with the theory of Lorentz. A. J. M.

Mean free path of metal electrons. M. SATO (Sci. Rep. Tôhoku, 1935, 24, 14—25).—The mean velocity, collision no. of electrons with atoms, and mean free path, l , have been calc. by Fermi statistics. If the electron gas is in a highly degenerate state, l decreases with the square of the abs. temp. The results are applied to calculate electrical conductivity of metals and Brownian motion. R. C.

Liberation of electrons from molybdenum surfaces by positive mercury ions. S. D. GVOZDOVER (Physikal. Z. Sovietunion, 1934, 6, 415—423).—Hg ions, with velocities 100—500 volts, set free 1/6 as many electrons as do Ne ions (cf. Penning, A., 1931, 139). There may be an adsorbed Hg layer on the Mo surface analogous to that on W (cf. Sonkin, A., 1933, 657). CH. ABS. (e)

Energy distribution of secondary electrons from molybdenum. L. J. HAWORTH (Physical Rev., 1935, [ii], 48, 88—95).—Energy distribution curves, obtained by magnetic analysis with primary electron energies > 150 volts, are given and their max. and irregularities are classified and explained. Results are correlated with curves for the no. of elastically reflected electrons as a function of primary energy. N. M. B.

Secondary emission of electrons from complex targets. P. L. COPELAND (Physical Rev., 1935, [ii], 48, 96—98; cf. A., 1934, 1149).—Investigation of secondary emission from complex targets formed by the condensation of Pt on Al, Ca on Au, and oil on Au indicate that the change in the secondary emission with the primary energy depends on the overlying element at low energies and on the base metal at high primary energies. N. M. B.

Polarisation effects in the positron theory. E. A. UEHLING (Physical Rev., 1935, [ii], 48, 55—63).—Mathematical. An investigation of some of the consequences of the positron theory for the special case of impressed electrostatic fields. N. M. B.

Bragg curve of H -rays. R. GREGOIRE (Compt. rend., 1935, 200, 2164—2166).—In determining the ionisation curve for α -rays from Po, approx. 1% of the particles gave a max. ionisation at 31 cm. in air, the val. being 50% of that for the α -particle. These rays consist of H atoms with unit charge and the same velocity as the α -particles. H. J. E.

Electron scattering by atoms. M. GHOSH (Phil. Mag., 1935, [vii], 20, 234—242).—Theoretical. A wave-statistical formula for the scattering of elec-

trons by atoms is deduced, based on Born's method, but taking into account the excluded phase-space of the scattered electron. A. J. M.

Effective cross-section of helium with respect to He^+ . F. WOLF (Ann. Physik, 1935, [v], 23, 285—303).—Apparatus for determining the effective cross-section of gas mols. with respect to 20—1000-volt gas ions is described. The effective cross-section of He with respect to He^+ decreases linearly with increasing velocity of ions, from $60 \text{ cm}^2 \text{ per cm}^3$ for 30-volt to $35 \text{ cm}^2 \text{ per cm}^3$ for 980-volt ions. The effective cross-section of He with respect to H^+ is considerably < this. Discharge of He^+ accounts for a considerable fraction of the cross-section. A. J. M.

Atomic mass of potassium. II. Potassium chloride-silver ratio. C. R. JOHNSON (J. Physical Chem., 1935, 39, 781—789).—Fifteen titrimetric determinations of the $\text{KCl}:\text{Ag}$ ratio give $K=39.100$ ($\text{Ag}=107.880$, $\text{Cl}=35.457$). J. W. S.

Systematics of isotopes. G. BECK (Physical Rev., 1935, [ii], 48, 47—48).—A comparison and discussion of the older and the recent views on the structure of nuclei. N. M. B.

Isotopic constitution of palladium and gold. A. J. DEMPSTER (Nature, 1935, 136, 65).—The new mass spectrograph (cf. this vol., 909) shows that Pd consists of six isotopes with at. masses 102, 104, 105, 106, 108, and 110. No trace of Au^{199} could be detected and it is probable that the accepted at. wt. of Au is too high. L. S. T.

Isotopic constitution of uranium. A. J. DEMPSTER (Nature, 1935, 136, 180).—Using the spark source recently described (this vol., 677) a faint companion of at. wt. 235 to the main component at 238 has been observed with long exposures. The intensity given by the new isotope is probably < 1% of that of U^{238} . U^{235} is probably actino-U, the parent of the Ac series. L. S. T.

Chemical elements and their atomic numbers as points on a spiral. N. OPOLONICK (J. Chem. Educ., 1935, 12, 265—267).—The at. nos. of the elements are arranged as points on the spiral $P=4\theta$, where P is the position in radians and θ the at. no. Six concentric circles are drawn through He, Ne, A, Kr, Xe, and Rn, dividing the elements into seven periods, and three additional concentric circles drawn through Ni, Pd, and Pt divide the 4th, 5th, and 6th periods into A and B series. Difficulties encountered in previous periodic arrangements of the elements are eliminated. L. S. T.

Connexion between the emanating power of radium-containing metals and the characteristic properties of these metals. O. WERNER (Naturwiss., 1935, 23, 456—459).—A method of using radioactive elements as indicators in metallography is described. A measured amount of the radioactive solution is evaporated to dryness on the polished metal surface, and reduced in H_2 at 750—1000°. The activity of the substance is then determined by the streaming method. The variation of activity with temp. for different metals has been determined. The temp. coeff. of the activity is inversely \propto Debye

characteristic temp. of the metal. From the temp. coeff. curves it is possible to derive the energy content and sp. heat of alloy systems. The effect of small quantities of impurities on the characteristic temp., and the reaction velocity at transition points, may be followed. The temp. coeff. of the activity is smaller in the neighbourhood of an allotropic transition point than above or below it. A. J. M.

Scattering of polonium α -particles by oxygen and neon. W. RIEZLER (Ann. Physik, 1935, [v], 23, 198—206).—Scattering between angles 55° and 90° was investigated, the range of incident particles being varied from 12 to 37 mm. and the energy from 3.3 to 8.6×10^{-6} erg. With Ne the classical scattering law was obeyed; with O_2 the scattering was abnormally low for energies $> 7 \times 10^{-6}$ erg. The radius of the nuclear trough is 4.5×10^{-13} cm. for O_2 and 4.6×10^{-13} cm. for Ne. W. R. A.

Anomalous scattering by suitable nuclear fields. L. H. HORSLEY (Physical Rev., 1935, [ii], 48, 1—6).—A schematic nuclear model representing Pose's data (cf. A., 1934, 1151) on the collision of α -particles and protons leads to results consistent with data on the position of nuclear energy levels and on the scattering of α -particles by light elements. N. M. B.

Registration of the ionisation curve of a single α -particle. H. ALFVEN (Nature, 1935, 136, 70).—An experimental arrangement is described. L. S. T.

β -Radiation of actinium- C'' , mesothorium 2, and of uranium X_1 and its derivatives. M. LECOIN (Compt. rend., 1935, 200, 1931—1934; cf. A., 1933, 995).—Curves showing the distribution of energy among the β -rays from each source are recorded, mean energies being calc. H. J. E.

Fermi theory of β -radioactivity. E. J. KONOPINSKI and G. E. UHLENBECK (Physical Rev., 1935, [ii], 48, 7—12).—Mathematical. A wt. factor is introduced into Fermi's energy distribution formula to provide required asymmetry. N. M. B.

β -Decay theory. R. L. DOLECEK (Physical Rev., 1935, [ii], 48, 13—17).—Mathematical. A method of calculating the energy distribution of the β -electrons for any assumptions on the angular momentum balance is developed. N. M. B.

Disintegration constant and the upper limit of the continuous β -spectrum. G. J. SIZOO (Nature, 1935, 136, 142; cf. this vol., 804). L. S. T.

γ -Radiation from uranium-X. E. STAHEL and D. J. COUMOU (Physica, 1935, 2, 707—718).—The absorption coeff. in Fe and Pb was measured. The calc. val. for the energy is 950,000 e.v. The abs. intensity of the radiation corresponds with the emission of 1.4 quanta per 100 atoms decomposed. H. J. E.

Determination of self-absorption for the evaluation of weak radium-containing substances by the γ -ray method. H. FRANZ and C. WEISS (Physikal. Z., 1935, 36, 486—489).—The dependence of absorption of γ -rays on thickness of absorbing layer has been determined, and is used as the basis

of a method for determining R_a in substances containing small quantities. A. J. M.

Levels of the neutron. E. SEVIN (Compt. rend., 1935, 200, 2070—2072; cf. this vol., 1050).—An expression for a series of quantised electron levels is deduced, leading to variation in mass of the neutron between 1.00784 and 1.01235 according to the electron orbit. H. J. E.

Capture of slow neutrons by a nucleus. L. ARTSIMOVITSCH, I. KURTSCHATOV, L. MIČOVSKI, and P. PALIBIN (Compt. rend., 1935, 200, 2159—2162).—The % of neutrons absorbed by Ag and Rh was measured after the neutrons had traversed varying thicknesses of H_2O (6—20 cm.) to reduce their energy. A const. val. of the absorption coeff. of the metals was not observed. H. J. E.

Selective absorption of slow neutrons. J. R. TILLMAN and P. B. MOON (Nature, 1935, 136, 66—67; cf. this vol., 802).—The absorption coeffs. of Ag, Cu, and I for slow neutrons vary with the element used as detector, indicating that selective absorption of neutrons of different velocities takes place. The ratio of the activity at 90° and 290° abs. is given for these three elements, and factors which must be considered in determining the effect of temp. on the activity of neutrons are discussed. L. S. T.

Energy spectrum of the neutrons from the disintegration of beryllium by deuterons. T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1935, [ii], 47, 910—913).—The energy distribution investigated by the method of recoil protons in a high-pressure cloud chamber gives max. neutron energies corresponding with a disintegration of 4.14×10^6 e.v. The calc. mass of Be^9 , assuming the reaction ${}^4_2Be + {}^1_1H^2 \rightarrow {}^5_{10}B + {}^0_{-1}e$, is 9.0123 ± 0.0008 . Other observed neutron groups of lower energy indicate that the B^{10} nucleus is left in one of several possible excited states and probably falls to the normal state by the emission of a γ -ray. N. M. B.

Neutrons of mass 2? S. FLUGGE (Z. Physik, 1935, 95, 312—317).—Evidence is given to indicate a possible existence of particles of two neutrons combined with antiparallel spins. A. B. D. C.

Nuclear transformations and bi-neutrons. S. FLUGGE and A. KREBS (Z. Physik, 1935, 95, 319—320).—Transformation phenomena observed with Be, B, Na, Cl, F, and Al nuclei are readily explained by the presence of bi-neutrons. A. B. D. C.

Mechanism of capture of slow neutrons by light nuclei. F. PERRIN (Compt. rend., 1935, 200, 1749—1751).—Theoretical. Diffraction may explain the large effective cross-sections in Li and B for slow neutrons. H. J. E.

Non-observance of induced β -radioactivity with the light elements. H. J. WALKER (Phil. Mag., 1935, [vii], 20, 266—274).—The possible reactions of the nuclei of light elements with neutrons are considered, with special reference to the stability of the products, and the possibility of β -ray disintegrations. Failure to observe β -radioactivity on bombarding light elements with neutrons can be

explained by their nuclear structure and isotopic constitution. A. J. M.

Attempts to detect γ -radiation excited by the impact of α -particles on heavy elements. W. B. LEWIS and B. V. BOWDEN (Phil. Mag., 1935, [vii], 20, 294—304).—No γ -radiation could be detected when Sn and Pb were bombarded with α -particles from Rn and Ra-C'. Ra-C' produces in Pb < 1 pair of positive and negative electrons for 10,000 α -particles, and Rn < 1 pair for 100,000 α -particles. A. J. M.

Interaction between a neutron and a proton and the structure of H^3 . L. H. THOMAS (Physical Rev., 1935, [ii], 47, 903—909).—Mathematical. N. M. B.

Nuclear processes in lithium on bombardment with α -rays. K. SCHNETZLER (Z. Physik, 1935, 95, 302—311).—Excitation functions on bombardment with Po α -rays are given for neutrons and α -rays. A. B. D. C.

Artificial disintegration of elements. P. SÄVEL (Ann. Physique, 1935, [xi], 4, 88—136).—The nature, energy, and conditions of emission of the radiation excited in Li, F_2 , Na, Mg, Al, and N_2 by α -particles from Po have been studied with a 40-atm. ionisation chamber. All emit photons and all but N, neutrons. The origin of the former is ascribed to (1) excitation without capture of α -particles and without transmutation (Li, N_2 , Al, F_2), (2) excitation with capture of α -particles and emission of groups of protons and neutrons (F_2 , Al, Na, Mg), and (3) annihilation of the positron (Al). The mechanism of neutron emission is discussed. T. G. P.

Life period of activated magnesium. A. ECKARDT (Naturwiss., 1935, 23, 527).—The rate of decay of the activity of Mg activated by α -rays from Th-C' is not exponential. Between 1 and 10 min. the curve is made up of two components, due to processes originating with ${}^{25}_{12}Mg$, ${}^{24}_{12}Mg$, and ${}^{26}_{12}Mg$. The half-life periods of the two processes are 1.95 ± 0.4 and 7.5 ± 1.5 min., respectively, in agreement with Fahlenbrach (this vol., 803). A. J. M.

Artificial radioactivity of the rare-earth elements. J. K. MARSH and S. SUGDEN (Nature, 1935, 136, 102—103).—Additional results (cf. this vol., 559) for the half-life periods and relative intensities ($Ag=1$) are: La 1.9 ± 0.2 days, 0.5; Pr 19 ± 0.5 hr., 0.9; Sm approx. 40 min., 0.03, and a much longer period; Eu 9.2 ± 0.1 hr., 19; Tb 3.9 ± 0.1 hr., 0.6; Dy 2.5 ± 0.1 hr., > 30 ; Ho 2.6 ± 0.2 hr., > 30 ; Er approx. 7 min., 0.03 and 1.6 ± 0.2 days, 0.3; Yb approx. 3.5 hr., 0.03; and Lu 4.0 ± 0.1 hr., 1.0. With Ce, Nd, and Gd the activity is < 0.01 that of Ag. The results previously given (*loc. cit.*) for Er and Yb were probably due to contamination by a small amount of Ho. A specimen of ytterbia separated electrolytically from lutecia as $YbSO_4$ gives a feeble activity indistinguishable in period from that of Lu, and probably due to residual traces of Lu. The intense activity produced by neutron bombardment of Eu, Dy, and Ho suggests a use of these elements as neutron detectors. Certain inconsistencies with Fermi's results are pointed out and the similarity in periods for Ho and Dy is discussed. L. S. T.

Artificial radioactivity of dysprosium and other rare-earth elements. G. VON HEVESY and H. LEVI (*Nature*, 1935, **136**, 103; cf. preceding abstract).—Bombardment by slow neutrons gives the following half-life periods and relative intensities ($A_g=8$): Dy 2.5 hr., 100; Ho 35 hr., 20; Er 12 hr., 0.35; Yb 3.5 hr., 0.25; Lu approx. 5 days, approx. 1. The half-val. thicknesses in Al of the β -rays emitted are also recorded. The upper limit of the continuous β -spectrum of Dy has an energy of 1.4×10^6 e.v. and that of Ho, 1.6×10^6 e.v. The activities of Dy and Ho obtained with fast neutrons are, respectively, 0.01 and 0.05 of those obtained with neutrons slowed down by passage through paraffin wax. L. S. T.

Artificial radioactivity of ruthenium bombarded by neutrons. I. KURTSCHATOV, L. NEMENOV, and I. SELINOV (*Compt. rend.*, 1935, **200**, 2162—2163).—Bombardment of Ru with neutrons, slowed down by passage through H_2O , gave four new radioactive products of periods 40 and 100 sec. and 11 and 75 hr., respectively. Their nature is discussed. H. J. E.

Radioactive elements formed by irradiating thorium with neutrons. (MME.) I. CURIE, H. VON HALBAN, and P. PREISWERK (*Compt. rend.*, 1935, **200**, 2079—2080; cf. this vol., 911).—The radioelement of period 1 min. formed on irradiating Th with neutrons was shown, by pptn. with $BaSO_4$, to be an isotope of Ra. A new radio-element of period 2—3 min. was observed, which was an isotope of Pa, and was formed by disintegration of another radioelement, probably the isotope of Th of period 25 min., previously described. H. J. E.

Artificial transformation products of uranium. O. HAHN, L. METTNER, and F. STRASSMANN (*Naturwiss.*, 1935, **23**, 544—545).—The substance of half-life 13 min. produced by the bombardment of U is probably eka-Re (at. no. 93). Comparison of the properties of the substance with those of Re shows that both form oxides sol. in NaOH [eka-Re better in $(NH_4)_2CO_3$]. Both are readily pptd. by H_2S from 20% HCl solution. Like Re, eka-Re is easily converted into the septavalent form, and in this state it can be pptd. from AcOH solution by nitron, whereas the other transformation products are not pptd. The substance previously assigned half-life 50—70 min. is now assigned 100 min. It differs from the 13-min. substance in being pptd. by NaOH, and by H_2S from more strongly acid solutions. In contrast to Os, distillation with conc. HNO_3 gave no volatile product. The substance is not an isotope of Pa. A third product of the bombardment of U has a half-life of 3.5 days. A. J. M.

Artificial radioactivity. E. FØYN (*Tidsskr. Kjemi*, 1935, **15**, 69—70).—A review. R. P. B.

Transmutation of elements, and artificial radioactivity. F. BEHOUNEK (*Chem. Listy*, 1935, **29**, 2—5, 17—24).—A review. R. T.

Absorption of cosmic-ray electrons. J. C. STREET, R. H. WOODWARD, and E. C. STEVENSON (*Physical Rev.*, 1935, [ii], **47**, 891—895).—The interpretation that the coincident discharge of 3 Geiger-Müller counters in line represents the passage

of a single ionising particle through the counters and any intervening material is checked by two experimental methods. Data for absorption in Pb, Fe, and marble are extended. N. M. B.

(A) Comparison of the intensity decrease of primary cosmic radiation in different materials.

(B) Absolute intensity of cosmic rays. J. CLAY (*Physica*, 1935, **2**, 645—649, 650—651).—(A) Absorption data are recorded for H_2O , Pb, Fe, and air. The decrease in intensity of cosmic rays for equiv. layers of different materials is greatest when the density of the latter is least.

(B) A correction (cf. this vol., 426). H. J. E.

Absorption of the soft fraction of corpuscular cosmic rays. P. AUGER, L. LEPRINCE-RINGUET, and P. EHRENFEST (*Compt. rend.*, 1935, **200**, 1747—1749).—Vals. of the absorption coeff. of Pb, Sn, Cu, and Al are recorded. The nature of the rays is discussed. H. J. E.

Elements of the quantum theory. I. Quantum phenomena. II. Differential equation for a wave motion. S. DUSHMAN (*J. Chem. Educ.*, 1935, **12**, 217—224, 274—284). L. S. T.

Waves and spin. E. SEVIN (*Compt. rend.*, 1935, **200**, 1744—1746).—Theoretical. H. J. E.

Quaternions, semi-vectors, and spinors. J. BLATON (*Z. Physik*, 1935, **95**, 337—354).—Mathematical. A. B. D. C.

Form and symmetry of the electromagnetic equations; equivalence of energy and mass. J. URBANEK (*Compt. rend.*, 1935, **200**, 2067—2070).—Theoretical. H. J. E.

Absolute field constant in Born's new field theory. H. ERTEL (*Naturwiss.*, 1935, **23**, 512).—The val. of the abs. field const. is calc. to be $b = 6.9015 \times 10^{15}$ dynes¹ per cm. A. J. M.

Some conclusions from the Born-Schrödinger electron radius. J. MEIXNER (*Ann. Physik*, 1935, [v], **23**, 371—379).—Changes in the fine structure of H and He^+ lines are calc., taking into account electron spin by using Pauli's equation, and employing the Born-Schrödinger electron radius, $r_0 = 13.6 e^2/mc^2$. Agreement with experiment shows that the use of this radius is justified. A. J. M.

Work functions of univalent metals. E. WIGNER and J. BARDEEN (*Physical Rev.*, 1935, [ii], **48**, 84—87).—An approx. formula, neglecting the effect of the electric double layer on the surface, is deduced for the work functions of univalent metals in terms of heats of sublimation. Results for the alkali metals agree closely with experiment. N. M. B.

Stokes phenomenon for the differential equations which arise in the problem of inelastic atomic collisions. O. K. RICE (*J. Chem. Physics*, 1935, **3**, 386—398).—Mathematical. H. J. E.

Relative transition probabilities for almost closed shells. C. W. UFFORD (*Physical Rev.*, 1935, [ii], **47**, 931; cf. A., 1934, 1148).—Three simplifications for calculating the relative transition probabilities of different multiplets in Russell-Saunders coupling

from spectroscopic stability are given for configurations involving almost closed shells. N. M. B.

Isotopes and nuclear structure. M. ELSASSER (J. Chim. phys., 1935, 32, 431—432).—By relating the no. of neutrons in a nucleus to the no. of associated protons, the nuclei fall into a no. of fairly distinct groups indicating the formation of successive levels of neutrons. Certain nuclear properties are functions of the no. of neutrons. J. G. A. G.

Masses of Be⁸ and C¹². H. S. W. MASSEY and C. B. O. MOHR (Nature, 1935, 136, 141).—The relationship between the mass of the at. nuclei of C and Be and the binding energy of the constituent α -particles is discussed. L. S. T.

Cassiopeium (lutecium) atomic nucleus and spherical symmetry. H. SCHULER and T. SCHMIDT (Z. Physik, 1935, 95, 265—273).—The nucleus deviates from spherical symmetry approx. as the \cos^2 law; its spin is 7/2. A. B. D. C.

Nuclear model. W. V. HOUSTON (Physical Rev., 1935, [ii], 47, 942—946).—A solution in terms of normal vibrations of the problem of a no. of bodies which attract each other with forces \propto distance gives expressions for the frequencies, and hence the quantum-mechanical energy levels, leading to a nuclear model. The instability of Be⁸ composed of two α -particles is attributed to the high zero-point energy of the system. The Pauli exclusion principle applied to the neutrons explains the limited no. of observed isotopes. N. M. B.

Absorption spectrum of ozone in the photographic infra-red. (MME.) L. LEFEBVRE (Compt. rend., 1935, 200, 1743—1744).—Data from 6500 to 10,000 Å. are recorded. H. J. E.

Absorption spectrum and mechanism of the photochemical decomposition of N₂O. L. A. M. HENRY (J. Chim. phys., 1935, 32, 437—446).—The absorption spectrum of 0.5—3.5 atm. of N₂O at 293—950° abs. is continuous. The long- λ limit, 2300 Å. approx. at 20°, is displaced to longer λ as the temp. rises. $\lambda < 2300$ Å. decompose N₂O into NO, and NO₂ is produced more slowly. The energy difference between the lowest vibration level and the unstable excited state is 132,000 g.-cal., approx., and the most probable mechanism of decomp. is N₂O(¹ Σ) + $h\nu \rightarrow$ NO(² Π_a) + N(²D). J. G. A. G.

Phosphorescence of nitrogen peroxide. Intensity of bands of the second positive group of nitrogen. M. DUFFIEUX (Compt. rend., 1935, 201, 53—55).—The spectrum of the afterglow on interrupting a discharge in streaming NO₂ was continuous in the visible, and in the violet and ultra-violet showed bands of the second positive group of N₂ and the γ group of NO. The intensity distribution is discussed. H. J. E.

Molecular emission spectra of some metallic salts. P. MESNAGE (Compt. rend., 1935, 200, 2072—2074).—Band emission spectra from AgCl, ZnCl₂, and NiCl₂ were excited in a high-frequency discharge in presence of a little Ne or Ar (to start the discharge). H. J. E.

Band spectra of the hydrides of lithium. F. H. CRAWFORD and T. JORGENSEN, jun. (Physical Rev., 1935, [ii], 47, 932—941; cf. this vol., 561).—Data for about 1000 lines, comprising 26 bands, of Li⁷H, with quantum assignments, are tabulated. Important consts. for the ground and upper states are given and discussed. The electronic origin isotope shift of the ¹ $\Sigma \rightarrow$ ¹ Σ system is 0.0 (± 0.5) cm.⁻¹ N. M. B.

Band systems of copper hydride. T. HEIMER (Z. Physik, 1935, 95, 321—327).—Two new band systems are analysed. A. B. D. C.

Band spectrum of bismuth hydride. A. HEIMER (Z. Physik, 1935, 95, 328—336).

A. B. D. C.

Influence of the addition of calcium chloride on the absorption of solutions of Cu⁺, Cu²⁺, Fe³⁺, Ru³⁺, and Sm³⁺; chromophore theory. M. PESTEMER and (FRL.) P. BERNSTEIN (Z. anorg. Chem., 1935, 223, 121—128).—Absorption data for chlorides of the above metals, with and without the addition of CaCl₂, are given. The formation of chromophores as the result of incompleting electron groups is discussed. M. S. B.

Spectrum of CO⁺. H. BULTHUIS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 604—617; cf. A., 1934, 1055).—Data for the comet-tail bands are tabulated and discussed. D. R. D.

Band spectrum of zirconium oxide. F. LOWATER (Phil. Trans., 1935, A, 234, 355—376).—A full rotational analysis of the 0,0, 0,1, and 1,0 bands due to Zr⁹⁰O and the isotope of next abundance Zr⁹⁴O is given. No A-type doubling was found. Mol. consts. for the upper and lower states are deduced. N. M. B.

Behaviour of SiF bands in stellar spectra. P. SWINGS (Ark. Mat. Astron. Fys., 1935, 25 B, No. 2; Chem. Zentr., 1935, i, 1010).—The intensity of the SiF bands rises continuously with the spectral type, but more slowly than that of the TiO bands. J. S. A.

Band systems and structure of CaCl. R. K. ASUNDI (Proc. Indian Acad. Sci., 1935, 1, A, 830—840).—Full data and vibrational analysis of the red doublet and orange band systems are given and discussed. The normal mol. dissociation energy is 3.5 volts. N. M. B.

Causes of colour changes of cobalt salts in neutral salt solutions. A. VON KISS and M. GESZNER (Acta Lit. Sci. Univ. Francisco-Josephinae, Sect. Chem. Min. Phys., 1934, 4, 124—146).—Mol. extinction coeffs. for the visible spectrum were measured for CoCl₂, Co(NO₃)₂, and CoSO₄ in various conc. solutions of neutral salts, HCl, HNO₃, and H₂SO₄. Colour changes are due to the Stark effect and ion deformation. Constitutional chromophoric changes may also occur. CH. ABS. (e)

Colour of paramagnetic crystals and solutions of the iron group. S. DATTA (Sci. and Cult., 1935, 1, 113—114).—In hydrated crystals as well as in solutions at low temp. the absorption centres are hydrated complexes; in crystals of anhyd.

chlorides and in solutions at higher temp. the centres are undissociated mols. C. W. G.

Zeeman effect of the absorption lines of chrome alum. F. H. SPEDDING and G. C. NUTTING (J. Chem. Physics, 1935, 3, 369—375; cf. A., 1934, 940).—Measurements are recorded at 20° and 50° abs. with fields of 12,000—25,000 gauss. At 50° abs., but not at 20° abs., the pattern depends on the orientation of the crystal lattice with respect to the magnetic field. The energy levels appear in groups of closely spaced levels, the lowest group belonging to the quartet system. These levels split in a magnetic field, and have a *g* factor of 2. Interaction between the levels is small. H. J. E.

Photo-dissociation of the vapours of some organo-metallic compounds. A. TEREININ and N. PRILESHAIEVA (Acta Physicochim. U.R.S.S., 1935, 1, 759—776).—The absorption spectra of HgMe₂, ZnMe₂, PbEt₄, HgMeI, and HgMeBr were all continuous and at $\lambda\lambda < \text{approx. } 2800 \text{ \AA}$. For HgMe₂ diffuse bands at 2125—1965 Å. were also observed. Photo-dissociation occurs at the metal-C linking. Zn and Pb were deposited on irradiating ZnMe₂ and PbEt₄ with light of $\lambda < 2650$ and 2400—2300 Å., respectively. On illuminating the vapours of HgMeI and HgMeBr, the band fluorescence of HgCl and HgBr was observed, showing these mols. to be liberated in an excited state by photo-dissociation. H. J. E.

Ultra-violet absorption spectrum of methylamine in the vapour state. V. HENRI and W. LASAREFF (J. Chim. phys., 1935, 32, 353—370).—The absorption spectrum of NH₂Me at 0.1—432 mm. and 18—290° lies between 2529 and 1986 Å. As the pressure is increased, the series of bands with structure change to general absorption, except on the long- λ side of the system. Rise of temp. produces similar effects and extends the absorption to the long- λ limit. The band spacings 650 and 2050 cm.⁻¹ are interpreted as vibration frequencies of the normal mol. (cf. A., 1933, 997) and the band spacing 1000 cm.⁻¹ is referred to the excited state. J. G. A. G.

Relation between general absorption and residual affinity: heterocyclic compounds. J. HOUSTON, G. CANNING, and H. GRAHAM (J.C.S., 1935, 965—966).—Pentamethylene sulphide and oxide, 1:4- and 1:3-dioxan, 1:4-thioxan, and 1:4-dithian with cyclohexane for comparison were examined spectrographically. The more chemically reactive compounds have the greater light-absorptive power. N. M. B.

Fluorescence spectra of some hydrocarbons of the rubene family. C. DHERÉ and (MLEL.) A. RAFFY (Bull. Soc. chim., 1935, [v], 2, 1424—1430).—The visible fluorescence spectra of tetraphenyl-, triphenyl-, and dehydro-rubene, in the solid state and in C₆H₆ solution, have been examined. T. G. P.

Spectrographic investigation of dyes of the benzopyrylium type.—See this vol., 1129.

Absorption spectra of metal complexes of dithizone and their analytical significance. H. FISCHER and W. WEYL (Wiss. Veroff. Siemens-Werken, 1935, 14, 41—53).—The absorption spectra

of the complexes with Cu^{II}, Cu^I, Ag, Zn, Cd, Hg^{II}, Tl^I, Sn^{II}, Pb^{II}, Bi^{III}, Co^{II}, and Ni^{II} in CCl₄ have been determined between 400 and 700 m μ . The possibilities of application to analysis and the structures of the complexes, are discussed. E. S. H.

Absorption spectrum of malachite-green leucocyanide and the mechanism of the dark reaction after photolysis. L. HARRIS, J. KAMINSKY, and R. G. SIMARD (J. Amer. Chem. Soc., 1935, 57, 1151—1154).—The absorption of the leucocyanide, base, chloride, and photo-compound of malachite-green and crystal-violet, respectively, have been determined. The fading of the coloured photo-compound in the dark has been studied and a mechanism of reaction is proposed. E. S. H.

Fluorescence and absorption spectra of simple aromatic amines. N. PRILESHAIEVA and R. TSCHUBAROV (Acta Physicochim. U.R.S.S., 1935, 1, 777—784).—The absorption and fluorescence spectra of NH₂Ph and NHPH₂ have been photographed. For each the absorption bands are in the region of 2800 Å. (C₆H₆ absorption) and at $< 2400 \text{ \AA}$. (NH₂ absorption). The bands for NHPH₂ are diffuse. H. J. E.

Pyrrole-blues. Absorption spectra. See this vol., 1134.

Vitamin-E. Measurement of absorption band.—See this vol., 1037.

Chlorophyll derivatives [absorption spectra]. See this vol., 1177.

Spectrometric measurements on various carotenoids. A. E. GILLAM (Biochem. J., 1935, 29, 1831—1836).—Spectrometric data are recorded for the absorption bands in the visible and ultra-violet of various carotenoids in CHCl₃ and in CHCl₃-SbCl₃ solution. W. O. K.

Absorption spectra of adsorbed materials.
I. Adsorption spectra of dyes adsorbed on colloids. E. B. FODIMAN and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1934, 1, 220—231).—The absorption of methylene-blue (I), thionine, Me-blue, and erythrosin, adsorbed on Al₂O₃, SiO₂, TiO₂, and gelatin sols, are modified in cases where the dye ion is charged oppositely to the colloid particles, but not when similarly charged. The absorption of dyes adsorbed on SiO₂ and TiO₂ changes on removal of the charge from the sol particles, but (I) on gelatin shows no corresponding change. J. W. S.

OH band in the very near infra-red. A. NAHERNIAC (Compt. rend., 1935, 200, 1742—1743).—A band at $\lambda\lambda$ 9500—9800 Å., attributed to OH, was observed in the absorption spectrum of the vapours of HCO₂H, AcOH, other fatty acids, BzOH, cyclohexanol, resorcinol, (CH₂·OH)₂, and glycerol. It is not observed in the absorption spectra of the liquids or their solutions. This fact may be due to association. H. J. E.

Far infra-red spectrum of H₂O. R. B. BARNES, W. S. BENEDICT, and C. M. LEWIS (Physical Rev., 1935, [ii], 47, 918—921).—The absorption of atm. H₂O vapour mapped in the range 38—170 μ is in good

agreement with Mecke's analysis of the vibration-rotation bands, and these results are extended.

N. M. B.

Extreme infra-red absorption of D_2O , ice, and D_2O in dioxan. C. H. CARTWRIGHT (Nature, 1935, 136, 181).— D_2O and H_2O have the same absorption between 60 and 200 cm^{-1} . The absorption band near 160 cm^{-1} can therefore be assigned to a hindered translational frequency of D_2O or H_2O mols. as predicted by Bernal and Tamm (this vol., 432). The existence of the 160 cm^{-1} band in ice at -10° provides additional evidence for a quasi-cryst. structure in H_2O , and indicates that the intermol. forces in H_2O and ice are approx. the same. The 160 cm^{-1} band disappears for H_2O dissolved in dioxan, confirming the view that its presence is due to a structure in H_2O rather than to the individual mols.

L. S. T.

Vibration frequencies of ethylene and ethane. E. TELLER and B. TOPLEY (J.C.S., 1935, 885—889).—From a summary of existing experimental data on the infra-red and Raman spectra, sets of vibration frequencies for the C_2H_4 and C_2H_6 mols. are derived.

N. M. B.

Absorption of acetylene and dideuteroacetylene in the photographic infra-red. C. A. BRADLEY, jun., and A. MCKELLAR (Physical Rev., 1935, [ii], 47, 914—917; cf. A., 1934, 1288).—Using an absorbing column 9 m. long and $C_2D_2 > 90\%$ pure at 85 cm. pressure, no absorption bands in the range 7000—11,500 Å. were observed. A 7.5-m. column of C_2H_2 at 90 cm. pressure gives a new absorption band with origin at 7859 Å. Possible vibrational transitions giving rise to this are discussed.

N. M. B.

Low-frequency fundamental bands of methyl chloride, bromide, and iodide. E. F. BARKER and E. K. PLYLER (J. Chem. Physics, 1935, 3, 367—368; cf. A., 1934, 1288).—The ν_5 bands of MeCl, MeBr, and MeI have been observed at λ 13.7, 16.4, and 18.8 μ , respectively, that of MeI having a sharp zero branch suitable for use in calibration. Isotope effects were observed.

H. J. E.

Vibration frequencies of chlorine derivatives [of some aliphatic compounds]. H. C. CHENG and J. LECOMTE (Compt. rend., 1935, 201, 199—201).—A discussion of the Raman and infra-red spectra of halogenated derivatives of MeR. The influence of the radical R on the C-Cl vibrational frequency is small in the Cl_1 , considerable in the Cl_2 , and preponderant in the Cl_3 -derivatives. The C-H vibrational frequency undergoes no systematic variation with change in R or the no. of Cl atoms in the mol.

H. J. E.

Modes of vibration of dihalogen derivatives of ethane. H. C. CHENG and J. LECOMTE (Compt. rend., 1935, 201, 50—52).—Raman and infra-red spectra of $(CH_2Cl)_2$, CH_2Cl-CH_2Br , $(CH_2Br)_2$, CH_2Cl-CH_2I , and $(CH_2I)_2$ support the hypothesis of *cis*- and *trans*-forms of these mols. One infra-red frequency is observed in the infra-red which should theoretically be inactive. Factors causing this anomaly are discussed.

H. J. E.

Infra-red absorption spectra of proteins. F. VILÈS and E. HEINTZ (Compt. rend., 1935, 200, 1927—1929).—Data are recorded for serin, oxy-hæmoglobin, excelsin, edestin, gelatin, and casein. The chief absorption regions were at approx. 3—5 μ and 6. The calc. and observed positions of bands corresponding with the isoelectric points agreed (cf. this vol., 444).

H. J. E.

Raman spectra of some metallic halides. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 1, A, 850—858).—Raman data for the halides of Cd and Zn and for $MgCl_2$, $MgBr_2$, and $AlCl_3$ are given. $ZnCl_2$ and $ZnBr_2$ and the halides of Cd give lines showing the existence of homopolar binding. The spectra of $ZnCl_2$ and CdI_2 were fairly intense and indicate a linear triat. model analogous to those of the Hg^{II} halides. Intensity, sharpness, and frequency for $ZnCl_2$, $CdBr_2$, and CdI_2 vary markedly from crystal to solution, and with different solvents; the presence of halogen ions in solution also affects the spectra. Results are attributed to the change in degree of ionisation in different solvents and to the influence of solvent mols. on the fundamental oscillation frequencies of the compounds. $MgCl_2$, $MgBr_2$, and $AlCl_3$ gave no Raman lines; a marked effect on the H_2O bands was found in each case.

N. M. B.

Raman spectra of bromine compounds of germanium and tin. A. TCHAKIRIAN and H. VOLKRINGER (Compt. rend., 1935, 200, 1758—1760).—Data are recorded for $GeBr_4$. $GeHBr_3$ gave results similar to a solution of $SnBr_2$ in HBr . Formation of the acidic compounds $HSnBr_3$ and $HGeBr_3$ is indicated.

H. J. E.

Raman spectra in solutions. I. Solutions of arsenic trichloride in carbon tetrachloride and benzene. A. E. BRODSKI, A. M. SACK, and S. F. BESUGLI (Ber. Ukrain. Wiss. Forsch. physikal. Chem., 1935, 4, 135—142).—Raman frequencies are given for $AsCl_3$, CCl_4 , C_6H_6 , a 39% solution of $AsCl_3$ in CCl_4 , and a 35% solution of $AsCl_3$ in C_6H_6 . The CCl_4 and C_6H_6 frequencies appear unchanged in the mixtures, but the $AsCl_3$ vals. show deviations which are attributed to the polar character of $AsCl_3$.

R. S.

Doppler effect in light scattered by liquids. I. Variation with temperature. B. V. R. RAO (Proc. Indian Acad. Sci., 1935, 1, A, 765—767; cf. this vol., 565).—For CCl_4 at 70° , the Doppler components become fainter and broader, merging with the central undisplaced component which increases in intensity; at 0° the components become sharper and move away from the central component. Results support the hypothesis of loosely-bound, or "vapour," and closely-bound or "cryst.," mol. groups in a liquid.

N. M. B.

Raman spectrum of heavy chloroform. R. W. WOOD and D. H. RANK (Physical Rev., 1935, [ii], 48, 63—65).—The spectrum was photographed and line shifts were measured. Three types of isotope effects were observed. Calc. and observed vals. for the isotope displacements agree.

N. M. B.

Vibrational Raman scattering in liquids. S. BHAGAVANTAM and A. V. RAO (Physical Rev., 1935, [ii], 47, 1935, 921—923).—The intensity distribution in the wings accompanying the depolarised vibrational Raman line 656 cm^{-1} in CS_2 is similar to that in the wings accompanying the Rayleigh lines and falls to zero from a max. near the centre. Results are contrary to the predictions of theories of the rotational Raman effect. N. M. B.

Raman frequency of the C:C linking in alkylidene-cyclohexanes and -cyclohexenes. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 99—108).—The Raman frequency of the C:C linking in nerol was 1670 cm^{-1} and in geraniol 1669 cm^{-1} . No effect of the spatial arrangement of the CH_2OH on the C:C frequency was observed, indicating that the latter is mainly determined by the no. of substituents. The frequencies in methylen-, ethylidene-, and isopropylidene-cyclohexanes were 1655 , 1676 , and 1674 cm^{-1} , respectively, showing that when one C of the C:C linking is a member of the cyclohexane ring, the inner frequencies near 1665 cm^{-1} , due to the valency oscillation of the various C:C linkings, remain nearly the same as those corresponding in the aliphatic olefines. The frequency in 1:2-dimethylcyclohexene was 1675 cm^{-1} , hence when the C:C linking is part of the cyclohexene ring the inner C:C frequencies near 1665 cm^{-1} are nearly as in the corresponding aliphatic series types. N. M. B.

Raman spectra of the isomeric cis- and trans-1:3- and 1:4-dimethylcyclohexanes and of 1:1-dimethylcyclohexane. O. MILLER and L. PIAUX (Compt. rend., 1935, 201, 76—77; cf. A., 1933, 998).—Data are recorded, the spectra of the cis- and trans-isomerides having certain lines in common, but showing characteristic differences.

H. J. E.

Raman spectra of the esters of some derivatives of β -ketobutyric acid. II. M. MILONE (Gazzetta, 1935, 65, 339—349).—Raman spectrum of derivatives of the type $\text{COMe}\cdot\text{CRR}'\cdot\text{CO}_2\text{Et}$ show that the enolic form is present in large amount when $\text{R}=\text{H}$ and $\text{R}'=\text{Cl}$ or COPh , in small amount when $\text{R}=\text{H}$ and $\text{R}'=\text{CH}_2\cdot\text{CH}(\text{CH}_3)$ or CH_2Ph , and absent when both R and R' are alkyl. O. J. W.

Raman effect of organic substances. IV. Raman effect of cedrene. K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1935, 10, 220—231).—A complicated spectrum of 119 lines is discussed, and by correlating with existing data an attempt is made to assign the various Raman frequencies. It is impossible to decide from Raman effect measurement whether cedrene contains a 1-methylcyclopentene or -hexene ring. W. R. A.

Raman effect of some organic substances. G. B. BONINO and R. MANZONI-ANSIDEI (Mem. R. Accad. Sci. Ist. Bologna, 1934, [ix], 1, 10 pp.; Chem. Zentr., 1935, i, 1197).—The Raman spectra of 96 compounds of various classes are described.

H. N. R.

Anti-Stokes fluorescence of aniline vapour. N. PRILESHAIEVA (Acta Physicochim. U.R.S.S., 1935, 1, 785—794).—The anti-Stokes fluorescence of NH_2Ph

reaches max. at 250° , and disappears at $350\text{--}400^\circ$. The spectral region for excitation is at $\lambda 2900\text{--}3900\text{ \AA}$. (max. 3600). The excitation mechanism is discussed. On irradiating a mixture of NH_2Ph and indigotin vapours with white light, the blue indigotin fluorescence bands and those of NH_2Ph are observed, indicating a sensitised anti-Stokes fluorescence.

H. J. E.

Depolarisation factor of light scattered by liquids. A. BOUTARIC and PEYROT (Rev. gen. Sci., 1934, 45, 564—565; Chem. Zentr., 1935, i, 858).—Vals. for the depolarisation factor (ρ) of various liquids are recorded. ρ is raised by introduction of a C:C linking. Introduction of Me or Et in a saturated cyclic series increases $\rho >$ does a corresponding increase in the no. of ring C atoms. ρ can be used as a test of purity and, in certain cases, for studying binary mixtures. Very pure H_2O shows a small fluorescence, but pure C_6H_6 does not.

H. J. E.

Depolarisation of light by colloidal solutions, crystalline precipitates, and solid deposits on glass. S. PROCOPIU (Compt. rend., 1935, 201, 55—58).—Observations are recorded for the depolarisation produced by various colloids and suspensions and by films on glass. The min. particle size to produce depolarisation is approx. $0.8\text{ }\mu$. The method may be used to study cryst. ppt. formation or the orientation of thin solid films.

H. J. E.

Raman spectrum of rubber. S. D. GEHMAN (J. Amer. Chem. Soc., 1935, 57, 1382—1383).—A spectrum, with intense frequencies at 1672 , 1460 , and 1382 cm^{-1} , has been observed. E. S. H.

Quenching of iodine fluorescence by benzene vapour. J. P. HOWE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1935, 57, 1262—1265).—The quenching is not of the simple type encountered in monat. vapours. Probably several excited states are involved.

E. S. H.

Fluorescence of some pure substances. E. CANALS, P. PEYROT, and R. NOEL (Compt. rend., 1935, 201, 208—210; cf. A., 1934, 830).—Vals. for the depolarisation factors (ρ) and the relative intensities of fluorescence for a series of fatty acids are recorded. ρ decreases as the homologous series is ascended, except in the case of $\text{Pr}^*\text{CO}_2\text{H}$ and BuCO_2H . The fluorescence spectrum in each case was at $4400\text{--}4900\text{ \AA}$.

H. J. E.

Influence of nitrogen on the fluorescence of cyanogen. A. JAKOVLEVA (Acta Physicochim. U.R.S.S., 1934, 1, 296—304).—The presence of 20 mm. pressure of N_2 decreases to half the intensity of the blue fluorescence of $(\text{CN})_2$, produced by illumination of ICN with ultra-violet light. The changes in relative intensities of the (1,1) and (0,0) bands indicate that a transition from the state $v'=1$ to $v'=0$ occurs on collision. The probabilities of quenching and of the transfer of vibration on collision are about 0.1.

J. W. S.

Fluorescence spectra of hepatoflavin before and after irradiation.—See this vol., 1145.

Connexion between absorption and luminescence in concentrated dye solutions. V. L.

LEVSCHIN (*Acta Physicochim. U.R.S.S.*, 1935, 1, 685—712; cf. A., 1931, 1353).—Measurements on the absorption and fluorescence of rhodamine-G (extra) solutions are recorded. The absorption spectrum changes with increasing concn., due to association. The associated mols. are incapable of fluorescence and the intensity decreases. The concn. solutions on heating resemble dil. solutions. In Bu²OH solution changes in absorption spectrum occur only at high concn. This method of studying association is discussed. H. J. E.

Temperature optima of phosphorescent dye solutions. P. FROELICH (*Acta Lit. Sci. Univ. Francisco-Josephinae, Sect. Chem. Min. Phys.*, 1934, 4, 1—17).—Vals. of the temp. at which max. phosphorescence was observed are recorded for EtOH and glycerol solutions of erythrosin, eosin-A, rhoduline-orange, and rhodamine-S. There was a steady transition between fluorescence and phosphorescence phenomena. CH. ABS. (e)

Fluorescence of zinc oxide-iron oxide mixtures and its dependence on the temperature of heat-treatment. A. KUTZELNIGG (*Z. anorg. Chem.*, 1935, 223, 251—252; cf. this vol., 1085).—The fluorescence of equimol. ZnO+Fe₂O₃ mixtures heated at different temp. passes through a min. for mixtures heated at 500—550° as does that of ZnO, but rises to a max. at about 700°. J. S. A.

Influence of the passage of an electric current on the phosphorescence of zinc sulphide. G. DECHÊNE (*Compt. rend.*, 1935, 201, 139—142).—The phosphorescence of thin layers of various types of phosphorescent ZnS, spread on metal electrodes separated by conducting Cellophane, was reduced on passing a current after illuminating. The effect increased with the applied voltage (1000—3000 volts). H. J. E.

Light-dark effect, with reference to the adsorptive power of phosphors. J. A. HEDVALL and I. AFZELIUS (*Svensk Kem. Tidskr.*, 1935, 47, 156—161).—Phosphorescent ZnS containing Ag or Cu adsorbed 10—75% more lanasol-green when illuminated than when in the dark. Non-phosphorescent ZnS or BaSO₄ gave no such effect. H. J. E.

Radiation accompanying the dehydration of quinine sulphate. M. PROST (*Compt. rend.*, 1935, 201, 143—144; cf. A., 1931, 996).—A magnetic field of 600 gauss produced a 90% reduction in the ionisation current. The effect may be due to the production of large ions during the dehydration. H. J. E.

Emission of radiation in chemical and biological phenomena. R. AUDUBERT and O. VIKTORIN (*Coll. Czech. Chem. Comm.*, 1935, 7, 261—272; cf. A., 1933, 764).—Audubert and Van Doormaal's results were confirmed. Data are recorded for the dependence on time of the no. of photons emitted in the anodic polarisation of Al, and on the applied voltage. The intensity of the radiation at the anode c.d. Preliminary vals. are given for the spectral distribution of the radiations, using photocathodes of Al and CuI. Radiation was observed from nerves excited electrically or mechanically. H. J. E.

Hyperbolic law of decay of phosphorescence. M. CURIE (*Compt. rend.*, 1935, 201, 142—143).—Theoretical. H. J. E.

Quantitative tetrachromatic theory [of colour vision]. I. J. F. SCHOUTEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 590—603). D. R. D.

Ionisation potential of acetone vapour. W. A. NOYES, jun. (*J. Chem. Physics*, 1935, 3, 430—432).—The val. found by the electron bombardment method was 10.1 volts, agreeing with one val. predicted from spectroscopic data. H. J. E.

Electrical behaviour of the rectifying layer of lead sulphide. W. SCHADE (*Physikal. Z.*, 1935, 36, 499—508).—On varying the tuning of a circuit in which a PbS detector was connected in series with a milliammeter, the current in the circuit at first increased, reached a max., then decreased to zero, and finally the current was reversed. The greatest current flows in the detector for small alternating p.d. if the positive half-phase travels from the point to the surface. A virgin spot is less sensitive than one which has been previously used. Direct photographic demonstration of the emission of electrons from the PbS surface has been obtained. A. J. M.

New photo-electric effect of cuprous oxide. I. K. KIKOIN (*Physikal. Z. Sovietunion*, 1934, 6, 478—489; cf. A., 1934, 1291).—Experiments on the dependence of the effect on magnetic field strength, light intensity, λ , and temp. are described. CH. ABS. (e)

External photo-electric effect in cuprous oxide. E. VASSER (*Physikal. Z. Sovietunion*, 1934, 6, 351—367).—Vals. for the long- λ limit and photo-electric yield are recorded and discussed. CH. ABS. (e)

Influence of occluded gas and vapours on the electrical conductivity of cuprous oxide. L. DUBAR (*Compt. rend.*, 1935, 200, 1923—1925).—The conductivity decreases as a result of adsorption of gases, particularly H₂O, which produces approx. a tenfold decrease. H. J. E.

Electrical conductivity of water. A. KLING and A. LASSIEUR (*Compt. rend.*, 1935, 201, 203—204).—The conductivity of H₂O varies, distillation in Pt giving a higher val. than that in glass. The presence of small quantities of dissolved CO₂ cannot be detected conductometrically. H. J. E.

Dipole moment of deuteroammonia. J. M. A. DE BRUYNE and C. P. SMYTH (*J. Amer. Chem. Soc.*, 1935, 57, 1203—1205).—The triple point of ND₃ is at -73.6° and 48.6 mm. The dipole moments of NH₃ and ND₃, calc. from dielectric const. measurements, are 1.46×10^{-18} and 1.49×10^{-18} , respectively. E. S. H.

Dipole moment and structure of organic compounds. Moment of the N:C group.—See this vol., 976.

Electrical moments of isobutyl, isopropyl, and phenylchlorosulphites. P. TRUNEL (*Compt. rend.*, 1935, 200, 2186—2187; cf. this vol., 430).—Vals. of 2.66, 2.83, and 2.43 Debye units, respectively, were obtained. The difference between the vals. for

the Pr^{α} and Pr^{β} derivatives is attributed to their different influences on the free rotation of $\text{O}\cdot\text{SO}\cdot\text{Cl}$. The change due to the introduction of the Ph group is discussed. H. J. E.

Electric moments of alkyl monohalides. P. C. MAHANTI (Phil. Mag., 1935, [vii], 20, 274—287).—The effect of temp. on the dielectric const. of the vapours of Me, Et, and Pr halides and of $\text{C}_3\text{H}_5\text{Cl}$ has been determined by a heterodyne method, and the dipole moments have been calc. Since the moment of EtCl is $>$ that of MeCl , and the moment of $\text{Pr}^{\alpha}\text{Cl}$ is approx. the same as that of EtCl , the induction effect due to the principal doublet associated with the C-halogen linking of a n -alkyl monohalide is transmitted only as far as the second C in the chain. A. J. M.

Dielectric constants of acetylenic compounds. VI. **Acetylenic acids.** C. J. WILSON and H. H. WENZKE (J. Amer. Chem. Soc., 1935, 57, 1265—1267; cf. A., 1934, 1292).—Electric moments have been determined for propiolic, tetrolic, phenyl-, o - and p -chlorophenyl-, o - and p -nitrophenyl-propionic, phenyl-acetic, benzoic, p -nitro-, o -, m -, and p -hydroxybenzoic acids. The presence of the triple linking has a pronounced effect on the moments of CO_2H in the propiolic acids and on the ionisation consts. of these acids. H is more positive in CO_2H of the acetylenic acids than in AcOH . E. S. H.

Covalency angles of oxygen and sulphur in organic compounds. L. E. SUTTON and G. C. HAMPSON (Trans. Faraday Soc., 1935, 31, 945—957).—The dipole moments of Ph_2O , p -mono- and pp' -dibromodiphenyl ether, and PhBr in n -hexane at 25° are 1.18, 1.75, 0.65, and 1.60, respectively; those of p -bromophenyl p -tolyl ether, p -mono- and pp' -dichlorobenzophenone in C_6H_6 at 25° are 1.98, 2.71, and 1.70, respectively. The valency angles of O and S in Ph_2O and Ph_2S are $128 \pm 4^\circ$ and $113 \pm 3^\circ$, respectively. An explanation for the abnormally high val. for O is proposed, based on the probable resonance of the ordinary structure with others in which O forms a double linking with one nucleus. E. S. H.

Dipole moments of vapours. II. L. G. GROVES and S. SUGDEN (J.C.S., 1935, 971—974; cf. A., 1934, 944).—The following vals., in Debye units, were obtained: H_2O 1.84 ± 0.01 , D_2O 1.84 ± 0.01 , PhCl 1.73 ± 0.01 , PhBr 1.71 ± 0.01 , EtOBz 1.95 ± 0.02 , COPhMe 3.00 ± 0.01 , PhNO_2 4.24 ± 0.02 , PhCN 4.37 ± 0.02 , Bu^nCN 4.09 ± 0.01 . A survey of available data shows that in homologous series the moment of the terminal group tends to approach a const. val. on passing from Me to higher homologues and that Sutton's relation (cf. A., 1931, 1354) is confirmed. N. M. B.

Dipole moments of 1:4-dinitro-, 1:3:5-trinitro-, and certain 2:4:6-trisubstituted 1:3:5-trinitro-benzenes. (MRS.) C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1935, 957—965).—Measurements were made at 25° and 45° , in C_6H_6 , CHCl_3 , and dioxan solution, having regard to at. polarisations in the evaluation of the final moments. For the two first-named compounds moments were finite but >0.5 ; for the other compounds vals. were

larger. Results are explained by reference to a non-planar configuration of the NO_2 group. N. M. B.

Molecular polarisation of solutes and dielectric constant of solvents. R. J. W. LE FEVRE (Nature, 1935, 136, 181—182).—From the Raman-Krishnan formula for the vol. polarisation of a dielectric (A., 1928, 348) it is deduced that the polarisations of most substances in solution should be $<$ those in the vapour state. Substances with a negative Kerr const. should exhibit polarisations which are greater in the dissolved than in the gaseous condition. L. S. T.

Density and refractive index of benzene at varying temperatures. ("Allotropy" of benzene.) B. PESCE (Gazzetta, 1935, 65, 440—447).— d and n of are measured from 25° to 79° : $d_4^0 = 0.89983 - 1.0193 \times 10^{-3}t - 1.252 \times 10^{-6}t^2 - 6.044 \times 10^{-9}t^3$; $n_D^{20} = 1.51431 - 0.644 \times 10^{-3}t + 0.033 \times 10^{-6}t^2 - 2.391 \times 10^{-9}t^3$. The graphs of these functions present no singular points, and give no evidence of two liquid forms of C_6H_6 . E. W. W.

Spectrochemistry of organic fluorine compounds. K. VON AUWERS (Z. physikal. Chem., 1935, 173, 345—348).—Schiemann's (A., 1931, 1355) vals. for the equiv. refractive power of F are confirmed for o -, m -, and p - $\text{C}_6\text{H}_4\text{F}\cdot\text{NO}_2$ and o -, m -, and p -fluoronitroaniline, but his dispersion equiv. is too large. T. G. P.

Origin of optical rotatory power. T. M. LOWRY (Nature, 1935, 136, 191—192).—A review of recent theoretical investigations, with illustrative examples. L. S. T.

Analysis of rotatory dispersion of chemically analogous substances. P. A. LEVENE and A. ROTHEN (Science, 1935, 81, 623—624).—The partial rotations of the individual absorption regions in substances of the general type of $\text{CHRR}'\cdot[\text{CH}_2]_n\text{X}$, where R and R' are alkyl, and X is a functional group CHO, N_3 , SH, halogen ($n=0$ or an integer), are tabulated and discussed. L. S. T.

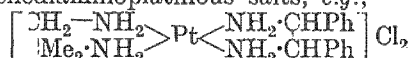
The NO^+ radical. W. R. ANGUS and A. H. LECKIE (Trans. Faraday Soc., 1935, 31, 958—962).—Conductivity measurements show that solutions of NOHSO_4 or NOCIO_4 in nitromethane are electrolytes, confirming the deduction from band spectra and Raman spectra data that NO^+ is a stable radical. E. S. H.

Shape of the NO_2 molecule. G. B. H. M. SUTHERLAND and W. G. PENNEY (Nature, 1935, 136, 146—147).—Closer investigation (cf. A., 1934, 829) of the electronic structure indicates a $\text{O}\cdot\text{N}\cdot\text{O}$ angle of approx. 110 — 120° . A wide-angled structure for NO_2 is also to be preferred from a study of force fields in triat. mols. Difficulties regarding the contours of the infra-red bands suggest that a re-examination of these bands is necessary. L. S. T.

Structure of telluric acid. L. PASSERINI and M. A. ROLLIER (Atti R. Accad. Lincei, 1935, [vi], 21, 364—368; cf. A., 1934, 1161).—Cubic H_6TeO_6 has a 15.68 \AA , d_{calc} 3.158, 32 mols. in the unit cell, and space-group O_h^8 . The structure is $\text{Te}(\text{OH})_6$, with the OH arranged symmetrically around the Te, and not $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$. D. R. D.

Structure of phosphorus pentachloride and phosphorus pentamide. H. MOUREU and P. ROCQUET (Compt. rend., 1935, 201, 144—147).— PCl_5 (fused, gaseous, or in solution) may consist of mols. in which P is surrounded by a shell of 10 electrons, in equilibrium with a small proportion of mols. with two singlet linkings, the latter being responsible for the ready dissociation and the formation of POCl_3 . Similar considerations may apply to $\text{P}(\text{NH}_2)_5$, which readily loses 2 mols. of NH_3 forming a polymeride of PN_3H_4 . It is shown from the electronic structures that PN_3H_4 , PNCl_2 , and $\text{PN}(\text{OH})_2$ should all polymerise readily. H. J. E.

Configuration of the valencies of 4-covalent platinum. Optical resolution of *meso*-stilbene-diaminoisobutylenediaminoplatinous salts. W. H. MILLS and T. H. H. QUIBELL (J.C.S., 1935, 839—846).—The diphenyldimethyl derivatives of bisethylenediaminoplatinous salts, e.g.,



have been resolved, by means of diacetyltartaric acid, into antimeric optically active forms showing a high degree of optical stability. This shows that the 4-covalent Pt must have a planar configuration of its valencies, since the regular tetrahedral arrangement would give a symmetrical configuration for the complex cation. The planar arrangement also gives a practically strainless five-ring system composed of C and N atoms and one Pt. O. J. W.

Wave-mechanical treatment of the Mills-Nixon effect. L. E. SUTTON and L. PAULING (Trans. Faraday Soc., 1935, 31, 939—945).—Theoretical. E. S. H.

Dissociation of some molecules with free valencies. H. LESSHEIM and R. SAMUEL (Current Sci., 1935, 3, 610; cf. A., 1934, 477).—Conclusions reached from the correlation between the electronic terms of mols. of the type BeO , BeF , and NO and those of the constituent atoms are summarised. L. S. T.

Electronic structure and valency. C. PRÉVOST (Bull. Soc. chim., 1935, [v], 2, 1119—1148).—Current views of valency are modified. The no. of electronic doublets in the outer shell, except for the *K* ring, is regarded as equal to the no. of corners of a polyhedron (4, 6, etc.), and electronic shells can be completed by borrowing from an inner shell even when this is the *K* ring. Ionic forces are inferior to covalent. O may be singly covalently linked, as in $\text{O} \cdot \text{P}(\text{OH})_3$ [the electrostatic energy between O^- and P^+ in the formulation $\text{O}^- \cdot \text{P}^+(\text{OH})_3$ is considered to be negligible], $\text{O} \cdot \text{S} \cdot \text{O}$, $\text{O} \cdot \text{S}(\cdot \text{O})_2$, etc. Co-ordination is represented on the basis of covalency and not as electrostatic action on dipoles, and the co-ordination no. never exceeds 4 when the underlying ring is *K*, and when the central atom and satellites belong to the same row of the periodic table. Deficient octets, as in BF_3 , are considered to be completed from the *K* ring, except in the active form, and thus possess tetrahedral symmetry. Oxidation and autoxidation are discussed. Prototropy is generalised on the basis of the structural insignificance of the electrovalent linking, the stable structure not necessarily

corresponding to the neutralisation by the H^+ of the effective charge, e.g., in the ion $\text{O}^-\text{N}^+\text{O}^+$ the negative charge is carried by O, but the stable form is $\text{O} \cdot \text{N}(\cdot \text{O}) \cdot \text{H}$; so with $(\text{HO})_2\text{P}(\cdot \text{O}) \cdot \text{H}$. Many mols. usually written with triple linkings are supposed to have singlet linkings, e.g., $\cdot \text{N} : \text{N} \cdot$, electrons being drawn from the *K* rings, explaining the acidity of C_2H_2 and HCN . The theory is supported by stereochemical evidence. R. S. B.

Electronic theories of Lewis and Kossel. W. A. NOYES (Science, 1935, 81, 628—629).—Lewis' theory provides a simple explanation for many facts which are less easily reconciled with that of Kossel. L. S. T.

Orientation of unsymmetrical molecules at interfaces. S. H. BAUER and A. POLLACK (J. Chem. Physics, 1935, 3, 401—405).—Theoretical. H. J. E.

Electronic structures of polyatomic molecules and valency. VI. Method of molecular orbitals. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 375—378; cf. A., 1934, 14).—Theoretical. A qualitative framework into which chemical and spectroscopic data can be fitted is described. H. J. E.

Vibrations of polyatomic molecules in excited electronic states. A. B. F. DUNCAN (J. Chem. Physics, 1935, 3, 384—385).—The strongest vibrational frequencies observed in the excited states of CO_2 , CS_2 , H_2O , ClO_2 , SO_2 , O_2 , NH_3 , PCl_3 , C_2H_2 , C_6H_6 , and COMe , are totally symmetrical. These are usually the only frequencies observed. H. J. E.

Molecular structure of benzene. G. B. BONINO (Gazzetta, 1935, 65, 371—423).—Modern conceptions of the structure of the C_6H_6 ring are reviewed, with special reference to results obtained from the study of spectra (including infra-red and Raman) and to the application of quantum mechanics to the problem. It is considered that a conception of structure which is both acceptable on physical grounds and useful in interpreting the chemical behaviour of cyclic compounds is now available. H. F. G.

Calculation of the fundamental frequencies of vibration of a molecule X_6Y_6 , having plane hexagonal symmetry. C. MANNEBACK (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 129—159).—Mathematical. W. R. A.

Calculation of the vibration frequencies of C_2H_4 by the method of symmetrical co-ordinates. J. M. DELFOSSE (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 114—128).—Mathematical. W. R. A.

Periodic groups of non-hydride di-atoms. C. H. D. CLARK (Trans. Faraday Soc., 1935, 31, 1017—1036; cf. this vol., 432).—Non-hydride di-atoms are classified into periods (determined by non-bonding groups of electrons) and groups or sub-groups (dependent on electrons derived from the incomplete systems of the constituent atoms). Regularities and progressions of spectroscopic consts. are traced through different groups and periods. E. S. H.

Rational systematisation of chemical compounds. H. G. GRIMM (Z. ges. Naturwiss., 1935, 1,

178—186; cf. this vol., 448).—A review of the author's method of classification. H. J. E.

Maximum valency of elements and atomic structure. I, II. B. ORMONT (*Acta Physicochim. U.R.S.S.*, 1935, 1, 745—751, 752—758).—A general discussion of the influence of electron arrangements in compounds on their stability. Numerous compounds are discussed. H. J. E.

Electron affinity of the radicals HO₂ and OH, and the oxygen molecule. J. WEISS (*Trans. Faraday Soc.*, 1935, 31, 966—969).—Theoretical. The electron affinities, calc. with the aid of certain assumptions, are HO₂ +4.6, OH +3.7, O₂ +2.7 electron volts. E. S. H.

Constitution of water in solutions of weak electrolytes. I. Formic and acetic acids. C. S. S. RAO (*Phil. Mag.*, 1935, [vii], 20, 310—322).—The effect of dissolving weak electrolytes in H₂O on its constitution has been investigated in the case of AcOH and HCO₂H by examining the intensity distribution along the Raman H₂O band in these solutions. With increasing concn. of solute the band sharpens, and the max. moves towards higher frequencies. Addition of a weak electrolyte to H₂O causes a decrease in [(H₂O)₃] and an increase in [H₂O]. The proportion of (H₂O)₃ in HCO₂H is > in AcOH at the same concn. A. J. M.

Electron affinity of free radicals. V. Aromatic derivatives of dixanthyl and *pp'*-diphenylenedi(diphenylmethyl). H. E. BENT and R. G. GOULD, jun. VI. **Strength of the carbon-carbon linking in certain substituted dixanthyls.** H. E. BENT and E. S. EBERS. VII. **Triphenylboron and tri- α naphthylboron.** H. E. BENT and M. DORFMAN (*J. Amer. Chem. Soc.*, 1935, 57, 1217—1220, 1242—1246, 1259—1261; cf. A., 1932, 1191).—V. The electron affinities of phenylxanthyl and α -naphthylxanthyl differ little from the vals. for org. free radicals previously reported. Na is added more easily to *pp'*-diphenylenedibenzhydryl than to CPh₃. This observation is interpreted in terms of single linking energies and resonance energy.

VI. The electron affinities of dibenzyl-, diphenylethyl-, and di-*n*-butyl-dixanthyl have been determined. The heat of dissociation of C-C in these compounds is calc. as 16—17 kg.-cal. The variability of single linking energies is discussed.

VII. BPh₃ and tri- α -naphthylboron (I) behave like free radicals in adding Na, but the reaction is slow and the free energy change small. (I) adds 2 Na atoms, the second of which is held much less firmly than the first. E. S. H.

Concept of "chemical compound." J. A. A. KETELAAR (*Chem. Weekblad*, 1935, 32, 58—64).—The structure of intermetallic compounds and of cryst. substances in general is discussed in relation to the conception of a compound as containing certain elements in const. stoichiometric proportions. Thermal analysis alone does not adequately reveal the composition of all phases which may occur in the former case; the application of e.m.f. measurements and of activity considerations is demonstrated. H. F. G.

Nature of chemical force. H. HELLMANN (*Acta Physicochim. U.R.S.S.*, 1934, 1, 333—353).—A summary of recent news. J. W. S.

Theory of liquids. III. T. S. WHEELER (*Proc. Indian Acad. Sci.*, 1935, 1, A, 795—814; cf. A., 1934, 1295).—An examination of Edser's theory regarding a liquid as composed of a no. of force centres or mols. each vibrating within an associated spherical space kept free from other mols. by the thermal motion of the occupying mol. The vibratory motion is considered, and the amplitude has been linked with density, internal latent heat of vaporisation, surface tension, viscosity, and v.p. Formulæ relating viscosity with surface tension, and v.p. with internal latent heat, and equations for the coeff. of thermal expansion and compressibility are derived. Results are verified for a no. of substances. N. M. B.

Mechanical requirements and complementary anisotropy of ferromagnetic materials. A. PERRIER (*Helv. phys. Acta*, 1934, 7, 665—668; *Chem. Zentr.*, 1935, i, 1015).—Theoretical. The production of anisotropy by mechanical working is related to the author's theory of ferromagnetic induction.

J. S. A.
Comparison of action of heat on platinum oxide obtained chemically and in the electric discharge. J. PIAZZA (*An. Soc. cient. Santa Fe*, 1934, 6, 23—25; *Chem. Zentr.*, 1935, i, 1028).—Pt oxide (I) obtained by electric discharges in O₂ at low pressure decomposes between 530° and 600°; Pt(OH)₂ at 560°; PtO₂ at 630°. (I), of composition Pt₂O₃, is probably a mixture of Pt and PtO₂.

J. S. A.
Compound of platinum and helium. Probable size of colloidal particles. H. DAMIANOVICH (*An. Soc. cient. Santa Fe*, 1934, 6, 17—19; *Chem. Zentr.*, 1935, i, 1027—1028).—The mol. size calc. from at. dimensions is of colloidal order. To obtain products of high He content, rapid condensation on a cooled surface is desirable.

J. S. A.
Electronic states of the carbon atom and the calculation of binding energies. W. LASAREFF (*Physica*, 1935, 2, 737—742).—The energies of the C-C linking in diamond and in aliphatic compounds are 132±3.5 and 128 kg.-cal., respectively. H. J. E.

(C-C) diamond linking energy. W. LASAREFF (*J. Physical Chem.*, 1935, 39, 913; see preceeding abstract).—From recent data the energy of the C(⁵S)-C(⁵S) linking in the diamond lattice is calc. as 123±5 kg.-cal. J. W. S.

Dynamical theory of the diamond lattice. II. Elastic constants of diamond. N. S. NATH (*Proc. Indian Acad. Sci.*, 1935, 1, A, 841—849; cf. this vol., 150).—Mathematical. Expressions for the three elastic consts. of the diamond in terms of the mol. force consts. and approx. numerical vals. are deduced. N. M. B.

Variation method of calculating the energy of atomic systems. A. A. SCHUCHOVITZKI (*Acta Physicochim. U.R.S.S.*, 1934, 1, 212—219).—Mathematical. J. W. S.

Correction to the Eötvös constant. D. G. DERVICHIAN (*Compt. rend.*, 1935, 200, 2065—2067).—

The val. of the Eotvos const. for a series of fatty acids and alcohols is approx. 1.2 if, in place of the expression $(M/N\rho)^{2/3}$ for the surface area, the val. of the cross-section of the mol., deduced from X-ray measurements, is used. These substances all give discordant vals. using the normal method of calculating the const. H. J. E.

Interpretation of the Eotvos constant and of its different values. D. G. DERVICHIAN (Compt. rend., 1935, 201, 130—133; cf. preceding abstract).—Theoretical. An expression is derived similar to the Eotvos equation with the Ramsay and Shields correction term. Vals. for the const. are calc. and compared with experimental vals. H. J. E.

Surface tension of heavy water. H. LACHS and I. MINKOW (Nature, 1935, 136, 186—187).—Preliminary measurements with 94—99.2% D_2O indicate that the surface tensions of H_2O and D_2O are probably equal. L. S. T.

Parachor and chemical constitution. II. Structure of the triphenylmethane dyes. S. K. RAY (J. Indian Chem. Soc., 1935, 12, 248—257; cf. this vol., 283).—The surface tension and d of the hydrochlorides and coloured carbinol bases of rosaniline, crystal-violet, and malachite-green have been determined in solution. The parachor vals. support the quinonoid structure. O. J. W.

Additivity of the parachor. A. H. W. ATEN, jun. (Rec. trav. chim., 1935, 54, 666—670).—From the law of corresponding states it is shown that the parachor defined by $P = \gamma^{1/4} M / (D - d)$ should also be given by $P = K a^{1/4} b^{1/2}$, where a and b are the van der Waals consts. for the substance and K is a const. for all substances. Vals. of P calc. by the two formulæ show satisfactory agreement for the 30 substances examined. Additivity of P is traced to the additivity of the function $a^{1/4} b^{1/2}$. S. J. G.

Fine structure of X-ray absorption edges in close-packed cubic and close-packed hexagonal crystal lattices. D. COSTER (Physica, 1935, 2, 606—610).—The cubic close-packed and the hexagonal close-packed crystal lattices give the same X-ray absorption edge fine structure as regards the position of max. and min. relative to the main edge. The form of the max. and min. show typical differences. Data for Ca and Ti and for α - and ϵ -brass are quoted. H. J. E.

Lattice state of reacting crystal phases in the X-ray diagram. W. BUSSEM (Naturwiss., 1935, 23, 469—472).—The methods of obtaining F -curves for reacting crystal phases are discussed. A. J. M.

X-Ray extinction in piezoelectrically oscillating crystals. G. W. FOX and W. A. FRASER (Physical Rev., 1935, [ii], 47, 899—902). N. M. B.

New crystallography. W. L. BRAGG (Proc. Roy. Soc. Edin., 1934—1935, 55, 62—71).—Bruce-Preller lecture. N. M. B.

Photo-elastic effect of cubic crystals. H. MUELLER (Physical Rev., 1935, [ii], 47, 947—957).—Assuming that elastic deformations produce optical anisotropy, the Ewald-Born theory of double refraction of crystals is applied to the calculation of

the photo-elastic properties of D lattices. An explanation of the change of n with density, and of the different photo-elastic properties of NaCl, KCl, CaF_2 , and diamond is deduced. N. M. B.

Equilibrium form and growth form of crystal. I. N. STRANSKI and R. KAISCHEV (Ann. Physik, 1935, [v], 23, 330—338).—Theoretical. The equilibrium and growth forms of a crystal and the effect of degree of supersaturation on the equilibrium form are discussed on the basis of the theory of crystal growth previously put forward (this vol., 816). A. J. M.

Growth of very thin crystals. I. Qualitative investigation. II. Quantitative study. III. Theoretical. L. KOWARSKI (J. Chim. phys., 1935, 32, 303—331, 395—405, 469—495; cf. A., 1930, 1111, 1366; 1932, 796).—I. Full details are given of the growth, contraction, and drop phenomena observed with p -toluidine (I) crystals sublimed on to the edge of a razor blade, and mica, using the apparatus described. Two types of crystals are distinguished. Type (i) are large isolated crystals of uniform sp. thickness (approx. $1\ \mu$) with geometrically definable curved edges. These crystals grow when a carefully cleaned blade and rapid cooling are employed. When a disturbance occurs, such as making contact with a growing crystal, increments of thickness spread radially over the surface from the point of contact. Type (ii) occur in oriented groups. Each crystal is in stratified layers of different thickness and grows simultaneously in thickness and area. The edges are rectilinear. Such crystals are produced on blades contaminated with (I) and by slow cooling. Liquid drops formed below the m.p. are mobile and do not enlarge on type (ii), but are stationary and enlarge on type (i) (cf. A., 1933, 557). The unit cell of (I), $a\ 5.93$, $b\ 8.91$, $c\ 23.3\ \text{\AA}$, contains 8 mols.

II. Growing crystals of (I) are photographed at intervals of 10—15 sec.. Each crystal passes through three stages of growth. Initially, the area, S , increases parabolically with respect to time, then linearly, and finally the rate tends to zero; concomitantly, the ratio $S^{\frac{1}{2}}/\text{breadth}$ ($=f$) decreases, becomes const., and then increases. In general, these phenomena are independent of changes of thickness.

III. The theories of crystal growth are reviewed. The surface of a "curve-type" crystal of (I) is covered with a film of mobile mols. of which the surface density probably increases with time, and "homothetic" growth (f const.) is interpreted as an isotropic phenomenon. The theory leads to a growth equation of the form $S = S_{\infty}$ which accords with the above data, where S is the surface area at time t . In general, crystal growth is anisotropic, but isotropy supervenes when the velocity of crystallisation is in the neighbourhood of its max. J. G. A. G.

Oriented intergrowth and overgrowth in relation to the modification of crystal habit by adsorption. C. FRONDEL (Amer. J. Sci., 1935, [v], 30, 51—56).—In the case of regular intergrowths of crystals of different kinds, the lattice dimensions on certain planes are comparable; it is suggested that the same is true when impurities adsorbed from solu-

tion have an influence on the habit of the growing crystal. L. J. S.

Analytical method for determining preferred orientations of crystals in mechanically worked cubic metals. C. B. POST (Z. Krist., 1935, 90, 330—340).—An addition to the established method, which involves X-ray pinhole photographs along and perpendicular to the direction of rolling. Mainly mathematical, with detailed reference to the orientation analysis of rolled Ag. B. W. R.

Recrystallisation of silver of different degrees of purity. E. OSSWALD (Z. Metallk., 1935, 27, 101—104).—The recrystallisation temp. of Ag determined by X-ray methods agrees closely with that determined from curves showing the recovery of physical properties with annealing temp. Chemically pure Ag recrystallises at room temp. within 24 hr. of rolling and is completely recryst. in about 3 weeks. Even minute quantities of impurity raise the recrystallisation temp. considerably. Ag with 0.1% Fe recrystallises at 80° when annealed immediately after rolling, but will recrystallise at 20° in 14 days. A. R. P.

Twinning of single crystals of tin. B. CHALMERS (Proc. Physical Soc., 1935, 47, 733—746).—The conditions under which parts of the crystals can be caused to twin by impact or tension are investigated, and the determination of the energy relations for certain controlled cases is described. The energy of twinning is 8×10^5 ergs converted into heat per c.c. of crystal twinned. The process is discussed in relation to the crystal structure of Sn. N. M. B.

Microstructure of platinum after action of helium, oxygen, and hydrogen in the electric discharge. H. DAMIANOVICH (An. Soc. cient. Santa Fe, 1934, 6, 20—22; Chem. Zentr., 1935, i, 1028).—After the action of He, Pt shows a fine-grained structure with isolated coarse growths due to the ease of recrystallisation of Pt in He. In H₂ and other gases a uniform large-grained structure results. J. S. A.

Properties of crystalline magnesium oxide. R. W. DITCHBURN and J. HARDING (Nature, 1935, 136, 70—71).—Heating for 1 hr. in a vac. with metals at the specified temp. had no effect on cryst. MgO in the case of K (400°), Na (500°), Pb (1050°), Mg (1100°), and Al (1100°); Ca (1050°) and Cu (1100°) etched the surface slightly. The crystal is thus more resistant to metallic vapours than is glass or quartz. It can be ground and polished, and sealed into soda-glass of high expansion coeff. L. S. T.

Crystal structure of Au₂Bi. T. JURRIANSE (Z. Krist., 1935, 90, 322—329).—A definite phase Au₂Bi exists; its structure is cubic face-centred, space-group O_h^1 , a_0 7.942 Å., d (X-ray) 15.70, m.p. $373^\circ \pm 2^\circ$. The equilibrium diagram of the system Au—Bi is revised accordingly. B. W. R.

X-Ray investigation of austenite and martensite in some special steels. Z. NISHIYAMA (Sci. Rep. Tôhoku, 1935, 24, 128—140).—Steels containing Cr, Ni, or Mn and quenched from the γ -phase have been examined. The austenite has a face-centred cubic and the α -martensite a body-centred tetragonal

lattice, the consts. of each lattice varying with C content as in C steels. The martensite formed from austenitic Ni steel by cooling in liquid N₂ has the same tetragonal lattice. The martensite-like structure observed in quenched and tempered high-C high-Mn steel has a hexagonal lattice and has been formed from austenite during polishing. R. C.

Structure of manganite. J. GARRIDO (Bull. Soc. Franç. Min., 1935, 58, 224—241).—Manganite from Illfeld has a 4.42, b 5.23, c 2.87 Å. The X-ray diagram indicates the existence of a multiple cell with A 8.84, B 5.23, C 5.74 Å., and 4 mols. of Mn₂O₃·H₂O making 1 mol. of Mn₂O₃·H₂O in each of the four smaller cells. Each Mn is surrounded by 6 O at 1.95 Å. L. S. T.

Transition point of sodium cyanide due to rotation of the CN group. J. M. BIJVOET and H. J. VERWEEL (Rec. trav. chim., 1935, 54, 631—632).—The lattice of NaCN is of the rock-salt type at room temp., but changes to orthorhombic on cooling, the transition point being 11—16°, since the kinetic energy is no longer sufficient to permit the free rotation of the CN groups, which become oriented parallel to one another. This also explains why the crystal does not fall to pieces when the lattice form changes, despite a contraction of 1.5%. S. J. G.

Crystallography of complex salts. E. STOICOVICI (Bull. Soc. Ştiinţe Cluj, 1934, 8, 140—144; Chem. Zentr., 1935, i, 997).—[Cu en₂][Mn(SCN)₄] is triclinic holohedral, $a : b : c = 1.260 : 1 : 0.972$, α 90° 32', β 115° 59', γ 101° 32'. [Ni en₂][Ni(SCN)₆] is monoclinic holohedral, $a : b : c = 1.067 : 1 : 1.143$, β 111° 50'. J. S. A.

Crystal structure of calcium chloride. A. K. VAN BEVER and W. NIEUWENKAMP (Z. Krist., 1935, 90, 374—376).—By cooling fused dehydrated CaCl₂ slowly in vac., single crystals were obtained, having rhombic pseudotetragonal structure, a_0 6.24, b_0 6.43, c_0 4.20 Å., space-group $Pnmm$. At. parameters are given. A powder photograph does not agree with this structure, but corresponds with a second modification, arising from the first by mechanical disturbance. B. W. R.

Crystal structure of aluminium arsenate AlAsO₄. Isomorphy of Si and As^v in crystals. F. MACHATSCHKI (Z. Krist., 1935, 90, 314—321).—Powder diagrams of AlAsO₄ indicate a hexagonal structure, a_0 5.030, c_0 5.612 Å., disagreeing with the tetragonal structure previously found, and corresponding with that of quartz if the 3 Si of quartz are replaced by Al^{III} and As^v statistically in the ratio 1 : 1. B. W. R.

Crystallographic relations of aluminium iodate nitrate. K. SZTRÓKAY (Z. Krist., 1935, 90, 381—382).—Morphological and optical properties of the crystals Al(IO₃)₂NO₃·6H₂O are described. R.

Complex anion formation by tervalent elements: structure of caesium thallic enneachloride. H. M. POWELL and A. F. WELLS (J.C.S., 1935, 1008—1012).—The structure of Cs₃Tl₂Cl₉ has been determined. The rhombohedral unit cell has 2 mols.; space-group C or D_{3d}^2 . The structure is

based on a hexagonal close-packing of the Cs and Cl ions, with Tl occupying some of the positions between 6 Cl. The complex anion $\text{Tl}_2\text{Cl}_9^{3-}$, distinguished in the structure, is formed by two octahedral groups of 6 Cl around one Tl sharing the 3 Cl of one face between two octahedra. The comparative instability of As_2MHl_6 halides is attributed to the structure, and the formation of more complex compounds to greater structural compactness. The relation of the structure to that of $\text{Cs}_3\text{As}_2\text{Cl}_9$ is discussed.

N. M. B.

Scattering of X-rays in solutions of heavy molecules and the structure of complex ions. V. DANILOV, V. FINKELSTEIN, and D. SIROTENKO (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 125—133).—The theory of the scattering of X-rays by gases can be applied to a solution of heavy mols. in a solvent of light mols. A study of X-ray scattering by aq. $\text{K}_2\text{Hg}_2\text{I}_4$ indicates that HgI_4^{2-} consists of 4 I' arranged tetrahedrally about a central Hg".

R. S.

Crystallographic investigation of $2[\text{HgClMnO}_4] \cdot 3\text{HgO}$. C. LAURO (Rend. Fac. Sci. Cagliari, 1933, 3, 148; Chem. Zentr., 1935, i, 1027).—The compound has $a : b : c = 1.74805 : 1 : 0.62872$.

J. S. A.

Two-dimensional crystals of cristobalite. W. NIEUWENKAMP (Z. Krist., 1935, 90, 377—380).—Photographs are given which confirm the author's theoretical treatment of two-dimensional X-ray diffraction. The cristobalite specimens examined have a two-dimensional lattice, with only arbitrary phase relations between adjacent sheets.

B. W. R.

Crystal structure of lepidocrocite. F. J. EWING (J. Chem. Physics, 1935, 3, 420—424).—The crystals are orthorhombic (a 3.87, b 12.51, c 3.06 Å.; space-group V_h^{17} -*Amam*; 4 mols. of $\text{FeO}(\text{OH})$ in the unit cell). Interat. distances are calc. The structure consists of Fe-centred O octahedra, joined by the sharing of edges into two-dimensionally infinite layers, with the successive layers held together by H linkings.

H. J. E.

Crystallography and structure of hexamethylenetetramine salicylate. A. ŁASZKIEWICZ (Arch. Chem. Farm., 1935, 2, 219—236).—Crystallographic data are recorded.

R. T.

Crystal structure of dodecahydrobenzanthracene. J. IBALL (Chem. and Ind., 1935, 716).—The cell is triclinic, a_0 7.84, b_0 8.71, c_0 11.71 Å., α 108.0°, β 96.6°, γ 81.5°, d (floatation) 1.123. Space-group probably $P1$. The probable shape of the mol. is discussed.

B. W. R.

X-Ray studies of products of nitration of starch. I. M. KOŁACZKOWSKA and T. URBANŃSKI (Rocz. Chem., 1935, 15, 339—342).—Starch nitrates prepared from potato and sol. (amorphous) starch show the formation of similar crystallites in both cases.

R. T.

Molecular structure in sisal, coir, and oak. E. N. M. THOMAS and J. HEWITT (Nature, 1935, 136, 69—70).—X-Ray photographs are reproduced. Sisal fibres give the usual cellulose pattern and stretch-

ing appears to act on the crystallites (or micelles) in the same way as it does on cotton. The coir pattern gives two cellulose patterns at right angles to each other, and may be interpreted either as one spiral of crystallites running at 45° around the fibre, or as two spirals at right angles to each other, each running at 45° in opposite directions around the fibre. Chlorination has no great effect on the X-ray patterns, supporting the view that lignin is amorphous. In oak, it is inferred that the crystallites lie parallel to the longitudinal axis of the tracheids and that they are almost perfectly oriented. The results for oak agree, to some extent, with those for the summer wood of ash and the spring wood of fir (A., 1931, 1360).

L. S. T.

Electron diffraction as a means for determining the structure of organic substances. G. NATTA, M. BACCAREDDA, and R. RIGAMONTI (Monatsh., 1935, 66, 64—75).—The electron diffraction diagrams of many highly polymerised org. substances are very susceptible to the presence of thin films of fatty impurities. Special precautions are necessary to obtain characteristic diagrams of such substances.

O. J. W.

Structure of the benzene molecule and some of its methyl derivatives. P. L. F. JONES (Trans. Faraday Soc., 1935, 31, 1036—1039).—The vapours of C_6Me_6 , mesitylene, *p*-xylene, and C_6H_6 have been examined by the electron-diffraction method. The results are in agreement with the assumption of a plane mol. with a regular hexagonal structure for the C_6H_6 nucleus.

E. S. H.

Scattering of fast electrons from thin foil. H. SAEGUSA and K. KIKUCHI (Sci. Rep. Tōhoku, 1935, 24, 30—44).—The angular distribution of electrons scattered at angles of 30—120° by non-elastic collision from celluloid films has been determined, with accelerating voltages of 1 to 2.8×10^4 volts; the no. of electrons so scattered passes through a max. at about 53° and a min. at 45°, and at 90° is about 110% of the no. scattered by elastic collision. For angles of 30—50° the results agree with Moller's theory (A., 1931, 1100) as well as do Klemperer's (A., 1933, 109).

R. C.

Diffraction of X-rays and electrons by carbon tetrachloride vapour. C. DEGARD, J. PIERARD, and W. VAN DER GRINTEN (Nature, 1935, 136, 142—143; cf. A., 1934, 946, 1163).—New X-ray and electron-diffraction analyses of CCl_4 agree with theory and give the same vals. for interat. distances, viz., Cl-Cl 2.85 ± 0.03 Å., 2.86 ± 0.03 Å., and C-Cl 1.74 ± 0.02 Å., 1.75 ± 0.02 Å., respectively. The influence of thermal vibrations could be detected in the electron-diffraction photographs.

L. S. T.

Contact difference of potential between tungsten and barium. External work function of barium. P. A. ANDERSON (Physical Rev., 1935, [ii], 47, 958—964).—Highly rigorous conditions of outgassing and of obtaining clean surfaces lead to the vals. 2.13 ± 0.05 volts for the contact p.d. between W and Ba, and 2.39 ± 0.05 equiv. volts for the external work function of Ba.

N. M. B.

Molecular orientation in thin layers of anisotropic liquids and measurement of constants characterising their elastic properties. V. FREDERIKS and V. ZVETKOV (Physikal. Z. Sovietunion, 1934, 6, 490—504; cf. A., 1934, 948).—Experiments with *p*-azoxyanisole are described, vals. for its elasticity const. as a function of temp. being given.

CH. ABS. (e)

Plasticity of crystals. E. W. ZECHNOWITZER (Naturwiss., 1935, 23, 511).—Recrystallisation of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ from HNO_3 solution gives large prismatic crystals which can be bent in the fingers. When thus treated, the crystals become opaque and rough. Undeformed crystals lose their plasticity on keeping in air.

A. J. M.

Elastic modulus of ferromagnetic metals. M. KÆRSTEN (Z. Metallk., 1935, 27, 97—101).—Recent work on the effect of internal stress on the elastic modulus of metals is reviewed and its bearing on the variation of the modulus of ferromagnetic metals under the influence of magnetic fields is discussed mathematically.

A. R. P.

Weakening of a deformed single crystal by annealing. M. O. KORNFELD (Physikal. Z. Sovietunion, 1934, 6, 329—342; cf. A., 1934, 1296; this vol., 433).—Single-crystal wires of Al were strengthened by tensile deformation and then weakened by annealing for various periods at temp. (*t*) from 150° to 650°. The velocity of weakening rises rapidly with *t* in the range 150—250°, but does not vary greatly with the initial degree of deformation for *t*=200°. For 20-hr. annealing periods the flow limit decreases linearly with fall of *t* up to 400° and above 550°, but the state of the crystal does not vary with *t* in the interval 400—550°. Annealing near the m.p. restores the deformed crystal to its initial state.

CH. ABS. (e)

Continuity of the solid and the liquid states. J. FRENKEL (Nature, 1935, 136, 167—168).—The solid, liquid, and gaseous states must be regarded as forming one continuous sequence, the sharp transition points, i.e., m.p. and b.p., being substitutes for continuous transitions through unstable intermediate states corresponding with the hook-like parts of the *p-v* curve.

L. S. T.

Coalescence in stages between two drops of a liquid. I. W. WARK and A. B. COX (Nature, 1935, 136, 182).

L. S. T.

Determination of mol. wt. of cellulose by a dynamic osmotic method. J. MARCHLEWSKA (Rocz. Chem., 1935, 15, 331—338).—A dynamic method is described, which gives vals. of 27,000—37,000 for various samples of cellulose acetate.

R. T.

Relation between vitrification temperature and mol. wt. of organic compounds. F. K. GORSKI (Physikal. Z. Sovietunion, 1934, 6, 513—514).—The relation $T_g - BM^{2/3}$ (T_g —abs. temp. of vitrification, *M*=mol. wt., *B*=const.) holds for 17 org. compounds with T_g =94—250° abs., the mean val. of *B* being 6.77. A similar expression is proposed for two-component systems.

CH. ABS. (e)

Absorption of sound in gases. V. O. KNUDSEN (Science, 1935, 81, 578—581).—A summary.

L. S. T.

Tracing of standing sound and ultra-sonic waves in gases. O. BRANDT and H. FREUND (Z. Physik, 1935, 95, 415—416).

A. B. D. C.

Rendering visible ultra-sonic waves in gases and determination of their intensities. R. POHLMAN (Naturwiss., 1935, 23, 511).—A method for photographing ultra-sonic waves of small intensities is described. The intensity can be determined photo-metrically.

A. J. M.

Effect on supersonic dispersion in gases, of (A) pressure. W. RAILSTON and E. G. RICHARDSON. (B) Temperature. H. L. PENMAN (Proc. Physical Soc., 1935, 47, 533—542, 543—548).—(A) Measurements of $\lambda\lambda$ and absorption for supersonic radiation of frequencies 40—2000 kc. per sec. at pressures ≥ 2 atm. were made in CO_2 , N_2O , and SO_2 .

(B) Measurements of $\lambda\lambda$ of supersonic radiation of frequencies 40—140 kc. per sec. were made in CO_2 , N_2O , and SO_2 for the range room temp.—200°. Calc. velocities at const. density plotted against temp. show supersonic dispersion by a sharp fall of velocity in CO_2 at a temp. which increases with the frequency of the source. The relation of results to theories of supersonic dispersion is discussed.

N. M. B.

Crystal structure and electrical properties. VI. The eight principal parameters of electrical conductivity of bismuth single crystals in magnetic fields. O. STIERSTADT (Z. Physik, 1935, 95, 355—364).

A. B. D. C.

Influence of pressure on the electrical resistance of hard-drawn gold wire in different stages of annealing, and of soft gold wire. A. MICHELS and M. LENNSEN (Physica, 1935, 2, 591—596; cf. A., 1930, 281).—Measurements are recorded from 1 to 2900 atm. of the resistance of drawn Au wire at 25°, 50°, 75°, and 100° after annealing at 25—400°. After the application of pressure hysteresis was observed.

H. J. E.

Theory of electrical resistance anomaly of ferromagnetic substances. T. HIRONE (Sci. Rep. Tôhoku, 1935, 24, 122—127).—The accelerated decrease of the resistance with temp. below the crit. temp. is attributed to the mean free path of the conduction electron being decreased by the rotational vibration of the mol. magnets in the Honda-Ôkubo model of a ferromagnetic substance (Physical Rev., 1917, 10, 705). This is confirmed by existing data.

R. C.

Electrical resistance of iron below the Curie point and the resistance anomaly of ferromagnetic materials. A. DRIGO (Atti R. Ist. Veneto Sci., 1934, 93, 1163—1172; Chem. Zentr., 1935, i, 1186—1187).—The electrical resistance of Fe below the Curie point depends on the spontaneous magnetisation and is \propto the temp. Fe resembles Ni, the observations agreeing with theory.

H. J. E.

Thermo-electric effect and the superconducting state. E. F. BURTON, F. G. A. TARR, and J. O. WILHELM (Nature, 1935, 136, 141).—With Sn and

Pb no thermo-electric effect exists when both junctions are in the superconducting state. The effect appears when either one of the junctions is raised above the superconducting point of one of the metals. L. S. T.

Thermo-electromotive force produced by magnetisation. T. KOUSMINE (Helv. phys. Acta, 1934, 7, 732—772; Chem. Zentr., 1935, i, 863).—Data are recorded for the thermo-e.m.f. in the system Fe or Ni-Cu, with a const. temp. gradient, when the ferromagnetic material was magnetised up to saturation. H. J. E.

Influence of magnetisation while hot and of crystallisation on the shape of the thermo-magnetic curves. A. MICHEL and G. CHAUDRON (Compt. rend., 1935, 200, 2171—2173).—The stabilisation temp. for rhombohedral Fe_2O_3 and for ferrites of Ba and Pb are 1250° and 950° , respectively. H. J. E.

Thermomagnetic behaviour of ferromagnetic powders. H. FORESTIER (Compt. rend., 1935, 201, 45—47; cf. A., 1926, 566).—The effects of grain size and of crystal structure are described for Fe_3O_4 and Fe_2O_3 . H. J. E.

Mechanical damping of ferromagnetic materials in magnetisation. M. KERSTEN (Z. tech. Physik, 1934, 15, 463—467; Chem. Zentr., 1935, i, 1186). H. J. E.

Transition metals on the basis of quantum mechanics. N. F. MOTT (Proc. Physical Soc., 1935, 47, 571—588).—Theoretical. The magnetic susceptibilities and electrical conductivities of Co, Ni, and Pd and of their alloys with Cu, Ag, and Au are considered. The no. of electrons in the outermost s state must be about 0.6 per atom in the transition metals and 1 in the noble metals, explaining certain magnetic properties. A quantum-mechanical explanation, supported by resistance measurements, is given of the relatively high resistance of the transition metals. N. M. B.

Magnetic resistance variation of metal crystals. M. KOHLER (Z. Physik, 1935, 95, 365—382).—Magnetic variation of resistance depends on the current passing and on crystallographic orientation (cf. Stierstadt, this vol., 1062). A. B. D. C.

Number of electrons contributing to the paramagnetism of nickel. L. NEEL (Compt. rend., 1935, 201, 135—137).—The effects of metals alloyed with Ni on its paramagnetism are \propto the nos. of their valency electrons. The electrons of the alloyed metal annul the magnetic contribution of the Ni electrons. H. J. E.

Gadolinium, a new ferromagnetic metal. G. URBAIN, P. WEISS, and F. TROMBE (Compt. rend., 1935, 200, 2132—2134).—The Curie point is at $16 \pm 2^\circ$. The sp. magnetisation of Gd in strong fields is $>$ that of Fe. Data are recorded. The at. moment of Gd is 35.4 magnetons, that of Fe being 11. H. J. E.

Diamagnetism of elements in the powdered state. M. R. VERMA and I. C. GUPTA (Current Sci., 1935, 3, 611).—Red and grey Se powdered under C_6H_6 or PhMe showed only in an extreme case a fall

in diamagnetic susceptibility from -3.03×10^{-7} to -2.69×10^{-7} at a particle size of 0.4μ (cf. A., 1934, 1159). Washing with dil. HCl restored the original val. Red Se passes into the black form on prolonged exposure to light, and the decrease in diamagnetic susceptibility reported in certain cases may be due to transition to a metastable allotrope on powdering. Rao's results (A., 1931, 1357) are criticised. L. S. T.

Magnetic properties of solutions of cadmium in molten cadmium chloride and of molten calomel. J. FARQUHARSON and E. HEYMANN (Trans. Faraday Soc., 1935, 31, 1004—1010).—The absence of paramagnetism excludes the existence of CdCl ; the probability of the existence of either Cd_2Cl_2 or an at. solution of Cd in CdCl_2 is discussed. Comparison of the magnetic properties with the electrical conductivity of molten calomel suggests that it consists of Hg_2Cl_2 mols. which are partly dissociated into Hg_2^{++} and Cl^- . A marked rise in diamagnetic susceptibility occurs when CdCl_2 , PbCl_2 , or Hg_2Cl_2 melts. E. S. H.

Magnetic susceptibilities of salts of the iron group elements. R. B. JANES (Physical Rev., 1935, [ii], 48, 78—83).—Measurements of paramagnetic susceptibilities of powdered crystals over the temp. range 80 — 300° abs. are given for $\text{K}_3\text{Cr}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO})_2 \cdot 4\text{NH}_3$, $\text{Ni}(\text{CN})_2 \cdot \text{C}_6\text{H}_5\text{NH}_2$, NiO , $\text{K}_3\text{Co}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{NH}_3$, $\text{CoSO}_4 \cdot 6\text{NH}_3$, $\text{Co}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuK}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$. The results agree with Van Vleck's predictions. N. M. B.

Magnetic susceptibility of cerium chloride in aqueous solution and its variation with temperature. J. LIQUIER-MILWARD (Proc. Physical Soc., 1935, 47, 559—570).—Using a slightly modified Quincke ascension method, measurements were made for the concn. range 8 — 37.5% anhyd. salt, and temp. 7 — 70° . The variation of mol. susceptibility with temp. follows a Curie-Weiss law, $\chi_c(T + \Delta) = C$, where $C = 0.762$ irrespective of concn.; Δ , however, \propto no. of ions present per unit vol., and increases from 45 to 63 in the range considered. The effective magneton no. of the ion Ce^{++} , if calc. from $\mu_{\text{eff}} = 14.07 \sqrt{\chi_c(T + \Delta)}$, has a const. val. 12.36. Results are compared with available data from the spectroscopic ground states of the rare-earth group. N. M. B.

Determination of the m.p. of calcium, strontium, and barium. F. HOFFMANN and A. SCHULZE (Z. Metallk., 1935, 27, 155—158).—Determinations in an A atm. using vac.-sublimed metal gave the following vals.: Ca 851° , Sr 771° , Ba 704° ($\pm 1^\circ$ in each case). Vals. are also given for the commercial metals. A. R. P.

Heat capacities at low temperatures. I. Heat capacities of some organic substances. S. AOYAMA and E. KANDA (Sci. Rep. Tôhoku, 1935, 24, 116—121).—The mol. heats of C_6H_6 , Et_2O , PhMe, PhOH, and PhI have been determined at 80 — 230° abs. R. C.

Heat capacity of potassium chloride from 2.3° to 17° abs. W. H. KEESOM and C. W. CLARK

(Physica, 1935, 2, 698—706).—Data are recorded. Blackman's theory (this vol., 573) is partly confirmed.

H. J. E.

Heat capacity of methane and its halogen derivatives from spectroscopic data. R. D. VOLD (J. Amer. Chem. Soc., 1935, 57, 1192—1195).—The mol. heat capacities of CH_4 , MeCl , CH_2Cl_2 , CHCl_3 , and CCl_4 over the range 0—500° have been calc., with an accuracy of about 3%, from their Raman spectra, using the equation for a polyat. gas. E. S. H.

Relationships between constitution and magnitude of mol. heat of fusion of organic compounds. II. Synthesis of 1:4-endoazocyclohexane.—See this vol., 1133.

Homology in long-chain compounds. I. Oleic acid and *n*-alkyl oleates. L. KEEFLER and J. H. McLEAN (J.S.C.I., 1935, 54, 178—185t).—The prep. of oleic acid and the *n*-alkyl oleates is described, and densities, mol. vols., and heat of combustion have been determined.

Vapour pressures of solid krypton. W. H. KEESOM, J. MAZUR, and J. J. MEIHZIJEN (Physica, 1935, 2, 669—672).—Data are recorded from the triple point (115.94° abs., $p=54.9$ cm.) to 78° abs. Vals. agree with theory except near 115° abs.

H. J. E.

Vapour pressures of the isotopic forms of water. M. H. WAHL and H. C. UREY (J. Chem. Physics, 1935, 3, 411—414).—The ratio of v.p. of H_2O^{16} and HDO^{16} and that of H_2O^{16} and H_2O^{18} has been measured at 11.25°, 23.00°, 35.6°, and 46.35°, using the method of fractional distillation of dil. solutions of D_2O in H_2O under conditions such that the Rayleigh distillation formula held. Separation of the H isotopes by fractional distillation of H_2O is possible; that of the O isotopes would be more difficult.

H. J. E.

Certain physical properties of cyanogen and its halides. R. P. COOK and P. L. ROBINSON (J.C.S., 1935, 1001—1005).—The prep. and purification of C_2N_2 , CNCl , CNBr , and CNI , used for obtaining vals. for v.p. and density, liquid density, and surface tension, are described. The temp. coeff. of the liquid density and surface tension is given. Physical properties of these compounds and of HCN are tabulated, and are discussed with reference to structure and association in the liquid state.

N. M. B.

Comparison of physical properties of hydrogen and deuterium iodides. J. R. BATES, J. O. HALFORD, and L. C. ANDERSON (J. Chem. Physics, 1935, 3, 415—420).—Data for the absorption coeffs. and v.p. of HI and DI are recorded. Absorption by HI occurs at longer λ than that of DI . The v.p. of DI is slightly > that of HI at a given temp. Theoretical reasons for these differences are discussed.

H. J. E.

Vapour pressure of hexachloroethane. P. J. VAN DER LEE (Z. anorg. Chem., 1935, 223, 213—216).—Between 62° and 216°, the v.p. of solid C_2Cl_6 is given by $\log_{10} p = 8.640 - 2636.1/T$; for the liquid, $\log_{10} p = 7.483 - 2103.6/T$. The triple point is 186.8°. Latent heats of sublimation, evaporation,

and fusion are 12.0, 9.6, and 2.4 kg.-cal. per mol., respectively.

J. S. A.

Sublimation pressures of solid oxygen and nitrogen. S. AOYAMA and E. KANDA (Sci. Rep. Tôhoku, 1935, 24, 107—115).—The v.p. of O_2 has been measured at 37—65° and that of N_2 at 35—70° abs. The results agree well with the calc. vals.

R. C.

Structure of betaine. E. NORDT and H. G. TRIESCHMANN (Z. ges. Naturwiss., 1935, 1, 197—198; cf. this vol., 436).—The approx. heats of sublimation of the betaines of $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$ and sulphanilic acid are 24—44 and 12—20 kg.-cal., respectively, showing the mols. to be heteropolar.

H. J. E.

Volume coefficient of expansion of deuterium. J. B. M. COPPOCK (Trans. Faraday Soc., 1935, 31, 913—914).—Within the limits of experimental error (1 in 4000) α_p for D_2 is identical with the val. for H_2 .

J. W. S.

Approximate determination of the critical constants of unassociated substances. A. FERGUSON and S. J. KENNEDY (Trans. Faraday Soc., 1935, 31, 1000—1003).—Simple relations are developed to assist in the approx. calculation of crit. data from available data.

E. S. H.

Real gases according to the thermodynamic equation of state. VII. Boyle's law for helium. W. JACYNA (Z. Physik, 1935, 95, 409—414).—The positions of Amagat's minima are discussed.

A. B. D. C.

Equation of state of liquids. Negative internal pressure at high temperatures. P. WEISS (Compt. rend., 1935, 200, 1700—1702).—Theoretical. At a sufficiently high temp. the internal pressure is shown to become negative.

H. J. E.

Rotational entropy of non-rigid polyatomic molecules. M. L. EIDINOFF and J. G. ASTON (J. Chem. Physics, 1935, 3, 379—383).—Theoretical.

H. J. E.

Thermal conductivity of quartz at low temperatures. W. J. DE HAAS and T. BIERNASZ (Physica, 1935, 2, 673—682).—Measurements parallel to the crystal axis are recorded at 90—2.7° abs. The thermal resistance rises rapidly below 10° abs. The vals. at low temp. were increased by first heating at 340° and 570°.

H. J. E.

Viscosity of liquid nitrogen, carbon monoxide, argon, and oxygen, and its dependence on temperature. N. S. RUDENKO and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1934, 6, 470—477).—Data for the m.p.—b.p. ranges are recorded.

CH. ABS. (e)

Viscosity of sulphuric acid and its chlorides. G. P. LUCHINSKI (J. Phys. Chem. U.S.S.R., 1934, 5, 848—853).—Vals. of η as a function of temp. are given for H_2SO_4 by $\eta_t = 0.001236/(v_t - 0.5411)$, for SO_2Cl_2 by $\eta_t = 0.000759/(v_t - 0.5114)$, and for ClSO_3H by $\eta_t = 0.000698/(v_t - 0.5440)$, v being the sp. vol. The limiting v at low temp. is given by $\omega = pM - qM^2$, where $p = 0.010135$, $q = 0.000047$, and $M = \text{mol. wt.}$ ω/M for ClSO_3H is the arithmetic mean of ω/M for H_2SO_4 and SO_2Cl_2 .

CH. ABS. (e)

Viscosity and heat conduction according to the geometrical weight method compared with other treatments. W. S. KIMBALL (Phil. Mag., 1935, [vii], 20, 355—390).—Theoretical. The mathematical treatment of Chapman and Enskog is shown to be inadequate for the problem of viscosity and heat-conductivity distribution.

A. J. M.

Logarithmic increments of fluidity. R. LAUTIE (Bull. Soc. chim., 1935, [v], 2, 1467—1470).—The log. of fluidity is an additive function. Consts. assigned to C, H, and to various rings are used to calculate the fluidities of certain hydrocarbons. Anomalies between the calc. and experimentally determined vals. for higher cyclanes are discussed.

T. G. P.

Dispersing and condensing tendencies in a viscous, compressible gas. G. STROMBERG (Astrophys. J., 1935, 81, 474—478).—Certain conditions for general and local expansion and condensation in a viscous, compressible gas have been formulated.

L. S. T.

Complex viscosity. A. GEMANT (Naturwiss., 1935, 23, 406—407).—The increase of damping with frequency, in so far as it affects the theory of dipole losses due to mol. rotation, and of sound waves in solids, may be explained by an extension of the theory applied to liquids by Hencky, depending on Maxwell's conception of relaxing elasticity.

A. J. M.

Physical properties of surfaces. I. Kinetic friction. W. G. BEARE and F. P. BOWDEN (Phil. Trans., 1935, A, 234, 329—354).—Measurements of kinetic friction, using a modified Hardy apparatus, showed that for highly polished unlubricated surfaces of mild steel, Ni, and glass the coeff. of kinetic friction μ_K is independent of load, area of contact, and velocity; contaminating films give rise to apparent deviations from these results. For lubricated surfaces a transition from "fluid" to "boundary" lubrication is shown, and in the latter state μ_K is independent of velocity and area of contact. With some lubricants (notably octyl alcohol on steel) μ_K decreases with increasing load, with others it is const.; μ_K -load is not connected with viscosity of the lubricant. No latent period was found for kinetic friction. The effect of chemical composition on μ_K was investigated for homologous series of hydrocarbons, alcohols, and acids.

N. M. B.

X-Ray examination of barium-aluminium alloys. K. R. ANDREAS and E. ALBERT (Z. Metallk., 1935, 27, 126—128).—No solid solutions exist and only one compound, Al_4Ba , is formed; this has a body-centred tetragonal lattice, a 4.53, c 11.14 Å.

A. R. P.

Optical constants of the copper-nickel alloys. H. LOWERY, J. BOR, and H. WILKINSON (Phil. Mag., 1935, [vii], 20, 390—410).—Vals. of n , absorption coeff., and reflexion coeff. for the complete range of alloys have been determined for λ 5780, 5461, and 4358 Å. The specimens were prepared by a method of polishing which gives a very thin flowed layer. The various property-composition curves are continuous, but not linear.

A. J. M.

Structure of nickel-cobalt alloys. W. BRONIEWSKI and W. PIETREK (Compt. rend., 1935, 201, 206—208; cf. A., 1933, 771).—The variation of the electrical conductivity, thermoelectric properties, Curie points, expansion coeffs., hardness, and magnetic properties of alloys affords no evidence of compound formation. The alloys with <75% Co are solid solutions of γ -Co in α -Ni, and those with >75% Co solutions of α -Ni in Co.

H. J. E.

Equilibrium diagrams of binary alloys of tin. E. S. HEDGES and C. E. HOMER (Tech. Publ. Int. Tin Res. Dev. Council, B, No. 2, 90 pp.).—A compilation of equilibrium diagrams of binary systems containing Sn with Al, Sb, As, Ba, Bi, Cd, Ca, Ce, Cr, Co, Cu, Ga, Au, I, Fe, La, Pb, Li, Mg, Mn, Hg, Ni, P, Pt, K, Se, Si, Ag, Na, Sr, S, Te, Tl, and Zn, respectively, with notes on the transformations occurring in each system, and a discussion of the interpretation of the diagrams.

E. S. H.

Kinetics and mechanism of the allotropic transformation in the Pd-Cu system. (X-Ray investigation with single crystals containing 40—50 at.-% of palladium.) L. GRAF (Physikal. Z., 1935, 36, 489—498).—The transition of the α -phase (stable at room temp.) of Pd-Cu alloys containing 40—50 at.-% Pd into the β -phase (stable at temp. >600°) has been investigated by the X-ray method. It is a two-phase transition. The transition point is the higher, and the transition velocity the smaller, the higher is the Pd content, and for single crystals < for polycryst. specimens. The transition starts at points of instability in the crystal, e.g., on the surface, at nuclear boundaries, or where there has been plastic deformation. Previous heat-treatment of the alloy has no effect on the kinetics of the transition. There are certain exact geometrical relationships between the cryst. forms of the two phases. $[311]_\alpha$ is parallel to $[100]_\beta$, and $(001)_\alpha$ is parallel to $(113)_\beta$. This suggests that the breakdown of the β -crystal starts from quite definite energy-labile planes, the atoms set free arranging themselves in definite positions with respect to the β -crystal.

A. J. M.

Cubic sodium tungsten-bronzes. G. HAGG (Z. physikal. Chem., 1935, B, 29, 192—204).—These have the composition Na_xWO_3 , where $x=0.3-1$, and all their lattices are of the perovskite type. When $x=1$ the unit cell contains 1 NaWO_3 mol., $a \approx 3.850$ Å., and the colour is yellow. As x falls the colour changes through red to violet, being deep bluish-violet when $x \approx 0.3$, and a falls steadily, but the original W-O lattice is retained. The deepening in colour is due to progressive oxidation of W^{VI} to W^{VII} ions. This is compensated by a fall in the no. of Na^+ ions, an increasing no. of Na^+ ion positions in the lattice being left empty. The colours are surface colours, not body colours. At 20—350° the bronzes are electronic semi-conductors with high conductivity and small temp. coeff. Tetragonal W-bronzes contain less Na than the cubic bronzes so far examined.

R. C.

X-Ray analysis of binary metallic alloys at higher temperatures. G. F. KOSOLAPOV and A. K. TRAPEZNIKOV (J. Tech. Phys. U.S.S.R., 1934, 4, 1622—1624).—A 7 : 3 Cu-Pb alloy at 320° gave both

Cu and Pb lines, but at 340° only Cu lines. Those of Pb reappeared on cooling. CH. ABS. (e)

Equilibrium relations in the copper corner of the ternary system copper-tin-beryllium. E. S. ROWLAND and C. UPTHEGROVE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., 1935, Tech. Publ. 613, 26 pp.).—Data based on thermal analysis, X-ray studies, and quenching experiments are given for Cu-Sn-Be alloys ($\geq 32\%$ Sn, $\geq 1\%$ Be). CH. ABS. (e).

X-Ray examination of α -iron magnet alloys. R. GLOCKER, H. PFISTER, and P. WIEST (Arch. Eisenhüttenw., 1934—1935, 8, 561—563).—The effect of heat-treatment on the X-ray patterns of Fe alloys containing (a) Al 12 and Ni 30% and (b) Al 10, Ni 22.5, and Co 13% has been determined and the results correlated with the changes in coercivity (C). No line-broadening or change in lattice parameter (a) occurs up to the point at which max. C is obtained; only very prolonged annealing at high temp., by which C is reduced to a very low val., causes any change in a. At still higher temp. a phase with a γ -Fe lattice is pptd. Hence the characteristic magnetic properties of these alloys cannot be ascribed to a favourable particle size of the pptd. phase; the optimum magnetic properties are obtained when the alloy is in a similar condition to that in which duralumin shows its max. hardness, i.e., when the new phase is ready to be pptd. but before its pptn. can be detected by X-ray or micrographic examination. A. R. P.

System iron-cobalt-tin. W. KOSTER and W. GELLER (Arch. Eisenhüttenw., 1934—1935, 8, 557—560).—The system has been investigated by thermal and micrographic methods up to 40% Sn. The compounds Fe_2Sn and Co_2Sn form a continuous series of solid solutions (δ). The peritectic equilibrium $\alpha + \text{liquid} \rightleftharpoons \text{Fe}_2\text{Sn}$ is displaced to higher temp. by addition of Co and merges with the $\alpha + \text{liquid} \rightleftharpoons \gamma$ equilibrium of the Fe-Co system, the temp. of which falls rapidly with addition of Sn, and with the equilibrium $\text{liquid} \rightleftharpoons \gamma + \text{CoSn}_2$, the temp. of which falls only slightly with addition of Fe, to form the 4-phase equilibrium: $\text{liquid} + \gamma \rightleftharpoons \alpha + \delta$. The solubility of δ in the α - and γ -phases decreases with fall in temp. and these alloys can therefore be pptn.-hardened. Hardness and coercivity vals. for some alloys with 15 and 20% Co are tabulated and some characteristic microstructures are shown. A. R. P.

Induction period of the austenite transformation. E. SCHEIL (Arch. Eisenhüttenw., 1934—1935, 8, 565—567).—The degree to which a transformation can be suppressed depends on the time that elapses before nuclei of the new phase form. This induction period can be calc. from the relation between the transformation temp. and the rate of cooling; for the austenite transformation the relation between induction period and transformation temp. passes through a min. the position of which has not yet been satisfactorily determined. A diagram has been constructed showing the relation between induction period, transformation temp., and the C content of steels based on the work of Sato (A., 1931, 557); this consists of three zones: ferrite, cementite, and pearlite. The formation of a pearlite nucleus in the

pearlite zone takes place more readily than that of a ferrite or cementite nucleus, and the influence of already formed crystals of these constituents is small, being greatly exceeded by the influence of the C content of the austenite. The inoculating effect of various substances on ferrite decreases in the order: sulphides, austenite grain boundaries, oxides.

A. R. P.

Chemical stability of metallic solid solutions. V. V. SKORCHELETTI and B. M. IDELICHIK (Metallurg, 1934, 9, No. 2, 30—43; No. 3, 27—38).—The dissolution of Mg-Cd alloys in dil. H_2SO_4 , NaCl, and aq. NH_3 has been studied. At 10° there is a sharp reaction limit at 25 mol.-% and a less sharp limit at 12.5 mol.-% Cd. At 25° these limits lose their sharpness, owing to the diffusion of Cd atoms above 20°. When the Mg atoms are dissolved from the Cd-rich planes the holes left are large enough for H^+ to pass, but not for SO_4^{--} . It is inferred that the attack must be due to SO_4^{--} . With Ni-Cu alloys and aq. NH_3 there are reaction limits at 12.5, 25, and 50 mol.-% Ni; no such limits are observed with S_2Cl_2 . CH. ABS. (e)

Thermo-electric forces of some alloys at 2.5—17.5° abs. W. H. KEESOM and C. J. MATTHIJS (Physica, 1935, 2, 623—632; cf. A., 1932, 683).—Data are recorded for Ag with 0.91 at.-% Au, and for Au with small additions of Fe, Co, Ni, Mn, and Cr.

H. J. E.

X-Ray study of the inter-diffusion of copper and zinc. E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1935, A, 149, 282—298).—With ungraded particles, Cu-Zn alloys can be prepared in powder form by the inter-diffusion of filings at temp. $< \text{m.p.}$ of Cu but $>$ that of Zn. The photographs show, in addition to the α -phase, the production and disappearance of the β -phase from its reflexion lines. The γ -phase is not revealed. The rate of diffusion is not affected when the particles are exposed to the atm. for short intervals of time. Inter-diffusion takes place more readily between unannealed than between annealed particles. With graded particles the amount of inter-diffusion in a given time is the greater the smaller is the size or the lower the grade of the particle. A linear relation exists between the parameter val. and the grade val. for a given time of inter-diffusion.

L. L. B.

Molecular volumes of electrolytes in concentrated solutions. B. PESCE (Gazzetta, 1935, 65, 448—452).—The variation of the mol. vol. with the concn. has been studied for solutions of $\text{Sr}(\text{ClO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Na}_2\text{Cr}_2\text{O}_7$. Deviations from linearity are observed in some cases. O. J. W.

Viscosity formula for binary mixtures, the association degrees of constituents being taken into consideration. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1935, 10, 248—252; cf. this vol., 817).—The author's formula (A., 1934, 723) has been applied successfully to the data for molten C_{10}H_8 and molten Ph_2 . When it is applied to molten KCl good agreement is also found. Extrapolation of the formula to temp. $< \text{m.p.}$ suggests differences between electrolytes and non-electrolytes. W. R. A.

Influence of sexatomic rings on the viscosity of solutions of polymerides with filiform molecules. S. BEZZI (Atti R. Accad. Lincei, 1935, [vi], 21, 372—380).—Solutions of various polymerides, $(C_6H_4 \cdot CH_2)_n$, obtained by condensing CH_2PhCl under different conditions, have been examined. The results indicate that hydrocarbons with aromatic nuclei in the chain have the same viscosity as paraffins of equal length, and that the high vals. shown by cellulose must be due to some other cause.

T. H. P.

Molecular association and polarisation of ethyl alcohol in various solvents. P. MORTIER (Bull. Acad. roy. Belg., 1935, [v], 21, 594—605).—Polarisation-composition curves for binary mixtures of EtOH with C_6H_6 , CCl_4 , C_6H_{14} , $C-H_{16}$, and CS_2 agree with the theory of Wolf and Herold (this vol., 24).

D. R. D.

B.p. of the constant-boiling mixture $HCl-H_2O$. W. E. CADBURY, jun. (J. Chem. Educ., 1935, 12, 292).—A crit. examination shows that the val. 110° usually quoted should be replaced by $108.584^\circ/760$ mm.

L. S. T.

System pyridine-acetic acid. IV. B.p. L. E. SWEARINGEN and R. F. ROSS (J. Physical Chem., 1935, 39, 821—827).—B.p. and d vals. are recorded. The max. b.-p. mixture at 760 mm. contains 58.4 mol.-% AcOH (b.p. 138.35°), but its composition varies with pressure. No complexes are indicated by the b.p.-composition curve.

J. W. S.

Properties of ternary heterogeneous mixtures. P. MONDAIN-MONVAL (Bull. Soc. chim., 1935, [v], 2, 1106—1118).— n_D^{20} and d_4^{20} have been determined for mixtures of EtOH, *iso*- $C_5H_{11}OH$, and H_2O in the region of the crit. point, at which, contrary to Brun (cf. A., 1934, 357), no irregularities occur.

R. S. B.

Intermetallic solid solutions. E. R. JETTE (Trans. Amer. Soc. Min. Met. Eng., Inst. Met. Div., 1934, 111, 53—74).—The conditions which must be fulfilled by solute and solvent atoms in solid solution if Vegard's law holds are identical with those which are required by Raoult's law for liquid solutions. The results of a no. of accurate determinations of lattice consts. for intermetallic systems in which a range of solid solutions exist show that positive and negative deviations from Vegard's law occur.

W. P. R.

Detection of dilute solid solution formation with the iron oxides by means of thermomagnetic analysis. A. MICHEL and A. GIRARD (Compt. rend., 1935, 201, 64—65).—The solid solution of Fe_3O_4 in rhombohedral Fe_2O_3 shows a greatly increased susceptibility, although the X-ray diagram and Curie point of the Fe_2O_3 are unchanged by the solute.

H. J. E.

Influence of the addition of salts on the temperature of [complete] miscibility in the system water-phenol. A. BANCHETTI (Atti Soc. Toscana Sci. Nat., 1935, 44, 1—7).—The temp. is raised by addition of KCl. Over the concn. range 0.0004—0.06 mols. per 1000 g., $t = Ac^B$; if $c > 0.02$, $t = a\sqrt{c+b}$, where t = temp. elevation, c = concn. of KCl, and a , b , A , and B are consts.

D. R. D.

Solubility of noble gases in aqueous salt solutions at 25° . G. ÅKERLÖF (J. Amer. Chem. Soc., 1935, 57, 1196—1201).—The solubility of He and A in several aq. salt solutions has been determined. The salting-out consts. are of the same order of magnitude as those for other non-electrolytes.

E. S. H.

Transition of gas from the dissolved to the dispersed state. N. N. ANDREEV and L. E. KULIKOVA (J. Gen. Chem. Russ., 1935, 5, 366—370).—The relation of the degree of dispersion of bubbles of gas liberated from solutions by reducing the pressure to the solubility of the gas has been determined.

R. T.

Dependence of mist absorption by liquids on the bubble size. I. H. REMY and W. SEEMANN (Kolloid-Z., 1935, 72, 3—12).—The absorption of SO_3 mists by Et_2O , MeOH, EtOH, H_2O , 10% aq. $AgNO_3$, 5% and 20% KOH, and glycerol, respectively, has been investigated. For a given velocity of streaming the absorption decreases as the size of the bubbles carrying the mist increases. The pure solvents are better absorbers than the solutions. The absorption varies almost linearly with the reciprocal of streaming velocity over a wide range, but deviations occur when the velocity is low. A method for determining the no. of bubbles passing, when these exceed a rate of 2000 per min., is described.

E. S. H.

Heptane and its solutions. VI. Solubility of halogens in heptane. J. SEMB (J. Amer. Pharm. Assoc., 1935, 24, 547—553).—The solubilities of Cl_2 , Br, and I in C_7H_{16} have been determined from -23° to 85° , -67° to -12° , and -21° to 78° , respectively. Cl_2 and Br react with the solvent to a variable extent, HCl and HBr probably being catalysts. Reaction of the solutions with various metals is described.

R. S. C.

Absorption of hydrogen chloride into various organic liquids and the calculation of the heat of absorption. II. S. HAMAI (Bull. Chem. Soc. Japan, 1935, 10, 207—211; cf. this vol., 441).—The absorption of HCl by $CHCl_3-CH_2Cl$ and by C_2HCl_3 at 12° , 15° , and 20° and the respective heats of absorption have been determined. Solubilities \propto total bond energies of the solvent.

W. R. A.

Determination of solubility of ethylene, propylene, and butylene in certain solvents at -20° to 40° , at pressures less than atmospheric. V. V. A. KIREEV, S. I. KAPLAN, and M. A. ROMANTSCHUK (J. Gen. Chem. Russ., 1935, 5, 444—449).—Solubility data are recorded for xylene, cracking benzene, kerosene, $C_2H_4Cl_2$, crude C_6H_6 , and heavy solvent naphtha at -20° to 40° , and at 50—760 mm.

R. T.

Solubility of non-electrolytes. II. Influence of polar group on the free energy of hydration of aliphatic compounds. J. A. V. BUTLER and C. N. RAMCHANDANI (J.C.S., 1935, 952—955; cf. this vol., 441).—Partial pressures of NH_3 , Et NH_3 , Pr , NH_2Bu , $EtCO_2H$, $PrCO_2H$, $EtCN$, $PrCN$, $MeOAc$, $EtOAc$, $(CH_2 \cdot OH)_2$, and glycerol over their dil. aq. solutions have been determined and the free energy of hydration, F , calc. Vals. of F for ethers, hydro-

carbons, COMe_2 , AcOH , and PrOAc are calc. from existing data. F for simple compounds is approx. an additive function of the groups present, and is represented by $F - 0.5n \cdot \gamma_{A-W} - \sum a\gamma_{A-W} + 8600$, where n is the no. of H_2O mols. on the surface of the cavity containing the solute mol. and a the no. of H_2O mols. in contact with group A . Vals. are derived for the interaction consts., γ_{A-W} , between various groups and the H_2O mol. The effects of successive OH groups are not additive.

J. G. A. G.

Periodicity in the series of saturated fatty acids. [Solubility.] A. DE KUTHY (J. Chim. phys., 1935, 32, 406—409).—The solubility of digitoxin, cholesterol, $\text{Ca}_3(\text{PO}_4)_2$, and CaC_2O_4 in $2N$ aq. solutions of Na salts of the fatty acids varies periodically as the series is ascended. Salts with an odd no. of C atoms afford solubilities > those afforded by contiguous members with an even no.

J. G. A. G.

Precipitation colorimetry. Effect of ammonium chloride on solubility of $\text{ZnHg}(\text{SCN})_4$ and of $(\text{Co,Zn})\text{Hg}(\text{SCN})_4$. B. V. J. CUVELIER (Z. anal. Chem., 1935, 102, 16—20).—The solubility of $\text{ZnHg}(\text{SCN})_4$ has been determined by a colorimetric method. The solubility of $\text{ZnHg}(\text{SCN})_4$ is increased in presence of NH_4Cl ; the latter must not be present when $\text{Na}_2\text{Hg}(\text{SCN})_4$ is used for the determination of Zn.

S. J. G.

Distribution of saturated aliphatic monocarboxylic acids between two contiguous liquid phases. N. A. DE KOLOSOVSKI, A. BEKTUROV, and F. S. KULIKOV (J. Gen. Chem. Russ., 1935, 5, 319—326).—Data are recorded for the systems H_2O - PhNO_2 - HCO_2H and $-\text{AcOH}$; H_2O - $\text{iso-C}_5\text{H}_{11}$ - OH - EtCO_2H , $-\text{PrCO}_2\text{H}$, and $-\text{Bu}^i\text{CO}_2\text{H}$; H_2O - $\text{Bu}^i\text{CO}_2\text{H}$ - CCl_4 and $-\text{EtBr}$, at 25° .

R. T.

Mechanism of electrodiffusion of hydrogen through palladium. N. I. KOBOSEV and V. V. MONBLANOVA (Acta Physicochim. U.R.S.S., 1934, 1, 611—650).—In the electrodiffusion of H into various gases (H_2 , H_2O , C_6H_6 , etc.) on the other side of the Pd cathode, the following stages are considered: (a) adsorption of H on the Pd surface (polarisation surface), (b) occlusion of the adsorbed H atoms in the inner layers of the metal, (c) transport of occluded atoms through the metal, and (d) the reverse processes of (b) and (a) at the surface of the Pd in contact with the diffusion medium (diffusion surface). The rate of diffusion of H under various conditions has been measured experimentally. The main conclusions are: (1) diffusion is independent of the physical properties of the diffusion medium; (2) poisoning of the polarisation surface accelerates, whereas poisoning of the diffusion surface retards, diffusion; (3) electrolytes, especially KCl and KOH, in the solution on the polarisation side accelerate diffusion; (4) diffusion takes place through the inter-cryst. spaces and the edges of the crystals form the diffusion centres.

O. J. W.

Ionisation of hydrogen in contact with platinum, copper, and nickel. C. Y. MENG, P. A. ANDERSON, and Y. M. HSIEH (J. Chinese Chem. Soc., 1935, 3, 103—114; cf. J.C.S., 1922, 121, 1153).—

The ionisation current i obtained when H_2 is passed over Pt, Cu, and Ni and between Al electrodes has been measured. i increases rapidly with rise of temp. It is inferred that the activity of H desorbed from Pt is not due to ionisation.

R. S.

Adsorption of hydrogen by palladium in presence and absence of water. M. I. TEMKIN and A. N. BAKH (J. Phys. Chem. U.S.S.R., 1934, 5, 809—811).—Neither H_2O nor O_2 has any effect on the rate or amount of H_2 adsorbed by Pd or Pd-black at 15 — 20° . The total adsorption is 67.5 c.c. per g.

CH. ABS. (e)

Adsorption of hydrogen by supported copper poisoned with carbon monoxide. C. W. GRIFFIN (J. Amer. Chem. Soc., 1935, 57, 1206—1208).—A very small quantity of CO causes an increase in adsorption of H_2 up to 1 atm. With greater amounts of CO the adsorption of H_2 increases at low pressure and decreases at higher pressures. By using supported Cu the secondary factors of sorption are eliminated.

E. S. H.

Adsorption of oxygen and the catalysis of hydrogen peroxide by platinum. V. A. ROITER and M. G. LEPERSON (Ber. Ukrain. wiss. Forsch.-Inst. physikal. Chem., 1934, 4, 41—48).—Most of the O adsorbed by Pt in anode polarisation and all the H adsorbed by Pt in cathode polarisation reacts with H_2O_2 . In the electrolysis of dil. H_2SO_4 there is no sorption of electrolytic gas at either electrode if a sufficient $[\text{H}_2\text{O}_2]$ is maintained (anode 0.5%, cathode 1.8% of H_2O_2). Cathodic polarisation increases the catalytic activity of Pt in the decomp. of H_2O_2 . Anodic polarisation lowers it. The activity is const. if electrolysis occurs in presence of H_2O_2 .

CH. ABS. (e)

Sorption of water vapour from a current of air by inorganic gels. E. V. ALEXEEVSKI and F. J. RATSCHINSKI (J. Gen. Chem. Russ., 1935, 5, 299—306).— $\text{Al}(\text{OH})_3$ gel is the best adsorbent for H_2O at low (0—3 mm. pressure), and SiO_2 gel at higher, concns. $\text{Fe}(\text{OH})_3$ gel is at all pressures an inferior adsorbent.

R. T.

Adsorption of dilute organic vapours by active charcoal and their desorption in pure air. A. AKERMANN (Compt. rend., 1935, 201, 210—212).—Data are recorded for a no. of org. substances. Factors controlling adsorption and the retention of the adsorbate are discussed.

H. J. E.

Adsorption by wood charcoal in solutions and gases. H. FISCHER (Kolloid-Beih., 1935, 42, 125—183).—Adsorption velocity and equilibrium have been determined with 11 kinds of C in aq. succinic acid, I in aq. KI, I in EtOH, and methylene-blue in H_2O . The samples of C can be divided into three groups according to their adsorptive power and wettability. The adsorptive power of the samples is in the same order for the above solutions, and also for SO_2 . Adsorption velocity increases as the particle size of the adsorbent is decreased. The adsorption velocity of C_2H_4 and CO_2 is > with solutions, and the order of adsorptive power of the different kinds of C is different. The general phenomena of adsorption of solutes and gases are the same.

E. S. H.

Chemisorption on charcoal. VI. p_H of charcoal suspensions. A. KING (J.C.S., 1935, 889—894).—The p_H vals. of aq. suspensions of sucrose-C activated in O_2 increase linearly with rise of temp., t , of activation, corresponding with the transition from an acidic to a basic condition. The p_H decreases at $t > 900^\circ$ and is slightly dependent on the surface area of the C. Activation equilibrium is rapidly established at low t , but several hr. are required at the higher t . The effects are reversible, and C activated at t_2 when reactivated at t , affords the p_H characteristic of t_1 . The forms of C are stable in vac., but exposure to air decreases the p_H given by the basic type. Similar results are shown by graphite and by commercial animal (I) and vegetable (II) C, and also by activating with CO_2 at higher t . The adsorption of $EtCO_2H$ and $NaOH$ by (I) and (II) varies with p_H in the manner predicted. The interpretation of the phenomena is discussed.

J. G. A. G.

Influence of certain physical and chemical factors on the activity of charcoal. VI. Influence of carriers on the adsorptive properties of charcoal. E. V. ALEXEEVSKI and T. G. PLAT-SCHENOV (J. Gen. Chem. Russ., 1935, 5, 294—298).—The adsorptive capacity of C (from sucrose, starch, albumin, and blood) for C_6H_6 vapour is increased when the C is formed by heating ceramic rings or spheres (kaolin 15, diatomite 55, clay 15, wood-C 15%) saturated with aq. solutions of the source of C, when the porosity of the carrier $\leq 70\%$. R. T.

Sugar charcoal. I. Grain structure of sugar charcoal. II. Sugar charcoal as irreversible colloid. B. L. VANZETTI (Rend. Fac. Sci. Cagliari, 1933, 3, 141—142, 142—144; Chem. Zentr., 1935, i, 942).—The grain structure of charcoal produced by the action of H_2SO_4 on carbohydrates is detectable ultramicroscopically after progressive replacement of H_2O by $EtOH$, $PhMe$, and paraffin.

II. After dehydration in vac. at 120° , only 7.7% of the original H_2O was taken up again. J. S. A.

Examination of positively- and negatively-charged carbon surfaces by adsorption of thorium-B. H. R. KRUYT and T. KRUYT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 570—577).—Th-B in acid solution (as Th-B'') is far more strongly adsorbed by active C with a negatively-charged surface (A., 1931, 796) than by positively-charged C. The reverse is true in alkaline solution (Th-B as Th- BO_2''). D. R. D.

Chemical reactions of water adsorbed on glass. H. E. BENT and G. J. LESNICK (J. Amer. Chem. Soc., 1935, 57, 1246—1250).—The amount of H_2O has been measured by the discharge of the red colour of CPh_3Na (I) in Et_2O . The results show that the amount of H_2O , n , removed by (I), expressed as thickness of a layer in mols., is given by $n = 5(0.25 \times 10^{-10} t + 1)$, where t is the time in hr. during which the glass has been in contact with (I). The v.p. of H_2O in equilibrium with (I) is $< 10^{-12}$ mm., and probably of the order of 10^{-26} mm. E. S. H.

Loss of hydrogen atoms on water-poisoned glass surfaces. W. STEINER (Trans. Faraday Soc.,

1935, 31, 962—966).—From published results (cf. this vol., 587) the calc. adhesion coeff. of H on a glass surface poisoned by adding 2.3—3.5% of H_2O vapour to the flowing mixture of H and H_2 is 2.6×10^{-6} — 9×10^{-6} . E. S. H.

Adsorption of organic substances at crystal surfaces. III. Adsorption of sodium laurate by barium sulphate. N. A. HELD and K. N. SAMOCHVALOV (Kolloid-Z., 1935, 72, 13—17; cf. A., 1934, 359).—The sp. surface of $BaSO_4$ powder has been determined (1) by microscopical measurement, and (2) by adsorption measurements with Na laurate in H_2O and lauric acid in C_6H_6 . Comparison of the results shows that Na laurate is absorbed by $BaSO_4$ in H_2O as a bimol. film. The stabilisation of $BaSO_4$ and flotation phenomena are explained by assuming that the second mol. layer has its polar end turned towards the solution. E. S. H.

Transference of surface changes inside crystal systems. IV. D. BALAREV [with K. ANDREEV, E. ZANKOVA, and P. DAMOVA] (Kolloid-Z., 1935, 72, 25—26; A., 1934, 485).—The addition of small amounts of $CaFe_2O_4$, $CaTiO_3$, $CaMoO_4$, $CaZnO_2$, or $CaCdO_2$ lowers the decomp. temp. of $CaCO_3$ throughout the whole system. E. S. H.

Exchange adsorption of ions on colloidal arsenic trisulphide. V. A. KARGIN and H. B. KLIMOVITZKAJA (Acta Physicochim. U.R.S.S., 1935, 1, 729—740).—The Ba, Ca, Mg, and Cl adsorbed in the coagulation of As_2S_3 sols by 0.2N- $BaCl_2$, - $CaCl_2$, and - $MgCl_2$, and the acid content of the filtrate have been determined gravimetrically and potentiometrically, respectively. Adsorption of Cl is very small. There is no equivalence in the exchange adsorption, the quantity of strong acid in the filtrate being $>$ the adsorbed cation. The filtrate contains H_3AsO_3 , initially present in the intermicellar liquid of the As_2S_3 sol, and acting as a stabiliser. H_2S is not responsible for stabilisation. H. J. E.

Adsorptive property of silica gel. I. Chemical activity of residual water in activated silica gel. M. R. A. RAO and B. S. RAO. II. Adsorptive properties of silica gel containing residual hydrogen chloride. III. Volume changes produced on displacement of adsorbed liquids in silica gel by water. IV. Liberation of air from silica gel capillaries during adsorption of liquid. V. Specific gravity of silica gel under various liquids. M. R. A. RAO (J. Indian Chem. Soc., 1935, 12, 322—325, 326—330, 331—335, 336—339, 340—342).—I. CCl_4 vapour reacts with the residual H_2O in activated SiO_2 gel. The reaction is perceptible at 110° and fairly rapid at 300° , forming $COCl_2$ and HCl . By this reaction all the residual H_2O can be removed; the resulting gel retains HCl very firmly.

II. The adsorptive capacity of the gel for CCl_4 and its selective adsorption from a mixture of $EtOH$ and C_6H_6 have been determined. The HCl gel takes up less liquid, but the selectivity is enhanced.

III. The vol. changes caused by displacement of adsorbed C_6H_6 , $PhMe$, CCl_4 , $PhNO_2$, or NH_4Ph by H_2O have been determined. Selective adsorption of C_6H_6 from a mixture with CCl_4 has been observed.

IV. Measurement of the vol. of air liberated when H_2O wets SiO_2 gel shows that the air has a pressure of 2 atm. in the gel space.

V. The apparent sp. gr. varies with the liquid in which SiO_2 gel is immersed. It is assumed that the liquids vary in their power of penetrating into the capillaries present in the gel. E. S. H.

Selective adsorption and its significance. I. **Nature of selective adsorption.** M. R. A. RAO (J. Indian Chem. Soc., 1935, 12, 345—355).—Selective adsorption by SiO_2 gel in the mixtures $\text{EtOH}-\text{C}_6\text{H}_6$, $\text{EtOH}-\text{CCl}_4$, C_6H_6 - and $\text{C}_5\text{H}_5\text{N}$ -heptane has been investigated. Assuming that the liquid held in the capillaries of the gel is identical in composition with the bulk liquid, whilst that adsorbed at the gel surface is responsible for the selectivity, a method of calculating the true adsorption of each constituent has been developed. E. S. H.

Adsorption of aluminium hydroxide by kieselguhr. E. C. C. BALY and W. P. PEPPER (Nature, 1935, 136, 28).—The curve obtained when the adsorption of $\text{Al}(\text{OH})_3$ is plotted against the electrokinetic potential (ζ) of the preps. in 0.1N-AcOH indicates that $\text{Al}(\text{OH})_3$ is first adsorbed as a unimol. layer by the kieselguhr surface and when this layer is completed the ζ val. is 75.4 mv. When a second unimol. layer is deposited ζ falls to 61.2 mv. and this layer has the same properties as the unadsorbed surface. The enhanced ζ val. of the first layer indicates that the mols. in the adsorbed unimol. layer must be activated in some way. L. S. T.

Selective adsorption from soap solutions. H. A. NEVILLE and M. HARRIS (Amer. Dye stuff Rep., 1935, 24, 312—314, and J. Res. Nat. Bur. Stand., 1935, 14, 765—770).—In the production and removal of foam from a neutral 0.25% aq. solution of pure olive oil soap (p_H 10.0) by a current of air the residual liquor becomes more alkaline (p_H 10.5) and less conc. (0.08% soap), whilst the condensed foam becomes more acid (p_H 9.6) and more conc. (1.13% soap) and is turbid until the addition of alkali. These changes are due to the formation of an acid soap at the air-solution interface. The composition of the foam is const. during its continuous removal from olive oil soap. Similar changes occur when Na_2CO_3 is present in the soap, but the foam is less stable due to repression of hydrolysis. When various substances are added to olive oil soap followed by filtration the residual liquor increases in alkalinity (p_H 10.1—10.4) with lampblack, paraffin, and olive oil (0.33% free fatty acid), and decreases in alkalinity (p_H 9.2) with fuller's earth, cotton, silk, and wool. The last two show pronounced selective adsorption of alkali, but cotton adsorbs equal but relatively small amounts of alkali and fatty acid. Silk adsorbs the greatest amount of alkali, as might be anticipated from its low isoelectric point (p_H 2.5). Olive oil soap becomes immediately turbid when in contact with silk and wool, but remains clear for 24 hr. with cotton. A. J. H.

Equation of state of monolayers. J. S. MITCHELL (Trans. Faraday Soc., 1935, 31, 980—986).—Theoretical. The equation of state of an imperfect

gas film is obtained and a method of correlating the surface potential with the deviation from the perfect gas laws is suggested. E. S. H.

Interaction of atoms and molecules with solid surfaces. I. **Activation of adsorbed atoms to higher vibrational states.** J. E. LENNARD-JONES and C. STRACHAN. II. **Evaporation of adsorbed atoms.** C. STRACHAN (Proc. Roy. Soc., 1935, A, 150, 442—455, 456—464).—I. Mathematical. Formulae are found for the mean interval between successive excitations from the state of lowest vibrational energy to various excited states, and for the mean time during which the atom remains in an excited state. This time is of the order of a few periods of the vibrating atom. The results are applied to the theory of surface migration.

II. The theory is extended to calculate the probabilities of evaporation of atoms or mols. from surfaces. A formula is derived for the interval of time that an atom (or mol.) remains in the adsorbed condition. The theory is applied to the evaporation of H_2 , HD, and D_2 from a metal, and it is shown that over a wide temp. range the average length of time spent by HD on Cu is 4—6 times that of H_2 , whilst that spent by D_2 is about 20 times that of H_2 . L. L. B.

Interfacial tension between two liquids. D. G. DERVICHIAN (Compt. rend., 1935, 201, 333—334).—Relationships between the interfacial tension of two liquids and their cohesive forces and mutual affinity are discussed. J. W. S.

Temperature coefficients of surface tension and thermal expansion. T. S. WHEELER (Current Sci., 1935, 3, 550).—The constancy of the ratio of these coeffs. follows from the observed validity of the parachor law. A. B. D. C.

Temperature coefficients of surface tension and thermal expansion. L. SIBAIYA (Current Sci., 1935, 3, 550—551).—The parachor law (cf. preceding abstract) gives the ratio of these coeffs. as 4, and observed vals. are quoted for various liquids including org. compounds and elements. C_6H_{12} , H_2O_2 , H_2O , Hg, and H_2 do not behave as normal liquids. A. B. D. C.

Change in the surface tension of a solution of methyl acetate due to hydrolysis. B. H. HANDORF and E. R. WASHBURN (J. Amer. Chem. Soc., 1935, 57, 1201—1203).—In the hydrolysis of 2M-MeOAc the surface tension, measured by the ring method, varies linearly with the amount of change determined by titration with $\text{Ba}(\text{OH})_2$.

E. S. H.

Formation of multimolecular layers on the partition surface mercury-solution. A. FRUMKIN, A. GORODETZKAJA, and P. CHUGUNOV (Acta Physicochim. U.R.S.S., 1934, 1, 12—21).—At 25° decioic acid and PhOH lower the surface tension of the Hg-solution boundary layer (using a capillary electrometer method). They are adsorbed in conc. solution giving layers with an average thickness of 2 mols., but actually consisting of "islands" of termol. layers in the general unimol. layer. These effects are not observed at the air-solution interface.

CH. ABS. (e)

Interfacial tensions between solutions of palmitic acid in benzene and aqueous solutions of sodium salts. L. GAY and M. CERVEAU (*J. Chim. phys.*, 1935, **32**, 371—384; cf. A., 1932, 1200).—Dissolved NaCl, Na₂SO₄, NaNO₃, Na₂CrO₄, and Na₂Cr₂O₇ have only very slight effects on the interfacial tension, γ , between H₂O and 1% palmitic acid in C₆H₆ at 20°, but with increasing concn. of Na₂CO₃, NaHCO₃, and NaOAc, γ decreases slowly to the Adam point and then decreases more rapidly. The data obtained with aq. NaOH alone and in presence of Na salts of strong acids suggest that Na palmitate is responsible for the interface effect. The discrepancies observed with Na salts of weak acids are attributed to dissolution of these salts in the interfacial soap film. J. G. A. G.

Surfaces of separation. Saponification at interfaces. J. WAJZER (*J. Chim. phys.*, 1935, **32**, 429—430).—The interfacial tension between arachis oil containing 1% of oleic acid and aq. NaOH decreases with increasing [NaOH]. It is inferred that the interface is occupied by a unimol. layer of Na oleate in the expanded (gaseous) state. J. G. A. G.

Rigidity with which two solid phases adhere along their interface. V. P. KONSTANTINOVA (*Acta Physicochim. U.R.S.S.*, 1934, **1**, 286—295; cf. A., 1933, 900).—The effect of unimol. layers of alcohols, acids, and amines on the adherence at quartz-paraffin and calcite-paraffin interfaces has been studied. In homologous series the effect increases with the mol. wt. of the "mol. solder." The mol. solder increases the solidity of thin films of paraffin, probably by sp. conditioning of the crystallisation. J. W. S.

Heat of wetting. II. Influence of adsorbed air on the heat of wetting. A. DUMANSKI and M. V. TSCHAPEK (*Kolloid-Z.*, 1935, **72**, 55—58; cf. this vol., 930).—The heat of wetting of peat, soil, SiO₂ gel, and charcoal by H₂O and C₆H₆ is increased when adsorbed air is first removed by evacuation. The difference between the vals. determined in air and in vac. is taken as a measure of the heat of adsorption of air. E. S. H.

Infiltration method for the investigation of the wetting power of mineral dispersoids. Comparative wetting powers of corundum powders. Z. V. VOLKOVA (*Acta Physicochim. U.R.S.S.*, 1934, **1**, 247—255).—An apparatus is described for measuring the velocity of penetration of liquids into dispersoids and for the saturation of powders with large hysteretic wetting angles. Results for the penetration of H₂O and PhMe into corundum powders are recorded and discussed. J. W. S.

Mechanism of flotation. Rôle of highly disperse powder in the flotation process. Z. V. VOLKOVA and A. V. SAPOROSHEZ (*Kolloid-Z.*, 1935, **72**, 82—86).—In the flotation of S, talc, BaSO₄, and CaCO₃ powders in H₂O containing a little iso-amyl alcohol it is shown that no adsorption of the alcohol occurs at the surface of the particles and no increase in coagulation occurs. The finely powdered substances stabilise the air-liquid dispersion, although coarser particles do not. The

fine particles play a part in aiding the flotation of the larger particles. E. S. H.

Insolubility of thin films of albumin. H. DEVAUX (*Compt. rend.*, 1935, **201**, 109—111; cf. this vol., 161).—A thin oriented film of albumin, which is capable of considerable expansion or compression, forms on the surface. When removed from the solution and dried, the film is insol. if again treated with H₂O. H. J. E.

Albumin membranes: their rigidity, elasticity, and insolubility. H. DEVAUX (*Compt. rend. Soc. Biol.*, 1935, **119**, 1124—1125).—A unimol. film of albumin forms on the surface of its solutions: it behaves as a solid membrane, perfectly elastic, and has a solubility $< 10^{-8}$. R. N. C.

Significance of structure of a membrane for its selective permeability. W. WILBRANDT (*J. Gen. Physiol.*, 1935, **18**, 933—965).—The pore and solubility theories advanced to explain selective ion permeabilities of membranes may be reconciled if the arrangement of the dipoles of the membrane mols. is considered. The behaviour of collodion membranes under various conditions is explained. Membranes of Cellophane and ethylcellulose are negatively, and those of cellulose acetate positively, charged. Membranes of collodion impregnated with basic dyes or alkaloids become more permeable to anions than to cations, in contrast to ordinary collodion membranes. A combination of these two types of membranes gives an asymmetric membrane giving a high potential between two identical electrolyte solutions. F. A. A.

Electrical transport through phase boundaries. System II: glass-molten metal (mercury). System III: glass-molten salt (silver nitrate). E. MANEGOLD and C. STUBER (*Z. physikal. Chem.*, 1935, **173**, 321—344; cf. this vol., 705).—Changes produced by a d.c. in the anode surface of a heated glass diaphragm coated on both sides with Hg or molten AgNO₃ have been examined chemically and under the microscope, and their influence on the electrical properties of the diaphragm has been measured. Transport occurs either with or without the wandering of material particles. To the former class belong the systems glass-Na vapour, -molten AgNO₃, -K vapour, -H₂, and -N₂, and to the latter glass-He, -O₂, -CO₂, and -Hg. The conditions necessary for the processes are discussed, and mechanisms are suggested. T. G. P.

Colloidal ultra-filter containing hydrated silica. G. A. BLANC (*Atti R. Accad. Lincei*, 1935, [vi], **21**, 296—301; cf. A., 1931, 1253).—Negatively-charged colloidal Au passes through the filter without adsorption, whereas positively-charged Au does so only if protected by addition of gum arabic. The adsorbed Au can be washed out by means of 1% aq. Na₂CO₃ (which dissolves the surface layer of the SiO₂), the particle size undergoing no change in the process. D. R. D.

Heats of dilution and osmotic pressures of non-electrolyte solutions. C. FRENZEL, R. BURIAN, and O. HAAS (*Z. Elektrochem.*, 1935, **41**, 419—429).—The sp. heats of aq. sucrose, glue, and CO(NH₂)₂,

solutions have been determined over a range of concn. and temp., and the temp. coeffs. of the mol. differential heats of dilution calc. therefrom. Neglect of the heat of dilution may lead to an error of 10% in the calculation of osmotic pressure. E. S. H.

Increase in the rotatory power of mannitol in water by means of zirconium salts. (MLLE.) M. FALINSKI (Compt. rend., 1935, 201, 69—71).—Addition of aq. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (I) to mannitol produced a large increase in the rotatory power. With low $[\text{Zr}]$ at room temp. an equilibrium val. is not reached until after several months. The solutions with 20—50% of (I) show a large increase in η and are colloidal. H. J. E.

Physico-chemical properties of picric acid with varying p_{H} . J. MOLNAR (Compt. rend., 1935, 201, 59—62).—At const. p_{H} , Beer's law holds for concns. of 5—40 mg. of picric acid (I) per litre, and for λ 2200—4900 Å. Variations of the absorption spectrum and solubility with p_{H} are recorded. At high p_{H} (I) is negatively charged, but in HCl and H_2SO_4 it becomes positive at the p_{H} at which the min. solubility occurs in the same acid. Seven mol. modifications are suggested to account for these results. H. J. E.

Temperature variation, of the viscosity of aqueous solutions of strong electrolytes. W. J. SULSTON (Proc. Physical Soc., 1935, 47, 657—666).—Accurate data for KCl and K_2SO_4 over the temp. range 18—85° are recorded. The results agree with the Debye-Hückel theory. N. M. B.

Determination of hydration of magnesium chloride ions. F. BOURION and E. ROUYER (Compt. rend., 1935, 201, 65—67; cf. A., 1934, 728).—Hydration decreases in the order $\text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{BaCl}_2$. H. J. E.

Metastructures of matter. WO. OSTWALD (Kolloid-Beih., 1935, 42, 109—124).—A lecture on the colloidal state. E. S. H.

Somatoids. I. K. HUBER (Helv. Chim. Acta, 1935, 18, 858—891).—A summary of published work on the non-crystallographic morphology of inorg. substances. E. S. H.

Use of colloidal cobaltinitroso- β -naphthol in a general chemistry experiment. G. H. DAMON (J. Chem. Educ., 1935, 12, 193—195).—Colloidal cobaltinitroso- β -naphthol (prep. described) provides an excellent sol for the elementary study of colloids. Coagulation experiments with Na_2SO_4 , BaCl_2 , Fe_2O_3 sol, and As_2S_3 sol show that it is positively charged. Flocculation vals. in millimols. per litre are HCl 9.0, NaCl 6.0, NaBr 5.5, NaNO_3 4.8, H_2SO_4 1.6, Na_2SO_4 1.0, K_2CO_3 2.0, Na_2HPO_4 1.6, Na_2HAsO_4 2.0, Na_3PO_4 1.2. Gelatin has a marked protective action on the colloid. Na_2SO_4 and AcOH, respectively, are recommended in place of NH_4Cl and HCl in determining Co by means of nitroso- β -naphthol. L. S. T.

Method of comparing magnitudes of molecules and colloidal micelles. A. BOUTARIC (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 101—106).—Equal masses of the same adsorbent were introduced into solutions of Na oleate (I) and, after equilibrium, the

surface tension was measured. The mol. cross-section of (I) can be determined and hence the total surface of adsorbent. Similar experiments have been made with colloidal solutions instead of (I). Modification in the degree of association of the solution can be followed and the micellar magnitudes at various stages can be compared. The mathematical theory is discussed. W. R. A.

Consolidation of charged clay particles. M. BIOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 110—113).—Theoretical. W. R. A.

Integrability of non-linear equations [in the theories] of heat [transfer] and of the consolidation of clay sediments. M. BIOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 106—109).—Mathematical. W. R. A.

(A) Study of degree of dispersion of dyes by the diffusion method. (B) Adsorption of dyes of varying degrees of dispersion. N. S. SCHEINKER (J. Phys. Chem. U.S.S.R., 1933, 4, 860—864, 865—870).—(A) The coeff. of diffusion of dyes dissolved in various H_2O -EtOH solutions has been measured by the Quast-Ostwald method. The radii of the methylene-blue particles varied from 0.39×10^{-7} cm. in H_2O to 0.21×10^{-7} cm. in 70% EtOH, that of crystal-violet from 0.57 to 0.26×10^{-7} cm., and that of neutral-blue from 2.4 to 0.34×10^{-7} cm. Aggregation occurs in the H_2O solutions (max. for neutral-blue).

(B) For dyes dissolved in H_2O in the mol. dispersed form, adsorption on glass is unimol. If the dye mols. are aggregated, the adsorbed layer is unimicellar. Methylene-blue B extra showed the first type of adsorption, and neutral-blue and crystal-violet the second (2.18 and 1.6 mols. per micelle, respectively). CH. ABS. (e)

Diffusion of compounds of high mol. wt. and related compounds. I. Glucose penta-acetate, cellobiose acetate, and quinol in organic fluids. II. Calculation of molecular size. III. Measurements in cellulose nitrate solution. M. TANGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 241—245B, 245—246B, 246—248B).—I. Diffusion coeffs. (D) have been determined for glucose penta-acetate (I), cellobiose acetate (II), and quinol (III) at 20° in org. solvents. D varies slightly from layer to layer, as in the case of a colloidal solution. It follows that the explanation given for colloids (cf. A., 1934, 483), viz., polydispersion, is incorrect, since the above solutions are mol. D increases with concn. except for (I) in MeOAc and $\text{C}_5\text{H}_5\text{N}$, and (III) in H_2O , but becomes approx. const. above a certain concn.

II. Vals. of the mol. radius calc. by the Einstein and Sutherland formulæ, respectively, are (I) 4.26 and 6.39, (II) 4.96 and 7.44, and (III) 2.91 and 4.36 Å. It is almost independent of the solvent, and the vals. given for (I) by Einstein's formula are close to those calc. from d , and from (cf. A., 1933, 670). It follows that solvation is small.

III. D is unaffected by dissolving in the org. solvent approx. 0.1—0.2% of cellulose nitrate (IV), in spite of the large increase in η , owing to the enmeshing of solvent by (IV). D for (I) in COMe_2 + (IV) does not

vary from layer to layer, and becomes const. at a concn. much < in pure COMe_2 . R. S. B.

Nature of the nucleus in hygroscopic droplets. J. H. COSTE and H. L. WRIGHT (Phil. Mag., 1935, [vii], 20, 209—234).—Nuclei for the condensation of moisture are produced in air, previously freed from nuclei, SO_2 , and other acid gases, by heating, irrespective of the source of heat. Since nuclei are produced when Pt foil is electrically heated in air, they probably consist of droplets of HNO_3 formed from atm. N_2 and O_2 . HNO_3 can exist in air both as a gas and as a liquid. The latter acts as a source of nuclei and can be detected in air collected after various combustions. Results of spraying various liquids into air show that fuming H_2SO_4 and sea- H_2O produce many nuclei. Many nuclei are also formed when fuels containing S (coal gas, and CS_2 +EtOH) are burnt. H_2SO_4 produced by the oxidation of SO_2 in air may therefore be one of the nucleus-forming substances in ordinary air. A. J. M.

Mechanism of division of small liquid systems which are the seats of physicochemical reactions. N. RASHEVSKY (Physics, 1934, 5, 374—379; cf. A., 1932, 294).—The mechanism of division of small liquid drops has been studied from the kinetic viewpoint. Crit. sizes calc. by this method agree with thermodynamic computations. CH. ABS. (c)

Mol. wt. of linear macromolecules by ultracentrifugal analysis. III. Mol. wt. analysis of mixtures by sedimentation equilibrium in the Svedberg ultracentrifuge. W. D. LANSING and E. O. KRAEMER (J. Amer. Chem. Soc., 1935, 57, 1369—1377; cf. this vol., 688).—Three types of average mol. wt. are distinguished, viz., "no.-average" (deduced from usual physico-chemical methods), "wt.-average" (Staudinger's viscosity method), and "z-average" (ultracentrifuge data). These can all be calc. from data on sedimentation equilibrium. The methods used are now applied to Krishnamurti and Svedberg's data (A., 1930, 1198) for gelatin. The significance of the results in connexion with other macromol. substances is discussed. H. B.

Preparations of emulsions and colloidal solutions by ultra-sonic waves. S. N. RSCHEVKIN and E. P. OSTROVSKI (Acta Physicochim. U.R.S.S., 1935, 1, 741—744).—With a frequency of 4×10^5 Hertz, obtained by means of a quartz-plate oscillator, emulsions of Hg, Sn, Bi, Cu, Ag, S, paraffin, and various oils in H_2O have been obtained. Conductivity measurements for the Hg emulsions are recorded. H. J. E.

Mode of formation and composition of colloidal and precipitated copper sulphides. E. SAUER and D. STEINER (Kolloid-Z., 1935, 72, 41—46).—Under certain conditions of concn. etc., H_2S gives a sol of Cu_2S with Cu^I salts; with Cu^{II} salts under similar conditions a mixture of Cu_2S and S in colloidal form is obtained, which on warming changes to CuS . E. S. H.

Formation and properties of acidoid gold sols with charging mixed complexes. W. PAULI, E. RUSSE, and E. BRUNNER (Kolloid-Z., 1935, 72, 26—35). Au sols prepared by electro-dispersion in

HCl are stable to boiling and are stabilised by the charging complex $[\text{Au}^I\text{Cl}_2]\text{H}$. Progressive electro-decantation converts them into sols which are not stable to boiling and are charged by the complex $[\text{Au}^I(\text{OH})\text{Cl}]\text{H}$. The more stable sol is re-formed by adding HCl in accordance with the equilibrium $[\text{Au}^I(\text{OH})\text{Cl}]\text{H} + \text{HCl} \rightleftharpoons [\text{Au}^I\text{Cl}_2]\text{H} + \text{H}_2\text{O}$. Similar relations have been observed in Au sols prepared by reduction of HAuCl_4 with P or H, in presence of K_2CO_3 . E. S. H.

Dissolution of titanite hydroxide in hydrogen peroxide. S. KATZOFF and R. ROSEMAN (J. Amer. Chem. Soc., 1935, 57, 1384).—Freshly pptd. and washed $\text{Ti}(\text{OH})_4$ dissolves in H_2O_2 giving a colloidal sol, which is pptd. by electrolytes. Gels can be formed by evaporating the sols and cooling. E. S. H.

Electrical conductivity of colloidal solutions. J. J. BIKERMAN (J. Chim. phys., 1935, 32, 460—465; cf. this vol., 700).—The equation derived from the diffuse double layer theory shows that the fraction of the observed conductivity of aq. sols which is due to micelles is, in general, negligible when κ is $> 10^{-5}$ ohm $^{-1}$ cm. $^{-1}$. J. G. A. G.

Preparation of colloidal ferric hydroxide solutions with the aid of tetra-alkylammonium hydroxides containing several vicinal hydroxyl groups in one alkyl residue. W. TRAUBE and K. E. STUMPF (Ber., 1935, 68, [B], 1394—1398).—Solutions of trimethyl- $\beta\gamma$ -dihydroxypropylammonium hydroxide dissolve $\text{Fe}(\text{OH})_3$ in large amount which increases with the concn. of the alkali solution. The greater amount of $\text{Fe}(\text{OH})_3$ is present as colloid, only a small portion being in complex union. The amount of $\text{Fe}(\text{OH})_3$ dissolved depends on its previous history. Treatment of the solutions with BaCl_2 or BaSO_4 causes pptn. of all the colloiddally dissolved $\text{Fe}(\text{OH})_3$. Similar solvent power is shown by $\beta\gamma\delta\epsilon$ -tetrahydroxy-*n*-hexyleneditrimethylammonium hydroxide. The presence of the NH_4 base does not appear to hinder the formation of Fe^{III} -mannitol complexes but, unexpectedly, the colloidal $\text{Fe}(\text{OH})_3$ thus prepared appears to react more slowly than that obtained by other methods. Sorbitol behaves similarly to mannitol but somewhat more rapidly. H. W.

Viscometric investigation of structure formation in $\text{Fe}(\text{OH})_3$ sols. II. Influence of warming. A. RABINERSON (Acta Physicochim. U.R.S.S., 1934, 1, 256—265).—Viscosity-pressure curves for a sol containing 10.07 g. of Fe_2O_3 per 100 c.c. show that the viscosity increases with lapse of time, this change being accelerated by heating to 55—60°. Further heating to 70—72° yields a jelly; this on shaking yields a thick sol which on keeping returns partially to the thixotropic state. This effect is increased after frequent warming. The phenomena are explained by the diminution in $[\text{Fe}^{III}]$ in the solution due to hydrolysis on warming, modifying the adsorption equilibrium with ions on the particles and leading to partial coagulation, these processes being partially reversible at lower temp. J. W. S.

Anomalous variations of viscosity during the coagulation of positive ferric oxide sol by col-

loidal arsenious sulphide sol. S. S. JOSHI and K. P. N. PANNIKAR (J. Chim. phys., 1935, 32, 455—459).—Large and irregular changes of viscosity occur during the coagulation of colloidal $\text{Fe}(\text{OH})_3$ (1.5 g. Fe_2O_3 per litre) by colloidal As_2S_3 at various dilutions (cf. A., 1934, 597). J. G. A. G.

Influence of concentration and age on some colloidal properties of ferric chloride solutions. H. L. ELLISON and F. HAZEL (J. Physical Chem., 1935, 39, 829—835).—The no. of nuclei initially present in 0.1—0.001M- FeCl_3 solutions increases with increasing concn. On ageing the no. of colloidal particles increases in a stepwise manner with abrupt discontinuities. The increase in $[\text{H}^+]$ during ageing is approx. \propto the increase in no. of particles. The electrophoretic velocity decreases with ageing. The no. of particles produced in the high-temp. hydrolysis product depends on the no. of particles in the initial solution. J. W. S.

Investigation of solvation and aggregation. N. S. SCHEINKER, R. E. NEUMANN, and G. A. SCHIROV (Acta Physicochim. U.R.S.S., 1935, 1, 795—804).—Diffusion observations show that addition of C_6H_6 to an EtOH solution of Et-violet causes first a decrease in the size of colloidal particles due to desolvation, and then an increase, due to aggregation. With MeOH solutions an increase only is observed, the particles being aggregated but not solvated. The behaviour in EtOH- H_2O mixtures resembles that in EtOH. The solvation in EtOH corresponds with a unimol. layer of solute. H. J. E.

Theory of coagulation. N. FUCHS (Z. physikal. Chem., 1935, 173, 387).—A correction (cf. this vol., 164). T. G. P.

Kinetics of coagulation of colloidal gold. K. JABŁCZYŃSKI and W. KOSCHANY (Rocz. Chem., 1935, 15, 283—289).—A spectrophotometric study of Au sols indicates that the dimensions of the particles do not vary during 21 days of observation, but their negative charge increases. Different samples of identically prepared Au sols exhibit different initial rotations. The spectrophotometric method is not applicable to quant. study of sols which change colour with time. R. T.

Spontaneous formation of ordered aggregates in sols containing non-spherical particles. W. HELLER (Compt. rend., 1935, 200, 2082—2084).—By the mechanical coagulation of $\text{Fe}(\text{OH})_3$ sols under conditions such that coagulation is difficult, a small no. of aggregates is formed which show anisotropy. These are not formed in presence of electrolyte. H. J. E.

Structure viscosity of solutions of highly polymerised substances. J. COUMOU (Chem. Weekblad, 1935, 32, 426—429).—Solutions of gelatin, starch (if not heated for too long a period), dextrin, carotin, gum tragacanth, linseed, and pectin in H_2O , lichenin in dil. alkali, and polystyrene in tetrahydronaphthalene show structure viscosity (change in η with rate of flow). Solutions of sucrose, glucose, gum arabic, and gum acajou in water and of PhOH- and cresol- CH_2O resins in COMe_2 or EtOH do not show this effect. The difference is attributed to the

long-chain structure of the former and relatively compact form of the mols. of the latter. D. R. D.

Reaction [between] metal hydroxide solution [and] cellulose fibre. II. X-Ray investigation of the reversibility of the lattice transformation in sodium-cellulose. W. SCHRAMMEK and H. GORG (Kolloid-Beih., 1935, 42, 302—330; cf. this vol., 29).—Equilibrium in the system cellulose-NaOH has been studied by X-ray examination. The phase rule is not applicable. Five kinds of Na-cellulose have been recognised, and the conditions of inter-conversion determined. Na-cellulose I is assigned the mol. ratio $2\text{C}_6 : 1\text{NaOH}$. E. S. H.

Relative precipitating effect of alcohols on organosols. B. YAMAGUCHI (Kolloid-Z., 1935, 72, 51—55).—The pptg. effect of a series of homologous aliphatic alcohols on solutions of cellulose acetate in COMe_2 and of polystyrene in C_6H_6 or PhCl increases with increasing mol. polarisation (P) of the alcohol, but with polystyrene in EtOAc the pptg. effect is independent of the alcohol. The general relation is expressed by $a - 1/(P - 36.8)^n = k$, where n and k are consts. characteristic of the sol. The relation between the pptn. curve and the solvation of the solute is discussed. E. S. H.

Influence of alcohols on structure formation in ferric hydroxide sols. A. RABINERSON (Kolloid-Z., 1935, 72, 58—62).—Addition of about 40% of EtOH to conc. $\text{Fe}(\text{OH})_3$ sols causes a great increase of η and, eventually, solidification. Small amounts of EtOH have no appreciable effect. $(\text{CH}_2\text{OH})_2$ (I) and glycerol (II) do not behave like EtOH, although they have a dehydrating action. Conc. sols of $\text{Fe}(\text{OH})_3$ in (I) or (II) can be prepared by direct dispersion, but not in EtOH, which gives a coarse dispersion. E. S. H.

Chemical reactions between colloids. I. Copper and sulphur. E. SAUER and D. STEINER (Kolloid-Z., 1935, 72, 35—40).—Sols of Cu and S, prepared in different ways, react to form Cu_2S , which later reacts with more S, forming CuS. The participation of electrolytes in the chemical change was excluded. E. S. H.

Thixotropy in suspensions of coarsely disperse aluminium compounds. T. HENNIG (Kolloid-Z., 1935, 72, 63—66).—The thixotropic properties of Al formate and acetate and Ca and Mg aluminates are described. The terms negative and positive thixotropy, according to whether the change is in the direction of forming solid or liquid, are introduced. E. S. H.

Structure viscosity and thixotropic properties of cellulose ester solutions. I. Dependence of structure viscosity and thixotropic properties of alcohol-ether solutions of cellulose nitrate on specific viscosity. S. ROGOVIN and V. IVANOVA (Kolloid-Z., 1935, 72, 86—92).—Structure viscosity generally increases with increasing sp. viscosity, especially in conc. solutions, but several contrary results in solutions containing large amounts of degradation products are noted. There is no direct relation between thixotropy and sp. viscosity. E. S. H.

Amorphous and crystalline oxide hydrates and oxides. XXII. Hydroxide gels and oxide hydrate gels, and their amphoteric properties. A. KRAUSE (Kolloid-Z., 1935, 72, 18—25; cf. this vol., 946).—A discussion of published work.

E. S. H.

p_H measurements in gelatin solutions. I. PETROV and A. PASINSKI (J. Appl. Chem. Russ., 1935, 8, 165—171; cf. A., 1932, 700).—The of buffered gelatin solutions can be reproduced with an accuracy of ± 0.05 potentiometrically (H, quinhydrone, glass electrodes), and ± 0.1 colorimetrically with Michaelis' and with Clarke and Lubs' indicators. In unbuffered solutions the corresponding vals. are ± 0.15 for purified, and -0.25 and -0.50 for impure, gelatin.

R. T.

Response of electrolytes in gelatin to an applied electric field. (MLLE.) S. VEIL (J. Chim. phys., 1935, 32, 429).—For a p.d. that required to cause decomp. the applied field gives rise to a periodic distribution of electrolyte in a layer of gelatin spread on glass, suggesting the existence of zones of unequal rates of diffusion.

J. G. A. G.

Residual water in activated silica gel. S. S. KISTLER and K. KEARBY (Acta Physicochim. U.R.S.S., 1934, 1, 354—364).—By treatment with SiCl_4 , about 94% of the residual H_2O can be removed from SiO_2 gel below 350° without reducing its activity seriously, indicating that most of the H_2O is within reach of the surface. Adsorption activity, as measured by heat of wetting, is almost independent of H_2O content. Approx. free energies of reaction of SiCl_4 , BCl_3 , TiCl_4 , SnCl_4 , and AlCl_3 with H_2O are calc.

J. W. S.

Structure of silica gel. M. V. POLJAKOV, P. M. STADNIK, M. V. PARITZKI, and I. M. MALKIN (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 71—73).—The activity of SiO_2 gel prepared in presence of C_6H_6 , PhMe, xylene, C_{10}H_8 , and S has been determined. Vals. for C_6H_6 , PhMe, and xylene are \propto their mol. wts.

R. S.

Gelatinisation and polymerisation. Explanation of a case of thixotropy. B. A. TALMUD and D. L. TALMUD (Acta. Physicochim. U.R.S.S., 1934, 1, 282—285).—The formation of thixotropic gels from non-aq. Ba malonate sols is attributed to rearrangement of the mols. into chains, each Ba atom being linked to two CO_2 groups of different malonate mols.

J. W. S.

Hydrophilic colloids. I. Calorimetric investigation of the hydration of hydrophilic colloids in ethyl alcohol-water mixture and in ethyl alcohol-ether-water mixture. M. V. TSCHAPEK (Kolloid-Z., 1935, 72, 46—50).—Experiments with agar, potato starch, peat, and gelatin show that the hydration is not reduced by EtOH until $> 80\%$ is present. Throughout the ternary liquid mixture the hydration is always $>$ half that in H_2O . Addition of Et_2O increases the hydration, apparently by removing some of the EtOH.

E. S. H.

Storage of polonium solutions. C. ROSENBLUM and E. W. KAISER (J. Physical Chem., 1935, 39, 797—

801).—The storage of Po solutions in paraffin-coated glass vessels decreases the formation of colloids.

J. W. S.

Influence of salts on the potential and charge of inert and protein surfaces. H. A. ABRAMSON (J. Physical Chem., 1935, 39, 749—760).—The electrokinetic potential (ζ) and density of surface charge (σ) of colloids in aq. salt solutions of various concns. (c) have been calc. from mobility measurements. The ζ -c curves for graphite, quartz, collodion, cellulose, and paraffin oil in solutions for which the sign of σ is not reversed show max. for about $10^{-5}M$ solutions, but the σ -c curves follow a simple form resembling a typical adsorption curve, with an initial steep slope and reaching saturation at about $0.01M$. The ζ -c curves for proteins are in agreement with the view that the net charge on the protein surface depends primarily on the p_H and that ζ in dil. solution depends on the thickness of the electrical double layer.

J. W. S.

Electrokinetic potential and the stability of colloids. H. MUELLER (J. Physical Chem., 1935, 39, 743—747).—The electrostatic forces of the double layer on hydrophobic colloid particles are sufficient to account for the existence of a stable protective layer of H_2O mols. The theory indicates that the stability of such colloids should decrease rapidly at temp. $> 80^\circ$.

J. W. S.

Cataphoresis of particles of the fatty acids and related compounds. T. ALTY and O. JOHNSON (Phil. Mag., 1935, [vii], 20, 129—145).—The mobility of particles of fatty acids and other related compounds in H_2O and in aq. HCl depends on the nature of the H_2O -sol. group and on the length of the hydrocarbon chain. For const. chain length the mobility follows the order $\text{CO}\cdot\text{NH}_2 > \text{CO}_2\text{H} > \text{CH}_2\cdot\text{OH}$, whilst in the series of acids the mobility decreases with increasing length of the chain. The mobility is increased by a double linking near the middle of the chain. The mobilities decrease with increasing $[\text{H}^+]$ of the solution.

J. W. S.

Cataphoresis of Chinese ink in water containing deuterium oxide. T. TERADA and R. YAMAMOTO (Proc. Imp. Acad. Tokyo, 1935, 11, 214—215).—Differences from the behaviour in ordinary H_2O are attributed to substitution of D for H in the NH_2 groups of the gelatin protecting the ink.

C. W. G.

Thermodynamical treatment of base-exchange equilibria. Real solid solutions of two zeolite components. J. KIELLAND (Tidsskr. Kjemi, 1935, 15, 74—76).—Theoretical.

E. S. H.

Thermodynamics of base-exchange equilibria of some different kinds of clays. J. KIELLAND (J.S.C.I., 1935, 54, 232—234t).—A thermodynamic method of treating base-exchange equilibria is given which takes account of the activity coeffs. of the zeolitic components. The method is shown to give const. K_a vals. Free energies for various components are calc. In exchange reactions with H- and Tl-clays, the occurrence of the compound $2\text{HZ}, \text{TlZ}$ is indicated.

Reciprocity theorem in colloid optics. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 1, A, 782—788).—A previous algebraic relation (cf. this vol.,

821) is deduced from the Helmholtz-Rayleigh principle of reciprocity and supported by experimental evidence. N. M. B.

Possible determination of state of degeneracy of a gas. M. SATÔ (Sci. Rep. Tôhoku, 1935, 24, 26—29).—For the Brownian motion in a degenerate gas, the motion deduced for $A < 1$ by means of the Bose-Einstein statistics is $<$ that derived by the classical theory. R. C.

Intensity parameter and stable thermodynamic equilibrium. T. EHRENFEST-AFANASSJEVA and G. L. DE HAAS-LORENTZ (Physica, 1935, 200, 743—752).—Theoretical. H. J. E.

Mass action. N. A. BRUNT (Chem. Weekblad, 1935, 32, 446—448). I. M. KOLTHOFF (*ibid.*, 448—449).—Polemical (cf. this vol., 702). D. R. D.

Formulation of the law of mass action in homogeneous and heterogeneous systems with particular regard to metallurgical equilibria. A. SKAPSKI (Bull. Acad. Polonaise, 1935, A, 174—188).—Theoretical. J. W. S.

Equilibrium and heat of the reaction $C_2H_4 + H_2 = C_2H_6$. E. TELLER and B. TOPLEY (J.C.S., 1935, 876—885; cf. A., 1934, 254).—The most trustworthy val. of the equilibrium const. is $\log_{10} K_{P(atm.)} = 1.613$ at 863° abs. Within the limits of spectroscopic and sp. heat data, assumptions relating to the potential energy of the restricted rotation of Me in C_2H_6 and also to the frequencies of C_2H_4 and C_2H_6 not fixed spectroscopically lead from K_P to $-\Delta H_{298} = 31,050 \pm 300$ g.-cal. per mol. The thermodynamic evaluation of $-\Delta H_{298}$ from the temp. coeff. of K_P is less trustworthy. The max. and the probable errors in the statistical mechanical vals. are ± 600 and ± 300 g.-cal., respectively, and the origin of the discrepancy between the experimental (cf. this vol., 304) and the calc. vals. of $-\Delta H_{298}$ is obscure. The heat of reaction at 0° abs. is $-\Delta E_0 = 29,420 \pm 100$ g.-cal. per mol. J. G. A. G.

Solvation and equation of state of dissolved substances. M. AF HALLSTROM (Suomen Kem., 1935, 8, A, 53—57).—The influence of solvation on the mol. wt. (M) calc. from the f.p. is given by $M - M_0(1 - Sc)$, where M_0 = theoretical mol. wt., S = solvated solvent in kg., and c = wt. concn. This leads to an equation of state of the same form as that used by Sackur, $p(v - b) = RT$ (cf. A., 1910, ii, 273). The degree of hydration is calc. from the consts. b given by Sackur, and also from the quantities of solvent in isotonic solutions. The vals. obtained agree with those calc. by Tammann from hydration pressure and Öholm (A., 1912, ii, 564) from diffusion. In solvents other than H_2O a term must be included in the equation of state to allow for mol. attraction. R. S. B.

Electrolytic dissociation of heavy water. E. ABEL, E. BRATU, and O. REDLICH (Z. physikal. Chem., 1935, 173, 353—364; cf. A., 1934, 1173).—The e.m.f. of the cells $D_2[DCl(0.1M)|AgCl|Ag]$ and $D_2[NaOD(0.1M) + NaCl(0.1M)|AgCl|Ag]$ have been measured. The ratio of the dissociation consts. $D_2O : H_2O$ is 0.16 at 21°. The product of the different "hydrogen-ion" and "hydroxyl-ion" concns. is

strictly dependent on the stoichiometric isotopic composition, and is the same for acid or alkali in the same water. This product plays a similar rôle for mixtures of D_2O and H_2O as does the dissociation const. in pure H_2O . For D_2 in D_2O ${}_0E_h = -0.0034$ volt; for $Ag, AgCl, Cl^-$ in D_2O ${}_0E_h = -0.218(7)$ volt. DCl is less sol. in D_2O than HCl in H_2O in the ratio 0.62 : 1. T. G. P.

Influence of substituents on the dissociation constants of carboxylic acids. J. F. J. DIPPEY and H. B. WATSON (Chem. and Ind., 1935, 735—737).—The relation between the dissociation const. of substituted acetic acids and the dipole moment of the substituent (cf. A., 1933, 890) has been applied to substituted phenylacetic acids. Deviations from the relation are discussed. R. S.

Dissociation constants of organic acids. XII. New buffer: phenylacetic acid-sodium phenylacetate. W. L. GERMAN and A. I. VOGEL (J.C.S., 1935, 912—914).—Measurements of have been made with the quinhydrone electrode at 25°. The H electrode affords unsteady and drifting potentials owing to the catalytic reduction of $CH_2Ph \cdot CO_2H$ to cyclohexylacetic acid. The buffer solutions cover the range p_H 3.16—4.66 and lead to $K_a = 4.89 \times 10^{-5}$, in good agreement with other vals. J. G. A. G.

Electrometric titration curves of dibasic acids. V. Dissociation constants of cyclopentanedicarboxylic acids [at 25°]. Attempted check on methods proposed for calculating mol. dimensions. C. K. INGOLD and H. G. G. MOHRHENN (J.C.S., 1935, 949—952).—The first and second dissociation consts., $K_1 \times 10^5$ and $K_2 \times 10^6$, of the isomerides are: *cis*-1 : 2-, 3.7, 0.27; *trans*-1 : 2-, 11, 1.4; *cis*-1 : 3-, 5.5, 3.1; *trans*-1 : 3-, 4.8, 3.8, respectively. The extended equation (A., 1931, 1126) gives vals. for the distances between the charges of the bivalent anions in closer agreement with the requirements of the mol. models than the vals. calc. from Bjerrum's original equation. J. G. A. G.

Classical dissociation constant of benzoic acid in various salt solutions. L. C. RIESCH and M. KILPATRICK (J. Physical Chem., 1935, 39, 891—899).—The classical dissociation const. of $BzOH$ has been determined in solutions of $LiCl$, $NaCl$, KCl , $LiNO_3$, $NaNO_3$, KNO_3 , $NaClO_4$, $PhSO_3Na$, and $p-C_6H_4Me \cdot SO_3Na$. The mean activity coeffs. of OBz ions are calc. from the activity coeff. of mol. $BzOH$ and the thermodynamic dissociation const. J. W. S.

Rôle of *o*-substitution in the ionisation of organic acids and bases. A. W. WALDE (J. Physical Chem., 1935, 39, 885—889).—The increase in acidity of *o*-substituted $BzOH$ and NH_2Ph is attributed to the restriction of the free rotation of the CO_2H or NH_2 . J. W. S.

Solubilities, apparent dissociation constants, and thermodynamic data of dihalogenated tyrosine compounds. P. S. WINNER and C. L. A. SCHMIDT (J. Gen. Physiol., 1935, 18, 889—903).—The solubilities and differential heats of solution of *d*-, *dl*-, di-iodo-*dl*-, dibromo-*l*-, (I), and dichloro-*l*-tyrosine (II) are given. There is evidence that

dl-tyrosine is a compound. From solubility determinations at 25° and 40° at different p_H the apparent acid and basic dissociation consts., and the apparent heats of ionisation, of (I) and (II) are calc.

F. A. A.

Reaction of malonic acid with metallic bases. C. W. DAVIES (J.C.S., 1935, 910—912).—Anomalies of Cu malonate and Cu H malonate solutions are explained by the low dissociation consts., K , of the salts and there is no reason for inferring the presence of colloidal basic aggregates (cf. this vol., 449). The Cu salts of disubstituted malonic acids are largely hydrolysed, and the recorded vals. of K (A., 1931, 1126) are therefore uncertain. K for the reaction $\text{CuOH}^+ \rightleftharpoons \text{Cu}^{++} + \text{OH}^-$ is 3×10^{-8} , approx.

J. G. A. G.

Activity coefficients of the alkali bromides and iodides in aqueous solution from vapour-pressure measurements. R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 1161—1165).—The concns. of solutions of LiBr, NaBr, KBr, RbBr, CsBr, NaI, KI, RbI, and CsI which are isopiestic with KCl solutions of known concn. at 25° have been measured. Activity coeffs. of the above salts have been calc. at concns. from 0.1*M* to 4*M*. The results agree satisfactorily with those from e.m.f. and f.-p. data. E. S. H.

Activity coefficients of alkali nitrates, acetates, and *p*-toluenesulphonates in aqueous solution from vapour-pressure measurements. R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 1165—1168; cf. preceding abstract).—The activity coeffs. have been calc. from determinations of the concns. of aq. alkali nitrates, acetates, and *p*-toluenesulphonates which are isopiestic with KCl solutions of known concn. at 25°. The results agree with those obtained from f.-p. data. E. S. H.

Liquid ammonia as a solvent. IV. Activities of ammonium nitrate, iodide, bromide, and chloride at 25°. W. E. LARSEN and H. HUNT (J. Physical Chem., 1935, 39, 877—883).—Vals. of the relative mean ionic activity coeffs. are calc. from the v.p. of solutions of these salts in liquid NH_3 . It is suggested that deviations from Raoult's law are due to partial association of the solutes and solvation of the ions. J. W. S.

Activity of ammonium ions in liquid ammonia. V. A. PLESKOV and A. M. MONOSSOHN (Acta Physicochim. U.R.S.S., 1935, 1, 713—728; cf. A., 1934, 1309).—The activities of NH_4NO_3 (0.0001—1.0*N*) and NH_4Cl (0.005—0.5*N*) in liquid NH_3 have been measured with the H electrode at -50°. A discrepancy exists with vals. from conductivity measurements. The Debye-Hückel theory is unsatisfactory in this case. The dissociation const. of NH_3 at -50°, determined potentiometrically, is 1.9×10^{-33} . Results of Zintl and Neumayr and of Fredenhausen (A., 1930, 297, 537) are criticised. H. J. E.

Complexes of aromatic nitro-compounds with acids. B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1935, 5, 401—412).—Measurements of the e.m.f. obtained on immersing a Na electrode in C_6H_5 solutions of PhNO_2 , $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$, or $1\text{-C}_{10}\text{H}_7\text{NO}_2$ and AcOH , EtCO_2H , $\text{Pr}^n\text{CO}_2\text{H}$, $\text{Pr}^i\text{CO}_2\text{H}$,

or $\text{Bu}^i\text{CO}_2\text{H}$ indicate potential max. corresponding with complexes of 1 mol. of NO_2 -compound with 1—2 mols. of acid. The e.m.f. of systems containing AcOH is greatly increased by adding 1% of H_2O . R. T.

System calcium nitrite-water. J. BUREAU (Compt. rend., 1935, 201, 67—69).—Data obtained by thermal analysis and solubility methods are recorded. The hydrates $\text{Ca}(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ are formed. H. J. E.

System bismuth iodide-ammonium iodide. (MLLE.) M. L. DELWAULLE (Compt. rend., 1935, 201, 341—344).—This system has been investigated at 11°, 35°, and 50°, the existence of $\text{BiI}_3 \cdot \text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$ and $\text{BiI}_3 \cdot 4\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$ being confirmed and a further compound $\text{BiI}_3 \cdot 2\text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$ identified. J. W. S.

Equilibrium diagram of system barium fluoride-magnesium fluoride. M. OKAMOTO and U. NISIOKA (Sci. Rep. Tôhoku, 1935, 24, 141—149; cf. A., 1933, 782).—The compound $\text{BaF}_2 \cdot 2\text{MgF}_2$ is formed at 930° in accordance with $\text{MgF}_2 + \text{melt} \rightleftharpoons \text{BaF}_2 \cdot 2\text{MgF}_2$. R. C.

System $\text{MnO} \cdot \text{SiO}_2$ -FeS. A. S. GINZBERG, B. P. SELIVANOV, and S. I. NIKOLISKI (Soob. Vsesoy. Inst. Met., 1931, No. 8, 25—29).—A m.-p. diagram is given. CH. ABS. (e)

Thermodynamics of the binary system: *p*-cresol-benzoic acid. G. CHAPAS (J. Chim. phys., 1935, 32, 466—468).—The liquid probably consists of double mols. of each component (cf. this vol., 35). J. G. A. G.

Purification and physical properties of organic compounds. IX. Some binary freezing-point diagrams and a study of their ideality. E. L. SKAU (J. Physical Chem., 1935, 39, 761—767; cf. A., 1930, 543).—The system $\text{NH}_2\text{Bz}-m\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ shows a eutectic point at 42.1° with 56.6 mol.-% of $m\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. The system acenaphthene- $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ has two eutectics at 68.7° and 66.5° with 36 and 68 mol.-% of $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$, respectively. An equimol. compound, m.p. 71.9°, is formed. $\beta\text{-C}_{10}\text{H}_7 \cdot \text{NH}_2$ and $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ also form a compound. The greatest deviations from ideality occur with the first mixture and it is suggested that a compound does form but that conditions are such that it does not crystallise. The m.p. obtained are generally > those given by other authors. J. W. S.

System antimony iodide-ammonium iodide-water. F. FRANÇOIS (Compt. rend., 1935, 201, 215—216).—Solubility data at 11°, 20°, 35°, 50°, and 75° are recorded. The compound $\text{SbI}_3 \cdot 4\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$ is formed below 75°. $\text{SbI}_3 \cdot 2\text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$ and an unidentified orange-red compound, stable below approx. 20°, have also been observed. H. J. E.

System iron-phosphorus-oxygen. H. WENTRUP (Arch. Eisenhüttenw., 1935—1936, 9, 57—60).—The system $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ has been examined by thermal and micrographic methods in the range 30—50.6% Fe; FePO_4 (I) melts without decomp. at 1240° and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ (II) at 1270°. (I) and (II) form a eutectic with 34.6% Fe at 964° and (I) also forms a eutectic at 42.6% Fe and 968° with the compound $2\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.

(III) formed by a peritectic reaction between Fe_2O_3 and (I) at 1095° . (I) exists in three forms, the γ -form crystallising in grey transparent crystals from the melt and changing at 889° into the grey β -form, which changes at 784° into white needles of the α -form. (II) exists in two forms with a transformation point at 865° and (III) also exists in two forms, the grey α being converted into lighter-coloured β at 869° . There appears to be no solid solution range in the system. The system $\text{FeO}-\text{P}_2\text{O}_5$ has been examined in the range 46.9—59.8% Fe; $3\text{FeO}, \text{P}_2\text{O}_5$ (IV) exists in two forms, the grey α being converted at 942° into white rhombic crystals of β which melt without decomp. at 1238° and form with FeO a eutectic at 1008° and 53.9% Fe. (IV) and (II) appear to form a quasibinary system with a eutectic at about 1040° and 38.7% Fe. Characteristic microstructures of mixtures in the above systems are shown.

A. R. P.

Ferric oxide and aqueous sulphuric acid at 25° . W. H. BASKERVILLE and F. K. CAMERON (J. Physical Chem., 1935, 39, 769—779).—Dissolution of Fe_2O_3 , hydrated Fe_2O_3 , or basic Fe^{III} sulphates in aq. H_2SO_4 is slow and its rate depends on the composition, physical properties, and previous history of the solid. Equilibrium is reached the more slowly the more conc. is the acid. The solubility of $\text{Fe}_2\text{O}_3 \propto$ the $[\text{SO}_3]$ up to a max. val. of 20.5% with 26.4 g. of SO_3 per 100 g. of solution, but decreases at higher $[\text{SO}_3]$. Below this $[\text{SO}_3]$ the solids in equilibrium with the solutions form a continuous series of solid solutions, but at higher $[\text{SO}_3]$ the following solid phases have been identified: $\text{Fe}_2\text{O}_3, 2.5\text{SO}_3, 7\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 9\text{H}_2\text{O}$, and $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$. The solutions in equilibrium with $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 8\text{H}_2\text{O}$ are unstable. There are no congruent points in this system.

J. W. S.

Thermal equilibria in ternary systems. VI. Phenacetin-antipyrine-menthol. VII. Phenacetin-urethane-menthol. VIII. Resorcinol-pyrocatechol-quinol. K. HRYNAKOWSKI and F. ADAMIANIS (Rocz. Chem., 1935, 15, 311—317, 318—324, 325—330).—VI. Compounds are not formed. The eutectic, f.p. 31.0° , contains antipyrine 16, phenacetin 1.5, and menthol 82.5%.

VII. The eutectic, f.p. 24.8° , contains phenacetin 2, menthol 72, and urethane 26%.

VIII. The eutectic, f.p. 58.7° , contains quinol 15, resorcinol 49, and pyrocatechol 36%. R. T.

Double decomposition in the absence of a solvent. XXVII. Complex mutual systems of a higher order. A. G. BERGMAN (J. Gen. Chem. Russ., 1935, 5, 432—437).—Possible methods of study of systems of 6 or more salts are considered. R. T.

Heats of formation of certain sulphides. H. ZEUNER and W. A. ROTH (Z. physikal. Chem., 1935, 173, 365—382).—The heats of formation of FeS and Ag_2S have been determined by synthesis in a calorimeter, and of PbS by pptn. of dil. aq. $\text{Pb}(\text{NO}_3)_2$ with aq. H_2S . At 20° , $\text{Fe}(\alpha) + \text{S}(\text{rhomb.}) = \text{FeS} + 22.8 \text{ kg.-cal.}$, $2\text{Ag} + \text{S}(\text{rhomb.}) = \text{Ag}_2\text{S} + 6.6 \text{ kg.-cal.}$, $\text{Pb} + \text{S}(\text{rhomb.}) = \text{PbS} + 23.1 \text{ kg.-cal.}$ The heat of dissolution of PbCl_2 has also been determined.

T. G. P.

Transition point and thermodynamic values of silver sulphide. G. KIMURA (Sci. Rep. Tôhoku, 1935, 24, 77—90).—The rhombic changes to the cubic form at $175\text{—}176^\circ$, the vol. increasing by 0.00065 c.c. per g. From the e.m.f. of the cell $\text{H}_2(p)|\text{HCl}(m)|\text{HCl}(m), \text{H}_2\text{S}(p), \text{Ag}_2\text{S}|\text{Ag}$ the vals. $\Delta F_{298} = -9542$ and $\Delta H_{298} = -7512 \text{ g.-cal.}$ are obtained for $2\text{Ag} + \text{S}(\text{rhomb.}) = \text{Ag}_2\text{S}$ (cf. A., 1934, 148).

R. C.

Transference numbers of aqueous solutions of some electrolytes at 25° by the moving boundary method. L. G. LONGSWORTH (J. Amer. Chem. Soc., 1935, 57, 1185—1191).—Data for aq. KBr , KI , KNO_3 , NH_4Cl , NaOAc , CaCl_2 , and Na_2SO_4 over the concn. range 0.01—0.2N are recorded. E. S. H.

Conductivity of silver, thallium, magnesium, and alkaline-earth metal hydroxides in aqueous solution. M. HŁASKO and A. SALITÓWNA (Rocz. Chem., 1935, 15, 273—282).—Direct measurements indicate that λ_∞ is attained in $2 \times 10^{-8}\text{N-Ca}(\text{OH})_2$, $5 \times 10^{-8}\text{N-Sr}(\text{OH})_2$, $1 \times 10^{-7}\text{N-Ba}(\text{OH})_2$, and $2 \times 10^{-6}\text{N-TlOH}$; these vals. differ by $> 0.2\%$ from those calc. from Kohlrausch's equation. λ_∞ cannot be measured directly for AgOH and $\text{Mg}(\text{OH})_2$, although very approx. vals. are obtained. The cationic mobilities are: $\text{Mg}^{++} 56$, $\text{Ca}^{++} 60.1$, $\text{Sr}^{++} 60.3$, $\text{Ba}^{++} 65.05$, $\text{Ag}^+ 63.3$, $\text{Tl}^+ 78.7$. The measured conductivity coeffs. ($f\mu$) differ by $> 1\%$ from those calc. from Onsager's equation, except for AgOH and $\text{Mg}(\text{OH})_2$, which are not completely ionised even at very high dilutions. The vals. of $f\mu$ for a no. of hydroxides rise in the order $\text{NH}_4 < \text{Ag} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{Tl} < \text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.

R. T.

Conductance of potassium chloride and of hydrochloric-deuterochloric acid in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures. Viscosity of $\text{H}_2\text{O}-\text{D}_2\text{O}$. W. N. BAKER and V. K. LA MER (J. Chem. Physics, 1935, 3, 406—410).—Conductivity measurements for 0.01N-KCl and HCl-DCl in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures and of η for $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures at 25° are recorded. The η of D_2O is 23% $>$, the conductance of KCl in D_2O 17% $<$, and that of DCl in D_2O 26% $<$, corresponding vals. in H_2O . The η and conductance of KCl solutions and of HCl-DCl solutions show max. deviations of 0.4, 0.8, and 5.4% from linearity. The decreased conductance of KCl in D_2O is due mainly to the increased η of the solvent. H. J. E.

Electrical conductivity of glass-like alkali borates. B. I. MARKIN and R. L. MULLER (Acta Physicochim. U.R.S.S., 1934, 1, 266—281; cf. A., 1930, 1511).—The conductivities of glasses composed of B_2O_3 and Li_2O , K_2O , Rb_2O , or Cs_2O follow the law $\log k = -A/T + B$, excepting at low alkali concn. where the curves show breaks near the crit. softening point. At low alkali concn. the mol. conductivity remains almost const., but with increasing concn. a min. is first reached followed by a sharp rise. The min. is most marked with K_2O . Empirical relations between the consts. for the various alkalis are evolved. The mobilities of the alkali metal ions decrease with increasing mol. wt. of the ion.

J. W. S.

Influence of temperature on the electrical conductivity of saccharin solutions. A. IMBESI and V. DE ANGELIS (Annali Chim. Appl., 1935, 25,

254—262).—In the variation of degree of ionisation and dissociation const. with temp. and concn., saccharin behaves similarly to aliphatic and aromatic carboxylic acids.

T. H. P.

Magnetic fields and electrolytic conductors. K. KRISHNAMURTI (*Current Sci.*, 1935, 3, 351—352).—The decrease in the current on application of a magnetic field normal to the current has been studied by following the movements of streams of fine gas bubbles.

A. B. D. C.

Contact cells and their short-circuiting. (MLLE.) S. VEIL (*Compt. rend.*, 1935, 200, 2013—2015; cf. A., 1932, 226; this vol., 822).—A general discussion of e.m.f. phenomena in conducting gels.

H. J. E.

Ammonia gas electrode. V. FINKELSTEIN, M. SCHELUDKO, and A. TERESCHTSCHENKO (*Acta Physicochim. U.R.S.S.*, 1935, 1, 805—816).—E.m.f. measurements are recorded for the cells

$\text{Pt}|\text{NH}_3|\text{aq. NH}_4\text{NO}_3|\text{aq. KNO}_3|\text{aq. NH}_4\text{NO}_3|\text{Pt}|\text{O}_2$, and $\text{Pt}|\text{NH}_3|\text{aq. NH}_4\text{NO}_3|\text{aq. KNO}_3|\text{N-aq. KCl}+\text{Hg}_2\text{Cl}_2|\text{Hg}$; the vals. agree with those calc. from thermochemical data. The potential of the NH_3 gas electrode $\Pi_{\text{NH}_3} \rightarrow \text{NO}_3 = -0.17 \pm 0.01$ volt.

H. J. E.

Argentite salts in acid solution. II. Oxidation state of argentite salts. A. A. NOYES, K. S. PITZER, and C. L. DUNN. **III. Oxidation potential of argentous-argentite salts in nitric acid solution.** A. A. NOYES and A. KOSSIAKOFF (*J. Amer. Chem. Soc.*, 1935, 57, 1229—1237, 1238—1242).—II. Chemical and magnetic methods of examination confirm that the substance produced by oxidising AgNO_3 in HNO_3 solution with O_3 contains Ag^{++} , but not Ag^{+} .

III. The oxidation potential determined by e.m.f. measurements is 1.914 ± 0.002 volts, and it remains const. when $[\text{Ag}^{++}]:[\text{Ag}^{+}]$ is varied 2-fold and over the $[\text{HNO}_3]$ range 1—4*N*. Further evidence is adduced that the oxidation product consists almost entirely of Ag^{++} .

E. S. H.

Relations between oxidation-reduction potentials and acidity potentials in organic derivatives of arsenic acid. H. ERLENMEYER and E. WILLI (*Helv. Chim. Acta*, 1935, 18, 733—740).—In the series of acids represented by $\text{C}_6\text{H}_4\text{X} \cdot \text{AsO}_3\text{H}_2$, where $\text{X} = \text{NH}_2$, Me, Cl, or NO_2 , the oxidation-reduction potential is practically const., but there are considerable differences in acidity potential.

E. S. H.

Polarographic studies with the dropping mercury cathode. XLVIII. Overpotential in heavy water. J. HEYROVSKY and O. H. MULLER. **XLIX. Electro-reduction and determination of bromates and iodates.** A. RYLICH (*Coll. Czech. Chem. Comm.*, 1935, 7, 281—287, 288—298).—XLVIII. Solutions of HCl , TiCl_3 , and KCl in 3—99.2% D_2O have been studied polarographically with a dropping Hg cathode. Compared with H_2O solutions no differences are found in the $b \log i$ term of the overvoltage relation, in current oscillations due to the change of surface of the Hg drops, in the catalytic lowering of the overpotential due to a trace of quinine, in the currents due to deposition of alkali metals,

in the reduction of atm. O_2 , in the depolarising action of OH^{\cdot} , or in the electro-reduction of maleic acid. The inflexion points, characterising the process of electro-reduction, are 20—25 mv. more negative for dil. HCl solutions in 99.2% D_2O than for the same concn. in H_2O .

XLIX. Vals. for the reduction potentials of IO_3^{\cdot} and BrO_3^{\cdot} have been determined in presence of Na^{\cdot} , K^{\cdot} , Ca^{\cdot} , Sr^{\cdot} , Ba^{\cdot} , and La^{\cdot} . They vary with the cation valency in the same way as for NO_3^{\cdot} and NO_2^{\cdot} . The process of electro-reduction is $\text{IO}_3^{\cdot} + 6\text{e}^- + 3\text{H}_2\text{O} = \text{I}^{\cdot} + 6(\text{OH})^{\cdot}$. ClO_3^{\cdot} and ClO_4^{\cdot} are not reducible at the dropping Hg cathode. The reducibility of IO_3^{\cdot} , BrO_3^{\cdot} , and ClO_3^{\cdot} is given by their order of deformability. Simultaneous polarographic determination of IO_3^{\cdot} and BrO_3^{\cdot} is very sensitive, IO_3^{\cdot} being determinable with any excess of BrO_3^{\cdot} and ClO_3^{\cdot} , and BrO_3^{\cdot} with any excess of ClO_3^{\cdot} . IO_3^{\cdot} , BrO_3^{\cdot} , and NO_3^{\cdot} are simultaneously determinable.

H. J. E.

Maxima of the polarisation curve of mercury cathodes. A. FRUMKIN and B. BRUNS (*Acta Physicochim. U.R.S.S.*, 1934, 1, 232—246).—Previous theories are discussed and considered as unsatisfactory. It is suggested that the charge and discharge of the double layer and disturbances in the neighbourhood of the cathode, occasioned by local differences in the surface potential, are the primary factors in the polarisation phenomena.

J. W. S.

Polarisation capacity and constitution of the conducting layer at the electrode. N. THON (*J. Chim. phys.*, 1935, 32, 430—431).—With 0.5*M*- $\text{Hg}_2(\text{NO}_3)_2$, the apparent capacity of the Hg electrode $\sim 1/(\text{frequency})^2$, which is incompatible with the Warburg-Kruger theory. An electrode model for a.c. consistent with the results consists of a capacity and a resistance in parallel.

J. G. A. G.

Influence of the electrode surface on anodic processes. O. J. WALKER and J. WEISS (*Trans. Faraday Soc.*, 1935, 31, 1011—1017).—The phenomena observed by Glasstone and Hickling (cf. this vol., 176) on the addition of certain salts in the anodic oxidation of $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , and OAc^{\cdot} is traced to a change in the anode surface through the formation of oxide layers. The mechanism of evolution of O_2 at the anode and of the anodic oxidation of inorg. and org. ions and mols. is discussed.

E. S. H.

Oxygen overvoltage in the electrolysis of liquid mixtures of KNO_3 - NaNO_3 - LiNO_3 . S. KARPATSCHEV and V. PATZUG (*Z. physikal. Chem.*, 1935, 173, 383—387).—The anode overvoltages in eutectic mixtures have been measured.

T. G. P.

Theory of passivity phenomena. XXVII. Time phenomena in the anodic polarisation at smooth platinum in 2*N*-sulphuric acid. W. J. MULLER and O. HERING (*Monatsh.*, 1935, 66, 35—56).—An arrangement is described for measuring both the current-time and potential-time curves in the anodic polarisation of smooth Pt in 2*N*- H_2SO_4 . For the range 1.8—3.5 volts the two curves are similar. The ratio of initial current (after 0.005 sec.) to final current (after 20 min.) depends largely on the applied

potential, but the amount of current which passes during the period of the initial rapid decrease is practically const. (about 18×10^{-4} coulomb). Up to potentials of 2 volts the main process in the anodic polarisation consists in the dissolution of Pt in the pores of the metal. During this stage the current falls rapidly. Above 2 volts O_2 evolution commences.

O. J. W.

Electrolysis of sodium chloride in liquid ammonia. I. E. I. ACHUMOV and B. B. VASILIEV (J. Gen. Chem. Russ., 1935, 5, 334—342).—The conductivity of solutions of NaCl in liquid NH_3 rises with the [NaCl]; the decomp. potential of NaCl is 3.54 volts. Electrolysis with a diaphragm leads to production of NH_4Cl in the anode, and of $NaNH_2$ in the cathode, section.

R. T.

Formation of alloys from galvanic elements. V. A. PLOTNIKOV and D. P. ZOSIMOVITSCH (J. Gen. Chem. Russ., 1935, 5, 327—333).—On closing the circuit between two electrodes immersed in a fused salt, or in its aq. solution, the baser metal is deposited on the nobler one, yielding an alloy. The e.m.f. of the cell $Zn|fused\ ZnCl_2|Cu$ changes with time to that of $Zn|fused\ ZnCl_2|\beta\text{-brass}$. A deposit of brass forms on the Pt electrode of a Daniell cell containing $CuSO_4$ and $ZnSO_4$.

R. T.

Determination of the mechanism of chemical reactions. M. BODENSTEIN (Helv. Chim. Acta, 1935, 18, 743—759).—A lecture.

E. S. H.

Kinetics of polymerisation processes. G. GEE and E. K. RIDEAL (Trans. Faraday Soc., 1935, 31, 969—979).—Theoretical. A steric factor provides a sufficient mechanism for chain termination. Induction periods, points of max. reaction, and variations of chain length are discussed.

E. S. H.

Calculation of energy loss in combustion. J. VILLEY (Compt. rend., 1935, 200, 1921—1923).—Theoretical. A thermodynamical treatment.

H. J. E.

Ignition temperatures of gases.—See B., 1935, 660.

Thermal decomposition of ozone. H. J. SCHUMACHER (Proc. Roy. Soc., 1935, A, 150, 220—223).—Polemical. If the reaction scheme given by Ritchie (this vol., 39) were correct, the kinetics of the thermal decomp. would be identical with those of the photochemical decomp.; this is not the case, and it is concluded that his mechanism is incorrect. The high velocities obtained by Ritchie indicate that he was measuring the catalytic, not the homogeneous, decomp. of O_3 .

L. L. B.

Mechanism of hydrogen-oxygen explosions. M. V. POLJAKOV, I. I. MALKIN, and V. A. ALEXANDROVITSCH (Acta Physicochim. U.R.S.S., 1935, 1, 821—832).—Data are recorded for the dependence of the H_2O_2 yield in H_2-O_2 explosions initiated by a Pt wire (the reaction vessel being dipped in liquid air) on the vessel dimensions and pressure. O_3 was also detected. Increase in total pressure or in vessel dimensions lowers the H_2O_2 yield. Increase in the H_2 pressure raises it. Increase in the O_2 raises the

O_3 . The reaction mechanism is discussed. The chain mechanism probably changes with the conditions.

H. J. E.

Detonation in gas mixtures. II. Influence of pressure on the velocity of a detonation wave. A. SOKOLIK and K. SHTSHOLKIN (Acta Physicochim. U.R.S.S., 1934, 1, 311—317).—The velocities of detonation waves in $2H_2+O_2$, CH_4+2O_2 , CH_4+O_2 , and H_2+Cl_2 mixtures have been determined between atm. pressure and the min. explosion pressure. The val. changes with initial pressure for $2H_2+O_2$ and CH_4+2O_2 mixture in the direction indicated by Jouguet's theory, whereas the velocity is independent of initial pressure for H_2+Cl_2 . The results are in accord with the theory that dissociation occurring in the wave front causes the change in the velocity of detonation with pressure.

J. W. S.

Combustion of H_2+O_2 at room temperature in the presence of oxygen atoms. A. NALBANDJAN (Acta Physicochim. U.R.S.S., 1934, 1, 305—310).—An arrangement for introducing a H_2+O_2 mixture into a reaction vessel 0.07 sec. after switching off a discharge in the vessel is described. Contrary to previous data, the length of the reaction chain (calc. from the no. of O atoms present on introduction of the gases) is about 70, and reaction is complete in 0.1 sec. These observations are explained by assuming that when there is a large no. of initial centres the chains interact, thus increasing chain length.

J. W. S.

Explosion regions at reduced pressure. I. Pressure limits in the system $H_2-O_2-N_2$. J. DROR (Rec. trav. chim., 1935, 54, 671—679).—The explosion limits were determined for a series of $[H_2-O_2]-N_2$ mixtures, in which the $H_2:O_2$ ratio varied from 25:75 to 80:20, whilst for each $H_2:O_2$ ratio the N_2 ranged from 0 to 60%. Pressure throughout was 60 cm. The results agreed with those deduced theoretically, from the law of mass action, by van Heinigen (Diss., Leyden, 1934), the explosion limits being represented by the surface $q=Kp^2x(1-x-y)$ where q is the reaction rate just yielding explosion, K is a const., p is the pressure, and x , $1-x$, and y are the concns. of H_2 , O_2 , and N_2 , respectively.

S. J. G.

Experimental determination and theoretical calculation of flame temperatures and explosion pressures. B. LEWIS and G. VON ELBE (Phil. Mag., 1935, [vii], 20, 44—65).—Anomalies between theoretical flame temp. calc. from band spectra and experimental vals. are discussed and attributed to effects such as time dependency of sp. heats and radiation losses. The results and conclusions of David and others (A., 1930, 865; 1932, 25; 1934, 258, 1073) are criticised.

J. W. S.

Flame temperatures and explosion pressures. W. T. DAVID (Phil. Mag., 1935, [vii], 20, 65—68).—Polemical against Lewis and von Elbe (cf. preceding abstract).

J. W. S.

Kinetics of carbon monoxide combustion. II. Heat of activation with respect to different catalysts. V. FINKELSHTEIN, I. CHRISMAN, and M. RUBANIK (Ber. Ukrain. wiss. Forsch.-Inst. physik.

Chem., 1934, 4, 19—27; cf. A., 1929, 515).—For oxidation of CO on Fe_2O_3 , Cr_2O_3 , ZnO , porcelain, Al_2O_3 , CuO , pyrolusite, and MnO_2 , the heats of activation were respectively 29.1, 25.2, 26.1, 24.9, 24.9, 22.0, 8.3, and 10.7 kg.-cal. The reaction, especially with the weaker catalysts, is initially third order, but is later retarded owing to poisoning by CO_2 . The mechanism is firstly an activation of adsorbed O_2 , followed by a three-body collision on the catalyst surface: $\text{O}_2 + 2\text{CO} = 2\text{CO}_2$. For more active catalysts intermediate higher oxides may be formed.

CH. ABS. (e)

Explosions of carbon disulphide-nitric oxide mixtures and their practical applications. J. A. M. VAN LIEMPT (Chem. Weekblad, 1934, 31, 706—708).—There is a crit. point for the mixtures at 3.5 cm. pressure and a mol. ratio ($\text{CS}_2:\text{NO}$) of 1:2.3. The max. light output ($I \times t$) at a given pressure is obtained with a ratio between 1:2.25 and 1:2.75, and varies with the square of the pressure. The reaction is $5\text{CS}_2 + 10.8\text{NO} \rightarrow 5.4\text{N}_2 + 2.6\text{CO} + 2.4\text{CO}_2 + 1.7\text{SO}_2 + 8.3\text{S} + 784 \text{ kg.-cal.}$ At 11 cm. the light output is 16.7% of the theoretical, and at 70 cm. 41.5%. The spectrum of the radiation is continuous between 3200 and 6300 Å., with the max. intensity between 3700 and 4200 Å. For photography with panchromatic plates, Na, Ca, Ba, and Sr salts should be used to raise the intensity at the longer λ . Experiments on the speed of the reaction, and its practical significance, are described.

H. F. G.

Explosion ranges. W. P. JORISSEN (Chem. Weekblad, 1934, 31, 694—699).—The rates of reaction and reaction limits for various binary and ternary mixtures of gases and solids (e.g., Fe and S, Fe, Mg, and S) are given and discussed.

H. F. G.

Explosive reactions between combustible gases and nitrous and nitric oxides. M. J. VAN DER WAL (Chem. Weekblad, 1934, 31, 708—711).—The explosion limits in the systems $\text{CH}_4\text{-NO}$, $\text{CH}_4\text{-N}_2\text{O}$, $\text{CH}_4\text{-NO-N}_2\text{O}$, $\text{CO-N}_2\text{O}$, $\text{CH}_4\text{-CO-N}_2\text{O}$, $\text{CO-N}_2\text{O-NO}$, $\text{H}_2\text{-N}_2\text{O}$, $\text{H}_2\text{-N}_2\text{O-NO}$, and $\text{H}_2\text{-CO-N}_2\text{O}$ have been determined. No closed explosion region could be found for ternary gas mixtures, but the model for the quaternary system $\text{H}_2\text{-CO-NO-N}_2\text{O}$, derived from the three three-component systems, appears to contain a closed explosion range.

H. F. G.

Theory of combustion of hydrocarbons. R. G. W. NORRISH (Proc. Roy. Soc., 1935, A, 150, 36—57).—The slow and explosive combustion of CH_4 , C_2H_6 , C_2H_4 , and olefines in general can be described by representing the reaction in terms of an atom-chain mechanism involving alternately O and free radicals. At low temp. (300—500°) the chains start at the surface from O generated from traces of aldehyde initially formed on the surface during the induction period: $\text{R}\cdot\text{CHO} + \text{O}_2 \rightarrow \text{R}\cdot\text{CO}_2\text{H} + \text{O}$. At high temp. free radicals may be directly generated from hydrocarbons (e.g., CH_2 from CH_4 at 800°) and these may form chains directly. The propagation of the CH_4 chain may be represented by the alternating reactions: $\text{O} + \text{CH}_4 = \text{CH}_2 + \text{H}_2\text{O}$; $\text{CH}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$. Branching may also occur through $\text{CH}_2\text{O} + \text{O}_2 = \text{HCO}_2\text{H} + \text{O}$. The chains end at the wall or by ternary

collision, e.g., $\text{X} + \text{CH}_4 + \text{O} \rightarrow \text{X}' + \text{MeOH}$. This is the origin of MeOH in combustions at high pressures. This hypothesis affords an explanation of the varied kinetic and analytical data of the oxidation of hydrocarbons.

L. L. B.

Rate of combustion of pentane[-oxygen] mixtures. N. N. GUSEV and M. B. NEUMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 377—382).—Mean velocities of flame propagation in pentane- O_2 mixtures ignited by an electric spark have been determined. At a given initial pressure and temp., velocity \propto composition, and within a narrow pressure range there are two velocity max., which were also found with other air-hydrocarbon mixtures, in accord with the semi-quant. theory outlined.

T. G. P.

Pyrogenetic reactions of condensation of hydrocarbons. II. Kinetics of polymerisation and decomposition of ethylene. III. Kinetics and mechanism of polymerisation of propylene. IV. Kinetics of polymerisation of butylenes and amylenes. M. V. KRAUZE, M. S. NEMTZOV, and E. A. SOSKINA (J. Gen. Chem. Russ., 1935, 5, 343—355, 356—360, 382—387).—II. A detailed account of work already noted (A., 1934, 736). The products are chiefly unsaturated aliphatic hydrocarbons, together with *iso*-paraffins; aromatic, naphthenic, and cyclohexene hydrocarbons are absent. The reactions $\text{CH}_4 + \text{C} + 28,200 \text{ g.-cal.} \leftarrow \text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2 + 8600 \text{ g.-cal.}$ take place under the conditions of cracking of liquid hydrocarbons.

III (see *ibid.*, 1179). The products are chiefly olefines and saturated aliphatic hydrocarbons; gaseous olefines (C_2H_4 and butenes) and cyclic hydrocarbons are not formed.

IV. The results (*loc. cit.*) indicate that substitution of one H per C of C_2H_4 retards reaction, owing to steric hindrance, whilst substitution of both H modifies the energetic character of the mol., raising its activation energy.

R. T.

Kinetics of the thermal decomposition of methylamine. H. J. EMELEUS and L. J. JOLLEY (J.C.S., 1935, 929—935; cf. this vol., 172).—The decomp. of 375—33 mm. of NH_2Me at 540—670° consists mainly of (a) $\text{NH}_2\text{Me} \rightarrow \text{HCN} + 2\text{H}_2$ and (b) $\text{NH}_2\text{Me} + \text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_3$. (a) is largely homogeneous with an energy of activation 58,000 g.-cal., and is unimol. at pressures as low as 33 mm., corresponding with ≤ 13 degrees of freedom being involved in the activation process. (b) is heterogeneous and the yield of CH_4 is increased by lowering the temp. and by packing the vessel, but is not affected by the products of decomp. or added H_2 . (a) and (b) are consistent with a chain reaction initiated by $\text{NH}_2\text{Me} \rightarrow \text{Me} + \text{NH}_2$.

J. G. A. G.

Thermal decomposition of diethylamine. H. A. TAYLOR and C. R. HERMAN (J. Physical Chem., 1935, 39, 803—810).—The rate of increase of pressure during the decomp. of NHEt_2 at 510—540° indicates a homogeneous reaction with, in the early stages, an energy of activation of 49,000 g.-cal. per mol. Analysis of the intermediate products indicates that the decomp. involves the formation and subsequent decomp. of $(\text{NHEt})_2$ and C_4H_{10} .

J. W. S.

Polymerisation and hydrogenation of acetylene. H. A. TAYLOR and A. VAN HOOK (J. Physical Chem., 1935, 39, 811—819).—The principal processes in the homogeneous thermal polymerisation of C_2H_2 and the hydrogenation of C_2H_2 at 495—535° are bimol., with energies of activation of 40,500 and 42,000 g.-cal. per mol., respectively. The efficiency of collisions between activated mols. is high. J. W. S.

Chlorination of propane. I. Homogeneous reaction. S. YUSTER and L. H. REYERSON (J. Physical Chem., 1935, 39, 859—875).—The homogeneous reaction between C_3H_8 and Cl_2 at 100—300° is a chain reaction, and a chain mechanism is suggested which accounts for the results obtained. Chains are stopped by the walls of the reaction vessel and to a smaller extent are initiated by them, but the walls become poisoned at high $[Cl_2]$. High rates of flow and high $[Cl_2]$ favour explosions. The heat of activation calc. from the temp. coeff. and from the collision efficiency is about 20,000 g.-cal. per mol. J. W. S.

Velocity of reaction of sodium atoms with chloro-, bromo-, and iodo-benzene. F. FAIRBROTHER and E. WARHURST (Trans. Faraday Soc., 1935, 31, 987—998).—The rates of reaction of $PhCl$, $PhBr$, and PhI with Na vapour, determined by the "life-period" method, are of the same order as in the aliphatic series. The effect of the change of halogen atom is also similar in the two series. E. S. H.

Kinetic derivation of the mass action expression. H. G. DEMING (J. Chem. Educ., 1935, 12, 195). L. S. T.

Velocity of oxidation of sodium arsenite by atmospheric oxygen under pressure. V. S. MALINOVSKI and E. P. LOPATINA (J. Appl. Chem. Russ., 1935, 8, 425—428).—The reaction of oxidation of $NaAsO_2$ by atm. O_2 at 100—250°, under pressure, is one of the first order. R. T.

Velocity of formation of an amorphous precipitate of sulphur in a certain simple case. W. JACEK (Rocz. Chem., 1935, 15, 258—272).—The velocity of formation of a ppt. of S from aq. $Na_2S_2O_3$ or $KCNS$ is expressed by $dx/dt = Kx^{5/3}(1-x)/(x+k_1)$, where $x = (r/r_0)^3$, r and r_0 are the radii of the particles at time t , and after completion of the process, $K - h_0/3r_0$, h_0 is the increase in the radius of the particles in unit time during the initial stages of the process, and k_1 is a const. R. T.

Oxidation of stannous sulphate by oxygen. D. STEPANOV and F. MARSHAK (J. Gen. Chem. Russ., 1935, 5, 289—293).—The velocity of oxidation of aq. $SnSO_4$ by atm. O_2 falls with increasing $[H_2SO_4]$; the reaction in no case proceeds to completion. Oxidation is inhibited by traces of phenols [$C_6H_4(OH)_2$, guaiacol, $C_{10}H_7OH$, vanillin, $C_6H_3(OH)_3$, $PhOH$, cresol] or alkaloids (morphine, papaverine), whilst neutral sulphates ($MgSO_4$, Na_2SO_4) are without effect. R. T.

Rate of reaction between ferric and stannous salts in solution. R. A. ROBINSON and N. H. LAW (Trans. Faraday Soc., 1935, 31, 899—906).—The reaction between $Fe(ClO_4)_3$ and $Sn(ClO_4)_2$ is termol. owing to hydrolysis of the $Fe(ClO_4)_3$. With $FeCl_3$ and $SnCl_2$ in acid or neutral solution a bimol. reaction occurs simultaneously, being accelerated by Cl^- ,

probably owing to polymerisation of $FeCl_3$. The temp. coeff. of the reaction velocity suggests that reaction occurs between one Sn^{++} ion and one $Fe_2(OH)_2^{+++}$ ion present in small concn. relative to the total amount of hydrolysed $FeCl_3$. J. W. S.

Variation of reaction velocity with temperature. J. A. MULLER and (Mlle.) E. PEYTRAL (Bull. Soc. chim., 1935, [v], 2, 1462—1467).—The relationship $k = \alpha\beta^{-1/T}$, where α and β are two parameters which depend on the reaction, is applied to the reaction between salicylic acid and Ac_2O , $H_2C_2O_4$ and $KMnO_4$ in the presence of H_2SO_4 , and to the saponification of Et lactate. T. G. P.

Effect of pressure on reactions in solution. I. Sodium ethoxide and ethyl iodide to 3000 kg. per sq. cm. II. Pyridine and ethyl iodide to 8500 kg. per sq. cm. R. O. GIBSON, E. W. FAWCETT, and M. W. PERRIN (Proc. Roy. Soc., 1935, A, 150, 223—240).—Vals. are given for the velocity coeffs. for the reaction between $NaOEt$ and EtI in $EtOH$ for pressures of 1 and 3000 kg. per sq. cm. at 15—30° in a 0.1M solution, and at 25° with initial concns. of $NaOEt$ of 0.05—0.5M; and for the reaction between C_5H_5N and EtI in $COMe$, for pressures of 1, 3000, 5000, and 8500 kg. per sq. cm. at 20—60°. A marked difference is found in the effect of pressure on the typical "normal" and "slow" reactions studied. Whilst a pressure of 3000 kg. per sq. cm. increases the velocity coeff. of the normal reaction only 1.6 times, it increases that of the slow reaction 7.2 times. In the normal reaction, only the val. of the "collision term" A of the Arrhenius equation is increased by pressure, whilst in the slow reaction the vals. of both A and of the "activation energy" E are increased by pressure. L. L. B.

Kinetics of rapid reactions. I. H. VON HALBAN and H. EISNER (Helv. Chim. Acta, 1935, 18, 724—733).—Using an optical method, preliminary observations have been made with several inorg. oxidation-reduction reactions. The method has been applied to the study of the kinetics of the reaction of $C_6H_4(NO_2)_2$ with $NPhMe_2$ or $NPhEt_2$ in $EtOH$ solution. E. S. H.

Velocity of absorption of propylene by sulphuric acid. V. PIGULEVSKI and N. RUDAKOVA (Materials on Cracking, 1933, No. 1, 67—77; cf. A., 1930, 549).—Absorption of C_3H_6 by H_2SO_4 follows the law for unimol. reactions. The amount absorbed by unit surface in unit time \propto the partial pressure of C_3H_6 , and is independent of its vol. The absorption is an autocatalytic process. Vals. of the velocity coeff. at 5—25° were determined for 75—88% acid. CH. ABS. (e)

Velocity of decomposition of diazo-compounds in water. XVII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 275—280B; cf. this vol., 173).—Sunlight increases the velocity coeff. (k) of decomp. of $1-C_{10}H_7-N_2Cl$. Results on the naphthalenediazo-compounds are collated and discussed. The order of the reaction is 0 or 1 according as the diazo-compound is pptd. or dissolved. Temp. coeffs., k , temp. of diazotisation, and the influence of sunlight and added substances are compared. R. S. B.

Oxidation of quinol solutions. III. Effect of alkali salts and metallic hydroxides. A. SAINT-MAXEN (J. Chim. phys., 1935, 32, 410—428).—Details of earlier work (A., 1930, 1128; 1932, 578) are given. The log. of the initial rate of oxidation of quinol (I) in a given type of buffer solution increases linearly with increasing p_H and is independent of [salt], but in borate buffers is $>$ in phosphate buffers of equal p_H . Carbonate buffers give similar results. The oxidation catalysed by alkalis and $Mg(OH)_2$ is interpreted in terms of sol. compounds formed with (I). The rate of oxidation induced by equiv. proportions of $La(OH)_3 > Y(OH)_3 > Ni(OH)_2$, prepared by hydrolysing the acetates, increases during re-hydration and decreases during the subsequent coagulation of the hydroxide. These hydroxides do not form compounds with (I) and are insol. in aq. (I) and probably catalyse the fixation of O_2 on the acceptor, (I). Equiv. amounts of KOH and $Ni(OH)_2$ have approx. equal catalytic effects.

J. G. A. G.

Physicochemical study of the reducing action of glucose. W. B. WOOD, jun. (J. Biol. Chem., 1935, 110, 219—232).—A potentiometric method for studying the irreversible oxidation of glucose (I) by $Fe(CN)_6'''$ (II) is described. Decreasing the p_H , lowering the temp., or increasing the salt content slows down the reaction rate but increases the final amount of (II) reduced. The final amount of (II) reduced \propto the concn. of (I) (within the limits of blood-sugar determinations), but the time for complete reaction also increases with the (I) concn. An increase in the (II) concn. slightly increases the final amount of (II) reduced. There is a great similarity in the oxidising action of Cu^{++} and (II) in alkaline solution. As changes in p_H affect reduction of (II) by (I) and fermented blood filtrate to about the same extent, it is concluded that there is no optimum p_H at which the non-(I) reducing substances exert a min. effect. An enhancement by NaCN of the reducing action of (I) accounts for the lower, and more accurate, blood-sugar vals. obtained by the Folin microcolorimetric method.

E. A. H. R.

Isomerisation of cyanogenic heterosides. V. PLOUVIER (Compt. rend., 1935, 200, 1985—1987).—The rates of isomerisation of amygdalin and of amygdonitrileglucoside (I) are increased by rise in temp. and in p_H . (I) is isomerised to prulaurasin (II). Both have been isolated from the leaves of *Photinia serrulata* (A., 1912, ii, 675), but the (II) may be due to isomerisation of (I) during the extraction process.

H. G. M.

Rates of racemisation of acids of the type $CHRR'CO_2H$. B. K. MENON and D. H. PEACOCK (J. Indian Chem. Soc., 1935, 12, 268—272).—The rates of racemisation of six acids of the above type have been measured, in which R and R' are, respectively: Bu^a , CH_2Ph ; Bu^a , $p-C_6H_4Br-CH_2$; CH_2Ph , $p-C_6H_4Br-CH_2$; CH_2Ph , $m-C_6H_4Br-CH_2$; CH_2Ph , $p-C_6H_4Cl-CH_2$, and CH_2Ph , $m-C_6H_4Cl-CH_2$. Replacement of Bu^a by CH_2Ph or $p-C_6H_4Br-CH_2$ greatly increases the rate of racemisation. With the *m*-substituted acids the Br-acid racemises faster than the Cl-acid, but with the *p*-substituted acids

the rates are equal for Cl- and Br-derivatives. The results are discussed.

O. J. W.

Salt activation. I. Influence of neutral salts on the enzymic hydrolysis of starch.—See this vol., 1162.

Kinetics of the decomposition process and the problem of chains in the solid phase. S. M. MOSKOVITSCH (Uspekhi Khim., 1934, 3, 752—760).—A discussion. Chain mechanisms in solids differ from those in a homogeneous gas phase because chains can be broken on the phase boundaries, and because of anisotropic properties of the crystals.

CH. ABS. (e)

Thermal dissociation of silver nitrite. M. CENTNERSZWER and T. CHĘCIŃSKI (Bull. Acad. Polonaise, 1935, A, 156—165).—In a vac. or at low pressure the dissociation of $AgNO_2$ follows the equation $AgNO_2 \rightleftharpoons Ag + NO_2$, but at higher pressure it is a reversible reaction: $2AgNO_2 \rightleftharpoons Ag + AgNO_3 + NO$. The dissociation pressures above 150 mm. follow the Nernst equation $\log p = (15365.6/4.571T) + 1.75 \log T + 3.716$.

J. W. S.

Kinetics of the thermal dissociation of silver nitrite. M. BLUMENTHAL and T. CHĘCIŃSKI (Bull. Acad. Polonaise, 1935, A, 166—173; cf. preceding abstract).—The thermal decomp. of $AgNO_2$ occurs in two stages, viz., $AgNO_2 = Ag + NO_2$ and $NO_2 + AgNO_2 = AgNO_3 + NO$, the velocity of each reaction being dependent on pressure. In a vac. the reaction is of the first order, and at atm. pressure of the second order. Rise in temp. diminishes the order of the reaction. An induction period is observed near the equilibrium state.

J. W. S.

Kinetics of decomposition of sodium mercurisulphide by water. A. LOTTERMOSER and E. HAENEL (Abh. nat. Ges. Isis, Festschr., 1934, 195—203; Chem. Zentr., 1935, i, 1026—1027).—The rate of decolorisation of Na mercurisulphide (I) solutions was followed photometrically; it is compounded of the rate of decomp. of (I) and the rate of separation of HgS , and is independent of the concn. of (I), \propto the amount of H_2O and of neutral salts, and $\propto 1/[Na_2S]$.

J. S. A.

Rate of dissolution of zinc in acids. C. V. KING and M. SCHACK (J. Amer. Chem. Soc., 1935, 57, 1212—1217).—The rate of dissolution of rotating Zn cylinders in dil. AcOH \propto the peripheral velocity up to 163,000 cm. per min. In presence of KNO_3 the rate is at first nearly $\propto [AcOH]$ and almost independent of $[KNO_3]$. In presence of $p-OH \cdot C_6H_4 \cdot NO_2$, benzoquinone, or H_2O_2 the rate increases with the concn. of oxidising agent and is nearly independent of $[AcOH]$. NaCl accelerates the rate at low concn. but retards it at higher concn.; NaOAc has a retarding effect throughout.

E. S. H.

Kinetics of anode film formation on metals. L. J. KURTZ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 383—389).—The formation and nature of AgCl and AgBr films deposited on a Ag anode by the electrolysis of KCl and KBr solutions have been studied through the polarisation curve of the electrode, the conductivity of the films, and their appearance under the microscope. Deposition begins in isolated islets

which spread until the surface is covered at a definite mean film thickness, which decreases with increasing c.d., as does the size of the crystals deposited and the sp. resistivity of the film. There is an unexplained discontinuity in the polarisation curve. T. G. P.

Corrosion of aluminium by sodium hydroxide. Y. K. HENG and Y. TA (Compt. rend., 1935, 200, 2153—2155; cf. A., 1933, 240).—Corrosion by NaOH was measured in presence of Na tartrate by determining the α of the Na aluminotartrate produced. Preliminary data are given for the rate of corrosion of Al specimens of varying purity and for Al alloys.

H. J. E.

Catalytic and induced reactions in micro-chemistry. I. M. KOLTHOFF and R. S. LIVINGSTON (Ind. Eng. Chem. [Anal.], 1935, 7, 209—213).—Mainly a discussion. Observations on the catalytic influence of Ag on the reduction of Mn^{III} and of Hg on the reduction of As^V are recorded.

E. S. H.

Polymerisation of ethylene induced by methyl radicals. O. K. RICE and D. V. SICKMAN (J. Amer. Chem. Soc., 1935, 57, 1384—1385).— C_2H_4 is rapidly polymerised at about 300° by small amounts of azomethane (I). Under the conditions studied the initial rate depends on \sqrt{p} of (I) and $p^{3/2}$ of C_2H_4 ; k is 3.0 and 6.5×10^{-6} mm.⁻¹ sec.⁻¹ at 290° and 310° , respectively. A chain decomp. is also set up in EtCHO (II) and isobutane by (I); the use of 6.5% of (I) leads to 60—70% decomp. of (II), showing that the reaction is not a "degenerate explosion" (Semenov, this vol., 451).

H. B.

Enzyme catalysis of the exchange of deuterium with water. G. H. BOTTOMLEY, B. CAVANAGH, and M. POLANYI (Nature, 1935, 136, 103—104; cf. A., 1934, 738).—The first-order velocity coeff. is inversely \propto the square root of the pressure of the hydrogen. The reaction takes place in two stages, $HD + 2B \rightleftharpoons HB + DB$ and $DB + H_2O \rightleftharpoons HB + DHO$, where B represents a catalytic centre. During the reaction the no. of living bacteria (*B. acidilactici*) diminishes rapidly without affecting the catalytic power.

L. S. T.

Influence of small amounts of agar-agar and gelatin on the KG [crystallisation velocity] of cathode deposits of silver. A. GLAZUNOV, J. TEINDL, and J. HALÍK (Chem. Listy, 1935, 29, 117—118, 131—133).—The velocity of crystallisation (linear) of Ag at the cathode during electrolysis of $AgNO_3$ is reduced by presence of 0.03—0.15% of agar or gelatin in the electrolyte; the effect is not due to viscosity changes. The colloids are present in small amount in the deposit, either in the residual electrolyte between the crystallites, or in the crystal lattice.

R. T.

Reactions between oxalic and permanganic acids in presence of dilute sulphuric acid, and the velocities of these reactions. J. A. MULLER and (MLLE.) E. PEYTRAL (Bull. Soc. chim., 1935, [v], 2, 1457—1462).—The nature and velocities of the intermediate reactions occurring in the autocatalytic oxidation of $H_2C_2O_4$ by $KMnO_4$ in presence of H_2SO_4 have been studied.

T. G. P.

Catalytic decomposition of formic acid in presence of selenic acid. R. DOLIQUE (Bull. Soc. chim., 1935, [v], 2, 1489—1491).— H_2SeO_4 catalyses the decomp. of HCO_2H into CO and H_2O , CO_2 appearing only towards the end of the reaction, or when the H_2SeO_4 is in excess.

T. G. P.

Intermediate stages of aldehyde oxidation.

I. Catalytic action of manganese catalyst in the various stages of the process of acetaldehyde oxidation. M. J. KAGAN and G. D. LUBARSKY. **II. Kinetics of the interaction between peracetic acid and the aldehydes.** G. D. LUBARSKY and M. J. KAGAN (J. Physical Chem., 1935, 39, 837—846, 847—857).—I. The oxidation of MeCHO by O_2 in AcOH solution in presence of Mn^{II} salts proceeds rapidly after production of the dark brown $Mn(OAc)_3$ (through action of AcO_2H on Mn^{II}) which acts as a catalyst. Presence of H_2O increases the induction period, owing to decomp. of the catalyst, and in absence of H_2O the induction period can be eliminated by addition of a Mn^{III} salt. It is suggested that the catalyst may hasten the decomp. of an intermediate peroxide produced by addition of AcO_2H to MeCHO, as well as decompose AcO_2H to yield active O which can oxidise MeCHO directly. AcO_2H is decomposed vigorously and exothermically by Mn^{III} in AcOH, yielding mainly CO_2 , and only slowly in H_2O , yielding mainly O_2 . The latter process is a first-order reaction with an energy of activation of about 12,000 g.-cal. per mol.

II. The reaction between AcO_2H and MeCHO in AcOH, C_6H_6 , $PhNO_2$, $CHCl_3$ or PhMe at 10 — 30° has an energy of activation of 15,400—16,300 g.-cal. per mol. It follows a second-order equation but there is a short initial period of rapid decrease of $[MeCHO]$, attributed to the formation of an intermediate compound, probably $OH \cdot CHMe \cdot O \cdot O \cdot COMe$, which exists in equilibrium with the reactants and decomposes relatively slowly. This intermediate compound separates on carrying out the reaction at -40° to -60° , the energy of activation of this stage of the reaction being 7000 g.-cal. per mol. Its decomp. is unimol. The behaviour of Bu^sCHO is similar to that of MeCHO.

J. W. S.

Benzoin reaction. II. Negative catalysis. D. R. NADKARNI and S. M. MEHTA. **III. Effect of water.** D. R. NADKARNI (J. Physical Chem., 1935, 39, 901—906, 907—912).—II. KCl, NaCl, KI, and quinol inhibit the benzoin reaction through stopping the heterogeneous reaction, but they do not affect the homogeneous autocatalytic reaction.

III. Addition of H_2O to KCN first increases and then decreases its rate of reaction with PhCHO, autocatalysis disappearing gradually. This is attributed to the extraction of CN^- from solution in the PhCHO. Inhibition of the reaction by KI is less marked in presence of H_2O .

J. W. S.

Kinetics of heterogeneous catalysis and of enzyme action. E. C. C. BALY (Nature, 1935, 136, 146).—Theoretical. Equations are given, and it is suggested that enzyme reactions are of the two-stage activation type. Neither the crit. increment of a heterogeneous reaction nor that of the deactivation of an enzyme system can be determined directly from

measurements of reaction velocity at two different temp.

L. S. T.

Velocity of absorption of unsaturated gases by sulphuric acid in presence of catalysts. M. B. MARKOVITSCH, V. G. MOOR, and M. I. DEMENTIEVA (Materials on Cracking, 1933, 1, 77—102).—Data are recorded for the effect of numerous substances (e.g., alkali sulphates, As_2O_3 , Se, COMe_2 , $\text{C}_5\text{H}_5\text{N}$) on the absorption. Ag compounds gave the best results. Some of the salts had a retarding action. Addition of liquids insol. in H_2SO_4 increased the rate of physical dissolution of the gases.

CH. ABS. (c)

Spin-isomerisation of hydrogen in paramagnetic and diamagnetic surfaces. H. S. TAYLOR and H. DIAMOND (J. Amer. Chem. Soc., 1935, 57, 1251—1256).—Rapid interconversion of ortho- and para- H_2 at low temp. is obtained on surfaces of paramagnetic metals, oxides, and salts. The velocity is reduced by decreasing magnetic susceptibility or adsorptive capacity. Slow conversion at liquid-air temp. on diamagnetic catalysts may be due to paramagnetism of surface atoms or residual low-temp. activated adsorption. A new high-temp. conversion involving an exchange reaction with H_2O has been observed. Sintering of Cu catalysts affects the low-temp. activity for the H_2 conversion < for the hydrogenation of C_2H_4 .

E. S. H.

Catalytic exchange reaction between deuterium and water. H. S. TAYLOR and H. DIAMOND (J. Amer. Chem. Soc., 1935, 57, 1256—1259).—Rapid exchange has been observed at high temp. between D_2 and H_2O retained by catalysts of Cr_2O_3 , ZnO , ZnCr_2O_4 , Al_2O_3 , and Pt-asbestos. The reverse reaction between H_2 and D_2O has also been demonstrated. The variation of reaction velocity with temp. has been approx. determined with Cr_2O_3 . The mechanism is discussed.

E. S. H.

Heterogeneous-homogeneous catalysis. Hydrogen and oxygen in presence of platinum. III. M. V. POLJAKOV, P. M. STADNIK, and A. T. ELKENBARD (Acta Physicochim. U.R.S.S., 1935, 1, 817—820; cf. this vol., 588).—Interaction of H_2 and O_2 on a Pt wire at 400—450° leads to formation of H_2O_2 , yield depending in the same manner on the H_2 pressure as does that in the homogeneous explosive reaction. The mechanism in the two cases is the same, the heterogeneous process initiating homogeneous H_2O_2 formation. The no. of active centres, and hence the abs. H_2O_2 yield, is much greater in the explosive reaction.

H. J. E.

Active oxides. LXXXIX. Course of formation of zinc ferrite from zinc oxide and iron oxide. G. F. HUTTIG, H. E. TSCHAKERT, and H. KITTEL (Z. anorg. Chem., 1935, 223, 241—250; cf. A., 1934, 850).—The catalytic activity of equimol. $\text{ZnO} + \text{Fe}_2\text{O}_3$ mixtures for both the $2\text{CO} + \text{O}_2$ reaction and the N_2O decomp. plotted as a function of the temp. of heating shows two max. The higher corresponds also with the onset of paramagnetism, and with fluorescence different from that of ZnO , with a min. d , and with the threshold of crystallisation of ZnFe_2O_4 . The formation of two states of max. catalytic activity

is discussed in relation to the theory of solid reactions.

J. S. A.

Primary decomposition of hydrocarbon vapours on carbon filaments. L. BELCHETZ and E. K. RIDEAL (J. Amer. Chem. Soc., 1935, 57, 1168—1174).—The primary products of decomp. of CH_4 at heated C or Pt filaments are CH_2 and H_2 . CH_2 radicals condensing on a cooled surface readily unite to form C_2H_4 . TeCH_2 is readily reduced to TeMe_2 and Te_2Me_2 . The energy of activation for the decomp. of CH_4 on C is 95 kg.-cal. per mol., and for the decomp. of C_2H_6 to C_2H_4 on C is 94.6 kg.-cal. per mol. There is no evidence of the formation of Me or the ethylidene radical.

E. S. H.

Oxidising faculty of nitrogen oxide. J. BJERRUM and L. MICHAELIS (J. Amer. Chem. Soc., 1935, 57, 1378—1379).—The oxidation of reduction products of dyes by NO in presence of colloidal Pd is described.

E. S. H.

Effects of fluorides on the thermal synthesis of calcium silicates. VI. S. NAGAI and Y. KOSAKI (J. Soc. Chem. Ind. Japan, 1935, 38, 229—232b; cf. this vol., 49).—A mixture of $2\text{CaCO}_3 : \text{SiO}_2$ was heated for 1 hr. at 1000—1400°, and the product analysed by Jander and Hoffmann's method (cf. B., 1933, 270) for free CaO and SiO_2 , $3\text{CaO}.\text{SiO}_2$ (I), $2\text{CaO}.\text{SiO}_2$ (II), $3\text{CaO}.\text{SiO}_2$, and $\text{CaO}.\text{SiO}_2$. The ratio of combined CaO to combined SiO_2 is const. at 1100—1400°, but the % of (II) increases with temp. 1% of CaF_2 was then added to the same mixture, and the product analysed after heating as before. The % of (I) is greatly increased at 1000—1100° by the addition of CaF_2 , but the effect falls with rise in temp. owing to decomp. of (I) into (II). The % of (II) and of total silicate is greatly increased by CaF_2 , approx. 75—80% of which remains unchanged.

R. S. B.

Effect of fluorides on the thermal synthesis of calcium silicates. VII. S. NAGAI and Y. KOSAKI (J. Soc. Chem. Ind. Japan, 1935, 38, 294—298b).—Prolonged heating at 1200° of mixtures of CaCO_3 and SiO_2 (2 : 1) is not so effective in causing silicate formation as is the addition of 1% of CaF_2 ; more CaF_2 is still more effective. At 1300° the yield of Ca_3 silicate from the mixture $\text{CaCO}_3 : \text{SiO}_2 = 3$ is 90% when 1% of CaF_2 is present, and complete combination is not obtainable at a lower temp.

A. G.

Catalytic preparation of hydrochloric acid from chlorine and water.—See B., 1935, 722.

Poisoning of molybdenum-zinc catalyst. G. N. MASLIANSKI and M. S. NEMTZOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 404—408).—The catalytic activity of a mixture of MoS_2 and ZnO in the C_2H_4 - H_2 reaction is diminished in the presence of O_2 . If poisoning occurs below 300°, the activity returns completely after the O_2 is removed. At 400° poisoning is partly irreversible, and the greater is $[\text{O}_2]$ in the gas, the lower is the residual activity of the catalyst. H_2O vapour induces similar effects, but the deceleration of the reaction diminishes with rising temperature. Preheating the catalyst to 450° in H_2 enhances, and the use of C_2H_4 -rich mixtures diminishes, the activity of the catalyst.

T. G. P.

Direct oxidation of platinum and the nitriding of metals (Cu, Al, Mg, Zn, Fe, Ni, and W). P. GRANDADAM (Ann. Chim., 1935, [xi], 4, 83—146).—Pt-black heated at 450° in O₂ at 170 kg. per sq. cm. gives PtO₂, *d* 10, insol. in mineral acids, which decomposes in air at 380—400° to give Pt, and catalyses the combustion of slightly heated coal gas and the combination of H₂ and O₂ at room temp., and is fully reduced after 1 hr. in H₂ at 90°. Pt-black heated at 430° at 8.25 kg. per sq. cm. gives PtO, *d* 15, little attacked by HCl in absence of air, easily sol. in aqua regia, does not decompose in air below 500°, catalyses instantaneously the combustion of coal gas and H₂ at room temp., and is instantly reduced by H₂ at room temp. with incandescence. PtO₂ is a better reduction catalyst for C:C and C:O than the well-known Pt-blacks; PtO is good for C:C linkings, but less effective for C:O. Pt-black heated between 100° and 200° in O₂ at 150 kg. per sq. cm. becomes three times as active for the reduction of C:C or C:O linkings, and is recommended for laboratory use.

Li combines with N₂ at room temp. by an autocatalytic process. Ni reacts with NH₃ at 530° to give a product of uncertain stoichiometric composition, but the reaction between NiCO₃ and Li₃N appears to yield the nitride. The sp. electrical conductances and temp. increments have been determined for Al, Fe, Ni, Zn, W, and Mg, which also exhibited an allotropic transition at 280°. By examining the conductivity of a filament heated at various temp. in NH₃, dissolution and chemical combination were discriminated, the exact temp. at which nitriding commenced was ascertained, and the reversible process of nitriding was followed for each of these metals. The action of Ni and Fe in the synthesis of NH₃ is discussed. T. G. P.

Reactivity and catalytic activity of solid substances in transition states. J. A. HEDVALL (Svensk Kem. Tidskr., 1935, 47, 161—188).—A comprehensive review and discussion of previous work bearing on various factors (*e.g.*, changes in magnetic state or in crystal structure) which influence the reaction of solids. H. J. E.

Kinetics of the catalytic dehydrogenation of methylcyclohexane with a nickel-aluminium oxide catalyst. A. A. BALANDIN and N. I. SCHUKIN (Acta Physicochim. U.R.S.S., 1934, 1, 200—211).—The effects of temp. of 200—350° and of the presence of reaction products on the dehydrogenation of methylcyclohexane has been investigated. The energy of activation is 12,300 kg.-cal. per mol. The data are compared with those for cyclohexane and dimethylcyclohexane (*cf.* A., 1933, 234; this vol., 310).

J. W. S.

Function of carriers in heterogeneous catalysis. IV. Dehydrogenation and hydrogenation of ethyl alcohol on zinc oxide deposited on charcoal. I. E. ADADUROV and P. Y. KRAINI. V. Decomposition of formic acid on lead oxide deposited on birchwood charcoal. I. E. ADADUROV (J. Phys. Chem. U.S.S.R., 1934, 5, 1132—1138, 1139—1145).—IV. The carrier may alter the magnitude and even the sign of the field of the catalyst. Data for ZnO catalysts are discussed. Easily deformed cations of catalysts are most subject to carrier effects.

V. HCO₂H decomposes almost 100% into CO₂ and H₂ on pure birch C at 200—350°, or on PbO prepared from Pb(NO₃)₂ up to 360°. A catalyst prepared by adsorption on the C from 0.01*N*-Pb(NO₃)₂, drying, and heating to 360°, gave 100% of CO₂+H₂ at 200—360°. A similarly treated catalyst prepared from 0.05*N*-Pb(NO₃)₂ gave at 255°, 75 and 25%, respectively, of CO₂ and CO, at 275°, 50 and 50%, at 305°, 37 and 63%, at 325°, 2 and 98%, and at 350°, 67 and 33%, respectively, of the two gases.

CH. ABS. (e)

Catalytic reduction reactions.—See this vol., 1120.

Physicochemical conditions of the production of potassium persulphate. V. P. ILJINSKI, A. F. SAGAJDATSCHNUI, and E. K. HELIGREN (Trans. State Inst. Appl. Chem. U.S.S.R., 1934, 19, 2—12).—Saturated (NH₄)₂SO₄ is used. When the solution becomes alkaline, powdered KHSO₄ is added. It reacts with (NH₄)₂S₂O₈, K₂S₂O₈ crystallising out. The optimum anode and cathode c.d. are 5 amp. and 1 amp. per sq. cm., respectively (optimum temp. 30°).

CH. ABS. (e)

Chemical stability of the terminal faces of acicular crystals. D. W. PEARCE, T. T. QUIRKE, and B. S. HOPKINS (Amer. J. Sci., 1935, [v], 30, 116—120).—In the electrolytic reduction of YbCl₃ in the presence of H₂SO₄ (A., 1931, 51; 1933, 37) the pptd. YbSO₄ has the form of radiating tufts of acicular crystals, but with slower pptn., with a weaker current and in the presence of more acid, a granular ppt. of spherulites was obtained. The latter is more resistant to acids, probably owing to the lower solubility of the ends of the acicular crystals. It is argued that acicular crystals of various substances are of slower growth than crystals of other habits.

L. J. S.

Theory and practice of chromium plating.—See B., 1935, 678.

Electrolysis of chlorides of nickel and cobalt dissolved in mixtures of water and ethyl alcohol. C. CHARMETANT (Compt. rend., 1935, 201, 43—45; *cf.* this vol., 456).—For NiCl₂ and CoCl₂ the anodic phenomena resemble those for ZnCl₂, a large proportion of the Cl oxidising EtOH to MeCHO. At the cathode, for NiCl₂, Ni oxides are first deposited, and dissolve later owing to diffusion of HCl from the anode. In 0.006*N*-acid pure Ni is deposited, the yield decreasing with time and with increasing c.d. The acid concn. needed to avoid oxide formation increases with the [EtOH]. The Ni yield passes through a min. with 150 g. of EtOH per litre. Co is deposited from an EtOH-H₂O solution of CoCl₂ even in neutral solution.

H. J. E.

Electrochemical production of aluminium oxide from aqueous aluminium sulphate.—See B., 1935, 723.

[Electrolytic] preparation of mercuric oxide. See B., 1935, 723.

Electrodeposition of alloys of copper and tin.—See B., 1935, 730.

Electrodeposition of noble-metal alloys.—See B., 1935, 730.

Electrolytic deposition of cerium from anhydrous organic solvents (i) alone, and (ii) in presence of reducing agents.—See B., 1935, 730.

Chemical reactions in electrical discharges.
I. Reactions of free atoms. Recombination of oxygen and hydrogen atoms on metal wires. S. ROGINSKI and A. SCHECHTER (*Acta Physicochim. U.R.S.S.*, 1934, 1, 318—332).—The velocities of recombination of O and of H atoms on heated Pt and Pd filaments have been determined comparatively from the currents required to maintain the filament at a specified temp. The usual method of determination, using a thermometer coated with a catalyst, is untrustworthy, the low thermal conductivity of the catalyst powder generally causing autocatalysis of the recombination. J. W. S.

[Cathodic catalysis in the electrical discharge.] **Application to ammonia.** P. JOLIBOIS and F. OLMER (*Compt. rend.*, 1935, 201, 62—64; cf. this vol., 446).—The equilibrium concn. of NH_3 formed from a $\text{N}_2\text{—H}_2$ mixture at 1.1—3.5 mm. in the gas near the Pt cathode of a discharge tube varies from 3.3 to 24% with the discharge conditions. Data are recorded for the energy input needed to obtain 1 g. of NH_3 using cathodes of Fe, Cu, Ni, Cu—Hg, Al, and Pt. The gas circulating in the positive column contains no NH_3 . The catalysis is attributed to the action in the gas phase of metal particles ejected from the cathode. The same explanation applies to formation of NH_3 in the spark. H. J. E.

Photochemical decomposition of hydrogen peroxide in aqueous solution. G. KORNFELD (*Z. physikal. Chem.*, 1935, B, 29, 205—214).—Following Haber and Weiss (*A.*, 1933, 234) the mechanism of decomp. proposed is: $\text{H}_2\text{O}_2 + h\nu = 2\text{OH}$, $\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2\text{H}$, $\text{H}_2\text{O}_2 + \text{O}_2' = \text{O}_2 + \text{OH}' + \text{OH}$, $\text{OH} + \text{O}_2\text{H} = \text{H}_2\text{O} + \text{O}_2$. This requires that the rate $\propto \sqrt{I[\text{H}_2\text{O}_2]}$, which accords with the experimental data for the reaction in absence of acid (*A.*, 1921, ii, 670). The observed decline in the rate of increase of the velocity with $[\text{H}_2\text{O}_2]$ at higher concns. in presence of acid is also quantitatively predicted from the above. The retardation by alkali is, however, not fully accounted for. R. C.

Photochemical oxidation-reduction equilibrium in methylene-blue solutions. H. VON EULER, H. HELLSTRÖM, and K. BRANDT (*Naturwiss.*, 1935, 23, 486—489).—The photochemical processes in methylene-blue (I)—EtOH and (I)— Fe^{II} —EtOH systems have been investigated. The quantum efficiency of the reduction of (I) in the first system is considerably < 1 . In the second system, reduction velocity is dependent on p_{H} , increasing with increasing acidity to a max. at p_{H} 3.6. Light favours the formation of the leuco-base (II) in the equilibrium $\text{H}_2 + \text{(I)}$ (II). The quantity of (II) in the irradiated substance is not \propto intensity of absorbed light. A. J. M.

Fog formation by dyes. LUPPO-CRAMER (*Phot. Ind.*, 1934, 32, 974).—Sensitising nuclei are removed with H_2CrO_4 after application of the dye. Results vary with the dye used, and apparently depend on a secondary reaction between the dye and the oxidant. CH. ABS. (e)

Action of various elements and compounds on photographic plate. II. S. AOYAMA and T. FUKUROI (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 481—496).—Direct chemical reaction of activated gases on the photographic plate is a more plausible view than emission of radiation when the gases associate. W. R. A.

Photo-reaction in tropical sunlight. B. J. MALAVIYA and S. DUTT (*Proc. Acad. Sci. Agra and Oudh*, 1935, 4, 319—329).—The products of the action of intense sunlight on a large no. of org. compounds have been identified. C. W. G.

Mechanism of the activation of oxygen by irradiated pigments. II. **Photo-oxidation in the near infra-red.** H. GAFFRON (*Ber.*, 1935, 68, [B], 1409—1411).—Solutions of bacterio-chlorophyll or bacterio-phaeophytin resemble chlorophyll (I) in sensitising ability and are active in the infra-red. A solution of these pigments in COMe_2 with thiosinamine as acceptor vigorously absorbs O_2 when exposed to light of $\lambda < 760$ m μ . The absorption limit of (I) in the red is therefore certainly not the limit of such photochemical reactions. H. W.

Exchange reactions with deuterium atoms. K. H. GEIB and E. W. R. STEACIE (*Z. physikal. Chem.*, 1935, B, 29, 215—224).—At. D enters into exchange reactions with H_2O , NH_3 , and C_2H_2 , the energies of activation being 12 ± 1 , 11 ± 1 , and < 5 kg.-cal., respectively. No exchange was observed with CH_4 ; contrary to Taylor's findings (this vol., 457) the energy of activation of $\text{CH}_4 + \text{D} = \text{MeD} + \text{H}$ is < 11 kg.-cal. At 20° the reaction with H_2O apparently occurs partly on the wall. R. C.

Production of light water and determination of the deuterium concentration in normal water. N. MORITA and T. TITANI (*Bull. Chem. Soc. Japan*, 1935, 10, 257—258).—Light H_2O was prepared from Osaka conductivity water (I) by fractional electrolysis and was 19.3γ lighter than (I). The D : H ratio in (I) is $1 : 5500 \pm 200$. W. R. A.

Distillation and rectification of dilute solutions of volatile substances. I. **Heavy water.**—See B., 1935, 609.

Separation of lithium [sulphate] from spodumene by heating with alkali-metal salts.—See B., 1935, 723.

Hydrolysis of alkali chlorides. C. R. JOHNSON (*J. Physical Chem.*, 1935, 39, 791—795).—Carefully purified NaCl and KCl contain $< 1\text{—}2$ p.p.m. of alkali after fusion in N_2 under specified conditions. Such fused salts can be weighed in air of low or moderate R.H. without absorbing weighable amounts of H_2O . NaCl hydrolyses $>$ KCl when fused in moist air. J. W. S.

Preparation of sodium persilicate.—See B., 1935, 671.

Ammines from phenylenediamines and metallic salts. M. PAPAFLI (*Ann. sci. Univ. Jassy*, 1934, 20, 139—153; cf. *A.*, 1934, 66).—The prep. and properties of the following compounds are described [*Bo*, *Bm*, and *Bp* representing *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$]: $\text{CuSO}_4 \cdot \text{Bm}$; $\text{Cu}(\text{NO}_3)_2 \cdot \text{Bm}$; $\text{Cu}(\text{NO}_3)_2 \cdot \text{Bp}$;

$\text{CuCl}_2, \text{Bo}, \text{H}_2\text{O}$; $\text{CuCl}_2, \text{Bm}, 2\text{H}_2\text{O}$; $\text{CuCl}_2, \text{Bp}, \text{H}_2\text{O}$; $\text{Co}(\text{NO}_3)_2, 4\text{Bo}$; $\text{Co}(\text{NO}_3)_2, 4\text{Bm}$; $\text{Co}(\text{NO}_3)_2, 2\text{Bp}, \text{H}_2\text{O}$; CoCl_2, Bo ; CoCl_2, Bm ; $\text{NiSO}_4, \text{Bm}, \text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2, 2\text{Bo}$; $\text{Ni}(\text{NO}_3)_2, 4\text{Bm}$; $\text{Ni}(\text{NO}_3)_2, 2\text{Bp}, \text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2, 3\text{Bo}$; $\text{NiCl}_2, 4\text{Bo}$; $\text{NiCl}_2, 2\text{Bm}, \text{H}_2\text{O}$; $\text{NiCl}_2, 2\text{Bp}$ and $\text{CuCl}_2, m\text{-NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2, 2\text{H}_2\text{O}$. CH. ABS. (e)

Behaviour of copper on fusion with sodium carbonate and sulphur. R. HOLTJE and W. KAHMEN (Z. anorg. Chem., 1935, 223, 234—240).—On fusion of material containing Cu with $\text{Na}_2\text{CO}_3 + \text{S}$, and subsequent extraction with H_2O , the Cu dissolved increases with the proportion of S, and is augmented by the presence of Sn. Most is reprecipitated on addition of NaOH , Na_2S , Na_2SO_3 , or KCN , but is best separated by acidifying and then redissolving As, Sb, and Sn with $\text{Na}_2\text{S} + \text{NaOH} + \text{Na}_2\text{SO}_3$. A quant. separation of Cu is not possible. J. S. A.

[Electrolytic] method of studying complexes. C. DUVAL (Compt. rend., 1935, 200, 2175—2177; cf. this vol., 716).—The double chloride of Cu and Cd has the formula $\text{Cu}[\text{CdCl}_4]$. Kainite behaves as a binary electrolyte with the formula $\text{K}[\text{MgClSO}_4(\text{H}_2\text{O})_3]$. The complex from AgCl and NH_3 is $[\text{Ag}(\text{NH}_3)_4]\text{Cl}$. Other applications of the method are briefly indicated. H. J. E.

Action of water vapour on metallic fluorides. L. DOMANGE (Compt. rend., 1935, 200, 2180—2182; cf. this vol., 448).— H_2O vapour at 200—400° converts AgF into Ag. At 400—650° it converts ZnF_2 into ZnO (heat of reaction at const. pressure at 525—625° = -25,930 g.-cal.). With PbF_2 attack was incomplete at 500—750°, a mixture of PbO and PbF_2 remaining (heat of reaction at const. pressure at 625—725° = -37,200 g.-cal.) H. J. E.

"Electron transfer" theory applied to the reactions in the (photographic) developing bath. K. M. PANDALAI (J. Indian Chem. Soc., 1935, 12, 216—219).—The reactions occurring in the developing bath are considered as typical oxidation-reduction processes in which there is a transfer of electrons from the reducing to the oxidising agent. O. J. W.

Influence of hydrogen ions in the phenomena of reduction and hydrogenation. A. A. GUNTZ and E. BELTRAN (Compt. rend., 1935, 200, 2011—2013).—In a mechanism suggested for the reduction of Ag_2O , H^+ is attracted, and then causes disruption of the mol. by electrostatic repulsion. This will explain the action of an electric field in facilitating the reduction when the oxide is the cathode, and in retarding reduction when the oxide is the anode. H. J. E.

Argentate salts in acid solution. I. Oxidation and reduction reactions. A. A. NOYES, J. L. HOARD, and K. S. PITZER (J. Amer. Chem. Soc., 1935, 57, 1221—1229).—Solutions of AgNO_3 in aq. HNO_3 are oxidised at room temp. by O_3 , forming a black, sol. Ag^{II} salt. The reaction ceases before completion, due to reduction of Ag^{II} by H_2O with evolution of O_2 . At 0° the initial rate of oxidation of Ag^+ is $\propto [\text{Ag}^+]$ and $[\text{O}_3]$ and only slightly affected by $[\text{HNO}_3]$. The rate of decomp. of Ag^{II} is approx. $\propto [\text{Ag}^+]$ and inversely $\propto [\text{Ag}^{\text{II}}]$, and is greatly diminished by increasing $[\text{HNO}_3]$. The temp. coeff. is high. The mechanism is discussed. E. S. H.

Hydrothermal experiments with gold. S. P. OGRYZLO (Econ. Geol., 1935, 30, 400—424).—Between 250° and 600°, 20% HCl has no action on Au when passed over it. AuCl_3 is formed when Cl_2 and steam are passed over Au, the max. amount being formed at 200°. Volatilisation of AuCl_3 in $\text{Cl}_2 + \text{H}_2\text{O}$ begins at 125°, increases rapidly to a max. at 200°, and decreases sharply to practically zero at 400°. Au is sol. in dil. HCl at high temp. (300°) and pressures and the amount dissolved increases with rise in temp., pressure, and concn. of the acid. More Au is dissolved in presence of air than in that of CO_2 or N_2 . Aq. solutions of alkali chlorides under pressure at 200—300° have no appreciable solven action on Au and aq. Na_2CO_3 at 200° under pressure has no action. Au is sol. in HCl solutions of FeCl_3 at 200° under pressure in absence of O_2 ; it is pptd. on cooling. Aq. Na_2S dissolves only traces of Au at 175—300° under pressure and none at room temp. Some Au is dissolved by NaSH at room temp. in considerable amounts at 200—300° under pressure. The results show that in nature, Au may be transported either in acid or slightly alkaline aq. solution and also in the vapour phase as AuCl_3 . L. S. T.

Basic magnesium carbonates. (MME.) L. W. LEVY (Compt. rend., 1935, 200, 1940—1942).—The compounds $8\text{MgO}, \text{K}_2\text{O}, 5\text{CO}_2, 5\text{H}_2\text{O}$ and $4\text{MgO}, 3\text{CO}_2, 3\text{H}_2\text{O}$ were prepared by the decomp. of $\text{MgCO}_3, \text{K}_2\text{CO}_3, 4\text{H}_2\text{O}$ in a sealed tube at 100—200° by aq. K_2CO_3 or KHCO_3 . H. J. E.

Action of carbon dioxide on lime water and of alkali carbonate on calcium salt solutions. II. O. SPENGLER and G. DORFMULLER (Z. Wirts. Zuckerind., 1935, 65, 263—281; cf. A., 1933, 1020).—When CO_2 reacts with aq. CaO the first product is a sol. hydrated carbonate, which is fairly stable up to 100°, and can be crystallised at 0—2°. E. S. H.

Wet preparation of calcium chromate. J. MILBAUER and J. DOŠKAŘ (Chem. Listy, 1935, 29, 113—116).— CaCrO_4 is pptd. by adding 1.6 times the theoretical amount of CaCl_2 (as a solution of 40—45 g. per 100 c.c. of H_2O) to saturated aq. Na_2CrO_4 at 20°. The product obtained using K_2CrO_4 is contaminated with difficultly eliminable K^+ and Cl^- . R. T.

Mechanism of precipitation processes. XVII. $\text{Ba}(\text{NO}_3)_2$ and H_2SO_4 . Z. KARAOGLANOV and P. SAGORTSCHEV (Z. anorg. Chem., 1935, 223, 217—221; cf. this vol., 317).—When $\text{Ba}(\text{NO}_3)_2$ is pptd. by H_2SO_4 in presence of HNO_3 , the ratio of Ba to SO_4 in the ppt. increases with the total $[\text{NO}_3^-]$, up to a max. corresponding with the presence of 38% of $(\text{BaNO}_3)_2\text{SO}_4$. Addition of EtOH lowers the ratio by suppressing the ionisation of $\text{Ba}(\text{NO}_3)_2$. J. S. A.

Deposition of artificial radio-elements by electrochemical exchange. M. HAISSINSKY (Nature, 1935, 136, 141—142).—Radio-Cu (I) (period 10 hr.) has been separated from Zn by the following method. 8—12 g. of neutron-irradiated Zn powder are treated with conc. HCl until 0.2—0.3 g. remains. Practically all the activity is conc. on this residue, which is dissolved separately in conc. HCl and diluted

with 2 vols. of H_2O . Rotation for 30 min. of a Pb plate insulated on one side collects $>$ half of (I) on the plate. Strong sources of (I) can thus be prepared in very thin layers without co-pptn. L. S. T.

Preparation of zinc chloride solutions. A. RAUSCH (Arch. Chem. Farm., 1935, 2, 237—243).—The difference in $[\text{ZnCl}_2]$ between filtered and unfiltered aq. ZnCl_2 [containing suspended $\text{Zn}(\text{OH})\text{Cl}$] is $> 0.02\%$. R. T.

Isomeric amines from cyclic diamines and metallic salts. II. M. PONI (Ann. sci. Univ. Jassy, 1934, 20, 154—172; cf. A., 1934, 66).—The prep. and properties of the following compounds are described $[\text{T}=\text{C}_6\text{H}_5\text{Me}(\text{NH}_2)_2; \text{N}=\text{C}_{10}\text{H}_8(\text{NH}_2)_2]$: $\text{CdBr}_2, 2(2:4\text{-T}), 2\text{H}_2\text{O}$; $\text{CdBr}_2, 2(2:4\text{-T})$; $\text{CdBr}_2, 2(2:5\text{-T})$; $\text{CdI}_2, 2(2:4\text{-T}), 2\text{H}_2\text{O}$; $\text{CdI}_2, 2(2:4\text{-T})$; $\text{CdI}_2, 2(2:5\text{-T})$; $\text{Cd}(\text{NO}_3)_2, 2(3:4\text{-T})$; $\text{Cd}(\text{NO}_3)_2, 2(2:4\text{-T})$; $\text{CuCl}_2, 2(3:4\text{-T})$; $\text{CuCl}_2, 2(2:5\text{-T})$; $\text{CuBr}_2, 2(2:4\text{-T})$; $\text{CuBr}_2, 2(2:5\text{-T})$; $\text{Cu}(\text{NO}_3)_2, 2(3:4\text{-T})$; $\text{Cu}(\text{NO}_3)_2, 2(2:4\text{-T})$; $\text{CoCl}_2, 2(3:4\text{-T})$; $\text{CoCl}_2, 2(2:5\text{-T}), 2\text{H}_2\text{O}$; $\text{CoCl}_2, 2(2:5\text{-T})$; $\text{NiBr}_2, 3(2:4\text{-T})$; $\text{NiCl}_2, 2(2:5\text{-T}), 2\text{H}_2\text{O}$; $\text{NiCl}_2, 2(2:5\text{-T})$; $\text{CdCl}_2, 2(1:2\text{-N})$; $\text{Cd}(\text{NO}_3)_2, 2(1:8\text{-N})$; $\text{CdBr}_2, 2(1:2\text{-N}), 2\text{H}_2\text{O}$; $\text{CdBr}_2, 2(1:2\text{-N})$; $\text{Cu}(\text{NO}_3)_2, 2(1:5\text{-N})$; $\text{CuCl}_2, 2(1:8\text{-N})$; $\text{CuBr}_2, 2(1:8\text{-N})$; $\text{Cu}(\text{NO}_3)_2, 2(1:8\text{-N})$; $\text{Cu}(\text{NO}_3)_2, 2(2:7\text{-N})$; $\text{NiCl}_2, 2(1:2\text{-N})$; $\text{NiCl}_2, 2(1:8\text{-N})$; $\text{NiBr}_2, 2(1:8\text{-N})$; $\text{Ni}(\text{NO}_3)_2, 3(1:8\text{-N})$; $\text{NiSO}_4, 2(1:8\text{-N})$; $\text{CoCl}_2, 2(1:2\text{-N})$; $\text{CoI}_2, 2(1:2\text{-N})$; $\text{CoCl}_2, 2(1:8\text{-N})$; $\text{CoBr}_2, 2(1:8\text{-N})$; $\text{CoI}_2, 2(1:8\text{-N})$; and $\text{Co}(\text{NO}_3)_2, 2(1:8\text{-N})$. CH. ABS. (e)

Constitution of compounds formed by cyclic diamines and metallic salts. R. CERNATESCU, (MME.) M. PAPAFL, and M. PONI (Ann. Sci. Univ. Jassy, 1934, 20, 175—189; cf. preceding abstract).—In $\text{CdCl}_2, 2(1:8\text{-N})$, $\text{CdBr}_2, 2(1:8\text{-N})$, and $\text{CdBr}_2, 2(1:2\text{-N})$ each mol. of base is replaceable by INH_3 , and in $\text{NiSO}_4, 2(1:8\text{-N})$, $\text{CdBr}_2, 2(1:5\text{-N})$, $\text{CdCl}_2, 2\text{Bp}$ (I), $\text{CdI}_2, 2\text{Bp}$ (II), and $\text{Cd}(\text{NO}_3)_2, 2\text{Bp}$ (III), $\text{NiCl}_2, 2\text{Bp}$ (IV) [$\text{Bp}=\text{p-C}_6\text{H}_4(\text{NH}_2)_2$], and $\text{CdBr}_2, 2(2:5\text{-T})$ each mol. of base is replaceable by 2NH_3 . Formula are assigned to (I)—(IV). CH. ABS. (e)

Mercuriammonium chromate. S. AUGUSTI (Boll. Chim. farm., 1935, 76, 505—508, 511—513).—The new prep. of $(\text{Hg}_2\text{N})_2\text{CrO}_4, 2\text{H}_2\text{O}$ from $(\text{Hg}_2\text{N})\text{NO}_3$ and K_2CrO_4 , and from aq. NH_3 and HgCrO_4 , is described. The substance reacts with Na_2S to form Hg_2S , NH_3 , NaOH , and Na_2CrO_4 . With KI it gives K_2HgI_4 and KOH ; with $\text{Na}_2\text{S}_2\text{O}_3$, $\text{Na}_2\text{Hg}(\text{S}_2\text{O}_3)_2$ and NaOH ; with HCl and KBr , K_2HgBr_4 and KCl ; and with KCN , $\text{K}_2\text{Hg}(\text{CN})_4$ and KOH . In each of these reactions $(\text{NH}_4)_2\text{CrO}_4$ is also formed. E. W. W.

Orange modification of mercuric iodide. V. S. GORSKI (Physikal. Z. Sovietunion, 1934, 6, 515).—Orange crystals of HgI_2 were obtained from COMe_2 solution at room temp., together with the known red and yellow forms, this being a new metastable modification (tetragonal; a 8.70, c 23.44 Å.; body-centred; space-group D_{2h}^{12} or C^{11}). CH. ABS. (e)

Modification of Carpenter and Elam's method of producing single crystals of aluminium by

deformation and annealing. V. H. STOTT (Trans. Faraday Soc., 1935, 31, 998—1000).—Modified procedure, involving greater extension of the specimen, is recommended. E. S. H.

"Decaying" [inter]metallic compounds. G. TAMMANN and A. RUHENBECK (Z. anorg. Chem., 1935, 223, 288—296).—Numerous alloys and inter-metallic compounds of Al, Ca, Mg, Ce, and Si with moderately base metals (e.g., FeAl_3 , AlSb , PbCa , AgCa , SnMg_2 , BiCe , but not Al_3Mg_4 or AuMg) decompose on exposure to moist air, probably forming hydroxide and free metal. The effect is attributed to the non-formation by such alloys of protective coatings, either of coherent hydroxide (as on Al, Mg, or Al-Mg alloys) or of the nobler metal. J. S. A.

Rare earths. XLIV. Preparation of anhydrous rare-earth compounds by the action of fused and solid "-onium" salts on the oxides. J. B. REED [with B. S. HOPKINS and L. F. AUDRETH] (J. Amer. Chem. Soc., 1935, 57, 1159—1160; cf. A., 1934, 373).—Rare-earth oxides react with NH_4Cl or NH_4Br at 200—300°, yielding the corresponding halides. Rare-earth sulphides, prepared by reducing the sulphates with C, react partly with NH_4I at 450—500°. The action of NH_4I on the rare-earth oxide yields basic iodides. E. S. H.

Complex iodides of bivalent germanium. T. KARANTASSIS and L. CAPATOS (Compt. rend., 1935, 201, 74—75).—A HI solution of $\text{Ge}(\text{OH})_2$ when added to solid CsCl_2 gave a black microcryst. ppt. of the compound CsGeI_3 , which was readily hydrolysed by H_2O . With aq. NMe_4I , $\text{Ge}(\text{OH})_2$ gave the compound NMe_4GeI_3 , white needles, and with a solution of cocaine hydrochloride gave white needles of $\text{GeI}_2, 3(\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{HI})$ (decomp. in air). H. J. E.

Reactions of zirconium tetrabromide and thorium tetrabromide with potassium and with potassium amide in liquid ammonia. R. C. YOUNG (J. Amer. Chem. Soc., 1935, 57, 1195—1196).—A solution of ZrBr_4 in liquid NH_3 is reduced by K; further reaction occurs with evolution of H_2 and formation of $\text{Zr}(\text{NK})_2, \text{NH}_3$, which is also formed by the action of excess of KNH_2 on ZrBr_4 . Equiv. proportions of KNH_2 and ZrBr_4 yield a mixture of $\text{Zr}(\text{NH})_2$ and $\text{Zr}(\text{NH})\cdot\text{NK}$. When ThBr_4 in liquid NH_3 is treated with K, the product is $\text{Th}(\text{NH})\cdot\text{NK}, \text{NH}_3$. The action of excess of KNH_2 on ThBr_4 yields $\text{Th}(\text{NK})_2, \text{KNH}_2$. E. S. H.

Lead acetatobromide. E. GRILLOT (Compt. rend., 1935, 200, 2177—2179; cf. this vol., 50).—The compound $\text{PbBr}\cdot\text{OAc}$ was isolated from a solution containing PbBr_2 , $\text{Pb}(\text{OAc})_2$, and AcOH . It hydrolyses to form $\text{PbBr}\cdot\text{OH}$. Solubility data are recorded. H. J. E.

Action of nitrogen on metals. Electric discharge at low pressures. G. BERRAZ (An. Soc. cient. Santa Fe, 1933, 5, 54—56; Chem. Zentr., 1935, i, 1020).—Cathodic sputtering of Ag and Au in N_2 at 0.5 mm. is attended with combination of N. With Pb a nitride is formed which evolves NH_3 with H_2O . J. S. A.

Preparation and properties of phosphorus nitride. V. F. POSTNIKOV and L. L. KUZMIN (J. Appl. Chem. Russ., 1935, 8, 429—438).— P_3N_5 is obtained in good yield by Stock's method (A., 1903, ii, 207), and is also formed in traces from P and N_2 by the silent electrical discharge, or at 600° (Ni and Pt catalysts). P_3N_5 is conveniently analysed by the Kjeldahl method, being quantitatively converted into H_3PO_4 and NH_3 with H_2SO_4 at the b.p. or with H_2O at $\leq 180^\circ$. The P_3N_5 may be dried in air at 120° without decomp.; at 800° conversion into N_2 and P_2O_5 takes place, whilst in N_2 the products are N_2 and P. Conc. HNO_3 and dil. H_2SO_4 cause only inconsiderable decomp. at the b.p., aq. HCl and aq. alkalis have no effect, whilst fusion with NaOH affords Na phosphate and N_2 or NH_3 . R. T.

Additive compounds of arsenic [tri]chloride. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1365—1367).— $AsCl_3$ combines with C_5H_5N , NH_2OH , NH_2Ph , piperazine, $(CH_2)_6N_4$, quinoline, NaCl, NH_4Cl , and $CoCl_3$. No reaction occurs with $MgCl_2$, $ZnCl_2$, or $CrCl_3$. T. G. P.

Action of liquid ammonia on tantalum pentachloride. H. MOUREU and C. HAMBLET (Compt. rend., 1935, 200, 2184—2186).—Interaction of anhyd. NH_3 at its b.p. with $TaCl_5$, followed by removal of excess of NH_3 at low temp., yields the compound $Ta(NH_2)_2Cl_3 \cdot 7NH_3$ together with NH_4Cl . On heating this product to $> 170^\circ$ $Ta(NH_2)_2Cl_3$ is formed; this, when heated in NH_3 at 1100° , forms TaN . Two of the Cl in $TaCl_5$ are particularly reactive. H. J. E.

Laboratory preparation of oxygen and of chlorine. F. C. KRAUSKOFF (J. Chem. Educ., 1935, 12, 293—294).—Details are given for the prep. of O_2 from $Ca(OCl)_2$ and a Co salt and of Cl_2 from a suspension of bleaching powder or $Ca(OCl)_2$ and HCl. L. S. T.

Formation of dithionate by oxidation of sulphurous acid and sulphites. H. BASSETT and A. J. HENRY (J.C.S., 1935, 914—929).—The hydrolytic decomp. of $H_2S_2O_6$ (I) is not reversible, and oxidising agents have no action unless conditions are such as to cause hydrolysis. Cl_2 , I, and H_2O_2 oxidise sulphite (II) solutions rapidly, and in acid, but not in neutral or alkaline, solutions traces of (I) are formed. This introduces an error in the iodometric determination of SO_2 . O_2 reacts with (II) by a chain mechanism, and (I) is formed in acid solution only. The proportion of (I) increases with increase of [(II)] and for a given [(II)] there is an optimum acidity. Free SO_3'' is oxidised to SO_4'' and the (I) is produced by oxidation of S_2O_5'' . Methylene-blue inhibiting the atm. oxidation of H_2SO_3 is gradually oxidised, and the inhibition is thus removed. In moist O_2 , alkali pyrosulphites yield a mixture of sulphate and approx. 25% of dithionate (III), and in solution, the ratio of (I) formed to total S_2O_5'' oxidised rises to a const. val. with increasing $[S_2O_5'']$.

Of the H_2SO_3 oxidised by $H_2Cr_2O_7$ and $HMnO_4$, approx. 4% and 19%, respectively, is converted into (I) under all conditions of concn. and acidity. The SO_2 mols. in the solution probably form, with the oxid-

ising ions, complexes which subsequently break down, producing SO_4'' and S_2O_5'' in proportions which are function of the metal forming the complex. Analogous considerations are applied to numerous cases in which metal ions, easily reducible to a lower valency state, or the metal, form complexes with SO_3'' and give similar results. In alkaline solution, MnO_4' afford no (III), and SO_4'' formation is probably accompanied by the process $MnO_4' \rightarrow MnO_4'' \rightarrow MnO_4''' \rightarrow MnO_2$. (III) is not produced during the photo-decomp. of H_2SO_3 to H_2SO_4 and S, but traces are produced during the dark decomp.

Electrolytic formation of (III) probably proceeds by the process $2SO_3'' \rightarrow (2SO_3' + 2e) \rightarrow S_2O_6'' + 2e$. There is no evidence from these data for the existence of a sulphurous-sulphonic equilibrium in H_2SO_3 solutions. J. G. A. G.

Loss of selenium in the reduction of selenite by hydrazine. V. HOVORKA (Coll. Czech. Chem. Comm., 1935, 7, 273—280; cf. A., 1933, 1102).—The loss of Se, due to H_2Se formation, in reducing H_2SeO_3 by N_2H_4 in acid media has been determined for a series of acids. With mineral acids the loss is 0.17—0.29%, and with tartaric or citric acid it is 0.07—0.1%. H. J. E.

Nomenclature of the telluric acids. M. PATRY (Compt. rend., 1935, 201, 71—73; cf. this vol., 593).—The two acids H_2TeO_4 and $(H_2TeO_4)_n$ are termed ortho and meta, respectively. The val. of n in aq. solution is approx. 3. The conditions for obtaining the two acids, and their properties, are reviewed. H. J. E.

Preparation of iodine. C. E. WHITE (J. Chem. Educ., 1935, 12, 169).—9 ml. of 0.25M-NaIO₃ are mixed with 10 ml. of 0.5M-Na₂SO₃. 3 ml. of 2N- H_2SO_4 are added and the whole is carefully shaken. L. S. T.

Intermediate product of long life between iodine and oxalate (ion). E. ABEL and H. SCHMID (Naturwiss., 1935, 23, 501; cf. A., 1933, 237).—In the photochemical reaction between I and C_2O_4 an intermediate product of long life, probably $(O_2C \cdot CO_2)'$ ("oxalato-ion") is produced. This may be connected with the "activated form of $H_2C_2O_4$ " previously described (A., 1928, 505). A. J. M.

Decomposition of permanganic acid in certain acid media. Thermal decomposition of manganic carbonate, and its products. (A) J. KOTRBA. (B) J. CHLOUPEK (Chem. Listy, 1934, 28, 137—140, 140—142).—Criticism and a reply (cf. A., 1933, 919, 1022). R. T.

Anhydrous ferric orthophosphate. P. BRASSEUR (Compt. rend., 1935, 200, 2182—2184). $FePO_4$ was prepared by adding aq. $(NH_4)_3PO_4$ to aq. Fe alum containing NH_3 , evaporating to dryness, and heating gradually to 800° . $FePO_4$ is white and micro-cryst. Its magnetic properties were studied. No anhyd. basic phosphates were isolated, mixtures of $FePO_4$ and Fe_2O_3 being always obtained. E.

Reaction of carbon dissolved in liquid iron with oxides. F. KORBER and W. OELSEN (Naturwiss., 1935, 23, 462—465).—The removal of C from liquid Fe by the oxidising action of the oxides of the

slag is not entirely governed by mass action, but by a no. of external phenomena, such as the formation of CO bubbles in the melt. There is delayed formation of these bubbles, giving rise to local superheating. Spontaneous formation of the first CO bubbles rarely occurs in the bulk of the melt or at the surface of contact with the slag, but almost exclusively where the melt comes in contact with the walls of the containing vessel.

A. J. M.

New group of complex compounds. Compounds with a complex anion, the central ion of which is a complex cation. I. Complex sulphato- and oxalato-anions with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 223, 253—256).—Determination of ionic wts. by electrodialysis in solutions of complex salts in aq. K_2SO_4 and $K_2C_2O_4$ shows that complex sulphato- and oxalato-ions may be formed, in which the central atom of the usual acido-complex is replaced by a central complex ion. The following such complexes were shown to exist: ($R=SO_4''$ or C_2O_4'') $[[Co(NH_3)_5H_2O]R_4]^{5-}$; $[[Co(NH_3)_4(H_2O)_2]R_4]^{5-}$; $[[Co(NH_3)_4SO_4]R_4]^{7-}$; $[[Co(NH_3)_6](SO_4)_4]^{5-}$; $[[Co(NH_3)_5Cl](SO_4)_4]^{6-}$; $[[Co(NH_3)_4CO_3](SO_4)_4]^{7-}$. In aq. $K_2C_2O_4$, $[Co(NH_3)_4CO_3]^+$ forms the anion $[Co(NH_3)_4(CO_3)(C_2O_4)]$.

J. S. A.

Recent advances in applied microchemistry. J. B. NIEDERL (Ind. Eng. Chem. [Anal.], 1935, 7, 214—218).—A review.

E. S. H.

Role of analytical chemistry in industrial research. II. Microanalysis. B. L. CLARKE and H. W. HERMANCE (Ind. Eng. Chem. [Anal.], 1935, 7, 218—222).—A review.

E. S. H.

Material testing by flame analysis. F. WAIBEL (Z. tech. Physik, 1934, 15, 454—456; Chem. Zentr., 1935, i, 1274).—Flame spectra are more accurate and convenient for quant. spectral analysis than spark spectra.

J. S. A.

Chromatographic adsorption analysis. N. A. SØRENSEN (Tidsskr. Kjemii, 1935, 15, 53—55).—A review.

R. P. B.

Determination of p_H with the glass electrode. K. BENNEWITZ and E. KELLNER (Z. anal. Chem., 1935, 102, 1—3).—This method dispenses with the use of an electrometer. The glass electrode and a potentiometer are connected in opposition to a condenser, which is discharged through a mirror galvanometer. The potentiometer is adjusted to give zero galvanometer deflexion. A p_H accuracy of ± 0.003 is attainable.

S. J. G.

Buffer action and reciprocity of the acid-base function. S. KILPI (Z. physikal. Chem., 1935, 173, 223—236).—In acid-alkali titration with one reactant weak, $[H']$ or $[OH']$ at the point of min. p_H change $\sim K$ and the point of max. p_H change practically coincides with the equiv. point if $Kc \ll 10^{-10}$, where c is the concn. of weak reactant. If Kc is smaller, the points of max. and min. p_H change approach and coincide when $Kc=$

If both reactants are weak the point of max. or min. buffer action towards strong acids and strong bases generally coincides with the equiv. point, the buffer action being a min. or max. according as

$K_{HA}K_{BOH}$ is $>$ or $< 15 K_w$. When the salt of a weak acid or base is titrated with a strong base or acid the change in potential has both a max. and a min. if $K/c < 1/27$. In displacement titration the solution of a salt of weak acid (base) behaves like a base (acid) with dissociation const. equal to the hydrolysis const. of the salt.

R. C.

Use of antimony electrode for p_H determination and acidimetric titration in aqueous or organic solutions. E. VELLINGER (Ann. Off. nat. Comb. liq., 1934, 9, 673—701; Chem. Zentr., 1935, i, 1274).—An Sb rod electrode is recommended for acidimetric titrations. Acids insol. in H_2O may be titrated in EtOH, $C_5H_{11}OH$, EtOH+Et₂O, or EtOH+ C_6H_6 . Alcoholic LiCl may be added to increase the conductivity.

J. S. A.

Direct determination of the absolute water-vapour content of gases.—See B., 1935, 705.

Determination of chloride, bromide, and iodide by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 175—177B).— Cl' , Br' , and I' may be titrated photometrically with $AgNO_3$, using starch as protective colloid. The light absorption attains a const. val. when pptn. of Ag halide is complete.

J. S. A.

Determination of bromine in brine.—See B., 1935, 671.

Electrometric determination of bromine in the presence of large quantities of chlorine. G. E. VLADIMIROV and J. A. EPSTEIN (Mikrochem., 1935, 18, 58—65).—The method depends on the separation of NaCl from NaBr by pptn. with $COMe_2$ and centrifuging, removal of the solvent, and titration of the solution with 0.01N- $AgNO_3$ potentiometrically, the NaCl not pptd. having no effect on the potential jump at the end-point of the NaBr titration. For the analysis of org. materials, e.g., blood, the org. matter is destroyed with fuming HNO_3 and $AgNO_3$, the $AgCl+AgBr$ ppt. washed and decomposed by shaking with Na amalgam, the alkaline solution neutralised with H_2SO_4 , and the Na_2SO_4 pptd. with EtOH before making the $COMe_2$ separation.

A. R. P.

Micro-iodometric determinations. I. M. KORENMAN (Mikrochem., 1935, 17, 361—364).—Titration of Na_2SO_3 and $SnCl_2$ with aq. KIO_3 gives vals. in agreement with I titrations.

R. S.

Identification of halides in presence of thiocyanates. G. B. HEISIG and L. K. HEISIG (Ind. Eng. Chem. [Anal.], 1935, 7, 249—250).—The sensitivity of the test for I' is greatly increased by adding $K_2S_2O_8$ to a cold 10-c.c. sample containing 1—2 c.c. of CCl_4 . If aq. Na_2CO_3 is then added and the solution evaporated to dryness the CNS' is destroyed. Br' is then determined colorimetrically in a CCl_4 extract after adding conc. HNO_3 . Cl' is determined by $AgNO_3$ after removing Br by adding $KMnO_4$ and boiling. By this procedure ≤ 0.25 mg. I' , 0.5 mg. Br' , and 0.25 mg. Cl' can be detected in presence of 100 mg. CNS'.

E. S. H.

Penfield's method for determining fluorine. O. KALLAUNER and K. KURAŠ (Stavivo, 1933, 65).—The Penfield method is modified: into the vessel

in which decomp. occurs, dehydrated Cu uranate is added to ensure complete binding of H_2O formed in the reaction. A second V-shaped pipe filled with glass balls is used to keep any H_2SO_4 from the gas stream. 0.02N-KOH is used. The titration is performed in an alcoholic medium in presence of excess of KCl (Mc-red indicator). CH. ABS. (e)

Determination of small quantities of oxygen in gases.—See B., 1935, 724.

Oxidation-reduction indicators. I. Diphenylbenzidinesulphonic acid. L. A. SARVER and W. VON FISCHER (Ind. Eng. Chem. [Anal.], 1935, 7, 271).—The prep. of diphenylbenzidinesulphonic acid (cf. this vol., 462) is described. The product contains 10 SO_3H groups. A 0.1% aq. solution of the Na salt is recommended as an indicator; when oxidised in 0.5–1.0N- H_2SO_4 the pale yellow solution becomes green and finally violet. On reduction the colour changes are reversed. The absorption spectra of the different forms have been determined.

E. S. H.

Determination of atmospheric ozone by fluorescein. W. HELLER (Compt. rend., 1935, 200, 1936–1938; cf. Maché, this vol., 836).—A discussion of factors which influence the determination. N_2 and O_2 have no influence, and NO , NO_2 , and CO_2 are much less effective in destroying the fluorescence than is O_3 .

H. J. E.

Potentiometric titration of sulphite and sulphonylate alone and in the presence of hyposulphite. J. LÖBERING (Z. anal. Chem., 1935, 101, 392–398).— SO_3'' and derivatives of HSO_3' with aldehydes can be titrated potentiometrically with $\text{K}_2\text{Cr}_2\text{O}_7$ in 2% H_2SO_4 using a Pt indicator electrode, the reaction being $2\text{HSO}_3' + \text{HCrO}_4' + \text{H}^+ \rightleftharpoons 2\text{SO}_4'' + \text{Cr}^{3+} + 2\text{H}_2\text{O}$. Similarly, $2\text{HSO}_2' + \text{HCrO}_4' + \text{H}^+ \rightleftharpoons \text{Cr}^{3+} + 2\text{H}_2\text{SO}_4$. $\text{Na}_2\text{S}_2\text{O}_4$ does not interfere unless the solution is heated or the acidity is high. A. R. P.

Argentometric determination of (A) sodium sulphide and hydrosulphide present together, (B) sodium hydroxide and sulphide in sodium aluminate.—See B., 1935, 723.

Conductometric titration of selenates with lead nitrate and with barium chloride. R. RÍPAN-TILICI (Z. anal. Chem., 1935, 102, 28–31).—The aq. selenate solution (approx. 0.05M) is made 40% in EtOH and is then titrated with 0.5M- $\text{Pb}(\text{NO}_3)_2$, the conductivity being measured after each addition. Selenic acid can be determined if first made slightly alkaline with KOH, but heavy metal selenates are unsuitable. For titration with 0.5M- BaCl_2 the selenate solution must contain 50% of EtOH.

S. J. G.

Determination of ammoniacal and urea-nitrogen. J. Y. YEE and R. O. E. DAVIS (Ind. Eng. Chem. [Anal.], 1935, 7, 259–261).—Modifications of the urease method, which enable $\text{CO}(\text{NH}_2)_2$ to be determined even in highly-coloured solution, are described. NH_3 is determined by distillation at 40° with NaOH in MeOH under reduced pressure with aeration.

E. S. H.

Determination of ammonia. S. ŠKRAMOVSKÝ (Lékárn., 1934, 14, 249–251; Chem. Zentr., 1935,

i, 933).—A modified NH_3 distillation apparatus is described.

J. S. A.

Colorimetric determination of nitric acid and nitrates. R. CERNATESCU and E. GHELLER (Z. anal. Chem., 1935, 101, 402–406).—The method depends on the formation of a red colour when the solution (0.5 c.c.) is treated with 4 vols. of conc. H_2SO_4 to which has been added 0.5 g. per 100 c.c. of *m*-diaminophenol hydrochloride. Fe^{3+} and Fe^{2+} must first be removed by pptn. with NaOH and NO_2' by treatment with $\text{CO}(\text{NH}_2)_2$.

A. R. P.

Colorimetric determination of phosphorus in presence of silica, arsenic, iron, and nitrates. C. ZINZADZE (Ind. Eng. Chem. [Anal.], 1935, 7, 227–230).—Modifications in the Mo-blue method are described. In the SnCl_2 reduction method the use of MoO_3 is recommended in place of NH_4MoO_4 . SnCl_2 may be replaced by *p*-OH- $\text{C}_6\text{H}_4\cdot\text{NHMe}$, H_2SO_4 , quinol, or aminonaphtholsulphonic acid. E. S. H.

Colorimetric determination of arsenic in phosphorus-free solutions. C. ZINZADZE (Ind. Eng. Chem. [Anal.], 1935, 7, 230).—The modifications described for the determination of P (see above) are applicable to As.

E. S. H.

Use of conductometric titrations with visual observation in microchemical tests: titration of minute amounts of arsenic. G. JANDER and J. HARMIS (Angew. Chem., 1935, 48, 267–271).—Quantities of As of the order of 0.1 mg.— 0.1×10^{-6} g. can be rapidly determined by visual conductometric titration with an EtOH solution of I using Pt electrodes and a Wheatstone bridge and galvanometer. Addition of NaHCO_3 is unnecessary and undesirable, CO_2 -free H_2O must be used when the As is $1-20 \times 10^{-6}$ g. and A must be passed into the titration vessel when $< 1 \times 10^{-6}$ g. of As is being titrated. The graphs obtained consist of two straight lines, that obtained after the end-point being horizontal to the axis giving c.c. of I. AsPhO can be determined similarly. The necessary apparatus and its connexions are illustrated.

A. R. P.

Modified procedure for the arsenic group. A. T. LINCOLN and E. OLSON (J. Chem. Educ., 1935, 12, 264–265).—The solution of thio-salts in $(\text{NH}_4)_2\text{S}_x$ is evaporated until it becomes turbid and then 20 ml. of a saturated solution of $\text{H}_2\text{C}_2\text{O}_4$ and 5 ml. of 3% H_2O are added. The solution is boiled for 5 min., diluted to 25 ml., saturated with H_2S , filtered, and washed. The Sn is confirmed with HgCl_2 after reduction of the oxalate in the filtrate with HCl and Al. As_2S_5 is extracted from the ppt. by treatment with 20 ml. of 0.5N- $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 4 ml. of 5M aq. NH_3 , repptd. with HCl and H_2S , and confirmed as the arsenomolybdate. Sb_2S_5 from the residue is boiled with 5 ml. of HNO_3 , diluted with 20 ml. of H_2O , filtered from S, and repptd. with H_2S . Determinations of the relative solubilities of the sulphides of As and Sb in the common NH_4 salts show that only ammoniacal $(\text{NH}_4)_2\text{C}_2\text{O}_4$ dissolves those of As completely and is practically without action on those of Sb. 0.9 mg. of As in < 3 ml. can be readily detected by dilution with 24 ml. of this reagent.

L. S. 1.

Volumetric determination of small amounts of boron in natural solutions. N. V. TAGEEVA (J. Appl. Chem. Russ., 1935, 8, 528—535).—Thomson's method (J.S.C.I., 1896, 12, 432) serves for the determination of ≤ 2 mg. of B_2O_3 (error 0—3%), and Foote's method (A., 1932, 242) of ≤ 0.7 mg. (error 1—3%). B may be determined in presence of interfering substances by evaporating the solution (containing 1—15 mg. of B_2O_3) to dryness, and distilling the residue with 10 ml. of MeOH and 5 drops of conc. H_2SO_4 (to evolution of SO_3). The distillate is hydrolysed with NaOH, the solution evaporated to dryness, the residue dissolved in H_2O , the solution made acid with HCl, boiled, and B_2O_3 is determined by Foote's method. The error is $\pm 1.4\%$. R. T.

Volumetric determination of boron nitride. B. ORMONT and A. SAMOILOW (Z. anal. Chem., 1935, 102, 20—24).—0.05—0.1 g. of the BN together with ≈ 6 times its wt. of KOH are heated at 250° in a porcelain crucible held in a test-tube through which a stream of pure H_2 can be passed. The NH_3 formed is collected in excess of HCl, which is titrated.

S. J. G.

Determination of carbon dioxide in air.—See B., 1935, 671.

Direct and indirect determination of cyanates with adsorption indicators. R. RIPAN-TILICI (Z. anal. Chem., 1935, 102, 32—34).—(a) Direct: 25 c.c. of the approx. 0.01M-CNO' solution are titrated with M-AgNO₃ in presence of 4—5 drops of 0.2% fluorescein solution as adsorption indicator, until a marked red colour appears. 1% accuracy is attainable. (b) Indirect: To the KCNO solution, excess of 0.2M-AgNO₃ is added, and the whole diluted to 50 c.c. After filtration the excess of AgNO₃ is pptd. with excess of 0.4M-KCNS and the excess of the latter titrated with AgNO₃, using fluorescein as indicator.

S. J. G.

Fractional detection of potassium. C. N. POTSCHINOK (J. Appl. Chem. Russ., 1935, 8, 524—527).—0.5 ml. of aq. CH_2O is added to 1 ml. of solution, and 2N-Na₂CO₃ is added to the appearance of a red coloration with phenolphthalein; the solution is filtered, the filtrate is decolorised with AcOH, and a few drops of aq. Na₂Co(NO₂)₆ are added, when a ppt. is obtained in presence of ≤ 0.6 mg. of K. Other cations do not interfere.

R. T.

Colorimetric determination of potassium according to Lebermann. H. RIEHM (Z. Pflanz. Dng., 1935, 39, 309—314).—Modifications of the original method (colorimetric comparison of the solution of cobaltinitrite in HCl) are described and a new process for the prep. of the standard tint is given. 0.03—2.0 mg. of K may be determined with 10% accuracy.

A. G. P.

Determination of small amounts of potassium by means of sodium cobaltinitrite. H. W. LOHSE (Ind. Eng. Chem. [Anal.], 1935, 7, 272—273).—The composition of the ppt. varies between $KNa_2[Co(NO_2)_6]$ and $K_2Na[Co(NO_2)_6]$, according to the conditions of pptn.

E. S. H.

Drop reaction for caesium and its use in drop colorimetry. E. S. BURKSER and M. L. KUTSCH-

MENT (Mikrochem., 1935, 18, 18—21).—The solution under test (1 drop) is placed on a filter-paper impregnated with a solution of AuBr₃ and PtBr₃ containing 3% Au and 1.5% Pt; a black spot due to Cs₂Au₂PtBr₁₂ forms in the presence of 0.25×10^{-6} g. of Cs per cu mm. K, NH₄, Na, and Li give no reaction and Rb gives a similar reaction only when the Cs solution contains $> 2\%$ Rb.

A. R. P.

Application of a drop reaction to determination of traces of silver in galenites and in Pribram flotational concentrates. R. JIRKOVSKY (Chem. Listy, 1935, 29, 133—136).—The ignited ore is extracted with HNO₃, and a drop of extract is added to a layer of collodion containing Feigl's reagent (A., 1928, 1108), when the dimensions and intensity of coloration of the spot produced are approx. \propto the Ag content.

R. T.

Test-tube method for flame testing. A. R. CLARK (J. Chem. Educ., 1935, 12, 242—243).—New flame tests for certain of the commoner metals obtained by the test-tube method are described and compared with those obtained by using Pt wire.

L. S. T.

Volumetric micro-determination of calcium (precipitated as picrolonate) with methylene-blue. A. BOLLIGER (Austral. J. Exp. Biol., 1935, 13, 75—78).—0.05N-Li picrolonate is added in known excess to the neutral solution, Ca picrolonate is removed after 24 hr., and excess of picrolonate in the filtrate is titrated against methylene-blue in presence of CHCl₃ (A., 1934, 1017).

F. O. H.

Volumetric determination of beryllium and silicon in solutions of their complex fluorides. J. A. TSCHERNICHOV and E. J. GULDINA (Z. anal. Chem., 1935, 101, 406—413).—The neutral solution is treated with a large excess of neutral CaCl₂ solution which decomposes the Na₂SiF₆ with the formation of HF, which can be titrated (Me-orange) with 0.5N-NaOH (1 c.c.=7.5 mg. of SiO₂). The solution is then diluted to 250 c.c., again titrated with the same NaOH to a pale pink with phenolphthalein, heated to the b.p., and titrated to a permanent pink (1 c.c.=6.25 mg. BeO). If much Na₂SiF₆ is present the ppt. obtained in the first step must be removed before making the second titration.

A. R. P.

Determination of magnesium as magnesium ammonium phosphate hexahydrate. J. P. MEHLIG (J. Chem. Educ., 1935, 12, 288—290).—The determination of Mg by this method gives results which compare favourably with those obtained by the pyrophosphate method. The method is also recommended for the determination of P.

L. S. T.

Experiments with Hahn's reagent. (A) J. ČERVINKA. (B) A. OKAČ (Chem. Listy, 1935, 29, 35—37, 148).—(A) Mg cannot be distinguished from Ca, Sr, and Ba by means of 1:2:5:8-tetrahydroxy-anthraquinone (A., 1924, ii, 784). Zn, Al, and Fe^{III} interfere with the development of the colour reaction.

(B) Specificity was not claimed by Hahn *et al.* R. T.

Pyrophosphate method for the determination of zinc. Z. H. PAN and C. H. CHIANG (J. Chinese Chem. Soc., 1935, 3, 118—121).—The decomp.

$\text{ZnNH}_4\text{PO}_4 \rightarrow \text{Zn}_3\text{P}_2\text{O}_7$, begins at 350° and is complete at 520° in 1.5 hr. R. S.

Quinaldinic acid as a micro-reagent. III. Determination of zinc in the presence of iron, aluminium, uranium, beryllium, and titanium. P. RAY and M. K. BOSE (*Mikrochem.*, 1935, 18, 89—91).—The ammoniacal tartrate solution is treated with Na quinaldinate, the excess of NH_3 removed by blowing air over the solution at 60° , the solution cooled and filtered, and the washed ppt. dried at 125° , and weighed as $\text{Zn}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$. A. R. P.

Micro-determination of zinc with anthranilic acid. C. CHERMAN and P. WENGER (*Mikrochem.*, 1935, 18, 53—55).—The method of Funk and Ditt (A., 1933, 244) is adapted to microchemical work. A. R. P.

Determination of zinc in water by means of sodium diethyldithiocarbamate.—See B., 1935, 752.

Determination of lead. Removal of bismuth interference in the dithizone method. C. E. WILLOUGHBY, E. S. WILKINS, jun., and E. O. KRAEMER (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 285—286).—Bi is separated from Pb by extracting a HNO_3 solution of the metals, adjusted to p_H 2.0, with a solution of dithizone in CHCl_3 . Pb remains in the aq. phase, whilst Bi forms a CHCl_3 -sol. org. complex. E. S. H.

Determination of lead. Modification of the Fischer-Leopoldi method. O. B. WINTER, H. M. ROBINSON, F. W. LAMB, and E. J. MILLER (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 265—271).—Pb is determined colorimetrically by extraction with a solution of dithizone in CHCl_3 . The method is sensitive to approx. 0.001 mg. Pb in biological material. With suitable modifications the determination may be made in presence of Bi or Sn^{II} , which normally interfere. E. S. H.

Determination of lead in drinking water.—See B., 1935, 752.

Iodometric determination of copper. J. BRTSKETI (*Z. anal. Chem.*, 1935, 102, 35—38).—The method is based on the reaction $2\text{Cu}^{II} + 2\text{S}_2\text{O}_3^{II} + 2\text{SCN}^- = 2\text{CuSCN} + \text{S}_4\text{O}_6^{II}$. To 10 c.c. of the approx. 0.1N solution of Cu^{II} , previously neutralised, excess of 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ is added together with 10 c.c. of 10% AcOH and 1—2 g. of NaOAc . 3 g. of KI , 10 c.c. of 10% KCNS , and 5 c.c. of starch solution are next added and the excess of $\text{S}_2\text{O}_3^{II}$ is titrated with 0.1N-I. Any Fe^{II} must be previously oxidised with conc. HNO_3 , the excess of this being removed with $\text{CO}(\text{NH}_2)_2$. S. J. G.

New reagent [thiolbenzthiazole] for gravimetric determination of certain metals. I. Copper. G. SPACU and M. KURAŠ (*Z. anal. Chem.*, 1935, 102, 24—28).—An excess of a 5% EtOH solution of the reagent is added to a warm aq. solution of the Cu salt. After heating and shaking, the orange-yellow ppt. is washed and dried at 110 — 120° , then ignited to CuO and weighed as such. The method is applicable in presence of Ni, Co, Zn, Cd, Mn, alkaline-earth and alkali metals, but Bi, Pb, Hg, Ag, Au, and Tl are quantitatively pptd. S. J. G.

Dimercaptothiodiazole as an analytical reagent. P. RAY and J. GUPTA (*J. Indian Chem. Soc.*, 1935, 12, 308—317).—1:4-Dithiolthiodiazole forms coloured ppts. with most elements in the H_2S analytical group; by its use 2×10^{-8} g. of Cu and 1×10^{-7} g. of Bi can be identified. Methods for separating Cu from As, Sb, Sn, Mo, W, Fe, Zn, and all metals in or following analytical group III, and for separating Pb from As, Sb, Sn, Mo, and alkaline earths are described. E. S. H.

Colorimetric determination of aluminium with eriochrome-cyanine. II. F. ALTEN, B. WANDROWSKI, and E. HILLE (*Angew. Chem.*, 1935, 48, 273—275).—A portion of the substance containing 10 — 100×10^{-6} g. of Al is heated with conc. H_2SO_4 to destroy org. matter and expel halides, the residue is ignited and fused with NaKCO_3 , the melt dissolved in H_2O , acidified with HNO_3 and treated with $(\text{NH}_4)_2\text{MoO}_4$ mixture to ppt. P_2O_5 , the Al pptd. by addition of $\text{UO}_2(\text{OAc})_2$ and aq. NH_3 (bromothymol-blue), and the ppt. extracted first with aq. Na_2CO_3 then with aq. NaOH . The combined extracts are acidified with HCl , treated with 15 c.c. of 0.1% eriochrome-cyanine solution, neutralised with NaOH , and buffered to p_H 6 with NaOAc - NH_4OAc - AcOH mixture. The extinction coeff. is then determined as usual and the Al content read from a graph constructed from standards prepared in the same way. A. R. P.

Volumetric determinations in strongly alkaline solutions. II. Titration of manganese with ferricyanide. O. TOMIČEK and J. KALNY (*J. Amer. Chem. Soc.*, 1935, 57, 1209—1211; cf. this vol., 838).—The influence of glycerol, mannitol, $(\text{CH}_2\text{OH})_2$, and tartaric acid on the oxidation of Mn^{II} salts by $\text{K}_3\text{Fe}(\text{CN})_6$ in presence of NaOH has been investigated. Using tartaric acid, Mn^{II} can be determined by potentiometric titration by this method in presence of Cu^{II} , Zn^{II} , Ni^{II} , Co^{II} , As^{III} , As^V , Sb^V , Fe^{III} , Al^{III} , PO_4^{III} , and MoO_4^{II} . E. S. H.

Volumetric determination of manganese by induced oxidation of Mn^{II} salts to Mn^{III} metaphosphoric acid [complex]. R. LANG (*Z. anal. Chem.*, 1935, 102, 8—16).—The chloride-free Mn^{II} solution containing definite quantities of H_2SO_4 or of NO-free HNO_3 is treated with sufficient dil. HPO_3 . 3 drops of NHPh_2 indicator (1% solution in syrupy H_3PO_4) are added, then excess of $\text{K}_2\text{Cr}_2\text{O}_7$, followed by excess of arsenite solution. The Mn, now in the Mn^{III} condition, is titrated with 0.1N- FeSO_4 until the solution becomes grass-green. Small quantities of NaCl, of Mg, Ca, Al, Ni, Co, Pb, Cu, and Ti do not interfere. In presence of Fe special precautions are necessary as to concns. S. J. G.

Spectral analysis as accessory in material testing and production. W. GERLACH (*Z. tech. Physik*, 1934, 15, 451—453; *Chem. Zentr.*, 1935, i, 1273—1274).—Spectral analysis using the interrupted arc is recommended for the detection and determination of impurities, and their distribution, in metals, and for the rapid approx. determination of minor constituents in rocks. The distribution of Fe in Au-Ag alloys is irregular, points of high [Fe] being also low in Ag. J. S. A.

Cerimetric titration of small amounts of iron by means of 2 : 2'-dipyridyl as indicator. C. J. VAN NIEUWENBURG and (Miss) H. B. BLUMENDAL (Mikrochem., 1935, 18, 39—42).—The HCl solution is reduced by passing it through a Ag sponge reductor and titrated with 0.002—0.015*N*-Ce(SO₄)₂ using as indicator a 0.25% solution of 2 : 2'-dipyridyl in 1 : 1 aq. NH₃. A. R. P.

Use of indigo-carmin in micro-volumetric analysis. I. M. KORENMAN (Mikrochem., 1935, 18, 31—38).—In Na₂CO₃ solution 0.001*N*-indigo-carmin (I) can be used for the titration of Fe(CN)₆^{'''} and in H₂SO₄ solution for the titration of KMnO₄ and, indirectly, of Fe^{'''}. (I) retains its titre for about a month if 20 c.c. of 1 : 5 H₂SO₄ per litre are added. A. R. P.

Detection of ferricyanides in the presence of ferrocyanides. I. M. KORENMAN (Z. anal. Chem., 1935, 101, 417—419).—The method depends on the power of Fe(CN)₆^{'''} to bleach the blue colour of indigo-carmin solution in the presence of Na₂CO₃; sensitivity 1 in 6 × 10⁵. MnO₄['], OCl['], OBr['], and H₂O₂ interfere by giving similar reactions. A. R. P.

Detection of cobalt in presence of other cations. R. V. VORONTZOV (J. Appl. Chem. Russ., 1935, 8, 555—556).—The solution is made acid with HCl, excess of NH₄CNS is added, the solution is decolorised with SnCl₂, C₅H₁₁·OH in COMe₂ is added, and the mixture is shaken. A blue coloration of the alcohol layer indicates Co. R. T.

Determination of chromium. I. Volumetric and colorimetric micro-determination of hexavalent chromium. D. BRARD (Ann. Chim. Analyt., 1935, [iii], 17, 201—207).—Quantities of Cr > 0.2 mg. can be determined by addition of slight excess of titred FeSO₄ solution, and titrating the excess with 0.005*N*-KMnO₄. For colorimetric determination of > 0.001 mg. Cr, the solution is treated with H₃PO₄ and H₂SO₄ and then with a 2% EtOH solution of diphenylcarbazine, the rose-violet colour being compared with standards. J. W. S.

Potentiometric determination of molybdenum in ores and rocks.—See B., 1935, 677.

Potentiometric determination of molybdenum and titanium in steel, ferro-alloys, slags, and ores in presence of iron and other metals.—See B., 1935, 677.

Rapid determination of polonium in a natural radio-lead by direct measurement of α-rays and Ra. (MLLE.) M. LEBLANC (J. Chim. phys., 1935, 32, 332—341).—Po was incorporated with PbCl₂ and PbCO₃ and subsequently extracted and determined by the Ag-plate and ionisation chamber method. PbCl₂ afforded results deviating widely from the mean which, however, agreed with the calc. val., but PbCO₃ afforded concordant results disagreeing with the calc. val. In presence of Ra, the Po was determined as above, and the Ra content was deduced from the emanation accumulated in a definite time after separating the Ra with Ba from the Pb. The activity due to Po in the chlorides and carbonates of natural Ra-leads is approx. equal to the total activity, compared with that of UO₃, of the material collected

in a thick layer from suspension, diminished by the activity due to the Ra, providing no emanation is lost. The nitrates give anomalous results.

J. G. A. G.

Centigram (semi-micro-)analysis of inorganic substances. I. General considerations. T. MIŁOBĘDZKI. II. Brass. III. Dolomite. W. JANCAK (Rocz. Chem., 1935, 15, 294—297, 298—303, 304—310).—I. Introductory.

II. Sn, Pb, Cu, and Zn are determined in brass by the centigram and decigram methods; the results are of the same order of accuracy, but the former procedure involves an economy of > 50% in time, and of 90% in reagents.

III. Centigram analysis of dolomite for Fe, Ca, Mg, CO₂, and insol. residue requires 9—10 hr., as compared with 15 hr. for the decigram procedure. R. T.

Precipitation of titanium as phosphate. CHENG DA-TCHANG and L. HOVONG (Compt. rend., 1935, 200, 2173—2175, and J. Chinese Chem. Soc., 1935, 3, 115—117).—Pptn. of Ti as phosphate is complete in presence of > 10% of HCl, and with excess of (NH₄)₂HPO₄. The factor for determining TiO₂ from the wt. of phosphate is 0.5234. Previous conclusions as to the formula are criticised (cf. A., 1922, ii, 91).

H. J. E.

Detection of small quantities of germanium with a drop reaction. A. S. KOMAROVSKY and N. S. POLUEKTOV (Mikrochem., 1935, 18, 66—73).—The alkaline solution of GeO₂ is evaporated to dryness with H₂O₂ and the residue distilled with KMnO₄ and 3.5—4*N*-HCl. The distillate is mixed with NH₄OAc and a few drops are placed on a piece of filter-paper, which is then heated with a drop of a 7.5% solution of (NH₄)₂MoO₄ in 1 : 1 HNO₃ and a drop of 0.1% aq. benzidine acetate. A blue colour is perceptible with > 0.25 × 10⁻⁶ g. of GeO₂ in 0.025 c.c. Procedures are given for the detection of Ge in ores and Zn electrolytes. A. R. P.

Reactions for germanic and boric acids. N. S. POLUEKTOV (Mikrochem., 1935, 18, 48—52).—H₂GeO₄ gives similar reactions to H₃BO₃ with mannitol, quinalizarin in conc. H₂SO₄, and *p*-nitrobenzenazo-chromotropic acid in conc. H₂SO₄, but the reactions are not so sensitive. A. R. P.

Spectrographic determination of traces of germanium. Application to copper and metallic iron. R. BRECKPOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 160—173).—The extraction and determination of Ge by the spectrographic method of Geilmann and Brünger (A., 1931, 455) are discussed. The extraction of Ge by co-pptn. with Fe(OH)₃, and as GeCl₄ by distillation, is reviewed and its application to the determination of Ge in Cu and Fe is discussed. W. R. A.

Gravimetric determination of vanadium by means of ammonium benzoate. F. M. SCHEMJAKIN and V. F. TSCHAPIGIN (J. Appl. Chem. Russ., 1935, 8, 536—542).—10 ml. of 2*N*-HCl are added to 25 ml. of solution containing > 0.1—0.15 g. of V₂O₅, aq. (NH₄)₂SO₃ is added to the boiling solution to complete reduction of V^V to V^{IV}, which is pptd. by adding excess (< 1 g.) of NH₄OBz, boiling for 1 min., and filtering after 3 hr. The ppt. is washed

with aq. 0.37% BzOH, ignited, and weighed as V_2O_5 . Fe and Cr should be absent; Mg, Al, Cu, Mo, W, and Ti do not interfere. R. T.

Spectrographic determination of traces of bismuth, arsenic, antimony, tin, and lead in electrolytic copper. R. BRECKPOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 173—194).—Bi, As, Sb, Sn, or Pb present to 10^{-5} or $10^{-6}\%$ can be determined. The occlusion of Cu by $Fe(OH)_3$ is influenced by the $[NH_3]$ and $[NH_4Cl]$. The impurities are also occluded and methods of determining them in absence of Cu and in presence of Cu are outlined. W. R. A.

Bismuth-characterising groups. J. V. DUBSKY, A. OKAČ, and J. TRTILEK (Mikrochem., 1935, 17, 332—343; cf. A., 1934, 377).—Bi salts give a yellow colour with thiocarbamides (I) and an orange-yellow or red cryst. ppt. with compounds containing the groups $NH\cdot CS\cdot S\cdot C(SH)\cdot N\cdot$ or $NH\cdot CS\cdot NR\cdot C(SH)\cdot N\cdot$ (II), attributed to the formation of a six-membered ring in which Bi is linked to two S. 24 reagents have been examined and their behaviour is accounted for on this basis. Microchemical tests with (I) and (II) are described and the influence of other ions is discussed. R. S.

Tantalum and niobium. I. Analysis of mixtures of the pentoxides. K. R. KRISHNASWAMI and D. S. MURTHI (J. Indian Inst. Sci., 1935, 18A, 69—73).— Nb_2O_5 is reduced to Nb_2O_4 on heating at 800 — 1000° in H_2 for 1 hr.; the product is oxidised back to Nb_2O_5 at 600° in air. Since Ta_2O_5 remains unchanged the method can be used for determining Nb_2O_5 in mechanical mixtures of the two oxides. No tests were made on co-pptd. mixtures. A. R. P.

Microchemical determination of gold in presence of palladium and tin. J. DONAU (Mikrochem., 1935, 18, 11—17).—The alloy is inquarted with Zn—Cd eutectic in a small glass tube in a current of H_2 and the bead is parted first in 0.5 c.c. of 1:1 HNO_3 and then in 0.5 c.c. of conc. HNO_3 . In presence of much Pd a second inquartation and parting are necessary and in presence of Sn the $Au+SnO_2$ are collected by centrifuging and the SnO_2 is volatilised by heating with NH_4Cl . A. R. P.

Micro-determination of gold and silver in alloys.—See B., 1935, 678.

Highly sensitive reaction of indole and pyrrole [with gold].—See this vol., 998.

Detection and determination of gold in solutions.—See B., 1935, 729.

Microscopical identification of the elements of the platinum group and gold. W. F. WHITMORE and H. SCHNEIDER (Mikrochem., 1935, 17, 279—319).—The microscopical behaviour of Ru, Rh, Pd, Os, Ir, Pt, and Au with various reagents has been investigated. The most characteristic test reagents are: for Ru, NEt_4Br and $NH_2Me\cdot HCl$; for Pd, dimethylglyoxime and caffeine; for Ir, $NH_2Me\cdot HCl$; for Pt, $m\text{-}C_6H_4Me\cdot NH_2\cdot HCl$, $m\text{-}C_6H_4(NH_2)_2$, and $NH_4Et_2\cdot HCl$; for Au, caffeine. Qual. analysis is effected by extraction of Au with $EtOAc$ and distillation of Os, the remainder being detected by the sp. tests. R. S.

Assay and analysis of metals of the platinum group. W. SAVELSBERG and A. FISCHER (Metall u. Erz., 1934, 31, 451—456; Chem. Zentr., 1935, i, 935).—Sources of error in the assay of Pt metals are discussed. Fusion is effected in a fireclay or graphite crucible, Fe filings being added. The Pb regulus is re-fused with Na_2CO_3 +borax to remove Ni, which prevents complete removal of Pb during cupellation. The addition of 10—15-fold amount of Ag is advantageous. J. S. A.

Spectro-analytically detected elements adsorbed on ferromagnetic colloidal γ -ferric oxide as biological indicators.—See this vol., 1182.

Liquefaction of hydrogen by the expansion method. F. SIMON, A. H. COOKE, and H. PEARSON (Proc. Physical Soc., 1935, 47, 678—683).—Conditions for the satisfactory application of the expansion method to H_2 are examined. N. M. B.

Oxygen liquefier. C. R. MARSH and C. T. KNIPP (Rev. Sci. Instr., 1935, [ii], 6, 203—204).—Gaseous O_2 circulates around a tube containing liquid air boiling at atm. pressure. C. W. G.

Apparatus for the thermal decomposition of small quantities of materials in an inert atmosphere. R. A. SMITH (Mikrochem., 1935, 18, 98—99).—A one-piece glass apparatus for the pyrolysis of small amounts of org. compounds in an inert atm. is illustrated. A. R. P.

Electric micro-muffle. C. J. RODDEN (Mikrochem., 1935, 18, 97).—The wire gauze on the horizontal tube of a Pregl micro-muffle is replaced by an electric heater made by winding 18-gauge nichrome wire around a porcelain form 9 cm. long and covering the wire with asbestos paper for insulation. The heater is connected in series with a 660-watt heater of the sun-bowl type to act as a resistance and operated with 110 volts a.c. A. R. P.

Modified boiling vessel for micro-ebullioscopic mol. wt. determinations by Pregl's method. A. REŽEK (Mikrochem., 1935, 18, 109—111).—The vessel is broadened slightly at one side, from just below the meniscus of the solvent, to permit easier introduction of the pastille of solute. A. R. P.

Production of temperatures below 1° abs. by adiabatic demagnetisation of gadolinium sulphate. W. F. GIAUQUE and D. P. MACDOUGALL (J. Amer. Chem. Soc., 1935, 57, 1175—1185).—Apparatus and procedure are described. Starting at 1.29° abs., using a field of about 8000 gauss, the lowest temp. reached was $0.242 \pm 0.0003^\circ$ abs. Tables showing the change of temp., differential susceptibility, energy and heat content accompanying adiabatic magnetisation from temp. below 1° abs. are given. E. S. H.

Simplified mixture calorimeter. H. S. VAN KLOOSTER (J. Chem. Educ., 1935, 12, 285—286).—In the apparatus described only 25 c.c. of acid and base are used. Heats of mixing H_2O and alcohols, and heats of gelation for rapidly forming gels can also be determined. L. S. T.

Micro-burner. V. T. JACKSON (J. Chem. Educ., 1935, 12, 216).—A method of converting a Bunsen

burner into a micro-burner giving a hot non-luminous flame which can be varied in height from a few mm. to approx. 3 cm. is described. L. S. T.

Determination of ultra-violet absorption. R. FABRE and L. AMY (*J. Pharm. Chim.*, 1935, [viii], 22, 1—15).—The method involves the use of a variable no. of quartz laminations to cut out the spectrum of the solvent for both qual. and quant. work. H. G. R.

Adjustment of Lovibond red glasses. R. S. ESTEY (*Oil and Soap*, 1935, 12, 135—138).—The methods used in the Electrical Testing Laboratories are described. Lovibond red glasses can be lightened by re-polishing the coloured surface so as to adjust them (for use with 35 yellow) to exact integral vals. on the Priest-Gibson *N''* grading scale. E. L.

Apparatus for microscopical work at low temperatures. S. ERK (*Physikal. Z.*, 1935, 36, 451—452).—The formation of dew etc. on a microscope objective is prevented by placing the lower part of the microscope surrounded by a cooling jacket in a Dewar vessel containing evaporating liquefied gases. Observations can be made down to -120° . A. J. M.

Simple filters for isolating lines in the mercury spectrum. A. J. MADDOCK (*J. Sci. Instr.*, 1935, 12, 218—219).—Compositions of solutions, mainly inorg., are given. C. W. G.

Standard conditions for precise prism refractometry. L. W. TILTON (*J. Res. Nat. Bur. Stand.*, 1935, 44, 393—418).—The precision necessary in the control and measurement of the temp., pressure, humidity, and CO_2 content of air used as a standard reference medium for accurate measurements of n is discussed, and expressions and tables for the reduction of observed vals. of n to standard conditions of reference are given. The range of temp. effects on the abs. val. of n and the range of pressure effects on liquids are indicated, an empirical relation between n and d for elastically deformed glass is derived, and the character of annealing and permissible degree of striation of glasses are considered. By suitable corrections it is possible to determine the n of a liquid to $\pm 3 \times 10^{-6}$ by the classical method of min. deviation. A. R. P.

Precision actinometer for the ultra-violet region (including an exact test of the Einstein equivalence law). L. HARRIS and J. KAMINSKY (*J. Amer. Chem. Soc.*, 1935, 57, 1154—1159).—The Einstein equivalence law holds for the photolysis of malachite-green leucocyanide with an accuracy of 2.5% in abs. val. An actinometer using this solution is suitable for measuring very small light energies. E. S. H.

Photo-electric colorimeter. J. H. YOE and T. B. CRUMPLER (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 281—284).—Apparatus and technique are described. Results are given for the determination of Cu in $\text{Cu}(\text{NH}_3)_4\text{SO}_4$. E. S. H.

Photo-electric colorimetry in micro-analysis. Photo-electric methods in macro- and micro-analysis. R. H. MULLER (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 223—226).—Apparatus, technique, and applications are described. E. S. H.

Photo-electric photometers for use in colorimetry. C. ZINZADZE (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 280—281).—Two instruments of the two-cell form are described. E. S. H.

Colorimeter. J. WOUDE (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 585—589).—The colour of a reflecting surface, transparent medium, or coloured light is determined directly in trichromatic units by means of a visual spectrophotometer fitted with an automatic calculating device. D. R. D.

Determination of the indices of refraction of liquids. J. L. SHELDON (*J. Chem. Educ.*, 1935, 12, 183—186).—The method involves the use of a thin, plano-focus, meniscus lens, and a cover slip. Results showing the accuracy attained are given. L. S. T.

Current lead-in for vacuum vessels. H. HANDEK (*Z. tech. Physik*, 1934, 15, 494—496; *Chem. Zentr.*, 1935, i, 1282).—Ceramic materials are described with linear expansion coeffs. $2.5\text{--}9 \times 10^6$ which give gas- and water-tight seals with glazes. Using glass as an intermediate, massive metal seals may be made into ceramic vessels. Examples are given. H. J. E.

Sensitive a.c. vacuum-tube relay. E. L. ELLIS (*Science*, 1935, 81, 568—569).—A relay suitable for temp. control is described. L. S. T.

Simple cell for glass electrode work. J. H. HIGHBERGER and F. D. THAYER (*J. Amer. Leather Chem. Assoc.*, 1935, 30, 339—341).—The glass electrode bulb is mounted in a rubber stopper fitting into a glass tube of slightly larger diameter, provided with a side arm for filling and at its lower end with a three-way tap so arranged that the cell may be emptied or connected through a short KCl-agar tube with a Hg_2Cl_2 half cell. D. W.

Syringe hydrogen electrode. W. HERMANOWICZ (*Rocz. Chem.*, 1935, 15, 290—293).—A H electrode requiring > 0.2 c.c. of solution is described; the potential becomes const. after 5 min. in buffered, and after 35—45 min. in unbuffered, solutions. The electrode is suitable for p_{H} measurements of biological fluids containing CO_2 . R. T.

Increasing the accuracy of electrolytic conductance measurements made with student-type equipment. L. NUTTING (*J. Chem. Educ.*, 1935, 12, 286—288).—A vac.-tube oscillator and amplifier, replacing the usual microphone hammer and headphones, are described. L. S. T.

Micropolarographic tests. I. Apparatus and technique. V. MAJER (*Mikrochem.*, 1935, 18, 74—88).—Apparatus for carrying out polarographic tests in air or H_2 , using > 0.005 c.c. of solution, is described and illustrated. A. R. P.

Sensitive method of measuring the e.m.f. of high-resistance [galvanic] elements. F. MULLER and W. DURICHEN (*Z. physikal. Chem.*, 1935, 173, 349—352; cf. A., 1932, 814, 999).—The anode current of an electrometer tube is controlled by the unknown e.m.f., and is split into pulsating d.c. by means of a leaf contact-breaker, and suitably amplified. T. G. P.

Cæsium photo-electric cells.—See B., 1935, 681.

Arrangement for demonstrating and studying the Zeeman effect. P. KIRKPATRICK (Rev. Sci. Instr., 1935, [ii], 6, 205).—Transverse and longitudinal beams are obtained from a capillary discharge tube mounted between the poles of a magnet.

C. W. G.

Improvements in microchemical laboratory technique. H. K. ALBER (Mikrochem., 1935, 18, 92—96).—A modified frame, forceps, and wash-bottle for working with the Emich filter-stick, a sharpening block for glass knives, and an improved method of determining the ash of org. substances in the micro-muffle are described.

A. R. P.

Micro-shaking apparatus and stirrer for micro-titrations. K. SCHWARZ (Mikrochem., 1935, 18, 106—108).—Use is made of the magnetic system of a wireless loud speaker, a non-rusting steel wire replacing the membrane and terminating in a ring to hold the vessel to be shaken or in a stirring device.

A. R. P.

Modification of the Bunsen burette. E. W. BLANK (J. Chem. Educ., 1935, 12, 291).—The glass bead is replaced by a small hole in the side and near the sealed mouth of the burette.

L. S. T.

Modified bulb pipette. J. C. LOTZE (Science, 1935, 81, 596).

L. S. T.

Apparatus for the quantitative recovery of dialysates. P. LOCH (Z. anal. Chem., 1935, 101, 385—388).—To avoid the accumulation of large vols. of solution in quantitatively separating crystalloids from colloids by dialysis, the solution outside the membrane is siphoned continuously into a flask from which the solvent is distilled back through a condenser into the dialysing vessel and in which a conc. solution of the crystalloid accumulates.

A. R. P.

Mechanically operated valve designed to withstand atmospheric pressure, for use in high-vacuum work. J. A. CHILES (Rev. Sci. Instr., 1935, [ii], 6, 202—203).—A ground-glass float is raised by means of Hg.

C. W. G.

Mercury-vapour pumps with low primary vacuum. L. HENRY (Bull. Soc. chim. Belg., 1935, 44, 307—310).—A simple pump to be backed by a filter-pump is described.

C. W. G.

Vacuum pump check valve. R. L. MOBLEY (Ind. Eng. Chem. [Anal.], 1935, 7, 222).

E. S. H.

Volume, shape, and roundness of quartz particles. H. WADELL (J. Geol., 1935, 43, 250—280).—Methods for measuring these properties of sedimentary quartz particles are described.

L. S. T.

Determination of moment of passage of vapour through a layer of sorbent by the method of gravimetric indication. E. V. ALEXEEVSKI and Z. I. AZARCH (J. Appl. Chem. Russ., 1935, 8, 577—579).—The air, after passing through the layer of sorbent, passes through dry C in a cylinder suspended from one arm of a balance. The moment when H₂O vapour ceases to be totally adsorbed is indicated by an increase in wt. of the cylinder.

R. T.

Apparatus for measuring the drying power of the atmosphere. J. R. BAKER (J. Sci. Instr., 1935,

12, 214—216).—Direct readings are obtained from a modified hair hygrometer.

C. W. G.

Soldering aluminium-brass joints. F. H. SIMS (J. Sci. Instr., 1935, 12, 233).—The Al is first tinned with special solder and the brass with ordinary solder.

C. W. G.

Double liquid-air trap. R. W. CONWAY (J. Sci. Instr., 1935, 12, 234).—One trap is made to serve for two circuits.

C. W. G.

Microchemical balances. M. FURTER (Mikrochem., 1935, 18, 1—10).—Temp. changes and other disturbing factors in making microchemical weighings are eliminated by using an all-metal balance with a glass front; the back, sides, and base are made of hard Al sheet and the remainder of brass, and the swing is damped by means of two light metal cylinders below the pans. Means for keeping the temp. const. are described.

A. R. P.

Portable chemical balance. H. LLOYD (J. Sci. Instr., 1935, 12, 222—224).—250 mg. can be weighed to 2% on the spring balance described.

C. W. G.

Apparatus for micro-distillation. L. V. REAKES, jun. (Mikrochem., 1935, 18, 100—102).—The flask is made by blowing a 1-c.c. bulb at the end of a piece of 10-mm. (outside diameter) tubing and the side-tube is connected to the condenser with a ground-glass joint; the apparatus gives good results with 0.5 c.c. of liquid.

A. R. P.

Vacuum distillation device. G. LODE (Chem.-Ztg., 1935, 59, 624).—Definite wts. of distillate may be collected during a vac. distillation by having the tubes in a Brühl receiver fixed and counterpoised on small balance arms.

E. H. S.

Pressure regulator for vacuum distillation. O. J. SCHIERHOLTZ (Ind. Eng. Chem. [Anal.], 1935, 7, 284—285).—The regulator operates on the flutter-valve principle and is actuated directly by the vac.

E. S. H.

Fractional distillation. Analysis of organic liquids. H. S. KING (Proc. Nova Scotian Inst. Sci., 1933—1934, 18, 272—275; cf. A., 1934, 398).—The apparatus and its use are described.

J. L. D.

Hoppler viscosimeter in connexion with the standardisation of viscosity measurements. D. CANNEGIER (Chem. Weekblad, 1935, 32, 403—405).—The Hoppler viscosimeter is described. Its accuracy is 0.1% between 10 and 600 and 0.27% between 0.01 and 10⁵ centipoises. Its rapidity, simplicity, and universal applicability make it the ideal standard instrument for measuring η .

S. C.

Micro-viscosimeter. F. M. LIDSTONE (J.S.C.I., 1935, 54, 189—190r).—Viscosity is evaluated by timing the movement of a meniscus in a straight capillary tube. On account of the small quantity of liquid necessary the test is applicable to micro-analysis. The derivation of the equation in abs. units is given. τ^2 (instead of τ^4) occurs in the dimensional const., thus allowing a greater tolerance in calibration. The cause and prevention of the clogging of fine capillaries are discussed.

Permanent aqueous microscopic mounts. H. R. SMITH (Ind. Eng. Chem. [Anal.], 1935, 7, 286).—

The sealing composition recommended is made by heating anhyd. wool fat with $\approx 20\%$ of rosin.

E. S. H.

Hydrogenator. J. O. RALLS and W. H. HAMMERSLEY (J. Chem. Educ., 1935, 12, 290—291).

L. S. T.

Sodium press. M. W. PARKER and C. E. WHITE (J. Chem. Educ., 1935, 12, 232).

L. S. T.

Apparatus and method used in measuring the compressibility of gases at 0—325°. J. A. BEATTIE (Proc. Acad. Arts Sci., 1934, 69, 389—405).

CH. ABS. (e)

Fractional ultrafiltration. I. Preparation of collodion membranes of varying permeability.

II. Glass apparatus for ultrafiltration under pressure. P. GRABAR (Bull. Soc. Chim. biol., 1935, 17, 965—990).

A. L.

Measurement of low pressures with the elastic manometer. L. HENRY (Bull. Soc. chim. Belg., 1935, 44, 311—314).—The sensitivity of a glass Bourdon gauge is increased by means of a valve circuit so that 2 can be detected.

C. W. G.

Training in microchemistry and chemical microscopy. A. A. BENEDETTI-PICHLER (Mikrochem., 1935, 17, 320—331).

R. S.

Scientific contributions of Don Andres Manuel Del Rio. M. E. WEEKS (J. Chem. Educ., 1935, 12, 161—166).—Historical.

L. S. T.

Geochemistry.

Mineralisation of water in the R. Sakma basin (Pugatschev province, Lower Volga region). V. S. VASILIEV (Trans. Saratov Univ., 1934, 10, No. 3, 79—112).—Analytical data are recorded.

R. T.

Variability of concentration of natural waters of European Russia. F. F. SELIVANOV (J. Appl. Chem. Russ., 1935, 8, 445—470).—Variations in the content and concn. of salts in river- and spring-waters, over a no. of years, are recorded.

R. T.

Isotopic composition of water from petroleum sources. K. OKABE and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 259).—Ten samples of water from petroleum sources, 30—1500 m. deep, have been analysed and d compared with standard Osaka conductivity water at 21°. The difference in d is not more than $\pm 2 \gamma$.

W. R. A.

Effect of organic colloids on the behaviour of substances in natural waters. W. OHLE (Naturwiss., 1935, 23, 480—484).—The salts present in waters containing colloidal org. matter (humus) are in part combined with the colloid, the cations being more available in acid and the anions, more particularly PO_4''' , in alkaline solution. The bearing of the existence of such associations of inorg. ions with colloids on the problems of soil and water chemistry is discussed.

W. O. K.

Problems of radio-geology. V. I. VERNADSKI (Bull. Acad. Sci. U.S.S.R., 1935, 1—18).—A discussion.

R. T.

Age of the earth from the changes in its temperature and elastic properties. B. GUTENBERG (Science, 1935, 82, 52).

L. S. T.

Age of the earth from radioactive disintegration and related problems. R. D. EVANS (Science, 1935, 82, 52).—A summary. The age is estimated to lie between 1850 and 3500×10^6 years. The ages of 23 Fe meteorites, many of which are probably of extra-solar origin, are uniformly distributed between 2800×10^6 years and nearly zero and show no tendency to group about any particular age.

L. S. T.

Age of the earth from sedimentation. G. D. LOUDERBACK (Science, 1935, 82, 51—52).—For the time from the Cambrian to the present, a first approximation of sp. sedimentation rates for separate di-

visions of geological history gives results of the same order of magnitude as the radioactive method.

L. S. T.

Composition and contraction of the earth. I. I. SASLAVSKY (Tsch. Min. Petr. Mitt., 1935, 46, 331—341).—Further discussion and repetition (A., 1931, 1389; 1932, 1107).

L. J. S.

Quantitative spectral determination of germanium in the Brazilian meteorites from Bendego and Santa Luzia de Goyaz. A. BETIM (Ann. Acad. Brasil. Sci. 1935, 7, 177—179).—Ge (determined by the author's method of spectral analysis; cf. A., 1934, 380) is present to the extent of 0.00272 and 0.00419% in the S. Luzia and Bendego meteorites, respectively.

E. L.

Stages in the metamorphism of Samos emeries. J. DE LAPPARENT (Compt. rend., 1935, 201, 154—157; cf. A., 1934, 386).—The rocks are described and their metamorphism is discussed.

H. J. E.

Definition of sepiolites. H. LONGCHAMON and G. MIGEON (Compt. rend., 1934, 200, 1946—1949; cf. this vol., 842).—Ampandrandava sepiolite is monoclinic pseudo-orthorhombic (c 5.32 Å.). All sepiolites are attacked completely by cold 10% HCl. Data are recorded for the changes on heating to 1000°. The general formula is $\text{Si}_4\text{O}_{11}(\text{Mg}, \text{H}_2)_3 \cdot \text{H}_2\text{O} \cdot (\text{H}_2\text{O})_x$. H_2O is driven off at $< 350^\circ$. $\text{Si}_4\text{O}_{11}(\text{Mg}, \text{H}_2)_3 \cdot \text{H}_2\text{O}$ decomposes progressively at $> 350^\circ$. $\text{Si}_4\text{O}_{11}(\text{Mg}, \text{H}_2)_3$ decomposes at 750° . Recrystallisation of enstatite and cristobalite occurs at 800° and 1100—1200°, respectively.

H. J. E.

Origin of potash-rich rocks. R. D. TERZAGHI (Amer. J. Sci., 1935, [v], 30, 141—142).—Further note and correction (this vol., 601).

L. J. S.

Synthesis of magnesioferrite: observations on "mineralisation." R. B. DRAPER (Amer. J. Sci., 1935, [v], 30, 106—115).—HCl gas was passed over Fe_2O_3 and MgO in a long porcelain tube along which the temp. was graded. At 800—950° FeCl_3 vapour reacts with MgO giving sharp octahedra of magnesioferrite ($\text{MgO}, \text{Fe}_2\text{O}_3$). Further along the tube hæmatite is deposited as equidimensional crystals at 700° grading to scaly crystals at 500°. Excess of MgO yields a minutely crystalline aggregate of

periclase. FeCl_2 vapour in the absence of H_2O and air reacts with MgO , with production of magnesioferrite and MgCl_2 , at a lower temp. (500°). In these experiments HCl is acting as a "mineraliser."

L. J. S.

Ilmenite sands on the Azov Sea. P. G. PANTILEEV (Min. Suir., 1934, 9, No. 10, 12—16).—The radioactive sands in some sections contain TiO_2 35.02, Fe 37.32, and V_2O_5 0.13%. Garnet, zircon, etc. were present in some specimens. CH. ABS. (e)

Methods of petrographic investigation. V. V. ARSCHINOV (Trans. Inst. Econ. Min. U.S.S.R., 1933, 287—298).—A review. CH. ABS. (e)

Heavy minerals in Finnish rocks. III. Kakola granite. A. LAITAKARI (Tekn. Aikakaus., 1934, 24, 399—402).—The minerals found were garnet, ilmenite, sillimanite, anatase, monazite, zircon, spinel, and smaller amounts of apatite, dumortierite, tourmaline, and andalusite.

CH. ABS. (e)

Eastern end of the Newry igneous complex. D. L. REYNOLDS (Quart. J. Geol. Soc., 1934, 90, 585—636).—Peridotite and biotite-pyroxenite were the earliest intrusives in the area. Analyses are given for the unaltered greywacke and shale, fused sedimentary rocks, peridotite, biotite-pyroxenite, augite-biotite-diorite, shonkinitic monzonite, hypersthene-monzonite, and granodiorite.

CH. ABS. (e)

Thomsonised inclusion from Blackness sill. (Sir) J. FLETT (Prog. Repts. Geol. Survey Gt. Britain, 1934, (1933), Pt. II, 85—90).—Analytical data are given for a xenolith consisting of a matrix of thomsonite containing smaller amounts of other minerals.

CH. ABS. (e)

Isotopic composition of the leads of Great Bear Lake. C. S. PIGGOT (J. Geol., 1934, 42, 641—645).—Pb from three pitchblende specimens and one of galena within the pitchblende vein contained the isotopes 206, 207, and 208 (in order of abundance), indicating pure U-Pb. A second galena from outside the vein had isotopes Pb 208, 207, and 206, indicating contamination of ordinary Pb by U-Pb.

CH. ABS. (e)

Native iron from West Greenland. (Sir) H. C. H. CARPENTER (Nature, 1935, 136, 152—153).—Native Fe from Oviak, Disco Island, West Greenland has Fe 93.9, Ni 2.50, C 1.63, Co 0.98, Cu 0.21, SiO_2 0.24%; CO_2 is absent. The C is much > that found in meteoric Fe and the Ni is considerably lower. Photomicrographs of structures obtained by etching with 1% HNO_3 in EtOH and with alkaline Na picrate are reproduced. The structure consists mainly of a white massive constituent, cementite (I), in a finely-divided duplex matrix, which is probably a eutectoid of ferrite and (I). The origin of the metal is discussed.

L. S. T.

Topaz. J. W. HOWARD (J. Chem. Educ., 1935, 12, 153—156).

L. S. T.

Sulphated minerals of Chili. H. UNGEMACH (Bull. Soc. Franç. Min., 1935, 58, 97—221).—The geometrical crystallography, chemical analyses, optical properties, and densities of the following minerals from Tierra Amarilla and Sierra Gorda are described:

botryogene, hohmannite, amarantite, copiapite, pseudo-copiapite, melanterite, romerite, coquimbite, paracoquimbite, quenstedtite, amarillite, leucoglaucite, lapparentite, and chalcantite. Origin and paragenesis of the sulphates are discussed. L. S. T.

Killarnean and earlier granite. A. C. LANE (Science, 1934, 82, 60—61).—A discussion concerning age. L. S. T.

Composition of lavrovite. E. A. RATZBAUM and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 409—410).—The diopside lavrovite (Sludianka, L. Baikal) has been analysed spectroscopically, and contains, apart from Si, Ca, and Mg, Cr 1.5, Al 0.7, V 0.5, Fe 0.15, Mn 0.001%, and traces of Na, K, and Ti.

T. G. P.

Minerals of Poeloe Berhala (Malacca Strait, Sumatra). J. H. DRUIF (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 639—650).—The minerals found on this island are described. D. R. D.

Chemical analyses of minerals from Poeloe Berhala. W. VAN TONGEREN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 634—639; cf. preceding abstract). D. R. D.

Colorado pegmatites. K. K. LANDES (Amer. Min., 1935, 20, 319—333).—Microcline (I), white bull quartz (II), and riebeckite are the dominant minerals in the pegmatite at St. Peter's Dome, Pike's Peak region. The fluorides in order of deposition are cryolite; pachnolite, the most abundant mineral in the pegmatite after the feldspar and quartz; prosopite; and fluorite. A small amount of silicification and kaolinisation has occurred. At Florissant, white or pink (I), milky (II), some albite (III) and phenacite occur in the pegmatites. In the Arkansas River Valley pegmatites at Eight-Mile Park, feldspar [(I) (III)] is the dominant constituent, (II) is next in abundance, and muscovite is present in amount sufficient to yield commercial mica. Beryl (IV) and subordinate tourmaline (V) also occur. Albitisation is the main feature in the paragenesis of these pegmatites. Pegmatites at other localities in this district are described. In Ohio City, Gunnison County, the main pegmatites are complex. The principal minerals are (I), (III), lepidolite, topaz (VI), and (IV). (I) and (V) are subordinate and columbite and samarskite are minor accessory minerals. (VI) and (IV) are unusually abundant. L. S. T.

Absorption and refraction of light by aquamarine and some yellow and green beryls. H. KLANG (Neues Jahrb. Min., 1934, A, 69, 93—116; Chem. Zentr., 1935, i, 872).—Measurements are recorded. The absorption was always continuous, four types being observed. The coloration is attributed to Fe^{II} and Fe^{III} .

H. J. E.

Realgar from Komana (Albania). C. LAURO (Rend. Sem. Fac. Sci. Cagliari, 1933, 3, 147—148; Chem. Zentr., 1935, i, 872).—Five new cryst. forms are described. H. J. E.

New mineral from Langban (sahlinite). G. AMINOFF (Geol. Foren. Stockholm, 1934, 56, 493—494; Chem. Zentr., 1935, i, 872).—A sulphur-yellow mineral of the formula $12\text{PbO} \cdot \text{As}_2\text{O}_5 \cdot 2\text{PbCl}_2$ is

described. It has a very high μ , hardness 2—3, and d 7.95. H. J. E.

Determination of direct and inverse forms in pyrites. E. ONORATO (Rend. Sem. Fac. Sci. Cagliari, 1933, 3, 145—146; Chem. Zentr., 1935, i, 848).—X-Ray analysis of the two forms of pyrites of different thermoelectric behaviour shows both to be direct forms. H. J. E.

Quantities of radioactive materials from radium and thorium emanations in air of Santa Fe. F. E. URONDO (An. Soc. cient. Santa Fe, 1933, 5, 48—53; Chem. Zentr., 1935, i, 1032).—Results are given over a period of four months. J. S. A.

Stochastic relations in argillaceous sediments. F. E. KLINGNER (Neues Jahrb. Min., 1934, 69, A, 5—41; Chem. Zentr., 1935, i, 1031).—Stochastic=derived from theory of probability. A correlation between CaCO_3 content and p_H of the suspension is derived. Rise of p_H with fall in CaCO_3 indicates maritime deposits from saline waters. The method is applied to the deduction of the p_H etc. of seas of geological age. J. S. A.

Microscopical investigation of Friedensville, Pennsylvania, zinc ore. D. M. FRASER (Amer. Min., 1935, 20, 451—461).—The microscopical features of the primary minerals, sphalerite (I) and pyrite and some greenockite (II), the secondary minerals calamine [$\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$], and some smithsonite and (I) are described. Associated minerals in the oxidised ore are limonite, (II), quartz, calcite, dolomite, melanterite, and probably goslarite. Conditions of primary replacement are discussed. L. S. T.

Copper ores of Orange County, Vermont. N. W. BUERGER (Econ. Geol., 1935, 30, 434—443).—The ores from this Cu district represent a deposit of high-temp. type. The silicate minerals of the ore and wall rock are similar to those in the country rock. The most abundant are quartz, microcline, oligoclase-andesine, calcite, phlogopite, muscovite, and garnet. Pyrrhotite (I) is the principal ore mineral occurring intimately associated with chalcopyrite (II). The Cu content ~ 0.3 —20%. Pyrite was the first mineral to be deposited, followed by (I), (II), and sphalerite. Cubanite, valleriite, galena, and haematite are also present. The deposit is similar in many respects to those of Ducktown, Tennessee. L. S. T.

Variations in optical properties with chemical composition in the monoclinic pyroxenes. T. TOMITA (J. Shanghai Sci. Inst., II, 1934, 1, 41—58).—Data from the lit. are tabulated and plotted on triangular diagrams CaSiO_3 — MgSiO_3 — FeSiO_3 . The diagrams do not apply to pyroxenes containing >2.5 mol.-% R_2O_3 and >1 mol.-% TiO_2 . L. J. S.

Artificial transformation of feldspars into pyrophyllite. R. SCHWARZ and G. TRAGESER (Naturwiss., 1935, 23, 512; cf. A., 1934, 42).—Pyrophyllite has been synthesised by treatment of orthoclase or anorthite with 0.5N-HCl under pressure in a steel bomb, at temp. $>400^\circ$. A. J. M.

Milowite. An unusual form of silica. J. N. WILSON (Chem. Trade J., 1935, 97, No. 2512, 28).—The composition and physical properties of milowite,

an unusually soft form of SiO_2 occurring naturally in Milos, are given. It is suitable for use as an abrasive, as a filler for paints and rubber, a base for lake pigments, and a constituent of ceramic glazes.

D. R. D.

Composition of some African granitoid rocks. F. F. GROUT (J. Geol., 1935, 43, 281—296).—Analyses and brief petrographic notes are given for 21 large intrusives from the African Shield. They indicate that Central Africa is largely granite and is not abnormal in composition as indicated by analyses of alkalic and basic rocks near the coasts. Analyses of granites from Northern and Southern Rhodesia, the Transvaal, and the southern part of the Union of South Africa are tabulated and classified. L. S. T.

Silver mine of Colquijirca, Peru. W. LINDGREN (Econ. Geol., 1935, 30, 331—346).—The mineralisation is of the epithermal type and was probably effected at temp. gradually falling from 250° to approx. 100° . High-temp. minerals are absent. The shale has been replaced by chalcedonic SiO_2 giving a brown chert. Other early gangue minerals are kaolin, dolomite, and ankerite. Barite is a later and abundant gangue especially in the Cu-Ag ores. Pyrite, poor in Ag, is the earliest metallic mineral and is followed by sphalerite, enargite, tennantite (I), galena, and chalcopyrite. Bi minerals follow (I). Hypogene stromeyerite follows and with supergene native Ag is the principal mineral in the rich argentiferous ores. Argentite and chalcocite are not abundant. Analyses of wittichenite, stromeyerite, and tennantite are recorded. L. S. T.

Structural features of gold deposits in certain intrusives of Western Quebec. L. V. BELL and A. M. BELL (Econ. Geol., 1935, 30, 347—369).—The well-defined structural features which characterise the Au deposits in the plutonic rocks of the eastern part of the Abitibi Belt of Western Quebec are described. L. S. T.

Influence of tertiary intrusive structural features on mineral deposits at Jamestown, Colorado. E. N. GODDARD (Econ. Geol., 1935, 30, 370—386).—The general geology, the structure, and the mineral deposits of fluor spar, Pb-Ag, pyritic Au and Au-Te veins are described. The structural relations of the mineral deposits to tertiary intrusives are discussed. L. S. T.

Petrography of the Roy, Harding County, New Mexico, meteorite. R. E. S. HEINEMAN (Amer. Min., 1935, 20, 438—442).—The Roy aerolite is a cryst. chondrite; the chondrules are the chrysolite, bronzite, and porphyritic types. The ground-mass silicate is mainly chrysolite. Irregular grains of a Ni-Fe alloy of const. composition showing alteration to and replacement by oxidation products are present together with considerable troilite. The trias could not be distinguished. Analysis of the stone gives SiO_2 36.95, Al_2O_3 2.92, Fe_2O_3 13.29, FeO 12.57, MgO 23.10, CaO 2.50, Na_2O 0.26, K_2O 0.06, TiO_2 0.12, P_2O_5 0.31, SO_2 0.69, MnO 0.16, NiO 1.27, CoO 0.14, CuO 0.10, Cr_2O_3 0.43, FeS 3.58, loss on ignition 1.88, total 100.33%. L. S. T.

New Hampshire garnet deposits. L. C. CONANT (Econ. Geol., 1935, 30, 387—399).—The associated rocks, the petrology, paragenesis, physical and chemical properties of the garnets, the deposits and their origin are described. Garnet from Wilmot, New Hampshire, has SiO_2 37.35, Al_2O_3 20.36, Fe_2O_3 2.27, FeO 31.36, MgO 2.22, CaO 2.55, $\text{Na}_2\text{O} + \text{K}_2\text{O}$ 1.69, $\text{H}_2\text{O} + 0.16$, $\text{H}_2\text{O} - 0.04$, P_2O_5 0.59, TiO_2 0.79, MnO 1.18, S 0.36, NiO 0.01, and CuO 0.05, total 100.98%. The garnet rock is probably the result of contact metamorphic alteration of certain Fe- and Al-rich portions of sedimentary rocks which had been previously dynamically metamorphosed. The schists have been impregnated by igneous material and the garnet has developed subsequent to the formation of the biotite and sillimanite with which, together with quartz, magnetite, and minor amounts of feldspar, zircon, and rutile, it is associated.

L. S. T.

Tektites without figured shapes from Indo-China. A. LACROIX (Compt. rend., 1935, 200, 2129—2132).—Specimens are described. H. J. E.

Origin of tektites. F. WATSON, jun. (Nature, 1935, 136, 105—106; cf. A., 1933, 1268).—Theories dealing with the origin of tektites are critically discussed. No satisfactory meteoritic theory of their origin has yet been advanced. L. S. T.

Mourne Dyke Swarm. S. I. TOMKEIEFF and C. E. MARSHALL (Quart. J. Geol. Soc., 1935, 91, 251—292).—The petrology of the intrusions, petrogenesis, and igneous sequence are described. The mineral compositions of basic and intermediate rocks of this region are tabulated. Chemical analyses are recorded. L. S. T.

Charnockite series of Uganda. A. W. GROVES (Quart. J. Geol. Soc., 1935, 91, 150—207).—Distribution, mode of occurrence, distinguishing features, and the constituent minerals, quartz, potash feldspar, plagioclase, pyroxenes, amphiboles, biotite, and garnet, are described. Chemical and micrometric analyses of the principal types are recorded. Geochemical characters are summarised and compared with the geochemistry of similar rocks from India and Ceylon. The variation diagram is discussed. Modifications due to dynamic metamorphism are described, the mineralogical changes being classified into (i) amphibolisation of pyroxenes, (ii) conversion

of hypersthene into garnet, and (iii) formation of reaction rims and kelyphitic borders. Petrogenesis and age are discussed, and a comparison with similar rocks in other parts of Africa is made.

L. S. T.

Dispersion of the double refraction of a muscovite. J. P. MATHIEU (Bull. Soc. Franç. Min., 1934, 57, 233—240; Chem. Zentr., 1935, i, 1194).—Vals. are recorded. H. J. E.

Generative metamorphism of folds. R. PERLIN (Compt. rend., 1935, 200, 1951—1952).—A discussion. H. J. E.

Constitution of senonian phosphates from Egypt. L. CAYEUX (Compt. rend., 1935, 200, 2134—2137).—A general description. H. J. E.

Constitution of senonian phosphates from Palestine and Transjordan. L. CAYEUX (Compt. rend., 1935, 200, 1893—1896).—A review and discussion of the chief characteristics of the deposits, compared with those of similar deposits in Syria. H. J. E.

Geochemical frequency of strontium. C. J. VAN NIEUWENBERG and R. H. DEWALD (Rec. trav. chim., 1935, 54, 633—638).—According to existing data the geochemical frequency of Ba is approx. the same as that of Sr, whereas in most other groups it falls markedly with increasing at. no. To test whether this is due to analytical underestimation of Sr, two independent methods of determining small amounts of Sr in presence of excess of Ca were worked out: (a) 1 c.c. of the solution was evaporated to dryness in a Pyrex tube with capillary end, taken up in 1 c.c. of HNO_3 , d 1.40, and centrifuged until the height in the capillary tube was const. The apparatus was previously calibrated with known amounts of Ca and Sr. (b) A fulgurator was devised enabling the spark spectra of solutions of 15% $\text{Ca}(\text{NO}_3)_2$ containing known amounts of Sr to be taken on the same plate as the unknown solution, the Sr content being evaluated by direct comparison. Samples of five different rocks were tested and the vals. for each rock by the two methods agreed well, but varied from one rock to another between 1 and 6 atoms Sr per 1000 atoms Ca. Since these are close to the accepted average val. for all rocks (3—4) it would appear that the above-mentioned anomaly is not due to analytical underestimation of the Sr content of the earth.

S. J. G.

Organic Chemistry.

Chlorination of propane. I. Homogeneous reaction.—See this vol., 1082.

Isomerisation of hydrocarbons. I. Chlorination of isomerides of hexane and octane by means of antimony pentachloride, as a method for their determination. B. L. MOLDAVSKI and S. E. LIVSCHITZ (J. Gen. Chem. Russ., 1935, 5, 422—431).—0.25 ml. of a 5—10% solution of isoparaffin in $n\text{-C}_6\text{H}_{14}$ or $n\text{-C}_8\text{H}_{18}$ are diluted to 15—25 ml. with 0.5N-SbCl₅ in CHCl_3 , and SbCl₅ formed is titrated after 2 hr. (in 3 ml. of solution) with 0.1N-KBrO₃.

0.5 ml. of the mixture under analysis is treated similarly, when the content of isohydrocarbons is given by $acef/bdg$, where a and b are the vols. of 0.1N-KBrO₃ used for titration of the unknown and known solutions, respectively, c and d are the vols. of 0.5N-SbCl₅ added to the corresponding solutions, e and f are the % content (by wt.) and the no. of ml. of isohydrocarbon in the known mixture, and g is the vol. of unknown solution taken. The solutions should be completely H_2O -free. Induction of chlorination of n -paraffins is not observed under the above conditions.

R. T.

Ozone as an oxidising catalyst. VIII. Ozonation of propane and butane. E. BRINER and J. CARCELLER (Helv. Chim. Acta, 1935, 18, 973—981).—Appreciable oxidation of a mixture of *n*- and *iso*-C₄H₁₀ occurs with ozonised O₂ at 20°, yielding CH₂O and HCO₂H. At temp. up to 330° the oxidation of the mixture and of C₃H₈ proceeds more rapidly in presence of O₃. The excess of oxidation due to the O₃ is > the amount of O₃ consumed (cf. A., 1933, 680). F. R. G.

Oxidation of unsaturated hydrocarbons by peracetic acid. J. BÖESEKEN [with VAN ASPEREN, C. AUCHY, C. MATERS, and P. OTTENHOFF] (Rec. trav. chim., 1935, 44, 657—665).—Δ^α-Heptene is much more slowly oxidised by AcO₂H than are Δ^γ-heptene or β-methyl-Δ^α-hexene, thus confirming the view that oxidation occurs most rapidly when alkyl groups are adjacent to the double linking. Diallyl is relatively slowly oxidised. The first O atom is very rapidly absorbed by isoprene in comparison with the second atom. The product of the action of O is mainly a monoacetate, reduced and hydrolysed to β-methylbutane-αβ-diol, which gives a CMe₂ ether, b.p. 135°, and a Hg compound with HgSO₄-H₂SO₄. β-Methyl-Δ^{βγ}-butadiene yields mainly a diol monoacetate, which, after hydrolysis, is converted into γ-keto-β-hydroxy-β-methylbutane, decomposed into CHBr₃ and OH·CMe₂·CO₂H. H. W.

Mechanism of the nitration process. A. MICHAEL and G. H. CARLSON (J. Amer. Chem. Soc., 1935, 57, 1268—1276).—Additive compounds are not formed when C₂H₄, CPh₂·CH₂ (I), Δ^α-butene, and cyclohexene are treated with 98.6% HNO₃ (II) at -30° to 0° usually in presence of CH₂Cl₂, CHCl₃, or CCl₄. CMe₂·CHMe and (II) or abs. HNO₃ at -20° give *tert*-amyl nitrate [also formed from *tert*-amyl alcohol and (II)]; similarly, (II) and CMe₂·CH₂ afford Bu^γO·NO, [also obtained from Bu^γOH and (II)]. (I) is polymerised by (II) at 0°; the same polymeride is also obtained from CPh₂Me·OH and (II) (2 equivs.). Phenanthrene and (II) at -20° give NO₂-derivatives and about 25% of an additive product (constitution not proved). The formation of nitroalkenes and nitroalkyl nitrates from alkenes (III) and HNO₃ (cf. Wieland *et al.*, A., 1920, i, 280; 1921, i, 782) is due to the reaction of (III) with nitrous gases formed during side reactions. Wieland's views (*loc. cit.*) on the addition of HNO₃ (as OH+NO₂) and H₂SO₄ (as OH+SO₃H) to (III) and the mechanism of the nitration of C₆H₆ are criticised and held to be untenable. The view (cf. A., 1896, i, 593; 1902, i, 69; 1904, ii, 164) that aromatic nitration proceeds primarily by aldolisation is revived; various data supporting this process are given. H. B.

Influence of substituents on the additive reactivity of ethylene derivatives. II. Effects of catalysis on the relative rates of addition of bromine. S. V. ANANTAKRISHNAN and C. K. INGOLD (J.C.S., 1935, 984—987; cf. A., 1931, 1267).—The previous results and new data are considered in relation to the catalytic effect of HBr on the addition of Br in competition experiments to CR₂·CHR' (R=H, Me, Ph) and shown to be consistent with theory. F. R. G.

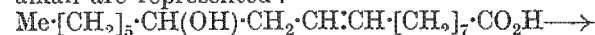
Polymerisation of ethylene induced by methyl radicals.—See this vol., 1084.

Pyrogenetic reactions of condensation of hydrocarbons. II—IV.—See this vol., 1081.

Catalytic decomposition of alkyl bromides. J. B. SENDERENS (Compt. rend., 1935, 200, 2137—2139).—HBr is removed from Bu^βBr by ThO₂ at 260°, from Bu^αBr by ThO₂ or Al₂O₃ at 280—300°, from Pr^αBr by Al₂O₃ at 250—270°, by ThO₂ at 235—255°, and by kaolin at 260—280°, from Pr^βBr by Al₂O₃ at 220—240° or ThO₂ at 180—210°, and from EtBr by ThO₂ at 215—230°. C₄H₈ is obtainable only with difficulty from Bu^βBr and not at all from Bu^αBr owing to recombination with the HBr liberated. EtI and ThO₂ react at about 240° to give complex products. Bromides react only at higher temp. than do the corresponding chlorides. The catalysts do not react with the liberated acids. R. S. C.

Analysis of mixtures of monochlorides of *n*- and *iso*-pentane. H. B. HASS and P. WEBER (Ind. Eng. Chem. [Anal.], 1935, 7, 231—233).—The mixture of α- (I), β- (II), γ- (III), and 8-chloro-β-methylbutane (IV) obtained by the chlorination of CHMe₂Et (V), is separated from polychlorides and unchanged (V) by fractional distillation. (II) is determined by aq. hydrolysis below 35°, and (III) by treatment with 0.1N-AgNO₃ during 60 hr. (methods: Whitmore and Johnstone, A., 1934, 168). The remaining mixture of (I) and (IV) is characterised (after redistilling) by an adaptation of Conant and Kirner's method (A., 1924, i, 273) for determination of velocity coeffs. with COMe₂-KI at 60°. By fractional distillation of the chlorination products of *n*-C₅H₁₂, α-, b.p. 108.2°/760 mm., is separated quantitatively from the mixture of β- and γ-chloropentanes, analysis of which is effected by thermal examination of the resultant mixed anilides (cf. A., 1934, 753). The prep. of (I), b.p. 99.8—100°/760 mm., and (IV), b.p. 98.7—98.9°/760 mm., is described. F. N. W.

Existence of β-epoxy-tautomerism in degradative reactions of organic compounds. A. BARBOR (Bull. Soc. chim., 1935, [v], 2, 1438—1452).—The degradation of numerous org. compounds can be regarded from a homogeneous viewpoint if the formation of intermediate αγ-oxides is assumed. Thus the scissions of ricinoleic acid by heat and alkali are represented:



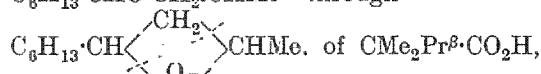
$\text{Me} \cdot [\text{CH}_2]_5 \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH} \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$, with fission represented by the dotted lines. At 450°/atm.

pressure, $\text{CH}_2 \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$ gives C₂H₄ and CH₂O

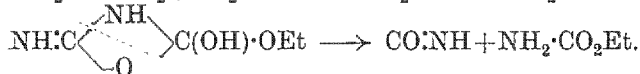
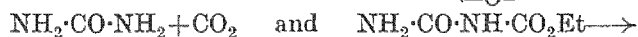
and $\text{CET}_2 \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$ affords CET₂·CH₂ and CH₂O.

The degradation of αγ-glycols by dil. H₂SO₄ at 130—180° is represented $\text{OH} \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \longrightarrow$
 $\text{CHR} \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$ [and $\text{CH}_2 \begin{array}{c} \diagup \text{CHR} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$]
 whence CH₂R·CH₂·CHO and R·COEt; thus

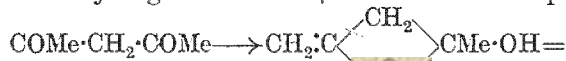
$\text{OH} \cdot [\text{CH}_2]_3 \cdot \text{OH}$ affords EtCHO when passed over pumice at 500° and $\text{OH} \cdot [\text{CMe}_2]_3 \cdot \text{OH}$ gives COMe_2 and $\text{CMe}_2 \cdot \text{CMe}_2$. The degradation of β -ethylenic alcohols is similarly explained. Scission in two directions as indicated by the author's hypothesis is illustrated by the decomp. of $\text{C}_6\text{H}_{13} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$ at 500° into $\text{C}_6\text{H}_{13} \cdot \text{CH} \cdot \text{CH}_2 + \text{MeCHO}$ and $\text{C}_6\text{H}_{13} \cdot \text{CHO} \cdot \text{CH}_2 \cdot \text{CHMe}$ through



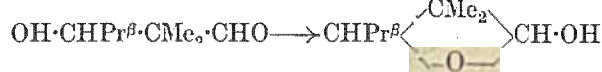
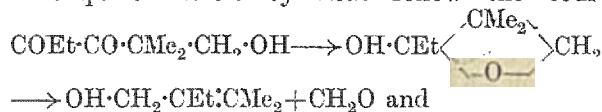
$\text{OH} \cdot \text{CHEt} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, $\text{OH} \cdot \text{CHMe} \cdot \text{CMePr} \cdot \text{CO}_2\text{H}$, $\text{OH} \cdot \text{CHMe} \cdot \text{CET}_2 \cdot \text{CO}_2\text{H}$, hexahydrosalicylic acid, and $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$. The same considerations apply to β -ketonic acids and esters and to allophanic acid,



The hydrogenation of β -diketones is explained,



$\text{CH}_2 \cdot \text{CO} (\longrightarrow \text{MeCHO}) + \text{CH}_2 \cdot \text{CMe} \cdot \text{OH} (\longrightarrow \text{CHMe}_2 \cdot \text{OH})$, and a similar mechanism is involved in their fission by alkali. Scission of β -OH-ketones by alkali and decomp. of aldols by heat follow the courses,



$\longrightarrow \text{Pr}^\alpha \text{CHO}$. If the mol. contains several functions which can react among themselves with the formation of a β -epoxy-ring under conditions under which it is unstable it is shown by a series of examples that the expected products of scission are obtained.

H. W.

Heterogeneous catalysis. IV. Dehydrogenation and hydrogenation of ethyl alcohol. V. Decomposition of formic acid.—See this vol., 1086.

Dehydration of ethyl alcohol by mixed catalysts. Z. E. KOSOLAPOV (J. Gen. Chem. Russ., 1935, 5, 307—318).—Dehydration of EtOH at 286 — 368° in presence of Al_2O_3 , $\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$, $-\text{CaO}$, and $-\text{Fe}_2\text{O}_3$ leads to production of C_2H_4 , C_2H_6 , CH_4 , CH_2O , and MeCHO thus: $2\text{C}_2\text{H}_5\text{CHMe} \cdot \text{CHMe} + 2\text{EtOH} \rightarrow \text{CHMeEt} \cdot \text{OH} \rightarrow \text{MeCHO} + \text{C}_2\text{H}_6$; $\text{EtOH} \rightarrow \text{CH}_4 + \text{CH}_2\text{O}$.

R. T.

Synthesis and constitution of a dimethylhexitol. J. WIEMANN (Compt. rend., 1935, 200, 2021—2023; cf. this vol., 605).—Oxidation of Δ^8 -octadiene- δ -diol (cf. A., 1934, 277) gives a dimethylhexitol (I), m.p. 161 — 162° (dibenzacetal, m.p. 237 — 238° ; Ac_6 derivative, m.p. 108°). A stereochemical formula is suggested. J. L. D.

Oils from marine animals. New group of lipins. Ether-esters of glycerol.—See this vol., 1145.

Preparation of mixed formals by direct acetalisation. H. WUYTS and P. DOCQUIER (Bull. Soc. chim. Belg., 1935, 44, 297—306).— ROH heated with $\text{R}'\text{OH}$ (1 mol.) (R , $\text{R}' = \text{alkyl}$), CH_2O (1 mol.), and 0.5% of H_2SO_4 gives $\text{OR} \cdot \text{CH}_2 \cdot \text{OR}'$, $\text{CH}_2(\text{OR})_2$, $\text{CH}_2(\text{OR}')_2$, and H_2O . The mixed formal is separated from the other products by fractional distillation with CS_2 . $\text{OMe} \cdot \text{CH}_2 \cdot \text{OEt}$ and $\text{OEt} \cdot \text{CH}_2 \cdot \text{OPr}^\alpha$ were obtained in this way. The b.p. and d of these compounds, and the d and b.p. of their azeotropic mixtures with other products of the reaction, are recorded.

F. R. G.

Constitution of benzylidene- d -sorbitol. II. p -Toluenesulphonyl and anhydro-derivatives of d -sorbitol. L. VON VARGHA (Ber., 1935, 68, [B], 1377—1384; cf. this vol., 325).—Treatment of benzylidene- d -sorbitol (I) with 1 mol. of acyl chloride gives mixtures of at least 3 compounds, whereas by use of 2 mols. of BzCl a compound (II), m.p. 172° , $[\alpha]_D^{20} -10.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$, is smoothly obtained. This is hydrolysed by 50% AcOH to d -sorbitol α -dibenzoate (III), m.p. 141° , $[\alpha]_D^{20} +1.54^\circ$ in $\text{C}_5\text{H}_5\text{N}$. The possibility of acyl migration during hydrolysis is excluded, since (II) and (III) give the same d -benzylidene- d -sorbitol α -dibenzoate, m.p. 208° , $[\alpha]_D^{20} -1.9^\circ$ in CHCl_3 , when treated with ZnCl_2 and PhCHO . Further the presence of 2 primary OH in (I) is established by the ready formation of α - ζ -triphenylmethylbenzylidene- d -sorbitol diacetate, m.p. (indef.) 112° , $[\alpha]_D^{20} +21.3^\circ$ in CHCl_3 . Since (II) and benzylidene- d -sorbitol α - ζ - p -toluenesulphonate (IV), m.p. 148° , $[\alpha]_D^{20} +17.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$, are indifferent towards $\text{Pb}(\text{OAc})_4$, vicinal OH are not present. (I) is therefore β -benzylidene- d -sorbitol instead of the α - γ -compound as described previously; the nomenclature of the derivatives (*loc. cit.*) requires corresponding alteration. The p - $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2$ groups of (IV) are readily removed by $\text{NaOH} \cdot \text{EtOH}$, but several anhydro-compounds appear to be produced, one of which is readily isolated as its *Et ether*, m.p. 75° . (IV) in CHCl_3 with $\text{NaOMe} \cdot \text{MeOH}$ affords β -benzylidene- ϵ - ζ -anhydro- d -sorbitol α - p -toluenesulphonate, m.p. 137° , $[\alpha]_D^{20} +4.0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, converted by $\text{NaOMe} \cdot \text{MeOH}$ at 15 — 20° into β -benzylidene- ζ -methyl- d -sorbitol α - p -toluenesulphonate, m.p. 128° , $[\alpha]_D^{20} -1.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and by 50% AcOH at 100° into β -anhydrohexitol α - p -toluenesulphonate, m.p. 146° , $[\alpha]_D^{20} +3.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (non-cryst. CPh_3 derivative, $[\alpha]_D^{20} +16.3^\circ$ in $\text{C}_5\text{H}_5\text{N}$).

H. W.

Polymerisation and ring-formation. XXVII. Polydecamethylene oxide. J. W. HILL (J. Amer. Chem. Soc., 1935, 57, 1131—1132; cf. this vol., 844).—Depolymerisation of decamethylene carbonate sometimes (? when the pressure rises too high) gives much rubbery non-volatile material (I) and some Δ^4 -decen- α -ol (II). Hydrolysis of (I) gives a little $\text{OH} \cdot [\text{CH}_2]_{10} \cdot \text{OH}$ and much linear polydecamethylene oxide, m.p. 58 — 60° , the structure of which is proved by conversion by HI into $\text{I} \cdot [\text{CH}_2]_{10} \cdot \text{I}$; the oxide is probably formed by way of (II).

R. S. C.

β -Chloro-derivatives of esters of oxy-acids of sulphur. A. SPORZYŃSKI (Arch. Chem. Farm., 1935, 2, 243—247).— SOCl_2 and $\text{CCl}_3 \cdot \text{CH}_2 \cdot \text{OH}$ (I) afford $(\text{CCl}_3 \cdot \text{CH}_2 \cdot \text{O})_2\text{SO}$, m.p. 6 — 7° , b.p. 133 — $139^\circ/5 \text{ mm.}$

oxidised by KMnO_4 in COMe_2 to the sulphate, $(\text{CCl}_3\cdot\text{CH}_2\cdot\text{O})_2\text{SO}_2$, m.p. 118.5—119.5°, also prepared from (I) and SO_2Cl_2 in $\text{C}_5\text{H}_5\text{N}$ at 100°. $(\text{CBr}_3\cdot\text{CH}_2\cdot\text{O})_2\text{SO}$, m.p. 81—81.5°, is prepared analogously. R. T.

Alkyl- and aryl-sulphinic esters. P. CARRE and D. LIBERMANN (Compt. rend., 1935, 200, 2086—2089).— ClSO_2Et (I) (1 mol.) (cf. A., 1934, 48, 696) in dry Et_2O (3 mols.) at 0° with MgEtCl (1.2 mols.) gives *Et ethylsulphinic*, b.p. 60°/18 mm. The following are prepared similarly and are stable in air (cf. A., 1931, 64): *Buⁿ ethylsulphinic*, b.p. 90—92°/13 mm.; *Et propylsulphinic*, b.p. 69—71°/13 mm.; *Et*, b.p. 89—91°/18 mm., and *Buⁿ*, b.p. 112°/13 mm., *n-butylsulphinic*; *Buⁿ n-octylsulphinic*, b.p. 167—172° (partial decomp.). (I) in dry Et_2O with MgPhBr affords *Et phenylsulphinic* which decomposes when heated, and with excess of MgPhBr gives mainly SOPh_2 , but also Ph_2S and PhCl . The reaction mechanisms are discussed. J. L. D.

Isomerides of the butadienesulphones. H. J. BACKER and J. STRATING (Rec. trav. chim., 1935, 44, 618—621).—The isomerisation of the sulphones of β -alkylbutadienes in alkaline solution under the influence of ultra-violet light consists in a displacement of the double linking in the ring towards the alkyl. The isomeric sulphone of isoprene is ozonised to γ -keto-*n*-butylsulphonic acid (*Ba* salt). *tert*-Butylbutadiene-sulphone is isomerised to the compound,

$\text{SO}_2\text{C} \begin{array}{c} \text{CH}_2\text{CH}_2 \\ \text{CH}=\text{CBu}^n \end{array}$, m.p. 96—97°, ozonised to γ -keto- $\delta\delta$ -dimethyl-*n*-amylsulphonic acid [*Ba* (+2H₂O) salt]. H. W.

Volumetric determination of sodium glycerophosphate: calcium glycerophosphate. S. BABITSCH (Z. anal. Chem., 1935, 101, 398—401).—Na glycerophosphate may be determined by boiling the solution with an excess of 0.5*N*- $\text{Pb}(\text{NO}_3)_2$, removing the pptd. Pb salt, and titrating the excess of $\text{Pb}(\text{NO}_3)_2$ with 0.1*N*- Na_2CO_3 (phenolphthalein). Na cacodylate does not interfere, since it gives no ppt. with Pb salts. Ca glycerophosphate gives low results by the Pb method and low results for Ca by the oxalate- KMnO_4 method, indicating that part of the Ca exists as an internal complex; good results are, however, obtained acidimetrically. A. R. P.

Dehalogenation of $\alpha\beta$ -dibromo-acids. II. Influence of acid structure on yields of bromo-olefines. J. K. FARRELL and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 1281—1283).—The yields of $\text{CR}'\text{R}''\text{CBrR}'''$ from $\text{CBrR}'\text{R}''\text{CBrR}'''\cdot\text{CO}_2\text{H}$ and aq. $\text{C}_5\text{H}_5\text{N}$ or Na_2CO_3 (cf. A., 1933, 1275) vary from 0 (when $\text{R}'=\text{R}''=\text{R}'''=\text{H}$) to 70—90% (when $\text{R}'=\text{R}''$ or $\text{R}'''=\text{Alk}$); when R' or $\text{R}'''=\text{Alk}$ (variation of which has little effect), the yield is usually about 30%. $\text{CR}'\text{R}''\text{CBr}_2$ are similarly obtained in yields of 70—90% ($\text{R}'=\text{R}''=\text{Alk}$ or $\text{R}'=\text{Alk}$ and $\text{R}''=\text{H}$); when $\text{R}'=\text{R}''=\text{H}$, the yield is 30%. The following are new: α -bromo- γ -methyl- Δ^{α} -butene, b.p. 99—101°; β -, b.p. 108—110°, and γ -, b.p. 110—111°, -bromo- Δ^{β} -pentene; $\alpha\alpha$ -dibromo- β -methyl- Δ^{α} -propene, b.p. 156—157°; $\alpha\alpha$ -dibromo- γ -methyl- Δ^{α} -butene, b.p. 159—160°; α -bromo- Δ^{α} -isohexenoic acid, b.p. 152°/23 mm., m.p. 80.5°, converted with difficulty into $\alpha\alpha\beta$ -tribromoiso-

hexoic acid; $\alpha\alpha\beta$ -tribromo- β -methylbutyric acid, decomp. 230°. $\alpha\beta$ -Dibromo- $\alpha\beta$ -dimethylbutyric acid has m.p. 222° (corr.; decomp.) (lit. 190—191°). H. B.

Relative mobilities of *n*-alkyl radicals from C_1 to C_{16} in their chloroformates. P. CARRE and H. PASSEDOUET (Compt. rend., 1935, 200, 1767—1769; cf. this vol., 606).—The decomp. temp. of ClCO_2R into RCl and CO_2 in presence of quinoline ($\text{R}=\text{n-alkyl}$, $\text{C}_1\text{—C}_{16}$) shows an alternation effect with the no. of C in the radical for $\text{C}>7$. The results are compared with those for $\text{ClSO}_2\text{R}=\text{RCl}+\text{SO}_2$, and are discussed in terms of the mobility of the radicals. H. J. E.

Electrolysis of nitrate-acetate mixtures. F. FICHTER and F. METZ (Helv. Chim. Acta, 1935, 18, 1005—1007; cf. this vol., 472).—By electrolysis a solution containing NaOAc (3.7*N*), NaNO_3 (1.4*N*), and AcOH (3.2*N*) with c.d. 0.130 amp. per sq. cm. at the Pt anode, 1.8 c.c. of an oil, mainly MeNO_3 and MeNO_2 , was obtained during the passage of 14 amp.-hr.

F. R. G.

Action of sodium ethoxide on γ -halogenocrotonic esters. R. RAMBAUD (Compt. rend., 1935, 200, 2089—2091).— $\text{CH}_2\text{Cl}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ with NaOEt in $\text{EtOH-Et}_2\text{O}$ or in C_6H_6 gives *Et γ -chloro- β -ethoxybutyrate*, b.p. 108—108.5°/20 mm., hydrolysed to β -ethoxy- γ -butyrolactone, b.p. 131.5°/20 mm. Et and Me γ -bromocrotonate when similarly treated give *Et*, b.p. 82°/18 mm. (cf. A., 1905, i, 406), and *Me 2-ethoxycyclopropanecarboxylate*, b.p. 61—62°/16 mm., respectively, which react with Br and KMnO_4 , but not with H_2 or O_3 . J. L. D.

Highly unsaturated acids of the kernels of *Parinarium laurinum*.—See this vol., 1141.

Highly unsaturated acids in sardine oil. III. Isolation and constitution of moroctic acid, $\text{C}_{18}\text{H}_{28}\text{O}_2$. IV. Separation of highly unsaturated C_{20} -acids. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 232—241, 241—248; cf. this vol., 960).—III. The $\text{C}_{18}\text{H}_{28}\text{O}_2$ acid of sardine oil called moroctic acid (I) is separated from hiragonic acid by the insolubility of the bromide of its Me ester in C_6H_6 ; this was debrominated (Zn, EtOH , HCl), saponified to remove unsaponifiable substance, hydrolysed (HCl), and esterified to give *Me moroctate*, $\text{C}_{18}\text{H}_{28}\text{O}_2$, b.p. 208—213°/15 mm. (octabromide, m.p. 215°), ozonolysed to EtCO_2H , EtCHO , succinic acid and semialdehyde and their Me esters, CO_2 , AcOH , MeCHO , and $\text{CH}_2(\text{CO}_2\text{H})_2$. (II) with $(\text{CNS})_2$ in AcOH gives *Me tetrathiocyanomoroctate*, obtained as its solution in CHCl_3 , ozonolysis of which yields EtCO_2H , EtCHO , CO_2 , AcOH , MeCHO , and an oily CNS-compound which with Zn- EtOH-HCl and subsequent hydrolysis yields Δ^7 -decadiene- $\alpha\kappa$ -dicarboxylic acid, hydrogenated to decane- $\alpha\kappa$ -dicarboxylic acid; hence (I) is $\Delta^{7/12}$ -octadecatetraenoic acid.

IV. The Et ester fraction, b.p. > 215°/10 mm., from sardine oil was converted into Na soap and the COMe_2 -sol. portion successively hydrolysed and esterified; the Me esters were fractionally distilled and the corresponding Na soaps fractionally pptd. from COMe_2 . An eicosatetraenoic acid, $\text{C}_{20}\text{H}_{32}\text{O}_2$ (octabromide, blackens 240°; Me ester, b.p. 217—220°/10 mm.), and an impure eicosapentenoic acid, $\text{C}_{20}\text{H}_{30}\text{O}_2$ (decabromide,

blackens 240°), were obtained and the acid $C_{20}H_{34}O_2$ may be present. F. R. G.

Oxidation of fatty acids *in vitro*, with especial reference to that of β -hydroxybutyric and acetoacetic acids. R. O. JONES and I. S. MACLEAN (Biochem. J., 1935, 29, 1690—1701).—The fatty acid is heated with H_2O_2 and acid with or without $CuSO_4$ as catalyst, and the amounts of H_2O_2 and acid to be added at intervals to maintain the initial $[H_2O_2]$ and $[H^+]$ are determined. From the curves of H_2O_2 and H^+ added against time it is deduced that $CuSO_4$ increases oxidation; β -hydroxybutyric acid (I) is more readily oxidised than $CH_3Ac\cdot CO_2H$; lactic acid and (I) may be first oxidised to $MeCHO$ and fatty acid. The oxidation of glucose is inhibited by Na salts of fatty acids; glucose does not favour the decomp. of fatty acids. H. D.

Intermediate product of long life between iodine and oxalate ion.—See this vol., 1090.

Reaction between ethyl oxalate and ethylene-diamine. W. GAARDE (Chem. Weekblad, 1935, 32, 347—348).—When $Et_2C_2O_4$ and $(CH_2\cdot NH_2)_2$ react the tendency is to form long-chain compounds and not ring systems. 2 mols. of $Et_2C_2O_4$ and 1 mol. of $(CH_2\cdot NH_2)_2$ give *Et*₂ ethylene- $\alpha\beta$ -dioxamate, m.p. 129°, and Hofmann's "ethyleneoxamide," which is $(\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CO_2Et)_2$. By interaction of $Et_2C_2O_4$ and $(CH_2\cdot NH_2)_2$ under different conditions esters or amines are formed by the successive condensation of $\cdot CO\cdot CO\cdot$ groups (A) and $\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot$ groups (B) in long chains; the following are described: *di-esters* A : B = 4 : 3, m.p. 345°; A : B = 3 : 2, m.p. about 400°; *diamines* A : B = 1 : 2 (carbonate, m.p. 375°); A : B = 2 : 3 [carbonate, m.p. 300° (decomp.)]. S. C.

Dehydrogenation of succinic acid by charcoal. Model of the mode of reaction of succinodehydrase.—See this vol., 940.

Ethyl acetone-*d*-tartrate and its optical activity. V. TSUZUKI (Bull. Chem. Soc. Japan, 1935, 10, 255—256).—Et tartrate in $COMe_2$ heated with anhyd. $CuSO_4$ gives *Et*₂ d-isopropylidenedioxysuccinate, b.p. 150° (corr.)/19 mm., $[\alpha]_D^{25} -51.19^\circ$. F. R. G.

Decarboxylation of mesoxalic acid by glycer-aldehyde and methylglyoxal. K. BALLOWITZ and R. MEIER (Z. physiol. Chem., 1935, 233, 204—208).—In presence of glyceraldehyde (I) and Cu^{++} , mesoxalic acid (II) is decarboxylated, but malonic (III) and tartronic acid (IV) are unaffected. The O_2 uptake by (I) is increased by small and decreased by larger amounts of (II). (III) and (IV) produce no change in O_2 uptake. AcCHO behaves similarly to (I). J. H. B.

Condensation of α -formylsuccinic esters with esters of α -halogenated acids. I. L. KNUNIANZ and M. P. GERTSCHUK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 133—139).—Et formylsuccinate with $CHBrEt\cdot CO_2Et$ in C_6H_6 - Et_2O containing NaOEt affords (cf. A., 1905, i, 563) *Et* $\gamma\delta$ -oxido-*n*-hexane- $\alpha\beta\delta$ -tricarboxylate, b.p. 196°/10 mm., hydrolysed (10% HCl) to δ -keto-*n*-hexane- $\alpha\beta$ -dicarboxylic acid, b.p. 194—197°/16 mm., which with conc. HNO_3 affords $(\cdot CH_2\cdot CO_2H)_2$. J. L. D.

Absorption spectra of the metabolic acids of *Penicillium charlesii* and their relationship to the absorption of ascorbic acid. R. W. HERBERT and E. L. HIRST (Biochem. J., 1935, 29, 1881—1886).— α -Ethyltetronic acid (I) has bands at 258, 233, and 258 $m\mu$ in neutral, acid, and alkaline solutions, respectively, similarly to ascorbic acid. α -Acetyltetronic acid (II) has two bands at 265 and 230 $m\mu$ independent of p_H . Carlic (III), carolic (IV), carolinic, and carlosic acids have spectra similar to that of (II) which change to single-banded spectra like that of (I) on reduction. (III) and (IV) have single-banded spectra in EtOH corresponding with their dehydrated forms. The spectra of *l*- γ -methyl- and γ -carboxymethyl-tetronic, ramigenic, and verticellic acids are also examined. The spectral evidence is considered to support the structures suggested by Clutterbuck (A., 1935, 327, 662, 898) for the tetronic acids. H. D.

Ascorbic acid (vitamin-C) and hydroxytetronic acid. F. MICHEEL and W. SCHULTE (Annalen, 1935, 519, 70—80).—Hydroxytetronic acid Me_2 ether (I) heated with 0.2N-NaOH under H_2 yields the corresponding 2-*Me* ether, $O\begin{array}{c} \diagup CO-C\cdot OMe \\ \diagdown CH_2\cdot C\cdot OH \end{array}$, m.p. 141°,

which when ozonised and treated with NH_3 gives $(\cdot CO\cdot NH_2)_2$ and $OH\cdot CH_2\cdot CO_2NH_4$. Hydroxytetronic acid with CH_2N_2 gives the 3-*Me* ether, $O\begin{array}{c} \diagup CO-C\cdot OH \\ \diagdown CH_2\cdot C\cdot OMe \end{array}$

m.p. 139°, which similarly yields $NH_2\cdot CO\cdot CO_2NH_4$ and $OH\cdot CH_2\cdot CO\cdot NH_2$. Acidic properties are therefore more pronounced in 3-OH than in 2-OH. Dimethyl-ascorbic acid, unlike (I), is readily isomerised by cold 0.1N-alkali to a product of which the mononitrobenzoate has m.p. 181°, $[\alpha]_D +18.9^\circ$, and, probably, the annexed structure. F. R. G.

***l*- β -Methylxylonic acid.** W. BOSSHARD (Helv. Chim. Acta, 1935, 18, 956—959).—3-Methyl-1 : 2-isopropylidene-*d*-glucose oxidised with $KMnO_4$ gives *d*- β -methyl- $\gamma\delta$ -isopropylidenexyluronic acid ($+H_2O$), m.p. 63—67°, $[\alpha]_D^{25} -67.5^\circ$ in H_2O , hydrolysed with dil. H_2SO_4 and subsequently reduced ($Na-Hg$) to *l*- β -methylxylonic acid, isolated as a salt $[Cd(C_6H_{11}O_6)_2 + CdBr_2 + 2H_2O]$, $[\alpha]_D^{25} -8.43^\circ$ in H_2O . *Me* d - $\gamma\delta$ -isopropylidenexyluronate, obtained by Reichstem *et al.* (this vol., 731), when methylated with dry Ag_2O and MeI gives *Me* *d*- β -methyl- $\gamma\delta$ -isopropylidenexyluronate, b.p. 151°/12 mm. F. R. G.

Hydrolytic fission of the disulphide linking. A. SCHÖBERL and H. ECK (Naturwiss., 1935, 23, 391).—The fission of disulphides by hydrolysis ($RS\cdot SR + H_2O = RSH + RS\cdot OH$) takes place not only in alkaline but also in neutral solution. Solutions of dithiodiacetic acid and of disulphidodisuccinic acid (I) in acetate buffers and neutral solutions of their Na salts are hydrolysed when boiled. Hydrolysis of (I) also occurs even in acid solution. The decomp. of proteins containing $\cdot S\cdot S\cdot$ by irradiation with ultra-violet light is a similar type of fission. A. J. M.

$\beta\beta$ -Disulphopropionic acid. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 44, 601—606).—

The prep. of $\beta\beta$ -disulphopropionic acid ($+2\text{H}_2\text{O}$), m.p. $91-93^\circ$, from KHSO_3 and *cis*- or *trans*- $\text{SO}_3\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $\text{CH}_3\text{C}\cdot\text{CO}_2\text{H}$, or $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ is described, action in the last-named case being represented $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{K} + \text{K}_2\text{SO}_3 \rightarrow \text{SO}_3\text{K}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{K} \rightarrow \text{SO}_3\text{K}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{K} \rightarrow (\text{SO}_3\text{K})_2\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$. The K_3 ($+2\text{H}_2\text{O}$) (crystallographic data), Ti_3 , and Ba_3 ($+3\text{H}_2\text{O}$ and $+7\text{H}_2\text{O}$) salts are described. During unsuccessful attempts to resolve the acid, the normal *quinine* ($+5\text{H}_2\text{O}$) salt, decomp. about 160° , *quinine H* ($+5\text{H}_2\text{O}$) salt, m.p. $120-121^\circ$ (decomp.), *brucine H*, and *strychnine H* salts have been obtained. H. W.

$\beta\beta$ -Disulphobutyric acid. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 44, 621-626).— $\beta\beta$ -Disulphobutyric acid ($+2\text{H}_2\text{O}$), m.p. $83-84^\circ$, obtained by the action of NH_4HSO_3 on *cis*- or *trans*- $\text{CMeCl}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $\text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{H}$, or $\text{SO}_3\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, is characterised as the K_3 ($+6\text{H}_2\text{O}$ and $+2\text{H}_2\text{O}$), Ti_3 ($+2\text{H}_2\text{O}$), Ba , and *strychnine H* salts. Its structure is proved by its inability to afford optical antipodes and its difference from $\alpha\beta$ -disulphobutyric acid. The $\alpha\beta$ -dibromobutyric acids and $(\text{NH}_4)_2\text{SO}_3$ afford β -sulphobutyric acid (Ba and NH_3Ph , m.p. 162° , salts). H. W.

Intermediate stages of aldehyde oxidation. I, II.—See this vol., 1084.

Polarographic examination of aqueous solutions of formaldehyde. F. G. JAHODA (Časopis čechoslov. Lék., 1934, 14, 225-234; Chem. Zentr., 1935, i, 1091-1092).—The mol. reduction potential of CH_2O is 1.50 volts. Reduction is an irreversible process and is facilitated by an alkaline medium. 0.07×10^{-6} g. of CH_2O may be determined with 10% accuracy. The method is suitable for the examination of pharmaceutical preps. which contain EtOH , MeOH , MeCHO , COMe_2 , or PhCHO in addition to CH_2O .

A. G. P.

Gravimetric determination and identification, by elementary analysis, of small quantities of formaldehyde at great dilutions. R. FOSSE, P. E. THOMAS, and P. DE GRAEVE (Compt. rend., 1935, 201, 105-109).— CH_2O (2 mg. at a dilution of 40-200 mg. per litre) may be determined gravimetrically and identified as methylenedi- β -naphthol (cf. this vol., 877). This is converted by boiling conc. HCO_2H into dinaphthoxanthene, the tribromide (A., 1904, i, 816) and aurichloride (A., 1905, i, 541) of which are also suitable for the identification of CH_2O . H. G. M.

Thermal reaction between chlorine and formaldehyde. R. SPENCE and W. WILD (J. Amer. Chem. Soc., 1935, 57, 1145-1146).—The production of HCOCl is considered to be small (cf. this vol., 586).

E. S. H.

Reaction between chlorine and formaldehyde. K. B. KRAUSKOPF and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1935, 57, 1146).—Polemical (cf. preceding abstract).

E. S. H.

Metacetaldehyde: its preparation and influence on the rotation of ethyl tartrate. T. S. PATTERSON and G. M. HOLMES (J.C.S., 1935, 904-906).—Metacetaldehyde (improved prep.) enhances the rotation of Et tartrate.

F. R. G.

Constitution of the rhodinol from rose oil. J. DŒUVRE (Parfums de France, 1934, 12, 197-202; Chem. Zentr., 1935, i, 1310-1311).—The O_3 method for examination of unsaturated compounds (A., 1928, 542) is modified to avoid the further oxidation of the CH_2O produced. The reaction is carried out in AcOH-EtOAc at -15° , excess of the Grosse-Bohle reagent is added immediately, and CH_2O is determined colorimetrically. The semicarbazone of *l*-citronellal from geranium oil contains $> 2\%$ of the α -[methylene]-form. The alcohol $\text{C}_{10}\text{H}_{18}\text{O}$ from geranium oil is almost exclusively in the β -[isopropylidene]-form. The composition of rhodinol from rose oil and that from geranium oil are practically the same.

A. G. P.

Dicyclic derivatives of simple aliphatic ketones. F. E. KING (J.C.S., 1935, 982-984).—The following ketones were prepared by dry distillation of the appropriate Pb salts: *s*-di- Δ^1 -cyclohexenylacetone, b.p. $165^\circ/12$ mm. (semicarbazone, m.p. 112°), *s*-di-cyclopentenylacetone, b.p. $139^\circ/12$ mm. (semicarbazone, m.p. $155-156^\circ$), *s*-di- β -cyclopentyl *Et* ketone, b.p. $182^\circ/15$ mm., m.p. 25° . cyclopentanone-2- β -propionic acid (A., 1934, 1002) is reduced (Zn-Hg , conc. HCl) to β -cyclopentylpropionic acid, b.p. $135^\circ/15$ mm., (phenylhydrazide, m.p. 162° ; Pb salt, cryst.).

F. R. G.

Aliphatic thioketones. I. Action of phosphorus pentasulphide on aliphatic ketones. A. E. KRETOV and J. F. KOMISSAROV (J. Gen. Chem. Russ., 1935, 5, 388-391).— P_2S_5 and ketones in PhMe at 100° yield disulphides of the general formula $\text{CRR}'\langle\text{S}\rangle\text{CRR}'$: with COMe_2 , $\text{R}=\text{R}'=\text{Me}$; with COMeEt , $\text{R}=\text{Me}$, $\text{R}'=\text{Et}$, b.p. $120-130^\circ/15$ mm. (salt with HgCl_2), and with COEt_2 , $\text{R}=\text{R}'=\text{Et}$, b.p. $135-150^\circ/9$ mm., whilst COPr_2 affords Pr^2 , b.p. $135-150^\circ/40$ mm., and COBu^3 , gives Bu^3 thio-ketone, b.p. $105-110^\circ/10$ mm.

R. T.

Demethylation of methylsugars. K. HESS and F. NEUMANN (Ber., 1935, 68, [B], 1371-1373).— HCl in any solvent with exception of the alcohols causes fission of only glucosidic OMe from methylated sugars. HBr removes all OMe groups without damaging the sugar component. HI not only demethylates but also reduces and resinifies and is therefore unsuitable for this purpose. 2:3:6-Trimethylglucose and $\text{HBr-Ac}_2\text{O}$ at 0° give 1- α -bromoglucose tetra-acetate, m.p. 87° , $[\alpha]_D^{25} +199.3^\circ$ in CHCl_3 , in good yield. Similarly, 2:3:6-trimethylglucoside 4-*p*-toluenesulphonate affords 1-bromoglucose 2:3:6-triacetate 4-*p*-toluenesulphonate, m.p. 168° (decomp.), $[\alpha]_D^{25} +137.4^\circ$ in CHCl_3 , $+147.3^\circ$ in C_6H_6 , $+135.6^\circ$ in COMe_2 . Profound demethylation takes place with 2:3:6-trimethyl-*l*-idose, but the product contains Br resistant towards AgOAc-AcOH .

H. W.

Oxidation of *d*-glucose with bromine and alkali. T. REICHSTEIN and O. NERACHER (Helv. Chim. Acta, 1935, 18, 892-896).—Contrary to Hönig and Tempas (A., 1924, i, 712) oxidation of *d*-glucose with Ba(OBr)_2 yields *l*-sorburonic acid (identified by its Ca salt and $[\alpha]_D^{25} -10.1^\circ$) with only a trace of *d*-ketogluconic acid.

F. R. G.

Alkalimetric determination of glucose. E. N. TARAN (J. Appl. Chem. Russ., 1935, 8, 562—576).—10 ml. of neutral solution, containing >0.1 g. of glucose, are added to 25 ml. of 0.1N-I in KI, 30 ml. of 0.1N-NaOH are gradually added, with const. mixing, 25 ml. of 0.12N-HCl are added after 10 min., the liberated I is removed by adding sufficient 10% aq. $\text{Na}_2\text{S}_2\text{O}_3$, and excess of HCl is titrated with 0.1N-NaOH (thymolphthalein indicator), when % glucose = $0.6(a-b)/v$, where a is the total vol. of 0.1N-NaOH taken, b that of 0.12N-HCl, and v is the vol. of solution. The method requires 15—18 min., and is more accurate than those ordinarily employed (0.05% error for 0.1% solutions). R. T.

Monomethylhexoses. I. Constitution of the supposed 4-methylglucose. J. MUNRO and E. G. V. PERCIVAL (J.C.S., 1935, 873—875).—4-Methyl- β -methylglucoside 2 : 3 : 6-triacetate (cf. A., 1933, 54) in COMe_2 with Me_2SO_4 in 30% NaOH and subsequent methylation with MeI and Ag_2O and hydrolysis yields 2 : 3 : 4 : 6-tetramethylglucopyranose, also obtained by direct methylation of 4-methylglucose (I), which is oxidised (Br, H_2O) to 4-methyl- δ -gluconolactone, $[\alpha]_D^{20} +54.6^\circ \rightarrow +33.9^\circ$ (const.) after 280 min., shown to be a δ -lactone by rate of hydrolysis; this is methylated (MeI, Ag_2O) to a lactone which with NHPh-NH_2 gives the phenylhydrazide of 2 : 3 : 4 : 6-tetramethylgluconic acid. Hence the structure of (I) is confirmed. F. R. G.

Acetone derivatives of methylglycosides. R. G. AULT, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1935, 1012—1020).—2 : 3-*iso*Propylidene- α -methylmannopyranoside (I) with MeI and Ag_2O yields 4 : 6-dimethyl-2 : 3-*isopropylidene*- α -methylmannopyranoside, b.p. $130^\circ/0.01$ mm. (bath temp.), $[\alpha]_{D}^{20} +80.5^\circ$ in H_2O , $+99^\circ$ in MeOH, hydrolysed (4% HCl) to 4 : 6-dimethylmannose, a glass, $[\alpha]_{D}^{20} +25^\circ$ in H_2O [2 : 3-*isopropylidene* derivative, b.p. $128^\circ/0.01$ mm., m.p. $76-77^\circ$, $[\alpha]_{D}^{20} +11^\circ$ in dry MeOH, $[\alpha]_{D}^{20} 0^\circ \rightarrow -9.5^\circ$ (equilibrium val.) in H_2O]; this with Br- H_2O gives a syrup, which when heated at $100^\circ/0.01$ mm. yields 4 : 6-dimethyl- δ -mannolactone, m.p. 55° , $[\alpha]_{D}^{18} +145^\circ$ in EtOH, $[\alpha]_{D}^{18} +165^\circ$ ($\rightarrow +70^\circ$ in 150 hr.) in H_2O [*amide*, m.p. 119° , $[\alpha]_{D}^{18} -3^\circ$ in MeOH, $[\alpha]_{D}^{18} +15^\circ$ in H_2O], phenylhydrazide, m.p. 151° , $[\alpha]_{D}^{18} -3.5^\circ$ in EtOH, $[\alpha]_{D}^{18} +14^\circ$ in H_2O ; 2 : 3-*isopropylidene* derivative, b.p. $130^\circ/0.01$ mm. (bath temp.), m.p. $112-113^\circ$, $[\alpha]_{D}^{19} +128^\circ$ in EtOH, $[\alpha]_{D}^{22} +121^\circ$ ($\rightarrow +52^\circ$) in 50% aq. MeOH (the mutarotation in MeOH was studied in detail), methylated to 2 : 3 : 4 : 6-tetramethyl- δ -mannolactone, identified as the corresponding phenylhydrazide.

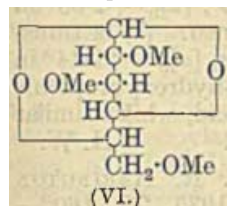
α -Methylmannopyranoside (II) shaken with anhyd. CuSO_4 and dry COMe_2 gives (I) and α -methyl-2 : 3 : 4 : 6-diisopropylidenemannopyranoside (III), b.p. $125-130^\circ/0.03$ mm. (bath temp.), m.p. $76-77^\circ$, $[\alpha]_{D}^{22} +3^\circ$ in MeOH, hydrolysed (HCl, H_2O , MeOH) to (II). β -Methylmannopyranoside (IV) with 1% HCl in COMe_2 gives 2 : 3 : 5 : 6-diisopropylidenemannose, but with anhyd. CuSO_4 and COMe_2 yields β -methyl-2 : 3-*isopropylidene*mannopyranoside, b.p. $145^\circ/0.03$ mm., $[\alpha]_{D}^{18} -80^\circ$ in MeOH, $[\alpha]_{D}^{20} -72^\circ$ in H_2O , and β -methyl-2 : 3 : 4 : 6-diisopropylidenemannopyranoside,

b.p. $105^\circ/0.03$ mm., m.p. $76-77^\circ$, $[\alpha]_{D}^{20} -124^\circ$ in MeOH, both of which with HCl in aq. MeOH yield (IV). α -Methylmannofuranoside (V) with anhyd. CuSO_4 and COMe_2 gives α -methyl-2 : 3 : 5 : 6-diisopropylidenemannofuranoside (VI), b.p. $125^\circ/0.04$ mm. (bath temp.), m.p. 24° , $[\alpha]_{D}^{18} +68^\circ$ in MeOH, hydrolysed (HCl, aq. MeOH) at room temp. to (V). (II) with COMe_2 containing 5% MeOH and 1% HCl yields a mixture of (I), (III), and (VI). α -Methylgalactopyranoside (VII) (improved prep.) with 1% HCl in COMe_2 gives α -methyl-3 : 4-*isopropylidene*galactopyranoside, b.p. $145-150^\circ/0.02$ mm. (bath temp.), m.p. $101-102^\circ$, $[\alpha]_{D}^{20} +162^\circ$ in H_2O , hydrolysed by 0.01N-HCl to (VII) and oxidised (KMnO_4 , KOH) to K α -methyl-3 : 4-*isopropylidene*galacturonate. β -Methylfructopyranoside with 1% of HCl in COMe_2 gives *isopropylidene*- β -fructose, and with anhyd. CuSO_4 and COMe_2 yields *isopropylidene*- α -fructose, also obtained in quant. yield from ethylfructofuranoside. The structures and spatial configurations of the above *isopropylidene* derivatives are discussed. Vals. of n_D are recorded in some cases. F. R. G.

Acetylated sugars with a free α -position, and synthetic experiments with 2 : 3 : 4 : 6-tetraacetylglucose and similar compounds. M. WEIZMANN and L. HASKELBERG (J.C.S., 1935, 1022—1024).—2 : 3 : 4 : 6-Tetraacetylglucosidyl bromide in COMe_2 shaken with an aq. solution of NaNO_2 yields after 24 hr. the *nitrite*, m.p. 108° , $[\alpha]_D -4.2^\circ$ in CHCl_3 , but after 5 days gives glucose 2 : 3 : 4 : 6-tetraacetate (I) in 70% yield. Galactose and lactose tetraacetates were obtained by a similar reaction. (I) with $\text{CH}_2\text{Br-COBr}$ (II) in CHCl_3 - $\text{C}_6\text{H}_5\text{N}$ yields glucose 2 : 3 : 4 : 6-tetraacetate 1-bromoacetate, m.p. 127° , $[\alpha]_{D}^{19} -1.17^\circ$ in CHCl_3 (cf. Brauns, A., 1925, ii, 633), converted by NaI and COMe_2 into the 1-iodoacetate, m.p. $125-126^\circ$, $[\alpha]_{D}^{19} -16.3^\circ$ in CHCl_3 ; this with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in C_6H_6 gives an *isomeride*, m.p. 146° , $[\alpha]_{D}^{19} -10.14^\circ$ in CHCl_3 . Similarly diisopropylideneglucose gives diisopropylideneglucose 1-bromoacetate, m.p. 136° , and isopropylideneglucose 1-iodoacetate, m.p. 74° . *iso*Propylideneglucose yields isopropylideneglucose tribromoacetate, m.p. 115° , $[\alpha]_{D}^{19} -0.4^\circ$ in CHCl_3 , and the I_3 -compound, m.p. 116° , $[\alpha]_{D}^{19} -1.44^\circ$ in CHCl_3 ; (I) with α -bromoisohexoyl bromide similarly yields 1- α -glucose 2 : 3 : 4 : 6-tetraacetate 1- α -iodoisohexoate, m.p. $112-113^\circ$, $[\alpha]_D -2.2^\circ$. F. R. G.

Glucosyl-ketimines, ternary compounds of sugars with ammonia and β -diketones. E. VOTOCEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1935, 7, 299—308).—The following are obtained by the interaction of NH_3 and the appropriate sugar and β -diketone in MeOH or EtOH : *Me* ($+1\text{H}_2\text{O}$), m.p. $190-192^\circ$, $[\alpha]_D -125.5^\circ$ in MeOH, and *Et*, m.p. 185° , $[\alpha]_D -121.0^\circ$ in MeOH, β -rhamnosyliminocrotonate; *Et* β -mannosyliminocrotonate, m.p. 179° , $[\alpha]_D +159^\circ$ in EtOH; *Me*, m.p. $192.5-193^\circ$, $[\alpha]_D -111^\circ$ in MeOH, and *Et*, m.p. $191.5-192.5^\circ$, $[\alpha]_D -107.5^\circ$ in EtOH, β -rhamnosylimino- α -ethylcrotonate; *Et* rhamnosylimino- α -methylcrotonate, m.p. 182° , $[\alpha]_D -112.5^\circ$ in EtOH; δ -rhamnosylimino- Δ^7 -penten- β -one, m.p. 209° (decomp.), $[\alpha]_D -172.50^\circ$ in MeOH. F. N. W.

Synthetic sugar anhydrides. VIII. 2:3:6-Trimethyl-*l*-idose anhydride from 2:3:6-trimethylglucose. K. HESS and F. NEUMANN (Ber., 1935, 68, [B], 1360—1370).—Contrary to Haworth *et al.* the complete methylation of cellulose acetate cannot be effected by a single treatment with Me_2SO_4 and NaOH. After repeated treatment the product is hydrolysed at 0° with HCl saturated at -20° and the crude material is methylated, distilled, and then hydrolysed, thus giving 2:3:6-trimethylglucose (I), m.p. 114° , $[\alpha]_D^{20} +70.5^\circ$ (equilibrium) in H_2O in 60% yield. (I) is converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ at $15\text{--}20^\circ$ into 4-*p*-toluenesulphonyl-2:3:6-trimethylglucosido-1-pyridinium *p*-toluenesulphonate, m.p. 140° , $[\alpha]_D^{20} +14.5^\circ$ in H_2O , $+27.1^\circ$ in COMe_2 , $+21.3^\circ$ in CHCl_3 . Under similar conditions, 2:3:6-trimethylmethylglucoside affords 2:3:6-trimethylmethylglucoside 4-*p*-toluenesulphonate (II), $[\alpha]_D^{20} +20.1^\circ$ in CHCl_3 , which is only incompletely hydrolysed by HCl. It is therefore transformed by HCl in Ac_2O into 1- α -chloro-2:3:6-trimethylglucose 4-*p*-toluenesulphonate (III), $[\alpha]_D^{20} +85.6^\circ$ in CHCl_3 , which is converted by pptd. Ag_2CO_3 in $\text{COMe}_2\text{--H}_2\text{O}$ into non-cryst. 2:3:6-trimethylglucose 4-*p*-toluenesulphonate (IV), $[\alpha]_D^{20} +51.3^\circ$ in CHCl_3 (II) and $\text{AcOH--Ac}_2\text{O--H}_2\text{SO}_4$ at $15\text{--}20^\circ$ afford 2:3:6-trimethylglucose 1-acetate 4-*p*-toluenesulphonate, $[\alpha]_D^{19} +52.5^\circ$ in CHCl_3 . (III) is converted by AgOAc in AcOH at 100° into 2:3:6-trimethylglucose 1- β -acetate 4-*p*-toluenesulphonate, $[\alpha]_D^{19} +4.8^\circ$ in CHCl_3 , isomerised by $\text{Ac}_2\text{O--AcOH--H}_2\text{SO}_4$ to 2:3:6-trimethylglucose 1- α -acetate 4-*p*-toluenesulphonate (V), $[\alpha]_D^{18} +49.4^\circ$ in CHCl_3 . Hydrolysis of (IV) or (V) with NaOMe yields 2:3:6-trimethyl-*l*-idose anhydride (VI), b.p. $76^\circ/0.015$ mm., $[\alpha]_D^{19} +111.3^\circ$, $[\alpha]_D^{18} +114.2^\circ$ in H_2O , $+103.6^\circ$ in MeOH , $+90.8^\circ$ in CHCl_3 , hydrolysed by 1% HCl at 100° to 2:3:6-trimethyl-*l*-idose, $[\alpha]_D^{19} +98.5^\circ$ in H_2O , and by saturated HBr at 0° to *l*-idose, identified as the phenylosazone, m.p. 168° , and by oxidation to *l*-idonic acid. Unexpectedly therefore Walden inversion takes place at C5 instead of C4, change taking place as a consequence of anhydride formation and not of elimination of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$. H. W.



Decomposition of fructose in glass vessels by ultra-violet light of wave-length 366 $m\mu$ from the quartz-mercury vapour lamp. R. CANTIENI (Helv. Chim. Acta, 1935, 18, 933—935).—The presence of CO could be detected spectroscopically as its haemoglobin compound, 8 times as rapidly in a 10% solution of fructose in quartz as in glass.

F. R. G.

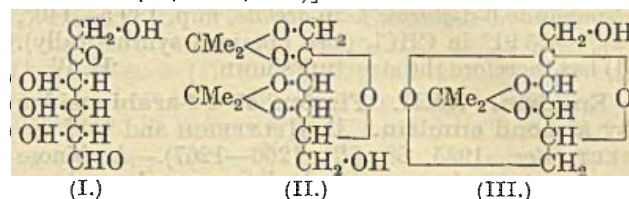
Formation of hydrogen cyanide and carbamide by the oxidation of fructose in ammoniacal solution at room temperature. J. PARROD (Compt. rend., 1935, 200, 1884—1886).—Fructose (not glucose) and $\text{Cu}(\text{OH})_2$ in aq. $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_3$ at 18° give slowly a little CuCN and a trace of $\text{CO}(\text{NH}_2)_2$.

R. S. C.

***l*-Psicose (2-keto-*l*-ribohexose, ψ -fructose), diacetone-*l*-psicose, and diacetone-*l*-psicuronic acid.** M. STEIGER and T. REICHSTEIN (Helv. Chim.

4 E

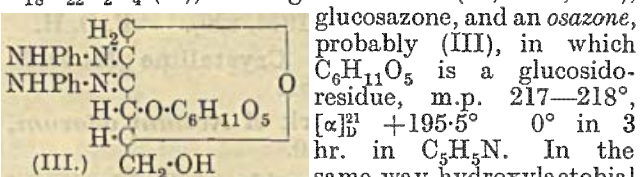
Acta, 1935, 18, 790—799).—*alloDulcitol* (improved prop.), m.p. $148\text{--}150^\circ$, with a sorbose bacteria culture gives *l*-psicose (I) [phenylosazone, m.p. $173\text{--}174^\circ$ (decomp.), probably identical with *l*-allosazone (A., 1934, 759)].



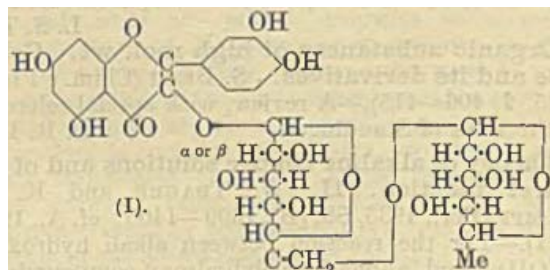
(I) with COMe_2 and anhyd. CuSO_4 in conc. H_2SO_4 gives diisopropylidene-*l*-psicose (II), m.p. $56.5\text{--}57^\circ$, $[\alpha]_D +99^\circ$, together with a compound, $\text{C}_9\text{H}_{11}\text{O}_5$, m.p. $137\text{--}137.5^\circ$, $[\alpha]_D^{21} +97.2^\circ$, regarded as (III). (II) in an aq. solution of $\text{Ca}(\text{OH})_2$ oxidised with KMnO_4 yields diisopropylidene-*l*-psicuronic acid, m.p. $80\text{--}81^\circ$, $[\alpha]_D^{20} +80.5^\circ$. F. R. G.

4-Methyl-*l*-sorbose. W. BOSSHARD and T. REICHSTEIN (Helv. Chim. Acta, 1935, 18, 959—961).—3-Methyl-*d*-glucose hydrogenated in aq. solution in presence of Ni gives γ -methyl-*l*-sorbitol, a syrup (*di*formal, m.p. $133.5\text{--}134^\circ$), oxidised with sorbose bacterium to 4-methyl-*l*-sorbose, m.p. 133° (corr.), $[\alpha]_D^{12} -30.9^\circ$ in H_2O . F. R. G.

New reactions of lactobiose and cellobiose. M. BERGMANN and K. GRAFE (J. Biol. Chem., 1935, 110, 173—180).—Hydrolysis of hydroxycellobial hepta-acetate (I) with NaOMe and treatment of the product with $\text{NHPh}\cdot\text{NH}_2$ gives the phenylosazone, $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_4$ (II), of Bergmann *et al.* (A., 1931, 939),



Constitution and synthesis of rutinose, the biose of rutin. G. ZEMPLEN and A. GERECES (Ber., 1935, 68, [B], 1318—1321).—Enzymic fission of rutin (I) affords an amorphous biose, transformed by Ac_2O



and NaOAc at 100° into β -1-*l*-rhamnosido-6-*d*-glucose β -hepta-acetate (II), m.p. $168.5\text{--}169^\circ$, $[\alpha]_D -28.54^\circ$

in CHCl_3 . Rutinose acetate and TiCl_4 in CHCl_3 afford α -chloroaceto- β -1-1-*rhamnosido*-6-d-*glucose*, m.p. 150.5—151° after softening at 149°, $[\alpha]_D^{20} +66.50^\circ$ in CHCl_3 [also obtained from synthetic (II)], converted by Ag_2CO_3 in boiling MeOH into 1-methyl- β -1-1-*rhamnosido*-6-d-*glucose hexa-acetate*, m.p. 139.5—140°, $[\alpha]_D^{20} -45.91^\circ$ in CHCl_3 (also obtained synthetically). (I) has therefore the structure shown. H. W.

Emulsin. XXII. Fission of α -l-arabinosides by almond emulsin. B. HELFERICH and U. LAMPERT (Ber., 1935, 68, [B], 1266—1267).—Arabinose tetra-acetate is converted by *o*-cresol and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ at 100° and hydrolysis of the product with NaOMe in MeOH into *o*-tolyl- α -l-arabinoside (I), m.p. 114—116°, $[\alpha]_D^{20} +2.1^\circ$ in H_2O . The increase in the rate of fission by almond emulsin between phenyl- α -l-arabinoside and (I) is comparable with that between phenyl- and *o*-tolyl- β -d-galactosides.

H. W.

Composition of Bourdaine bark.—See this vol., 1141.

Glucoside from *Betula alba*, L. Betuloside and its aglucone, betuligenol. A. SOSA (Arch. Mus. Hist. Nat. Paris, 1935, 12, 341—345).—Betuloside (A., 1933, 811) is hydrolysed to glucose and betuligenol, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_4\text{H}_8\cdot\text{OH}$, m.p. 81° [B_2 , m.p. 135° (Maquenne block), B_2 , m.p. 59° (block), and *Me* derivatives]. F. O. H.

Thevetin, crystalline glucoside of *Thevetia nerifolia*. N. GHATAK (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 173—174).—Thevetin, the correctness of the formula $\text{C}_{20}\text{H}_{30}\text{O}_6$ for which is upheld, is hydrolysed to glucose and thevetigenin, $\text{C}_{14}\text{H}_{20}\text{O}$ (cf. A., 1933, 877; 1934, 820). F. O. H.

***Butea frondosa* flowers.** Crystalline glucoside of butin.—See this vol., 1181.

Constituents of the bark of *Nerium odorum*, Soland.—See this vol., 1180.

Sophoricoside, a heteroside of the fruits of *Sophora japonica*, L.—See this vol., 1141.

Isomerisation of cyanogenic heterosides.—See this vol., 1083.

Products of hydrolysis of glycogen. C. H. GRAY (Nature, 1935, 135, 1002).—Attempts to isolate a trisaccharide from the products of hydrolysis of glycogen (I) by glycerol extracts of muscle have failed (cf. this vol., 533). A hydrolytic product with a reducing power equiv. to 30—33% of (I) disappearing and yielding a phenylosazone similar to that previously described (A., 1930, 249) has, however, been obtained.

L. S. T.

Organic substances of high mol. wt. Cellulose and its derivatives. S. BEZZI (Chim. e l'Ind., 1935, 1, 406—415).—A review, with special reference to the work of Staudinger.

D. R. D.

Theory of alkaline copper solutions and of the biuret reaction. II. W. TRAUBE and K. E. STUMPF (Ber., 1935, 68, [B], 1399—1405; cf. A., 1930, 1421).—For the reaction between alkali hydroxide, $\text{Cu}(\text{OH})_2$, and aliphatic polyhydroxy-compounds or substances of the type of biuret it is essential that the latter should have a (generally weak) acidic reaction.

It then reacts in part with the alkali to form a salt the anion of which can unite with $\text{Cu}(\text{OH})_2$. According to the law of mass action, the reaction is continued and may eventually involve all the cupriphile compound. It is further important that the reaction proceeds with pronounced evolution of heat and that the complex Cu compound is more strongly acidic than the initial material. Measurements of conductivity show that the complex Cu compounds of diguanide, guanyl-carbamides, and substances such as trimethyldihydroxypropylammonium hydroxide are to be formulated as inner salts or zwitterions.

H. W.

Kinetics of the thermal decomposition of methylamine.—See this vol., 1081.

Removal of hydrogen chloride from aldchloro-imines by sodium hydroxide.—See this vol., 939.

Mechanism of action of glycine on potassium platinichloride. A. A. GRUNBERG and L. M. VOLSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 488—491).—Glycine reacts with K_2PtCl_4 at room temp. if sufficient alkali is added to neutralise the $\cdot\text{CO}_2\text{H}$, giving mainly the *cis*-diglycine complex, with only a small amount of the usual *trans*-form. The following mechanism is proposed ($\text{Gl}=\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot$): $\text{K}_2\text{PtCl}_4 + 4\text{GIH} \rightarrow [\text{Pt}(\text{GIH})_4]\text{Cl}_2 \rightarrow [\text{Pt}(\text{GIH})_2\text{Cl}_2] \rightarrow [\text{Pt}(\text{GIH})_2(\text{OH})_2] \rightarrow [\text{PtGl}_2]$. The compounds H_2PtGl , BaPtGl_4 , and $[\text{Pt}(\text{GIH})_4]\text{Cl}_2$ are described. E. W. W.

Synthesis of optically active isoserine. S. TSUNOO (Ber., 1935, 68, [B], 1341—1343).— β -Chloro- α -hydroxypropionic acid is resolved into its optical antipodes by brucine in H_2O , whereby *d*-3-chloro- α -hydroxypropionic acid (I), m.p. 91.5°, $[\alpha]_D^{18} +2.60^\circ$ in H_2O , $[\alpha]_D^{18} +3.45^\circ$ in H_2O , is obtained. (I) is transformed by 30% NH_3 into *l*-isoserine, $[\alpha]_D^{10} -29.44^\circ$ in H_2O . Treatment of *dl*- β -chloro- α -hydroxypropionic acid with Na-Hg yields *dl*-lactic acid, whilst similar treatment of (I) affords *d*-lactic acid.

H. W.

Synthesis of glutathione. C. R. HARRINGTON and T. H. MEAD (Biochem. J., 1935, 29, 1602—1611).—A method is described for deacylation by means of PH_4I of *N*-carbobenzyloxy-compounds, carbobenzyloxyglycylglycine and the CH_2Ph ester of carbobenzyloxyglutamine giving yields of glycylglycine and glutamine of 80 and 35%, respectively. The method is then applied in the synthesis of glutathione and γ -glutamylcysteine. The acid chloride of *N*-carbobenzyloxycystine on coupling with glycine ester gave *N*-carbobenzyloxycystylglycine Et ester, which with PH_4I yielded cysteylglycine Et ester hydriodide (I), m.p. 115°. *N*-Carbobenzyloxyglutamic anhydride with MeOH and Na in MeOH gave α -Me *N*-carbobenzyloxyglutamate (II), an oil, the acid chloride of which on condensation with (I) in NHEt_2 gave α -Me *N*-carbobenzyloxyglutamato-cysteylglycine Et ester, m.p. 173°, hydrolysed with *N*- NaOH in aq. dioxan to *N*-carbobenzyloxy- γ -glutamylcysteylglycine, m.p. 166°, which in AcOH with PH_4I and subsequent treatment with NaOH gave glutathione, m.p. 190°, $[\alpha]_{5461} -21.0^\circ$ in H_2O [natural product -18.5° (Hopkins)]. The compound titrates with I, and with H_2O_2 is converted into the oxidised form, $[\alpha]_{5461} -107^\circ$ (natural product under same conditions -108°). Like the natural product,

it gave with extreme ease on boiling in aq. solution glutamic acid (largely as pyrrolidone-2-carboxylic acid) and cystylglycyl anhydride, m.p. 261—262° (decomp.). The structure of naturally occurring glutathione as γ -glutamylcysteylglycine, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{SH})\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, is thus confirmed. Further, the acid chloride of (II) on condensation with cystine Et ester hydrochloride in $\text{CHCl}_3\text{-NH}_4\text{Et}$ and purification by reduction to the thiol with pptn. as the Cu^+ mercaptide gave α -methyl-N-carbobenzoyloxyglutamocysteine Et ester, m.p. 97°, hydrolysed in aq. dioxan with NaOH to N-carbobenzoyloxy- γ -glutamylcysteine, which with PH_4I in AcOH yielded γ -glutamylcysteine (III), m.p. 167°, $[\alpha]_{5461} + 13.6^\circ$. The compound has marked acidic properties, an aq. solution having p_{H} 2.5. The oxidised form has m.p. 187° (decomp.), $[\alpha]_{5461} - 120^\circ$. The results suggest that Stewart and Tunnicliffe (A., 1925, i, 795) probably isolated an impure prep. of (III). P. W. C.

Preparation of aminohydroxypropanesulphonic acid and its derivatives. S. TSUNOO (Ber., 1935, 68, [B], 1334—1341).—Treatment of epichlorohydrin with NaHSO_3 at 100° and of the product with $\text{H}_2\text{C}_2\text{O}_4$ and then with $\text{Pb}(\text{OAc})_2$ leads to Pb γ -chloro- β -hydroxypropanesulphonate. The corresponding free acid is transformed by the requisite base at 100° into γ -amino- (I), m.p. 280° (decomp.), γ -methylamino-, m.p. 180° γ -dimethylamino-, m.p. 223°, γ -anilino-, m.p. 240°, and γ -methylanilino-, m.p. 235—238° (decomp.), β -hydroxypropanesulphonic acid. With the requisite *tert.*-base the following compounds are obtained: γ -trimethylamino-, m.p. 286—287° (decomp.), γ -pyridyl-, m.p. 242° (decomp.), γ -quinolyl-, m.p. >280°, and γ -isoquinolyl-, m.p. 270° (decomp.), β -hydroxypropanesulphonbetaine. Benzoylation of the dissolved acid in presence of $\text{Ba}(\text{OH})_2$ affords γ -benzamido- β -hydroxypropanesulphonic acid, m.p. 255° (decomp.) (Ba salt), hydrolysed by 48% HBr to (I), which gives the biuret and ninhydrin reactions. γ -Phenylureido- (Ba salt) and γ -2-naphthalenesulphonamido- [Na, m.p. 265° (decomp.), and Ba salts] β -hydroxypropanesulphonic acid are described. (I) and cholic acid afford the compound $\text{C}_{27}\text{H}_{47}\text{O}_8\text{NS}$, m.p. 185° after softening at 145°, decomp. 210°, $[\alpha]_{\text{D}}^{25} + 27.29^\circ$ in dil. EtOH. H. W.

Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. II. Reaction between phospho-18-tungstic acid reagent and other substances than thiol compounds. K. SHINOHARA (J. Biol. Chem., 1935, 110, 263—277).—The influence of a no. of compounds likely to occur together with cystine (I) and cysteine (II) on the development of colour with phospho-18-tungstic acid under conditions described earlier (this vol., 877) is studied. CH_2O and COMe_2 inhibit colour production due to (I) and (II) without influencing that due to AcCO_2H , furfuraldehyde, quinol, resorcinol, pyrocatechol, Fe^{3+} , and Sn^{4+} , thus providing a means of determining these substances in the presence of (I) and (II). Creatinine increases the rate of colour production in the presence

of (I) and (II) and CH_2O . Sn is a better reducing agent for (I) than is Zn. H. D.

Absence of dissociation of thiocarbamide and substituted thiocarbamides in dilute aqueous solution. P. CRISTOL, R. SEIGNEURIN, and J. FOURCADE (Compt. rend., 1935, 200, 2223—2225).—Thiocarbamide (I), its Me, Et, and allyl derivatives, and biuret are shown by cryoscopy, κ , and p_{H} to be undissociated in H_2O . (I) is thus not $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{SH}$, but probably $\text{NH}\cdot\text{C}(\text{NH}_2)=\text{S}$. R. S. C.

Preparation of guanidine nitrate from ammonium thiocyanate. H. GÖCKEL (Angew. Chem., 1935, 48, 430).—Guanidine nitrate is obtained in almost quant. yield by treating NH_4CNS (100 g.) with dry NH_3 (50 g.) at room temp. until liquefied, adding $\text{Pb}(\text{NO}_3)_2$ (400 g.), and heating the mixture in an autoclave to 120°. S. C.

Radial esters of tetrathio-orthosilicic and tetrathio-orthogermanic acids. H. J. BACKER and F. STIENSTRA (Rec. trav. chim., 1935, 44, 607—617).—Cryst. esters of tetrathio-ortho-silicic and -germanic acid are isomorphous with one another and with esters of tetrathio-orthostannic acid. Those with compact alkyl groups crystallise readily and simply and have a high m.p. In general the m.p. of the esters falls in the order $\text{C} > \text{Si} > \text{Ge} > \text{Sn}$, but the Me and Bu' compounds are exceptional. The m.p. of the latter increases with increasing wt. of the central atom, whereas those of the former apparently present a combination of the two opposed actions. The following tetrathio-orthosilicates are described with crystallographic data: Pr_4 , m.p. 33.5°; tetra-n-amyl, b.p. 230—232°/3—4 mm.; tetracetyl, m.p. 50—51°; tetracyclohexyl, m.p. 101.5—102.5°; Ph_4 , m.p. 114.5—115°; tetra-p-tolyl, m.p. 128.5—129°; tetra-p-tert-butylphenyl, m.p. 185—186°. The following tetrathio-orthogermanates have been obtained: tetra-n-amyl, b.p. 240—241°/3—4 mm.; tetracetyl, m.p. 50—51°; tetracyclohexyl, tetragonal, m.p. 84°, monoclinic, m.p. 88°; Ph_4 , m.p. 101.5°; tetra-p-tolyl, m.p. 110—111°; tetra-p-tert-butylphenyl, m.p. 155—156°; compound $\text{Ge}\left\{\begin{smallmatrix} \text{S}-\text{CH}_2-\text{CH}_2 \\ \text{S}-\text{CH}_2-\text{CH}_2 \end{smallmatrix}\right\} > \text{O}\}_2$, m.p. 159—159.5°. The physical consts. of the compounds are tabulated. H. W.

Simplified preparation of activated magnesium for Grignard reagents. H. GILMAN and R. H. KIRBY (Rec. trav. chim., 1935, 44, 577—583).—5 c.c. of Et_2O are added dropwise to a well-stirred mixture of Mg turnings or powder (5 g.), C_6H_6 dried over Na (100 c.c.), and 2.5 g. of I. As soon as the colour of the I has disappeared the solvent is distilled from an oil-bath finally at 150—160°. The product is cooled in a dry atm., powdered, and quickly transferred to a dry bottle fitted with a rubber stopper. Immediately before use the catalyst is re-activated by being heated in a test-tube until evolution of gas ceases and a faint colour of I appears. Usually about 0.2 g. of it is used in initiating Grignard reactions. The mechanism of the catalysis is discussed. H. W.

Yields of organomagnesium and organolithium compounds. H. GILMAN, E. A. ZOELLNER, W. M. SELBY, and C. BOATNER (Rec. trav. chim., 1935, 44, 584—594).—Yields of Grignard compounds are recorded (i) when the compound RX in Et_2O is gradually added to Mg turnings under Et_2O when reaction has been initiated by I and halide, (ii) when the compound RX is added all at once after reaction has started, and (iii) under special conditions for each reagent. Although good yields are frequently recorded by (i) and (iii), the optimal conditions have not been secured. The quality of the available Mg is very significant in the prep. of the less common Grignard reagents. Fine Mg is not generally essential, but is preferable to Mg turnings where an increase in yield is desired or for initiating actions when an activated Mg catalyst is not available. The yields of Grignard reagents $MgRHal$ decrease in the order $MgRCl$, $MgRBr$, $MgRI$. As reactant $MgRCl$ is preferred, since it is formed in better yield, its prep. involves little extra attention to details as there is no appreciable decline in yield with rapid addition of RCl to Mg in Et_2O , and it is more reactive and generally gives higher yields of product. The reaction is initiated by using an activated catalyst; its use with polyfunctional reactants may involve difficulties due to its greater reactivity. n -Alkyl bromides with an even no. of C atoms give higher yields than the preceding bromides with an odd. no. of C atoms. The reverse is the case with the iodides, but the medium here appears to exert a marked influence. Alternation appears to take place with the chlorides, but the evidence is at present insufficient. Generalisations with regard to the prep. of organolithium compounds cannot be made at present. H. W.

Relative rates of formation of some organomagnesium and -lithium compounds.—See this vol., 939.

Aldolising action of mixed secondary and tertiary organomagnesium compounds on certain ketones. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1935, [v], 2, 1435—1438).—Mixed *sec.* and *tert.* aliphatic organomagnesium derivatives give, in addition to the usual three types of reaction, an aldolisation of certain ketones of definite structure. The examples cited are the action of $MgPr^sCl$, $MgBu^sBr$, and $MgBu^sCl$ on $COMePr^s$, of $MgPr^sCl$, $MgBu^sBr$, and $MgBu^sCl$ on pinacolone, of $MgPr^sCl$ and $MgBu^sBr$ on cyclopentanone, and of $MgPr^sCl$ on cyclohexanone. H. W.

Complex iron compounds. I. Formation and solvation of ferrous chloride in non-aqueous liquids. D. R. CHESTERMAN (J.C.S., 1935, 906—910).—Purified Fe reacts rapidly with solutions of HCl in $MeOH$, $EtOH$, Pr^sOH , and $COMe_2$ forming sol. co-ordination compounds with $FeCl_2$; it reacts with HCl in $MeOAc$, $EtOAc$, Et_2O , and $CHCl_3$ forming insol. co-ordination compounds, but does not react with HCl in CCl_4 , CS_2 , C_6H_6 , or light petroleum. Solubility of HCl at 25° in the solvents and conductivities of the saturated solutions are recorded. The following cryst. co-ordination compounds are described: $FeCl_2$ dimethyl-, tetramethyl-, ethyl-, isopropyl-alcoholate, and monomethylacetate. F. R. G.

Triethylenediaminecobaltic salts with mixed anions.—See this vol., 946.

Organic compounds of gold. V. Cyano-compounds. Production of alkyl radicals. A. BURAWOY, C. S. GIBSON, and (in part) S. HOLT (J.C.S., 1935, 1024—1030; cf. this vol., 479).—Diethylmonobromogold in Et_2O with $AgCN$ gives diethylmonocyanogold ($C_5H_{10}NAu$)₄ (I), m.p. 103 — 105° , decomp. to $AuCN$ and C_4H_{10} , converted by boiling in $CHCl_3$ into diethyldicyanodigold (II), decomp. 110 — 120° . (I) in C_6H_6 with aq. $(CH_2NH_2)_2$ gives monoethylenediaminetetraethyldicyanodigold, $C_{12}H_{28}N_4Au_2$, m.p. 96 — 98° with evolution of C_4H_{10} to give monoethylenediaminodithyldigold aurocyanide, $C_8H_{18}N_4Au_2$, m.p. 161 — 162° (decomp.), which with aq. HCl yields (II). Monoethylenediaminetetra- n -propyldibromodigold with aq. HBr yields di- n -propylmonocyanogold ($C_7H_{14}NAu$)₄ (III), m.p. 94 — 95° decomp. to $AuCN$, converted by warming in $CHCl_3$ to di- n -propyldicyanodigold, decomp. 100° giving $AuCN$ and C_6H_{12} . (III) in C_6H_6 with $(CH_2NH_2)_2$ yields monoethylenediaminetetra- n -propyldicyanodigold, m.p. 84 — 85° with formation of C_6H_{12} and monoethylenediaminodi- n -propylgold aurocyanide, m.p. 151 — 152° (decomp.). Structures are given for the above compounds. F. R. G.

Mechanism of additions to double linkings. I. Thermochemistry and kinetics of a diene synthesis.—See this vol., 938.

2-Methyldicyclo-[2:2:2]-octane and its behaviour during dehydrogenating catalysis. B. A. KASANSKY and A. F. PLATE (Ber., 1935, 68, [B], 1259—1264).—The absence of strain in the mol. and consequent structural stability which do not facilitate elimination of H at a Pt contact do not hinder the catalytic decomp. of 2-methyldicyclo-[2:2:2]-octane (I) characteristic of all hydrocarbons with a hexamethylene ring. *cis*-Diethylenetetrahydrobenzaldehyde, b.p. 90 — $92^\circ/20$ mm., is obtained in 40% yield when acraldehyde (II) and $\Delta^{1:3}$ -cyclohexadiene are heated for $3\frac{1}{2}$ hr. at 100° and then treated with K_2CO_3 , whereby excess of (II) is polymerised. It is converted by successive treatment with $N_2H_4 \cdot H_2O$ and KOH into 2-methyldicyclo-[2:2:2]-octene, b.p. 147.5 — $149^\circ/756.7$ mm., hydrogenated (Pt -black in $EtOH$) to (I), m.p. 33 — 34° . Treatment of (I) in CO_2 with $Pt-C$ at 305 — 315° gives a mixture of hydrocarbons containing C_6H_6 and affording mainly $BzOH$ when oxidised, thus probably indicating the formation of $PhMe$. H. W.

Steric hindrance, a means of analysis of intermolecular forces. O. ZWECKER (Ber., 1935, 68, [B], 1289—1306).—The spatial conception of the effect of *o*-substituents on the reactivity of chemical compounds is inadequate, since it fails to explain the many instances of enhanced activity. A uniform view is obtained of the displacement of the chemical properties of simply substituted C_6H_6 derivatives caused by the entry of 1 or 2 *ortho*-substituents as compared with the differences in chemical properties of the corresponding "substitution pairs." The latter are the compounds obtained when the reacting substituent is regarded as united to one of the neigh-

bouring substituents. Replacement of an *ortho*-H in a simply substituted C_6H_6 derivative by a second substituent (*B*) causes an alteration in the properties of the reacting substituent (*A*). The displacement of reactivity is comparable in magnitude and direction with the difference in chemical behaviour of *AH* and *AB*. If a reaction occurs more rapidly with *AH* than with *AB*, the same difference in modified form is observed when in the mono-substituted C_6H_6 derivative an *ortho*-H is replaced by *B*. If the reaction of *AB* is slower than that of *AH*, retardation of the rate of reaction is caused by the *ortho*-substituent in the C_6H_6 derivative. Complete repression of a reaction by the *ortho*-substituent occurs only when the difference in the rates of reaction of the corresponding "substitution pairs" is unusually great. The phenomena of hindrance are particularly obvious with C_6H_6 derivatives because the reactions under consideration in the case of compounds without *ortho*-substitution usually occur more slowly than with the corresponding simple mols. At present the relationships are not quant.

H. W.

Action of magnesium phenyl bromide on dichloriodoaryl compounds. N. N. MELNIKOV (J. Gen. Chem. Russ., 1935, 5, 28—29).— $PhCl$, $PhBr$, PhI , and Ph_2 are formed when $MgPhBr$ in Et_2O is added to $C_6H_5Cl_2I$; the corresponding products with $C_6H_5MeCl_2I$ are phenyltolylidonium chloride, $PhCl$, $PhBr$, p - C_6H_4MeI , Ph_2 , and p - C_6H_4PhMe .

R. T.

Reduction of nitro-compounds with cast-iron filings. V. O. LUKASCHEVITSCH and M. A. VOROSHILOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 394—399).—Reduction by Fe filings involves the conversion of Fe into $Fe(OH)_2$ and of $Fe(OH)_2$ into $Fe(OH)_3$. The rate of reaction depends on the micro-structure of the filings and their chemical composition. Soft, grey cast iron gives highly active filings in contrast with the harder varieties or with those containing little graphite. Rate of reduction in presence of electrolytes increases with the concn. of the latter up to a certain point, after which it commences to decline. With about 0.78*N* solutions of the following electrolytes the yields of NH_2Ph from $PhNO_2$ after 32 min. boiling are as follows: NH_4Cl , 95.5%; HCl ($FeCl_2$), 91.3%; $(NH_4)_2SO_4$, 89.2%; $BaCl_2$, 87.3%; $CaCl_2$, 81.5%; $MgCl_2$, 68.5%; $NaCl$, 50.4%; Na_2SO_4 , 42.2%; KBr , 41%; $NaOAc$, about 10%; $NaOH$, 0.7%. During reduction in the presence of alkali and of certain alkaline-earth salts the solution is distinctly alkaline to phenol- and cresol-phthalein. In these cases the p_H of the medium depends on the temp. of reaction, usually decreasing with rise of temp. The amount of dissolved Fe decreases during reduction with $FeCl_2$ probably owing to adsorption of Cl^- by the residue. After a certain point increase of p_H almost entirely inhibits reduction; diminution of p_H has much less influence. The rate of reduction by $Fe(OH)_2$ depends on the p_H of the medium; reaction is greatly delayed by certain ions such as SO_4^{--} . The slowness of the oxidation-reduction process in presence of SO_4^{--} permits the oxidation of Fe to $Fe(OH)_3$ to be regarded as a stepwise process;

when fine Fe powder is shaken with $PhNO_2$ and $FeSO_4$, a loose, dark green residue is formed which is oxidised slowly when cold, rapidly when heated. The Fe residue consists of FeO and Fe_2O_3 in very varying ratio; Fe_3O_4 is not present. The ratio $FeO : Fe_2O_3$ depends mainly on the rate of oxidation of Fe and $Fe(OH)_2$ by org. products, but the degree of subdivision of the metallic Fe is also important.

H. W.

Reduction of aromatic nitro-compounds. I. V. O. LUKASCHEVITSCH (J. Gen. Chem. Russ., 1935, 5, 103—116).— β -Arylhydroxylamines are formed as intermediate products in the reduction of $R \cdot NO_2$ ($R=Ph$, *o*-, *m*-, and *p*-tolyl, *o*- C_6H_4Cl , *o*- $OEt \cdot C_6H_4$, and *o*- $OMe \cdot C_6H_4$); the velocity of their reduction to amines is greater in alkaline than in neutral media. Formation of azo-compounds commences after most of the NO_2 -groups have been reduced, and is due to interaction of azoxy- and hydrazo-compounds. An analytical procedure for the determination of the various products of reduction of NO_2 -compounds, present together, is described.

R. T.

Reactivity of halogen in halogenated nitrobenzenes. I. Reaction with piperidine. R. B. SANDIN and M. LISKEAR (J. Amer. Chem. Soc., 1935, 57, 1304—1306).—The % of *p*-halogen (I) replaced during treatment of the following mono-, di-, and tri-(II)-halogenonitrobenzenes (0.003685 mol.) with piperidine (0.1088 mol.) in boiling C_6H_6 (20 c.c.) for 8 hr. are: *p*-chloro- 18.5, *p*-bromo- 37.7, *p*-iodo- 11.8, 3:4-di-iodo- 55.4, 4-chloro- 50.6, and 4-bromo- 90.8, -3-iodo-, 3-chloro- 73.8, and 3-bromo- 77.2, -4-iodo-, 3:4:5-tri-iodo- 38.6, 4-chloro- 14.3, and 4-bromo- 66.1, -3:5-di-iodo-, 3:5-dichloro- 76.7, and 3:5-di-bromo- 77.9, -4-iodo-; little or no *m*-halogen (III) is replaced. The mobility of (I) is increased by (III). The decreased activity of (II) is ascribed to steric factors.

H. B.

Dichloronitroiodobenzenes. H. C. TUAN and N. WU (J. Chinese Chem. Soc., 1935, 3, 150—152).—2:5-Dichloro-4-nitroaniline is converted into the corresponding -iodobenzene, m.p. 81—82°, identical with that obtained by Herschmann (A., 1894, i, 330). 2:4-, m.p. 62—63°, and 3:6-Dichloro-2-iodonitrobenzene, m.p. 32°, b.p. 292°, are prepared from the corresponding amines.

F. R. S.

Hydrolysis of the aluminium benzenesulphonates.—See this vol., 934.

Constitution and reactivity. XII. Nitration and sulphonation of aromatic compounds. K. LAUER. XIII. Sulphonation of toluene and the directive action of the methyl group. K. LAUER and R. ODA (J. pr. Chem., 1935, [ii], 143, 127—138, 139—142; cf. this vol., 970).—XII. Cationoid substituents in C_6H_6 are considered as retarding normal further substitution, and favouring anionoid substitution; thus nitration of cationoid-substituted C_6H_6 tends to be abnormal. The "self-directive" property of NO_2 is assumed to be due to its capacity to react as cationoid or as anionoid. SO_3H is presumed to have a similar, though smaller, capacity, since sulphonation by H_2SO_4 does not give exclusively normal products. SO_3 , on the other hand, must as a dipole have a

cationoid reaction at the S atom, and anionoid (oxidising) reaction at the O atoms; sulphonation by SO_3 should therefore be exclusively at anionoid C atoms. This is confirmed experimentally. PhNO_2 and SO_3 at 140° yield pure $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$; PhSO_3H gives pure $m\text{-C}_6\text{H}_4(\text{SO}_3\text{H})_2$. BzOH yields $m\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ with no trace of *o*- or *p*-isomeride.

XIII. In contrast with the above, the 8% of $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ which is formed in the sulphonation of PhMe (A., 1911, i, 849), is obtained even when SO_3 is used. That this is due to H_2SO_4 formed as a result of the reaction $2\text{PhMe} + \text{SO}_3 \longrightarrow (\text{C}_6\text{H}_4\text{Me})_2\text{SO}_2 + \text{H}_2\text{O}$ is, however, proved by treating PhMe with SO_3 in presence of P_2O_5 or of Ac_2O , when the products are *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ and the *p*-sulphone, without $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$. E. W. W.

Exchange of sulphonyl groups in thiolsulphonon esters. J. D. LOUDON and A. LIVINGSTON (J.C.S., 1935, 896—898).—The exchange $\text{R}'\text{S}\cdot\text{SO}_2\text{R}'' + \text{R}'''\text{SO}_2\text{Na} \longrightarrow \text{R}'\text{S}\cdot\text{SO}_2\text{R}''' + \text{R}''\text{SO}_2\text{Na}$ (R' or $\text{R}'' = \text{Ph}$, $p\text{-C}_6\text{H}_4\text{Me}$, CH_2Ph , $p\text{-C}_6\text{H}_4\text{Cl}$, $p\text{-C}_6\text{H}_4\text{Br}$, 2:5- $\text{C}_6\text{H}_3\text{Cl}_2$, *o*- and *m*- $\text{C}_6\text{H}_4\text{NO}_2$) operates when the potential anion is more stable than the free sulphinate ion. The following thiolsulphonates were prepared: *Ph*, m.p. 74° , $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$, m.p. 120° , *p*, m.p. 65° , $p\text{-C}_6\text{H}_4\text{Br}$, m.p. 107° , 2:5- $\text{C}_6\text{H}_3\text{Cl}_2$, in two forms, m.p. $86\text{--}87^\circ$ and 103° , *p*-toluenethiolsulphonates, *o*-nitrophenyl benzenethiolsulphonate, m.p. 87° , and *p*-bromobenzenethiolsulphonate, m.p. 137° , 2:5-dichlorophenyl *m*-nitrobenzenesulphinate, m.p. 116° .

Electrochemical oxidation of toluene in aqueous-ethereal phosphoric acid solution. V. A. PLOTNIKOV, I. L. KATZNELSON, and S. G. FRIDMAN (J. Gen. Chem. Russ., 1935, 5, 378—381).—The most suitable solvent for PhMe is 2:5 $\text{H}_3\text{PO}_4\text{--Et}_2\text{O}$. Small (1%) yields of PhCHO are obtained by anodic oxidation (Pt anode); PhCHO is not obtained unless the anolyte is separated by a diaphragm. Relatively considerable amounts of CO_2 and CO are evolved, pointing to oxidation of the C_6H_6 ring. R. T.

Preparation of *m*-xylyl chloride. H. S. KING and M. K. MERRIAM (Proc. Nova Scotian Inst. Sci., 1933—1934, 18, 276—281).— $m\text{-C}_6\text{H}_4\text{Me}_2$ with Cl_2 (conditions described) gives *m*-xylyl chloride (64%) and 1:3:4- $\text{C}_6\text{H}_3\text{Me}_3\text{Cl}$ (7%). No Cl_2 -compounds are formed. O_2 greatly retards chlorination. J. L. D.

Halogenation. X. Preparation of mixed halogen derivatives of xylenes. P. S. VARMA and K. S. V. RAMAN (J. Indian Chem. Soc., 1935, 12, 245—248).—2-Chloro-5-iodo-*p*-xylene, m.p. 46° , is readily obtained when 2-chloro-*p*-xylene is heated with I in AcOH--CCl_4 and a mixture of nitrosulphonic (I) and fuming nitric acids (II). Similarly 4-chloro-*m*-xylene yields 4-chloro-6-iodo-*m*-xylene, m.p. 44° ; 4-bromo-*o*-xylene yields 4-bromo-5-iodo-*o*-xylene, m.p. $68\text{--}5^\circ$ (also obtained by bromination of 4-iodo-*o*-xylene); 4-bromo-*m*-xylene yields 4-bromo-6-iodo-*m*-xylene, m.p. 47° (also obtained by bromination of 4-iodo-*m*-xylene); and 2-bromo-*p*-xylene yields 2-bromo-5-iodo-*p*-xylene, m.p. 73° (also obtained by bromination of 2-iodo-*p*-xylene). In the foregoing brominations a little I was used as halogen-carrier. Good yields of 4-chloro-6-bromo-*m*-xylene (Noyes, Amer.

Chem. J., 1898, 20, 798) and of 2-chloro-5-bromo-*p*-xylene (A., 1889, 965) are obtained by brominating 4-chloro-*m*-xylene and 2-chloro-*p*-xylene, respectively, in presence of a mixture of (I) and (II). H. G. M.

Polymethylbenzenes. XI. Nitration of pentamethyl-, hexamethyl-, and hexaethylbenzene. L. I. SMITH and S. A. HARRIS. XII. Nitration of bromodurene and structure of the "dinitro-duroyl bromide" of Willstatter and Kubli. L. I. SMITH and D. TENENBAUM (J. Amer. Chem. Soc., 1935, 57, 1289—1292, 1293—1296).—XI. C_6HMe_5 added to HNO_3 (*d* 1.52) + conc. H_2SO_4 (large excess) and CHCl_3 at $< 10^\circ$ gives 65—74% of dinitrophenitene (I), m.p. $176\text{--}177^\circ$, converted by SnCl_2 + conc. HCl in boiling AcOH into 2:4:5:6:7-pentamethylbenziminazole, m.p. 264° [hydrochloride (+2 H_2O); hydriodide, m.p. $> 350^\circ$ (formed during the action of MeI in xylene); methiodide, m.p. $> 350^\circ$ (darkens at 310°); *MeH* sulphate, m.p. $258\text{--}261^\circ$ (decomp.) (darkens at 255°) (formed using Me_2SO_4 in MeOH)], methylated (Me_2SO_4 , NaOH , MeOH) to the 1:2:4:5:6:7- Me_6 derivative, m.p. 165° , and converted (method: Bogert and Bender, A., 1914, i, 579) into 2-styryl-4:5:6:7-tetramethylbenziminazole, m.p. $279\text{--}280^\circ$. Similar nitration of C_6Me_6 and 2:3:4:5- $\text{C}_6\text{HMe}_4\text{CO}_2\text{H}$ affords 22% and quant. yields, respectively, of (I), whilst C_6Et_6 gives a poor yield of 1:4-dinitrotetraethylbenzene (II), m.p. $143\text{--}145^\circ$. Reduction (SnCl_2 , HCl , AcOH) of (II) and subsequent oxidation (aq. FeCl_3) of the amine stannichloride gives tetraethyl-*p*-benzoquinone, m.p. $56\text{--}58^\circ$. Possible mechanisms for the formation of (I) are discussed.

XII. Bromodurene (I) and HNO_3 (*d* 1.52) at 0° give the "dinitroduroyl bromide" (II), m.p. $122\text{--}123^\circ$, of Willstatter and Kubli (A., 1909, i, 899), which is probably $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}_2\text{Br}$, is reduced to aminodurene, does not react with EtOH--AgNO_3 , and is converted by alkali into coloured products but no dinitroduroylic acid (III) [*Me*, m.p. $103\text{--}106^\circ$, and *Et*, m.p. $99\text{--}101^\circ$, esters; chloride (IV), m.p. $90\text{--}91^\circ$]. The bromide of (III) could not be prepared (PBr_3 or SOBr_2). (I) and HNO_3 (*d* 1.52) at 25° or HNO_3 (*d* 1.6) at 0° give 3-bromo-*o*:6-dinitro- ψ -cumene (V), m.p. $181\text{--}182^\circ$, also prepared from (a) bromonitrodurene and HNO_3 (*d* 1.52) at 0° , (b) (II) and HNO_3 (*d* 1.52) at 25° , (c) (II) and conc. H_2SO_4 , and (d) 3-bromo- ψ -cumene, HNO_3 (*d* 1.52), and conc. H_2SO_4 . (II) may be 3-bromo-6-nitro-2:4:5-trimethylbenzyl nitrate or (less probably) 3-bromo- α :6-dinitro-2:4:5-trimethylbenzyl alcohol. Reduction (SnCl_2 , conc. HCl , EtOH) of (V) gives 5:6-diamino- ψ -cumene, converted by boiling AcOH into 2:4:6:7-tetramethylbenziminazole. Chlorodurene and HNO_3 (*d* 1.52) at 0° similarly afford a compound, $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}_2\text{Cl}$, m.p. $93\text{--}94^\circ$ [which differs from (IV)], converted by conc. H_2SO_4 into 3-chloro-5:6-dinitro- ψ -cumene. H. B.

Decomposition of triphenylmethyl hyponitrite. M. A. SPIELMAN (J. Amer. Chem. Soc., 1935, 57, 1117—1119).— CPh_3Cl and $\text{Ag}_2\text{O}_2\text{N}_2$ at 18° give N_2 (0.9 mol.), resinous products, $(\text{CPh}_3\cdot\text{OPh})_2$, COPh , $(\text{CPh}_3\cdot\text{O})_2$, PhOH , CPh_3Me , $\text{CPh}_3\cdot\text{OH}$, and *p*- $\text{CPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, in amounts decreasing in the order

given. A reaction mechanism is postulated, based on the transitory formation of CPh_3O , which is held to be proved. R. S. C.

Hexa-*p*-alkylphenylethanes. Effect of *p*-alkyl group on dissociation of the ethane. J. W. COPENHAUER, M. F. ROY, and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1311—1314).— $p\text{-C}_6\text{H}_4\text{Alk}\cdot\text{MgBr}$ (0.5 mol.) and Et_2CO_3 (0.125 mol.) in Et_2O give $(p\text{-C}_6\text{H}_4\text{Alk})_3\text{C}\cdot\text{OH}$, converted by HCl in $\text{Et}_2\text{O} + \text{CaCl}_2$ into $(p\text{-C}_6\text{H}_4\text{Alk})_3\text{CCl}$ (I). The colours of the solutions of the ethanes obtained from (I) and mol. Ag in PhMe deepen with increase in wt. of Alk, thus indicating a progressive increase in the dissociation (cf. A., 1931, 1392). The following are described: *tri-p-ethyl*-, m.p. 157—158°, -*n*-, m.p. 88—89°, and -*iso*-, m.p. 167—168°, -*propyl*-, and -*n*-, m.p. 63°, -*iso*-, m.p. 135—136°, and -*sec*-, m.p. 132—133°, -*butyl-phenylmethyl chlorides*; *tri-p-ethyl*-, m.p. 159—160°, -*n*-, m.p. 140—141°, and -*iso*-, m.p. 162—163°, -*propyl*-, and -*n*-, m.p. 127—128°, -*iso*-, m.p. 135—136°, and -*sec*-, m.p. 147—148°, -*butyl-phenylmethyl peroxides*. The $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{Alk}$ (numerous physical data given) are prepared (i) from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{MgBr}$ (II) and Alk_2SO_4 or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Alk}$ and (ii) by reduction (H_2 , PtO_2 , EtOH) of *p*-bromoalkenylbenzenes. $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$ and (II) give γ -*p*-bromophenyl- β -methyl- Δ^2 -propene, b.p. 98°/5 mm. *p*-Bromoisopropenylbenzene is prepared by Ziegler and Tiemann's method (A., 1923, i, 30); dehydration of the intermediate carbinol occurs during isolation. COMeEt and (II) similarly afford β -*p*-bromophenyl- Δ^2 -butene, b.p. 111°/6 mm. H. B.

Behaviour of unsaturated hydrocarbons towards the Grignard reagent at elevated temperatures. C. R. KINNEY and R. G. LARSEN (J. Amer. Chem. Soc., 1935, 57, 1054—1056).— MgPhBr does not react with $\text{CPh}_2\cdot\text{CH}_2$ (I), $\text{CHPh}\cdot\text{CH}_2$, $\text{CPh}\cdot\text{CMe}$, or $\text{CPhMe}\cdot\text{C}\cdot\text{CMe}_2$ in xylene, Ph_2 , Ph_2O , or kerosene at 130—190°. In some experiments (I) yielded $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\text{Ph}$, probably formed, however, from $\text{CH}_2\text{Ph} > \text{O}$, present as impurity in (I). R. S. C.

Dipole moment and molecular structure. XIV. 2:2'-Difluorobisdiphenylene-ethylene. E. BERGMANN. XV. Spatial configuration of the allene system. E. BERGMANN and G. C. HAMPSON (J.C.S., 1935, 987—989, 989—993).—XIV. 9:9-Dichloro-2-fluorofluorene with Ag powder in xylene gives 2:2'-difluorobisdiphenylene-ethylene, m.p. 226—227°, which is shown to have a *cis* configuration by measurement of its dipole moment by extrapolation to infinite dilution in C_6H_6 solution at 16°, as 2.51D. The dielectric const. and d of bisdiphenylene-ethylene in C_6H_6 at 16° were also determined.

XV. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ with MgPhBr gives *p*-chlorophenyl $\beta\beta$ -diphenylethyl ketone, m.p. 131°, which with MgPhBr yields $\alpha\gamma\gamma$ -triphenyl- α -*p*-chlorophenyl-propyl alcohol, m.p. 127—128°; this with aq. HCl loses H_2O to give $\alpha\gamma\gamma$ -triphenyl- α -*p*-chlorophenyl- Δ^2 -propene, m.p. 120—121°, which with Br in CHCl_3 and subsequent treatment with boiling $\text{KOH}\cdot\text{EtOH}$ yields $\alpha\gamma\gamma$ -triphenyl- α -*p*-chlorophenylallene (I). $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ with $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{MgBr}$ gives

p-bromophenyl β -phenyl- β -*p*-bromophenylethyl ketone, m.p. 126.5°, which with MgPhBr in $\text{Et}_2\text{O}\cdot\text{PhMe}$ yields $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-(*p*-bromophenyl)propyl alcohol, m.p. 130—131°; this boiled with aq. HCl gives $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-(*p*-bromophenyl)- Δ^2 -propene, m.p. 126°, brominated and treated with KOH as above to give $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-(*p*-bromophenyl)allene (II), m.p. 139—139.5°. Dipole moments were measured as above for $\text{C}(\text{CPh}_2)_2$; $\text{C}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{C}\cdot\text{CPh}_2$, 1.57D; (I) 1.55D; (II) 1.92D. These results show that allene has the structure required by the van't Hoff theory and that $\text{C}(\text{CRR}')_2$ should be resolvable as found by Maitland and Mills (this vol., 968).

F. R. G.

Formation of the indene nucleus. Phenylbenzylidenes. (MRS.) O. BLUM-BERGMANN (J.C.S., 1935, 1020—1022; cf. A., 1932, 273).—2-Benzylhydrindone with MgPhBr in Et_2O gives 3-phenyl-2-benzylindene (I), m.p. 96—98°. The compound obtained by Orekhov (A., 1923, i, 454) by heating $\text{CHPhBr}\cdot\text{CBr}(\text{CH}_2\text{Ph})_2$ is 1-phenyl-2-benzylindene (II), m.p. 97—99°, also prepared by Roger *et al.* (A., 1929, 317). (II) when boiled with KOH in EtOH isomerises to (I). Both (I) and (II) with PhCHO give 3-phenyl-2-benzyl-1-benzylideneindene, m.p. 177.5—179°.

F. R. G.

Properties of unsaturated sulphur compounds.

I. $\alpha\beta$ -Unsaturated sulphones. E. P. KOHLER and H. POTTER (J. Amer. Chem. Soc., 1935, 57, 1316—1321).— $\alpha\beta$ -Unsaturated sulphones add Grignard reagents (I) in the same manner as $\alpha\beta$ -unsaturated ketones; the sulfoxides undergo fission. Contrary to Hepworth and Clapham (J.C.S., 1921, 119, 1188), saturated sulphones react with (I) to form MgHal derivatives; they behave as saturated ketones in which the hindrance to addition is prohibitive.

p-Tolyl styryl sulphide, two forms, m.p. 44° and 65°, prepared from $\text{CPh}\cdot\text{CH}$ and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SH}$ (II) at $\approx 100^\circ$, is oxidised (30% H_2O_2 , AcOH) to the sulphoxide (III), m.p. 64° and 60°, respectively, and thence (either form) to sulphones, m.p. 77° (IV) and 121° (V). Exposure of (IV) in $\text{CHCl}_3 + \text{I}$ to sunlight gives (V), which is also prepared (15% yield) from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Me}$ (VI), PhCHO , and KOH . (V) is incompletely reduced (H_2 , Pt , AcOH) to *p*-tolyl β -phenylethyl sulphone (VII), m.p. 75°. (IV) and (V) add Br in sunlight to give the same dibromide, m.p. 132°, and with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SNa}$ in $\text{C}_6\text{H}_6\cdot\text{Et}_2\text{O}$ afford *p*-tolyl β -*p*-tolylthiol- β -phenylethyl sulphone, m.p. 175—176°, oxidised (30% H_2O_2 , AcOH) to $\alpha\beta$ -di-*p*-toluenesulphonyl- α -phenylethane, m.p. $> 225^\circ$ (decomp.). $\alpha\alpha$ -Di-*p*-toluenesulphonyl- β -phenylethane, m.p. 103°, is prepared by benzylation (method: Shriner *et al.*, A., 1930, 900) of $(p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2)_2\text{CH}_2$. $\text{CHNa}(\text{CO}_2\text{Et})_2$ and (IV) or (V) in C_6H_6 give *Et* γ -*p*-toluenesulphonyl- β -phenylpropane- $\alpha\alpha$ -dicarboxylate, m.p. 78°; with MgPhBr in C_6H_6 , the Mg derivative, $[\text{CPh}_2\cdot\text{CH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4]\text{MgBr}$ (VIII), results. (VIII) is hydrolysed to *p*-tolyl $\beta\beta$ -diphenylethyl sulphone (IX), m.p. 149° [also prepared from (II) and $\text{CPh}_2\cdot\text{CH}_2$ with subsequent oxidation], and with Br , BzCl , AcCl , and CO_2 gives *p*-tolyl α -bromo-, m.p. 155°, α -benzoyl-, (X), m.p. 253°, and α -acetyl-, m.p. 205°, $\beta\beta$ -diphenylethyl sulphones and α -*p*-toluenesulphonyl- $\beta\beta$ -diphenylpropionic acid, m.p. 195—197° (decomp.).

respectively. (X) is also prepared from *Ph* α -bromo- α -*p*-toluenesulphonylmethyl ketone, m.p. 164° [which, contrary to Arndt and Martius (A., 1933, 146), is obtained from $\text{CH}_2\text{Bz}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ and Br in CHCl_3], by the procedure previously used (this vol., 493). *p*-Tolyl α -iodo- $\beta\beta$ -diphenylethyl sulphone, m.p. 186°, was obtained by the action of Br on the compound from (IX) and MgMeI . (VII) and (IX) do not react with MgMeI (modified Zerevitinov) at room temp.; at 50–75°, however, at least 1 mol. of CH_4 is evolved. (VI) reacts slowly at room temp. (VIII) is also obtained from (IX) and MgEtBr . Treatment of the product from (VI) and MgEtBr with BzCl gives *dibenzoyl-p*-toluenesulphonylmethane, m.p. 164°; $2[\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7]\text{MgBr} + 2\text{BzCl} \rightarrow \text{CHBz}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7 + \text{C}_7\text{H}_7\cdot\text{SO}_2\text{Me}$.

(III) and MgEtBr afford *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SEt}$ and $\alpha\delta$ -diphenylbutadiene: $2\text{MgEtBr} + 2\text{CHPh}\cdot\text{CH}\cdot\text{SO}\cdot\text{C}_7\text{H}_7 \rightarrow (\text{CHPh}\cdot\text{CH})_2 + \text{C}_4\text{H}_{10} + \text{C}_7\text{H}_7\cdot\text{SO}\cdot\text{MgBr}$; $\text{MgEtBr} + \text{C}_7\text{H}_7\cdot\text{SO}\cdot\text{MgBr} \rightarrow \text{C}_7\text{H}_7\cdot\text{SEt}$. A similar reaction occurs with MgPhBr ; oxidation (excess of H_2O_2) of the resulting oil gives *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Ph}$ and a little *p*-tolyl $\beta\beta\beta$ -triphenylethyl sulphone, m.p. 229–230° [(NO_2)₃-derivative, m.p. about 265° (decomp.)], which with PCl_5 at 200° affords $\text{CPh}_3\cdot\text{CH}_2\text{Cl}$ and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ (formed from the intermediate *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ by way of *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl}_3$). *p*-Tolyl desyl sulphide, m.p. 63–64°, from desyl chloride and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SNa}$ in EtOH , and MgPhBr give β -*p*-toluenesulphonyl- $\alpha\alpha\beta$ -triphenylethyl alcohol, m.p. 275° (sinters about 180°), reduced (P, I) to *p*-tolyl $\alpha\beta\beta$ -triphenylethyl sulphone, m.p. 187°. (IX) and PCl_5 at 200° afford *p*-tolyl $\alpha\alpha$ -dichloro- $\beta\beta$ -diphenylethyl sulphone, m.p. 157°, $\text{CPh}_2\cdot\text{CCl}_2$, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$. H. B.

Magnetochemical investigations of organic substances. II. Existence of diradicals. E. MULLER and I. MULLER-RODLOFF (Ber., 1935, 68, [B], 1276–1282).—Magnetochemical examination shows that triphenyl- α -naphthylquinodimethane, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_{10}\text{H}_7$, as solid or in 5% solution in C_6H_6 at 18° and 74° exists very preponderatingly in the quinonoid form. Diradicals, if existent in the thermal equilibrium, are present in concn. $\approx 2\%$. *pp'*-Tetramethyldiaminothiobenzophenone in CHCl_3 at 18° has certainly $\approx 2\%$, probably $\approx 1\%$, of the diradical form. H. W.

Colour reactions and the spectrophotometric determination of nitronaphthalenes. B. P. FEDOROV and A. A. SPRISKOV (J. Gen. Chem. Russ., 1935, 5, 450–453).—Three 0.025-g. portions of $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ (1-, 2-, and mixed) are dissolved in 25 c.c. of 93.8% H_2SO_4 , the solutions are kept in the dark for 4 hr. at room temp., and relative absorption of light ($\lambda=580\text{ m}\mu$) is determined spectrophotometrically, when the % 1- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ content is given by $(A_{\text{Be}}-A)/(B-A)$, where *A* and *B* represent relative absorption by solutions of 1- and 2- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$, respectively. 1:8- and 1:5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ in $\text{C}_5\text{H}_5\text{N}$ or quinoline give, respectively, intense red-brown and yellow-brown colorations with limited quantities of KOH in abs. EtOH ; 1- and 2- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ do not develop colorations in these conditions. The intensity of the colorations given by $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ is

not \propto concn. Colour reactions of nitronaphthalenes with KOH in COMe_2 are described. R. T.

Mechanism of monosulphonation of naphthalene. R. LANTZ (Compt. rend., 1935, 201, 149–152).—With 55–68% H_2SO_4 at 140° C_{10}H_8 is in equilibrium with its sulphonation products. The velocities of sulphonation and of desulphonation increase rapidly with increasing $[\text{H}_2\text{SO}_4]$, the former increasing the more rapidly. The velocity of desulphonation of 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ (I) is roughly an exponential function of the concn. (cf. A., 1907, ii, 855). The transformation of (I) into the 2-acid (II) is considered to occur in two stages—desulphonation of (I) followed by 2-sulphonation of the C_{10}H_8 formed—as it occurs only when the $[\text{H}_2\text{SO}_4]$ is such that both processes can take place. Thus, only C_{10}H_8 but no (II) is formed from (I) with 45.9% H_2SO_4 , which does not sulphonate C_{10}H_8 . The proportion (89:11) of (I) to (II) formed by sulphonation of C_{10}H_8 is independent of the $[\text{H}_2\text{SO}_4]$ between the limits of 81.7 and 94.4% H_2SO_4 . H. G. M.

1-Methylnaphthalene derivatives. K. DZIEWONSKI and M. OTTO (Bull. Acad. Polonaise, 1935, A, 201–208).—The methylnaphthalenesulphonic acid previously (A., 1930, 336; cf. A., 1933, 708) assigned the 1:7-configuration is the 1:6-isomere. Replacement of SO_3H by, in turn, OH , NH_2 , and $\text{CO}\cdot\text{NHMe}$, and oxidation, gave 6-amino- α -naphthoic acid identical with that prepared from 3-nitronaphthalic acid. Improved preps. of 1:6- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{SO}_3\text{H}$, 6-hydroxy- (I) and 6-amino-1-methylnaphthalene are given. 6-Hydroxy-1-methyl-5-naphthoic acid, m.p. 169–170° (decomp.), from (I) and CO_2 under pressure at 160° and 6-hydroxy-1-methyl-7-naphthoic acid, m.p. 229–230°, from (I) and CO_2 under pressure at 230–240°, are described. P. G. C.

Colour reactions for differentiating tetra- from deca-hydronaphthalene. A. CASTIGLIONI (Z. anal. Chem., 1935, 101, 414–417).—The liquid (1 c.c.) is diluted to 50 c.c. with 95% EtOH and 1 c.c. of the solution is boiled with 1 c.c. of 30% aq. CH_2O and 10 c.c. of conc. HCl ; decahydronaphthalene (I) produces a yellow colour on cooling, tetrahydronaphthalene (II) no colour. If the HCl is replaced by 2 c.c. of conc. H_2SO_4 (II) gives a brownish-red and (I) a very pale yellow colour. Under the same conditions with HCl and furfuraldehyde (II) gives a blue, (I) a pure yellow, and mixtures of both a green colour. A. R. P.

Hydrogenation of anthracene. A. MAILLARD (Compt. rend., 1935, 200, 1856–1880). Hydrogenation (Ni-pumice) of anthracene (I) vapour by the const.-vol. technique is similar to that of C_{10}H_8 (A., 1934, 178). It is slow at 20°. At 160° 4 O are rapidly absorbed and another 4 O more slowly. The H_4 -derivative is smoothly dehydrogenated to (I) at 160°, but the more hydrogenated compounds also partly decompose, yielding CH_4 and other products. R. S. C.

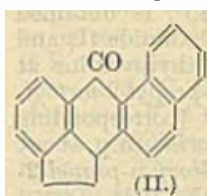
Synthetic uses of as-octahydrophenanthrene. I. J. W. COOK and G. A. D. HASLEWOOD (J.C.S., 1935, 767–770).—1:2:3:4:9:10:11:12-Octahydrophenanthrene [as-octahydrophenanthrene (A.,

1933, 1042)] with AlCl_3 and succinic anhydride in PhNO_2 at 0° affords β -6-as-octahydrophenanthrolylpropionic acid (I), m.p. $140-141^\circ$ (semicarbazone, m.p. $185-187^\circ$) [and other products, the semicarbazone, m.p. $144-146^\circ$ (decomp.), of one of which was isolated], oxidised by alkaline KMnO_4 to 6-as-octahydrophenanthroic acid, m.p. $226-228^\circ$, dehydrogenated (Se at 300°) to 3-phenanthroic acid. Clemmensen reduction of (I) yields γ -6-as-octahydrophenanthrylbutyric acid, m.p. $81-83^\circ$, b.p. $198^\circ/0.15$ mm., cyclised by $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at 100° to 5-keto-1:2:3:4:5:6:7:8:1':2':3':4'-dodecahydro-1:2-benzanthracene (II), m.p. $120-121^\circ$, reduced (Clemmensen) to the corresponding dodecahydro-1:2-benzanthracene, m.p. $87-88^\circ$, b.p. $180^\circ/0.2$ mm. [isomeric with that already described (A., 1934, 519)]. (II) with Mg , C_6H_6 , Et_2O , and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ affords a mixture of two unsaturated acids (the corresponding Δ^a - and Δ^b -substituted acetic acids) (*Me* esters, b.p. $195-212^\circ/0.2$ mm.), one of which was isolated by extraction with cyclohexane and had m.p. $226-232^\circ$ (efferv.). Both the mixture and this acid are hydrogenated (Pd-black) to the corresponding dodecahydro-1:2-benzanthryl-5-acetic acid (III), m.p. $163-165^\circ$. This acid and the foregoing mixture of acids are dehydrogenated and decarboxylated when heated at 300° with Pt-black and afford 5-methyl-1:2-benzanthracene (A., 1934, 180). Dehydrogenation (Se at $290-300^\circ$) of the *Me* ester of (III) gives a little 1:2-benzanthryl-5-acetic acid, m.p. $160-162^\circ$ (picrate, m.p. $170-173^\circ$). (III) is cyclised by $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at 100° to the corresponding ketodecahydrocholanthrene, m.p. $114-116^\circ$, reduced (Clemmensen) to dodecahydrocholanthrene, m.p. $62-63^\circ$, dehydrogenated by Pt-black at 300° to cholanthrene (cf. this vol., 968, and below). $\text{C}_3\text{H}_5\cdot\text{MgBr}$, Et_2O , and (II) give a crude carbinol, dehydrated by heating at $155-160^\circ$ to 5-allyl-1:2:3:4:7:8:1':2':3':-decahydro-1:2-benzanthracene, b.p. $174^\circ/0.1$ mm. This could not be used for the prep. of (III) as it was unaffected by Na in boiling $\text{C}_2\text{H}_5\cdot\text{OH}$, but on treatment with Pt-black at 300° it affords 5-n-propyl-1:2-benzanthracene, m.p. $91-91.5^\circ$ (picrate, m.p. $131.5-132.5^\circ$), oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to 5-n-propyl-1:2-benzanthraquinone, m.p. $104-105.5^\circ$. The use of (II) for the prep. of other 5-substituted 1:2-benzanthracenes is suggested. H. G. M.

Synthesis of 1:2-cyclopentenophenanthrene and related compounds. W. E. BACHMANN (J. Amer. Chem. Soc., 1935, 57, 1381-1382).— β -2-Phenanthrylpropionyl chloride (free acid, m.p. $177-177.5^\circ$) and SnCl_4 give 1'-keto-1:2-cyclopentenophenanthrene, m.p. $183-184^\circ$, reduced (Clemmensen) to 1:2-cyclopentenophenanthrene (Cook and Hewett, A., 1933, 1042). 1'-Keto-2:3-cyclopentenophenanthrene (?), m.p. $140-140.5^\circ$, is similarly prepared from β -3-phenanthrylpropionic acid, m.p. $156-157^\circ$. Beckmann rearrangement of the oxime, m.p. 186° , of 1-benzoylphenanthrene gives phenanthrene-1-carboxylanilide, m.p. 245° , converted by treatment with PCl_5 and subsequent reduction (SnCl_2 , HCl , abs. Et_2O) into 1-aldehydophenanthrene, m.p. $110-111^\circ$. This is reduced to 1-phenanthrylcarbinol, m.p. 165° , the bromide, m.p. 97° , of which is converted (malonate

method) into β -1-phenanthrylpropionic acid, m.p. $189-189.5^\circ$. 1-Hydroxy-1-methyl-, m.p. $86-86.5^\circ$, -1-ethyl-, m.p. $57-57.5^\circ$, and -1-n-propyl-, m.p. $86-87^\circ$, -1:2:3:4-tetrahydrophenanthrenes have been prepared. H. B.

Convenient synthesis of cholanthrene. J. W. COOK and G. A. D. HASLEWOOD (J.C.S., 1935, 770-771).—1- β -Naphthylhydrindene, m.p. $52-53^\circ$ [obtained by hydrogenation of the indene, m.p. 87° , prepared from α -hydrindone and $2\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ (cf. A., 1929, 562, where the two first-mentioned compounds are wrongly described as the α -compounds)] with Br in CS_2 and a little AlCl_3 affords 2-1'-hydrindyl-1-bromonaphthalene (I), b.p. $180-192^\circ/0.2$ mm., separated from compounds brominated in the five-membered ring by treatment with boiling $\text{C}_5\text{H}_5\text{N}$ and then with cold 80% H_2SO_4 . The Grignard reagent of (I) and CO_2

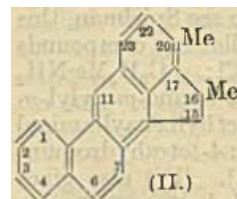


afford 2-1'-hydrindyl- α -naphthoic acid, m.p. $155-156^\circ$, dehydrated by H_2SO_4 at 0° to the crude anthrone (II), reduced by Zn in boiling 3*N*- NaOH to cholanthrene (cf. this vol., 968, and above). This is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in boiling AcOH to 1:2-benzanthraquinonyl-5-acetic acid, decomp. $245-265^\circ$, decarboxylated to 5-methyl-1:2-benzanthraquinone (*loc. cit.*). 1-Bromo-2-naphthylmagnesium iodide (prepared from 1:2- $\text{C}_{10}\text{H}_6\text{BrI}$, Mg , EtBr , and Et_2O) and α -hydrindone afford a compound, $\text{C}_{19}\text{H}_{14}\text{O}$, m.p. $142-143^\circ$, b.p. $210^\circ/0.1$ mm., which is probably a cyclic oxide. H. G. M.

Methylcholanthrene. J. W. COOK and G. A. D. HASLEWOOD (J. Amer. Chem. Soc., 1935, 57, 1380-1381).—A recapitulation of the work on the structure of methylcholanthrene (I). Fieser and Neuman's estimate (this vol., 859) of the over-all yield of (I) from deoxycholic acid is criticised. H. B.

Methylcholanthrene. L. F. FIESER (J. Amer. Chem. Soc., 1935, 57, 1381).—A reply to Cook and Haslewood (preceding abstract). H. B.

16:20-Dimethylcholanthrene. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1935, 57, 1377-1378).—The carbinol from 4-bromo-7-methylindanone and MgMeI heated to 190° gives 7-bromo-3:4-dimethylindene, b.p. $110-111^\circ/1.8$ mm., reduced (H_2 , PtO_2 , EtOH) to 4-bromo-1:7-dimethylindane (I), b.p. $98.5^\circ/1.5$ mm. The Grignard reagent from (I) with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{COCl}$ in Et_2O at -10° affords 4- α -naphthoyl-1:7-dimethylindane, m.p. $112-114^\circ$, which when heated at $400-405^\circ$ in N_2 for 30 min. passes into 16:20-dimethylcholanthrene (II), m.p. $169-170^\circ$ (corr.) [picrate, m.p. $179-180^\circ$ (corr.)]. The absorption spectrum of (II) is practically identical with that of methylcholanthrene. H. B.



Azides. III. *p*-Chlorobenzazide as a reagent for the identification of primary and secondary amines. C. KAO, H. FAN, and P. P. T. SAH (J. Chinese Chem. Soc., 1935, 3, 137-140; cf. this vol., 998).—By addition of *p*-chlorobenzazide to the appropriate amine, the following -4'-chlorophenylcarbamides

have been prepared: *phenyl*-, m.p. 237°, *4-bromo*-, m.p. 289—290°, *4-chloro* m.p. 285° (decomp.), *4-nitro*-, m.p. 261—263°, *2-nitro*-, m.p. 206°, *2-chloro-4-nitro*-, m.p. 227°, *3-nitro*-, m.p. 212—213°, *N-acetyl*-, m.p. 240° (decomp.), *4-bromo-N-acetyl*-, m.p. 163—164°, and *3-nitro-N-acetyl-phenyl*-, m.p. 293° (decomp.), and *4-tolyl*-, m.p. 267° (decomp.), *2-tolyl*-, m.p. 209°, *3-bromo-4-tolyl*-, m.p. 220°, *3-nitro-4-tolyl*-, m.p. 233—234°, *4-*-, m.p. 285—286°, and *2-tolyl-N-acetyl*-, m.p. 293—295°, α -, m.p. 235°, and β -*naphthyl*-, m.p. 264°, and *diphenyl*-, m.p. 162°. F. R. S.

Action of epichlorohydrin and chlorohydroxypropylphthalimide on α -picoline and aniline. T. FUKAGAWA (Ber., 1935, 68, [B], 1344—1346).—Epichlorohydrin and NH_2Ph react vigorously when gently warmed, giving α -*anilino- γ -diphenylamino- β -hydroxypropane*, m.p. 350° (decomp.). γ -*Anilino- β -hydroxy- n -propylphthalimide*, m.p. 145°, is obtained from γ -chloro- β -hydroxy- n -propylphthalimide (I) and NH_2Ph at room temp. (I) and 2-methylpyridine at 100° afford γ -*phthalimido- β -hydroxy- n -propyl-2-methylpyridinium chloride*, m.p. 123—124° [corresponding *picrate*, m.p. 205—207°, and *platinichloride*, m.p. about 225° (decomp.)]. γ -*Amino- β -hydroxy- n -propyl-2-methylpyridinium chloride* has m.p. 165—166°.

H. W.

Action of sulphur on aniline and similar amines. M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 1287—1289).—Improvements in the prep. of 4:4'-diaminodiphenyl sulphide (I) from NH_2Ph , S, and PbO (cf. Shukla, A., 1927, 1196; Hodgson and France, A., 1933, 497; 1934, 1096) are recorded; (I) is converted into the 4:4'-(OH)₂-derivative using a modification of the method previously described (A., 1930, 769). NPhMe_2 and CHPh:NPh do not react with S in presence of PbO; NHPhMe affords 4:4'-dimethyldiaminodiphenyl sulphide. These results together with those (lit.) for NHAcPh and $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ indicate the following mechanism: $2\text{NHPhR} + \text{S} \longrightarrow \text{S}(\text{NPhR})_2 \longrightarrow (\text{NHR}\cdot\text{C}_6\text{H}_4)_2\text{S}$; R=H, Me, Ac.

H. B.

Condensations of aromatic amines with formaldehyde in media containing acid. III. **Formation of Troger's base.** E. C. WAGNER (J. Amer. Chem. Soc., 1935, 57, 1296—1298; cf. A., 1934, 1211).—Troger's base (I) (for constitution see Spielman, this vol., 630) is prepared from the following compounds and 37% CH_2O in EtOH-conc. HCl: $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (II); $(p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH})_2\text{CH}_2$ (III); o -amino- m -xylyl- p -toluidine [p -tolyl-(2-amino-5-methylbenzyl)amine] (IV); 3- p -tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline (V) (cf. Spielman, loc. cit.). (IV) also gives some (V); in one case, an unidentified compound, m.p. 108—111° [also convertible (as above) into (I)], was also produced. (II), (III), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$, and PhNO_2 at 60° afford (IV). The production of (I) from (II) involves the changes: (II) \longrightarrow (III) or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{CH}_2$ (or its trimeride) \longrightarrow (IV) \longrightarrow (V) \longrightarrow (I).

H. B.

Preparation of ethyl- o -toluidine. H. E. FIERZ-DAVID (Helv. Chim. Acta, 1935, 18, 781).—The method of prep. of rhodamine esters previously used (cf. this vol., 206) is acknowledged as due to W. Ryser.

F. R. G.

Anomalous mutarotation of amine salts of d -camphor-10-sulphonic acid. Attempted resolution of trisubstituted nitrogen compounds. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1306—1311).—*N-Acetylbenzenesulphon-p-nitroanilide*, m.p. 198—199° [from $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ (I) and Ac_2O in $\text{C}_5\text{H}_5\text{N}$], is reduced (H_2 , PtO_2 , EtOH) to the *p-aminoanilide*, m.p. 162—163° [*d-camphor-10-sulphonate*, m.p. 174—177°, 207—208° (b)]. The Na derivative (II), m.p. 409—410° (b), of (I) and MeSO_2Cl give *N-methanesulphonylbenzenesulphon-p-nitroanilide*, m.p. 170—171.5°, similarly reduced to the *p-aminoanilide*, m.p. 163—164° [*d-camphor-10-sulphonate*, m.p. 153—156°, 195—196° (b)], whilst (II) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in COMe_2 afford *N-p-toluenesulphonylbenzenesulphon-p-nitroanilide*, m.p. 188—189°, reduced to the *p-aminoanilide*, m.p. 168—169° (slow), 154—156° (rapid heating) re-solidifying with m.p. 168—169° [*d-camphor-10-sulphonate*, m.p. 212—218°, 230° (b)]. The above salts are dextro-rotatory and exhibit mutarotation (towards —) in MeOH, EtOH, or CHCl_3 ; the final vals. are dependent on the solvent and concn. Mutarotation is not due to asymmetric N^{III} atom since *NH₂Ph* (III), m.p. 184—186°, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (+3 H_2O), m.p. 155—157°, $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 176—180°, 210° (b), and *p-aminoacetanilide* (IV), m.p. 188—194°, 208—211° (b), *d-camphor-10-sulphonates* all exhibit the same phenomenon. When (IV) is heated to 220° or when a MeOH solution is kept for 4 days, the levorotatory *d-camphor-10-sulphonic acid p-acetamidooanil*, m.p. 375—380° (b), is obtained; (III) heated to 200° gives the (—)-*anil* (V), m.p. 294—295° (b). Solutions of (III) or (V) in $\text{CHCl}_3 + \text{H}_2\text{O}$ (small amount) give the same final val., indicating the equilibrium (III) \rightleftharpoons (V). Decomp. of the salts and anils gives the inactive amine in each case. Deductions regarding resolution of a *r*-compound from mutarotation data alone must be made with caution.

NN-Dibenzenesulphonyl-p-nitroaniline, m.p. 213°, prepared from (II) and PhSO_2Cl (VI) in COMe_2 or, in small yield, from $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and an excess of (VI), is reduced to the corresponding amine, m.p. 166—167° [*d-camphor-10-sulphonate*, m.p. 210—218°, 244—245° (b)]. *Benzenesulphon-p-aminoanilide* [*d-camphor-10-sulphonate*, m.p. 196—198°, 230° (b)] has m.p. 171—172°. All m.p. (b) are on Maquenne bloc. H. B.

Acetylene derivatives. IX. **Catalytic hydrogenation of oo' -dinitrotolane.** P. RUGGLI and H. ZAESLIN (Helv. Chim. Acta, 1935, 18, 853—857).— oo' -Dinitrotolane hydrogenated in presence of Ni yields *cis- oo' -diaminostilbene*, m.p. 107° (lit., m.p. 123°) (*picrate*, m.p. 155—156°; Ac_2 derivative, m.p. 214—215°), which with a trace of acid gives the *trans-isomeride* (Ac_2 derivative, m.p. 304°). F. R. G.

Alkylated ethylenediamine derivatives. III. α -*Amino- β -benzylaminoethane*. J. VAN ALPHEN (Rec. trav. chim., 1935, 44, 595—598).—Treatment of PhCHO with a large excess of hydrated $(\text{CH}_2\cdot\text{NH}_2)_2$ in abs. EtOH at 0° gives mainly $\alpha\beta$ -dibenzylideneaminoethane (I); the presence of α -amino- β -benzylideneaminoethane in the residues from the isolation of (I) is established by addition of PhNCO , whereby β -benzylideneamino- α -phenylcarbamidoethane, m.p.

141°, is obtained, partly disproportionated to (I) and $\alpha\beta$ -diphenylcarbamidoethane, m.p. 298° (lit. m.p. 263°). Some α -amino- β -benzylaminoethane (II) is obtained when PhCHO and $(\text{CH}_2\text{NH}_2)_2$ are rapidly mixed in EtOH and Na is quickly added, but the main product is $\alpha\beta$ -dibenzylaminoethane (III), b.p. 222°/18 mm.; α - α' -benzyl- γ -phenylcarbamido- β - γ -phenylcarbamidoethane and β -benzamido- α -benzylbenzamidoethane have m.p. 180° and m.p. 187°, respectively. Treatment of (II) with PhCHO and of the product with Na in EtOH leads to (III). (II) and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ when similarly treated give α -benzylamino- β - p -methoxybenzylaminoethane (hydrochloride), characterised by conversion into α - α' -benzyl- γ' -phenylcarbamido- β - α'' - p -methoxybenzyl- γ'' -phenylcarbamidoethane, m.p. 141° (block), and α -benzylbenzamido- β - p -methoxybenzylbenzamidoethane, m.p. 156°. H. W.

Character of the combination of colours in an individual molecule of a dye. S. A. BARKOFF (Bull. Soc. chim., 1935, [v], 2, 1288—1295).—Comparison of the absorption spectra of p -fuchsin, diamine-blue 2B ($p\text{-R}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot$)₂, and ($p\text{-R}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4$)₂: $\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{Cl}$ [$\text{R}=1:8:3:6\text{-C}_{10}\text{H}_3(\text{NH}_2)(\text{OH})(\text{SO}_3\text{H})_2$ attached at 7] shows that although there is an appearance of additivity in the composition of the colours the mutual influence of the chromophores is apparent, this causing an individuality characteristic of the absorption of the compound dye. H. W.

Thiohydrazines. H. WUYTS and (MLLE.) A. LACOURT (Bull. Acad. roy. Belg., 1935, [v], 21, 618—627).—The following were prepared by methylating (MeI or Me₂SO₄) the appropriate thiohydrazines: β -thioacetyl-, m.p. 59°, β -hexahydrothiobenzoyl-, m.p. 108°, β -phenylthioacetyl-, m.p. 82°, and β - m -tolylthioacetyl-, m.p. 91°, α -phenyl- α -methylhydrazine; β - o -thiotoluoyl- α - o -tolyl-, m.p. 107°, β - p -thiotoluoyl- α - p -tolyl-, m.p. 63° (Bz derivative, m.p. 143.5°), and β - p -thiotoluoyl- α - o -tolyl-, m.p. 62°, S -methylhydrazine; β -thioacetyl- α -phenyl- α - S -dimethylhydrazine, b.p. 115—120°/2 mm.; β -thioacetyl- α -phenyl- α -benzyl- S -methylhydrazine, m.p. 78°; β -hexahydrothiobenzoyl-, b.p. 150°/1 mm., β -phenylthioacetyl-, m.p. 76°, and β - m -tolylthioacetyl-, m.p. 58°, α -phenyl- α - S -dimethylhydrazine. The N -Bz derivatives of thiobenz- (I), m.p. 160°, and thionaphth- (II), m.p. 181°, -phenylhydrazides, o -thiotolu- o -tolylhydrazide, m.p. 182°, and phenylthioacetphenylhydrazide (III), m.p. 171°, and the N - p -nitrobenzoyl derivatives of (III), m.p. 182°, and of the S -Me derivatives of (I), m.p. 188°, and (II), m.p. 151°, are described. Benzoylation occurs in all cases on the NH₂aryl. The reactions of $\text{R}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{NHR}'$ and $\text{R}\cdot\text{CS}\cdot\text{NMe}\cdot\text{NHR}'$ with the Grignard reagent are discussed. $\text{NHMe}\cdot\text{NHPh}$ with $\text{CH}_2\text{Ph}\cdot\text{CS}_2\text{H}$ gives β -phenylthioacetyl- α -phenyl- β -methylhydrazine, m.p. 99° (Bz derivative, m.p. 122°), which with MgEtI gives (probably) α -phenyl- β -(β -phenylethyl)- β -methylhydrazine, m.p. 182° (hydrochloride, m.p. 240°). $\text{CH}_2\text{Ph}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{NPhMe}$ similarly yields (probably) α -phenyl- β -benzyl- α -methyl- β -ethylhydrazine, m.p. 138° (hydrochloride, m.p. 235°). Demethylation (HI in Ac₂O at 325°) does not occur with $\text{R}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{NMePh}$, occurs to the extent of

48% with $\text{R}\cdot\text{CS}\cdot\text{NMe}\cdot\text{NHPh}$, and is complete with $\text{R}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{NHPh}$ and $\text{R}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{R}'$, whilst $\text{R}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{NMePh}$ loses 1 Me. F. R. G.

Resistance to heat of certain diazonium compounds and theory of the formation of azo-complexes. E. JUSTIN-MUELLER (Bull. Soc. chim., 1935, [v], 2, 1370—1376).—Diazobenzene and its $p\text{-NO}_2$ - and $p\text{-SO}_3\text{H}$ derivatives were studied. The unsubstituted amine gives the least stable diazo-compound. In AcOH the latter compound is decomposed completely by heat; in dil. HCl it slowly darkens, and after sufficient heating decomp. into phenol is complete, whilst in H₂SO₄ it darkens less when boiled and gives a purer phenol. The presence of SO₃H augments considerably the stability of the diazo-compound. The chloride can be heated to boiling without much change and is more resistant in presence of HCl. Prolonged boiling is necessary to effect complete replacement of N₂. In AcOH, it is transformed without other decomp. into azoxybenzene-4':4'-disulphonic acid (I). The $p\text{-NO}_2$ has the same effect as $p\text{-SO}_3\text{H}$ in HCl, but in AcOH there is no stabilising effect and azoxy-compound is not formed. The low resistance of diazo-compounds in weakly acid or somewhat alkaline solution is due to the transformation of the diazonium salt into the diazo-hydrate which, unstable in itself, is an intermediate in the formation of azo-compounds. The production of (I) from diazotised sulphanilic acid is explained as follows: $2\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{OH} \rightarrow 2\text{C}_6\text{H}_4\cdot\text{N}^+\text{SO}_3^- + 2\text{H}_2\text{O} + [\text{N}_2]$ $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}^+\text{SO}_3^- \rightarrow \text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N} + \text{OH} + \text{H}_2\text{O}$. H. W.

Replacement of the amino-group of aromatic amines by hydrogen. L. C. RAIFORD and F. W. OBERST (Amer. J. Pharm., 1935, 107, 242—244).—The yields of hydrocarbon or halogenated derivative obtained by treatment of diazotised aromatic amines with 10% excess of 10% H₃PO₂ below 5° during 4 days (cf. A., 1902, i, 245) are > those obtained by means of EtOH in those cases where both methods give the required product. H. G. M.

Iodo- m -nitrophenols. P. BRENANS and P. LARIVAILLE (Compt. rend., 1935, 201, 81—83).—The $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{OH}$ of Schlieper (A., 1894, i, 18) is a mixture of 6-iodo-3-nitrophenol (cf. Proc.C.S., 1901, 17, 131) (*Et* ether, m.p. 84°; $\alpha\beta$ -dihydroxypropyl ether, m.p. 113—114°; *Ac* derivative, m.p. 122°; *Na* salt, cryst.; *Ba* salt, cryst.) and a tri-iodo- m -nitrophenol, m.p. 135° (*Me* ether, m.p. 126°; *Et* ether, m.p. 92°; *Ac* derivative, m.p. 185°). F. R. G.

Manufacture of *tert*-alkylphenols.—See B., 1935, 716.

Manufacture of 3- and 5-chloro-2-hydroxydiphenyl.—See B., 1935, 716.

New method of fission of certain ethers. M. MOTTIER (Helv. Chim. Acta, 1935, 18, 840—845).—*o*-, *m*-, and *p*-OH·C₆H₄·OMe heated (6 hr.) under pressure with NaNH₂ (2 mols.) in tetrahydronaphthalene or PhMe give 75—100% yields of the corresponding C₆H₄(OH)₂. *o*-, *m*-, and *p*-C₆H₄Me·OMe, *o*-, *m*-, and *p*-C₆H₄(OMe)₂, PhOMe, and Ph₂O under similar conditions do not give phenols. F. R. G.

Physical constants and configuration of the stereoisomeric isoeugenols. K. VON AUWERS (Ber., 1935, 68, [B], 1346—1350).—Examination of the physical consts. of the stereoisomeric isoeugenols and their derivatives shows that according to m.p., b.p., and $E\Sigma$ vals. the solid variety has the *trans* configuration (I). As judged by the val. of n the reverse Me·C·H (I.) is the case, but in this instance H·C·C₆H₃(OH)·OMe the rules are based on the behaviour of hydroaromatic compounds. With aromatic substances of known configuration n of the *trans* forms is > that of the *cis* varieties.

H. W.

Catalytic reduction reactions. II. K. PACKEN-DORFF (Ber., 1935, 68, [B], 1251—1254).—Catalytic hydrogenation (PtO₂) of *m*-C₆H₄(OH)₂ in EtOAc at room temp. causes fairly rapid absorption of 4.5 H₂ with production of cyclohexane (I) and cyclohexanol, also obtained from *o*- and *p*-C₆H₄(OH)₂ and from pyrogallol. The yield of (I) increases with the activity of the catalyst. Similarly *o*-OH·C₆H₄·CO₂Et yields Et hexahydroalicylate and Et hexahydrobenzoate. OH is not protected by conversion into OAlk, since *m*- and *p*-C₆H₄(OMe)₂ yield (I) and hexahydroanisole. The product of these changes is invariably a mixture of completely and incompletely hydrogenated material. Completion of the reaction is not effected by use of fresh catalyst, addition of HCl, etc. The production of alcohols and hydrocarbons is therefore due to independent, parallel reactions. The view that catalytic reduction of OH is possible only when at. groupings which can be adsorbed at the surface of the catalyst are present in the mol. is supported by the observation that saturated aliphatic alcohols (glycerol, hexoses, n -hexyl alcohol) are not reduced under the experimental conditions, whereas elimination of OH is observed from olefinic alcohols (geraniol, citronellol, linalool).

H. W.

Molecular rearrangements of anilinothiols. T. B. JOHNSON and M. L. MOORE (Science, 1935, 81, 643—644).—Two types of reaction product can be formed by mol. rearrangement of a given anilinothiol. *o*-NO₂·C₆H₄·SCI gives with NH₂Ph a good yield of *o*-nitro-*S*-anilinothiophenol, which when heated at a definite temp. or digested with NH₂Ph at the b.p. is transformed into 2-nitro-4'-aminodiphenyl sulphide. When warmed with NaOH-EtOH it is transformed into *o*-nitro-*o*'-thioldiphenylamine.

L. S. T.

Synthesis of *p*-methoxybenzyl acetate. A. OFNER (Helv. Chim. Acta, 1935, 18, 951—956).—*p*-CH₂Cl·C₆H₄·OMe is prepared in bulk from anisole, CH₂O, and HCl gas (cf. Quelet, A., 1934, 290) and converted by NaOAc-AcOH into *p*-OAc·CH₂·C₆H₄·OMe accompanied by *o*-OAc·CH₂·C₆H₄·OMe and *pp*-CH₂(C₆H₄·OMe)₂.

F. R. G.

Action of iodides on sterol dibromides and the preparation of cholestenone. R. SCHOENHEIMER (J. Biol. Chem., 1935, 110, 461—462).—When sterol dibromides are heated in EtOH solution with NaI or KI, I is liberated with regeneration of the double linking. The reaction is quant. A method is given

for the prep. of cholestenone in 89% yield from cholesterol dibromide, by oxidation with CrO₃ in C₆H₆ and treatment with NaI.

J. N. A.

Action of mercuric iodide on cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1367).—HgI₂ and cholesterol at 145—150° afford α -cholesterylene and cholesteryl oxide. Under the same conditions HgCl₂ gives a non-cryst. mixture of saturated Cl-compounds retaining much unattacked HgCl₂.

H. W.

Degradation of sitostanol acetate by chromic acid. E. FERNHOLZ (Helv. Chim. Acta, 1935, 18, 1003—1004; cf. this vol., 542, 617).—A reply to Ruzicka *et al.* regarding priority.

F. R. G.

Degradation of sterol derivatives with chromic acid. L. RUZICKA (Helv. Chim. Acta, 1935, 18, 1004).—A reply (cf. preceding abstract).

F. R. G.

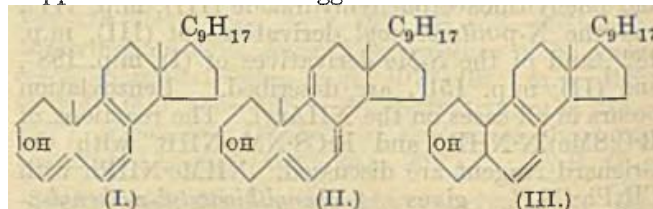
[Chemistry of] algæ.—See this vol., 1040.

Condensation of biosterol with maleic and citraconic anhydrides.—See this vol., 1176.

Ring structure of calciferol.—See this vol., 1036.

Vitamin-D and its reaction products.—See this vol., 1037.

Constitution of calciferol (vitamin-D). O. ROSENHEIM and H. KING (Chem. and Ind., 1935, 699—701).—Review of the lit. shows that the appended constitution expresses the distinctive properties of tachysterol (I), *i.e.*, (1) the intense absorption in the ultra-violet region at 280 m μ enhanced by the proximity of the 3 conjugated double linkings to OH at C3, (2) liability to autoxidation, and (3) lack of crystallising power. The ease with which calciferol (II) crystallises and its increased resistance to autoxidation appear incompatible with the presence of 3 conjugated double linkings in a 10-membered ring. In the reaction (I) \rightarrow (II) a migration of double linkings is postulated and (II) appears the most probable structure. In the conversion of (II) into pyrocalciferol (III)—*isopyrocalciferol* it appears that ring closure between C5 and C10 occurs, since the compound is oxidised by HNO₃ to C₆HMe(CO₂H)₄ and gives Diels' hydrocarbon C₁₈H₁₆ when dehydrogenated with Se. The ring system of the sterols is therefore present in (III) for which the appended structure is suggested.



H. W.

Molecular shape of calciferol and related substances. J. D. BERNAL and D. CROWFOOT (Chem. and Ind., 1935, 701—702).—Details are recorded of the cell size and approx. mol. shape of a no. of sterols and allied compounds. The crystallographic evidence for or against the formulæ of Rosenheim *et al.* (preceding abstract) is difficult to assess, since no compound with a

10-membered ring has been examined by X-ray methods. Since higher cyclic hydrocarbons do not differ essentially from the corresponding fused-ring compounds, it may be considered that these new suggestions do not conflict with the X-ray evidence, whereas those of Windaus *et al.* clearly do so. Suprasterol I cannot have the spiran form, but there is no direct evidence that it has the structure (I), which demands a definite lengthening of the axis not observed in this compound. Suprasterol II is crystallographically peculiar and resembles rather closely anhyd. cholesterol with a definitely crossed ring system.

Parachor and chemical constitution. Structure of triphenylmethane dyes.—See this vol., 1059.

Absorption spectrum of malachite-green leucocyanide and the mechanism of the dark reaction after photolysis.—See this vol., 1052.

Exchange of a halogen atom in the aromatic ring for a nitrile group under the influence of nickel cyanide. T. ŚLEBODZIŃSKI (J. pr. Chem., 1935, [ii], 143, 115—122; cf. A., 1920, i, 44).—PhCl with KCN and NiCl₂ in H₂O at 260—270° gives 1·8% of BzOH; from PhBr and PhI the yields are 81% and 72%, respectively. The following furnish the corresponding toluic acids in the yields noted: *o*-, *m*-, and *p*-C₆H₄MeCl (7·4%, 4·6%, 4·6%); *o*- and *m*-C₆H₄MeBr (15%, 6%); *o*-, *m*-, and *p*-C₆H₄MeI (35%, 32%, 32%). *p*-C₆H₄Cl₂ yields terephthalic acid (12%), and *m*-C₆H₄I·CO₂H, isophthalic acid (99%). 4 : 4'-Dibromodiphenyl gives 4 : 4'-diphenic acid (5%); 1-C₁₀H₇Br yields α -C₁₀H₇·CO₂H (20%). *p*-C₆H₄Br·NO₂ and *p*-C₆H₄Br·NH₂ do not give *p*-NO₂·C₆H₄·CO₂H or *p*-NH₂·C₆H₄·CO₂H.

Local anaesthetics. Phenylprocaine.—See this vol., 1155.

Oxidation of phenyl derivatives of fatty acids with hydrogen peroxide in presence of copper. R. O. JONES and I. S. MACLEAN (Biochem. J., 1935, 29, 1877—1880).—Phenylation of straight-chain aliphatic acids increases their rate of oxidation by H₂O₂ in the presence of Cu; CH₂Ph·CO₂H is readily attacked, whilst in the absence of Cu more acid is oxidised with increasing length of chain.

Configurative relationship of benzylmethylacetic [α -benzylpropionic] to benzylmethylpropionic [β -benzyl-*n*-butyric] acid. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 110, 299—309).—As part of a study of the effect of the distance of the CO₂H and Ph groups from the asymmetric centre of the series of Ph acids, the change in rotation on converting *d*- α -benzylpropionic acid (I), b.p. 155°/2 mm., [*M*]_D²⁵ -48·3°, into *d*- β -benzylbutane (II), b.p. 80°/20 mm., [*M*]_D²⁵ +2·67°, is determined; the effect of exhaustive hydrogenation of the Ph group is also determined. It emerges that in substances of the type CHMeR·[CH₂]_n·CO₂H (R=alkyl, Ph, benzyl, or phenethyl and their H₆-derivatives) the change from *n*=0 to *n*=1 causes a change in the direction of

rotation. (I) is converted into (II) through 1-*Et* α -benzylpropionate, b.p. 95°/1 mm., -25·7°, *d*- β -benzyl-*n*-propyl alcohol, b.p. 105°/1 mm., [*M*]_D²⁵ +4·3°, 1- α -bromo- β -benzylpropane, b.p. 85°/1 mm., [*M*]_D²⁵ -17·3°, *d*- β -benzylbutyric acid, b.p. 160°/1 mm., [*M*]_D²⁵ +0·94°, 1-*Et* β -benzylbutyrate, b.p. 110°/1 mm., [*M*]_D²⁵ -1·61°, *d*- γ -benzyl-*n*-butyl alcohol, b.p. 115°/1 mm., [*M*]_D²⁵ 0·59°, and 1- γ -benzyl-*n*-butyl bromide, b.p. 110°/1 mm., [*M*]_D²⁵ -9·51°. *d*- α -cyclohexylmethylpropionic acid, b.p. 136°/1 mm., [*M*]_D²⁵ +10·8°, is converted into *d*- β -cyclohexylmethyl-*n*-butane, b.p. 191°/760 mm., [*M*]_D²⁵ -2·82°, through its *Et* ester, b.p. 105°/15 mm., [*M*]_D²⁵ +13·2°, 1- β -cyclohexylmethylpropyl alcohol, b.p. 114°/15 mm., [*M*]_D²⁵ -5·36°, and bromide, b.p. 108°/10 mm., [*M*]_D²⁵ -2·06°, 1- β -cyclohexylmethyl-*n*-butyric acid, b.p. 148°/1 mm., [*M*]_D²⁵ -3·96°, and its *Et* ester, b.p. 122°/12 mm., [*M*]_D²⁵ -3·29°, γ -cyclohexylmethyl-*n*-butyl alcohol, b.p. 120°/1 mm., [*M*]_D²⁵ -4·03°, and bromide, b.p. 112°/1 mm., [*M*]_D²⁵ +0·61°.

Configurative relationship of acids of phenethyl series to those of normal series. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 110, 311—321).—To study the effect of the distances of the CO₂H and Ph from the asymmetric centre of the series of "phenyl" acids, the change in rotation on converting γ -phenyl- α -methylbutyric acid (I), b.p. 155°/2 mm., [*M*]_D²⁵ -48·3°, into ϵ -phenyl- γ -methylpentane (II), b.p. 112°/15 mm., [*M*]_D²⁵ -4·76°, has been determined; the effect of exhaustive hydrogenation of the Ph has also been determined. It is deduced that configuratively related α -methyldecoic and γ -phenyl- α -methylbutyric acids rotate light in the same direction; it is also shown that δ -phenyl- β -methylvaleric and γ -phenyl- α -methylbutyric acids have opposite directions of rotation, and that exhaustive hydrogenation of the Ph has no effect on the direction of rotation except in the case of α -bromo- ϵ -phenyl- γ -methylpentane. (I) is converted into (II) through *Et* γ -phenyl- α -methylbutyrate, b.p. 120°/2 mm., +7·6°, δ -phenyl- β -methylbutyl alcohol, b.p. 157°/17 mm., [*M*]_D²⁵ -2·7°, and bromide, b.p. 151°/17 mm., [*M*]_D²⁵ -5·8°, δ -phenyl- β -methylvaleric acid, b.p. 162°/2 mm., [*M*]_D²⁵ -6·04°, its *Et* ester, b.p. 131°/2 mm., [*M*]_D²⁵ -4·9°, ϵ -phenyl- γ -methyl-*n*-amyl alcohol, b.p. 157°/17 mm., [*M*]_D²⁵ -3·99°, and bromide, b.p. 160°/17 mm., [*M*]_D²⁵ -2·29°. γ -cyclohexyl- α -methylbutyric acid, b.p. 156°/2 mm., [*M*]_D²⁵ +3·4°, is converted into ϵ -cyclohexyl- γ -methyl-*n*-pentane, b.p. 110°/15 mm., [*M*]_D²⁵ -2·82°, through *Et* γ -cyclohexyl- α -methylbutyrate, b.p. 101°/1 mm., [*M*]_D²⁵ +4·92°, δ -cyclohexyl- β -methylbutyl alcohol, b.p. 141°/17 mm., [*M*]_D²⁵ -2·09°, and bromide, b.p. 142°/15 mm., [*M*]_D²⁵ 0°, δ -cyclohexyl- β -methyl-*n*-valeric acid, b.p. 158°/2 mm., [*M*]_D²⁵ -2·36°, its *Et* ester, b.p. 162°/17 mm., [*M*]_D²⁵ -1·85°, ϵ -cyclohexyl- γ -methylamyl alcohol, b.p. 157°/17 mm., [*M*]_D²⁵ -1·84°, and bromide, b.p. 151°/15 mm., [*M*]_D²⁵ -1·12°.

Configurative relationships of derivatives of benzylmethyl- and phenylethylmethyl-, methylheptyl-, and methyloctyl-acetic acids. P. A. LEVENE (J. Biol. Chem., 1935, 110, 323—328).—*d*- α -Methylbutyric acid (I) is converted into *d*- α -phenyl- β -methylpentane, and *d*- α -benzylpropionic acid (II) leads to *l*- α -phenyl- β -methylpentane; hence (I) and

(II) are configuratively related. Since (I) is related to *d*- α -methylnonoic acid (III), (III) is related to (II). Since also *d*- α -methyldecoic acid (IV) is related to *d*- γ -phenyl- α -methylbutyric acid (V) and (III) and (IV) are related, it follows that (II) and (V) are related. The correlation of the configuration of (I) and *d*- α -phenyl- β -methylbutane (VI), b.p. 80°/12 mm., $[M]_D^{25} + 1.85^\circ$, involved the conversion of *d*-valeraldehyde by MgPhBr into α -phenyl- β -methyl-*n*-butyl alcohol, b.p. 68—70°/0.3 mm., and this was converted into (VI) with HI. On the basis of the max. rotation of (VI) those of the derivatives of β -phenyl- α -methylpropionic acid are calc. H. D.

Maximum rotations of configuratively related carboxylic acids containing a phenyl or a cyclohexyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 110, 329—342; cf. A., 1933, 821).—The max. rotations for substances of the type $\text{CHPhR} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{H}$ (I) and of similar substances with Ph replaced by cyclohexyl (II) ($\text{R} = \text{Me}$ or Et) are determined. With (I) there is a periodicity in the changes in direction of rotation on increasing n for the acids and their derived esters, carbinols, and halides. The acids and their esters do not follow Freudenberg's rule. With (II) and its derivatives for $n=0$ and $n=1$ the direction of rotation for $\text{R} = \text{Me}$ is opposite to that for $\text{R} = \text{Et}$. *r*- β -Phenyl-*n*-valeric acid is resolved with quinine and converted through *l*-Et β -phenylvalerate, b.p. 105°/1 mm., $[M]_D^{25} - 8.88^\circ$, γ -phenyl-*n*-amylalcohol, b.p. 118°/1 mm., $[M]_D^{25} - 4.41^\circ$, and bromide, b.p. 102°/1 mm., $[M]^{25} - 29.5^\circ$, *l*- γ -phenyl-*n*-hexoic acid, b.p. 156°/4 mm., $[M]_D^{25} - 1.17^\circ$, its *Et* ester, b.p. 121°/1 mm., $[M]^{25} - 4.09^\circ$, *d*- δ -phenyl-*n*-hexyl alcohol, b.p. 125°/5 mm., $[M]^{25} + 0.37^\circ$, and *l*-bromide, b.p. 125°/3 mm., $[M]_D^{25} - 3.25^\circ$, *l*- δ -phenylheptoic acid, b.p. 161°/1 mm., $[M]_D^{25} - 6.04^\circ$, its *Et* ester, b.p. 135°/1 mm., $[M]^{25} - 4.00^\circ$, and *l*- ϵ -phenyl-*n*-heptyl alcohol, b.p. 123°/1 mm., $[M]_D^{25} - 4.96^\circ$, into *l*- α -bromo- ϵ -phenyl-*n*-heptane, b.p. 125°/1 mm., $[M]_D^{25} - 11.6^\circ$. β -Phenylbutyric acid is resolved with quinine and converted through *l*-Et β -phenylbutyrate, b.p. 111°/4 mm., $[M]_D^{25} - 2.92^\circ$, *l*- γ -phenyl-*n*-butyl alcohol, b.p. 117°/8 mm., $[M]_D^{25} - 2.60^\circ$, and bromide, b.p. 120°/11 mm., $[M]_D^{25} - 7.58^\circ$, *l*- γ -phenyl-*n*-valeric acid, b.p. 137°/1 mm., $[M]_D^{25} - 1.89^\circ$, its *Et* ester, b.p. 112°/1 mm., $[M]^{25} - 2.54^\circ$, and *l*- δ -phenyl-*n*-amyl alcohol, b.p. 109°/1 mm., $[M]_D^{25} - 1.48^\circ$, into *l*- α -bromo- δ -phenyl-*n*-pentane, b.p. 125°/15 mm., $[M]^{25} - 1.84^\circ$. *d*- α -cyclohexylpropionic acid, b.p. 105°/1 mm., $[M]^{25} + 8.1^\circ$, is converted through its *Et* ester, b.p. 100°/15 mm., $[M]_D^{25} + 11.6^\circ$, *l*- α -cyclohexyl-*n*-propyl alcohol, b.p. 110°/15 mm., $[M]_D^{25} - 0.55^\circ$, and bromide, b.p. 110°/15 mm., $[M]_D^{25} + 3.8^\circ$, into *d*- β -cyclohexylbutyric acid, b.p. 145°/4 mm., $[M]^{25} + 2.5^\circ$. H. D.

Synthesis of 4-iodo- α -naphthoic acid. H. GOLDSTEIN, R. MOHR, and T. BLEZINGER (Helv. Chim. Acta, 1935, 18, 813—816).—A diazotised solution of 4 : 1- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{CN}$ in dioxan with KI in dil. H_2SO_4 gives 4-iodo-1-naphthonitrile, b.p. 200°/12 mm., m.p. 128 (corr.), hydrolysed (H_2SO_4) to 4-iodo- α -naphthoic acid, m.p. 213° (corr.). α -Naphthyloxamic acid with ICl yields 4-iodo- α -naphthyloxamic acid, decomp. 198° (corr.), not convertible into 4-iodo- α -naphthyl-

amine, and with Br yields 4-bromo- α -naphthylloxamic acid, decomp. 193° (corr.), hydrolysed to 4-bromo- α -naphthylamine. F. R. G.

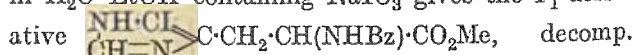
Substituted phenylacetoneitriles and derivatives. I. Phenyl-1-cyanocyclopropane, α -phenyl- γ -hydroxybutyronitrile, α -phenyl- γ -chlorobutyronitrile, and α -phenylcrotononitrile. E. C. KNOWLES and J. B. CLOKE (Rensselaer Polytech. Inst. Bull., Eng. Sci. Ser., No. 49, 24 pp.).—The substance, m.p. 177—178°, previously reported (A., 1932, 739) to be α -phenylacetacetamide is actually α -phenyl- β -methylglycidamide.

CH. ABS. (r)

*iso*Amyloxyvanadyl salicylates. P. BRAUMAN (Compt. rend., 1935, 200, 1854—1855).—Distillation of 50% aq. VOCl_2 with *iso*amyl alcohol until the temp. of the vapour reaches 129—130° gives an anhyd. solution of VOCl_2 , which with Li_2CO_3 affords probably $(\text{C}_5\text{H}_{11}\text{O})_2\text{VO}$; addition of *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{R}$ affords the following *iso*amyloxyvanadyl salicylates, $\text{C}_5\text{H}_{11}\text{O} \cdot \text{VO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{R}$, blue when solid, black or brown when molten (unchanged in absence of O_2 and H_2O): *Me*, m.p. 175.5—176.5°; *Et*, m.p. 179—180°; *iso*amyl, m.p. 149.5—151.5°; *Ph*, m.p. 252—253°; β - C_{10}H_7 , m.p. 179.5—180.5°. R. S. C.

Acetylation of phenolic hydroxyl groups. M. A. VJAZKOVA (J. Appl. Chem. Russ., 1935, 8, 471—475).—*o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, Ac_2O , and H_3PO_4 in C_6H_6 at room temp. afford *o*- $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, in 80% yield, and of high purity. The method is of general applicability. R. T.

Substitutions in tyrosine and histidine. H. BAUER and E. STRAUSS [with, in part, E. MASCHMANN] (Ber., 1935, 68, [B], 1108—1115; cf. A., 1932, 402).—Model experiments with NH_2 -acids in relationship to substitutions in proteins are recorded. Treatment of tyrosine (I) in $\text{H}_2\text{O} - \text{NaHCO}_3$ with I slowly affords di-iodotyrosine (II), m.p. 204° (decomp.). The corresponding *Me*, decomp. 190°, and *Et*, decomp. 171°, esters are similarly obtained. (I) cannot be iodinated in acid solution, but the influence of the "basic situation" is pronounced in the amide, which in AcOH gives di-iodotyrosineamide, decomp. 180°. Treatment of the Na salt of (I) with $\text{Hg}(\text{OAc})_2$ does not immediately yield a mercurated product, but if the mixture is warmed tyrosine-3-mercurihydroxide separates; it is transformed by $\text{I} - \text{KI}$ in H_2O into (II). A moniodotyrosine could not be obtained. Iodination of nitrotyrosine, its *Me* ester [m.p. 173° (slight decomp.)] (hydrochloride, decomp. 197°), or 3-nitrotyrosineamide, m.p. 196° (decomp.), could not be effected in presence of NaOH , NaHCO_3 , NH_3 , or $\text{C}_5\text{H}_5\text{N}$ or by HgO and I; similarly, the introduction of Hg appears impossible. Addition of $\text{I} - \text{KI}$ to a solution of *isobenzoyl*histidine *Me* ester in $\text{H}_2\text{O} - \text{EtOH}$ containing NaIO_3 gives the I_1 -derivative



The view that substitution of I in the glyoxaline ring occurs initially at N from which the halogen becomes transferred to C is supported by the non-occurrence of the reaction when the group is substituted and the inability of such compounds to couple with diazo-derivatives. *N*-Bromoacetyl-3-nitro-

tyrosine, m.p. 175° (decomp.), its *Me* ester, m.p. 127°, *N*-glycyl-3-nitrotyrosine, m.p. 247° (decomp.), and -nitro-4'-hydroxybenzylidiketopiperazine, decomp. 254°, are incidentally described. H. W.

Anacardic acid. I. Anacardic acid and tetrahydroanacardic acid. II. Constitution of tetrahydroanacardic acid. P. P. PILLAY (J. Indian Chem. Soc., 1935, 12, 226—231, 231—236).—I. Anacardic acid (I), $C_{22}H_{32}O_3$, m.p. 23—25° (improved method of purification described) (cf. J.C.S., 1887, 51, 663) has 2 active H (Zerevitnov) and 2 aliphatic double linkings. The *Et* ester [prepared from the Ag salt of (I) and *EtI*] decomposes on distillation. Oxidation of (I) with HNO_3 affords $H_2C_2O_4$, but with $KMnO_4$ cœnanthic acid and other dicarboxylic acids are also formed. (I) gives an intense violet coloration with $FeCl_3$ -*EtOH*, and has a phenolic OH, but is not acetylated by boiling Ac_2O nor methylated by Me_2SO_4 and alkali. (I) is hydrogenated (Pd-C) to tetrahydroanacardic acid (II), $C_{22}H_{36}O_3$, m.p. 92.5—93° [*Me*, m.p. 49°, and *Et* ester, m.p. 38°; *Ac* derivative (III), m.p. 78°; *Br*₁-derivative, m.p. 77°], oxidised by $KMnO_4$ in $COMe_2$ and H_2O to palmitic and oxalic acids.

II. When heated at about 200° in an atm. of N_2 (I) loses CO_2 and yields a resin and anacardol (IV), $C_{21}H_{32}O$, b.p. 215—220°/14 mm., hydrogenated (Pd-C) to tetrahydroanacardol (V), m.p. 53—54° [*Ac* derivative, m.p. 42°, also obtained when (III) is heated; *Bz* derivative, m.p. 54°; *phenylcarbamate*, m.p. 79—80°; *Na* derivative], also obtained together with some tetrahydroanacardyl tetrahydroanacardate, m.p. 49°, hydrolysed to (II) and (V). (V) is readily oxidised by $KMnO_4$ in $COMe_2$ to oxalic and palmitic acids. (IV) is decomposed by distillation under atm. pressure, and the resulting phenols on fusion with KOH give salicylic acid. From the foregoing reactions, together with the fact that (II) gives a violet coloration with $FeCl_3$, it is concluded that (II) is 2-hydroxy-3-*n*-pentadecylbenzoic acid.

H. G. M.

ψ -Chlorides and ψ -esters of *o*-dicarboxylic acids. A. KIRPAL, A. GALUSCHKA, and E. LASSAK (Ber., 1935, 68, [B], 1330—1334).—The action of PCl_5 on phthalic and 4-chlorophthalic anhydride leads exclusively to the normal chlorides, whereas under similar conditions the more highly substituted anhydrides yield ψ -chlorides which can only be partly isomerised to the true chlorides by prolonged heating at the b.p. $C_6H_4\langle\begin{smallmatrix} OCl \\ CO \end{smallmatrix}\rangle O$ is converted by $MeOH$ containing pptd. $CaCO_3$ at 15—20° into *Me*₂ phthalate, m.p. 53°, which passes below its b.p. into $C_6H_4(CO_2Me)_2$. as-3:6-Dichlorophthalyl chloride (I), m.p. 122°, is partly isomerised at its b.p. to 3:6-dichlorophthalyl chloride, m.p. 31°, which slowly when solid, more rapidly in solution, and instantaneously in the presence of animal C reverts to (I). Even in absence of a neutralising medium (I) is converted into *Me*₂ 3:6-dichloro- ψ -phthalate, m.p. 134°; *Me* 3:6-dichlorophthalate, from $C_6H_4(CO_2Ag)_2$ and MeI , has m.p. 82°. 3:4-Dichlorophthalic anhydride and PCl_5 give 3:4-dichloro- ψ -phthalyl chloride, m.p. 133°, whence *Et*₂ 3:4-

dichloro- ψ -phthalate (II), m.p. 79° (*Et*₂ 3:4-dichlorophthalate has m.p. 80°). (II) is hydrolysed by a small amount of H_2O to 1-*Et* H 3:4-dichlorophthalate (II), m.p. 184°, also obtained by esterification of 3:4- $C_6H_3Cl_2(CO_2H)_2$ with *EtOH* and H_2SO_4 . 2-*Et* H 3:4-dichlorophthalate, m.p. 164°, is obtained by partial hydrolysis of the *Et*₂ ester or by the action of abs. *EtOH* on 3:4- $C_6H_3Cl_2(CO_2H)_2$. (II) and $SOCl_2$ in CCl_4 yield chloroethoxy-3:4-phthalide, m.p. 87°. H. W.

Preparation of β -amino-acids. J. V. SOUDI (J. Amer. Chem. Soc., 1935, 57, 1279).—Slow evaporation of a mixture of $CHPh:C(CO_2Et)_2$ and 10% *EtOH*- NH_3 and passage of HCl into the *Et*₂O extract of the product, gives 47% of the hydrochloride of *Et* β -amino- β -phenylethane- $\alpha\alpha$ -dicarboxylate, which is hydrolysed (dil. HCl) to β -amino- β -phenylpropionic acid [also obtained by evaporation of a mixture of $CHPh:C(CO_2H)_2$ and 10% aq. NH_3]. H. B.

Condensation of homophthalaldehyde to 2-phenylnaphthalene-5:2'-dialdehyde. P. BAUMGARTEN (Ber., 1935, 68, [B], 1316—1317).—2-Phenylnaphthalene-5:2'-dialdehyde (I), m.p. 126.5°, is formed by the action of boiling 1% $NaOH$ on homophthalaldehyde (II), thus strengthening the hypothesis that (II) is an intermediate compound in the formation of (I) from *o*-aldehydo- ω -aminostyrene-*N*-sulphonic acid. H. W.

Synthesis of dimethoxycinnamaldehydes. K. FEUERSTEIN (J. pr. Chem., 1935, [ii], 143, 174—178).—Veratraldehyde and *o*-veratraldehyde condensed with $MeCHO$ ($MeOH$ - KOH) yield, respectively, 3:4-dimethoxycinnamaldehyde, m.p. 83.5°, b.p. 164°/3 mm. (semicarbazone, m.p. 185°; oxime, m.p. 82°; thiosemicarbazone, m.p. 182°; aldazine, m.p. 200°; phenylhydrazone, m.p. 133°), and 2:3-dimethoxycinnamaldehyde, m.p. 77.5°, b.p. 160—161°/5 mm. (semicarbazone, m.p. 198°; oxime, m.p. 115°; thiosemicarbazone, m.p. 200°; aldazine, m.p. 182.5°; phenylhydrazone, m.p. 134°). E. W. W.

Complete synthesis of dicyclo-[2:2:2]-octanone and dicyclo-[2:2:2]-octane. G. KOMPPA (Ber., 1935, 68, [B], 1266—1272).—Oxidation of *p*-isopropylphenylacetonitrile, b.p. 140—142°/16 mm., with boiling HNO_3 (*d* 1.21) gives homoterephthalic acid (I) accompanied by considerable amounts of terephthalic acid (II). Since oxidation of *p*-isopropylbenzyl chloride yields (II) exclusively, the best method of preparing (I) consists in treating $CN\cdot C_6H_4\cdot CH_2\cdot CN$ with H_2SO_4 - H_2O at 100°. Hydrogenation of *Me*₂ homoterephthalate, b.p. 161—165°/8 mm., in *AcOH* containing colloidal Pt at 45°/4 atm. and hydrolysis of the product with boiling HCl affords hexahydrohomoterephthalic acid, m.p. 146—147° (which is not dehydrated by $AcCl$), and small amounts of the (?) corresponding *cis*-acid, m.p. 121—125°. Dry distillation of *Mg* hexahydrohomoterephthalate (the *Ca*, *Ba*, *Zn*, and *Pb* salts are less satisfactory) gives dicyclo-[2:2:2]-octanone (III), m.p. 176°, in 50—60% yield. Reduction of dicyclo-[2:2:2]-octanoneoxime, m.p. 117—118°, with *Na* and *EtOH* yields dicyclo-[2:2:2]-octylamine, m.p. 138—140° in sealed tube (hydrochloride, m.p. > 300°; picrate, m.p. 222—223°;

corresponding *carbamide*, m.p. 182.5—183°. (III) is reduced by Na and EtOH to dicyclo-[2 : 2 : 2]-*octanol*, m.p. 216—217° in sealed tube (*phenylurethane*, m.p. 138—139°; *acetate*, b.p. 121—123°/15 mm.), converted by PCl₅ into dicyclo-[2 : 2 : 2]-*octyl chloride*, which is transformed by Na and abs. EtOH into dicyclo-[2 : 2 : 2]-*octane*, m.p. 168° (corr.). H. W.

Isomerism of halochromic compounds. III. P. PFEIFFER, K. SCHWENZER, and K. KUMETAT (J. pr. Chem., 1935, [ii], 143, 143—156).—Colourless NH₄ salts and coloured oxonium salts of unsaturated basic ketones, obtained with HClO₄ (A., 1933, 1052; 1934, 76), are similarly obtained with HBF₄ or H₂SiF₆. Thus *p*-dimethylaminostyryl Me ketone forms a blue *borofluoride*, m.p. 152° (decomp.), fairly stable to H₂O, which when dissolved in HCO₂H and treated with HBF₄ and Et₂O isomerises to the colourless *borofluoride*, m.p. about 150° (decomp.), immediately hydrolysed by H₂O. Ph *p*-dimethylaminostyryl ketone treated in EtOH with HBF₄ yields a colourless *borofluoride*, m.p. about 172° (decomp.), converted by CH₂Cl·CO₂H into the reddish-violet *borofluoride*. *p*-Chlorophenyl *p*'-dimethylaminostyryl ketone similarly gives a colourless and a bluish-violet *borofluoride*, the latter obtained by treating the former with AcOH and HBF₄. By treatment in AcOH with H₂SiF₆, *p*-dimethylaminostyryl Me ketone forms colourless and reddish-violet *silicofluorides*, and *p*-chlorophenyl *p*'-dimethylaminostyryl ketone a colourless *silicofluoride*.

From saturated ketones, only colourless NH₄ perchlorates are obtained. *p*-Dimethylaminobenzophenone gives a *perchlorate*, m.p. 162°, and *p*-dimethylamino-*p*'-methoxybenzophenone a *perchlorate*, m.p. 161°; in each case the solution of the perchlorate in AcOH or EtOH is bright yellow, suggesting the existence of a coloured form. Michler's ketone gives a colourless *diperchlorate*, m.p. 210°, and a yellow *perchlorate*, m.p. 147°. Ph *p*-dimethylaminophenylethyl ketone, m.p. 49.5—50.5° (*oxime*, m.p. 89—89.5°; *H sulphate*, m.p. 70°), obtained by reduction (PtO₂) of Ph *p*-dimethylaminostyryl ketone, yields a *perchlorate*, m.p. 167°. Ph *p*-nitrodiphenyl ketone, new m.p. 157° (cf. B., 1933, 662), obtained from *p*-nitrodiphenyl and BzCl (AlCl₃ in PhNO₂), is reduced (SnCl₂) to Ph *p*-aminodiphenyl ketone, m.p. 143°, which gives a *perchlorate*, decomp. 218°. *p*-Aminophenyl *p*-diphenyl ketone forms a *perchlorate*, m.p. 230°, and its Bz derivative, a yellow *perchlorate*. E. W. W.

α-Halogenoketones. α-Chlorodibenzyl ketone. C. PREVOST and A. SOMMIERE (Bull. Soc. chim., 1935, [v], 2, 1151—1165).—The reactivity of the halogen and CO of α-halogenoketones towards mildly alkaline reagents is compared. α-*Chlorodibenzyl ketone* (I) (prep. by S₂Cl₂), m.p. 68.5°, b.p. 195°/12 mm. (decomp.) (oxidised to > 1 mol. of BzOH), with HCN-EtOH gives the *cyanohydrin* (II), m.p. 135—136° (only the less sol. isomeride is isolated), but with NaOAc-AcOH the α-*OAc-ketone*, b.p. 197°/13 mm., hydrolysed by NaOH-EtOH (slightly > 1 mol.) to α-*γ-diphenylpropan-α-ol-β-one* (III), m.p. 116°; (III) is also obtained from (I) and hot aq. Na₂CO₃, is oxidised by CrO₃ to PhCHO and BzOH, and with alkali gives the dienolic form, OH·CPh·C(OH)·CH₂Ph, since acidification of its alkaline solution yields some

CH₂Ph·CH(OH)·COPh (IV); (IV) is equally isomerised by alkali to give some (III). (III) and S₂Cl₂ in CCl₄ give γ-*chloro-α-γ-diphenylpropan-α-ol-β-one*, m.p. 95°. With NaOMe at 100° (I) gives α-*phenoxydibenzyl ketone*, m.p. 68°, which is decomposed by distillation/11 mm. to give some PhOH and (?) α-*γ-diphenyl-β-γ-oxido-Δ^α-propylene* (V), b.p. 173°/11 mm. (I) and NaOMe under other conditions give (V), which, with 1 : 3-*diphenyl-1 : 3-dibenzylcyclobuta-2 : 4-dione*, m.p. 153° (obtained by polymerisation of CH₂Ph·CPh·CO initially formed), is also obtained by use of KOH in hot dry Et₂O. (I) and conc. aq. KCN (4—5 mols.) give αβ-*oxido-β-cyano-α-γ-diphenylpropane* (VI), m.p. 118.5°, hydrolysed by 5% H₂SO₄ or aq. HCl to a mixture of (IV) and β-*cyano-α-γ-diphenylpropane-αβ-diol*, m.p. 129°, also obtained from (III) and an excess of HCN in EtOH. (II) with KOH gives (I), but with KCN-EtOH affords (IV). (VI) and HCl in C₆H₆ give (I) and (II). R. S. C.

Fluorene series. II. 3-Nitrofluorenone and its derivatives. F. E. BARDOUT (Anal. Assoc. Quim. Argentina, 1934, 22, 123—132; cf. A., 1932, 153).—3-Hydroxyfluorenone [*oxime*, m.p. 188° (decomp.)] in 10% aq. NaOH with Me₂SO₄ gives 3-*methoxyfluorenone*, m.p. 96—97°. Diazotised 3-amino-fluorenone with Cu₂Br₂ (Sandmeyer) gives 3-*bromo-fluorenone*, m.p. 165° (corr.). Variations in the recorded m.p. of 3-nitrofluorenone and its oxime are discussed. F. R. G.

Addition reactions of phenyl vinyl ketone. V. Anthrone. C. F. H. ALLEN and S. C. OVERBAUGH (J. Amer. Chem. Soc., 1935, 57, 1322—1325).—Anthrone (I) and CH₂Cl·CH₂·COPh (II) in 70% H₂SO₄ at 100° (bath) for 10—15 min. give 63% of 9-β-*benzoyl-ethyl-* (III), m.p. 141—144°, and 15% of 9 : 9-*di-β-benzoyl-ethyl-10-anthrone* (IV), m.p. 187—188° (*dioxime*, m.p. 244—245°). (IV) is similarly obtained from (II) and (III). A solution of (III) in MeOH-NaOH (trace) slowly deposits (IV). (III) and (IV) are both oxidised (CrO₃, AcOH) to anthraquinone [also formed from (III) and Br in CHCl₃]. (III) is converted by 80% H₂SO₄ at 100° (bath) into Bz-1-*phenylbenzanthrone* (V), m.p. 182—183°, also formed from (I) and CHPh·CH·CHO in 1-C₁₀H₇Cl at 250—260°, which is oxidised (CrO₃, AcOH) to 1-benzoylanthraquinone. Mechanisms suggested (lit.) for the production of benzanthrone from (I) and unsaturated aldehydes are discussed. MgBu⁺Cl and (V) give 10-*tert-butyl-Bz-1-phenylbenzanthron-10-ol*, m.p. 159—160°; with other Grignard reagents 1 : 4-addition occurs (cf. this vol., 751) and affords 4-*ethyl-* (VI), m.p. 120—122°, 4-*n-butyl-* (VII), m.p. 81—82°, 4-*n-hexyl-* (VIII), m.p. 88°, 4-*cyclohexyl-*, m.p. 190—191°, 4-*phenyl-* (IX), m.p. 223—224°, 4-*benzyl-* (X), m.p. 179—180°, 4-β-*phenylethyl-*, m.p. 154—155°, and 4-*styryl-* (XI), m.p. 186—187°. Bz-1-*phenylbenzanthrone* (VI), (VII), and (VIII) are oxidised (method: *loc. cit.*) to 1-benzoyl-4-*ethyl-*, m.p. 198°, 4-*n-butyl-*, m.p. 123—124°, and 4-*n-hexyl-*, m.p. 128°, -*anthraquinone*, respectively; these are all oxidised (CrO₃, aq. AcOH) to 4-benzoyl-anthraquinone-1-carboxylic acid, also obtained directly from (IX). (X) similarly gives 1 : 4-dibenzoylanthraquinone. (IX) could not be oxidised. H. B.

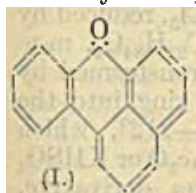
Addition of magnesium methyl iodide to benzylidenepropiophenone. L. I. SMITH and L. I. HANSON (J. Amer. Chem. Soc., 1935, 57, 1326—1328).—Decomp. of the product (I) from benzylidenepropiophenone and MgMeI with cold dil. HCl (method: Kohler, A., 1904, i, 595) gives 1-phenyl-2:3-dimethylindene (II), m.p. 68—69°, oxidised (2% KMnO_4) to $\alpha\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$. Decomp. of (I) with aq. NH_4Cl affords $\alpha\gamma$ -diphenyl- β -methyl- Δ^4 -buten- γ -ol, decomp. on attempted distillation, which is oxidised (KMnO_4 in H_2O or COMe_2 ; O_3) to BzOH and COPhMe and is converted by MeOH -conc. HCl into (II) [probably by way of $\text{CPhMe}\cdot\text{CMe}\cdot\text{CHPh}\cdot\text{OH}$ (or the chloride) and subsequent loss of H_2O (or HCl)]. 3-Phenyl-2-methylindene (III) and MgMeI (2 mols.) give 1-hydroxy-3-phenyl-1:2-dimethylindene, m.p. 107—109°, which could not be converted into 3-phenyl-1:2-dimethylindene. (III) is reduced (red P, HI , AcOH) to the indanone, which with MgMeI affords 1-hydroxy-3-phenyl-1:2-dimethylindane, m.p. 101—102°, dehydrated (AcOH - H_2SO_4) to (II).

H. B.

Nitration of 1:9-benzanthrone by nitrogen dioxide and formulation of 1:9-benzanthrone. K. LAUER and K. ATARASHI (Ber., 1935, 68, [B], 1373—1376).—Benzanthrone (I), solid or in solution, is very readily attacked by NO_2 giving Bz -1-nitro-

benzanthrone and small amounts a complex product, apparently a dihydroxydibenzanthronyl or dihydroxydibenzanthrone. The Bz -ring does not therefore exist in a radical form nor as part of the C_{10}H_8 system, but is an unsaturated arrangement with aliphatic properties. (I) has therefore the annexed constitution.

H. W.



Free radicals. R. A. LABRIOLA (Anal. Asoc. Quím. Argentina, 1934, 22, 109—122).—A solution of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ in $\text{C}_6\text{H}_5\text{N}$ heated with CPh_3Cl yields α -(β -phenylpropionyl)- β -triphenylmethylhydrazine, m.p. 165—166° (decomp.), oxidised ($\text{Br}\cdot\text{H}_2\text{O}$) to the corresponding azo-derivative (I), m.p. 55—56°, which when heated in xylene in an atm. of CO_2 gives N_2 and $\text{CPh}_3\cdot\beta$ -phenylethyl ketone, m.p. 125°. (I) when heated in C_6H_6 (O_2 atm.) yields CPh_3 peroxide; $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ similarly yields α -cinnamoyl- β -triphenylmethylhydrazine, m.p. 161—162°, which with saturated aq. CaCl_2 (CO_2 atm.) gives a compound, m.p. 185—186°, containing Cl and N , and $\text{CPh}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$. $\text{CPh}_3\cdot\text{C}\cdot\text{COCl}$ and $\text{CPh}_3\cdot\text{NH}\cdot\text{NH}_2$ in Et_2O give α -phenylpropionyl- β -triphenylmethylhydrazine (II), m.p. 158—159°, and in $\text{C}_6\text{H}_5\text{N}$ give α -(β -chlorocinnamoyl)- β -triphenylmethylhydrazine (III), m.p. 193—194°. (II) in CHCl_3 oxidised by aq. $\text{K}_3\text{Fe}(\text{CN})_6$ gives the corresponding azo-derivative, m.p. 70°. (III) in CHCl_3 with 2N- NaOH yields a Cl -free compound, m.p. 70°, which when heated in C_6H_6 (CO_2 atm.) gives N_2 and a resin.

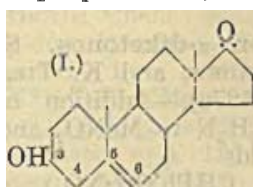
F. R. G.

Polyterpenes and polyterpenoids. XCVIII. Steric inversion of C 3 of sterols and male sexual hormones. L. RUZICKA, H. WIRZ, and J. MEYER (Helv. Chim. Acta, 1935, 18, 998—1003).—*epi*-Dihydrocholesterol is converted by PCl_5 into α -

cholestyl chloride, m.p. 114—115°, and by PBr_3 to α -cholestyl bromide, m.p. 115—115.5°; these with CrO_3 in AcOH give, respectively, 3-chloro- α -cholestan-17-one (I), m.p. 173°, obtained by Butenandt *et al.* (this vol., 413) and the 3-*Br*-compound, m.p. 163—164°, sublimes 130—140°/0.01 mm. [semicarbazone, m.p. 262° (decomp.)]. (I) has no activity in the capon test, but its isomeride, m.p. 128° (cf. A., 1934, 1221), is active. (I) is an intermediate of unknown orientation in the conversion of dehydroandrosterone (*trans*) into androsterone (*cis*).

F. R. G.

Sexual hormones. V. Artificial preparation of the male sexual hormone *trans*-dehydroandrosterone and of androstene-3:17-dione. L. RUZICKA and A. WETTSTEIN. VI. Androstane-diols and their methyl derivatives. Specificity of male sexual hormone activity. L. RUZICKA, M. W. GOLDBERG, and J. MEYER (Helv. Chim. Acta, 1935, 18, 986—994, 994—998; cf. this vol., 346).—V. Cholesteryl acetate dibromide with CrO_3 in AcOH gives Na 3-acetoxy- $\Delta^{5:6}$ -choleenate (3-*OAc*-acid, m.p. 186—187°; 3-*OH*-acid, m.p. 241—242°) and 3-acetoxy- $\Delta^{5:6}$ - α -cholestan-17-one, m.p. 171—172°, isolated as its semicarbazone, m.p. 273—275°, hydrolysed (H_2SO_4) to 3-hydroxy- $\Delta^{5:6}$ - α -cholestan-17-one (I) in



two readily interconvertible forms, m.p. 140—141° and 152—153°, of which the latter is identical chemically and physiologically with dehydroandrosterone isolated by Butenandt *et al.* (this vol., 413; cf. Schoeller *et al.*, this vol., 981) from men's urine. (I) brominated in AcOH , subsequently oxidised (CrO_3 , AcOH), and then reduced (Zn , AcOH) yields $\Delta^{4:5}$ - α -cholelene-3:17-dione.

VI. Androsterone (II) with MgMeI in Et_2O gives 3-*epihydroxy*-17-hydroxy-17-methylandrosterane (methyl-androstanediol) (III), m.p. 184—185°. Androstane-3:17-dione with MgMeI in Et_2O gives 3:17-*di*-hydroxy-3:17-dimethylandrosterane (dimethylandrostanediol) (IV), m.p. 150°. The monosuccinyl derivative, m.p. 185—185.5°, of (II) was hydrogenated (PtO_2 , H_2) to 3-monosuccinyl α -dihydroandrosterone, m.p. 207—208°. All m.p. are corr. The activity of the above compounds in the capon test is described. (III) is more active than (II) but (IV) is inactive.

F. R. G.

Constitution of dehydroandrosterone and its preparation from cholesterol. E. S. WALLIS and E. FERNHOLZ (J. Amer. Chem. Soc., 1935, 57, 1379—1380).—Dehydroandrosterone (I) has been prepared (as acetate) by oxidation (CrO_3) of cholesteryl acetate dibromide. The stereochemical arrangement of the OH in (I) is, therefore, the same as in cholesterol [but not as in androsterone (Butenandt and Dannenbaum, this vol., 413)].

H. B.

Androsterone. IV, V.—See this vol., 1033.

Action of alkali on acylated ketoximes. I. Effect of structure and configuration. R. P. BARNES and A. H. BLATT (J. Amer. Chem. Soc., 1935, 57, 1330—1332; cf. A., 1934, 773).— α -Benzoin-oxime propionate, benzoate, and cinnamate (I),

anisoyl-phenyl- and -*o*-chlorophenyl-carbinol oxime acetates, isobutyroinoxime acetate, and α -benzoyl- α -phenylethyl alcohol oxime acetate undergo fission (to aldehyde and nitrile; cf. *loc. cit.*) when treated with cold aq. 5% NaOH [for (I) aq. EtOH-NaOH is used]. β -Benzoinoxime propionate, benzoate, and cinnamate and β -benziloxime propionate and cinnamate similarly regenerate the oxime. From the above and other (*lit.*) data, it follows that the structural factor determining fission of an acylated ketoxime is the presence of OH, CO₂H, or CO in the α -position to the C:N linking. Furthermore, when one of these groups is *anti* to the OAcyl, fission (a second-order Beckmann rearrangement) occurs; hydrolysis takes place only if the group is *syn*. H. B.

Mechanism of the diacetyl reaction. H. MULLER (Z. physiol. Chem., 1935, 233, 276—280).—Lang's view (A., 1932, 834) of the reaction between creatine and AcBz could not be confirmed. Attempts to condense guanidine or derivatives with AcBz usually gave labile amorphous products. *as*-Phenylmethylguanidine (I) affords a compound containing (I) and AcBz in approx. the ratio 1 : 1 (not 3 : 2 as assumed by Lang). Condensation of AcBz with CO(NH₂)₂ in acid or alkaline solution gives a cryst. *bisglyoxalone* (?), C₁₁H₁₂O₂N₄. J. H. B.

Action of nitromethane on α -diketones. S. FUJISE, O. TAKEUCHI, T. KAMIOKA, and K. TIBA (Ber., 1935, 68, [B], 1272—1276).—Addition of benzil in powder form or in C₅H₅N to MeNO₂ and NaOEt in well-cooled EtOH yields OH·CHPh·CH·NO₂Na (whence CHPh·CH·NO₂), a little PhCHO, and considerable amount of EtOBz. With KOH as condensing agent, CH₂Bz·NO₂ is formed. Fural in presence of NaOEt affords α -nitro- β -furylethylene and Et furan-2-carboxylate (I), whereas Ph 2-furyl diketone gives CHPh·CH·NO₂ and (I). H. W.

Preparation of chloroacetylpyrocatechol. H. D. HOBERMAN (J. Amer. Chem. Soc., 1935, 57, 1382).—CH₂Cl·CO₂H (50 g.), *o*-C₆H₄(OH)₂ (50 g.), and freshly distilled POCl₃ (50 g.) heated in SO₂ for 1 hr. give chloroacetylpyrocatechol (53.6 g.), m.p. 173°. H. B.

2-Mesityl-1 : 4-naphthaquinone and its derivatives. H. C. TUAN (J. Chinese Chem. Soc., 1935, 3, 141—149).—Mesitylene and α -naphthaquinone condense (AlCl₃) to 2-mesityl-1 : 4-naphthaquinone (I), m.p. 172°, reduced to the -1 : 4-dihydroxynaphthalene, m.p. 168—169°. (I) is brominated to 3-bromo-2-mesityl-1 : 4-naphthaquinone, m.p. 147°, which with HNO₃ yields 3-bromo-2-(3 : 5-dinitro-2 : 4 : 6-trimethylphenyl)-1 : 4-naphthaquinone, m.p. 232—233°, with NaOEt forms 3-ethoxy-2-mesityl-1 : 4-naphthaquinone (II), m.p. 97—98°, and with CN·CH₂·CO₂Et affords *Et* 3-mesityl-2- α -naphthaquinonylecyanoacetate, m.p. 113—120°, hydrolysed to a substance, C₂₁H₁₇O₅N, m.p. 318—320°. (II) and AcCl lead (AlCl₃) to 3-hydroxy-2-(3-acetyl-2 : 4 : 6-trimethylphenyl)-1 : 4-naphthaquinone, m.p. 203°. F. R. S.

Blue-fluorescing substance in the corpus luteum.—See this vol., 1145.

Echinenone and pentaxanthin: two new carotenoids found in the sea-urchin.—See this vol., 1145.

Chemistry of heparin.—See this vol., 1144.

Lactone of sulphite waste and tsugaresinol. H. EMDE (Helv. Chim. Acta, 1935, 18, 807; cf. this vol., 623).—Tsugaresinol has the composition C₂₀H₂₀O₆ and not C₁₉H₁₈O₆ as stated by Slotta (this vol., 754). F. R. G.

Neutral saponins. II. Degradation of a genin of the neutral sapogenins to a derivative of the bile acids. R. TSCHESCHE and A. HAGEDORN (Ber., 1935, 68, [B], 1412—1420).—The relationship of the neutral saponins of *Digitalis* to the bile acids is established and the presence of 27 C atoms in the genin skeleton is placed beyond doubt. Tigogenin (isolation described) is converted by NaOAc and boiling Ac₂O into its acetate, m.p. 219°, [α]_D²⁵ -49.5° in CHCl₃, which when drastically oxidised with CrO₃ gives as main product an acid, C₂₇H₄₂O₅, m.p. 221—222° (oxidised by CrO₃ to a substance, C₂₇H₄₀O₅, m.p. 184.5°), one or more further acids, and (in 10% yield) an acetylated lactone, m.p. 219°, [α]_D²⁵ -49.5° in CHCl₃, hydrolysed to a lactone, C₂₂H₃₄O₃, m.p. 233.5, [α]_D²⁵ -41.2° in CHCl₃. Oxidation of the latter substance by CrO₃ in AcOH yields the ketolactone, C₂₂H₃₂O₃, m.p. 254°, [α]_D²⁵ -22.8° in CHCl₃, reduced by Zn-Hg and 15% HCl to the lactone, C₂₂H₃₄O₂, m.p. 199°, [α]_D²⁵ -44.4° in CHCl₃. This is transformed by MgPhBr with opening of the lactone ring into the diphenylcarbinol, C₃₄H₄₆O₂, m.p. 211—212°, which contains 2 OH; under the influence of Ac₂O or KHSO₄ it loses 1 H₂O giving a tetrahydrofuran derivative, C₃₄H₄₄O, m.p. 173.5°, the formation of which shows the OH to be in the 1 : 4-position to one another. Oxidation of the carbinol affords a neutral substance, an acid, C₃₄H₄₂O₄, m.p. 216—217° after softening at 132—133° (sparingly sol. Na salt; Me ester, m.p. 189.5°), and an acid, m.p. 253—254° (decomp.) (anhydride, m.p. 186°, [α]_D²¹ -58.7° in CHCl₃), identical with aetioallobilianic acid. H. W.

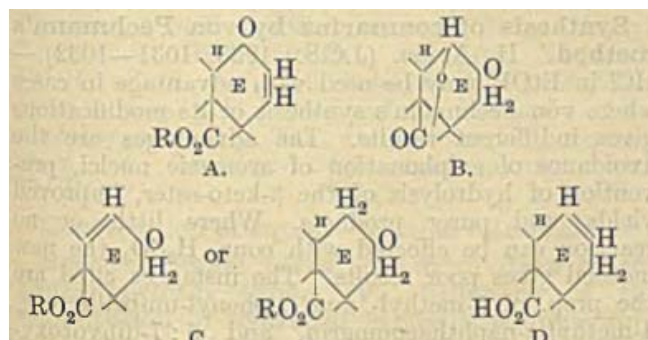
Constitution of hederagenin and oleanolic acid. VII, VIII, and IX. Z. KITASATO [with C. SONE] (Acta Phytochim., 1935, 8, 207—220, 254—262, 315—324).—VII. Treatment of the mother-liquor from the crystallisation of the Br-lactone (I), obtained by the action of HBr-AcOH on dehydrodiacetyl-hederagenin Me ester, with KOH-MeOH affords dehydrohederagenin, C₃₀H₄₆O₄, m.p. >300° (decomp.) (Ac₂ derivative, m.p. 152°, and its Me ester, m.p. 198°). (I) is transformed by KOH-MeOH, Zn dust and AcOH, or AcOH into the lactone of dehydrodiacetylhederagenin, m.p. 245—247°. The re-formation of a double linking by treatment of a Br-derivative with Zn dust and AcOH is further exemplified since oleanylene (II), readily obtained by heating acetyloleanolic acid at about 300°, adds HBr in AcOH-CHCl₃ giving the Br₂-compound, C₂₉H₄₈Br₂, m.p. 186—188° (decomp.), re-converted into (II). Oleanonic acid (III) and excess of Br in MeOH afford dibromo-oleanonolactone, m.p. 275° (decomp.), converted by KOH-MeOH into the substance, C₃₁H₄₅O₄Br or C₃₁H₄₇O₄Br, m.p. 195—198°. (III) is transformed

by conc. HCl in boiling AcOH into *oleanonolactone* (IV), $C_{30}H_{46}O_3$, m.p. 354° (*oxime*, m.p. $>300^\circ$). Me oleanonate and conc. HCl in AcOH at 100° afford (IV) and *Me epioleanonate*, m.p. $168-170^\circ$. *Oleanonolactone* has m.p. $335-337^\circ$ (decomp.). Treatment of (III) with P and HI in AcOH appears to lead to acetyloleanololactone, m.p. $337-338^\circ$, and anhydro-oleanyleno- or -oleaneno-lactone, m.p. 248° . Me_2 hederagenonedicarboxylate and HBr-AcOH at room temp. give the *monolactone*, m.p. 285° (decomp.), of hederagenonedicarboxylic acid. Bromination of the lactone of Me_2 oleanolate gives the *compound*, $C_{22}H_{49}O_7Br$, m.p. 244° (decomp.). $[\alpha]_D$ is recorded for many derivatives of hederagenin and oleanolic acid.

VIII. ψ -Ketohederagenin is transformed by $Ac_2O-NaOAc$ into the Ac_2 derivative (V), m.p. 215° . Treatment of the lactone of ketodiacylhederagenin (VI) with HBr-AcOH causes opening of the lactone ring, giving *isoketodiacylhederagenin* (VII), $C_{34}H_{50}O_7$, m.p. $275-279^\circ$, $[\alpha]_D^{25} -72.7^\circ$ in $CHCl_3$. Similar treatment of the monobromolactone of diacylhederagenin affords the *compound*, $C_{34}H_{49}O_6Br$, transformed by Me_2SO_4 and KOH-MeOH into the *substance*, $C_{31}H_{49}O_4Br$, m.p. 158° . Reduction of (V) with Na-Hg in boiling 90% EtOH yields the *compound*, $C_{30}H_{46}O_4$, m.p. 347° (Ac_2 derivative, m.p. $257-260^\circ$, $[\alpha]_D +39.6^\circ$ in $CHCl_3$), isomeric with the lactone of *aldehydehydroederagenin*. Similar treatment of (VII) affords the *substance*, $C_{30}H_{46}O_4$, m.p. 316° , $[\alpha]_D^{25} +228.2^\circ$ in $CHCl_3$.

IX. Ketoacetyloleanolactone and HBr-AcOH yield *isoketoacetyloleanolic acid*, m.p. $324-330^\circ$, $[\alpha]_D^{25} +46.6^\circ$ in $CHCl_3$, converted by CH_2N_2 into the *Me ester* (VIII), m.p. 205° . The following reductions with Na-Hg are described: (VII) to *isodehydro-oleanolic acid*, $C_{30}H_{46}O_3$, m.p. $295-300^\circ$, $[\alpha]_D +206.8^\circ$ in $CHCl_3$ (*Me ester*, m.p. 198° , and its Ac derivative (IX), m.p. $215-219^\circ$, $[\alpha]_D +229.7^\circ$ in $CHCl_3$); *Me isoketoacetyloleanolate* to (IX), transformed by HBr-AcOH in $CHCl_3$ into the *lactone*, $C_{32}H_{49}O_4Br$; *Me ψ -ketoacetyloleanolate* to *dehydro-oleanololactone*, $C_{30}H_{46}O_3$, m.p. 337° (Ac derivative, m.p. 347°); ketoacetyloleanolactone to a *substance* transformed by CH_2N_2 into *Me ketoacetyloleanolate*, m.p. $193-195^\circ$, $[\alpha]_D^{25} -9.5^\circ$ in $CHCl_3$.

The relationships of the various keto-compounds with regard to the structure of the E ring are therefore summarised as follows:

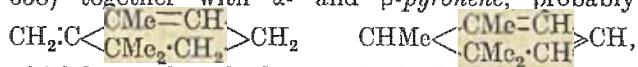


A is common to (VI), ketohedragonic acid, ketoacetyloleanolic acid, keto-oleanonic acid, and the Me esters of these substances, whilst all keto-lactones

from diacylhederagenin, hedragonic acid, hedragenonedicarboxylic acid, acetyloleanolic acid, and oleanonic acid have B in common. Structure C is shared by ketohedragenonedicarboxylic acid and Me ketohedratricarboxylate, all keto-acids (or Me esters) from Br-lactones (by action of EtOH-KOH) and those from keto-lactones (by action of Na-Hg), and by *isoketodiacylhederagenin Me ester* and (VIII). Structure D is common to ring E of hederagenin and oleanolic acid.

H. W.

Pyrolysis of pinene. Pyronenes, a new type of monocyclic terpene. G. DUPONT and R. DULOU (Compt. rend., 1935, 201, 219-221).—Examination of the Raman spectra of the products of pyrolysis of pinene vapour at 350° shows the presence of limonene and *alloocimene* (cf. Arbusov, A., 1934, 658) together with α - and β -pyronene, probably



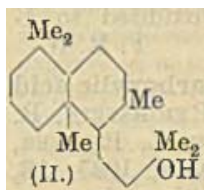
which by catalytic hydrogenation both give 1:1:2:3-tetramethylcyclohexane, also obtained by catalytic hydrogenation of methyl- γ -cuclogeraniolene (Escourrou, A., 1926, 1238).

F. R. G.

Optical activity and chemical constitution. I. Optically active bases and acids. M. SINGH (J. Indian Chem. Soc., 1935, 12, 219-225).— $[\alpha]_D$ of *p*-dimethylaminoanilocamphor (I), m.p. 135.5° , prepared by heating camphorquinone with *p*- $NH_2 \cdot C_6H_4 \cdot NMe_2$, EtOH, and anhyd. Na_2SO_4 , and $[\alpha]_D$, $[\alpha]_{3780}$, and $[\alpha]_{5461}$ of *m*-dimethylaminoanilocamphor, m.p. $125-126^\circ$, similarly prepared, have been determined in a no. of solvents. The effect of solvents of the type PhX ($X=NH_2$, NO_2 , halogen, H, Me) is discussed. (I) has a very high $[\alpha]_D$, viz., 3000° in NH_2Ph solution.

H. G. M.

Diterpene alcohol from the wood of *Dacrydium biforme*. I. J. R. HOSKING and C. W. BRANDT (Ber., 1935, 68, [B], 1311-1316).—Extraction of the wood with boiling EtOH gives a small amount of an acid, m.p. 158° , and 7% of a neutral oil which when fractionally distilled yields *manool* (I), $C_{20}H_{34}O$, m.p. 53° , b.p. $144-145^\circ/0.2$ mm., $[\alpha]_D^{25} +30.4^\circ$ in abs. EtOH. (I) is unsaturated and when hydrogenated (PtO_2) in neutral medium affords *tetrahydromanool* (II), m.p. $55-56^\circ$, whereas in presence of Pt-black *dihydromanool* (III), b.p. $151-152^\circ/0.2$ mm., m.p. $44-45^\circ$, is produced. (I) contains 1 OH (Zerevitinov) which is *tert.* since



it fails to react with $o-C_6H_4(CO)_2O$. It yields an acetate and a benzoate. With HCl in dry Et_2O (I) gives a trihydrochloride, m.p. 119° , identical with that from manoyl oxide, whilst the dihydrochloride, m.p. 120° , from (III) is identical with that from dihydromanoene or dihydroscleareol. Treatment of (I) with 98% HCO_2H yields a tricyclic hydrocarbon, $C_{20}H_{32}$, b.p. $121^\circ/0.3$ mm. (II) is converted by HCl in Et_2O into a non-cryst. hydrochloride, transformed by NH_2Ph at 100° into *tetrahydromanoene*, b.p. $141-142^\circ/0.2$ mm., which is ozonised and then transformed by H_2O into a ketone, $C_{18}H_{32}O$, b.p. $150^\circ/0.4$ mm.

(semicarbazone, m.p. 202°), and an acid, $C_{16}H_{28}O_2$, m.p. 129°. H. W.

Hinokinin as the enantiomorph of cubebinolide. L. H. BRIGGS (J. Amer. Chem. Soc., 1935, 57, 1383—1384).—The physical data for hinokinin (Yoshiki and Ishiguro, J. Pharm. Soc. Japan, 1933, 53, 73) and cubebinolide (I) (Mameli, A., 1922, i, 347) show that these are enantiomorphous. The structure

$\begin{array}{c} \text{CHR}\cdot\text{CH}_2 \\ \text{CHR}\cdot\text{CO} \end{array} \rightarrow \text{O}$ (II), $R=3:4\text{-CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2$, is suggested for (I). Matairesinol (Easterfield and Bee, J.C.S., 1910, 97, 1028) is probably (II), $R=4:3\text{-(OH)(OMe)C}_6\text{H}_3\cdot\text{CH}_2$. H. B.

Volatile vegetable substances. III. Constitution and synthesis of carlina oxide. A. S. PFAU, J. PICTET, P. PLATTNER, and B. SUSZ (Helv. Chim. Acta, 1935, 18, 935—951).—2-Furylacetylene (modified prep.) with MgEtBr and CH_3PhCl in Et_2O gives benzyl-2-furylacetylene, b.p. 115°/1 mm. (cf. Gilman *et al.*, A., 1933, 1055), which gives a Raman spectrum, and has α and β and oxidation products identical with those of natural carlina oxide, which was hydrogenated in presence of Ni to α -phenyl- γ -2-furylpropane (I), also obtained by hydrogenation of the crude extract of the roots of *Carlina acaules*, L. Hydrogenation of 2-furfurylideneacetophenone yields 2-furfurylacetylene, m.p. 37—37.5°, the semicarbazone, m.p. 104°, of which when distilled with KOH in EtOH gives (I) (Raman spectrum recorded), which with maleic anhydride in Et_2O gives (Diels-Alder) 3:6-endo-3- γ -phenylpropyl- Δ^4 -tetrahydrophthalic anhydride, m.p. 77.5—78° (decomp.); this in aq. Na_2CO_3 is hydrogenated (Ni) to 3:6-endo-3- γ -phenylpropylhexahydrophthalic acid, m.p. 146° (decomp.) (corr.) (anhydride, m.p. 96.5°). F. R. G.

Preparation of saturated tertiary carboxylic acids. T. REICHSTEIN, H. R. ROSENBERG, and R. EBERHARDT (Helv. Chim. Acta, 1935, 18, 721—724).—*tert.*- $\text{C}_6\text{H}_{11}\text{Cl}$ with Me pyromucate and AlCl_3 in CS, gives the Me ester, b.p. 108—110°/11 mm., of 5-*tert.*-amylfuran-2-carboxylic acid, m.p. 68.5—69°, oxidised (KMnO_4) to $\text{CMe}_2\text{Et}\cdot\text{CO}_2\text{H}$. Similarly 1-chloro-1-methylcyclohexane yields the Me ester, b.p. 145—146°/11 mm., of 5-(1-methylcyclohexyl)furan-2-carboxylic acid, m.p. 110°, oxidised to 1-methylcyclohexane-1-carboxylic acid. F. R. G.

Synthesis of coumarone-2-[1-]carboxylic acid and of hydroxycoumarones. T. REICHSTEIN, R. OPPENAUER, A. GRUSSNER, R. HIRT, L. RHYNER, and C. GLATTHAAR (Helv. Chim. Acta, 1935, 18, 816—830; cf. A., 1933, 281).—*o*-Vanillin with excess of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and NaOEt in EtOH gives the Me ether, m.p. 219.5—220.5° (corr.), sublimes 190—200°/low pressure, of 6-hydroxycoumarone-1-carboxylic acid, m.p. 229—230° (corr.), sublimes 190°/low pressure (Me ester, m.p. 78°; Na salt, cryst.), decarboxylated (Cu-quinoline) to 6-hydroxycoumarone, b.p. 71°/0.4 mm., m.p. 42° [Me ether, b.p. 68°/0.4 mm. (NO_2 -derivative, b.p. 135°/0.25 mm., m.p. 149—150°)]. 2:3:4-(OMe) $_3\text{C}_6\text{H}_2\cdot\text{CHO}$ heated with AlCl_3 in PhMe gives 2-hydroxy-3:4-dimethoxybenzaldehyde, m.p. 71—72°, which with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and NaOEt in EtOH yields 5:6-dimethoxycoumarone-1-carboxylic acid, m.p.

202° (corr.), sublimes 180—200°/0.2 mm., decarboxylated to 5:6-dimethoxycoumarone, m.p. 55°. Resorcyraldehyde with CH_2PhCl and NaOEt in EtOH gives 2-hydroxy-4-benzoyloxybenzaldehyde (I), b.p. 135—155°/0.1 mm., m.p. 77—80°, together with 2-hydroxy-4-benzoyloxy-3- or 5-benzylbenzaldehyde, b.p. 180—200°/0.1 mm., m.p. 94—95°, 2:4-dibenzoyloxybenzaldehyde, b.p. 220°/0.1 mm., m.p. 89—90.5°, 2:4-dibenzoyloxy-3- or 5-benzylbenzaldehyde, m.p. 230—240°/0.015 mm., m.p. 81.5—82.5° (semicarbazone, m.p. 180°), a compound, $\text{C}_{21}\text{H}_{18}\text{O}_3$, m.p. 154.5—155°, sublimes 185—195°/0.02 mm., and a compound, $\text{C}_{14}\text{H}_{12}\text{O}_3$ (?), m.p. 150—152°. (I) with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and NaOEt in EtOH yields 5-benzoyloxybenzaldehyde-1-carboxylic acid, m.p. 208—209° (corr.), the Me ester, m.p. 112° (corr.), of which with HCl in AcOH give 5-hydroxycoumarone-1-carboxylic acid, m.p. 255—270° (decomp.) [Me ester, m.p. 180° (corr.)], decarboxylated to 5-hydroxycoumarone, b.p. 85°/0.3 mm., m.p. 57—58°. 2:4-Dihydroxy-6-methoxybenzaldehyde (II) with CHPhN_2 gives 2-hydroxy-4-benzoyloxy-6-methoxybenzaldehyde (III), b.p. 190—195°/0.5 mm., m.p. 103° (corr.). (II) with CH_2PhCl gives 2:4-dihydroxy-6-methoxy-3- or 5-benzylbenzaldehyde, m.p. 201° (corr.), a compound, $\text{C}_{15}\text{H}_{14}\text{O}_4$, m.p. 91°, and a compound, $\text{C}_{22}\text{H}_{20}\text{O}_4$, m.p. 148°. (III) with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and NaOEt in EtOH yields 5-benzoyloxy-3-methoxycoumarone-1-carboxylic acid, m.p. 207—208° (corr.) [Me ester (IV) (two forms), m.p. 89—90° and 106—107° (corr.)]. Similarly 2-hydroxy-4:6-dimethoxybenzaldehyde gives 3:5-dimethoxycoumarone-1-carboxylic acid, m.p. 235—237° (corr.) [Me ester (V), m.p. 116—117°]. (IV) heated with HCl in AcOH gives 5-hydroxy-3-methoxycoumarone-1-carboxylic acid, m.p. 210°, sublimes [Me ester, m.p. 250° (corr.)], which with excess of CH_2N_2 yields (V) and is decarboxylated to 5-hydroxy-3-methoxycoumarone, b.p. 110°/0.6 mm., m.p. 55—57°. The Na salt of 5-hydroxycoumarone heated in CO_2 at 180—200° yields probably 5-hydroxycoumarone-4-carboxylic acid, m.p. 210—215° (decomp.). *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, Pr^iCOCl , and AlCl_3 in PhNO_2 give 2:4-dihydroxyisobutyrophenone, b.p. 150°/0.3 mm., which with 1 mol. Me_2SO_4 and NaOMe in MeOH yields 2-hydroxy-4-methoxyisobutyrophenone, b.p. 120—123°/0.2 mm., m.p. 27°, and this with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and NaOEt in EtOH gives 5-methoxy-2-isopropylcoumarone-1-carboxylic acid, m.p. 180°, decarboxylated to 5-methoxy-2-isopropylcoumarone, b.p. 95°/0.2 mm., m.p. —8° to —7° (picrate, m.p. 65°). F. R. G.

Synthesis of coumarins by von Pechmann's method. H. APPEL (J.C.S., 1935, 1031—1032).—HCl in EtOH may be used with advantage in cases where von Pechmann's synthesis or its modifications gives indifferent results. The advantages are the avoidance of sulphonation of aromatic nuclei, prevention of hydrolysis of the β -keto-ester, improved yields, and purer products. Where little or no reaction can be effected with conc. H_2SO_4 the new method gives poor results. The instances cited are the prep. of β -methyl- and β -phenyl-umbelliferone, 4-methyl- α -naphthacoumarin, and 6:7-dihydroxy-4-methylcoumarin. H. W.

Synthesis of flavonol and of dihydroflavonol. M. MURAKAMI and T. IRIE (Proc. Imp. Acad. Tokyo,

1935, 11, 229—231).—*o*-Hydroxychalkone is converted by alkali (2*N*-NaOH, NEt_3 , or dil. aq. NH_3) and H_2O_2 at room temp. into a mixture of flavonol (also obtained from flavanone with the above reagents) and dihydroflavonol, the latter being the main product.

P. G. C.

Yellow colouring matter from the wood of *Adina cordifolia*, Hook. J. B. LAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 257—261).—Extraction of the wood with EtOH gives cryst., optically active, yellow *adinin* (I), $\text{C}_{16}\text{H}_{14}\text{O}_7 \cdot 3\text{H}_2\text{O}$ ($3\text{H}_2\text{O}$ lost at 120°), which darkens at 195 — 196° , shrinks at 200° , and then gradually decomposes without melting (*hydrobromide*, $\text{C}_{16}\text{H}_{14}\text{O}_7 \cdot \text{HBr}$, decomp. without melting; NH_4 salt, m.p. 130°). Solutions of (I) in EtOH, PhOH, and H_2SO_4 are fluorescent. On treatment with Mg-EtOH-HCl and with $\text{Zn-NH}_3\text{-H}_2\text{O}$, (I) becomes colourless. (I) contains 1 OMe (Zeisel), and on demethylation with HI yields yellow *nor-adinin*, which shrinks at 213 — 214° and decomposes above 232° without melting. The absorption spectrum of (I) in 1% EtOH solution has a band between 4250 and 4650 Å., max. at 4590 Å. (I) may be a xanthone or an isoflavone. H. G. M.

Synthetical experiments in the chromone group. XVI. Chalkones and flavanones and their oxidation to flavones by selenium dioxide. H. S. MAHAL, H. S. RAI, and K. VENKATARAMAN (J.C.S., 1935, 866—868).—Flavones are conveniently prepared in one stage by the oxidation of *o*-hydroxy-chalkones with SeO_2 . 2-Hydroxy-4-benzoyloxyphenyl styryl ketone, m.p. 135° , is converted by prolonged boiling with P_2O_5 in EtOH containing a little H_2O into 7-benzoyloxyflavanone, m.p. 104° after softening at 102° . 2-Hydroxy-4-benzoyloxyphenyl 4-methoxystyryl ketone, m.p. 132 — 133° , similarly yields 7-benzoyloxy-4'-methoxyflavanone, m.p. 114° . 2-Hydroxy-4-benzoyloxyphenyl 4-benzoyloxy-styryl ketone has m.p. 139° . Protocatechualdehyde, CH_2PhCl , and K_2CO_3 in COMe_2 afford 3:4-dibenzoyloxybenzaldehyde, m.p. 93° , whence 2-hydroxy-4-benzoyloxyphenyl 3:4-dibenzoyloxy-styryl ketone, m.p. 137° . 2-Hydroxy-4-methoxyphenyl 4-benzoyloxy-styryl ketone, m.p. 125 — 126° , gives 7-methoxy-4'-benzoyloxyflavanone, m.p. 98 — 99° , debenzylated to 4'-hydroxy-7-methoxyflavanone, m.p. 160° . β -Naphthafavanone is oxidised by SeO_2 in xylene at 140 — 150° to β -naphthafavone, m.p. 163° . *o*-Hydroxyphenyl styryl ketone similarly yields flavone. 7-Benzoyloxyflavone, m.p. 187° , is debenzylated to 7-hydroxyflavone, m.p. 240° . 7-Benzoyloxy-4'-methoxyflavone has m.p. 137° . 1-Acetyl-2-naphthol, $\text{CHPh} \cdot \text{CH} \cdot \text{CHO}$, and 50% NaOH in EtOH afford 3-styryl-2:3-dihydro-1:4- β -naphthapyrone, m.p. 144° , oxidised to 3-styryl-1:4- β -naphthapyrone, m.p. 200° , also obtained by condensation of 3-methyl-1:4- β -naphthapyrone with PhCHO. H. W.

Constitution of equol.—See this vol., 1032.

Spectrographic investigation of dyes of the benzopyrylium type. IV. Influence of the substitution of hydroxyl in the benzopyrylium nucleus. K. HAYASHI (Acta Phytochim., 1935, 8, 179—206).—The relationships between absorption spectra and chemical constitution of hydroxy-

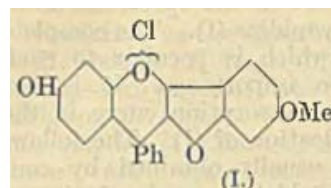
flavylium chlorides are extremely complicated. Not only the first well-developed band, but also the second and the third are important in the spectrochemical characterisation of anthocyanidins (I). The complete character of the graph, which is peculiar to each individual, is of decisive importance. It is not sufficient to determine the absorption curve in the visible end for the identification of (I). The following flavylium chlorides, usually obtained by condensation of the requisite aldehyde and substituted acetophenone in EtOAc saturated with HCl, are described: 4'-hydroxy-, decomp. 127 — 128° ; 7-hydroxy-, gradual decomp. $>140^\circ$ after becoming discoloured at 130° ; 7:4'-dihydroxy-, m.p. $>260^\circ$ after softening at 180° ; 7-hydroxy-4'-methoxy-, decomp. 182° ; 3:7:4'-trihydroxy-, decomp. $>290^\circ$ after shrinking at 260° ; 3:7-dihydroxy-4'-methoxy-, decomp. 211° after softening at 208° ; 7-hydroxy-4'-methoxy-*o*-methyl-, decomp. 242 — 243° after shrinking at 125° ; 4'-hydroxy-8-methoxy-, m.p. 138 — 139° after softening at 115° ; 6:4'-dimethoxy-, decomp. 138 — 139° ; 3:3':4'-trihydroxy-, decomp. 222 — 223° after softening at 160° ; 3:7:3':4'-tetrahydroxy-, m.p. $>270^\circ$; 3:6:7:4-tetrahydroxy:5'-dimethoxy-, decomp. 257 — 258° ; 7:8:4'-trihydroxy-, decomp. 267° after becoming brown at 100° and softening at 250° ; 7:8-dihydroxy-4'-methoxy-, decomp. 193 — 194° after softening at 180° . H. W.

Synthetical experiments in the chromone group. XVII. Further observations on the action of sodamide on *o*-acyloxyacetophenones. D. C. BHALLA, H. S. MAHAL, and K. VENKATARAMAN (J.C.S., 1935, 868—870).—Further examples of the NaNH_2 method of flavone synthesis are described (this vol., 90). The acid chlorides are prepared by SOCl_2 . *O*-Acyl derivatives (I) of ketones are made in $\text{C}_5\text{H}_5\text{N}$. Reaction with NaNH_2 is effected by shaking with (I) in Et_2O for 1—10 days. *o*-Benzoyloxyacetophenone and NaNH_2 afford *o*-hydroxydibenzoylmethane, m.p. 121 — 122° , and a substance, $\text{C}_{15}\text{H}_{12}\text{O}_3$, m.p. 110 — 111° , both of which are transformed by H_2SO_4 into flavone. The following are described: *o*-acetylphenyl *o*-methoxybenzoate, m.p. 81° ; *o*-acetylphenyl 2:4-dimethoxybenzoate, m.p. 77° ; 2-hydroxy-, m.p. 70° , and 2-benzoyloxy-, m.p. 68° ; 5-benzoyloxyacetophenone; 2-hydroxy-5-benzoyloxydibenzoylmethane, m.p. 68° ; 2-hydroxy-5-benzoyloxydibenzoylmethane, m.p. 103 — 104° ; 6-benzoyloxyflavone, m.p. 144 — 145° ; 1-acetyl-2-naphthyl benzoate, m.p. 85 — 86° ; β -naphthafavone, m.p. 165° , and small amounts of a substance, $\text{C}_{19}\text{H}_{14}\text{O}_3$, m.p. 171° ; 1-acetyl-2-naphthyl *o*-methoxybenzoate, m.p. 102 — 103° ; 2'-methoxy- β -naphthafavone, m.p. 188 — 189° ; 2-acetyl-1-naphthyl cinnamate, m.p. 111° ; ω -cinnamoyl-2-acetyl-1-naphthol, m.p. 158° ; 2-styryl-1:4- α -naphthapyrone, m.p. 177° ; 2-acetyl-1-naphthyl *p*-methoxycinnamate, m.p. 137 — 138° ; ω -*p*-methoxycinnamoyl-2-acetyl-1-naphthol, m.p. 176 — 177° ; 2-*p*-methoxystyryl-1:4- α -naphthapyrone, m.p. 207° ; 3-phenyl-2-methyl-1:4- α -naphthapyrone, m.p. 203 — 204° ; 2-phenylacetyl-1-naphthyl cinnamate, m.p. 146 — 147° ; 2-styryl-3-phenyl-1:4- α -naphthapyrone, m.p. 262 — 263° .

H. W.

Synthesis of chromylium salts. II. R. ROBISON and J. WALKER (J.C.S., 1935, 941—946).—The un-

saturated ketone is condensed with $m\text{-C}_6\text{H}_4(\text{OH})_2$ in EtOH containing HCl and chloranil. Thus 6-methoxy-2-benzylidenecoumaranone yields 7-hydroxy-6'-methoxy-4-phenyl-2:3-coumareno-(3':2')-

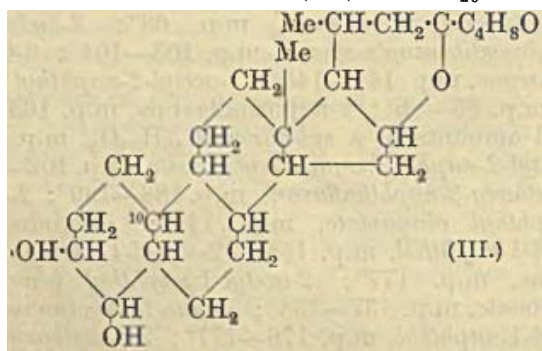


chromylium chloride (I), demethylated to 7:6'-dihydroxy-4-phenyl-2:3-coumareno-(3':2')-

chromylium chloride. 2-Benzoylcoumarone similarly affords 7-hydroxy-3:4-coumareno-(2':3')-flavylum chloride, and 7-hydroxy-4-p-dimethylaminophenyl-2:3-indeno-(3':2')-chromylium chloride hydrochloride is obtained from 2-p-dimethylaminobenzylidene-1-hydrindone. In order to examine the lake-forming properties of the product, the salicylic acid residue has been introduced into an oxonium salt. Thus, 5-aldehydsalicylic acid, 1-hydrindone, and KOH in EtOH yield the acid, $\text{C}_{17}\text{H}_{12}\text{O}_4$, m.p. 285°, the Et ester, m.p. 172°, of which is transformed by $m\text{-C}_6\text{H}_4(\text{OH})_2$ and chloranil in dioxan into 7-hydroxy-4-(4'-hydroxy-3'-carboxyphenyl)-2:3-indeno-(3':2')-chromylium chloride. 7-Hydroxy-4-p-hydroxyphenyl-flavylum chloride and 7:4'-dihydroxy-4-phenylflavylum chloride (+2H₂O) are obtained by demethylation of known substances. It is shown that the reactive phenol component can be varied within the usual limits by the prep. of the following: 5:7-dihydroxyflavylum chloride from $o\text{-C}_6\text{H}_4(\text{OH})_2$ and Ph vinyl ketone; 7:8-dihydroxy-4-phenylflavylum chloride (+3H₂O) from benzylideneacetophenone; 2-phenyl-4-anisyl-5:6-naphtha-(1':2')-pyrylium picrate, m.p. 204°, from anisylideneacetophenone; 6:7-dihydroxy-4-phenylflavylum picrate, m.p. 235°; 6-hydroxy-5:7-dimethoxy-4-phenylflavylum picrate, m.p. 220° (decomp.).

H. W.

Digitalis sapogenins. W. A. JACOBS and J. C. E. SIMPSON (J. Biol. Chem., 1935, 110, 429—438).—Oxidation of tigogenin (I), $\text{C}_{26}\text{H}_{42}\text{O}_3$, and tigogenone with CrO_3 in AcOH yields gitogenic acid (II) (Me ester, m.p. 210°; Me₂ ester, m.p. 145°; anhydride, m.p. 205—206°), identical with the acid obtained from gitogenin [provisional formula (III)]. (I) contains one of the two vicinal OH of (III). The C_{26} formul-



ation is more probable than C_{27} , but in the latter case the extra Me would probably be on C_{10} . The ketone obtained on dehydrogenation of (III) is not Me isohexyl ketone. Thermal decomp. of (II) or its anhydride yields a ketone, $\text{C}_{25}\text{H}_{38}\text{O}_3$ (oxime, m.p. 237—238°).

J. N. A.

Synthesis of rotenone and its derivatives. VI. Chromenochromones. H. I. KING and A. ROBERTSON (J.C.S., 1935, 993—996).—Treatment of 5-methoxysalicylaldehyde with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and anhyd. K_2CO_3 in boiling COMe_2 affords Et 2-aldehydo-4-methoxyphenoxyacetate, b.p. 187—188°/2 mm., m.p. 51° (semicarbazone, m.p. 171°), which condenses with hippuric acid in presence of NaOAc and Ac_2O to the azlactone (I), $\text{C}_{21}\text{H}_{19}\text{O}_6\text{N}$, m.p. 127°. (I) is hydrolysed by boiling 10% NaOH and, after removal of BzOH, is heated with conc. HCl, whereby 4-methoxyphenoxyacetic acid-2-pyruvic acid (II) is obtained; this is converted through the oxime, m.p. 150—151°, into 4-methoxyphenoxyacetic acid-2-acetonitrile (III), m.p. 140° (Me ester, m.p. 45°). The yield of (III) is greatly increased if crude (II) is directly oximated. (III), $m\text{-C}_6\text{H}_4(\text{OH})_2$, and ZnCl_2 in Et₂O saturated with HCl give 4-methoxyphenoxyacetic acid-2-resacetophenone, m.p. 163°, or (?) hydrated, m.p. 121—124°, cyclised by boiling Ac_2O containing NaOAc to 7-hydroxy-6-methoxychromeno-[3':4':2:3]-chromone, decomp. 248—249° after slight darkening at 243—245° (acetate, m.p. 190°). *o*-Vanillin, $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$, and K_2CO_3 in boiling COMe_2 yield Et 2-aldehydo-6-methoxyphenoxyacetate (IV), m.p. 75° (semicarbazone, m.p. 205°), converted by NaHSO_3 followed by NaCN into the corresponding cyanohydrin, which is transformed by SOCl_2 into Et 6-methoxyphenoxyacetate-2-chloroacetonitrile (V), m.p. 46°. Treatment of (V) with Zn dust, EtOH, AcOH, and H₂O affords Et 6-methoxyphenoxyacetate-2-acetonitrile (VI), m.p. 53°. (IV), hippuric acid, NaOAc, and Ac_2O give the corresponding azlactone, m.p. 126°, hydrolysed and transformed by boiling HCl into 6-methoxyphenoxyacetic acid-2-pyruvic acid, the oxime, m.p. 164°, of which is transformed by Ac_2O into 6-methoxyphenoxyacetic acid-2-acetonitrile, m.p. 93°. 6-Methoxyphenoxyacetic acid-2-resacetophenone, m.p. 180-5°, is transformed by boiling Ac_2O containing NaOAc into 7-hydroxy-8-methoxychromeno-[3':4':2:3]-chromone, m.p. 263—265° (decomp.) (acetate, m.p. 196°). (VI), $o\text{-C}_6\text{H}_4(\text{OMe})_2$, and ZnCl_2 in Et₂O give 6-methoxyphenoxyacetic acid-2:2':4'-O-dimethylphloracetophenone hydrate, m.p. 143—144° (whence 5:7:8'-trimethoxychromeno-[3':4':2:3]-chromone, m.p. 210°), and 6-methoxyphenoxyacetic acid-2:2':6'-O-dimethylphloracetophenone, m.p. 174°.

H. W.

Charcoal as a catalyst of stereoisomeric change in disulphoxides. T. W. J. TAYLOR and W. C. J. COUGHTREY (J.C.S., 1935, 974—976).—The isomerisation of oximes by charcoal has been attributed to the exchange of O atoms between the charcoal surface and the oxime group. A similar isomerisation is observed with thianthren disulphoxides in tetrahydronaphthalene containing blood-C at 180° but not in boiling C_6H_6 . A sufficiently accurate method is not available for the quant. analysis of mixtures of the two disulphoxides, but points of resemblance between the isomerisation and that of α -benzilmonoxime are traced.

H. W.

Additive compounds of arsenic trichloride.—See this vol., 1090.

Yellow coloration of mixtures of fructose and pyridine by ultra-violet light. R. CANTIENTI (Helv.

Chim. Acta, 1935, **18**, 808—812; cf. this vol., 68).—The yellow coloration of aq. solutions of C_5H_5N by irradiation is increased by addition of fructose (I). The colour of mixtures of C_5H_5N and (I) is more stable than the yellow coloration of pure C_5H_5N . Subsequent addition of (I) to irradiated C_5H_5N stabilises the colour, but the stability is not so great as that produced by irradiation of mixtures of C_5H_5N and (I).
F. R. G.

Synthesis of yellow tetrapyrroline ferrous thiocyanate. G. SPACU and V. ARMEANU (Bul. Soc. Stiinte Cluj, 1934, **7**, 566—567; Chem. Zentr., 1935, i, 1024).—An improved method of prep. is given.
J. S. A.

Dehalogenation of $\alpha\beta$ -dibromo-acids. III. Acids of pyridine and quinoline series. A. A. ALBERTS and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, **57**, 1284—1287).—The product (95% yield) from 2-methylquinoline, chloral, and C_5H_5N at 100° (bath) is hydrolysed (EtOH-KOH) to β -2-quinolylacrylic acid (I), m.p. 194—196° (hydrobromide, m.p. 218—220°; hydrochloride, m.p. 216—218°; acetate, m.p. 203°). The dibromide, m.p. 228—230° (corr.) (lit. 180—181°) (prepared under varying conditions), of (I) when treated with aq. KOH, Na_2CO_3 , or C_5H_5N , EtOH-KOH, anhyd. C_5H_5N , and boiling H_2O or EtOH, regenerates (I); contrary to Carlier and Einhorn (A., 1891, i, 83), 2-quinolylacetylene is not obtained using aq. Na_2CO_3 or K_2CO_3 . The product (16—18% yield) from 4-methylpyridine, chloral, and a little $ZnCl_2$ at about 34° (24 hr.) and 100° (2 hr.) is hydrolysed (method: Rabe and Kindler, A., 1922, i, 361) to β -4-pyridylacrylic acid (II), m.p. 293—295°, the dibromide, m.p. 258—260°, of which also regenerates (II) when treated with alkali. Dehalogenation of $CHBrPh\cdot CHBr\cdot CO_2H$ with anhyd. C_5H_5N gives a considerable amount of $CHPh\cdot CH\cdot CO_2H$; with aq. C_5H_5N and/or Na_2CO_3 , 65—75% of $CHPh\cdot CHBr$ results.

3-Acetylpyridine and PCl_5 in C_6H_6 give α -chloro- α -3-pyridylethylene, b.p. 112—114°/24 mm. (hydrochloride, m.p. 138—140°), converted by EtOH-KOH into 3-pyridylacetylene, b.p. 83—84°/30 mm., m.p. 38.5°.
H. B.

Syntheses of pyridiniummethanols. II. Mechanism of the condensation reaction. isoQuinoliummethanols. F. KROHNKE (Ber., 1935, **68**, [B], 1351—1359).—The condensation of phenacylpyridinium salts with aldehydes occurs according to the scheme $COR\cdot CH_2\cdot N(C_5H_5)X \xrightarrow{R\cdot CHO} COR\cdot CH(CHR\cdot OH)\cdot N(C_5H_5)X \rightarrow OH\cdot CHR\cdot CH_2\cdot N(C_5H_5)X$. Reactivity is due to the influence of COR on CH_2 and the reaction is therefore common to all pyridinium salts with activated CH_2 and hence to the allyl and CH_2Ph derivatives. The following are obtained by condensing phenacylpyridinium bromide (1 mol.) with NaOH (1 mol.) and excess of the requisite aldehyde in 90% EtOH at room temp.: β -hydroxy- β -p-chlorophenylethyl-, m.p. 182—183°; β -hydroxy- β -2:5-dichlorophenylethyl-, m.p. 259—261°; β -hydroxy- β -2-chloro-5-nitrophenylethyl- (hydrate and anhyd.), m.p. 238—239° after marked softening; β -hydroxy- β -o-methoxyphenylethyl-, m.p. 208°; β -hydroxy- β -3:4:5-trimethoxyphenyl-

ethyl-, m.p. 200—202°; β -hydroxy- β -p-ethoxyphenylethyl-, m.p. 166°; β -hydroxy- β -1-naphthylethyl-, m.p. 208—211° after softening (corresponding perchlorate, m.p. 181°); $\gamma\delta$ -trichloro- β -hydroxyamyl-, decomp. 219°, and β -hydroxy- β -n-hexylethyl-, m.p. 223° (decomp.) [hydrate, m.p. 53—54°; corresponding perchlorate, m.p. (indef.) 54°], -pyridinium bromide. β -Hydroxy- β -isobutylethylpyridinium picrate has m.p. 125—126°. Benzylpyridinium bromide and o- $C_6H_4Cl\cdot CHO$ yield β -hydroxy- α -phenyl- β -o-chlorophenylethylpyridinium bromide, m.p. 222° after softening at 160°. $CH_2\cdot CH\cdot CH_2Br$ and C_5H_5N at 0° give allylpyridinium bromide (I), m.p. 92—94° (corresponding perchlorate, m.p. 71.5—72.5°, and picrate, m.p. 69.5—70.5°). (I) and PhCHO in presence of NaOH afford α -hydroxyphenylmethyl- Δ^{β} -propenylpyridinium bromide, m.p. 227° after softening and becoming discoloured, reduced (Pd-BaSO₄) and converted by $HClO_4$ into α -hydroxyphenylmethyl-n-propylpyridinium perchlorate, m.p. 142—142.5°; the corresponding bromide, m.p. 199—202°, is obtained from n-propylpyridinium bromide and PhCHO. (I) and the requisite aldehyde yield the following substances: α -hydroxy-o-chlorophenylmethyl- Δ^{β} -propenyl-, m.p. 203—204° after much softening; α -hydroxy-o-nitrophenylmethyl- Δ^{β} -propenyl-, slow decomp. > 200°; α -hydroxy-1-naphthylmethyl- Δ^{β} -propenyl-, m.p. 190—192° after softening (corresponding perchlorate); α -hydroxy-2-furylmethyl- Δ^{β} -propenyl-, m.p. indef. 140°, -pyridinium bromide. Allylisoquinolinium bromide, m.p. 99—100° (corresponding perchlorate, m.p. 111°), gives the compounds: α -hydroxy-o-chlorophenylmethyl- Δ^{β} -propenyl-, decomp. about 225°; α -hydroxy-o-nitrophenylmethyl- Δ^{β} -propenyl-, decomp. 220° after becoming discoloured; α -hydroxy-m-nitrophenylmethyl- Δ^{β} -propenyl-, decomp. 213—215°, -isoquinolinium bromide. Benzylisoquinolinium bromide, m.p. 110—111.5° (corresponding picrate, m.p. 177° after softening, and perchlorate, m.p. 167—168°), gives β -hydroxy- α -phenyl- β -o-chlorophenylethyl-, m.p. 223° (decomp.), and β -hydroxy- $\alpha\beta$ -diphenylethyl-, m.p. 218° (decomp.), -isoquinolinium bromide. β -Hydroxy- β -phenylethyl-2-methylpyridinium bromide, m.p. 218—221° after softening, and β -hydroxy- β -phenylethyl-3-methylpyridinium bromide, m.p. 153—155°, are described. β -Hydroxy- β -p-isopropylphenylethylpyridinium bromide (monohydrate) has m.p. 190—192°.
H. W.

4:7-Dimethyloxindole. V. LIVOVSKI (Compt. rend., 1935, **201**, 217—219).—p-Xylidine with $CH_2Cl\cdot COCl$ and $AlCl_3$ gives 4:7-dimethyloxindole, b.p. 200°, m.p. 159° (3-benzylidene, m.p. 188°; 3-p-chlorobenzylidene, m.p. 212—215°; 3-o-sulphobenzylidene; 3:3'-benzylidenedi-, m.p. 172°; 3:3'-m-hydroxybenzylidenedi-, m.p. 164°, derivatives), which with isatin in $HCl\cdot AcOH$ yields 4:7-dimethylisoindigotin (I), cryst. (Na disulphonate, cryst.), but in EtOH with a trace of $C_5H_{11}N$ gives 4:7-dimethylisatin, dehydrated to (I).
F. R. G.

Constitution of abrin. T. HOSHINO (Proc. Imp. Acad. Tokyo, 1935, **11**, 227—228).—Abrin (I), m.p. 295°, $[\alpha]_D^{25} + 44.4^\circ$, an NH_2 -acid occurring in the seeds of *Abrus precatorius*, loses CO_2 when heated in vac. to give 3- β -methylaminoethylindole, m.p. 89—90°. Methylation of (I) and of l-tryptophan gives the same

Me β -3-indolylpropionate α -trimethylammonium iodide (picrates, m.p. 163—164° and 155—156°). (I) is therefore α -methylamino- β -3-indolylpropionic acid.
P. G. C.

Action of nitrous acid on tryptophan. N. J. DEMJANOV and N. I. PUTCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 390—393).—The action of HNO₂ on tryptophan affords 1-nitrosoindole-3-acrylic acid (dibromide). Absence of ring enlargement is ascribed to the attachment of NH₂ in the side-chain to C not directly united to the ring.
H. W.

Complexes of polynitro-compounds. I. Compounds of polynitro-hydrocarbons with 1-keto-1:2:3:4-tetrahydrocarbazole. A. KENT (J.C.S., 1935, 976—978).—1-Ketotetrahydrocarbazole (improved prep.) gives a *p*-nitrophenylhydrazone, m.p. 252—253° (also +1EtOH) (hydrochloride, decomp. 210—212°), and a picrate, m.p. 165—166°. It forms complexes with the following substances, the proportions being stated in parentheses: 1:3:5-C₆H₃(NO₂)₃ (1:2), m.p. 180—182°; 1:2:4-C₆H₃(NO₂)₃ (1:1), m.p. 129—131°; *m*-C₆H₄(NO₂)₂ (1:2), m.p. 120—139°; *p*-C₆H₄(NO₂)₂ (1:2), m.p. 140—142°; 2:4:6-C₆H₂Me(NO₂)₃ (1:1), m.p. 129—131°; 2:4:5-C₆H₂Me(NO₂)₃ (1:2), m.p. 127—140°; 2:4-C₆H₃Me(NO₂)₂ (1:1), m.p. 98—126°; 2:5-C₆H₃Me(NO₂)₂ (1:2), m.p. 142—143°; 3:5-C₆H₃Me(NO₂)₂ (1:1), m.p. 108—118°. No evidence is obtained that any of the compounds could be obtained cryst. with its components in alternative proportion.
H. W.

[Preparation of] bromine-substituted allyl 2-phenylquinoline-4-carboxylate.—See B., 1935, 750.

Asymmetric platinum atom. VI. H. REIHLEN and W. HUHN (Annalen, 1935, 519, 80—96; cf. A., 1933, 74).—*d*- and *l*-NH₂·CHPh·CH₂·NH₂ in Et₂O with K₂PtCl₄ in H₂O yield dichlorophenylethylenediamineplatinum (two forms), which when boiled with 3-methyl-2-aminomethyl-4-ethylquinoline hydrochloride and dil. NaOH gives (less sol.) α -phenylethylenediamine-3-methyl-4-ethyl-2-aminoethylquinolineplatinum chloride in two forms (+1½H₂O), [M]_D +855° in H₂O, converted into the nitrate, [M]_D +865° in H₂O, chloroplatate, cryst., low-rotating *d*-bromocamphor- π -sulphonate (+2½H₂O), [M]_D +1500° ([M]_D +864° for ion), and 1-bromocamphor- π -sulphonate (+4H₂O) [M]_D +220° ([M]_D +856° for ion), high-rotating *d*-bromocamphor- π -sulphonate (+2½H₂O), [M]_D +1720° ([M]_D +1080° for ion), and 1-bromocamphor- π -sulphonate (+4H₂O), [M]_D +440° ([M]_D +1075° for ion), and (+2H₂O) [M]_D -852° in H₂O, converted into the perchlorate, [M]_D -860°, low-rotating 1-bromocamphor- π -sulphonate, [M]_D -1490° ([M]_D -854° for ion), high-rotating *d*-bromocamphor- π -sulphonate, [M]_D -442° ([M]_D -1080° for ion), and 1-bromocamphor- π -sulphonate, [M]_D -1720° ([M]_D -1080° for ion), also (more sol.) β -phenylethylenediamine-3-methyl-2-amino-methyl-4-ethylquinolineplatinum chloride (acetate, [M]_D +470°; chloroplatate; bromocamphor- π -sulphonate). The structural relations of these isomerides are discussed.
F. R. G.

3:6-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-group on the 9-carbon atom. IV. Synthesis of 3:6-dialkoxy-9-arylamino-10-alkylacridinium chlorides. K. ISHIIHARA (J. Chem. Soc. Japan, 1934, 55, 858—877; cf. this vol., 93).—The following are prepared by condensing aromatic amines with 9-chloro-3:6-dialkoxy-10-alkylacridinium chlorides: 9-anilino-, decomp. 234—235°; 9-o-, decomp. 256—257°, 9-m-, decomp. 247°, and 9-p-toluidino-, decomp. 225—236°; 9-p-phenetidino-, decomp. 235—237°, -3:6-dimethoxy-10-methyl-, 9-anilino-, decomp. 212—214°; 9-o-, decomp. 223—224°, 9-m-, decomp. 205—206°, and 9-p-toluidino-, decomp. 200—201°; 9-p-phenetidino-, decomp. 203—204°, -3:6-dimethoxy-10-ethyl-, 9-anilino-, decomp. 250—251°; 9-o-, decomp. 253—255°, 9-m-, decomp. 256—257°, and 9-p-toluidino-, decomp. 225—226°; 9-p-phenetidino-, decomp. 228—230°, -3:6-diethoxy-10-methyl-, 9-anilino-, decomp. 239—241°; 9-o-, decomp. 242—244°, 9-m-, decomp. 237°, and 9-p-toluidino-, decomp. 219—225°; 9-p-phenetidino-3:6-diethoxy-10-ethyl-acridinium chloride.
CH. ABS. (r)

Synthesis of 8:9-benzoylene-3:4-phthalylphenanthridine-5-carboxylic acid. R. SCHOLL and H. K. MEYER (Ber., 1935, 68, [B], 1307—1309).—*Et* 1-chloroanthraquinone-2-carboxylate, m.p. 140—141°, is converted by Cu powder in boiling PhNO₂ into *Et*, 1:1'-dianthraquinonyl-2:2'-dicarboxylate, m.p. 264—266°. The corresponding acid is transformed by BzCl in boiling PhNO₂ into the anhydride, whence the monoamide (NH₄ salt) which passes under the influence of NaOCl, doubtless through the NH₂-acid, into 8:9-benzoylene-3:4-phthalylphenanthridine-5-carboxylic acid. 1:1'-Dianthryl-2:2'-dicarboxylic acid under dehydrating conditions passes into *amphi*-isopyranthrone, which is also obtained from 9:10:9':10'-tetrahydro-1:1'-dianthryl-2:2'-dicarboxylic acid, m.p. 288—290°, prepared by reduction (Zn dust-NaOH) of 1:1'-dianthraquinonyl-2:2'-dicarboxylic acid.
H. W.

Synthesis of antipyrene and pyramidone. A. L. KLEBANSKI and A. L. LEMKE (J. Appl. Chem. Russ., 1935, 8, 269—276).—Antipyrene (I) is obtained in 83—88% yield from 1-phenyl-3-methylpyrazole and Me₂SO₄ in PhMe at the b.p. (6—8 hr.), or in xylene (4—5 hr.). Directions for the purification of (I) are given. Pyramidone is prepared from Na sulphaminoantipyrene and CH₂O and HCO₂H, in 80% yield, at 100° (14 hr.).
R. T.

Pseudo-atoms and isoteric compounds. V. Relation between constitution and reactions of pyrazolone derivatives. H. ERLENMEYER and E. WILLI (Helv. Chim. Acta, 1935, 18, 740—743; cf. this vol., 431).—Pyramidone and isopropylantipyrene in which ·N· is replaced by ·CH· form mixed crystals and have similar pharmacological properties.
F. R. G.

5:5-Diphenylbarbituric acid. S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1303—1304).—Alloxan monohydrate (modified prep.; cf. Biltz and Heyn, A., 1917, i, 289), C₆H₆, and conc. H₂SO₄ at 75—80° give some 5:5-diphenylbarbituric acid (I), m.p. 290—292° (corr.) [hydrolysed (10% KOH) to NH₃, CO₂,

and $\text{CHPh}\cdot\text{CO}_2\text{H}$], and (mainly) an acidic substance, m.p. 320—325°. (I), in sub-lethal doses, is ineffective as a hypnotic.

H. B.

Derivatives of piperazine. IV. Reactions with derivatives of chloroacetic acid. D. E. ADELSON and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1280—1281).—Piperazine (I) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{R}$ in $\text{EtOH} + \text{Na}_2\text{CO}_3$ give *Me*, b.p. 156—157°/5 mm., m.p. 62·5°, *Et* (II), b.p. 158·5—159°/4 mm., m.p. 47·5° (*H sulphate*), *Pr*^a, b.p. 177—178°/5 mm. (*H sulphate*), *Bu*^a, b.p. 194—194·5°/4 mm. (*H sulphate*), and *n-hexyl*, b.p. 228—230° (slight decomp.)/5 mm., m.p. 39·5° (*H sulphate*), piperazine-1:4-diacetates, which with conc. aq. NH_3 afford piperazine-1:4-diacetamide (III), chars > 250°, also formed from (I), $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$, and Na_2CO_3 in *PhMe*. (III) is dehydrated to piperazine-1:4-diacetonitrile, m.p. 165°, and converted by NaNO_2 in conc. H_2SO_4 into piperazine-1:4-diacetic acid (+2 H_2O), decomp. > 250° (*H sulphate*; *Na salt*). Reduction (*Na*, *Bu*^a*OH*) of (II) gives 1:4-di- β -hydroxyethylpiperazine, m.p. 135—135·5°. *n-Hexyl chloroacetate* has b.p. 218·5—219·5°/758 mm.

H. B.

Relationships between constitution and magnitude of mol. heat of fusion of organic compounds. II. Synthesis of 1:4-endoazocyclohexane. J. PIRSON and J. JÖRGL (Ber., 1935, 68, [B], 1324—1330).—Evidence is adduced in favour of the view that, in addition to dependence on m.p., the type of space fulfilment is decisive for the magnitude of the mol. latent heat of fusion and the nature of the atoms constituting the compound has little if any influence. $\Delta^{1:3}$ -cyclohexadiene and Et_2 azodicarboxylate in ligroin yield *Et*, 1:4-endohydrazocyclohexene- NN' -dicarboxylate, b.p. 155°/1·5 mm. (slight decomp.), which in presence of Pd-C absorbs 2H with formation of cyclohexane and $(\text{-NH}\cdot\text{CO}_2\text{Et})_2$. After complete hydrogenation and treatment of the product with KOH , impure 1:4-endohydrazocyclohexane is obtained; it is transformed by CuCl_2 into the azo-cuprous complex, $\text{C}_6\text{H}_{10}\cdot\text{N}_2\text{CuCl}$, from which 1:4-endoazocyclohexane (I), m.p. 141·4°, is obtained by action of alkali. The mol. m.p. depressions of (I), endomethylenedehydropiperidazine, and endomethylenepiperidazine are 32·2, 29·4, and 32·4, respectively.

H. W.

Rearrangement of methoxy-pyrimidines and -purines. E. BERGMANN and H. HEDHOLD (J.C.S., 1935, 955—957).—4-Chloro-2:6-dimethoxypyrimidine is converted by MeI at 90° into 4-chloro-1:3-dimethyluracil, m.p. 113°. 2:6-Dimethoxy-7-methylpurine, m.p. 199°, from 2:6-dichloro-7-methylpurine and NaOMe-MeOH at 100°, is transformed into caffeine when heated at 210° or, preferably, with MeI at 100°. 2-Chloro-6-methoxy-7-methylpurine, m.p. 219° (decomp.), from 2:6-dichloro-7-methylpurine and NaOMe in boiling MeOH , has marked thermal stability but is transformed by MeI at 100° into 4-chloro-1:7-dimethylhypoxanthine methiodide, m.p. 228° (decomp.), a periodide, m.p. 158—160°, being also formed. In addition to the allyl derivatives only the methylpurine compounds appear capable

of rearrangement by heat; 2:6-dipropoxy-7-methylpurine, however, is stable at 150°.

H. W.

Action of aromatic aldehydes on the additive products obtained from aromatic amidines and glyoxal. J. B. EKELEY and A. R. RONZIO (J. Amer. Chem. Soc., 1935, 57, 1353—1356).— $\text{NH}\cdot\text{CPh}\cdot\text{NH}$ (I) and polyglyoxal (II) in aq. KOH give a compound, $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$ (III), m.p. 160° (all m.p. are on Maquenne block unless stated otherwise) [*hydrochloride*, m.p. 157—213° (decomp.) (tube)], which gives $(\text{CHO})_2$ when dissolved in H_2O and is converted by warm alkali into red compounds. (III) and PhCHO in aq. EtOH-KOH afford (probably) 5-hydroxy-2:4-diphenylpyrimidine (IV), m.p. 284° [*hydrochloride* (mixture of mono- and di-); *platinichloride* (+2 H_2O), m.p. 264° (decomp.) (tube)], also formed directly from equimol. amounts of (I), (II), and PhCHO in aq. EtOH-KOH , which is oxidised (alkaline KMnO_4) to NH_2Bz , BzOH , and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$. (IV) is considered to be stable in alkaline solution but to rearrange in acid (HCl) to

$\text{CH}=\text{N}-\text{CPh}$ (I), (II), and the appropriate ArCHO similarly give 5-hydroxy-2-phenyl-4-p-tolyl-, m.p. 319°, 4-o-hydroxyphenyl-, m.p. 338°, 4-5'-bromo-2'-hydroxyphenyl-, m.p. 335°, 4-o-, m.p. 283°, and -p-, m.p. 307°, -anisyl-, 4-m-nitrophenyl-, m.p. 262°, 4-m-, m.p. 241°, and -p-, m.p. 292°, -aldehydophenyl-, and -4-furyl-, m.p. 293·5°, -pyrimidines. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ and (II) similarly afford a compound, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$, m.p. 164°; 5-hydroxy-4-phenyl-, m.p. 310°, 4-p-tolyl-, m.p. 295°, 4-o-hydroxyphenyl-, m.p. 323·5—337°, 4-m-nitrophenyl-, m.p. 295°, 4-5'-bromo-2'-hydroxyphenyl-, m.p. 344·5—351·5°, and -4-furyl-, m.p. 310°, 2-p-tolylpyrimidines are prepared. The compound, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$, m.p. 148°, from $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ and (II) with PhCHO gives 5-hydroxy-4-phenyl-2-m-tolylpyrimidine, m.p. 258·5°, which with $\text{PCl}_5 + \text{POCl}_3$ affords the 5-Cl-derivative, m.p. 285·5°. Compounds, $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Cl}$, m.p. 188°, and $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$, decomp. 164—207°, are prepared from (II) and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ (V) and $\beta\text{-C}_{10}\text{H}_7\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ (VI), respectively. 5-Hydroxy-4-phenyl-2-p-chlorophenyl-, m.p. 331·5°, 2-p-nitrophenyl-, m.p. 326°, and 2- β -naphthyl-, m.p. 281°, -pyrimidines are formed from (II), PhCHO , and (V), $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NH})\cdot\text{NH}_2$, and (VI), respectively. When the mother-liquors from the prep. of (III) are kept for some weeks and then acidified, 5-hydroxy-2-phenylpyrimidine-4-carboxylic acid(?), m.p. 250° (tube), 310°, is pptd.; this arises from the $\text{CHO}\cdot\text{CO}_2\text{H}$ present in (II). Alkaline solutions of the hydroxypyrimidines often show fluorescence when EtOH is added.

H. B.

Indoles and isatogens. XVIII. Preparation of a vat dye from *oo'*-dinitrotolane and its conversion into indole. P. RUGGLI and H. ZAESLIN (Helv. Chim. Acta, 1935, 18, 845—852).—2:2'-Dinitrobenzil (I) in EtOAc , EtOH , and H_2O hydrogenated in presence of Ni gives 2-o-aminophenylindolone (II), m.p. 167° (*leuco*-compound; *Ac* derivative, m.p. 192°; *phenylhydrazone*, m.p. 186°; *semicarbazone*, decomp. 206°), and a compound, $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$, m.p. 344° (*Ac*, derivative, m.p. 220°). (I) and (II) when reduced with $\text{SnCl}_2\text{-HCl}$ both yield indole (cf. Heller, A., 1917 i, 708).

F. R. G.

isoIndigotin and related compounds. A. WAHL (Bull. Soc. chim., 1935, [v], 2, 1221—1244).—A lecture.

Quinazolines. XL. Synthesis of a quinazoline derivative structurally related to papaverine. E. B. MARR and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 1329—1330).—6-Aminoveratraldehyde, prepared in 90% yield by reduction (FeSO_4 , aq. NH_3) of the NO_2 -derivative (modified prep.), and homoveratryl chloride in 50% $\text{AcOH} + \text{NaOAc}$ give 6-homoveratramidoveratraldehyde, m.p. 141.2—142.2° (corr.), which with MeOH-NH_3 at 100—120° affords 6:7-dimethoxy-2-veratrylquinazoline, m.p. 134—135° (corr.). H. B.

Pyrrole-blues. I. Absorption spectra in visible light. II. Absorption spectra in the ultra-violet. P. PRATESI (Annali Chim. Appl., 1935, 25, 195—203, 203—208).—The spectra for 5-(2:3-dimethylpyrrolenyl)- β -isatin (2:3-dimethylpyrrole-blue), 5-(2:4-dimethyl-3-ethylpyrrolenyl)- β -isatin (cryptopyrrole-blue), and 5-(4-methyl-3-ethylpyrrolenyl)- β -isatin (opsopyrrole-blue) confirm the analogy in constitution of these three compounds.

T. H. P.

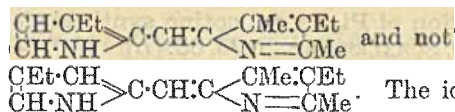
Flavins. R. KUHN (Bull. Soc. Chim. biol., 1935, 17, 905—926).—A lecture.

Improvement of the flavin synthesis. Boric acid process. R. KUHN and F. WEYGAND (Ber., 1935, 68, [B], 1282—1288).—The yields of flavins are increased almost tenfold when the corresponding diamines are condensed with alloxan in presence of H_3BO_3 . The action does not appear to depend on the formation of complexes of H_3BO_3 and the OH groups of the sugar-like side-chain, since lactoflavin forms such compounds in dil. aq. solution which are characterised by marked reversal of the sign of rotation, whereas in such solution H_3BO_3 has no influence on the yield of flavin provided the solution is acid. Further, the effect of H_3BO_3 is most marked in anhyd. media. Also it greatly increases the yield of flavins which do not contain OH suitable for condensation. The action of H_3BO_3 appears similar in the anthraquinone and flavin series. 4:5-Dinitro-*o*-xylene and *d*-arabamine in 80% EtOH at 135° yield 4-nitro-5-*d*-arabitylamino-*o*-xylene (I), m.p. 213—214° [corresponding di-compound (II), m.p. 203—204°]. The tetra-acetates of (I), (II), and 4-nitro-5-*l*-arabitylamino-*o*-xylene have m.p. 113—114°, 143—144°, and 113—114°, respectively. Treatment of (I) with Zn dust and H_3BO_3 in boiling AcOH followed by addition of alloxan in AcOH gives 6:7-dimethyl-9-*d*-araboflavin, m.p. 302—303° (decomp.), $[\alpha]_D^{20} +78.6^\circ$, $+70.9^\circ$, $+63.0^\circ$ in 0.1*N*-NaOH ($c=0.509$, 0.254, and 0.127, respectively), $[\alpha]_D^{20} -44.1^\circ$ in 0.05*N*-NaOH + $\text{Na}_2\text{B}_4\text{O}_7$ (tetra-acetate, m.p. 221—222°). 6:7-Dimethyl-9-*l*-araboflavin has m.p. 202—203° (decomp.), $[\alpha]_D^{20} -77.9^\circ$, -69.7° , -57.4° in 0.1*N*-NaOH ($c=0.488$, 0.244, and 0.122, respectively), $[\alpha]_D^{20} +44.8^\circ$ in 0.05*N*-NaOH + $\text{Na}_2\text{B}_4\text{O}_7$ (tetra-acetate, m.p. 221—222°). 6:7-Dimethyl-9-*dl*-araboflavin, m.p. 295—296°, and its tetra-acetate, m.p. 283—284°, are obtained by admixture of equal wts. of the optical antipodes. *o*-Aminodiphenylamine is converted into 9-phenylflavin, m.p. $> 370^\circ$, and 9-phenyl-3-methylflavin, m.p. $> 360^\circ$. H. W.

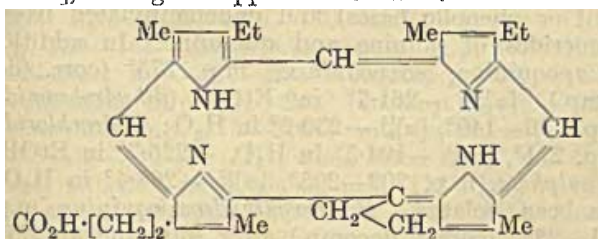
Flavin syntheses. VI. Synthesis of three further stereoisomerides of lactoflavin. P. KARRER, H. SALOMON, K. SCHOPP, F. BENZ, and B. BECKER (Helv. Chim. Acta, 1935, 18, 908—910; cf. this vol., 760).—By methods analogous to those already described the following new compounds are obtained from pentoses with 3-amino-4-carbethoxy-amino-*o*-xylene and alloxan: 2-carbethoxyamino-4:5-dimethylphenyl-1-ribamine, m.p. 172°, -*d*-arabamine, m.p. 175°, -*d*-lyxamine, m.p. 169°, hydrolysed by alkali to 1-*d*-lyxityl-2-hydroxy-5:6-dimethylbenzimidazole, m.p. 216°; 6:7-dimethyl-9-*l*-1'-ribityl-, m.p. 280°, -*d*-1'-arabityl-, m.p. 305° (corr.), -*d*-1'-lyxityl-isoalloxazine, m.p. 280—282° (*Ac*₁ derivative, m.p. 225—226°). F. R. G.

Fluorescence curves of lactoflavin and synthetic flavins. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1935, 18, 911—914; cf. preceding abstract).—6:7-Dimethyl-9-*d*-1'-ribityl- (I), -9-*d*-1'-sorbityl-, -9-*d*-1'-lyxityl-, -9-*d*-1'-rhamnityl-, and -9-*l*-1'-arabityl-, 7-methyl-9-*d*-1'-arabityl-, and 9-*l*-1'-arabityl-isoalloxazine in aq. solutions buffered with phosphate (pH 7.0) give fluorescence spectra having a max. intensity in 0.003% solution. The curves for (I) and natural lactoflavin practically coincide. F. R. G.

Chlorophyll. LVIII. Synthesis of β -unsubstituted deoxophyllerythrins and an isomeric deoxophyllerythrin. H. FISCHER and W. ROSE. LIX. Conversion of the vinyl group of chlorophyll and its derivatives into a hydroxyethyl group; oxopyrroporphyrin. H. FISCHER and J. HASENKAMP. LX. Fine structure of chlorophyll-*a* and -*b*. Detection of two asymmetric carbon atoms. H. FISCHER and A. STERN (Annalen, 1935, 519, 1—42, 42—58, 58—69; cf. this vol., 871).—LVIII. The *Me* ester (I), m.p. 98°, of 4-carbethoxy-2-methyl-3-ethylpyrrole-5-carboxylic acid (A., 1912, i, 899) with 2 mols. of SO_2Cl_2 in Et_2O gives the 2- α' - Cl_2 -derivative, cryst., hydrolysed (NaOH) to 2-aldehydo-4-carbethoxy-3-ethylpyrrole-5-carboxylic acid (II), m.p. 131° [*Me* ester, m.p. 82°; azine, m.p. 264° (decomp.); oxime, m.p. 188°]. (I) with 3 mols. of SO_2Cl_2 in Et_2O gives 5-carbomethoxy-4-carbethoxy-3-ethylpyrrole-2-carboxylic acid, m.p. 158°, which with 50% KOH yields 3-ethylpyrrole; this with cryptopyrrolealdehyde in EtOH and 48% HBr gives 3':5'-dimethyl-3:4'-diethylpyrromethene hydrobromide (III), m.p. 183° (decomp.) [*Br*₂-derivative (IV), m.p. $> 300^\circ$]. (II) hydrolysed with 6% NaOH gives 2-aldehydo-3-ethylpyrrole-4:5-dicarboxylic acid, blackens at 205°; this and (II) with cryptopyrrole (V) in 48% HBr and AcOH give, respectively, 4:5-dicarboxy-, decomp. 208°, and 5-carboxy-4-carbethoxy-3':5'-dimethyl-3:4'-diethylpyrromethene hydrobromide, m.p. 180° (decomp.). 2-Methyl-3-ethylpyrrole (VI) (improved prep.) with MgEtBr in Et_2O and ClCO_2Et gives *Et* 2-methyl-3-ethylpyrrole-5-carboxylate, m.p. 85°, the 4-*Br*-derivative, m.p. 117°, of which with SO_2Cl_2 in Et_2O yields the *Et* ester, m.p. 107° (azine, m.p. 239°), of 4-bromo-2-aldehydo-3-ethylpyrrole-5-carboxylic acid, m.p. 190°, which with (V) in AcOH gives 4-bromo-5-carboxy-, decomp. 265°, brominated to 4:5-dibromo-3':5'-dimethyl-3:4'-diethylpyrromethene hydrobromide, identical in appearance with (IV), showing that (III) is



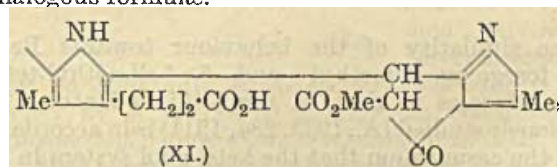
The identity of these Br_2 -derivatives is also shown by succinic acid fusion with 5-carboxy-4:4':5'-trimethyl-3-bromovinylpyrromethene-3'-propionic acid hydrobromide (VII), giving the same 1-demethyldeoxyphyloerythrin, the *Me* ester, m.p. 258°, of which, is oxidised with conc. H_2SO_4 to 1-demethylphyloerythrin. 1-Bromodeoxyphyloerythrin, m.p. 278°, 1:5-bisdemethyl-, 1-bromo-5-demethyl-, and 1:5-dibromo-actioporphyrin were also isolated from the melt. Similarly from (VII) and 3:5-dibromo-4:3':5'-trimethyl-4'-ethyl-, 5:3'-dibromo-4:5'-dimethyl-3:4'-diethyl- [blackens 180°, prep. from (VI) and 5-aldehydo-3-methyl-4-ethylpyrrole-carboxylic acid], and 5:4'-dibromo-4:3':5'-trimethyl-3-ethyl-pyrromethene hydrobromides, respectively, are obtained the following porphyrins: 2-de-ethyldeoxyphyloerythrin *Me* ester (VIII) (2-*Br*-derivative; *Fe* salt; *Cu* salt), identical with the product from chlorophyll-*a* (cf. A., 1934, 1371), the vinyl group of which must therefore be in position 2, and (VIII) with H_2SO_4 gives 2-de-ethylphyloerythrin; deuteractioporphyrin II (*Br*₁-derivative); 3-demethyldeoxyphyloerythrin *Me* ester (IX), m.p. 246° (*Br*-derivative), identical with the product from chlorophyll-*b*, the CHO of which must therefore be in position 3, and (IX) with H_2SO_4 yields 3-demethylphyloerythrin; 4-de-ethyldeoxyphyloerythrin *Me* ester, m.p. 259° (4-*Br*-derivative; *Fe* salt; *Cu* salt), which with H_2SO_4 yields 4-de-ethylphyloerythrin. Succinic acid fusion of 5-carboxy-4:3':5'-trimethyl-3-bromovinylpyrromethene-4'-propionic acid hydrobromide with 5-bromo-5'-bromomethyl-4:3'-dimethyl-3:4'-diethylpyrromethene hydrobromide gives a deoxyphyloerythrin, $\text{C}_{33}\text{H}_{36}\text{O}_2\text{N}_4$ [*Me* ester, m.p. 263°; *Fe* salt; *Cu* salt; phyloerythrin (*Me* ester, m.p. 264°); *rhodin*], having the appended formula:



LIX. Phæophorbide-*a* with red P and HBr in AcOH and subsequent treatment with 20% HCl yields 2- α -hydroxydihydrophæophorbide-*a*, which with CH_2N_2 in Et_2O gives 2- α -hydroxydihydrochlorin-*e*₆ *Me*₂ ester together with the *Me* ester, m.p. 261°, of 2- α -hydrodihydrophyrophæophorbin-*a* (X) decomp. 220°. Similarly pyrophæophorbide-*a* yields (X), which with MeOH yields the *Me* ester of its *Me* ether, m.p. 240°; this with HI in AcOH gives oxophylloerythrin *Me* ester, whilst reduction (H_2 , Pd, AcOH) and subsequent reoxidation yields phyloerythrin *Me* ester. Dihydrophæophorbide-*a* with HI in AcOH gives phæoporphyrin-*a*₅ but no oxophæoporphyrin-*a*₅. The colourless residue of *Rhodiovibrio* after extraction with COMe_2 (cf. this vol., 362) yields by further extraction (CHCl_3) a compound, $(\text{C}_4\text{H}_6\text{O}_2)_n$, depolymerised by sublimation to give crotonic acid together with (probably)

isocrotonic acid. $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ fusion of oxorhodoporphyrin gives oxopyrroporphyrin [*Me* ester, m.p. 255°; *oxime*, m.p. 272°; *hæmin*, cryst.; *Ac* derivative, m.p. 290°, identical with the Ac_2 derivative of 2-de-ethylpyrroporphyrin *Me* ester]. Data are given for the absorption spectra of most of the above compounds.

LX. Vals. of $[\alpha]^{20}$ in COMe_2 or $\text{C}_5\text{H}_5\text{N}$ are given for chlorophyll, ehlorophyllide-*a*, phæophorbide-*a*, methylphæophorbide-*b*, pyrophæophorbide-*a* and -*b* (XI), pyrophæophorbide-*a* *Me* ester (XII), 10-ethoxymethylphæophorbide-*a* and -*b*, 10-ethoxyethylphæophorbide-*a*, chlorin-*e*₄ *Me*₂ ester, chlorin *p*₆ *Me*₃ ester, phæoporphyrin-*a*₅, phyloerythrin, probophorbide-*a*, and oxochloroporphyrin-*e*₄. As (XII) is optically active it must contain an asymmetric C, which is considered to be C_γ ; hence (XI) must have asymmetric C at C_γ and C_{10} as shown. Derivatives of (XI) have analogous formulæ.



F. R. G.

Preparation of 4-methylthiazole-5-carboxylic acid. M. L. TOMLINSON (J.C.S., 1935, 1030—1031).— $\text{COMe}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ and $\text{HCS}\cdot\text{NH}_2$ give Et 4-methylthiazole-5-carboxylate, b.p. 215—220°, m.p. 27—28°, in 50% yield, hydrolysed to 4-methylthiazole-5-carboxylic acid (I), m.p. 280° (decomp.) after softening at 270° [*Me* ester (II), m.p. 74—75°]. (I) and (II) are identical with the products obtained by Windaus by degradation of vitamin-*B*₁. H. W.

Production of thiazole compounds.—See B., 1935, 749.

Formation and stability of polybromide derivatives of heterocyclic compounds. V. Bromination of some 2-arylimino-4-keto-3-aryl-5-methyltetrahydrothiazoles and their 3:5-dimethyl homologues: theory of singlet linkages. B. AHMAD, R. D. DESAI, and R. F. HUNTER (J. Indian Chem. Soc., 1935, 12, 237—245).—Treatment of 2-anilo-4-keto-3-phenyl-5-methyltetrahydrothiazole, m.p. 105° [from $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ (I), $\text{CS}(\text{NHPH})_2$ (II), NaOEt, and EtOH], with Br in CHCl_3 at 0—3° affords a hydroperbromide, $\text{C}_{16}\text{H}_{13}\text{ON}_2\text{SBr}\cdot\text{HBr}(\text{Br}_2)$, m.p. 149°, converted by H_2SO_3 into 2-anilo-4-keto-3-p-bromophenyl-5-methyltetrahydrothiazole, m.p. 121—122° [also obtained by heating $\text{NHPH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ (III), NaOEt, EtOH, and (I)]. Similarly 2-anilo-4-keto-3-phenyl-5:5-dimethyltetrahydrothiazole, m.p. 160° [from (II), NaOEt, EtOH, and $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (IV)], yields a hydroperbromide, m.p. 196° (decomp.), which loses Br on exposure to the air forming a hydro-tetrabromide. This is reduced by H_2SO_3 to 2-anilo-4-keto-3-p-bromophenyl-5:5-dimethyltetrahydrothiazole, m.p. 163° [also obtained from (III) and (IV)]. By similar methods 2-p-tolylimino-4-keto-3-p-tolyl-5-methyltetrahydrothiazole, m.p. 110°, affords an indefinite bromo-additive compound, m.p. 92°, reduced by H_2SO_3 to 2-p-tolylimino-4-keto-3-o-bromo-p-tolyl-5-methyltetrahydrothiazole, m.p. 157° [also obtained from

(I) and *s-p*-tolyl-*o*-bromo-*p*-tolylthiocarbamide, m.p. 168°; 2-*p*-tolylimino-4-keto-3-*p*-tolyl-5:5-dimethyl-tetrahydrothiazole, m.p. 167°, yields an indefinite hydroperbromide, m.p. 98°, reduced by H_2SO_3 to 2-*p*-tolylimino-4-keto-3-*o*-bromo-*p*-tolyl-5:5-dimethyl-tetrahydrothiazole, m.p. 109° [also obtained from *s-p*-tolyl-*o*-bromo-*p*-tolylthiocarbamide and (IV)]; 2-*p*-bromoanilo-4-keto-3-*p*-bromophenyl-5-methyltetrahydrothiazole, m.p. 120°, yields a hydrotribromide, m.p. 86° (decomp.), reduced by H_2SO_3 to 2-*p*-bromoanilo-4-keto-3-*op*-dibromophenyl-5-methyltetrahydrothiazole, m.p. 90° [also obtained from (I) and *s-p*-bromophenyl-*op*-dibromophenylthiocarbamide, m.p. 180°], and 2-*p*-bromoanilo-4-keto-3-*p*-bromophenyl-5:5-dimethyltetrahydrothiazole, m.p. 165–166°, yields a hydrotribromide, m.p. 84° (decomp.), reduced by H_2SO_3 to 2-*p*-bromoanilo-4-keto-3-*op*-dibromophenyl-5:5-dimethyltetrahydrothiazole, m.p. 140° [also obtained from the appropriate tribromothiocarbanilide and (IV)].

The similarity of the behaviour towards Br of the foregoing 5-methyl- and 5:5-dimethyl-tetrahydrothiazoles to that of the ψ -thiohydantoins (V) previously studied (A., 1933, 284, 1311) is in accordance with the assumption that the keto-enol system in (V) plays no part in their bromination.

1-Aminobenzthiazole hydrodibromide (A., 1934, 309) is not paramagnetic and hence does not contain a $[\text{Br}_2]^\circ$ ion which involves a "singlet linking"; a structure is proposed. The evidence for this type of linking is not conclusive. H. G. M.

Reaction of bismuth salts with the products of condensation of bis-phenylthiocarbamide. J. V. DUBSKY and J. TRTILEK (Chem. Listy, 1935, 29, 33–34).— BiCl_3 yields an orange-yellow salt with 3-anilino-5-thiol-4-phenyl-1:2:4-triazole, an orange-red salt, $\text{Bi}(\text{C}_6\text{H}_5\text{N}_3\text{S}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$, with 3:5-dithiol-4-phenyl-1:2:4-triazole, a white salt with 3:5-dianilino-4-thio-1:2-diazole, and a yellow salt with 3-anilino-5-thiol-4-thio-1:2-diazole. R. T.

***d*-Nornicotine, an alkaloid of *Duboisia Hopwoodii*, F. v. Muell.** E. SPATH, C. S. HICKS, and E. ZAJIC (Ber., 1935, 68, [B], 1388–1393).—Extraction of the dried leaves with EtOH and removal of non-basic material gives a crude alkaloid from which a fraction, b.p. 117°/3.6 mm., $[\alpha]_D^{25} + 38.3^\circ$, is isolated. Analyses indicating the formula $\text{C}_8\text{H}_{12}\text{N}_2$ and absorption spectrum point to the presence of *d*-nornicotine (I); this is confirmed by its oxidation to nicotinic acid. Methylation with CH_2O and HCO_2H gives a substance the dipicrate of which does not depress the m.p. of the dipicrate of *l*- or *dl*-nicotine. $[\alpha]$ of the volatile base from the *Duboisia* dipicrate shows the presence of 62% of *d*-nicotine and 38% of *dl*-nicotine. The presence of nicotine in the *Duboisia* base is excluded since it is quantitatively benzoylated by Bz_2O at 20°, and although (I) has a tendency towards racemisation under the influence of HCl (*d* 1.11) at 90–95° it is improbable that such change takes place under the much milder conditions of methylation. It must therefore be assumed that the *Duboisia* base contains about 62% of (I) and 38% of *dl*-nornicotine; this view is confirmed by comparison of its salts with those of *l*- and *dl*-nicotine. H. W.

[Simplification of Pictet's nicotine synthesis.] G. HAHN and O. SCHALES (Ber., 1935, 68, [B], 1310).—A reply to Spath *et al.* (this vol., 635). H. W.

Amination of alkaloids by sodamide and potassamide. α - and α' -aminoanabasines. IV. Nitration of α' -aminoanabasine. M. M. KATZNELSON and M. I. KABATSCHEV (Ber., 1935, 68, [B], 1247–1251).—Treatment of α' -aminoanabasine (I) in conc. H_2SO_4 at 0° with HNO_3 (*d* 1.4) affords 2-nitroamino-5-2'-piperidinopyridine [sulphate (II), m.p. 233° (decomp.)], isomerised by conc. H_2SO_4 at 70–80° to 3-nitro-2-amino-5-2'-piperidinopyridine, m.p. 178.5–179°, also obtained by direct nitration of (I) at a somewhat higher temp., whereby also a compound, m.p. 70°, is produced. (II) is transformed by boiling Ac_2O into 2-hydroxy-5-2'-piperidinopyridine [Na derivative; picrate, m.p. 241° (decomp.)], also obtained by diazotisation of (I). H. W.

Resolution of peganine (vasicine) into its optically active forms. E. SPATH, F. KUFFNER, and N. PLATZER (Ber., 1935, 68, [B], 1384–1388).—Treatment of peganine with *d*-tartaric acid in MeOH leads to the isolation of *l*-peganine (I), m.p. 211–212° (vac.) after marked softening at 197–200°, $[\alpha]_D^{25} - 159^\circ$, -189° , and -203° in CHCl_3 (*c*=1.04, 2.01, and 2.66, respectively), $[\alpha]_D^{25} + 31.4^\circ$ in HCl (1:35). The mother-liquors from (I) when treated with *l*-tartaric acid give *d*-peganine, $[\alpha]_D^{25} + 163^\circ$ (*c*=1.16), $[\alpha]_D^{25} + 188^\circ$ (*c*=2.33), $[\alpha]_D^{25} + 203^\circ$ (*c*=3.45), all in CHCl_3 , $[\alpha]_D^{25} - 30.7^\circ$ in HCl (1:35). Racemisation of the optically active forms occurs when they are repeatedly sublimed in high vac. or slowly when they are heated with 5% HCl at 100°. H. W.

Modified cinchona alkaloids. II. Action of sulphuric acid on quinine and quinidine. T. A. HENRY, W. SOLOMON, and E. M. GIBBS (J.C.S., 1935, 966–971).—The products of the action of 60% H_2SO_4 on the alkaloids are *apo*-bases (demethylated or phenolic bases) and undemethylated bases, isomerides of quinine and quinidine. In addition to *apo*quinine, *isoapoquinine*, m.p. 275° (corr., decomp.), $[\alpha]_D^{25} - 261.7^\circ$ in EtOH (*dihydrobromide*, m.p. 136–140°, $[\alpha]_D^{25} - 230.2^\circ$ in H_2O ; *hydrochloride*, m.p. 271°, $[\alpha]_D^{25} - 194.5^\circ$ in H_2O , -226.7° in EtOH); *H sulphate*, m.p. 202–205°, $[\alpha]_D^{25} - 268.4^\circ$ in H_2O), has been isolated. *Hydroxydihydroapoquinine*, m.p. 281–284° (corr.; decomp.) after softening at 277°, $[\alpha]_D^{25} - 205.4^\circ$ in 0.1N- H_2SO_4 [*hydrochloride*, m.p. 264–268° (corr.; decomp.), $[\alpha]_D^{25} - 177.3^\circ$ in 0.1N-HCl, -108.9° in H_2O , -110.4° in EtOH]; *sulphate*, m.p. 287–293° (corr.; decomp.), $[\alpha]_D^{25} - 175.5^\circ$ in 0.1N- H_2SO_4 ; *H sulphate*, blackens at 230° after darkening at 215°, $[\alpha]_D^{25} - 154^\circ$ in 0.1N- H_2SO_4 ; *dihydrobromide*, m.p. variable, $[\alpha]_D^{25} - 130.6^\circ$ in H_2O), has been obtained. From quinidine, in addition to *isoapoquinidine*, there is derived *apoquinidine*, m.p. 185–190° (corr.; decomp.), $[\alpha]_D^{25} + 291.4^\circ$ in 0.1N- H_2SO_4 , $+208.6^\circ$ in EtOH (also $+1\text{EtOH}$ and $+1\text{COMe}_2$) [*hydrochloride*, m.p. 183–185° (corr.; decomp.), $[\alpha]_D^{25} + 177.0^\circ$ in H_2O (also $+1\text{EtOH}$ and $+2\text{H}_2\text{O}$); *sulphate*, m.p. 260° (corr.; decomp.), $[\alpha]_D^{25} + 248.5^\circ$ in 0.1N- H_2SO_4 (also $+2\text{EtOH}$ and $+1\text{H}_2\text{O}$); *dihydrobromide*, m.p. 280° (corr.; decomp.), $[\alpha]_D^{25} + 192.5^\circ$ in H_2O ; *zincchloride*, m.p. 290° (corr.;

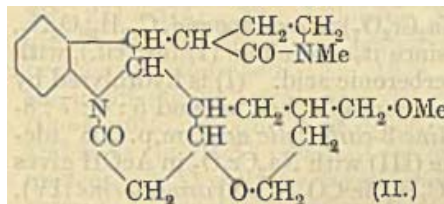
decomp.), $[\alpha]_D^{15}$ 175.3° in H_2O . A third isomeride, provisionally named *phenolic base A*, m.p. 250° (corr.; decomp.), $[\alpha]_D^{15}$ +209.5° in 0.1*N*- H_2SO_4 , +139.5° in EtOH [*hydrochloride*, m.p. 180—190° (corr.; decomp.), $[\alpha]_D^{15}$ +139.3° in H_2O (also +1EtOH)], has been isolated in small amount.

The undemethylated bases recovered from quinine have so far yielded only one cryst. product, *apoquinine Me ether*, m.p. 183—185°, $[\alpha]_D^{15}$ -201.9° in EtOH, which is the β -isoquinine of earlier workers. The *sulphate*, m.p. 220°, $[\alpha]_D^{15}$ -171.2° in H_2O , and *dihydrobromide*, m.p. 219° (corr.; decomp.), $[\alpha]_D^{15}$ -196° in H_2O (also +1*H*₂O), appear new. α -isoquinine has not been found. From quinidine two well-defined isomerides have been isolated, one of which is β -isoquinidine now shown to be *isoapoquinidine Me ether*, m.p. 180—181°, $[\alpha]_D^{15}$ +278.8° in 0.1*N*- H_2SO_4 [*hydrochloride*, m.p. 267° (corr.; decomp.), $[\alpha]_D^{15}$ +174.7° in H_2O]; *dihydrobromide*, m.p. 210—215° (corr.; decomp.), $[\alpha]_D^{15}$ +186.3° in H_2O . A possible third isomeride, m.p. 120°, $[\alpha]_D^{15}$ +233.5° in 0.1*N*- H_2SO_4 , +136.5° in EtOH, is described. H. W.

Third oxide base derived from quinidine. T. DOMAŃSKI and J. SUSZKO (Arch. Chem. Farm., 1935, 2, 205—219).— α -isoquinidine (I), as prepared by the method previously described (A., 1933, 517), contains up to 20% of a third isomeride, γ -isoquinidine (II), isolated as follows. The tartrates derived from the (I) fraction are converted into hydrochlorides, the aq. solution of which is allowed to crystallise during several weeks, the cryst. hydrochloride of (I) is separated, the mother-liquor is made alkaline with NaOH, excess of dil. HNO_3 is added, and the cryst. nitrate of (II), which then separates, is converted by aq. NH_3 into (II), +2*H*₂O, m.p. 70°, $[\alpha]_D^{15}$ +51.1° [*dinitrate*, m.p. 196°, $[\alpha]_D^{15}$ +50° in H_2O ; *oxalate*, m.p. 185—188° (decomp.), $[\alpha]_D^{15}$ -56.9° in H_2O ; *hydriodide*, m.p. 180—183°; *tartrate* (III), m.p. 160—161° (decomp.); *picrate*, m.p. 183—193°; *methiodide*, m.p. 227—235° (decomp.), $[\alpha]_D^{15}$ +12°; *dimethiodide*, m.p. 241—244° (decomp.), $[\alpha]_D^{25}$ -95°; *perbromide*, m.p. 213—216°; *aminoxide*, m.p. 80—100°, $[\alpha]_D^{15}$ +42°]. (III), when dried at 60° and then fused, affords γ -isoquinidine, m.p. 113°, $[\alpha]_D^{15}$ -40.0° [*tartrate*, *nitrate*, and *hydriodide*, oils; *N-NO*-, m.p. 103—105°, and *N-Me* derivative, an oil (*dinitrate*, m.p. 155°); *methiodide*, m.p. 90—100°, $[\alpha]_D^{15}$ -11.0°]. (II) and AcOH (100°; 32 hr.) give γ -hydroxydihydroquinotoxine, m.p. 110—118°, $[\alpha]_D^{15}$ -15.0° (*tartrate*, m.p. 60°; *N-NO*-derivative, an oil, $[\alpha]_D^{15}$ -17.0°; *p-nitrophenylhydrazone*, m.p. 90°). (II) is converted by heating at 70—80° with conc. H_2SO_4 into β -isoquinidine (IV), and by heating with conc. aq. HBr (100°; 14 hr.) into hydrobromocupreidine dihydrobromide. (II) differs from (I) and (IV) probably not structurally, but stereochemically. The optical data given above relate, unless otherwise specified, to solutions in 96% EtOH. R. T.

Strychnine and brucine. XXXIII. Methoxymethylchanodihydrostrychnanic acid and its resistance to facile dehydrogenation. (Miss) T. M. REYNOLDS and R. ROBINSON (J.C.S., 1935, 935—940).—Reply is made to Leuchs (this vol., 505).

The possibility that methoxymethylchanodihydrostrychnone (I) may be an aldehyde is not further entertained, since it is quantitatively recovered after being refluxed with HgO in H_2O . Oxidation of it with Br in HBr affords (?) *pentabromomethoxymethylchanodihydrostrychnonic acid hydrobromide*, decomp. 157° after darkening at 152°. Oxidation of methoxymethyl-dihydroeostrychnine with $KMnO_4$ in $COMe_2$ at -10° affords (I) in 10% yield, whereas use of BzO_2H leads to a remarkably pure product. It has been suggested that strychnine and its derivatives contain a blocked dihydroindole nucleus, but the stabilisation of the indole nucleus does not extend to methoxymethylchanodihydrostrychnane (II), and there appears no reason why it should not be readily oxidised to an indole derivative. Nevertheless it is



stable to $Hg(OAc)_2$ in AcOH at 100° and is not affected by S in boiling $C_{10}H_8$. In confirmation, *methoxymethylchanodihydrostrychnanic acid* (III), m.p. 205—206° (slight decomp.) after softening at 203°, has been compared with *cis*-hexahydrocarbazole (IV) in its behaviour towards dehydrogenating agents. Conditions are given under which (IV) is transformed into tetrahydrocarbazole by $Hg(OAc)_2$ in cold dil. AcOH or by S in quinoline at 175—180°; in parallel experiments (III) remains unchanged. (III) is prepared by the action of hot $Ba(OH)_2 \cdot MeOH$ in N_2 on (II) and the reverse change is effected by boiling (III) with 5% HCl or by heating it in $C_{10}H_8$ at 180—186°. The stability of the $\cdot N(b) \cdot CO \cdot$ group is remarkable, but its presence is confirmed since (III) is acid to litmus and gives a *nitrosoamine*, decomp. 190° after softening and darkening at 187°, which does not form a hydrochloride. The colour reactions of the acid show that the group $\cdot N(a) \cdot CO \cdot$ is the one that is hydrated.

H. W.

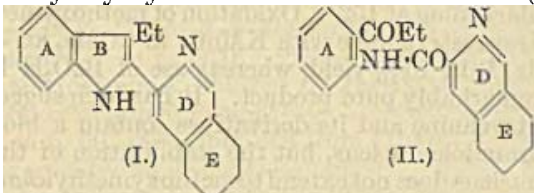
Ergot alkaloids. V. Hydrolysis of ergotinine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1935, 110, 521—530).—Alkaline hydrolysis of ergotinine (I) yields *isobutyrylformic acid* (II), *lysergic acid* (III), and a *dipeptide*, $C_{14}H_{18}O_3N_2$, m.p. 252° (decomp.), whilst acid hydrolysis gives (II), (III), phenylalanine, and proline. (I) and ergotoxine are regarded as being composed of proline and phenylalanine combined in peptide linking with (II) and (III) and perhaps NH_3 , and the structures are discussed. It is concluded that (III) is related biogenetically to tryptophan, for it may be degraded to simple indoles.

Alkaloid from ergot. W. A. JACOBS and L. C. CRAIG (Science, 1935, 82, 16—17).—Extraction with dil. acid of the ergot powder residue which remains after removal of Et_2O -sol. alkaloids, neutralisation with Na_2CO_3 , and extraction with $CHCl_3$ yields ergobasine (I) identical with that described by Stoll *et al.* (this vol., 995). Hydrolysis with KOH-EtOH yields lysergic acid (II), but no NH_3 , *isobutyrylformic* or *prruvic acid*. Hydrolysis with strong acid of the material left after removal of (II) gave an amino-propanol, isolated as the sulphate, $(C_3H_7ON)_2 \cdot H_2SO_4$.

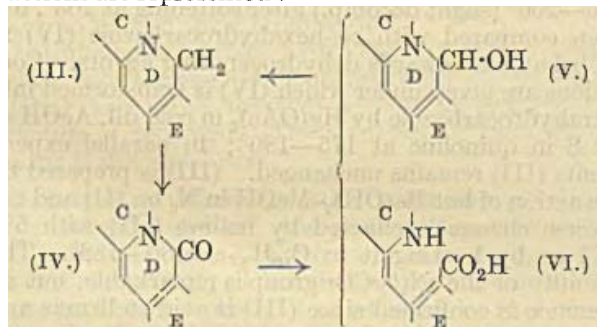
(di-*p*-bromobenzoate, $C_{17}H_{15}O_3NBr_2$, m.p. 155°, $[\alpha]_D^{25} +48^\circ$). (I) is the hydroxyisopropylamide of (II).

L. S. T.

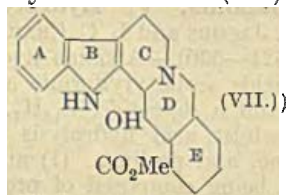
Constitution of yohimbine. C. SCHOLZ (Helv. Chim. Acta, 1935, 18, 923—933; cf. A., 1934, 89).—Tetrahydrobyrinerine is shown to have structure (I) by



oxidation (O_3 or $Na_2Cr_2O_7$) to a compound, $C_{19}H_{20}O_2N_2$, regarded as (II), since it, as well as (I) (*loc. cit.*), with dil. HNO_3 gives berberonic acid. (I) is hydrolysed by $10N-H_2SO_4$ to *o*-aminopropiophenone and 5 : 6 : 7 : 8-tetrahydroisoquinoline-3-carboxylic acid, m.p. 208° (decomp.). Yohyryne (III) with $Na_2Cr_2O_7$ in AcOH gives *o*- $C_6H_4(CO_2H)_2$, *o*- $C_6H_4MeCO_2H$, and oxyyohyryne (IV), m.p. 185°, reduced (KOH, amyl alcohol) to (III), a compound (V), $C_{19}H_{16}ON_2$, m.p. 193—194°, and an amphoteric compound (VI), m.p. 255°. These reactions are represented:

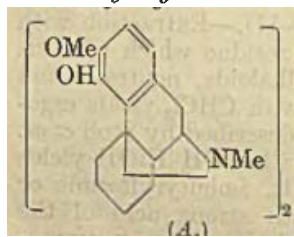


Tryptamine boiled with homophthalic anhydride in C_6H_6 gives indolyethylhomophthalimide, an oil, which when heated under reduced pressure yields a compound, $C_{19}H_{16}O_2N_2$, m.p. 210°, but no (IV). Yohimbine is consequently formulated as (VII).



F. R. G.

Sinomenine. XLI. *d*- and *l*-bis-1 : 1'-β-Tetrahydrodeoxycodeine. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1935, 10, 252—255; cf. A., 1934, 908).—Deoxodemethoxydihydrosinomenine (I) in EtOH with aq. $AgNO_3$ yields bis-1 : 1'-deoxodemethoxydihydrosinomenine (A), m.p. 230—237°, $[\alpha]_D^{20} +91.57^\circ$ in EtOH [methiodide, m.p. 275—279° (decomp.); hydrochloride, m.p. 293—297° (decomp.)]. Similarly β-tetrahydrodeoxycodeine (II) gives bis-1 : 1'-β-tetrahydrodeoxycodeine (A), m.p. 230—238°, $[\alpha]_D^{20} -91.32^\circ$ in EtOH (methiodide, m.p. 276—279°), and equal



codeine, m.p. 255—260°, $[\alpha]_D 0^\circ$ in EtOH. The following were prepared similarly to their optical isomerides (A., 1931, 1172): *de*-N-methyl-β-tetrahydrodeoxycodeine, m.p. 145—148°, $[\alpha]_D^{25} +65.45^\circ$ in MeOH; *dl*-*de*-N-methyl-β-tetrahydrodeoxycodeine, m.p. 133—136°, $[\alpha]_D 0^\circ$ in MeOH; *dehydro-d-thebanan*, m.p. 107—112°, $[\alpha]_D^{25} +175.54^\circ$ in MeOH; *dehydro-dl-thebanan*, m.p. 90—92°, $[\alpha]_D 0^\circ$ in MeOH; *dihydrode-N-methyl-β-tetrahydrodeoxycodeine*, m.p. 161°, $[\alpha]_D^{25} -78.42^\circ$ in MeOH- $CHCl_3$; *dl-dihydrode-N-methyl-β-tetrahydrodeoxycodeine*, m.p. 135—140°, $[\alpha] 0^\circ$ in MeOH- $CHCl_3$; *d-thebanan*, m.p. 48—54°, $[\alpha]^{25} +3.25^\circ$. F. R. G.

Tubocurarine. H. KING (Chem. and Ind., 1935, 739—740).—The active principle of tubocurarine (cf. A., 1928, 1264) is cryst. in the form of *tubocurarine chloride*, $C_{38}H_{44}O_6N_2Cl_2$. Hofmann degradation of *O-methylbebeerine methochloride* (I) gives three methine methiodides, two inactive and one dextrorotatory, which are also obtained, with a levorotatory form, from *O-methyltubocurarine chloride* (II); these methine methiodides, on further degradation, all give a substance, $C_{36}H_{32}O_6$. (II) and (I) are thus diastereoisomerides, and can be represented by the symbols *dl'* and *dd'*. This suggests that the botanical origin of tubocurarine is in a Brazilian *Chondodendron* (fam. Menispermaceae). E. W. W.

Mechanism of the preparation of tribenzylarsine according to Michaelis and Paetov. J. DODONOV and H. MEDOX (Ber., 1935, 68, [B], 1254—1258).—The action of Na on $AsCl_3$ and CH_2PhCl in Et_2O in an indifferent gas gives $As(CH_2Ph)_3$ (I) in 45.11% yield in contrast with a max. yield of 21.81% recorded by Michaelis *et al.*; the formation of $OH \cdot AsCl(CH_2Ph)_3$ (II) is not observed and > minimal amounts of $(CH_2Ph)_2AsO \cdot OH$ (III) are produced. Pure (I) is not rapidly oxidised by air at room temp., although catalytic impurities sometimes induce a vigorous oxidation giving (III), $PhCHO$, and As_2O_3 . (I) and O_2 in Et_2O containing HCl afford (III), $(CH_2Ph)_3AsCl \cdot OH$ (IV), and $PhCHO$. The change is therefore $3CH_2PhCl + AsCl_3 + 6Na \rightarrow (I) + 6NaCl$. $(I) + O + HCl \rightarrow (IV)$. $(I) + 3O \rightarrow (III) + PhCHO$. CH_2NaPh and $EtOAc$ are regarded as primary products. (II) and KBr in boiling H_2O afford the compound $OH \cdot As(CH_2Ph)_3 \cdot O \cdot AsBr(CH_2Ph)_3$, m.p. 162.5°, transformed by HBr into tribenzylarsine oxybromide, m.p. 129.5°. H. W.

Hydroxy-salts of secondary and tertiary arsines. G. J. BURROWS (J. Proc. Roy. Soc. New South Wales, 1934, 68, 72—79).—Oxidation of $AsPhMe_2$ in moist air yields $AsPhMeO \cdot OH$ (corresponding arsonium chloride, m.p. 111°, nitrate, m.p. 151°, and sulphate, m.p. 70°), whilst oxidation (H_2O_2 -EtOH) in HNO_3 or HCl gives *phenyldimethylhydroxyarsonium nitrate*, m.p. 152°, or *chloride*, m.p. 174°. $AsPh_2MeO$, m.p. 142°, is obtained by oxidation (H_2O_2 -EtOH) of $AsPh_2Me$, and *p*- $C_6H_4Me \cdot AsMeO \cdot OH$, m.p. 151° (corresponding arsonium chloride, m.p. 133°, nitrate, m.p. 157°, and sulphate, m.p. 85°), is obtained similarly from $(p-C_6H_4Me \cdot AsMe)_2O$ (I), b.p. 220°/12 mm. (prepared by methylation of Na tolyl arsenite), in AcOH solution. (I) with HCl gives $C_6H_4Me \cdot AsMeCl$, b.p. 147°/24 mm., 138°/14 mm.,

whilst $C_6H_4Me \cdot AsCl_2$, m.p. 42° (lit. 31°), with Na_2CO_3 yields $p-C_6H_4Me \cdot AsO$. F. N. W.

Catalytic reduction of nitroarylsarsinic acids. M. R. STEVINSON and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 1298—1299).—The NO_2 -acids (as Na salts in H_2O) (0.1 mol.) are reduced with H_2 (initial pressure 30 lb.) and Raney Ni (10 g.). *m*-Amino-, 2-chloro-5-amino-, 3-amino-4-hydroxy-, -4-isoamylamino-, -4- β -hydroxyethylamino-, -4- β -hydroxy-*n*-propoxy-, and -2-carboxymethylamino-, and 5-amino-2- β -hydroxyethylamino-phenylarsinic acids are thus prepared in 52—99% yield. The effect of various inorg. substances on the time of reduction (similar conditions) of $p-NO_2 \cdot C_6H_4 \cdot OH$ is studied; retardation is pronounced with KCN, Na_3AsO_3 , and $NaNO_2$, whilst slight acceleration is found with $CuSO_4$ (10% wt.). H. B.

Preparation and properties of 3 : 3'-bis(azo-*m*-phenylenediamine)- and 3 : 3'-bis(azo-2 : 6-diaminopyridine)-4 : 4'-dihydroxyarsenobenzene. A. E. JURIST and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 457—459).—The compounds named were prepared by treating diazotised salvarsan with $m-C_6H_4(NH_2)_2$ and 2 : 6-diaminopyridine, respectively. They are both rapid tissue penetrants, but are too toxic for therapeutic uses. The diaminopyridine derivative is bacteriostatic but not germicidal to *B. typhosus* and *B. staphylococcus*. E. H. S.

Arsenamides. Compounds containing the As-N linking. G. O. DOAK (J. Amer. Pharm. Assoc., 1935, 24, 453—457).—The compounds ("arsenamides") are obtained by treating the appropriate amines with arsenious halides, both in *n*-heptane solution. Trianilinoarsine trihydrochloride, $As(NH_2 \cdot PhCl)_3$, and anilindichlorarsine, $AsCl_2 \cdot NHPh$, m.p. 89° ; tripiperidinoarsine trihydrochloride, m.p. $240-242^\circ$ (trinitrate, m.p. 144° ; triacetate, m.p. 304°), and a yellow oil, b.p. $98^\circ/1$ mm. (piperidinodichlorarsine?); diethylaminodichloroarsine, b.p. $107^\circ/38$ mm.; di-(β -aminoethylamino)chloroarsine dihydrochloride, $AsCl(NH \cdot CH_2 \cdot CH_2 \cdot NH_2Cl)_2$ (chars $> 225^\circ$), methyl-anilindichloroarsine, b.p. $116^\circ/3$ mm. Tri(benzyl-amino)arsine trihydrochloride, m.p. 246° (decomp.); tri(dibenzylamino)arsine trihydrochloride, m.p. $252-254^\circ$ (decomp.); tri(tribenzylamino)chloroarsine, $As[N(CH_2Ph)_3Cl]_3$, m.p. $209-211^\circ$ (decomp.); di-piperidinoethylarsine dihydrochloride, m.p. 196° ; piperidinoethylchloroarsine, b.p. $108^\circ/8$ mm.; anilino-ethylchloroarsine, b.p. $110^\circ/10$ mm.; piperidinodimethylarsine, $C_5H_{10}N \cdot AsMe_2$, b.p. $75^\circ/8$ mm. E. H. S.

Reactivities of groups as revealed by hydrogen bromide cleavage of substituted germanes. J. K. SIMONS (J. Amer. Chem. Soc., 1935, 57, 1299—1302).—Ge tri-*m*-tolyl bromide (I) with $p-C_6H_4Me \cdot MgBr + ZnCl_2$ in xylene gives Ge tri-*m*-tolyl *p*-tolyl (II), m.p. $98.5-100.5^\circ$; Ge *o*-tolyl tri-*p*-tolyl, m.p. $164-166^\circ$, is similarly prepared from Ge tri-*p*-tolyl bromide. Ge tri-*p*-tolyl chloride, m.p. 121° , is formed from the oxide and EtOH-conc. HCl. Treatment of the following compounds with HBr in $CHCl_3$ gives the products quoted in square brackets and shows that the order of decreasing reactivity of

the following groups is *p*-tolyl, *m*-tolyl, Ph, benzyl: Ge tetra-*m*-tolyl [(I) 83.9%; PhMe 43.8%]; (I) [Ge di-*m*-tolyl dibromide (III), b. p. $189-190^\circ/4$ mm., 37.7%; PhMe 72.9%]; Ge tetra-*o*-tolyl [Ge tri-*o*-tolyl bromide 30.8%; PhMe 55.5%]; Ge tetrabenzyl [Ge tribenzyl bromide 10.3%; PhMe 18.6%]; Ge triphenyl *p*-tolyl [GePh₃Br 36%; PhMe 38.3%]; Ge triphenyl *m*-tolyl [GePh₃Br 15.8%; some C_6H_6]; (II) [(I) 27.4%; PhMe 72.2%; some impure (III)]. H. B.

Preparation of organo-mercury compounds of phenols and aromatic amines. II. P. NEOGI and G. K. MUKHERJEE (J. Indian Chem. Soc., 1935, 12, 211—215).—The following Hg derivatives of aromatic compounds are prepared by the method previously described (A., 1928, 783). They are sol. in dil. alkalis, couple with diazotised $\beta-C_{10}H_7 \cdot NH_2$ (the resulting products are described in parentheses), and have the $\cdot HgCl$ attached directly to the aromatic nucleus. β -Naphtholmercurichloride, m.p. 180° (decomp.) [β -naphthylazochloromercuri- β -naphthol, m.p. 170° (decomp.)]; α -naphthol-2-mercurichloride, m.p. 205° (decomp.) (4- β -naphthylazo-derivative, decomp. 180°); carvacrol-3-mercurichloride, m.p. 182° (decomp.) (5- β -naphthylazo-derivative, decomp. 160°); thymol-2-mercurichloride, m.p. 160° (decomp.) (6- β -naphthylazo-derivative, decomp. 195°), different from the compound prepared by Dimroth (A., 1902, i, 850), which is regarded as thymol-6-mercurichloride; 2-nitro-6(?)-chloromercuriphenol, m.p. 185° (decomp.); 4-nitro-2(or 6)-chloromercuriphenol, m.p. 180° (decomp.). 8-Hydroxyquinoline, however, affords quinoline-8-oxymmercurichloride, decomp. 205° . The following amines form coloured mercurichloride derivatives (decomp. temp. in parentheses) in which an $NH_2 \cdot H$ is replaced by $\cdot HgCl$: α - (125°) and β - $C_{10}H_7 \cdot NH_2$ (m.p. 170° [decomp.]); *o*- (165°), *m*- (180°), and *p*-toluidine (130°); xylidine (115°); *o*- (240°), *m*- (140°), and *p*-nitroaniline (225°). H. G. M.

Passage of phenyl radicals from metallo-organic compounds. G. A. RAZUVAYEV and M. M. KOTON (J. Gen. Chem. Russ., 1935, 5, 361—365).— $HgPh_2$ (I) and $(NHPh)_2$ in ligroin at 150° give Hg, C_6H_6 , and $(\cdot NHPh)_2$. (I) yields Hg and resinous products, but not C_6H_6 or Ph_2 , with isoprene, divinyl, or pyrrole. $HgPh \cdot OH$ and H_2 afford Hg, C_6H_6 , and H_2O . $SnPh_4$ or $PbPh_4$ and S at 150° afford $(SPh)_2$ and SnS_2 or PbS , whilst $Hg(CH_2Ph)_2$ and S yield dibenzyl and HgS . The above reactions indicate that Ph, but not CH_2Ph , derivatives liberate free radicals on thermal decomp. R. T.

Organic compounds of selenium. VI. W. E. BRADT (Proc. Indiana Acad. Sci., 1934, 43, 72—98; cf. A., 1933, 256).—An exhaustive bibliography of selenonium compounds. CH. ABS. (r)

Organic derivatives of thallium. I. Determination of thallium in organic compounds. II. Reaction of thallium chloride with diazo-compounds. S. S. NAMETKIN and N. N. MELNIKOV (J. Gen. Chem. Russ., 1935, 5, 371—372, 373—377).—I. Lehmann and Rupp's method (B., 1911, 508) is applicable to the determination of Tl.

II. The compounds, $R \cdot N_2 \cdot TiCl_4$, have been prepared by adding aq. $TiCl_3$ to aq. $R \cdot N_2 \cdot Cl$ at -5° : $R=Ph$, decomp. $68-69^\circ$; $R=m-C_6H_4Me$, decomp. 59° ; $R=p-C_6H_4Me$, decomp. 93° ; $R=p-OEt-C_6H_4$, decomp. 66° ; $R=p-NO_2-C_6H_4$, decomp. 91° ; $R=m-NO_2-C_6H_4$, decomp. $111-112.5^\circ$; $R=\alpha-C_{10}H_7$, decomp. $71-72.5^\circ$. $o-NO_2 \cdot C_6H_4 \cdot N_2 \cdot Cl$ affords $2(o-NO_2 \cdot C_6H_4 \cdot N_2 \cdot Cl) \cdot TiCl_3$, decomp. $98-98.5^\circ$. The compounds decompose thus: $R \cdot N_2 \cdot TiCl_4$ (I) $\rightarrow TiCl_3 + N_2 + RCl$; $2(I) \rightarrow 2TiCl_3 + N_2 + R_2 + Cl_2$; $TiCl_3 \rightarrow TiCl + Cl_2$; (I) + $H_2O \rightarrow TiCl \cdot R \cdot OH + N_2 + HCl$. R. T.

Complex salts of amino-acids and peptides.

II. Determination of *l*-proline with the aid of rhodanilic acid. Structure of gelatin. M. BERGMANN (J. Biol. Chem., 1935, 110, 471-479).—A new reagent for the determination is *tetrathiocyanatodanilidochromiato-acid*, $[Cr(CNS)_4(NH_2Ph)_2]H$, (termed "rhodanilic acid") [*aniline*, NH_4 , *pyridinium*, and *l*-proline salts, m.p. $133-134^\circ$ (decomp.)]. Proline rhodanilate is characterised by its slight solubility and rapid crystallisation. Hydroxyproline can be determined as Reineckate after removal of arginine and proline. It is suggested that in the gelatin mol. every third NH_2 -acid may be glycine, every sixth proline, and every ninth hydroxyproline. Such an arrangement could be represented as $\cdots G \cdot P \cdot X \cdot G \cdot X \cdot X \cdots$, where G =glycyl, P =prolyl, and X =other NH_2 -acids. J. N. A.

Azoproteins. W. C. BOYD and P. MOVER (J. Biol. Chem., 1935, 110, 457-459).—N and As analyses of proteins (I) coupled under different conditions with diazotised arsanilic acid agree with earlier results; i.e., the ratio As:N can be $>$ that calc. on the assumption that diazotised amines couple with (I) only through the tyrosyl and histidyl groups. No explanation has been found. J. N. A.

Unrecognised forms of sulphur in proteins. D. BLUMENTHAL and H. T. CLARKE (J. Biol. Chem., 1935, 110, 343-349).—Aq. Br converts compounds containing $\cdot CS$, or $\cdot SH$ with N or O on the same C, into SO_4^{4-} ; $C_6H_4Me \cdot SH$ is an exception. These compounds also yield PbS on treatment with $PbCO_3$. Cystine (I) is oxidised to SO_4^{4-} by boiling fuming HNO_3 , whilst methionine (II) is not. By applying these facts to the study of the hydrolysates of proteins it is concluded that besides (I) and (II) two other substances containing S are present, one yielding SO_4^{4-} with aq. Br and PbS with $PbCO_3$, and the other SO_4^{4-} with HNO_3 and no PbS with $PbCO_3$. H. D.

Preheater in the micro-analytical determination of carbon and hydrogen. W. F. BRUCE (Mikrochem., 1935, 18, 103-105).—To overcome the difficulty of obtaining satisfactory blanks when the combustion apparatus is not used constantly, the O_2 is first passed through a hard glass tube filled with CuO wire and supported on two layers of nichrome gauze which is heated by a micro-burner. Asbestos shields are provided to prevent the heat reaching other parts of the apparatus. A. R. P.

Chromic acid modification of the Kjeldahl method for determination of nitrogen in organic compounds. J. M. SHEWAN (J.S.C.I., 1935, 54,

172-174T).—With a wide variety of org. compounds it has been found that when $K_2Cr_2O_7-H_2SO_4$ is used the accuracy of N determinations is affected chiefly by the nature of the compound and the concn. of the reagents. This modification of the Kjeldahl method is therefore not recommended in soil analysis.

Micro-methods for determination of ammonia, carbamide, total nitrogen, uric acid, creatinine (and creatine), and allantoin. H. BORSOOK (J. Biol. Chem., 1935, 110, 481-493).—Improved micro-methods are described in detail for the determination of NH_3 , uric acid, creatinine, and allantoin. In every case, the procedure ends in a colorimetric measurement, and the improvements give greater stability of colour, increased sensitivity and specificity. The min. amounts of substances that can be determined are NH_3 (5×10^{-4} mg. of N per c.c.), urea-N (1×10^{-3} mg. per c.c.), creatinine (1×10^{-3} mg.), and allantoin (5×10^{-4} mg., in 2 c.c.). J. N. A.

Determination of ammoniacal and urea-nitrogen.—See this vol., 1092.

Detection of elements in organic compounds.

III. Detection of phosphorus, arsenic, and antimony. C. L. TSENG (J. Chinese Chem. Soc., 1935, 3, 122-136).—The solution from the Na fusion (cf. this vol., 876) is boiled (a) with 6N- HNO_3 ; a yellow ppt. obtained on boiling with tartaric acid and NH_4 molybdate indicates P; (b) with 6N-HCl; As_2S_3 or Sb_2S_3 is pptd. on passing H_2S after the addition of N-KI. R. S.

(A) Determination of small quantities of water in solid organic substances. W. ŚWIĘTOŚŁAWSKI and S. MIERNIK. (B) Ebulliometric measurements of the moisture content in standard benzoic acid. W. ŚWIĘTOŚŁAWSKI, M. WOJCIECHOWSKI, and S. MIERNIK (Bull. Acad. Polonaise, 1935, A, 53-58, 59-64; cf. A., 1933, 586).—(A) The method, based on the changes in b.p. and temp. of condensation of an azeotropic C_6H_6 -EtOH mixture produced by small amounts of H_2O , is described.

(B) Determinations of H_2O in standard BzOH are described. Adsorption of H_2O by BzOH does not give appreciable errors in calorimetric determinations of its heat of combustion. H. J. E.

Activity of sulphuric acid in the oxidation of organic substances with chromic acid. H. C. S. SNETHLAGE (Rec. trav. chim., 1935, 54, 651-656).—The optimum concn. of H_2SO_4 is 80% for the determination of mannitol, sucrose, BzOH, or other acids by oxidation with $K_2Cr_2O_7-H_2SO_4$ and titration with $Na_2S_2O_3$ after approx. neutralisation and addition of KI. P. G. C.

Crystal precipitation by salting out. II. L. ROSENTHALER (Mikrochem., 1935, 18, 50-52).—The following org. compounds yield characteristic cryst. ppts. on adding $(NH_4)_2SO_4$, $NaNO_3$, or alkali chlorides to their solutions: α - and β - $C_{10}H_7 \cdot OH$, quinol ($> 1\%$), veronal, luminal, chloramine, 1 : 2 : 5-tolylenediamine ($> 0.5\%$), *m*- and *p*- $C_6H_4(NH_2)_2$, 1 : 2 : 5-*p*-diaminoanisole. A. R. P.

Titration of organic acids with ferric chloride. W. D. TREADWELL and E. WETTSTEIN (Helv. Chim. Acta, 1935, 18, 981-986).—Solutions of Na citrate,

benzoate, malate, and oxalate can be titrated potentiometrically with FeCl_3 . E. S. H.

Volumetric micro-determination of *o*-nitrophenols with methylene-blue. A. BOLLINGER (J. Proc. Roy. Soc. New South Wales, 1934, 68, 51—57).—The method previously described for the determination of picric acid (A., 1934, 1017) is applicable to the micro-determination of 2 : 4- and 2 : 6-dinitrophenol, 2 : 4-dinitro-resorcinol and α -naphthol, and 2 : 6-dinitro-*p*-cresol in aq. solution as the alkali or alkaline-earth salt. F. N. W.

Macro-, micro-, and histo-chemical detection of cineole. R. WASICKY and E. GMACH (Sci. Pharm., 1934, 5, 113—120; Chem. Zentr., 1935, i, 1095).—Formation of the compound of cineole (I) with tetraiodopyrrole (II) (sublimes 120° , decomp. 135° on slow heating) is the most sensitive microchemical test. An excess of (II) is added, forming the (I)–(II) compound, which is washed with light petroleum. Addition of aq. KOH regenerates (I). J. S. A.

Microchemical identification of coniine and nicotine. R. FISCHER and W. PAULUS (Mikrochem., 1935, 17, 356—360).—Coniine vapour is allowed to react with picrolonic acid solution on a slide in a special apparatus. The picrolonate is characterised by micro-m.p. Sublimation of coniine hydrochloride and determination of the m.p. is less sensitive. Nicotine can be similarly identified as picrate. R. S.

Determination of pilocarpine and its salts. J. A. SANCHEZ (Ann. Chim. Analyt., 1935, [iii], 17, 122—123).—The pilocarpine (I) salt is dissolved in aq. EtOH and neutralised with 0.1*N*-NaOH (phenolphthalein); 10 c.c. of 0.1*N*-NaOH are added and the solution is boiled, hydrolysing (I) to Na pilocarpate. Excess of NaOH is then titrated. J. S. A.

Determination of alkaloidal salts by direct titration of their acid radicals. F. A. ROTONDARO (Amer. J. Pharm., 1935, 107, 237—241).—Alkaloidal salts may be determined by titrating (phenolphthalein) a solution in $\text{CH}_2\text{Ph}\cdot\text{OH}$ with KOH. H. G. M.

Biochemistry.

Regulation of the respiration of *Lumbricus*. J. B. THOMAS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 673—677).—In a closed vessel respiration of normal worms declines until the $[\text{O}_2]$ reaches 15%, and subsequently remains const. until $[\text{O}_2]$ becomes < 3%. In CO-poisoned worms, respiration does not exceed the level corresponding with 15% of O_2 even at high O_2 tensions. The role of hæmoglobin is discussed. A. G. P.

Fœtal respiration. J. BARCROFT (Proc. Roy. Soc., 1935, B, 118, 242—263).—A lecture. H. G. R.

Relation between oxygen capacity and molecular state of hæmoglobin. H. NAGAOKA (J. Biochem. Japan, 1935, 21, 355—365).—Denaturation and mol. aggregation (indicated by diminution in O_2 capacity and colloid-osmotic pressure, respectively) of hæmoglobin were determined in isotonic PO_4^{3-} buffer at p_{H} 6.7 at 55° or 59° for varying periods. Denaturation is more rapid than aggregation at 55° ; at 59° the reactions have more nearly equal velocities. F. O. H.

Micro-determination of hæmoglobin. Modification of the benzidine reaction. T. V. LETONOFF (J. Lab. Clin. Med., 1934, 20, 66—69).—To 1 c.c. of dil. blood (1 : 1000) in an isotonic solution containing 0.65% NaCl and 0.15% $\text{Na}_2\text{C}_2\text{O}_4$ are added 15 c.c. of 0.02% solution of benzidine, 3 c.c. of 0.25% aq. AcOH, and 1 c.c. of 1% H_2O_2 . The mixture is cooled in ice and after 30—40 min. is compared colorimetrically with a standard prepared by mixing 6.5 c.c. of 1% aq. $\text{K}_4\text{Fe}(\text{CN})_6$ in approx. 450 c.c. of H_2O with 5 c.c. of a 1% solution of gum ghatti and 10 c.c. of 1% aq. $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and diluting to 500 c.c. The standard is equiv. to the colour produced by 10 g. of hæmoglobin in 100 c.c. of blood. CH. ABS. (p)

Action of heat on proteins in solution. W. DUCE (Boll. Soc. Ital. Biol. sperim., 1935, 10, 73—75).—Exposure of solutions of hæmoglobin to temp.

close to the coagulation temp., or to those causing changes in η , produces no alterations of n_{D} . In partly coagulated solutions n_{D} of the uncoagulated protein is increased, or sometimes unchanged. R. N. C.

Treatment of methæmoglobin in the blood by glucose. M. M. BROOKS (Calif. and Western Med., 41, No. 2).—Methæmoglobin (I) was formed in rabbits by intravenous injection of 0.15 g. of NaNO_2 per kg. body-wt., and was determined spectrophotometrically. Injection of glucose converts (I) into oxyhæmoglobin. CH. ABS. (p)

Measurement of red-cell volume. VI. Different "fragility" of the red cells of various mammals. E. PONDER (J. Physiol., 1935, 83, 352—358).—The differences of fragility in hypotonic serum of the red cells of different mammals are due to the differences in crit. vol. H_2O content and the degree of perfection of the cell as an osmometer play only a minor part. The max. increase in cell area compatible with the integrity of the cell is a linear function of the cell vol. in sheep, ox, rabbit, and human red cells. R. N. C.

Relation of red-cell diameter and number to the light-transmission of suspensions. E. PONDER (Amer. J. Physiol., 1935, 111, 99—106).—Determination of the no. of red cells in a suspension by measurement of transmitted light can only be approx. The opacity of suspensions containing equal nos. of cells and the individual cell diameter are simply related, but variations in cell shape etc. make the determination of the cell diameter from opacity measurements untrustworthy. R. N. C.

Erythrocyte sedimentation rate. Comparison of the methods commonly employed for its determination. G. E. BEAUMONT and J. W. MAYCOCK (Lancet, 1935, 229, 19—20).—The Westergren, the modified Zeckwer–Goodell, and the micro-methods are compared. L. S. T.

Blood of domestic fowl. V. E. MORGAN and D. C. CHICHESTER (*J. Biol. Chem.*, 1935, **110**, 285—298).—The inorg. constituents and protein in erythrocytes and serum of fowl blood, the Donnan ratio of Cl^- and HCO_3^- , the buffer val. of serum (A., 1931, 753) and of oxygenated whole blood (A., 1930, 1053), the O_2 dissociation curves, and the effect of p_{H} on the affinity of blood for O_2 are compared with the corresponding properties of dog and human blood. A nomogram embodying the vals. obtained is constructed.

H. D.

Ageing of serum. A. ROCHE and F. MARQUET (*Compt. rend. Soc. Biol.*, 1935, **119**, 1147—1149).—The ppt. appearing in serum kept for a month at 0° is chiefly composed of lipins, proteins, and salts; cholesterol is present only in small quantities. The P/N ratio of the phospholipins is high as compared with that of the supernatant serum, suggesting that the ppt. is formed from phosphatides by the hydrolytic fission of the N-containing constituents.

R. N. C.

Mol. wt. of human serum-albumin. A. ROCHE, M. DORIER, and F. MARQUET (*Compt. rend. Soc. Biol.*, 1935, **119**, 1150—1151).—The osmotic pressure-concn. curve for human serum-albumin (I) is identical with that for horse-albumin. The mol. wt. of (I) is therefore 69,000.

R. N. C.

Crystallisation of seralbumins. R. WERNICKE (*Nature*, 1935, **136**, 30; cf. this vol., 508).—Photomicrographs of crystals of human and guinea-pig seralbumin (I) are reproduced. Cryst. (I) has also been obtained [by M. GRINSTEIN] from horses, asses, and mules but not from rabbits, llamas, pigs, oxen, dogs, and birds.

L. S. T.

Chemical and physical methods of determining [ethyl] alcohol in blood. A. GRONOVER (*Z. Unters. Lebensm.*, 1935, **70**, 34—40).—Widmark's (A., 1922, ii, 789) and Kionka and Hirsch's (A., 1924, i, 1366) methods are equally trustworthy. Small errors are introduced by the presence of COMe_2 , $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$, or MeCHO in blood.

E. C. S.

Blood-sugar regulation in exercise. D. B. DILL, H. T. EDWARDS, and S. MEAD (*Amer. J. Physiol.*, 1935, **111**, 21—30).—Blood-sugar remains near the rest level in easy work in which lactic acid does not accumulate, but increases in work that results in exhaustion after moderate time, continuing to increase for 5—10 min. after cessation of work. It does not change during activity that brings on exhaustion in < 3 min. with anaerobic energy production, but increases during recovery.

R. N. C.

Transplantation of endocrine glands and blood-sugar. V. PASSEK and M. RUBINSTEIN (*Compt. rend. Soc. Biol.*, 1935, **119**, 1019—1021).—Blood-sugar is not affected by transplantation of endocrine glands in rabbits except in the cases of the pituitary and the adrenal cortex, when it falls.

R. N. C.

Lactose in the plasma of pregnant and lactating women. R. S. HUBBARD and H. J. BROCK (*J. Biol. Chem.*, 1935, **110**, 411—420).—Lactose (I) was either absent from, or present in very small amount in, all specimens from normal and from pregnant women.

2 mg. of (I) per 100 c.c. of plasma were present in some specimens of blood from lactating women. It is concluded that the renal threshold for (I) is very low.

J. N. A.

Physico-chemical study of the reducing action of glucose.—See this vol., 1083.

Modification of the Folin-Wu blood-sugar method using permanent standards. H. BROWN (*J. Lab. Clin. Med.*, 1934, **20**, 86—89).—A solution containing 50 mg. of alizarin-blue GS and 10 mg. of alizarin-blue-black BG in 100 c.c. is mixed with a second solution of 20 mg. of alizarin-cyanine-green-B extra per litre of H_2O , in proportions to give the same colour as is obtained with known amount of glucose. The customary method is followed, using acid molybdate solution and heating for 8 instead of 6 min.

CH. ABS. (p)

Phospholipins of blood. C. P. STEWART and E. B. HENDRY (*Biochem. J.*, 1935, **20**, 1683—1689).—The determination of blood-phospholipins (I) by the Fiske-Subbarow (A., 1926, 443) determination of P in the ashed $\text{EtOH}\cdot\text{Et}_2\text{O}$ extract of blood is examined. The final $[\text{H}_2\text{SO}_4]$ in the ashed residue must be < 1.2N; large excess of H_2MoO_4 is to be avoided. That the P determined in this way represents (I) is shown by the fact that addition of a no. of non-lipin P-containing substances has little influence on the determined vals.; further, determination of P in the pptd. lipins (A., 1929, 837) gives vals. agreeing with those obtained as above. The ratio P:fatty acid in (I) is 1.5:1 and it is deduced that (I) contain equal proportions of sphingomyelin and a mixture of lecithin and kephalin.

H. D.

Determination of creatinine in urine and blood. H. LIEB and M. K. ZACHERL (*Wien. klin. Woch.*, 1934, **47**, 1572—1573; *Chem. Zentr.*, 1935, i, 937).—Creatinine is determined photometrically after treatment with picric acid.

J. S. A.

Volumetric determination of the nitrogen in 0.04—0.05 c.c. of blood (serum, plasma) without distillation. F. RAPPAPORT and R. PISTINER (*Mikrochem.*, 1935, **18**, 43—47).—The proteins are removed by warming with dil. H_2SO_4 and phosphomolybdic acid, an aliquot portion of the filtrate is evaporated with H_2SO_4 to destroy org. matter, diluted, neutralised (methyl-red) with NaOH, and treated with an excess of buffered NaOBr solution, and the excess is determined iodometrically.

A. R. P.

Determination of blood-chlorine. C. VAILLE and P. HAUTVILLE (*J. Pharm. Chim.*, 1935, [viii], **22**, 61—67).—After deproteinising with $\text{Zn}\cdot\text{Fe}(\text{CN})_6$, and pptg. as AgCl, excess of AgNO_3 is determined volumetrically. For normal children, the following results were obtained: total blood-Cl 2.86, plasma-Cl 3.42, erythrocyte-Cl 1.76 g. per litre. A method for determining corpuscle- and plasma-vol. is described.

H. G. R.

Exchange of mineral matter between corpuscles and plasma in blood. H. WAELSCH, S. KITTEL, and A. BUSZTIN (*Z. physiol. Chem.*, 1935, **234**, 27—53).—In human blood > 1.5—2.0 hr. after removal from the body Ca and Na pass from plasma

to corpuscles, whilst K and Mg pass from these to plasma. These elements move, in some cases in the same, in others in opposite, ways according to the state of health or disease of the subject. Such alterations always occur when mineral matter passes into or out of colloidal solutions. W. McC.

Calcium and inorganic phosphorus content of the blood-plasma of normal dairy cattle. J. R. HAAG and I. R. JONES (J. Biol. Chem., 1935, **110**, 439—441).—Ca ranged from 8.05 to 11.48 mg. per 100 c.c. Inorg. P for mature cattle is approx. 5.2 mg. per 100 c.c. J. N. A.

Graphic representation of ionic equilibria in blood-serum. J. F. McCLENDON (Science, 1935, **81**, 569—570). L. S. T.

Hydrogen-ion concentration in the blood of Europeans in temperate zones and in that of inhabitants of the tropics. G. M. STREEF (Arch. néerl. Physiol., 1935, **20**, 278—283).—The average p_H of the blood of Europeans in temperate zones was 7.57 ± 0.0013 at 30° (the subjects remained at 18°); this is the same as that of natives in Batavia, but $0.02 <$ that of Europeans in the tropics. P. G. M.

Determination of blood- p_H by the glass electrode. I. Acid change in shed blood. H. YOSHIMURA (J. Biochem. Japan, 1935, **21**, 335—353).—The so-called "first acid change" in shed blood (A., 1929, 1189) could not be confirmed. The whole course of diminution in p_H is due to glycolysis and is inhibited by $K_2C_2O_4$ and NaF, but not Na citrate, hirudin, or heparin. Lowering of temp. delays the acid change (cf. A., 1930, 1462). F. O. H.

Blood-coagulation as a chain reaction. A. FISCHER (Biochem. Z., 1935, **279**, 108—114).—Initiation of coagulation (hen's plasma) by heating or addition of HCl, active organ extracts, and lipins produces a continuous formation of coagulation-inducing substance. Coagulation in fresh plasma induced by addition of coagulating plasma occurs to an extent \propto the amount added and the duration of primary coagulation. Completion of coagulation is accompanied by a rapid decline in coagulation-promoting activity due to an "internal neutralisation" of the mol. concerned (cf. A., 1934, 795). F. O. H.

Coagulation of the blood as a chain reaction. H. J. FUCHS (Nature, 1935, **136**, 184; cf. this vol., 1002). L. S. T.

Concanavalin-A and hæmagglutination. J. B. SUMNER, S. F. HOWELL, and A. ZEISSIG (Science, 1935, **82**, 65—66).—Neutral suspensions of higher fatty acids, coconut, linseed, olive, almond, and jack-bean oils are agglutinated by the addition of a salt solution of concanavalin-A (I). Suspensions of butter, castor oil, lecithin, and cholesteryl acetate are not agglutinated by (I), and suspensions of lipins extracted from erythrocytes are only partly agglutinated. Suspensions of rice-starch, maize-starch, and baker's yeast are readily agglutinated by (I), and boiled starch is pptd. Glycogen (II) is completely pptd. at neutrality. Cow-erythrocytes are agglutinated only after a trace of (II) has been added. After laking, the erythrocytes of the horse, cat, and dog give a heavy ppt. with (I), but erythrocytes

which are not agglutinatable or only so with difficulty (e.g. cow, goat, sheep, man) give no ppt. Erythrocytes which agglutinate do so because of the formation of this ppt. The substance which forms the ppt. appears to be a protein. Agglutination appears to be due to an insol. compound formed by this substance and (I). When (II) is added to cow red cells it is adsorbed on their surfaces and forms a hydrophobic compound when (I) is added.

L. S. T.

Influence of neutral salts and sugar on hypertonic hæmolysis and formation of acid hæmatin. A. JODLBAUER (Arch. exp. Path. Pharm., 1935, **178**, 719—723).—Hypertonic salt solutions hæmolys erythrocytes: $Cl' < Br' < I' < SCN'$. Isolated stromata are lysed and liberated hæmoglobin is changed by hypertonic I' and SCN' . In 0.9% aq. NaCl, isotonic I' and SCN' enhance the acid-sensitivity of hæmoglobin, decomp. being initiated at p_H 4.9, 4.9, 5.3, and 6.2 with Cl' , Br' , I' , and SCN' , respectively. The increases in sensitivity and hæmolysis are inhibited by sucrose.

F. O. H.

Hæmolysis by Australian snake venoms. IV. Copperhead hæmolysin. H. F. HOLDEN (Austral. J. Exp. Biol., 1935, **13**, 103—112; cf. A., 1934, 1022).—Hæmolysis of rabbit's erythrocytes by copperhead venom is accelerated by lipins from rabbit's cells, by ovoidin, and by traces of $CaCl_2$ and inhibited by lipins from sheep's cells. Velocity curves for hæmolysis with and without $CaCl_2$ are given.

F. O. H.

Antigenic action of starch. S. FUJIMURA (J. Biochem. Japan, 1935, **21**, 371—380).—The antigenic action of starch is due to impurities and is not destroyed by amylolytic digestion. F. O. H.

(A) Formaldehyde and serum-proteins. Immunological characteristics. (B) Formaldehyde hypersensitiveness. F. L. HORSFALL (J. Immunol., 1934, **27**, 553—567, 569—581).—(A) Formolised serum-proteins (I), when injected into rabbits, produce precipitins for the homologous formolised serum, the homologous native serum, and heterologous formolised sera, and also anaphylactins which may be transferred passively to the guinea-pig uterus. Such uteri become sensitive to the homologous formolised serum, the homologous native serum, and heterologous formolised sera. Formolised NH_2 -acids do not saturate precipitins produced by injection of (I), although free CH_2O inhibits their action. Following injection of (I), rabbits show a progressive skin-hypersensitiveness to free CH_2O .

(B) Hypersensitiveness is attributed to the formation of a foreign substance by union of CH_2O with a constituent of the skin (probably protein).

CH. ABS. (p)

Lactogelification of blood-sera of immunised animals. J. BOUCEK (Compt. rend. Soc. Biol., 1935, **119**, 1134—1136).—The gelification of sera by *dl*-lactic acid is modified by the formation of antitoxins in the sera, the time of gelification being inversely \propto the quantity of antitoxin present. Gelification is also affected by the age of the serum and possibly the species, and by the presence of antiseptics.

R. N. C.

Concentration of antivenenen by the ammonium sulphate method. S. D. S. GREVAL (Indian J. Med. Res., 1934, 22, 365—371).—Immunised horse-plasma is fractionally pptd. with $(\text{NH}_4)_2\text{SO}_4$. The pseudoglobulin fraction, which contains antivenenen, is dialysed for 96 hr. against H_2O to remove $(\text{NH}_4)_2\text{SO}_4$. It is dissolved in 1% NaCl, adjusted to p_{H} 7.5—7.6 with Na_2CO_3 , preserved for 2 weeks under Et_2O and tricesol, and, if not toxic, filtered and bottled.

R. N. C.

Spontaneous super-contraction of animal hair. R. O. HALL (Nature, 1935, 136, 28—29).—Super-contraction in the guard-hairs of fur-bearing animals has been observed. Exposure to steam accentuates the deformation. Immersion in acid reduces and sometimes reverses the curvature, but washing and drying leads to an increase in the initial direction. The results are discussed in terms of the oxidation of the S-S' linking of the keratin.

L. S. T.

Composition of cartilage, bone, dentin, and enamel. M. A. LOGAN (J. Biol. Chem., 1935, 110, 375—389).—The inorg. constituents of cartilage, bone, dentin, and enamel are determined to elucidate the process of calcification. In rat bone the $\text{CO}_3^{''}$:Ca ratio increases from 10.7% to 15.8% with development, accompanied by increases in inorg. $\text{PO}_4^{'''}$. In human and dog dentin the ratio Mg:total base is 3—4 times that in enamel, and the Ca:total base is the same in both. The Mg content of dog dentin and enamel is not different from that of carious human teeth; in the latter, however, the $\text{CO}_3^{''}$ is > normal. In bone the total base=total acids, and it is concluded that the bases exist as tertiary phosphates. Na+K in cartilage is 50% > in plasma; Ca and Mg in cartilage are 3 to 4 times > in plasma with no corresponding increase in inorg. $\text{PO}_4^{'''}$, hence a large proportion of the base exists as salts of the org. constituents of cartilage. H. D.

Physicochemical factors affecting intraocular pressure. W. S. DUKE-ELDER (Physiol. Rev., 1934, 14, 483—513).—A review. CH. ABS. (p)

Chromosome micelle and the banded structure of chromosomes in the salivary gland. D. M. WRINCH (Nature, 1935, 136, 68—69; cf. this vol., 882).—The genetic identity of a chromosome is located in its protein constituent, and the protein pattern of an individual is defined as a sequence of protein mols. placed end to end in salt linkings. This meets the essential requirement of genetics that genes form a linear array. So far as concerns the protein constituent, the chromosome micelle is regarded as an aggregate of identical sequences of mols., the protein patterns lying side by side, and these will lie on and constitute a quasi-cylindrical surface. The nucleic acid will polymerise in rings around the micelle. The banded structure of certain salivary chromosomes is interpreted as due to the alternation of basic and non-basic units in the protein pattern. L. S. T.

Changes in the pancreas after ligation of the pancreatic duct. S. TSUNOO (J. Biochem. Japan, 1935, 21, 399—407).—Ligation of the pancreatic duct in dogs produces an increase in the $\text{EtOH}+\text{Et}_2\text{O}$ -sol. fat, whilst in the tissue-protein, lysine and $(\text{NH}_2)_1$ -acid decrease and arginine and histidine increase. Changes

also occur in $[\alpha]$ and N, NH_2 -N, and sugar contents of the pancreatic blood. F. O. H.

Composition of larval sacs of sacciferous larvae (Psyche). K. KUSUI (J. Biochem. Japan, 1935, 21, 453—455).—Hydrolysis of the sacs yields glycine (5.72%), glutamic acid (3.97%), alanine (3.62%), tyrosine (2.31%), approx. 13 other NH_2 -acids, and a reducing substance. F. O. H.

Fish and rabbit liver-glycogens. D. J. BELL (Nature, 1935, 136, 184—185).—Methylation of liver-glycogen from *Gadidae* by the method of Haworth and Percival gave a product (45.5% OMe) identical with the corresponding derivative from rabbit liver-glycogen. Hydrolysis with aq. HCl+AcOH gave similar amounts of tetramethylglucopyranose in each case, corresponding with 12 glucose units for the glycogen mol. Both methylated glycogens give a deep red-brown colour with I. These and other results with acylated glycogens show that fish and rabbit liver-glycogens are probably chemically identical.

L. S. T.

Chemistry of heparin. E. JORPES (Biochem. J., 1935, 29, 1817—1830).—Heparin prepared from ox-liver by the method of Charles and Scott contains Ac, hexuronic acid, hexosamine, and combined ethereal sulphate. By pptn. as the brucine salt, a fraction of high heparin activity was obtained having the composition of a chondroitintrisulphuric acid.

W. O. K.

Composition of the muscle of certain sea animals. I. Proteins of the muscle tissue of *Mugil cephalus*. A. CARTENI and A. MORELLI (Quad. Nutriz., 1934, 1, 185—191; Chem. Zentr., 1935, i, 1258).—The N distribution of the protein is examined and compared with that of other marine animals.

A. G. P.

A normal paraffin as a minor constituent in hydrogenated sardine oil. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1935, 38, 258—261B).—*n*-Heptadecane, m.p. 22—22.5°, has been identified in the distillate obtained during the vac. deodorisation (steam-distillation) of hydrogenated sardine oil.

E. L.

Whale-shark-liver oil. M. TSUJIMOTO and H. KOYANAGI (J. Soc. Chem. Ind. Japan, 1935, 38, 271—272B).—The liver of a specimen of *Rhinodon typicus*, Smith (Jap. "Jinbei" or "Ebisu-zame"), which died in captivity after 4 months' starvation, contained 61.6% of fat. By heating 54.9% of semi-solid fat was obtained having m.p. > 40°, d_{20}^{20} 0.8977, acid val. 25.0, sap. val. 182.5, I val. (Wijs) 108.6, Reichert-Meissl val. 0.11, unsaponifiable matter 5.04% [containing selachyl and (probably) batyl alcohol and 43.8% of cholesterol, and giving a blue coloration with SbCl_3]. The fatty acids had m.p. 41—42°, neutralisation val. 201.4, I val. 116.7, Et_2O -insol. bromides 27.8% (70.23% Br), and yielded 40.9% of solid acids (I val. 18.0; mainly palmitic acid) by the Pb salt- Et_2O method, and 19.5% of highly unsaturated acids (neutralisation val. 167.0, I val. 330.5) by the Li salt-COMe₂ method. The fatty acids consisted mainly of C_{16-22} acids, the unsaturation of the C_{20} and C_{22} acids being very high.

Shark-liver oils. M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 272—273B).—Analyses are detailed of the liver oils from "Aizame" (*Centrophorus* sp.), "Zaraka" or "Momijizame" (*Lepidorrhinus foliaceus*, Günther), "Togaritsunozame" (*Squalus japonicus*, Ishikawa), cat-shark or "Neko-zame" (*Heterodontus japonicus*, Dumeril), "Gaikotsuzame" (*Pristurus eastmani*, Jordan and Synder), "Yoshikirizame" (*Prionace glauca*, Linne), Porbeagle or "Nezumizame" (*Lamna cornubica*, Gmelin), and hammer-headed shark or "Shumokuzame" (*Sphyrna zygaena*, Linne). Aizame and Zaraka liver oils, which have a high squalene content, give a pale blue colour in the SbCl_3 test; squalene is absent from the other oils. E. L.

Oils from marine animals. New group of lipins. Ether-esters of glycerol. E. ANDRE and A. BLOCH (Bull. Soc. chim., 1935, [v], 2, 789—802).—The name "diglycerides-monoglyceroxides" (I) is suggested for the mixed ether-esters $\text{OR} \cdot \text{C}_3\text{H}_5(\text{O}_2\text{C} \cdot \text{R})_2$ of glycerol and batyl or selachyl alcohols present in elasmobranch-liver oils. Analysis of the liver oil of *Scymnorrhinus lichia*, Bonnaterre, and the Ac val. of the unsaponifiable matter indicate a composition hydrocarbons 57%, triglycerides 21.7%, (I) 21.3%, together with small amounts of free fatty acids and cholesteryl esters. By the method of fractional extraction (B., 1933, 353) using $\text{MeOH} \cdot \text{COMe}_2$ (3:1 by vol.), hydrocarbons are accumulated in the less sol. fractions, since the optical rotation of the latter fractions increases more rapidly than does their sap. val.; these fractions contain approx. hydrocarbons 1—2%, triglycerides 25%, and (I) 75—80%. Attempted separation of (I) from the less sol. fractions by fractional crystallisation at -4° afforded only a triglyceride, m.p. 40.8° , as a solid product. (I) are highly laevorotatory and, by hydrolysis, give alcohols of high Ac val. J. W. B.

Oil of the eggs of *Bombyx mori*. J. OZAKI and B. KASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 745—749).—The eggs contained 7.88—11.10% of crude fat, the fatty acids being palmitic, isopalmitic, stearic, myristic, oleic, linoleic, and β -linoleic. The eggs yielded a clear, red-brown, EtOH -insol. oil having n_D^{20} 0.9351, acid val. 29.07, sap. val. 199.05, I val. 138.84, Ac val. 39.04, Reichert-Meissl val. 2.13, unsaponifiable matter 0.35%, and insol. fatty acids 88.96%. CH. ABS. (e)

Occurrence of carotenoids in marine animals. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1935, 18, 915—921).—Cryst. astacene has been isolated from the sea-aster (*Echinaster sepositus*) and the red sponge (*Axinella crista-galli*) and is present in *Suberites domuncula*. No carotenoid was found in the coral (*Astroides calycularis*). That of the mussel (*Cardium tuberculatum*) is probably xanthophyll. The carotenoids of the molluscs, *Pecten jacobaeus* and *Pleurobranchus elegans*, the sea-lily (*Antedon rosacea*), and the sea-squirt (*Cynthia papillosa*) have also been examined. F. R. G.

Echinenone and pentaxanthin: two new carotenoids found in the sea-urchin (*Echinus esculentus*). E. LEDERER (Compt. rend., 1935, 201, 300—302).—The sexual glands of *E. esculentus* are

extracted with COMe_2 ; the product re-extracted with light petroleum and fractionated by adsorption yields a pigment, echinenone, $\text{C}_{40}\text{H}_{58}\text{O}$ ($\pm \text{H}_2$), m.p. $192\text{—}193^\circ$, with ill-defined absorption max. at 520, 488, and 450 $\text{m}\mu$ in CS_2 . The product from whole animals extracted with COMe_2 and with C_6H_6 , when fractionally adsorbed, yields pentaxanthin, $\text{C}_{40}\text{H}_{56}\text{O}_5$ ($\pm \text{H}_2$), a xanthophyll resembling lutein in its absorption. E. W. W.

Flavin from fish-eyes. P. KARRER, H. VON EULER, and K. SCHÖPF (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 54, 2 pp.).—Cryst. flavin may be isolated from the retina of fish-eyes. It is identical with lactoflavin and possesses vitamin-B₂ activity. E. A. H. R.

Blue-fluorescing substance in the corpus luteum. H. VON EULER and K. M. BRANDT (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 51, 5 pp.).—A blue-fluorescing substance is obtained from corpora lutea by extraction with COMe_2 and purified chromatographically. It is not reduced by Zn dust at p_H 2 nor appreciably by $\text{Na}_2\text{S}_2\text{O}_4$ at p_H 10. It is not extracted from aq. solution by Et_2O or CHCl_3 . It gives max. fluorescence at p_H 2—8. E. A. H. R.

Fluorescence spectra of hepatoflavin before and after irradiation. H. BIERRY and B. GOUZON (Compt. rend., 1935, 200, 2116—2118).—Hepatoflavin (greenish-yellow fluorescence) when irradiated in 0.5N-NaOH gives lumiflavin (green fluorescence), but in neutral solution affords lumichrome (blue fluorescence). The spectra of flavins from egg and adrenals are identical. J. L. D.

Determining the reducing substance of the anterior pituitary. W. T. SALTER, A. GREEN, and T. J. PUTMAN (J. Lab. Clin. Med., 1934, 20, 74—77).—The reducing substance is associated with the globulin fraction and its concn. is not paralleled by that of growth-promoting or other hormones present in this fraction. To determine the activity of the preps. the p_H is adjusted to 8.0 and the sample is placed in a Thunberg tube containing 0.1 c.c. of 1:1000 methylene-blue and 0.15 c.c. of *M*-phosphate buffer solution (p_H 8.0) and the whole diluted to 2.5 c.c. After evacuation the tubes are placed in boiling H_2O and the time required for bleaching is observed. CH. ABS. (p)

Role of lipins in the X-ray diffraction patterns of nerve. F. O. SCHMITT, R. S. BEAR, and G. L. CLARK (Science, 1935, 82, 44—45).—Large well-oriented spacings, apparently due to lipins, in the diffraction patterns of nerve, are described and discussed. L. S. T.

Solvation and desolvation of nerve. F. O. SCHMITT and L. J. WADE (Amer. J. Physiol., 1935, 111, 169—176).—Solvating agents such as $\text{HCO} \cdot \text{NH}_2$, NaCNS , acids, and alkalis produce shortening and increase in wt. of nerve at room temp., and lower the temp. of thermal shortening. On the other hand, PhMe , Et_2O , COMe_2 , and other desolvating agents produce shortening but increase the temp. of thermal shortening, as does also unification of the micellar structure by "tanning" with CH_2O or OsO_4 . R. N. C.

Potassium content of the human and animal nervous system. A. LEULIER, B. POMMÉ, and A.

BERNARD (Compt. rend. Soc. Biol., 1935, **119**, 1228—1229).—Normal nerve-K is < that of fresh brain or marrow, and falls still further in disease. Fresh brain- and marrow-K are of the same order as that of striated muscle, the vals. for the dry fat-free tissues agreeing still more closely.
R. N. C.

Chlorate-osmic-formalin method for staining degenerating myelin. R. L. SWANK and H. A. DAVENPORT (Stain Tech., 1935, **10**, 87—90).—An aq. solution containing 60 c.c. of 1% KClO_3 , 20 c.c. of 1% OsO_4 , 1 c.c. of AcOH , and 12 c.c. of 37% CH_2O is recommended. After fixation in CH_2O solution for 2 days, brain and spinal cord are stained in the solution for 7—10 days.
H. W. D.

Modification of the cresyl-violet technique for staining nerve cells. G. TRESS and M. TRESS (Stain Tech., 1935, **10**, 105—106).—After fixation in CH_2O the tissue is embedded in cellulose nitrate (I) and sections are stained in an aq. solution containing 0.5% of cresyl-violet and 4 drops of 10% AcOH . The sections are treated with 70% EtOH until the (I) is practically free from stain and then placed in a mixture of 60 c.c. of CHCl_3 , 10 c.c. of EtOH , and 10 c.c. of Et_2O for 2—5 min. The cells are differentiated in a solution made by adding 4 drops of 1% HCl to 100 c.c. of 95% EtOH . The sections are then neutralised in 95% EtOH containing a small quantity of NaHCO_3 , dehydrated in BuOH , and cleared in xylene.
H. W. D.

Iron in common sponge. P. ROBIN (J. Pharm. Chim., 1935, [viii], **24**, 600—604).—The yellowish-grey surface coloration and the brown coloration of the interior parts and of the foot of Mediterranean sponges are due to Fe^{III} . The average content of Fe according to the variety is 0.092—0.38% in the interior and 0.916—4.2% in the foot. In sponges from the Bahamas and Antilles the Fe content is 0.025—0.085% in the interior and 0.06—0.53% in the foot.
M. T.

Cryolysis, diffusion, and particle size.—See this vol., 932.

Constituents of mulberry leaves: proteins. VI. Variation in the amount of protein synthesised. VII. Indirect causes which affect the quantity, in the silkworm and the silk, of the proteins that have been accumulated from the proteins in mulberry leaves. VIII. Metabolism of the proteins in silkworms when the quantity of the soluble carbohydrates contained in the mulberry leaves is small. X. Quantity of sericin and fibroin in the silk due to difference in the constituents of the mulberry leaves and the growth of the leaves. Y. KISHI (Bull. Agric. Chem. Soc. Japan, 1935, **11**, 70—71, 71—72, 72—73, 76—77).—VI. The amounts and types of protein synthesised in mulberry leaves vary according to the amount of sunshine and the rate of growth of the leaves.

VII. The higher is the % of carbohydrate in the leaves, the greater is the amount of protein accumulated in the silkworm.

VIII. When the amount of carbohydrate is very small as in the youngest leaves soon after sprouting,

there is an increase in the metabolism of the protein, with a corresponding decrease in the % accumulated by the silkworm.

X. Young leaves produce less sericin (I) but more fibroin (II) than mature leaves. The amount of (I) increases with decrease in carbohydrate, but if sugars be given with the leaves, the amount of silk and (II) increases, whilst (I) decreases.
J. N. A.

Genetics of the silkworm. I. Colour of the cocoon. C. JUCCI (Mem. R. Accad. Italia, Cl. Sci. fis. mat. nat., 1934, **5**, 347—477; Chem. Zentr., 1935, i, 1145).—The colours of the blood, cocoon, and eggs of the silkworms arise from their nutrition, the "permeability" of the intestine permitting the absorption of pigments into the blood. The characteristic green or yellow of the cocoon is due to the ability of the silk gland to absorb flavones or carotenoids, respectively. Crossing of species with different blood- and cocoon-colours show that the permeabilities for carotenoids and flavones are Mendelian factors, which belong to different allelomorphic pairs.
R. N. C.

Silk fibroin. W. TRAUBE and H. HARTING [with V. SENFTNER and S. KELL] (Ber., 1935, **68**, [B], 1405—1408).—Silk fibroin is almost completely sol. in aq. NaOH (KOH)— $\text{Cu}(\text{OH})_2$ and from the solution EtOH ppts. a complex in which the ratio $\text{Cu} : \text{Na}(\text{K}) : \text{N} = 1.0 : 1.8 : 3.8—4.0$. Addition of acid to the moderately fresh solution ppts. the fibroin almost quantitatively, but if the solution is preserved the fibroin is degraded to compounds sol. in H_2O which are most readily isolated if KOH (NaOH) is replaced by $\text{Ba}(\text{OH})_2$. Degradation is due to the conjoint action of $\text{Cu}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ and does not occur in the presence of $\text{Ba}(\text{OH})_2$ alone. In the degraded and original products the ratio $\text{N} : \text{C} = 1.0 : 2.86$ and $1.0 : 3.2$, respectively. The degraded product gives an intense biuret reaction. Treatment with MeOH shows that it is not homogeneous. Unlike fibroin it is completely sol. in EtOH saturated with HCl .
H. W.

Saliva. F. DUYVENSZ (Proc. Roy. Soc. Med., 1934, **27**, 839—848).—The Ca and SCN' contents and of saliva are discussed. Pituitary hormones have been demonstrated in saliva.
CH. ABS. (p)

Alleged occurrence of acetylcholine and adrenaline in cat's saliva. P. S. LARSON (J. Pharm. Exp. Ther., 1935, **54**, 341—345).—Ultrafiltration removes the vascular activity, which cannot be due to acetylcholine or adrenaline, from cat's saliva.
H. G. R.

Variations in the saccharogenic power of human saliva. F. WALKER and L. SHEPPARD (Amer. J. Physiol., 1935, **111**, 192—195).—The activity of saliva samples from the same individual varies from day to day. It increases after ingestion of food, particularly in the morning, and declines slowly during the day but considerably at night. Saccharogenic power varies qualitatively, but not quantitatively, with rate of secretion of saliva, and possibly with total solids content.
R. N. C.

Secretory function of the stomach in the course of experimental hyperaminoacidæmia. J. LA BARRE and P. DESTREE (Compt. rend. Soc. Biol., 1935,

119, 1177—1179).—Intravenous injection of hypoglycaemic doses of glycine in the dog produces an increased total gastric secretion and an increased HCl content of the juice. The effect is abolished by vagotomy.

R. N. C.

Detection of free hydrochloric acid in stomach contents. M. WAGENAAR (Pharm. Weekblad, 1935, 72, 837—841).—A drop of a saturated solution of resorcinol and vanillin is evaporated to dryness and the "spot" treated with a drop of stomach fluid. A deep violet colour shows $>0.0015N\text{-HCl}$. Strong inorg. acids also give the colour, H_3BO_3 a pale coloration, and all org. acids except $\text{H}_2\text{C}_2\text{O}_4$ a negative test.

S. C.

Presence of taurocholate in the bile of cats and snakes. M. IWATO and K. WATANABE (J. Biochem. Japan, 1935, 21, 211—212).—Taurocholic acid was isolated.

F. O. H.

Liver diathermy and hepatic function. II. Excretion of dyes. Y. MITANI (J. Biochem. Japan, 1935, 21, 381—397).—Diathermy of the liver, which increases the vol. of bile secreted, does not affect the excretion of bile-pigments but tends to increase that of injected dyes, especially during pregnancy or following salvarsan injection.

F. O. H.

Liver diathermy and hepatic function. I. Bile secretion. Y. MITANI (J. Biochem. Japan, 1935, 21, 309—328).—Application of diathermic currents of 400—1500 milliamp. to the liver (dog) increases the excretion of bile, the excretion of bilirubin and bile acids being increased during and for some time after the application. The effect is inhibited by administration of atropine and adrenaline or by severe liver disease.

F. O. H.

Hæmoglobin and bile-pigment over-production in the splenectomised bile-fistula dog. R. E. KNUTTI, W. B. HAWKIN, and G. H. WHIPPLE (J. Exp. Med., 1935, 61, 127—138).—Blood destruction associated with *Bartonella* or with a drug (N_2H_4) produces a large amount of pigment in the bile. New hæmoglobin and bile-pigment are formed in large amounts on a diet which causes only small production of new hæmoglobin in anæmic dogs.

CH. ABS. (p)

Proof of a humoral control of intestinal secretion. E. S. NASSET, H. B. PIERCE, and J. R. MURLIN (Amer. J. Physiol., 1935, 111, 147—158).—Food in the digestive tract in dogs is accompanied by increased secretion in a completely isolated jejunal loop, thus proving the presence of a humoral control. Enzyme production in the loop is augmented by feeding.

R. N. C.

Physiology of milk secretion. V. N. NIKITIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 434—440).—Comparison of the composition of blood samples drawn from the jugular and from abdominal veins of lactating cows indicates that lactose is formed in the udder from blood-glucose, and that milk-protein is derived, at least in part, from the residual N of the blood. Variations in the amount of milk produced by different cows depend on the total amount of blood circulating in the udder and not on differences in the amount of constituent materials withdrawn from unit vol. of blood.

A. G. P.

Influence of thyroxine on milk secretion. E. L. JACK and S. I. BECHDEL (J. Dairy Sci., 1935, 18, 195—205).—Intravenous injection of thyroxine in cows resulted in increased milk production especially in the later stages of the lactation. The composition of the milk was not significantly altered.

A. G. P.

Seasonal variations in the lipase content of milk. J. L. HILEMAN and E. COURTNEY (J. Dairy Sci., 1935, 18, 247—257).—The lipase content of milk reaches a min. in early summer and a max. in early winter. The amount of lipase secreted increases as lactation is prolonged.

A. G. P.

Utilisation of the mercury-cadmium reagent for micro-determination of lactose in milk. M. BIERRY and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 119, 1029—1031).—The use of the $\text{Hg}(\text{NO}_3)_2\text{-Cd}(\text{NO}_3)_2$ reagent permits the determination of lactose in 1 c.c. of milk to an accuracy of 2%.

R. N. C.

Nutritional anæmia, calcium, phosphorus, and nitrogen balance of rats fed raw vs. pasteurised milk. H. A. LASBY and L. S. PALMER (J. Dairy Sci., 1935, 18, 181—192).—Milk pasteurised in glass showed no change in Cu or Fe contents and did not induce more severe anæmia than did raw milk. Commercially pasteurised milk sometimes caused less severe anæmia than did raw milk. No significant differences appeared in the Ca, P, and N retentions of rats receiving raw and pasteurised milks.

A. G. P.

Composition of human perspiration. B. A. MCSWINEY (Proc. Roy. Soc. Med., 1934, 27, 839—848).—Analyses are recorded. The presence of large amounts of lactic acid is not confirmed. Sweat glands are not affected by adrenaline, but are excited by pilocarpine and paralysed by atropine.

CH. ABS. (p)

Comparison of human with animal urine. M. TAKAMATSU (J. Biochem. Japan, 1935, 21, 427—433).—Comparative data for p_H , d , depression of f.p., κ , total ash and its solubility in H_2O , and the contents of CaO, MgO, P_2O_5 , SO_4 , Cl, total N, urea, uric acid, and creatinine are given for the urines of man, dog, cat, horse, ox, elephant, pig, goat, rabbit, guinea-pig, frog, toad, turtle, hen, and duck.

F. O. H.

Organic constituents of elephant's urine. M. TAKAMATSU (J. Biochem. Japan, 1935, 21, 435—438).—The principal N constituent is urea, whilst, unlike with most herbivores, hippuric acid forms a smaller part of the N excretion; creatinine is also present.

F. O. H.

Detection of protein and glucose in urine. E. SACHS (Deut. med. Woch., 1934, 60, 1923—1924; Chem. Zentr., 1935, i, 1280).—A no. of new tests using sulphosalicylic acid paper are described.

H. N. R.

Origin of *l*-xyloketose (urine-pentose). M. ENKLEWITZ and M. LASKER (J. Biol. Chem., 1935, 110, 443—456).—Administration of glycuronic acid causes a greatly increased elimination of *l*-xyloketose in the urine.

J. N. A.

Value of Gerhardt and Legal tests for determining ketonic compounds. A. ESCUDERO (Rev. méd. lat.-amer., 1931, 14, 877).—The Legal reaction

in urine is positive when the sum of COME_2 and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ (I) is > 0.25 g. per 1000. The Gerhardt reaction is positive when (I) is > 0.20 g. per 1000.

CH. ABS. (p)

Effects of carbon dioxide on urine formation and glomerular blood-flow. E. A. ADOLPH (Amer. J. Physiol., 1935, 111, 64—74).—High CO_2 tensions inhibit urine formation and decrease glomerular blood-flow in frogs.

R. N. C.

Oxygen tension and urine production in frogs. E. A. ADOLPH (Amer. J. Physiol., 1935, 111, 75—82).—The rate of urine production diminishes sharply with the O_2 tension in pithed frogs; it is independent of it in normal frogs, by virtue of their breathing, when the tension is $>$ that of room air, but declines rapidly in lower tensions. The response of the renal arterioles that reduces the blood-flow, and probably also the glomerular capillary pressure, is apparently under the influence of O_2 tension.

R. N. C.

Effect of hypertonic solutions of sodium chloride on the elimination of pigments by the kidney. E. MICHALOWSKI and Z. M. BIELINSKI (Compt. rend. Soc. Biol., 1935, 119, 1216—1218).—Hypertonic NaCl solutions accelerate the renal excretion of dyes in the dog through their diuretic action.

R. N. C.

Guanine in the excreta of arachnids. K. VAJROPALA (Nature, 1935, 136, 145).—Using the sp. deaminating enzyme guanase, 12 wt.-% of the excreta of the common garden spider is found to consist of guanine.

L. S. T.

Copper therapy in nutritional anaemia. J. C. HAWKSLEY (Proc. Roy. Soc. Med., 1934, 27, 1066—1068).—Among 80 cases of anaemia, 4 required addition of Cu to Fe medication to effect return to normal. Microcytosis occurred in Cu deficiency and was corr. by Cu administration.

CH. ABS. (p)

Basedow's disease and cholelithiasis. A. JUGENBURG and B. M. SCHLEPAKOV (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, No. 3, 200—209).—Irradiation of the thyroid and thymus produced better regulation of the disturbed cholesterol metabolism, lowered basal metabolism, and generally improved condition. Thyrotoxicosis creates all conditions favourable to development of cholelithiasis and may contribute to the formation of calculi. CH. ABS. (p)

Flocculating power of cancerous sera. M. L. CHEVREL-BODIN, F. CHEVREL, and M. CORMIER (Ann. Inst. Pasteur, 1935, 55, 108—123).—EtOH extracts of normal organs or of cancerous tissue diluted with aq. NaCl or KCl do not give sp. ppts. with cancerous sera but EtOH extracts of normal organs diluted with CaCl_2 or $\text{Ca}(\text{OAc})_2$ give increased pptn. with such sera, for which considerable specificity is claimed.

W. O. K.

Enzymes in cancer. β -Glycerophosphatase of the erythrocytes. J. W. SCHOONOVER and J. O. ELY (Biochem. J., 1935, 29, 1809—1816).—The optimum substrate p_{H} for normal and cancer human-erythrocyte- β -glycerophosphatase (I) activity in 0.2M-acetate buffer at 37° is 5.6—5.8. Over the p_{H} range 5.0—6.0 the (I) activity of erythrocytes from cancerous individuals is $>$ that of erythro-

cytes of normals of the same sex. The abs. increase of activity by Mg^{++} is the same for cancerous as for normal erythrocytes so that the % increase is smaller for the cancerous erythrocytes. Cancerous erythrocytes probably contain tissue- β -glycerophosphatase not activated by Mg^{++} .

W. O. K.

Tissue metabolism. VII. Action of tumour extracts on hexose diphosphate. E. BOYLAND and M. E. BOYLAND (Biochem. J., 1935, 29, 1910—1914).—Dialysed tumour (mouse, rat, rabbit) extracts contain zymo-hexase [converting hexose diphosphate (I) into dihydroxyacetone phosphate (II)] to an extent approx. 10% of that with muscle from the same animal. Dialysed tissue extracts aerobically oxidise (II) to a more stable P compound, a stage of glycolysis with which the Pasteur reaction is possibly concerned. Dialysed mouse tumour extracts convert (I) into lactic acid if sufficient adenylyl pyrophosphate is added to compensate for the rapid decomp. of the latter substance.

F. O. H.

Dental decay as an indicator of dietary fault. N. P. LARSEN, M. R. JONES, and G. P. PRITCHARD (Amer. J. Dis. Children, 1934, 48, 1228—1233).—Decay disappears when the usual diet of carbohydrates with an acid residue is replaced by one of alkaline starches with small amounts of vegetables. Resistance to other diseases is also increased.

CH. ABS. (p)

Blood-fats in diabetic lipaemia. F. K. HERBERT (Biochem. J., 1935, 29, 1887—1893).—In severe diabetic lipaemia increases in plasma-neutral fat, -cholesterol, and -phospholipins occurred, the greatest increase being in neutral fat, which also decreases most rapidly under treatment. Comparison of the I vals. of ingested and plasma-fatty acids indicates that a proportion of the fats is derived from the tissues.

H. D.

Attempts to reduce the symptoms of experimental diabetes by irradiation of the pituitary. W. A. SELLE, J. J. WESTRA, and J. B. JOHNSON (Endocrinol., 1935, 19, 97—104).—The fasting blood-sugar level of depancreatized dogs is not reduced by intensive X-irradiation of the pituitary; in some cases it is raised. The response to ingested glucose is always typical of severe diabetes. Sensitivity to insulin is not increased, and the min. quantity of insulin required to prevent glycosuria is unchanged.

R. N. C.

Dietary haemorrhagic disease in chicks. H. J. ALMQUIST and E. L. R. STOKSTAD (Nature, 1935, 136, 31).—The disease can be prevented by rice meal or bran which has been kept moist and by dehydrated lucerne. The antihaemorrhagic factor (cf. this vol., 903) is located in the unsaponifiable, Et_2O -extractable portion of lucerne.

L. S. T.

Depigmentation, a new dietary deficiency disease, cured by copper. F. J. GORTER (Nature, 1935, 136, 185; cf. A., 1934, 1132).—Depigmentation in rats is cured by addition of Cu to the diet. The min. dose varies considerably owing to its availability and the anti-Cu effect of certain growth-promoting food factors which should always be present in a satisfactory diet.

L. S. T.

Relation of the regulatory mechanism of respiration to clinical dyspnoea. D. W. RICHARDS, jun., A. COURNAND, and I. RAPPAPORT (Proc. Nat. Acad. Sci., 1935, 21, 498—501).—Dyspnoea is not determined by any physicochemical bodily function, but by local difficulty or disturbance in the mechanical function. H. G. R.

Blood chemistry in epilepsy. R. T. FLETCHER and O. D. PEDEN (Lancet, 1935, 228, 1382—1383).—There is no marked difference in composition of the blood during a convulsion, except possibly a greater variation in % vol. of red cells and a slight rise in serum-Ca. Serum-protein, -P, and -phosphatase and blood-Cl' remain practically unchanged. L. S. T.

Effect of cortin on intra-ocular tension in glaucoma. E. M. JOSEPHSON (Science, 1935, 82, 62).—Administration of cortin relieves the heightened intra-ocular tension in glaucoma, and reduces or arrests progressive myopia. The mechanism of both diseases can be explained as a disturbance of H₂O-salt metabolism. L. S. T.

Intermediary metabolism of purines in gout. M. LABBE, P. L. VIOLE, and F. NEPVEUX (Compt. rend. Soc. Biol., 1935, 119, 1095—1098).—Gout is accompanied by an increase in free and a decrease in combined purine-N of the serum, total purine-N remaining normal. The increase of uric acid in serum is probably due to its being in a form eliminated only with difficulty by a normal kidney. R. N. C.

Hepatectomy and nitrogenous substances in the blood. M. FRANKE, T. TOCZYSKI, and J. LANKOSZ (Compt. rend. Soc. Biol., 1935, 119, 1209—1211).—Hepatectomy in the dog provokes a fall of protein-N, urea, and creatinine, and a rise in other non-protein N substances. R. N. C.

Total cholesterol and its fractions in the blood after hepatectomy. M. FRANKE and S. MALCZYNSKI (Compt. rend. Soc. Biol., 1935, 119, 1212—1216).—Hepatectomy in the dog provokes a slow steady fall of total blood-cholesterol (I). Esterified (I) shows a more marked fall; in consequence, free (I) rises, whilst the esterified:total (I) ratio is diminished. Injection of isotonic glucose solution causes a fall of total and esterified (I). R. N. C.

Bromine level of the blood and maniacal-depressive insanity. H. FLEISCHACKER and G. SCHEIDERER (Mscr. Psychiat. Neurol., 84, 348—370; Chem. Zentr., 1935, i, 919).—Roman's method for determining blood-Br' is untrustworthy. The Zondek-Bier hypothesis is therefore founded on untrustworthy analytical results. R. N. C.

Tyrosine index of polypeptidaemia in mental illnesses. T. SIMON, J. C. ROUX, and R. GOIFFON (Compt. rend. Soc. Biol., 1935, 119, 926—928).—Polypeptide-tyrosine in human blood increases considerably in mental disorders. R. N. C.

Glucose tolerance test in leprosy. D. G. LAI (Amer. J. Trop. Med., 1934, 14, 575—584).—Apart from individual variations, leprosy without complications tends to give a normal blood-sugar curve. A low renal threshold is, however, common. CH. ABS. (p)

Atebrin in the treatment of malaria in the Philippine Islands. P. E. McNABB and S. C. SCHWARTZ (Amer. J. Trop. Med., 1934, 14, 309—317).—The action of atebrin on gametocytes and schizonts resembles that of quinine. CH. ABS. (p)

Observations in Panama with reference to control with atebrin. I. Malaria control with atebrin. W. H. W. KOMP and H. C. CLARK (Amer. J. Trop. Med., 1934, 14, 381—396).—Atebrin reduces fever as quickly as does quinine, but the parasite frequently remains and relapses are frequent. CH. ABS. (p)

Effect of saline ions on flocculation and superflocculation of the serum of paludics. F. TRENSZ (Compt. rend. Soc. Biol., 1935, 119, 966—968).—Saline ions interfere in melanoflocculation through their chemical nature; their actions on flocculation and superflocculation of the serum of paludics are different. R. N. C.

Different indicators replacing melanin in the Henry reaction. R. C. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 119, 1115—1117).—Melanin (I) can be replaced by carmine in the Henry reaction. The serum of paludics has no sp. affinity for (I), which acts as an indicator of the instability of the serum in distilled H₂O. R. N. C.

Relation of hypercholesterolaemia to increased tolerance for thyroid preparations in nephrosis. R. S. AITKEN (Clin. Sci., 1934, 1, 241—244).—In liver cirrhosis, hypercholesterolaemia did not inhibit thyroxine action or produce increased tolerance to thyroid preps. CH. ABS. (p)

Crystallisation of sodium chloride in the serum of pregnant women. V. BERGAUER, V. STICH, and Z. ZLABEK (Compt. rend. Soc. Biol., 1935, 119, 1131—1133).—NaCl crystallises from pregnancy serum in concentric circles, which change partly to the glaciated form from 10 days before, and completely to aggregates immediately before or after, parturition. This indicates that pregnancy is accompanied by hyperpituitarism, followed by hyperthyroidism. R. N. C.

Rickets. Control with 50 units (Steenbock) of cod-liver oil vitamin-D concentrate in milk. D. J. BARNES (Amer. J. Dis. Children, 1934, 48, 1258—1267).—Satisfactory control is recorded. The customary ratio 40:240 for the equiv. rat units of vitamin-D in irradiated milk to that in cod-liver oil is not confirmed. When the concentrate is given in milk the required units are approx. equal. CH. ABS. (p)

Phosphatase. V. Serum-phosphatase as a criterion of severity and rate of healing of rickets. A. BODANSKY and H. L. JAFFE (Amer. J. Dis. Children, 1934, 48, 1268—1278; cf. A., 1934, 560, 1129).—Serum-phosphatase increases in rickets and declines after effective therapy. It is a better criterion of the severity of the disease and of healing than are the serum-Ca and -P. CH. ABS. (p)

Experimental scurvy. XXV. Content of fatty acid, cholesterol, unsaponifiable matter, and nitrogen in faeces of scorbutic guinea-pigs. XXVI. Acid value of petrol extract of faeces.

XXVII. Serum-lipase. XXVIII. Volume and constitution of bile. Y. AIZAWA (J. Biochem. Japan, 1935, 21, 457—467, 469—475, 477—485, 487—504).—XXV. Scurvy produces an increase in the faecal fatty acids and in their ratio to the fatty acids ingested; the corresponding vals. for cholesterol and unsaponifiable material are diminished. The N balance is unchanged.

XXVI. The acid val. of the light petroleum extract of the faeces is decreased by approx. 23%.

XXVII. Scurvy diminishes the serum-lipase to an extent \propto the severity of the disease. The decrease does not depend merely on inanition.

XXVIII. The vol. of bile and its content of taurocholic acid and cholesterol in guinea-pigs are diminished in scurvy. F. O. H.

Diazo-urine. V. Small-pox urine. VI. Antoxyproteic acid. S. NAKAYAMA (J. Biochem. Japan, 1935, 21, 439—442, 443—448).—V. The urines of scarlet fever and small-pox patients give a positive diazo-reaction which, with the latter, appears to be due to a substance other than antoxyproteic acid (I).

VI. Urines from typhoid, scarlet fever, measles, or phthisis patients appear to contain the same (I) (13.05—13.39% N, 28.15—29.50% Ba in Ba salt, 0.46% $\text{NH}_3\text{-N}$, free from S, and not hydrolysed by erepsin). The relation between (I), oxyproteic acid (A., 1906, i, 122), urochromogen, chromogen, and kynurenic acid is discussed (cf. A., 1927, 170; 1934, 201). F. O. H.

Report of chemistry section. B. C. ASTON (New Zealand Dept. Agric. Ann. Rept. [1932—1933], 1933, 30—36).—The blood-Mg of cows suffering from "grass staggers" is markedly subnormal. In rats the blood-Mg level is directly related to the Mg of the diet and can be raised $>$ normal by supplementary feeding of MgCO_3 , MgSO_4 , MgCl_2 , or Mg phosphates.

No relationship exists between the enlarged thyroid glands of "bobby" calves and their I contents. The % of I in glands of lambs varied in the same direction as that of the soils and pastures of the district, high vals. occurring in rich limestone areas and low vals. in alluvial plains. CH. ABS. (p)

Calcium therapy in tropical diseases. P. BEREGOFF (Canad. Med. Assoc. J., 1935, 32, 177—178).—Prolonged residence in the tropics is associated with a deficiency in blood-Ca. Satisfactory treatment with Ca gluconate is recorded. CH. ABS. (p)

Isolation of an unsaponifiable substance from the spleen in a case of Werloff's disease. A. FIESCHI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 46—47).—The spleen contains an unsaponifiable substance that gives a greenish-yellow colour with EtOH. It is extracted from the dried spleen by saponification with Na, extraction with light petroleum, pptn. from EtOH solution with digitonin, and re-extraction with light petroleum. R. N. C.

Cod-liver oil salve treatment of fresh wounds, burns, and phlegmonous wounds. W. LOHR (Zentr. Chirurgie, 1934, 61, 1686).—Bacteria commonly occurring in infected wounds are destroyed by cod-liver oil. Salves prepared from the oil

rapidly liquefy necrotic tissue and stimulate growth. The effects are ascribed to the vitamin-A and -D in the oil. CH. ABS. (p)

Culture of whole organs. A. CARREL and C. A. LINDBERGH (Science, 1935, 81, 621—623).—In the method described an organ or any part of the body is transplanted to a sterile chamber in which it is fed artificially by a nutrient fluid through the arteries. L. S. T.

Metabolism of retina. H. LASER (Nature, 1935, 136, 184).—Respiration of rat retina and Crocker mouse sarcoma in HCO_3^- Ringer's solution is approx. twice that in PO_4^{3-} Ringer's solution. Respiration of the tumour is inhibited by approx. 90% in both media by small amounts of HCN, but respiration of retina is not inhibited by similar amounts of HCN in HCO_3^- Ringer's solution. L. S. T.

Rate of oxygen consumption of the isolated terrapin heart when perfused with various solutions. C. H. McDONALD and A. C. McDONALD (Amer. J. Physiol., 1935, 111, 51—54).— O_2 consumption is increased by perfusion with isotonic NaCl or NaCl- CaCl_2 solution, and decreased by isotonic NaCl-KCl or glucose solution. The effect of NaCl solution is inhibited by KCN in concn. 1 : 10,000. R. N. C.

Lability of the basal metabolism of the dairy cow. F. G. BENEDICT and E. G. RITZMAN (Proc. Nat. Acad. Sci., 1935, 21, 304—308).—The basal metabolism of the dairy cow is not const. even for short periods and in non-lactating animals is highest in the pasture season (June) and lowest in March. H. T.

Chemical reactions in muscle. VII. Dephosphorylation of phosphoglyceric acid in fluoride-poisoned muscle. T. MANN. VIII. Phosphoglyceric and adenylic acids. P. OSTERN, T. BARANOWSKI, and J. REIS. IX. Role of phosphagen. J. K. PARNAS and P. OSTERN (Biochem. Z., 1935, 279, 82—84, 85—93, 94—98; cf. A., 1934, 1027).—VII. The marked NH_3 production by frog's muscle in 0.02M-NaF is not influenced by 0.01M-K phosphoglycerate (I). With 0.005M-NaF, less NH_3 is formed, liberation of PO_4^{3-} increases, and adenosine triphosphate (II) remains unchanged. Higher concns. of (I) produce AcCO_2H , adenylic acid (III) being phosphorylated at the expense of (I).

VIII. Dephosphorylation of (I) does not occur in absence of (II) or (III). Creatine+(I) produce creatine phosphate only when formation and dephosphorylation of (II) in presence of (III) results in an accumulation of (II). Under certain conditions no liberation of PO_4^{3-} occurs in the system (I)-(II)-creatine-creatine phosphate but PO_4 is transferred from mol. to mol.

IX. The role of creatine phosphate (phosphagen) and possibly of arginine phosphate in the reaction (II) (III) is discussed. F. O. H.

Phosphate metabolism in muscular work. A. SZAKALL (Arbeitsphysiol., 1934, 8, 316—334).—During prolonged muscular work in the dog, PO_4^{3-} , after a small temporary increase, disappears from the urine, but reappears during recovery, the extent of these changes being dependent on the amount of work.

Work increases the PO_4''' balance. Inorg. PO_4''' in the blood, and also the leucocyte count, show no change during work, but increase considerably during recovery. Acid-sol. PO_4''' in the blood increases during work, but in cases of prolonged PO_4''' -deficiency is maintained at the normal level. R. N. C.

Reversible reactions in biological glycolysis. O. MEYERHOF (Naturwiss., 1935, 23, 490—493).—The chemical reactions occurring in muscle and involving org. phosphate compounds are of two types, (a) reversible, associated with small energy changes, and (b) irreversible, and yielding larger amounts of energy. The latter are especially associated with the adenylic acid—adenosinetriphosphoric acid system (cf. Lohmann, A., 1931, 1184), whilst characteristic examples of the former are the equilibria, hexose diphosphate \rightleftharpoons dihydroxyacetonephosphoric acid, glyceraldehyde-phosphoric acid and β -phosphoglyceric acid \rightleftharpoons α -phosphoglyceric acid \rightleftharpoons phosphopyruvic acid. W. O. K.

Influence of adenylic and cholic acids and secondary phosphate on liver-glycogenesis. K. WATANABE (J. Biochem. Japan, 1935, 21, 197—201).—The enhanced liver-glycogenesis in rabbits from glucose due to HPO_4'' is further increased by injection of adenylic acid; simultaneous oral administration of cholic acid effects a still further increase. F. O. H.

Comparative effect of adding different sugars to the perfusion liquid through frog's heart and the influence of insulin over it. R. K. PAL and S. PRASAD (J. Physiol., 1935, 83, 285—291).—Addition of glucose, fructose, lactose, maltose, or sucrose to the perfusing fluid increases the efficiency of the heart-beat, the effect being most lasting with glucose. The action of all these sugars is enhanced by insulin. Lowering of p_{H} in the course of perfusion produces a temporary dilatation of the heart with diminution of the amplitude, followed by true augmentation. Insulin scarcely affects the vagus when combined with suitable doses of any of the sugars. Injection of insulin, followed in 0.5 hr. by glucose, acts as an efficient cardiac stimulant. R. N. C.

Effect of creatine on carbohydrate metabolism. D. JAHN (Deut. Arch. klin. Med., 1934, 177, 121—138; Chem. Zentr., 1935, i, 1084).—After dosage with creatine (I) strong ketonæmia and depression of the blood-sugar level occur in cases of glycogen-poor liver. (I) stimulates the muscle-glycogen-forming action of insulin, and assists the blood-sugar-depressing action. H. J. E.

Metabolism of galactose. II. Synthesis of lactose by active mammary gland in vitro. G. A. GRANT (Biochem. J., 1935, 29, 1905—1909).—Glucose, but not fructose, mannose, or galactose, is readily converted into lactose (determined by fermenting with *S. fragilis*) when kept in 0.9% aq. NaCl at 37° with tissue-slices of lactating mammary gland (guinea-pig). A slight synthesis of org. PO_4''' from added glucose + PO_4''' on addition of yeast-hexokinase indicates the possible presence of a hexosephosphatase. F. O. H.

Fate of mannide and isomannide in the animal body. J. C. KRANTZ, jun., W. E. EVANS, jun., and

C. J. CARR (Quart. J. Pharm., 1935, 8, 213—217).—Mannide (I) and isomannide (II) cannot be stored as glycogen in rat-liver, do not relieve insulin shock in mice, and do not raise the fasting blood-sugar level of rabbits. (I) increases the R.Q. of rats, whereas (II) does not. H. G. R.

Fate of conjugated glycuronic acids in the body. M. KOIKE and Y. TOSAWA (Japan. J. Med. Sci., IV, 1933, 7, 110).—Orally administered phenyl- or benzoyl-glycuronic acid or urochloralic acid was largely excreted unchanged in urine by rabbits. No increase in ethereal sulphates occurred.

CH. ABS. (p)

Utilisation of variations of the respiratory quotient to determine the part played by ethyl alcohol in basal exchange. Case of carbohydrate diet. E. LE BRETON (Compt. rend. Soc. Biol., 1935, 119, 1014—1016).—The R.Q. method does not give trustworthy results, only direct measurement of the coeff. of EtOH oxidation being exact in all cases. R. N. C.

Transport of lipins in the animal organism. T. CAHN and J. HOUGET (Compt. rend., 1935, 201, 166—168).—Previous work supports the view that mobilisation of lipins occurs as cholesteryl esters, which are distributed from the liver to various tissues as phosphatides. H. G. R.

Carotenoid pigments in fishes. III. Effects of ingested carotenoids on the xanthophyll content of *Fundulus parvipinnis*. F. B. SUMNER and D. L. FOX (Proc. Nat. Acad. Sci., 1935, 21, 330—340; cf. A., 1934, 555).—When the fishes are fed a carotene-rich diet containing no xanthophylls the total xanthophyll content is increased. H. T.

Fat metabolism. XV. Biological degradation of fatty acids, esters, and fats to dicarboxylic acids. B. FLASCHENTRAGER and K. BERNHARD (Helv. Chim. Acta, 1935, 18, 962—972; cf. A., 1934, 1027).—When Na decanoate, Me or Et laurate is added to a dog's diet, only 0.5—1% is recovered as sebatic acid (I) in the urine. From Me decanoate the oxidation products are (I) and suberic acid. The results are attributed to ω -oxidation followed by successive β -oxidations. F. R. G.

Fat metabolism in fishes. VII. Depôt-fats of certain fish fed on known diets. J. A. LOVERN (Biochem. J., 1935, 29, 1894—1897).—The composition of the body-fats of *Ctenopharyngodon idellus* and of its dietary grasses, and of those of *Hypophthalmichthys nobilis* and *H. molitrix* and their dietary mud, was determined. Apparently the fishes synthesise their own body-fats. H. D.

Effect of choline on the liver-fat of rats in various stages of nutrition. C. H. BEST and M. E. HUNTSMAN (J. Physiol., 1935, 83, 255—274).—The liver-fat of white rats on a diet of grain and beef-fat rises to a steady max. in 3 weeks. Addition of choline (I) to the diet causes a rapid fall of liver-fat. Omission of the beef-fat also causes a fall, which is accelerated by (I). Liver-fat is maintained or increased by a complete diet with low (I) content, whether or not beef-fat is given. A diet of pure sucrose increases liver-fat in both normal and fatty-

livered animals, this effect being prevented by (I), which rapidly reduces liver-fat to normal. Liver-fat is reduced by a diet low in (I). Fasting in rats with fatty livers produces a rapid decrease of liver-fat, only slightly accelerated by (I). R. N. C.

Choline and liver-fat in phosphorus poisoning. C. H. BEST, D. L. MACLEAN, and J. H. RIDOUT (J. Physiol., 1935, 83, 275—284).—Choline (I) accelerates the disappearance of liver-fat in rats during recovery from P poisoning, but does not inhibit fat deposition after injection of large quantities of P. Liver-fat accumulation produced by complete diets poor in (I) is less rapid than that from P poisoning. Liver-fat does not decrease in rats with fatty livers produced by P poisoning when kept on a (I)-poor diet. The histological picture does not suggest that (I) affects the duration of the degenerative changes produced by P, apart from fat accumulation. R. N. C.

Excretion of exogenous fats through the intestinal mucosa. G. PERETTI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 79—81).—Oral administration of "iodipin" to a dog with a Thiry-Vella fistula results in secretion of considerable quantities of I-containing fat from the mucosa of the fistula, suggesting that part of the exogenous fat is normally excreted by this route. R. N. C.

Relation of the fat content of milk to the passage of the milk curd from the stomach of the calf. D. L. ESPE and C. Y. CANNON (J. Dairy Sci., 1935, 18, 141—147).—Curd from milk containing >6% of fat tends to leave the stomach more rapidly than skimmed milk as a result of the different texture of the curd formed. The fat in whole milk does not inhibit gastric secretion or motility. A. G. P.

Protein, fat, and carbohydrate metabolism in the white rat. I. In the normal rat. R. WETZEL, H. WOLLSCHITT, H. RUSKA, and T. OESTREICHER (Arch. exp. Path. Pharm., 1935, 179, 86—114).—Results of determinations of the dry wt., H_2O , total N, protein, fat, total reducing substances, carbohydrate, glycogen, and lactic acid contents of the organs of male rats are recorded. The respiration of the tissues was measured. W. McC.

Dog plasma-protein given by vein utilised in body metabolism of dog. Horse plasma and dog hæmoglobin not similarly utilised. W. T. POMMERENKE, H. B. SLAVIN, D. H. KARIHER, and G. H. WHIPPLE (J. Exp. Med., 1935, 61, 283—297).—Foreign plasma-protein (horse) introduced parenterally into the protein-fasting dog is not utilised but is eliminated as excess urinary N. Dog plasma, under similar conditions, will maintain the N equilibrium, and a small portion of dog hæmoglobin thus administered is used to maintain red-cell concn. Ch. Abs. (p)

Correlation between excess calories and excess urinary nitrogen in the specific dynamic action of protein in animals. H. BORSOOK (Proc. Nat. Acad. Sci., 1935, 21, 492—498).—The relation between the cal. and urine-N in excess of the basal in the sp. dynamic action of proteins (A., 1931, 648) is confirmed, contrary to the conclusions of Aubel and Schaeffer.

The steady state is attained 4 hr. after ingestion and is maintained for 20 hr. H. G. R.

Production of amino-acids from keto-acids and of urea in the liver. M. NEBER (Z. physiol. Chem., 1935, 234, 83—96).—Surviving liver (but not liver pulp) in presence of O_2 produces NH_2 -acid and urea from $AcCO_2H$ (I) and NH_3 in amounts which depend on the concn. of (I), urea production predominating when this concn. is low. The temp. coeff. of the process is high. After 6 hr. production of urea begins to decrease, but that of NH_2 -acid continues at undiminished rate. In N_2 , production of urea ceases but that of NH_2 -acid continues. Added ornithine (II) has no effect on the NH_2 -acid production but increases urea production if the concn. of (I) is low (e.g., in liver from fasting animals). (II) shifts the equilibrium between NH_2 -acid production and decomp. (to give urea). Lactic acid (III) and NH_3 in liver yield NH_2 -acid only after (III) is converted into (I). There is no increase in NH_2 -acid production when glucose, quinol, cysteine, or ascorbic acid is added. In kidney (I) + NH_3 yield NH_2 -acid. W. McC.

Perfusion of the stomach. V. Lactic acid formation from *d*-alanine. K. WAKASUGI. VI. Uricolytic processes. T. TSUTSUI. VII. Formation of ketonic substances. T. NAGAO. VIII. Fission of arginine. S. MURAOKA. IX, X, XI. Creatine. Y. HONGO. XII. Urease (II). S. SUMIDA (J. Biochem. Japan, 1935, 21, 243—248, 249—258, 259—269, 271—277, 279—287, 289—293, 295—299, 301—308).—V. *d*-Alanine added to blood perfused through the dog's stomach is decomposed, a small part being converted (mainly in the mucosa) into lactic acid. The NH_3 -N of the mucosa and urea-N of the muscular layer increase.

VI. Added uric acid is decomposed to allantoin especially in the mucosa.

VII. The ketonic substances, especially CH_3AcCO_2H , of perfused normal blood are diminished. Addition of leucine and fatty acids with an even no. of C atoms, however, produces an increase in ketonic substances on perfusion, indicating that β -oxidation occurs in the stomach wall.

VIII. Arginine is decomposed with formation of ornithine, urea, and histidine, unchanged arginine and its decomp. products appearing in the blood, gastric juice, mucosa, and, more especially, muscle.

IX. Perfused creatine is decomposed (mainly in the muscle), partly forming creatinine and partly by an unknown reaction.

X. Arginine in the perfusing blood is partly converted into creatine in the mucosa.

XI. Betaine and urea are not converted into creatine on perfusion (in blood) through the dog's stomach.

XII. Urease occurs in the stomach-tissues (dog) the cardiac and fundus regions having an activity > that of the pylorus. It is absent from the duodenal mucosa. F. O. H.

Nitrogen metabolism of the isolated tissues of the rat. H. BORSOOK and C. E. P. JEFFREYS (J. Biol. Chem., 1935, 110, 495—509).—Surviving slices of the isolated liver, kidney, diaphragm, spleen,

and small intestine of the rat were used in Ringer's solution. In every case there was an increase in non-heat-coagulable sol. N, free $\text{NH}_2\text{-N}$, and NH_3 ; uric acid, without any allantoin, was formed in every case except liver. Allantoin was formed only in liver and creatine in all the tissues except spleen. Deamination of $\text{NH}_2\text{-acids}$ occurred at approx. the same rate in liver and kidney. Urea is formed in the small intestine from arginine, and in liver probably from histidine. Liver quantitatively converts uric acid into allantoin. J. N. A.

Determination of glutathione in the tissues in the reduced form and in the oxidised form. L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1935, 119, 939—941).—Glutathione (I) is extracted from the tissue with aq. $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and reduced (I) determined by pptn. with Cd lactate, oxidation with I, and titrating excess of I with $\text{Na}_2\text{S}_2\text{O}_3$. Oxidised (I) is reduced with NaCN in neutral solution and total (I) then determined similarly, oxidised (I) being found by difference. R. N. C.

Effect of starvation on the glutathione of the tissues: rôle of the liver in glutathione metabolism. L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1935, 119, 941—943).—The glutathione (I) level in all tissues of the guinea-pig is maintained during starvation except in the liver, where it falls steadily, suggesting that the liver acts as a reserve store of (I) for the other organs. Reduced (I) generally follows total (I). R. N. C.

Cystinuria. IV. Metabolism of homocysteine and homocystine. E. BRAND, G. F. CAHILL, and R. J. BLOCK (J. Biol. Chem., 1935, 29, 399—410; cf. this vol., 775).—A cystinuric is fed with homocystine (I) or homocysteine (II) and the urinary total and urea-N, creatine, SO_4^{--} fractions, cystine (III), and (I) are determined. 18% of (I) fed is excreted as such, and the rest as inorg. SO_4^{--} ; 50% of (II) is excreted as (III), 24% as (I), and the remainder as inorg. SO_4^{--} . It is suggested that in the conversion of methionine into cysteine, (II) must be maintained in the reduced state. H. D.

Influence on metabolism of addition of small amounts of cystine to protein-deficient diets. L. LORENTE (Biochem. Z., 1935, 279, 76—81).—Determinations of N balance, C, and "vacate-O" vals. of the urine of rats fed on a diet deficient in quality and quantity of proteins indicate that small amounts (e.g., 0.0075 g. daily) of cystine influence the deoxidative metabolism (cf. A., 1930, 1613). F. O. H.

Tyramine and blood perfusion through the kidney. H. J. WOLF and H. A. HEINSEN (Arch. exp. Path. Pharm., 1935, 179, 15—23).—When the chief blood supply to one kidney in dogs (including those receiving protein-free diet) is cut off, outflow of blood being allowed to continue, tyramine (I) appears in the blood and the blood-pressure is increased. (I) is produced in the kidney from which the blood has been cut off. W. McC.

Uric acid synthesis in the bird. III. A purine synthesis. W. SCHULER and W. REINDEL (Z. physiol. Chem., 1935, 234, 63—82; cf. A., 1934, 104).—The kidney of the pigeon converts purines into

uric acid (I), but the pancreas and liver do not. A method of determining nucleosides, purines, and (I) in 4 c.c. of blood-serum is described. The precursor of (I) is enzymically produced in the liver (not in the kidney): it is not a mononucleotide or lactic, tartronic, mesoxalic, malonic, glutamic, aminomalonic, or β -hydroxyglutamic acid or hydantoin, glycerol, *d*-glucose, *d*-ribose, urea, carnosine, guanidine, creatine, creatinine, glycine, alanine, serine, glycylalanine, ornithine, arginine, histidine, cystine, reductone, or uracil. In the pigeon enzymic deamination of $\text{NH}_2\text{-acids}$ occurs chiefly in the liver but also in the kidney (not in pancreas and muscle). In the kidney the N thus liberated appears as NH_3 and (I) but in the liver part of it appears as NH_3 and the rest neither as (I), precursor, nor urea. The liver produces (I), the C source being the precursor, the N source $\text{NH}_2\text{-acid}$ (from NH_3). W. McC.

Nutritive value of Indian vegetable foodstuffs. V. Nutritive value of ragi (*Eleusine coracana*). S. P. NIYOGI, N. NARAYANA, and B. G. DESAI (Indian J. Med. Res., 1934, 22, 373—382).—4% NaCl or hot 70% EtOH removes about 20% of the total N of ragi, the remainder being inextractable. Analytical figures are given for eleusinins; it is a prolamine, sol. in EtOH, and containing S and P. The cystine, tyrosine, and tryptophan contents are > those of wheat gliadin. Prolonged hydrolysis causes little deamination. There is no relation between free $\text{NH}_3\text{-N}$ and the lysine-N of the prolamine. Ragi-proteins have biological vals. > those of rice and oats. The diastatic activity of ragi-malt is equal to that of barley-malt. R. N. C.

Nutritive value of the protein of cabbage and of sweet potato. H. C. KAO, W. H. ADOLPH, and H. C. LRU (Chinese J. Physiol., 1935, 9, 141—148).—Using Mitchell's method on a 10% protein basis, the biological vals. for cabbage- and sweet potato-protein are 76 and 72, respectively. The proteins contain arginine-N 13.0 and 11.8, histidine-N 3.1 and 2.1, lysine-N 8.3 and 5.3, tyrosine-N 2.2 and 2.4, tryptophan-N 1.2 and 1.8, cystine-N 1.1 and 1.8%, respectively. H. G. R.

"Digestibility" of common foodstuffs as determined by radiography. W. C. D. MAILE and K. J. L. SCOTT (Lancet, 1935, 228, 1500—1501).—Boiling is the only method found to shorten the stomach emptying-time for milk. Sugar is more rapidly absorbed from the stomach when fluid is drunk with it, and glucose disappears from the stomach more slowly than sucrose. L. S. T.

Biological value of proteins. VI. Balance-sheet method. H. CHICK, J. C. D. HUTCHINSON, and H. M. JACKSON. **VII. Influence of variation in level of protein in diet and of heating protein on its biological value.** H. CHICK, M. A. B. FIXSEN, J. C. D. HUTCHINSON, and H. M. JACKSON (Biochem. J., 1935, 29, 1702—1711, 1712—1719; cf. A., 1932, 182).—VI. The balance-sheet method of studying the biological val. for maintenance of N equilibrium in rats of proteins is examined. The excretion of endogenous N in the urine diminishes with the time the rat is on a N-deficient diet; the N excretion on a N-free diet during 4 days after a preliminary period of 2—3 days gives a measure of the endogenous

N output. Only an approx. proportionality exists between food intake and faecal N output. Results on rats with food intake < 6 g. per day are excluded.

VII. The biological vals. of whole wheat, white flour, wheat germ, maize endosperm, whole milk, lactalbumin (I), and caseinogen (II) are determined. With the exception of whole milk the biological vals. decrease with increased level of intake. Heating (II) at 150° for 66 hr. decreases its biological val. and digestibility; heating (I) at 120° for 72 hr. lowers its biological val. slightly and its digestibility considerably. H. D.

Fate of ethynal in animals and men. S. TSUNOO (J. Biochem. Japan, 1935, 21, 409—416).—Ingested "ethynal" (furylacrylyl-*p*-hydroxyphenylurea) is hydrolysed in the organism to furylacrylic acid [excreted both free and conjugated with glycine (dog, rabbit, man) or as the oxidation product, furoic acid (man)] and *p*-hydroxyphenylurea [excreted as glucuronate (dog, rabbit)]. F. O. H.

Fate of γ -phthalimido- β -hydroxybutyronitrile in animals. T. KAWADA (J. Biochem. Japan, 1935, 21, 417—421).—The compound fed to rabbits is hydrolysed (approx. 85%) to phthalic acid (approx. 11% excreted as such, the remainder oxidised to BzOH and excreted as hippuric acid) and γ -amino- β -hydroxybutyronitrile, which is converted into and excreted as \cdot SCN compounds and a thioaminopurine, $C_5H_7N_5S_2$ or $C_5H_7O_2N_5S$. F. O. H.

Fate of hydroxymethylfurfuraldehyde and of pyrrole in frogs. K. KUSUI (J. Biochem. Japan, 1935, 21, 449—451).—Subcutaneously injected hydroxymethylfurfuraldehyde is excreted as the corresponding hydroxymethylfuroic acid; with pyrrole no base can be isolated from the urine. F. O. H.

Nutrition and biochemical equilibrium in alimentary regime. L. RANDOIN (Chim. et Ind., 1935, 34, 10—21).—A review indicating applications of results to maintenance of balanced diets. W. McC.

Relation of food to regularity of nutritional response. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1935, 21, 434—436).—The coeff. of variability for rats at various stages on diets *A* and *B* are given. Diet *B* is superior to *A* in every respect and indicates the presence of an enrichment in an already adequate diet. H. G. R.

Metabolism trials with suckling pigs. G. SCHOLZ (J. Landw., 1935, 83, 107—156).—The S : N ratio of sow's milk averaged 1 : 11—12. Colostrum was relatively high in both elements but vals. reached normal after 3—4 days. The quantities of N and S eliminated in urine and faeces of piglings increased up to the age of 4 weeks and subsequently declined. The N : S ratio of the carcasses was 1 : 13.5 at birth and 1 : 14.0 at 4 weeks of age. The ratio varied considerably in the various organs. A. G. P.

Influence of the spleen on sulphur metabolism. K. IWABUCHI (Japan. J. Med. Sci., IV, 8; Proc. Japan. Pharmacol. Soc., 1933, 20—21).—Splenectomy increased all forms of urinary S and the total N in female dogs. Administration of 0.1 mg. of adrenaline caused further increases. CH. ABS. (p)

Influence of the spleen on inorganic mineral metabolism. H. KANEKO (Japan. J. Med. Sci., IV, 8; Proc. Japan. Pharmacol. Soc., 1934, 123—125).—Laparotomy had little effect on the composition of blood or urine in rabbits. Extirpation of the spleen decreased the erythrocytes, leucocytes, haemoglobin, K, Ca, and Mg in the blood and decreased the Ca and increased the K in urine. CH. ABS. (p)

Availability of calcium from some typical foods. M. L. FINCKE and H. C. SHERMAN (J. Biol. Chem., 1935, 110, 421—428).—The Ca of kale is nearly as well utilised as that of milk, but the Ca of spinach is utilised very poorly, if at all. This is due largely to the oxalate present in the spinach, and not to the presence of fibre. J. N. A.

Relation of vitamin-D to calcium and phosphorus retention in cattle as shown by balance trials. G. C. WALLIS, L. S. PALMER, and T. W. GULLICKSON (J. Dairy Sci., 1935, 18, 213—228).—Mineral retention was not increased by supplementary feeding of mineral matter with a vitamin-D-deficient ration. Administration of -D, however, increased the Ca retained to 14-fold and the P to 11-fold. The normal daily retention averaged 6.50 g. of Ca and 3.25 g. of P. The ratio of Ca : P retained was unaffected by the mineral content of the ration and was unchanged by -D deficiency. Calves store -D which may subsequently be utilised under adverse conditions. A. G. P.

Utilisation of different magnesium salts. J. C. FORBES and F. P. PRITS (J. Amer. Pharm. Assoc., 1935, 24, 450—452).—The average weekly Mg absorption and retention (by rats) of different Mg salts over a period of 5—6 weeks was approx. the same for each salt, i.e., 29—41% of the intake (av. 32.5%). Linseed meal, lucerne, $MgCl_2$, and Mg lactate were the sources of Mg. Addition of $\geq 2\%$ of Na_2CO_3 to the diet had no unfavourable effect on the Ca, P, or Mg utilisation. E. H. S.

Biological action of metals irradiated with a mercury-quartz lamp. II. Effect of irradiated iron on the growing organism. J. M. GOLDBERG (Acta med. Scand., 1934, 83, 573—595; Chem. Zentr., 1935, i, 919).— $Fe(OH)_3$ solution irradiated with a Hg-quartz lamp increases the rate of growth of chickens and children. R. N. C.

Iodine content of Indian foodstuffs. M. PATNAIK (Indian J. Med. Res., 1934, 22, 249—262). R. N. C.

Environmental selection of the fresh-water sponges (*Spongillidae*) of Michigan. M. C. OLD (Trans. Amer. Microscop. Soc., 1932, 51, 129—136).—Species distribution is examined in relation to pH ranges. Only *S. fragilis* tolerated the whole range examined (pH 4.2—9.2). Sponges occurred in H_2O having free CO_2 0—33, alkalinity to phenolphthalein of 0—22 (as $CaCO_3$) and to Me-orange 19—270 p.p.m. (as $CaCO_3$). All Michigan species preferred H_2O containing no carbonates. CH. ABS. (p)

Alcoholism. IV. Modification of blood-alcohol after intravenous administration of alcohol. R. FLEMING and D. REYNOLDS (J. Pharm. Exp. Ther., 1935, 54, 236—245).—Diathermic increase

in body-temp. appears to increase the rate of disappearance of EtOH from blood in man. Administration of adrenaline, insulin, caffeine, CO₂, O₂, olive oil, 0.9% aq. NaCl, or MgSO₄ is without effect.

F. O. H.

[Physiological effects of] cholesterol. S. MINOVICI and M. VANGHELOVICI (J. Chem. Educ., 1934, 11, 637—639).—Physiological effects are discussed. A biochemical synthesis of cholesterol from oleic acid by enzymes of liver or spleen is indicated.

CH. ABS. (p)

Lipin metabolism. I. Variation in cholesterol content of blood and of different organs in pigeons consequent on administration of chloroform. N. C. DATTA (Indian J. Med. Res., 1934, 22, 353—364).—Repeated inhalation of CHCl₃ in pigeons produces an increase in blood-cholesterol (I) during the first 2 months, followed by a fall. Body-wt. falls as blood-(I) rises. (I) in brain, lungs, heart, and kidney is not affected; liver-(I) falls slightly. Adipose tissue-fat is not formed during CHCl₃ administration. There is no definite relation between blood-(I) and the red-cell count, which remains const. as (I) increases, but falls considerably with (I).

R. N. C.

Relation of p_H and surface tension to the activity of local anæsthetics. J. H. GARDNER and J. SEMB (J. Pharm. Exp. Ther., 1935, 54, 309—319).—Although both the lowering of γ and the anæsthetic activity vary with p_H , no correlation was observed between these two factors for individual compounds (morpholine derivatives, procaine, cocaine).

H. G. R.

Relative anæsthetic effects of various carbamides. J. S. BUCK, A. M. HJORT, and E. J. DE BEER (J. Pharm. Exp. Ther., 1935, 54, 188—212; cf. this vol., 118).—With aliphatic carbamides the hypnotic potency decreases in the following order: monoalkyl-, *s*-dialkyl- (Me series) (methyl-*n*-propyl, m.p. 61°; -*n*-butyl-, m.p. 72°; -*n*-amyl, m.p. 79°), *as*-dialkyl- (ethyl-*n*-propyl, m.p. 54°; *di*-*n*-amyl, *s*-dialkyl- (Et series) (ethyl-*n*-propyl, m.p. 80°; -*n*-butyl-, m.p. 61°; -isobutyl-, m.p. 53°; -*n*-amyl, m.p. 59°), and trialkyl-carbamides (α -dimethylethyl-, m.p. ca. 58°; methyl- α -diethyl-, m.p. 49°; methyl- α -*di*-*n*-propyl-, m.p. 63°; ethyl- α -*di*-*n*-propyl-, m.p. 63°; methyl-, b.p. 134°/0.7 mm., and ethyl- α -*di*-*n*-butyl-, b.p. 123°/0.65 mm.). Mol. wt. is a determining factor with alkyl- but not aryl- (*m*-anisyl, m.p. 133°; 3:4-dihydroxy-, m.p. 171°, and 4-dimethylamino- β -phenylethyl, m.p. 129°) or alkylaryl-carbamides (α -ethyl- β -*m*-tolyl, m.p. 101°; α -ethyl- α -*p*-tolyl, m.p. 97°; α -ethyl- β -phenylethyl, m.p. 79°; α -*di*-*n*-butyl- β -phenyl, m.p. 86°).

γ -Hydroxypropyl-, m.p. 123°, *as*-*di*- β -hydroxyethyl-, m.p. 80°, cyclopentyl-, m.p. 197°, butanedi-, m.p. 226° (decomp.), *as*-*di*- γ -hydroxypropyl-, m.p. 148°, and 6:7-dimethoxytetrahydroisquinolyl-carbamide, m.p. 195°, are described.

F. O. H.

Cocaine, alcohol, dinitrophenol, and methylene-blue in experimental poisoning by barbiturics. A. ALLEGRI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 48—51).—Cocaine and C₆H₅(NO₂)₂·OH show slight therapeutic effects in guinea-pigs, and

EtOH in rabbits, poisoned by barbiturics; methylene-blue is without effect.

R. N. C.

Thiobarbiturates. E. MILLER, J. C. MUNCH, and F. S. CROSSLEY (Science, 1935, 81, 615).—Some thiobarbiturates show promise as sedatives, being free from the side actions and after-effects observed with their O analogues.

L. S. T.

Local anæsthetics. Phenylprocaine. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 358—363).—Phenylprocaine hydrochloride (I) is considerably more active than cocaine hydrochloride and novocaine in the guinea-pig and on the rabbit's cornea. (I) is the most active in a series of analogous Ph derivatives of procaine, although, owing to pptn. on the addition of buffers and irritation in corneal and intradermal tests, it does not appear to be of practical therapeutic val. 5-Nitro-2-cyanodiphenyl, m.p. 131—133° (from the 2-NH₂-compound in conc. HCl), is hydrolysed to the 2-carboxylic acid, reduced to the NH₂-compound (II), the hydrochloride, m.p. 230°, of which is converted into the 2- β -diethylaminoethyl ester dihydrochloride (I), hygroscopic, and the 2-dibutylaminopropyl ester, an oil (hydrochloride). (II) yields a chloride, b.p. 175—183°/2—3 mm., an *N*-Bu derivative (converted into the 2- β -diethylaminoethyl ester hydrochloride), and the 4-Cl-derivative, the 2- β -diethylaminoethyl ester of which was obtained as dihydrochloride, hygroscopic. 4-Amino-2- β -diethylaminoethylcarbamyldiphenyl hydrochloride was comparatively, and β -diethylaminoethyl 4-aminodiphenyl-2'-carboxylate was completely, inactive.

M. T.

[Pharmacological] activity of cocaine salts. J. REGNIER and R. DAVID (J. Pharm. Chim., 1935, [viii], 22, 16—22).—The anæsthetic activities of cocaine salts increase in the order hydrochloride, formate, acetate, salicylate, benzoate, phenylacetate. Salts of org. acids are more active than those of inorg. acids.

H. G. R.

Cardiac automaticity effects of caffeine and nicotine. Influence of (I) caffeine, (II) nicotine, and (III) caffeine-nicotine antagonism on the sino-aortic strip response. R. H. CHENEY (J. Pharm. Exp. Ther., 1935, 54, 213—221, 222—229, 230—235).—I. Low concns. of caffeine increase the amplitude of contractions in sino-aortic strips (frog); higher concns. diminish it and produce irregularities in rhythm.

II. Nicotine (0.2%) in Ringer's solution decreases frequency and amplitude and increases tonus. Only a slight stimulation occurs with a concn. of 0.05%.

III. The antagonism is investigated with reference to the automaticity of the strip and its physiological characteristics. Complete antagonism exists between 95 c.c. of 0.2% caffeine and 5 c.c. of 2.0% nicotine.

F. O. H.

Action of caffeine-containing and caffeine-free coffee on basal metabolism. E. MEYER (Z. Unters. Lebensm., 1935, 69, 563—570).—Ordinary coffee caused in six normal subjects and in four subjects suffering from hyperthyroidism or hypertonia a marked increase in basal metabolism, whilst caffeine-free coffee caused little or no increase.

E. C. S.

Action of drugs on liver-glycogen. Y. AOYAMA (Japan. J. Med. Sci., IV, 1933, 7, 21—22).—Perfusion of male toads with adrenaline, pilocarpine, or eserine increased sugar mobilisation, ergotoxine was without action, atropine caused slight inhibition, and choline a definite decrease. CH. ABS. (p)

Action of papaverine on blood-sugar of rabbits. A. RO (Japan. J. Med. Sci., IV, 1933, 7, 9—10).—Small doses of papaverine stimulate the adrenal gland, causing hyperglycaemia; larger doses inhibit adrenal action and induce hypoglycaemia. CH. ABS. (p)

Micro-determination of morphine in the brain. I. KABASAWA (Japan. J. Med. Sci., IV, 8; Proc. Japan. Pharmacol. Soc., 1934, 97—98).—Minced tissue is decomposed by papain at 65—70° for 20—80 min. Morphine (I) is extracted with dil. HCl, Et₂O-sol. matter is removed, and the tissue warmed with 3% HCl on a water-bath for 6 hr. After addition of NH₃ to pH 8.3 (I) is extracted (Soxhlet) with CHCl₃-EtOH mixture. (I) is recovered from the extract with dil. HCl and the vol. of the liquid adjusted to about 25 c.c. and to contain approx. 0.005N-HCl. The concn. of (I) is adjusted to approx. 1 mg. per c.c. and sufficient I solution is added so that after pptn. of (I) iodide 1 c.c. of the filtrate requires >1.1 c.c. of 0.005N-Na₂S₂O₃. The temp. must be <30°. CH. ABS. (p)

Hyperglycaemic action of opium alkaloids. H. GYOKU (Japan. J. Med. Sci., IV, 1933, 7, 101—103; cf. this vol., 528).—When injected intravenously into rabbits (2—50 mg. per kg.) morphine, codeine, and heroin were more potent hyperglycaemics than thebaine, although all contain the phenanthrene nucleus. *iso*Quinoline derivatives, papaverine, narcaine, and narcotine had a much weaker action. Pantopon produced the greatest response. CH. ABS. (p)

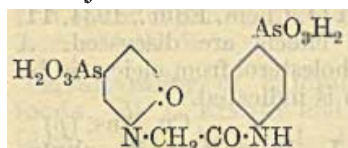
Action of opium alkaloids on the rabbit uterus *in situ*. S. HORIKOSHI (Japan. J. Med. Sci., IV, 1933, 7, 103—104).—Morphine (I), heroin (II), and codeine stimulated the uterus more strongly than did thebaine. Pantopon had a weaker action than (I) or (II). Narcotine and narcaine were without effect (cf. preceding abstract). CH. ABS. (p)

Pharmacology of arecoline. K. KYU (Japan. J. Med. Sci., IV, 1933, 7, 7—9).—The potency of arecoline was equal to that of acetylcholine and > that of pilocarpine, eserine, or muscarine. CH. ABS. (p)

Sedative action of antipyretics. T. YAO (Japan. J. Med. Sci., IV, 1934, 7, 103).—In experimentally induced toothache (electrical stimulation) antipyrene sedatives were more effective than those of the salicylic acid type. Na salicylate and salipyrine increased the stimulation threshold. CH. ABS. (p)

Biochemistry and medicinal significance of new pyridine derivatives. A. BINZ (Angew. Chem., 1935, 48, 425—429).—3-Iodopyridine, pyridine-3-antimony chloride, and, especially, pyridine-3-arsinic acid are more toxic than C₅H₅N. The hydroxypyridines, although more toxic than C₅H₅N, are not as toxic as PhOH; when they are condensed with CH₂Cl·CO₂H, the resultant pyridoneglycines,

and the corresponding I-derivatives, are (unexpectedly) very slightly toxic. 2-Pyridone-5- (I) and 4-pyridone-3-arsinic acids have an exceptionally high tolerance but 2-pyridone-5-stibinic acid is less stable and more toxic. N-Alkylation of (I) greatly increases the toxicity but the introduction of ·CH₂·CO₂H has



practically no effect. The compound (annexed formula), obtained by combining atoxyl (II) with (I) by means of CH₂Cl·COCl,

has twice the tolerance of (II). 3-Amino-2-pyridone-5-arsinic acid is similar to (I), but 2-amino-, 2-ethylamino-, and 2-diethylamino-pyridine-5-arsinic acids (from the 2-chloroarsinic acid and the alkylamine) are 0.5, 5, and 50 times as toxic as C₅H₅N, respectively. The therapeutic properties of the iodopyridones and the pyridonearsinic acids are discussed. S. C.

Toxicology of pyridine and its homologues (Wernicke encephalitis). H. LUDWIG (Arch. Gewerbepath. Gewerbehyg., 1934, 5, 654—664).—Symptoms are described. R. N. C.

Urobilinuria: false Ehrlich reaction caused by pyridium medication. J. W. FARTHING and J. S. P. BECK (J. Lab. Clin. Med., 1934, 20, 61—62).—The false positive reaction with Ehrlich's reagent given by urines containing pyridium is due to the action on this of HCl used in preparing the reagent. Urines giving a positive test should be treated with HCl alone to detect the dye. CH. ABS. (p)

Adrenolytic action of phenoxyamines in the rabbit. J. LEVY and L. OLSZYCKA (Compt. rend. Soc. Biol., 1935, 119, 899—902).—Phenoxyamines, ergot, and yohimbine—the so-called "sympatholytics"—antagonise, but do not invert, the pressor action of adrenaline. R. N. C.

Substances affecting the circulation in "eutonon" liver extract. H. A. HEINSEN (Klin. Woch., 1934, 13, 1597—1599; Chem. Zentr., 1935, i, 918).—"Eutonon" can be separated into a pressor and a depressor fraction by making strongly alkaline with Na₂CO₃ and extracting with C₅H₁₁·OH. The C₅H₁₁·OH fraction contains tyramine, and the H₂O fraction choline. R. N. C.

Action of certain new histamine derivatives. A. VARTIAINEN (J. Pharm. Exp. Ther., 1935, 54, 265—282).—All the alkylhistamines substituted in the NH₂ show some histamine-like activity. That of the Me₁ derivative is weaker on the blood-vessels but stronger on the uterine and intestinal muscles. The Me₂ derivative has 1/5—2/5 of the activity of histamine and a weak nicotine-like action, which becomes predominant in the NHMe₃ base. The derivative has 1/20 of the activity of histamine and hydroxyethylgloxaline a weak stimulating action on plain muscle. H. G. R.

Interaction between acetylcholine and sterols in tissues. G. S. CARTER and L. W. MAPSON (Nature, 1935, 136, 143—144).—Addition of a sterol or of acetylcholine (I) to the gastrocnemius muscle of a frog in the resting winter condition leads to a prolonged contraction. When added together in the

correct proportion, which, however, varies with different sterols, only a normal twitch is observed even when concn. is increased. Like (I), sterols weaken and retard the beat of the frog's heart, but when added together in the correct proportion the effect on the heart is reduced or disappears. The results suggest that sterols play a part in the same chemical processes as those in which (I) is concerned. L. S. T.

Occurrence of unstable choline esters in invertebrates. Z. M. BACQ (Nature, 1935, 136, 30—31).— $\text{CCl}_3\cdot\text{CO}_2\text{H}$ extracts of various tissues of *Octopus vulgaris* contain a substance, probably acetylcholine, which possesses the physiological properties of unstable choline esters. In some invertebrates, at least, conditions for cholinergic nervous action appear to be realised. L. S. T.

Action on the rabbit's isolated intestine of an acetylcholine-sensitising substance formed in the trunk of the pneumogastric nerve by electric excitation. C. NOCHIMOWSKI (Compt. rend. Soc. Biol., 1935, 119, 943—946).—Extracts of the peripherally or centrally excited pneumogastric of the dog increase the effect of acetylcholine on the isolated rabbit's intestine. Previous isolation of the nerve before excitation does not inhibit formation of the sensitising substance. R. N. C.

Colour changes in the catfish *Ameiurus* in relation to neurohumours. G. H. PARKER (J. Exp. Zool., 1934, 69, 199—233).—The nature of these secretions and their action on the chromatophores are examined. CH. ABS. (p)

New active principle of ergot. H. W. DUDLEY and J. C. MOIR (Science, 1935, 81, 559—560).—Concerning nomenclature. L. S. T.

New active principle(s) of ergot. M. S. KHARASCH and R. R. LEGAULT (Science, 1935, 81, 614—615).—A reply to the above. L. S. T.

New active principle of ergot. M. R. THOMPSON (Science, 1935, 81, 636—639).—Concerning nomenclature and priority (cf. preceding abstract). L. S. T.

New active principle of ergot. M. R. THOMPSON (Science, 1935, 82, 62—63).—A correction (cf. preceding abstract) and a reply to criticism. Pure ergotetrine, m.p. 161—163° (decomp.), is dextrorotatory in H_2O , EtOH , and CHCl_3 . L. S. T.

Pharmacological effects of ergometrine, a new alkaloid of ergot. RAYMOND-HAMET (Compt. rend., 1935, 201, 176—179).—The pharmacological effects are compared with those of other ergot alkaloids. H. G. R.

Ergobasine, a water-soluble alkaloid from ergot of rye.—See this vol., 995, 1137.

Action of ergoclavine and sensibamine. A. VARTIAINEN (J. Pharm. Exp. Ther., 1935, 54, 259—264).—The pharmacological activities of these alkaloids are identical with those of ergotoxine and ergotamine. H. G. R.

Vegetable extracts and blood-sugar. P. S. JORGENSEN and E. V. LYNN (J. Amer. Pharm. Assoc., 1935, 24, 389—392).—Contrary to previous reports no evidence could be found of activity of plant

extracts in reducing normal or high blood-sugar levels. M. T.

Some common [Indian] indigenous remedies. R. N. CHOPRA and S. GHOSH (Indian J. Med. Res., 1934, 22, 263—270).—The chemical composition, pharmacological actions, and therapeutic properties of a no. of plant extracts are described. R. N. C.

Phloridzin diabetes. II. E. S. LONDON, N. KOTSCHNEV, F. I. RIVOSCH, L. I. KRIZANOVSKAJA, R. R. PADVE, and N. B. MANUSSOVA (Arch. exp. Path. Pharm., 1935, 178, 700—718; cf. A., 1933, 746).—Continuous subcutaneous or single intravenous injection of phloridzin (I) into dogs produces disturbances in carbohydrate metabolism in which the kidney is not the only organ involved. Liberation of sugar occurs in the liver and retention in kidney, intestine, and muscle, whilst liberation of glycogen into the blood by the kidney is initiated. The arterial blood- AcCO_2H and -AcCHO decrease, whilst lactic acid increases. Determinations of P fractions in the blood from various vessels indicate that phosphorylation and dephosphorylation processes are significantly modified by (I); *in-vitro* experiments are misleading (cf. Lundsgaard, A., 1933, 1076). The blood- PO_4''' of young dogs (normal or phloridzinised) is $>$ that of adult dogs. (I) increases the blood contents of NH_2 -acid- and polypeptide-N and total glutathione. These and data from other tissues indicate that (I) diabetes is exclusively neither of renal origin nor concerned with P fractions, but is a general intoxication one symptom of which is glycosuria. F. O. H.

Pharmacological action of taxin. C. S. LIM (Japan. J. Med. Sci., IV, 1934, 8, 121—122).—Doses of 4 mg. per kg. decreased the normal blood-sugar and glucose-hyperglycæmia but did not affect adrenaline-hyperglycæmia. 50—200 p.p.m. of taxin caused depression of the isolated heart and tissue constriction in toads. CH. ABS. (p)

Active constituents of *Podophyllum plectanum*, Hance. S. To (Japan. J. Med. Sci., IV, 1933, 7, 15—16).—The active constituent resembles podophyllotoxin. Analytical data are given. CH. ABS. (p)

Polarimetric determination of physiological activity of hemp resin. M. N. GHOSE and S. N. BHATTACHARJEE (Analyst, 1935, 60, 313—316).—The physiological activity of charas and ganja, as estimated by a panel of experienced smokers from the degree of intoxication produced, \propto the $[\alpha]_D$ of the CCl_4 extract of the drug. E. C. S.

Relative toxicities of pyrethrins I and II. J. RIPERT and O. GAUDIN (Compt. rend., 1935, 200, 2219—2220).—Staudinger's method of isolating pyrethrins gives degraded products. The pure substances are best obtained by preferential extraction of pyrethrin II from ligroin by 82% MeOH . Pyrethrin I causes only slow paralysis of fish, but pyrethrin II causes also a preliminary excitation. Doses of pyrethrins I and II and a 1:1 mixture thereof which give a 50% mortality when injected into snails are 0.8, 0.75, and 0.66 mg. per kg. body-wt., respectively. R. S. C.

Action of cardiotonics on frog hearts. T. TAKABE (Japan. J. Med. Sci., IV, 1934, 8, 138—141).—In dynamic tests, digitalis, camphor (I), hexetone (II), and coramine (III) strengthened the abs. contractions and increased the beat vol., digitalis acting chiefly on the abs. contractile power. Cardiazole slightly affected the beat vol. Strophanthin, strychnine, and caffeine had a weak stimulative action on contractile power. (III) decreased, and digitalis and (I) increased, the rate, whereas (II) had no action. CH. ABS. (p)

Biological assay of digitalis preparations in the tropics. V. Potency of lanadigin (glucoside of *D. lanata*) and its relation to the standard powder (B.P. 1932). R. N. CHOPRA, J. S. CHOWHAN, and S. LAL (Indian J. Med. Res., 1934, 22, 279—283).—Lanadigin shows the same physiological potency as the glucosides of *D. purpurea*; it can be sterilised by boiling, and deteriorates less rapidly in the tropics than the *D. purpurea* glucosides.

R. N. C.

Potency of Oregon digitalis. D. K. LEE and E. T. STUHR (J. Amer. Pharm. Assoc., 1935, 24, 367—369).—A comparative study of seasonal physiological activity of wild *D. purpurea*, L.

M. T.

Bioassay of digitalis. III. Diuretic, oliguric cat method. J. H. DEFANDORF (J. Amer. Pharm. Assoc., 1935, 24, 369—374).

M. T.

Action and toxicity of retrorsine. K. K. CHEN, A. L. CHEN, and C. L. ROSE (J. Pharm. Exp. Ther., 1935, 54, 299—305).—Retrorsine has a depressor and a hyperglycæmic action and contracts the guinea-pig uterus. The guinea-pig is less susceptible than the mouse, the min. lethal dose being 0.32 g. per kg., whereas 0.2 g. per kg., injected intravenously, causes death in the mouse.

H. G. R.

Blood changes caused by ophidian venoms. III. Variations in alkaline reserve. J. VELLARD and M. MIGUELOTE-VIANNA (Ann. Inst. Pasteur, 1935, 55, 148—152; cf. this vol., 398).—A much smaller decrease in the alkaline reserve of the blood of dogs is observed on injection of *Naja tripudians* venom than with venoms from *Crotalinae*. This is attributed to the curarising effect of the former.

E. A. H. R.

Variations in the reaction of different parts of the central nervous system as influenced by depressant and stimulating drugs. D. E. JACKSON (J. Lab. Clin. Med., 1934, 20, 1—13).—The varied effects of metrazole on dogs anaesthetised with Et_2O , evipal, and with C_2HCl_3 are recorded.

CH. ABS. (p)

Influence of bile acids on phosphorylation of adenylic acid in liver and muscle. K. WATANABE (J. Biochem. Japan, 1935, 21, 203—209).—Phosphorylation of adenylic acid to adenylypyrophosphoric acid occurs in liver and muscle *in vitro* and is enhanced, especially in muscle, by 0.1% Na cholate. This agrees with the respective dephosphorylating activities (A., 1911, ii, 412).

F. O. H.

Influence of bile acids on urinary ammonia excretion. Y. KAWADA (J. Biochem. Japan, 1935, 21, 213—218).—Intravenous or oral administration of cholic acid to dogs produces a transient decrease in

the NH_3 content and sp. gr. of the urine; the vol. excreted tends to increase.

F. O. H.

Bile acids and calcium metabolism. X. Urine- and bile-calcium in normal and thyro-parathyroidectomised dogs. S. TUZIOKA (J. Biochem. Japan, 1935, 21, 219—241).—Excretion of Ca in urine and, more especially, in bile is increased in dogs by subcutaneous and, to a greater extent, oral administration of cholic acid. Thyro-parathyroidectomy diminishes the vol. of bile and Ca excretion in bile and urine; subsequent administration of cholic acid increases the vals. but not to normal levels. Following the operation, tetany occurs more readily in dogs with biliary fistulæ than in normal dogs, but is offset by injection of cholic acid. Thus tetany is related to liver function.

F. O. H.

Salt and water losses in diuretin diuresis and their relation to serum-non-protein-nitrogen and -electrolyte concentrations. E. KERPEL-FRONIUS and A. M. BUTLER (J. Exp. Med., 1935, 61, 157—172).—Losses are shown of Na, K, Cl, N, and H_2O together with changes in serum-Na, -Cl, -non-protein-N, and -total protein following administration of diuretin to rabbits. No relationship is apparent between the occurrence of azotæmia and the coincident hypochloræmia. Administration of H_2O without salt prevents N retention and lowers the serum-electrolyte and -protein. The efficiency of NaCl in preventing the withdrawal of K, Na, and Cl after diuretin treatment is examined.

CH. ABS. (p)

Effect, in the dog, of sinus blockage on the adrenaline, sugar, and calcium content of blood, and on the oxygen requirements. U.S. VON EULER and G. LILJESTRAND (Skand. Arch. Physiol., 1934, 71, 73—84).—Blockage of both carotids of anaesthetised dogs caused rise of blood-pressure, O_2 consumption, and adrenaline content of the blood. Blood-sugar and -Ca were unchanged. After extirpation of adrenals, blockage still caused rise of blood-pressure, but almost no rise in O_2 consumption.

G. H. F.

Effect of iodoacetic acid on rabbit muscle. Y. NISHITA (Japan. J. Med. Sci., IV, 1934, 8, 117).—Subcutaneous injection of 5% solution of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ in NaHCO_3 (50 mg. per kg. wt.) into rabbits increased the blood-sugar (I) and -lactic acid (II) and decreased the CO_2 -combining power. Section of both splanchnic nerves lowered the alteration in blood-(I) and -(II) but did not affect that of the CO_2 -combining power.

CH. ABS. (p)

Iodoacetic acid and glycosuria. G. PERETTI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 77—79).—Small doses of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ injected into rats or rabbits produce variable increases of urinary sugar. Injection of one kidney only with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ in the dog produces no difference between the sugar contents of the urine excreted from the two kidneys.

R. N. C.

Does methylene-blue form methæmoglobin? M. M. BROOKS (Proc. Soc. Exp. Biol. Med., 1934, 31, 1134—1137; cf. A., 1934, 912).—With rats and dogs, intravenous injection of methylene-blue (I) did not produce detectable amounts (spectrophotometer) of methæmoglobin (II). Only oxyhæmoglobin

was found. Hence recovery of HCN- and CO-poisoned animals treated with (I) is not due to formation of (II), but probably results from the catalytic action of (I) in transferring O_2 . CH. ABS. (p)

Basal metabolism and the dyestuffs methylene-blue, neutral-red, and malachite-green (in rats). A. H. ROFFO and R. L. RAMIREZ (Rev. Asoc. Med. Argentina, 1932, 46, 901—904).—Intravenous injection of methylene-blue reduces basal metabolism. Neutral-red and malachite-green have no action. CH. ABS. (p)

Action of hexenol from tea leaves. I. S. MURAKAMI (Japan. J. Med. Sci., IV., 1934, 8, 136—137).— Δ^6 -Hexen- α -ol obtained by distillation of raw leaves resembled hexyl alcohol in its action on the frog heart and in lowering the blood-pressure in rabbits. CH. ABS. (p)

Resistance of fixed tissue cells to the toxic action of certain chemical substances. W. DE B. MACNIDER (Science, 1935, 81, 602—605).—A lecture. L. S. T.

Influence of bromobenzene on the glutathione content of tissues. K. FUJII (Japan. J. Med. Sci., IV, 1933, 7, 84—86).—Following injection of PhBr (4500 mg. per kg.) into frogs, mice, and rats, the glutathione content was increased in heart, lungs, spleen, and pancreas and decreased in liver, kidneys, muscle, and testicles. CH. ABS. (p)

Excretion of sodium salicylate. C. MEI (Japan. J. Med. Sci., IV, 1933, 7, 98).—Acidosis delays and alkalosis increases excretion of Na salicylate (I). Injection of (I) lowers HCl-acidosis and delays excretion, but has no effect on $NaHCO_3$ -alkalosis although excretion is hastened. Administered alone (I) increases the plasma- pH over a 6-hr. period. CH. ABS. (p)

Toxicology of phenols. C. GERIN (Boll. Chim. farm., 1935, 74, 465—468).—With tissue-protein PhOH forms a compound which is decomposed by Na_2CO_3 but not by acids. Factors (e.g., putrefaction) influencing the content of phenolic substances in normal tissue and urine are discussed and a method for their determination in viscera etc. is described. F. O. H.

Anthelmintic properties of certain alkylphenols. P. D. LAMSON, H. W. BROWN, and P. D. HARWOOD (Amer. J. Trop. Med., 1934, 14, 467—478).—Comparison is made of *o*- and *p*-alkylphenols, 4-alkylresorcinols, and 6-alkylresols by the *Ascaris* method *in vitro*. The lower and higher members of each series were inactive whereas those having 4—7 C in the side-chain were active. With increasing length of the side-chain toxicity decreased, but irritation of the alimentary tract increased. *o*-Heptylphenol and hexyl-*m*-cresol gave best results *in vitro*, but on man infected with *Ascaris* and hook-worm were disappointing. CH. ABS. (p)

Effect of 2:4-dinitrophenol on oxygen consumption, blood-sugar, and cholesterol. V. EMMER (Compt. rend. Soc. Biol., 1935, 119, 1137—1140).—Administration of 2:4- $C_6H_3(NO_2)_2 \cdot OH$ to patients causes a rise of O_2 consumption, which reaches its max. in 4—5 hr. Blood-sugar rises steadily,

whilst cholesterol varies irregularly, diminishing in most cases. R. N. C.

Vago-inhibitory effects on the respiratory metabolism of the heart after treatment with dinitrophenol. W. E. GARREY and J. T. BOYKIN (Amer. J. Physiol., 1935, 111, 196—200).—The respiratory metabolism of resting cardiac muscle is augmented by $C_6H_3(NO_2)_2 \cdot OH$ *in vitro*, O_2 consumption being increased approx. 3 times. Vagus inhibition is still effective, stimulation causing a decrease of O_2 consumption in resting turtle's auricles, which is of the same order of magnitude as for normal resting auricles. R. N. C.

Spleen and experimental hyperthermia. M. RUBINSTEIN (Med. Doswiad. Spol., 1934, 19, 91—113).—Splenectomy diminished the fever response to 2:4-dinitrophenol (I). The glutathione content of the spleen of febrile dogs was < normal, the alkali reserve of the blood was lowered, and the red-cell-Cl increased. Alkaline solutions of (I) induced more intense fever than did neutral solutions. CH. ABS. (p)

Toxicology of aromatic nitro-compounds. I. 2:4-Dinitrophenol. A. I. TSCHERKESS, V. F. MELNIKOVA, and S. M. DUBASCHINSKAJA (Arch. exp. Path. Pharm., 1935, 179, 1—14).—The lethal dose of 2:4-dinitrophenol (I) (administered orally, subcutaneously, through the skin, or by inhalation) for dogs, cats, rabbits, pigeons is 15—50 mg. per kg. body-wt. The symptoms produced by lethal or nearly lethal doses are accelerated respiration, high fever (temp. up to 42—45°), hyperglycæmia, and increase of lactic acid and ketone contents with decrease in the alkali reserve of the blood, increased O_2 consumption, and increased CO_2 production. These results, which are not affected by preceding administration of drugs [$CCl_4 \cdot CH(OH)_2$, luminal, salicylate] which act on the central nervous system, indicate that (I) acts by stimulating tissue-oxidations. W. McC.

Effect of dinitro- α -naphthol on blood-cholesterol in man. L. F. GRANT and P. G. SCHUBE (J. Lab. Clin. Med., 1934, 20, 56—61).—Daily oral administration of dinitronaphthol causes a temporary increase of blood-cholesterol followed by a decline to < initial vals. and a slow return to normal. CH. ABS. (p)

Metabolism of naphthalene in adult and growing dogs. J. A. STEKOL (J. Biol. Chem., 1935, 110, 463—469).— α -Naphthylmercapturic acid was isolated from the urine; the latter also contained an ethereal sulphate, possibly a naphthol conjugation product with H_2SO_4 . There was an increased output of glycuronic acid in the urine after administration of $C_{10}H_8$. J. N. A.

Curative action of 2:4-diamino-4'-sulphonamidoazobenzene hydrochloride and similar derivatives in experimental streptococcal infection. C. LEVADITI and A. VAISMAN (Compt. rend. Soc. Biol., 1935, 119, 946—949).—The curative action of rubiazol is sp. for streptococcal infections. Azoi-4 is the most therapeutically active azo-derivative against streptococci. Rubiazol and prontosil are equally effective, whilst Na 4-sulphonamido-

benzeneazo-7-acetamido- α -naphthol-3:6 disulphonate is least effective. The action of azo-compounds is to inhibit encapsulation of the streptococci, and to facilitate phagocytosis.

R. N. C.

Combinations of different qualities of taste as a method of investigating the chemical sense of the earthworm. O. MANGOLD (Naturwiss., 1935, 23, 472—474).—Earthworms prefer pure gelatin (I) to (I) containing NaCl, quinine, or dulcitol, but (I) containing $\text{H}_2\text{C}_2\text{O}_4$ is preferred to pure (I). Combinations of the four taste substances exert in general an additive effect except that the preference for $\text{H}_2\text{C}_2\text{O}_4$ is specially effective in such combinations.

W. O. K.

Fate of oxalic acid in dogs. G. ORZECZOWSKI, P. GÖMÖRI, and M. HUNDRIESER (Arch. exp. Path. Pharm., 1935, 178, 739—748).— $\text{H}_2\text{C}_2\text{O}_4$ fed to dogs is excreted unchanged, no decomp. occurring in the organism.

F. O. H.

[Fate of oxalate in] oxalate-poisoned dogs. W. HEUBNER and R. HUCKEL (Arch. exp. Path. Pharm., 1935, 178, 749—754).—Histological appearance of the kidney and oxalate content of various organs in dogs poisoned with $\text{Na}_2\text{C}_2\text{O}_4$ are recorded. The prolonged retention of oxalate by the kidney is noteworthy.

F. O. H.

Toxicology of petrol. L. M. FRUMIN and S. S. FAIRSTEIN (Zentr. Gewerbehyg. Unfallverhütung, 1934, 21, 161—165; Chem. Zentr., 1935, i, 1087).—The toxic effects of petrol vapours on workers in the rubber industry are described.

R. N. C.

Propeptan therapy. E. URBACH and S. KITAMURA (Klin. Woch., 1934, 13, 1573—1578).—Egg-propeptan induces contraction of uterus from guinea-pigs sensitised with it; the reaction is sp. Anaphylactic shock in guinea-pigs can be prevented by administration of minimal doses of antigen, or of the sp. propeptan.

G. H. F.

Relationship between anaphylaxis and magnesium chloride. C. Y. CHOI (J. Chosen Med. Assoc., 1934, 24, 1249—1257).—Injection of 0.25 c.c. of 1% aq. MgCl_2 into guinea-pigs either before sensitisation with or before re-injection of horse-serum did not prevent anaphylaxis. The latter was inhibited by use of 0.25—0.5 c.c. of 3% aq. MgCl_2 .

CH. ABS. (p)

Methylene-blue, methæmoglobin, and cyanide poisoning. W. B. WENDEL (J. Pharm. Exp. Ther., 1935, 54, 283—298).—The author's previous conclusions are confirmed (cf. A., 1934, 1400).

H. G. R.

Importance of moisture in poisoning with carbon dioxide and with illuminating gas in mice. L. DI BELLA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 14—16).—The toxicities of the gases increase \propto their solubilities in H_2O when they are inhaled together with H_2O vapour.

R. N. C.

Anæsthetic properties of carbon monoxide and other gases in relation to plants, insects, and centipedes. P. W. ZIMMERMANN (Contr. Boyce Thompson Inst., 1935, 7, 147—155).—Min. anæsthetic concns. of CO , C_3H_8 , C_4H_8 , C_2H_4 , C_2H_2 , and CO_2 for various insects and centipedes are recorded. C_4H_8

was the most and C_2H_4 the least effective. Insects remained normal in N_2 or He mixtures with the O_2 content reduced to 2%. C_2H_4 was the most efficient plant anæsthetic, and retarded growth to extents \propto the concn. and differing with the plant species. C_2H_2 and C_3H_8 were equally active and approx. 10 times as active as CO .

A. G. P.

Purpura hæmorrhagica caused by gold and arsenical compounds. E. H. HUDSON (Lancet, 1935, 229, 74—77).—Two cases due to administration of allochrysine and sulpharsphenamine are recorded.

L. S. T.

Effect of mercury vapour on the upper air passages. A. STOCK (Naturwiss., 1935, 23, 453—456).—The effects of Hg poisoning by breathing the vapour are described and discussed.

A. J. M.

Lead content of human tissues and excreta. S. L. TOMPSETT and A. B. ANDERSON (Biochem. J., 1935, 29, 1851—1864).—Pb in bone tissue and excreta may be separated by ashing and extracting with Et_2O the complex of Pb with Na diethyldithiocarbamate. Pb in the extract after destruction of org. matter is determined colorimetrically with diphenylthiocarbazon in CCl_4 . A special modification is given for blood requiring 20 c.c. The mean concns. in mg. of Pb per kg. for adults not exposed to Pb were: liver 1.73, kidney 1.34, spleen 1.68, brain 0.5, rib 8.55, vertebra 7.09. Fœtal tissues gave vals. considerably below those for normal adults. The mean normal daily excretion in urine was 0.05 mg. and in fæces 0.22 mg. The blood-Pb in normals varied from $40\text{--}70 \times 10^{-6}$ g. per 100 c.c. with a mean of 55×10^{-6} g. per 100 c.c. The blood-Pb but not the excretion of Pb was markedly increased in a case of plumbism.

W. O. K.

Retrobulbar neuritis due to thallium poisoning. W. MAHONEY (Yale J. Biol. Med., 1933—1934, 6, 583—597).—Effects of TI poisoning from depilatory preps. are described.

CH. ABS. (p)

Toxicity of aluminium. I. Slight cumulative poisoning by ingestion of food prepared in aluminium cooking-vessels. L. TOCCO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 65—66).—Prolonged contact of food with Al vessels in presence of warm NaHCO_3 solution, followed by cooking without washing, results in contamination of the food with Al, which is cumulatively toxic, producing a gastro-intestinal syndrome.

R. N. C.

Effect of feeding high amounts of soluble iron and aluminium salts. H. J. DEOBALD and C. A. ELVEHJEM (Amer. J. Physiol., 1935, 111, 118—123).—Addition of large amounts of sol. Fe or Al salts to the normal diet in chicks produces severe rickets with fatal results in 3 weeks. Fe and Al levels equiv. to 50% and 75% of the amount necessary to convert the total P in the diet into FePO_4 and AlPO_4 reduce bone-ash to 25% and blood-P to 2—4 mg. per 100 c.c. of serum. Addition of sufficient Na_2HPO_4 to unite with the Fe and Al allows normal growth and bone formation. Blood-P falls 5 days after addition of Fe or Al, reaching 1.5—1.7 mg. per 100 c.c. of serum in 4 days.

R. N. C.

Influence of sodium fluoride on the phosphate metabolism of rabbit muscle. M. MIYOSHI (Japan. J. Med. Sci., IV, 1933, 7, 86—87).—Subcutaneous injection of NaF (80—120 mg. per kg.) induced hyperglycemia and changed the proportions of various P compounds in the muscles.

CH. ABS. (p)

Urine of phosphorus-poisoned men. T. KAWADA and F. YAMASAKI (J. Biochem. Japan, 1935, 21, 423—425).—Urine from P-poisoned men contained γ -butyrobetaine, tyrosine, and other NH_2 -acids.

F. O. H.

Action of mineral water on composition of the blood. IV. Karlsbad water and serum-anions. E. STRANSKY (Arch. exp. Path. Pharm., 1935, 178, 724—730; cf. A., 1934, 1254).—Continuous drinking of Karlsbad H_2O by rabbits produces no marked change in serum-Cl, -Na, $-\text{HCO}_3'$, or -total SO_4'' . Inorg. P and K increase in some cases, Ca increases by $<0.001\%$, and Mg correspondingly decreases, changes due to all and not merely one of the mineral constituents. The bearing of the data on those from men is discussed.

F. O. H.

Germicidal and antiseptic activity of some mercury compounds. E. MONESS, S. E. HARRIS, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 386—389).— β -4 : 4' - *Dihydroxydiphenylpropane*, b.p. 225—230°/4 mm., m.p. 144° (from PhOH , COMe_2 , and POCl_3), was converted into the 3 : 3-(NO_2)₂-derivative, m.p. 132° [which furnishes the 5 : 5'-(OAcHg)₂-compound (I)], and also into the 3 : 3'-*di*-bromo-5 : 5'-*di*-acetoxymercuri-compound (II), m.p. 250° (decomp.). A Hg derivative (III) of *di*-bromoresorcinoldiphenene was also prepared. (I), (II), and (III) all show germicidal activity.

M. T.

Effect of amebicidal drugs on tissue culture cells (arsenious trithiosalicylic acid, carbarsone, kurchi bismuth iodide, proparsamide, vioform). M. J. HOGUE (Amer. J. Trop. Med., 1934, 14, 443—456).—Toxic effects of the drugs are compared on tissues of the digestive tract of 8-day chick embryos *in vitro* at p_{H} 6.3—6.8.

CH. ABS. (p)

Influence of radon on internal secretion. N. P. KOCHNEVA (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, 243—248).—Increased retention of blood-sugar by the kidneys during insulin action is accelerated by intravenous injection of 20—25 millicuries of Rn and diminished by 1 millicurie. During absorption of protein derivatives Rn decreases the sugar level in renal and peripheral blood. In fasting dogs Rn does not accelerate the general hypoglycemic action of insulin, but augments sugar retention by kidneys, probably by decreasing the retention by other organs.

CH. ABS. (p)

Emission of radiation in chemical and biological phenomena.—See this vol., 1055.

Specificity of enzyme catalysis.—See this vol., 940.

Kinetics of heterogeneous catalysis and of enzyme action.—See this vol., 1084.

Enzyme catalysis of the exchange of deuterium with water.—See this vol., 1084.

Methods and applications of enzyme studies in histological chemistry of the Linderström-Lang-Holter technique. D. GLICK (J. Chem. Educ., 1935, 12, 253—259).

L. S. T.

Vitazymes and hormozymes. H. VON EULER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 45, 6 pp.).—It is suggested that animal and plant co-enzymes of carbohydrate decomp. have a common prosthetic group, adenosylphosphoric acid, and differ only in their ligatory group. Flavin (I) when bound to a protein is a typical vitazyme. The occurrence of light-stable (I) in green leaves is attributed to the protecting influence of chlorophyll and its colloidal carrier. Methylene-blue (II) may play a similar protective role in the photo-reduction of (I) by yeast extract and EtOH , which proceeds without lumiflavin formation, as the max. activation of this reaction is brought about by λ corresponding with the absorption bands of (II).

E. A. H. R.

Potentiometric study of catalase action. R. IRON (J. Biochem. Japan, 1935, 21, 329—334).—Purified catalase preps. from horse erythrocytes added to dil. aq. H_2O_2 have an oxidation potential (Pt electrode) $>$ that of the aq. H_2O_2 alone. A periodicity in the potential- $[\text{H}_2\text{O}_2]$ curve is related to the oxidation and reduction functions of H_2O_2 in presence of catalase.

F. O. H.

Chemical studies on enzymes. II. H. VON EULER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 42, 6 pp.).—In the pig, dehydrogenase (I) activity of the mucosa of the small intestine is accelerated (slightly) by EtOH , glucose, and HCO_2Na , and (greatly) by Na succinate. A-avitaminosis in rats increases (I) activity and the mucosa of the small intestine, and B_2 -avitaminosis also increases it. B_2 -avitaminosis in chickens has little action on the (I) activity of the small intestine. In the guinea-pig C-avitaminosis decreases (I) activity, suggesting that the influence of vitamin-C (II) is connected with enzymic activity. Phosphatase activity of the small intestine of the pig is inhibited by (II), whilst phosphatase activity is inhibited by cysteine and not by (II).

E. A. H. R.

Characterisation of three co-enzymes concerned in biological oxidation-reduction processes. H. VON EULER, E. ADLER, F. SCHLENK, and G. GUNTHER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 52, 6 pp.).—Adenyl pyrophosphate cannot function as a co-enzyme for EtOH -dehydrogenase (I) nor for hexose monophosphate-dehydrogenase (II). Cozymase (III) is identical with the activator of yeast-(I). Warburg's "co-ferment II" is a better activator of (II) than is (III), but does not activate (I); it is more thermolabile than (III).

E. A. H. R.

Dehydrogenation of succinic acid by charcoal. Model of the mode of reaction of succinodehydrazase.—See this vol., 940.

Influence of the yellow respiratory enzyme on the dehydrogenation of lactacidogen and hexose-diphosphoric acid by yeast-dehydrogenase. A. HAHN, H. NIEMER, and B. FREYTAG (Z. Biol., 1935, 96, 453—458).—The addition of the yellow enzyme (I) reduces the time of decolorisation of methylene-

blue (II) by lactacidogen (III) and hexosediphosphoric acid (IV) in the presence of yeast-dehydrogenase (V) to about one third. (I) has no influence on the rate of dehydrogenation of lactic acid (VI) by (II) and (V). Aerobically (I) does not accelerate the oxidation of (VI), but the O_2 uptake in the presence of (III) is about doubled. (IV) shows such a small O_2 uptake that its acceleration by (I) would not be significant.

E. A. H. R.

Citric acid dehydrase of liver. L. REICHEL [with A. NEEFF] (*Naturwiss.*, 1935, 23, 391).— $COMe_2$ -dried preps. from liver (man, calf, pig, horse) contain a citric acid dehydrase for which O_2 , methylene-blue, and lactoflavin do not function as intermediary acceptor. HCO_2H is the only true fission product, the formed acetonedicarboxylic acid being degraded by another enzyme system or non-enzymically. $p-C_6H_4Me \cdot SO_3H$ is introduced as a deproteinising agent.

F. O. H.

Active group of co-enzyme from erythrocytes. O. WARBURG, W. CHRISTIAN, and A. GRIESE (*Biochem. Z.*, 1935, 279, 143—144).—The C_5H_5N component (I) of the co-enzyme (this vol., 121, 249, 400), acting in a system converting hexose monophosphate into phosphohexonic acid, takes up 2 H. The hydrogenated (I) thus formed is oxidised not by O_2 alone, but by O_2 in presence of the alloxazine from yellow enzyme which acts as H_2 carrier. With $Pt+H_2$, 1 mol. of (I) takes up 3 H_2 , the product being inactive.

F. O. H.

Identity of xanthine-oxidase and Schardinger enzyme. V. H. BOOTH (*Biochem. J.*, 1935, 29, 1732—1748).—The identity of xanthine-oxidase (I) and the Schardinger enzyme (II) is claimed for the following reasons. With both aldehyde and purine substrates together only competition is observed; (I) is inhibited by the oxidation products of (II); activity ratios for the milk- and liver-enzymes are similar; in yolk-sac and whole embryo the first appearances of the two are coincident; no preferential destruction is caused by heat etc.; mixed dismutation occurs between uric acid and salicylaldehyde whereby the former is converted into hypoxanthine, no respiratory carrier being necessary. The change in the activity ratio of the two enzymes after adsorption (*A.*, 1930, 248) is not due to preferential adsorption of one component, but to the removal of an equal quantity of both, and to the fact that the relation between enzyme concn. and activity is not linear for either substrate. The change in ratio due to added protein is the result of preferential adsorption of one substrate.

H. D.

Action of hydrocyanic acid on oxidase of gum arabic. V. ZANOTTI (*Giorn. Farm. Chim.*, 1934, 83, 385—388; *Chem. Zentr.*, 1935, i, 1255).—Gaseous HCN inactivates the enzyme, which recovers its activity after aeration. Brief exposure to HCN may induce a stimulative effect and prolonged treatment (120 hr.) permanently destroys the enzyme.

A. G. P.

Enzymic hydrolysis *in situ* of intracellular tissue. H. COLIN and A. CHAUDUN (*Compt. rend.*, 1935, 201, 407—409).—Hydrolysis (by snail's hepato-

pancreatic juice) of pectin substances (I), determined by changes in the ratio of $[\alpha]$ to reducing val., in beetroot tissue indicates that a part of (I) adheres firmly to the cellulose walls; this agrees with the conception of a pecto-cellulose membrane.

F. O. H.

Activation of glycolysis by heat-inactivated cozymase preparations. H. VON EULER and G. GUNTHER (*Svensk Kem. Tidskr.*, 1935, 47, 189).—Cozymase preps. heated for 1 hr. at 100° and p_H 3.5 almost completely lose their activity on apozymase in fermentation, but retain their activity as indicated by lactic acid formation in extract of rat's muscle.

F. O. H.

Liver-amylase: effect of nutrition and of hormones. F. H. SCHARLES, P. D. ROBB, and W. T. SALTER (*Amer. J. Physiol.*, 1935, 111, 130—137).—Liver-amylase in mice is determined by incubation of glycogen (I) with liver extract at 45° . Amylase activity after feeding varies widely. Insulin (II) depresses the activity of the amylase to the fasting val. Thyroxine (III) increases the activity in the fasting state, but feeding of thyrotoxic animals causes a temporary fall in activity. Adrenaline does not affect the activity. (II) and (III) both lower liver-(I). In general, amylase activity increases when liver-(I) varies, but remains low when this is steady.

R. N. C.

Adsorption of malt α -amylase on calcium phosphate. O. HOLMBERGH (*Arkiv Kemi, Min., Geol.*, 1935, 11, A, No. 20, 12 pp.).—Pptn. of impurities from a crude malt extract with $Ca(OAc)_2$ and successive amounts of EtOH (final concn. 45%) gives a solution containing nearly all the amylase activity of the extract, which retains its activity unchanged at 0° for 2 months. Further impurities are adsorbed by Al subacetate. The optimum conditions for adsorption of α -amylase on rice-starch are temp. 2° , p_H 5.3, and time of adsorption 1 hr. 4% tannin ppts. the majority of α - and β -amylase at p_H 5.7 from malt extract to which acetate has been added. $Ca_3(PO_4)_2$ as a selective adsorbent for α -amylase (*cf. A.*, 1933, 1330) is prepared as follows. A lukewarm solution of 32 g. of Na_2HPO_4 in 200 c.c. of H_2O is added slowly to 29 g. of $CaCl_2 \cdot 6H_2O$ in 200 c.c. of H_2O , 40 c.c. of 4N- NH_3 are added, and after 1 day the $Ca_3(PO_4)_2$ is centrifuged off and washed. The ppt. obtained by increasing the EtOH concn. in malt extract to 80% is redissolved in H_2O and treated with a suspension of $Ca_3(PO_4)_2$ (0.025 g. per c.c.) at p_H 5.7, when 73% of the α -amylase is adsorbed. The adsorbate is washed with 0.0005N- H_3PO_4 and eluted with dil. aq. NH_3 .

E. A. H. R.

Amylosynthase. II. Rice amylosynthase. T. MINAGAWA (*Bull. Agric. Chem. Soc. Japan*, 1935, 11, 62—65).—Polished and unpolished rice yield amylosynthase (I), which differs from that obtained from yeasts, and it can be pptd. by EtOH or $COMe_2$ from aq. solution as a highly active powder. A similar enzyme has been detected in corn, millet, potato, and seed of panic-grass.

J. N. A.

Salt activation. I. Influence of neutral salts on the enzymic hydrolysis of starch. K. V. GRI and J. G. SHRIKHANDE (*J. Indian Chem. Soc.*, 1935,

12, 273—286).—The effect of neutral salts (NaF, NaCl, Na₂SO₄, NaNO₃) on the hydrolysis of starch by sweet-potato amylase is dependent on the p_H of the medium and on the concn. of the salt. At p_H 6.0 the salts do not affect the activity of the enzyme. At $p_H > 6.0$ the reaction is retarded at high salt concn., whereas below 6.0 it is accelerated to an extent \propto the acidity of the system. The accelerating effect at p_H 4.0 decreases in the order NaF > NaCl > Na₂SO₄ > NaNO₃. O. J. W.

Secretion of diastase and invertase by *Empoasae solana*, De Long (*Rhynchota*, *Homoptera*, *Jassidae*). G. V. B. HERFORD (Ann. Appl. Biol., 1935, 22, 267—278).—Adults and nymphs eject diastase into the feeding medium. The insect also secretes an enzyme which inverts sucrose. A. G. P.

Water relations of enzymes. II. Water concentration required for invertase action. Z. I. KERTESZ (J. Amer. Chem. Soc., 1935, 57, 1277—1279).—Hydrolysis of sucrose (I) in a solid reaction mixture [(I) 75%; invertase (II) 1%; dry apple pomace 20%; phosphate buffer 4%] by (II) occurs in presence of 4.75—5% H₂O at 25°. No enzyme action occurs with smaller concns. of H₂O, but with >5% hydrolysis is faster and more regular. H. B.

Emulsin. XX. Effect of neutral salts on the activity of almond-emulsin. B. HELFERICH and E. SCHMITZ-HILLEBRECHT (Z. physiol. Chem., 1935, 234, 54—62; cf. this vol., 783).—The rate of hydrolysis of phenol- β -*D*-glucoside by the emulsin is not appreciably altered by cations, but anions, in accordance with their position in the lyotropic series, increase it, in some cases greatly (e.g., ClO₄' threefold). The concn. of substrate is immaterial, but increasing concn. of salt causes corresponding increase until a max. is reached. Thereafter the rate remains const. or decreases. No change occurs in the form of the hydrolysis curve, the reaction remaining unimol. The increase in rate also varies with the p_H , being greatest at the p_H optimum. Emulsin damaged by O₃ behaves like undamaged. The extent of increase varies with the substrate chosen, being sometimes very slight with substrates which are very rapidly hydrolysed. W. McC.

Fission of α -*l*-arabinosides by almond emulsin.—See this vol., 1110.

[Esterase model.] S. C. J. OLIVIER (Rec. trav. chim., 1935, 44, 599—600).—A reply to Langenbeck (this vol., 784). H. W.

Destruction of acetylcholine by various organs of the guinea-pig, frog, and snail. N. HALPERN and E. CORTEGGIANI (Compt. rend. Soc. Biol., 1935, 119, 1049—1052).—The blood and organs of the guinea-pig, frog, and snail all contain a thermolabile substance that destroys acetylcholine, the action being inhibited by eserine. R. N. C.

Correlation between the splitting of fats and their oxidation. E. FREUDENBERG (Klin. Woch., 1934, 13, 723—724).—The lipase-zymogen of human milk is activated (reversibly) by bile acids, and (irreversibly and to a smaller extent) by COMe₂ and naturally-occurring products of fat oxidation, e.g.,

β -hydroxybutyric acid, CH₃Ac-CO₂H. If milk-fat or triolein is oxidised by shaking, the products can activate the pro-enzyme (I): on the contrary, cod-liver oil after shaking damages (I). Shaking does not activate (I) directly. G. H. F.

Proteins of foods. IV. Digestibility by proteolytic enzyme from viscera of eel. T. TOMIYAMA (J. Biochem. Japan, 1935, 21, 367—369).—Protein from soya bean is more readily hydrolysed at p_H 7.3 and 37° than that from sardine or silk-worm pupae. F. O. H.

Proteolytic digestion in the ammocœte larva. E. J. W. BARRINGTON (Nature, 1935, 136, 145).—Extracts of certain parts of the intestine and of the skin of brook-lamprey larva show strong proteolytic activity of the tryptic type, optimum p_H approx. 8. The intestinal extract is stronger than that of the skin. The proteolytic digestion is similar to that of the *Ascidacea*. L. S. T.

Natural activators of papain. W. GRASSMANN (Biochem. Z., 1935, 279, 131—136).—Phytokinase in papain preps. does not owe its activity to glutathione, but to a peptide consisting largely of cystine (and/or cysteine) and glutamic acid (cf. A., 1931, 328, 393; this vol., 122). F. O. H.

Glutathione and autolysis. S. LANG (Z. physiol. Chem., 1935, 234, 127—130; cf. A., 1934, 925).—The livers of fasting dogs poisoned with P do not contain increased amounts of reduced glutathione (I). During autolysis (I) passes from the reduced into the oxidised form. It is improbable that reduced (I) is the activator the protease which causes autolysis. W. McC.

***Coli*-tryptophan-indole reaction. I. Enzyme preparations and their action on tryptophan and indole derivatives.** F. C. HAPPOLD and L. HOYLE (Biochem. J., 1935, 29, 1918—1926).—Preps. of certain strains of *B. coli* killed by CHCl₃ contain an enzyme ("tryptophanase"), active at p_H 5.0—10.0 (optimum 8.5), which converts tryptophan (I) into indole (cf. this vol., 663). The enzyme occurs in *B. coli* grown on (I)-free media, but to a far greater extent when the media have a high (I) content or, more especially, when (I) is the sole source of N. Tryptophanase does not produce indole from indolyl-propionic, -acrylic, or -pyruvic acid, indole-carboxylic acid or -3-aldehyde. F. O. H.

Enzymic histochemistry. XV. Micro-determination of arginase. K. LINDERSTRØM-LANG, L. WEIL, and H. HOLTER (Compt. rend. Trav. Lab. Carlsberg, 1935, 21, No. 2, 7—14).—In presence of COMe₂-EtOH in high concn., arginine (I) at p_H 9.5 behaves as a strong base, whereas ornithine and urea are scarcely ionised. The enzymic cleavage of (I) can therefore be followed by the increase in the amount of base (0.05*N*-NMe₄OH) used in titrating to a standard p_H . This method is more convenient and rapid than a modified urease method also described, except that it cannot be used in the presence of excess of urease. Both methods give comparable results. E. A. H. R.

Ultrafiltration of ureases of different origin through membranes of graduated permeability.

P. GRABAR and A. RIEGERT (Compt. rend. Soc. Biol., 1935, 119, 1004—1006).—Commercial urease (Squibb) contains particles of varying sizes; cryst. urease is more homogeneous. Soya and *Canavallia* ureases differ greatly in particle dimensions, although prepared by identical methods. All ureases are retained by membranes non-permeable to particles $>15 \mu$.

R. N. C.

Ultrafiltration of urease after partial digestion by activated trypsin. P. GRABAR and A. RIEGERT (Compt. rend. Soc. Biol., 1935, 119, 1006—1007).—The active material of a urease solution partly digested by trypsin is retained by a membrane with 15μ pores. Hence the activity of urease is associated with the cryst. globulin isolated by Sumner, the digestion products of which are inactive.

R. N. C.

Enzymic fission of yeast-nucleic acid. A. CONTARDI and C. RAVAZZONI (R. Ist. lombardo Sci. Lett. Rend., 1934, 67, 503—517; Chem. Zentr., 1935, i, 1075).—Hydrolysis of the acid cannot be followed by changes in α of the Na salt, since observations are complicated by mutarotation. An enzyme system occurring in aq. extracts of rice chaff consists of a phospho-diesterase (optimum p_H 4.0) and a monoesterase (p_H 5.5). All P in nucleic acid is converted into inorg. forms by this system. The diesterase is not identical with choline-phosphatase.

A. G. P.

Enzymic conversion of glyceraldehyde- into dihydroxyacetone-phosphoric acid. O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 279, 40—48).—Dialysed muscle extracts rapidly convert (indicated iodometrically) 50% (i.e., the biologically active optical isomeride) of *dl*-glyceraldehydephosphoric acid (I) into dihydroxyacetonephosphoric acid (II). This supports the theory of the reaction chain (I) (II) hexosediphosphoric acid.

F. O. H.

Alkaline phosphomonoesterase of the mammary gland. S. J. FOLLEY and H. D. KAY (Biochem. J., 1935, 29, 1837—1850).—The phosphatase (I) of guinea-pig mammary glands hydrolyses $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ (II) in glycine buffer at a rate dependent on p_H and (II) concn., being max. at p_H 10.0 and at a (II) concn. of $0.009M$. At low (II) concns. the behaviour of (I) follows the theory of Michaelis with $K_m = 0.0006$ at p_H 10.0, whilst at higher concns. the data are in agreement with the theory put forward by Haldane to explain inhibition by high substrate concns. (I) is unstable in alkaline solution, has a marked stability max. at p_H 7.0, is activated by small concns. of Mg^{++} , and is able to synthesise glycerophosphate from glycerol and inorg. PO_4^{---} . Its properties agree closely with those of kidney-phosphatase, with which it is probably identical. W. O. K.

Phosphatase of the long bones during growth in the rat. J. ROCHE and A. LEANDRI (Compt. rend. Soc. Biol., 1935, 119, 1141—1144).—Phosphatase (I) increases rapidly in all parts of the bone in the initial period of development, but falls steadily after the animals have reached 80 g. wt. In the adult rat, (I) is α bone-protein. The diaphysis shows an exceptionally high (I) content. R. N. C.

Phosphatase of the red corpuscles. J. ROCHE and M. LATREILLE (Compt. rend. Soc. Biol., 1935, 119, 1144—1147).—The crude phosphatase of the red corpuscles shows a preferential action on α -glycerophosphates at an optimum p_H of 6.5. It can be adsorbed on kaolin at p_H 6.0 and eluted with $0.05N$ - NH_3 ; the purified product, however, shows a preferential action on β -glycerophosphates at an optimum p_H of 8—9, similar to the other animal phosphatases. The corpuscles contain a mixture of sp. α - and β -glycerophosphatases, and kaolin preferentially adsorbs the β -enzyme. R. N. C.

Urine- and blood-phosphatase. A. DMOCHOWSKI and D. ASSENHAJIM (Naturwiss., 1935, 23, 501).—Human urine contains a phosphatase (I) with an optimum activity at p_H 5.4—5.6 which is strongly inhibited by KCN, Cu^{++} , and NaF, more weakly by cysteine, and very slightly by phloridzin. Mg salts have no activating effect. It is partly inhibited by conc. urine, but with diluted or dialysed urine the inhibition is less marked. Urinary (I) is probably not derived from blood-(I), but from the kidney cells.

W. O. K.

Development of enzymes in malt. H. LUERS (Woch. Brau., 1935, 52, 249—254).—A lecture.

E. A. H. R.

Synthesis of reserve carbohydrate by yeast. I. **Synthesis from glucose and maltose and influence of phosphate thereon.** R. A. MCANALLY and I. S. MACLEAN (Biochem. J., 1935, 29, 1872—1876).—Yeast, incubated at 25° for 2 days, is examined for total carbohydrate, glycogen (I), insol. carbohydrate (II), and yeast-gum (III). With glucose or maltose media addition of HPO_4^{--} causes increased formation of (I), (II), and (III). The (I) produced on a maltose medium is much $>$ that on a glucose medium.

H. D.

Yeasts capable of fermenting trioses. C. NEUBERG and E. HOFMANN (Naturwiss., 1935, 23, 484—486).—Three varieties of yeast, *Schizosaccharomyces Pombe*, *Hansenula (Willia) javanica*, and *Willia anomala* (Hansen), fermented dihydroxyacetone (50—80%) and glyceraldehyde ($\approx 33\%$) with the formation of EtOH and CO_2 .

W. O. K.

Velocity of fermentation of sugar by zymase and the origin of the first fermentation equation of Harden and Young. O. MEYERHOF and W. KIESSLING (Naturwiss., 1935, 23, 501—502).—Phosphopyruvic acid (I) is fermented to CO_2 and MeCHO $\frac{1}{2}$ — $\frac{1}{10}$ as rapidly as is glucose (II), but addition of (II) to the yeast extract with NaF, which inhibits the fermentation of (II), results in an increase of the fermentation rate of (I) up to 10 times the original. The phosphate of (I) with an equal amount of inorg. phosphate combines in ester formation with (II), half appearing as hexose diphosphate (III) and half as phosphoglyceric acid (IV), whilst EtOH and not MeCHO is formed: $2(\text{II}) + 2(\text{I}) + 2\text{H}_3\text{PO}_4 \rightarrow (\text{III}) + 2(\text{IV}) + 2\text{CO}_2 + 2\text{EtOH}$. When the system is poisoned with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ instead of NaF the velocity of fermentation of (I) remains high, showing that the reaction limiting the velocity is not the oxidation of (IV) but the phosphorylation of hexose: $(\text{II}) + 2(\text{I}) \rightarrow (\text{III}) + 2\text{CO}_2 + 2\text{MeCHO}$. [NaF inhibits con-

version of α -(IV) into (I) and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ inhibits oxidation of triosephosphoric acid to (IV).] When various sugars are employed as PO_4''' acceptors in the fermentation of (I) the velocities correspond with the known velocities of fermentation of these sugars. The latter are therefore conditioned by their velocities of esterification. In yeast fermentation MeCHO is not reduced by the stable (III) esters but by an unstable ester formed from (II) in presence of (III). In the yeast extracts the reduction of MeCHO is sufficiently slow to allow a quantity of the (III) esters to assume the stable form instead of being oxidised to (IV). Extra (II) must then be esterified. W. O. K.

Fat and lipin metabolism of yeast. IV. Accumulation of sterols and fat in bottom yeast. M. SOBOTKA, W. HALDEN, and F. BILGER (*Z. physiol. Chem.*, 1935, 234, 1—20; cf. A., 1934, 1035).—It is the removal of H_2O which initiates and controls the increase in production of lipins and sterols, the predominating cause being the treatment of the yeast with EtOH vapour in a moderate supply of air. Better yields are obtained when the medium contains glucose than when no nutrient matter is present, apparently because of the action of the EtOH produced during the consequent fermentation. The yield of lipin is related to the dry wt. of the yeast, the yield of sterol, and the duration of the process, but not to the total N content of the yeast, which decreases owing to autolysis and removal of H_2O , loss of N beginning when the H_2O content has fallen to 73% of its initial val. The accumulation of lipin does not interfere with N equilibrium. W. McC.

Oligodynamic action of oxygen on the multiplication of yeast-cells. W. LIBBRECHT and L. MASSART (*Compt. rend. Soc. Biol.*, 1935, 119, 1193—1194).—The development of yeast-cells is accelerated by an O_2 pressure of 10^{-6} atm. R. N. C.

Phytochemical reduction of anthradiquinone. A. VERCELLONE (*Biochem. Z.*, 1935, 279, 137—139).—Yeast-sugar mixtures convert 1:4:9:10-anthradiquinone into quinizarin to an extent of approx. 80% when fermenting and approx. 30% when fermentation is inhibited by heating at 90° for 10 min. F. O. H.

Phytochemical reduction of *dl*-lactaldehyde. C. NEUBERG and A. VERCELLONE (*Biochem. Z.*, 1935, 279, 140—144).—*dl*-Lactaldehyde added to fermenting sucrose-yeast mixtures is converted into $\alpha\beta$ -propylene glycol, $[\alpha]_D +5.53^\circ$. F. O. H.

Action of ethylene on cell processes. F. H. SHAW (*Austral. J. Exp. Biol.*, 1935, 13, 95—102).— C_2H_4 increases the rates of fermentation and inversion by living yeast but not by dead yeast or cell-free enzyme preps. The stimulating action of C_2H_4 is due to increased production of enzyme and not to changes in cell permeability (cf. A., 1929, 1200; 1931, 468). F. O. H.

Activation of enzymic reactions. I. H. VON EULER and T. SVENSSON (*Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 47, 6 pp.).—If dried brewer's yeast be mixed with fructose and KH_2PO_4 within 6—7 hr. the greater part of the free PO_4''' is consumed (phosphatase action), after which the free PO_4''' again

increases up to nearly its original concn. (phosphatase action). The latter is accelerated by ascorbic acid and inhibited by Cu^{++} and cysteine. When $[\text{Cu}^{++}]$ is $> 10^{-3}N$ phosphatase and phosphatase action cannot be separated; both are strongly inhibited. The latter is accelerated by vitamin-D. E. A. H. R.

Oxidation-reduction potential of yeast suspensions. C. FROMAGEOT and P. DESNUELLE (*Biochem. Z.*, 1935, 279, 34—39).—Fermenting top yeast in buffered anaerobic suspension at p_H 6.4 or in unbuffered suspension at p_H 6.4—4.5 has $r_H=6.6$ —8.0. The significance of this val. is discussed with reference to the formation of lactic acid from AcCO_2H and to the non-formation of alanine from lactate and added NH_3 . F. O. H.

Changes in the flavin content of yeast. L. B. PÉTT (*Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 53, 6 pp.).—Yeast grown in a medium containing inorg. salts, glucose, and a trace of marmite develops flavin (I). A certain amount of PO_4''' ($> 4g.$ per litre) must be present for normal (I) development. CN^- produces a (I) content much $>$ normal. During autolysis very little (I) disappeared. Impoverishment of yeast-glycogen reserves by shaking with O_2 leads to a rapid reduction of the (I) content. E. A. H. R.

Changes in the concentration of cozymase, Z-factor, and flavin during the germination of peas. A. W. H. VAN HERK (*Arkiv Kemi, Min., Geol.*, 1935, 11, A, No. 22, 11 pp.).—The cozymase content of germinating peas is initially large and remains so for 4 days, but after 7 days it has fallen to $1/5$ — $1/6$ of its original val. The Z-factor remains const. for the first 2 days and then decreases, reaching a min. after 4 days, after which it again increases, reaching $1\frac{1}{2}$ times its original concn. in 2 weeks. The flavin (I) content remains const. for 2 days and then increases to 3 times its original val. In the etiolated plant (I) synthesis ceases after 12 days but increases again on exposure to light. A temporarily higher (I) content of the etiolated plant may be due to (I) destruction by light in the green plant. E. A. H. R.

Temperature stability and formation of cozymase. H. VON EULER and G. GUNTHER (*Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 50, 6 pp.).—Cozymase (I) preps. from yeast, horse-muscle, and peas vary considerably in thermostability. The (I) activity of rat-muscle is not appreciably increased by creatine feeding, nor is it affected by A-avitaminosis or -hypervitaminosis. E. A. H. R.

Distribution of growth-promoting factor (bios) in normal animal tissues and tumours. C. DITTMAR (*Biochem. Z.*, 1935, 279, 99—105).—Growth-promoting action on yeast in Reader's solution indicates that tissues contain the factor in relatively approx. const. amounts for the same species, the contents giving the series: kidney $>$ adrenal $>$ liver $>$ spleen, muscle, etc. $>$ blood. The content of any tissue (excepting blood) is independent of the animal's age and of the type of nutrition. Tumour implants have a content=that of kidney. Large necrosing growths have a very high content, indicating a relation between growth and content of growth factor. F. O. H.

Culture and physiology of marine dinoflagellates. H. A. BARKER (Arch. Mikrobiol., 1935, 6, 157—181).—Dinoflagellates examined are characterised by an adaptation to very poorly nutritive media. The P and N requirements are low. Org. compounds cannot be utilised to replace or supplement autotrophic nutrition. With 0.1 p.p.m. of N, max. rate of division occurs. A. G. P.

Nitrogen and carbon nutrition of *Polytomella agilis*. A. LWOFF (Compt. rend. Soc. Biol., 1935, 119, 974—976).—*P. agilis* grows very feebly with asparagine as the only N source, but readily in peptone at p_H 4.5—8.4. It can utilise as C source AcOH, propionic, *n*- or *iso*-butyric, *n*-valeric, or *n*-hexoic acid, or starch. R. N. C.

Photosynthesis in diatoms. H. A. BARKER (Arch. Mikrobiol., 1935, 6, 141—156).—Photosynthesis in *Nitzschia closterium* and *N. palea* is essentially similar to that in green plants. A. G. P.

Method for the study of crystals found in amoeba by means of X-rays. C. FOWLER (Science, 1935, 82, 45). L. S. T.

Cultivation of a sterile amoeba on media without solid food. K. REICH (J. Exp. Zool., 1934, 69, 497—500).—The culture of *Mayorella palestinensis* is examined. N is obtained from complex substances which cannot be replaced by NH_2 -acids. Sugars (glucose, fructose, sucrose, or lactose) are essential for good growth. The O_2 requirement is small. The organism develops at 12—27° (optimum p_H 6.8) and liquefies gelatin. CH. ABS. (p)

Decomposition of formic to oxalic and carbonic acids by various moulds. T. CHRZĄSZCZ and M. ZAKOMORNY (Biochem. Z., 1935, 279, 64—75).—Various moulds develop normally in media containing 2.5% of formate, which is decomposed with formation of $H_2C_2O_4$ and CO_2 to an extent varying with the species of mould; this is an alternative route to direct decomp. to CO_2 and H_2O (cf. A., 1934, 536, 982; this vol., 406). F. O. H.

Lactic acid formation by a fungus of the *Rhizopus* species. E. KANEL (Microbiol. [U.S.S.R.], 1934, 3, 259—265).—The organism, related to *R. japonicus*, produced a 40% yield of lactic acid on a medium containing 10% of sugar and 4% of chalk. CH. ABS. (p)

Starch formation in moulds. T. HIDA (J. Shanghai Sci. Inst., 1934, [iv], 1, 85—116).—Of 22 varieties of *Aspergillus* investigated, only 9 produced starch (I), acid also being generally developed. The most convenient variety is *A. niger*. (I) formation takes place only in strongly acid culture media; with *A. niger* the p_H must be < 2.2 for (I) to accumulate, but the optimum conditions for (I) formation are not those for the growth of *A. niger*. The accumulation of (I) in acid cultures is probably due to an inhibition of a diastatic factor rather than to a greater rate of (I) synthesis in acid solution. O_2 is essential for (I) formation and poisons which inhibit the respiration and rate of growth also inhibit (I) formation to the same extent. The best yields of (I) are obtained with a culture medium in which the source of C is glucose or sucrose. More carbohydrate is consumed during the

growth of *A. niger* than can be accounted for by the formation of (I) and other polysaccharides.

E. A. H. R.

Formation of fatty acids from glucose by *Aspergillus niger*. C. F. SCHMIDT, jun. (J. Biol. Chem., 1935, 110, 511—520).—A strain of *A. niger* in a glucose medium synthesised fatty acids under conditions in which further growth could not take place. The fatty acid content of the mycelium increased approx. 100% during 3 days. This increase is independent of p_H between 2.4 and 8.2. There is no relationship between p_H and degree of unsaturation of the acids. Formation of fatty acids takes place under aerobic and, to a smaller degree, under anaerobic conditions. J. N. A.

Sulphopeptidase of moulds. I. *Aspergillus niger*. II. Separation of sulphopeptidase from protease. III. Comparison of animal and plant sulphopeptidase. IV. Presence of sulphopeptidase in various species of moulds. H. OTANI (Acta Schol. Med. Univ. Kyoto, 1934, 17, 242—248, 249—259, 260—268, 269—287).—I. 2-Naphthalenesulphonylglycylglycine (I) was hydrolysed by a glycerol extract of mycelium of *A. niger*. Optimum p_H was 7.1—7.3. Naphthalenesulphonylglycine (II) is an end-product.

II. Sulphopeptidase (III) and erepsin were adsorbed at p_H 4 by animal C, kieselguhr, kaolin, and Al_2O_3 , and at p_H 5 by Al_2O_3 only. The two enzymes could not be separated. Protease was pptd. by acidification to p_H 5.

III. Heating at 70° destroyed (III) in 1 hr. Glycine inhibited the action of (III) from *A. niger*, whilst (II) and leucine were most effective against the (III) from pigs.

IV. Nine species of fungi hydrolysed (I) and *o*-toluene- and benzene-sulphonylglycine but not (II).

CH. ABS. (p)

Formation of hydroxylamine in cultures of *Aspergillus niger* in a medium containing ammonium nitrate. M. LEMOIGNE and R. DESVEAUX (Compt. rend., 1935, 201, 239—241).—Comparison of cultures of *A. niger* in an ordinary Czapek medium and also with 16 times the usual amount of NH_4NO_3 shows that in the latter case there is definite formation of NH_2OH with retardation of growth after 120—144 hr. F. R. G.

Nutritional requirements of *Aspergillus niger*. R. A. STEINBERG (Bull. Torrey Bot. Club, 1935, 62, 81—90).—Fe, Zn, Cu, and Mn are essential for normal growth and sporulation. CH. ABS. (p)

Gluconic fermentation. XI. Influence of iron on the gluconic fermentation of *Penicillium crustaceum* (L.), Fries. A. ANGELETTI and D. PONTE (Annali Chim. Appl., 1935, 25, 217—221).—Increasing small amounts of Fe (as $FeCl_3$) cause increasing retardation of the formation of gluconic acid from sucrose by *P. crustaceum* (cf. A., 1934, 1405).

T. H. P.

Utilisation of growth factors by micro-organisms. Biological synthesis of growth factors. W. H. SCHOPFER (Arch. Mikrobiol., 1935, 6, 196—207).—Vitamin- B_1 is absorbed by fungi from nutrient medium, which gradually loses its ability to activate

other media. Extracts of *Phycomyces* grown on an active medium can activate other media. This property is manifest as soon as a trace of $-B_1$ is added to the original culture. *Phycomyces* probably synthesises another growth factor in proportion to the supply of $-B_1$. Active extracts of *Phycomyces*, active cultures of *Mucorineæ*, and both, can activate *Sacc. cerevisiae*. A. G. P.

Chitinovorous bacteria. A. G. BENTON (J. Bact., 1935, 29, 449—465).—Numerous organisms are described and some biochemical reactions are recorded. A. G. P.

***Bacillus cellulose dissolvens* and thermophilic fermentation of cellulose.** Y. KHOUVINE and K. SOETERS (Compt. rend. Soc. Biol., 1935, 119, 1036—1037).—Certain strains grow only at 50—55°, and are responsible for the destruction of cellulose (I) in heaps of vegetable debris where the internal temp. has been raised by fermentation. The yellow pigment produced from (I) fermentation is not a carotenoid. R. N. C.

Products of the fermentation of glucose and arabinose by butyric acid anaerobes. A. F. LANGLYKKE, W. H. PETERSON, and E. MCCOY (J. Bact., 1935, 29, 333—347).—In yeast- H_2O media and with many strains of organisms, low yields of neutral products are associated with high final acidity in the cultures. The yield of BuOH is lowered when Pr^oOH replaces $COMe_2$ in the products. The formation of EtOH during fermentation proceeds more easily than that of BuOH or $COMe_2$. Fermentation of arabinose by nearly all cultures was poor. Acid production was high and yields of neutral substances relatively low. A. G. P.

Carbonic acid assimilation by red sulphur bacteria. II. H. GAFFRON (Biochem. Z., 1935, 279, 1—33; cf. A., 1934, 698).—Addition of NaSH to cultures of *Thiocystis* produces storage of S with concomitant loss of colour; lactate has the same effect, marked changes occurring in cell metabolism. The evolution of CO_2 by pure strains in $NaHCO_3$ -media in the dark is increased by addition of $SO_4^{''}$, butyrate, malate, pyruvate, or lactate; in the light assimilation of CO_2 occurs. With S-loaded cells, a marked evolution of CO_2 occurs in the light, probably due to storage of org. assimilation products coincidental with that of S. Formation of H_2S in the dark occurs at the expense of reserve material in the cell and is not sensitive to PhMe (A., 1934, 453) (which increases CO_2 formation). CO_2 is not assimilated by cultures in CO_2+H_2 in the dark; exposure to light increases absorption of H_2 and initiates that of CO_2 . The action of CO, HCN, and thymol was also investigated. The bearing of the data on the metabolism of S bacteria is discussed and the results of Roelofsen (this vol., 406) are criticised. F. O. H.

Nitrifying bacteria. T. Y. K. BOLTJES (Arch. Mikrobiol., 1935, 6, 79—138).—Winogradsky's medium prepared from pure substances is unsatisfactory for the growth of nitrifying bacteria owing to deficiency of Ca. The use of cooking-salt in place of pure NaCl brings improvement and substitution of tap- H_2O for distilled H_2O permits optimum growth. The

injurious effects of peptone on the organism are due to certain NH_2 -acids present therein. A. G. P.

Nitrogen-assimilating bacteria. II. **Fixation of atmospheric nitrogen by *Azotobacter*.** G. ENDRES (Annalen, 1935, 518, 109—126).—The fixation of N_2 in the form $>C:N\cdot OH$ by *Azotobacter* is proved by the following data. Oxidation of the culture solution, after removal of the bacteria by centrifuging, with I affords HNO_2 . Under similar conditions only solutions containing free NH_2OH or oximes (of $AcCO_2H$), but not solutions containing N_2H_4 , NH_3 , or alanine, afford HNO_2 . As the O_2 consumption and wt. increase Q_{O_2} decreases and approx. 10% of the total fixed N_2 occurs as $>C:N\cdot OH$, but increase of the latter with growth varies with different substrates. The concentrate (1:40) of the culture solution (method described) contains no NH_3 , HNO_2 , or NH_2OH , but affords NH_2OH ($1-3 \times 10^{-4}$ mol. per litre) after hydrolysis. Addition of NH_2OH in amounts $>2 \times 10^{-6}$ mol. has a growth-inhibiting effect on *Azotobacter*, which is greater the greater is $[NH_2OH]$; the effect begins at approx. the same concn. as that of HCN but increases more slowly with increasing concn. Oximes have a similar but smaller effect. In presence of NH_2OH growth of *Azotobacter* occurs only in presence of NH_4^+ : when $[NH_2OH]=10^{-5}$ mol. per litre, growth occurs only at the expense of NH_4^+ , but at 10^{-4} mol. per litre NH_3 assimilation is also inhibited. In the absence of N_2 (80% $A-20\% O_2$) neither growth nor oxime formation occurs; hence the latter is definitely associated with N_2 fixation. J. W. B.

Influence of ultra-violet rays on the physiological activities of *Azotobacter*. II. **Stimulation of *A. chroococcum* by ultra-violet rays.** A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1935, 6, 561—573).—The greatest no. of bacteria was found after 1 min. exposure to the Hg arc lamp; longer exposure caused increased acidity of the medium and a diminution in the no. of bacteria. The conductivity, $[H^+]$, and osmotic pressure were affected $>$ viscosity and surface tension, but these phenomena had little influence on bacterial growth. P. G. M.

Pantothenic acid and the nodule bacteria-legume symbiosis. C. H. MCBURNEY, W. B. BOLLEN, and R. J. WILLIAMS (Proc. Nat. Acad. Sci., 1935, 21, 301—304).—Pantothenic acid is one of the substances which passes from bacteria to host in symbiosis and effects the growth of plants. It is not alone responsible for N fixation but is an important factor in the carbohydrate anabolism. H. T.

Effect of temperature on bacterial ammonification of urea. S. P. TANDON (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 169—172).—Formation of NH_3 from urea by bacteria of tropical soils is optimum at approx. 40° and does not occur at temp. $> 50-55^\circ$. Hence ammonification in these soils cannot be of bacterial origin during summer. F. O. H.

Synergic gas production by bacteria. N. ATKINSON (Austral. J. Exp. Biol., 1935, 13, 67—73).—Symbiotic gas (H_2+CO_2) formation (A., 1928, 797) from xylose or mannitol occurs with *B. Morgani* and

B. typhosus especially in presence of CaCO_3 . Old cultures of *B. typhosus* contain a stable intermediate substance which liberates gas in presence of *B. Morgani*. A similar phenomenon occurs with gas production from lactose by *B. Morgani* and a hæmolytic or non-hæmolytic streptococcus. The possibility of HCO_2H being the precursor of the gas is discussed.

F. O. H.

Vitality of the typhoid bacillus in butter as a function of the acidity. J. BRISOU (Compt. rend. Soc. Biol., 1935, 119, 1221—1222).—The bacillus can grow in fresh or rancid butter containing $\geq 1\%$ of PrCO_2H . In peptone broth or peptone- H_2O it is destroyed by $p_{\text{H}} < 6.0$, and in H_2O by $p_{\text{H}} 4.0$. The increased resistance in butter is due to the buffers present.

R. N. C.

Cultural requirements of bacteria. V. Diphtheria bacillus. J. H. MUELLER (J. Bact., 1935, 29, 515—530).—The utilisation of certain energy sources and NH_2 -acids by a certain strain of the organism is examined.

A. G. P.

Diphtheria formol toxoid and the Moloney test. R. SWYER (Lancet, 1935, 229, 22).—The test is not an accurate index of the reactions to be expected in adults after the injection of formol toxoid.

L. S. T.

Existence of "complete" and "residual" antigens in various bacteria. A. BOIVIN and L. MESROBEANU (Compt. rend., 1935, 201, 168—170).—Extraction of capsulated bacteria (*Pneumococcus* type II) with $\text{CCl}_3\cdot\text{CO}_2\text{H}$ yields a sp. polysaccharide but no "complete" antigen. Digestion of the bacillus with trypsin prior to the extraction indicates that the complex is probably present in a very labile state.

H. G. R.

Immunising substances in *Pneumococci*. II. Separation of the organism into acid-soluble and -insoluble fractions. L. D. FELTON (J. Immunol., 1934, 27, 379—393).—Organisms of types I and II retain their antigenicity after drying with COMe_2 and desiccation in vac. The immunising agent occurs in the acid-sol. fraction of the cells, is pptd. (90%) by EtOH or COMe_2 , and is largely sp. A small amount of immunising substance occurring in the acid-insol. fraction produces heterologous immunity in mice.

CH. ABS. (p)

Chemo-immunological studies on the soluble specific substance of *Pneumococcus*. II. Chemical basis for immunological relationship between capsular polysaccharides of types III and VIII *Pneumococcus*. W. F. GOEBEL (J. Biol. Chem., 1935, 110, 391—398).—The constitution of the sp. polysaccharide (I) of *Pneumococcus* VIII is examined in relation to its immunological cross-reaction with type III. (I), prepared by an earlier method (A., 1931, 267), gives glucose and an aldobionic acid of which the *hepta-acetate*, m.p. $249-250^\circ$, $[\alpha]_{\text{D}}^{25} +40.0^\circ$ in CHCl_3 , of the Me ester gives no depression of m.p. with that of the (I) obtained from type VIII.

H. D.

Antigenic structure of *Vibrio cholerae*. VII. Two acid-soluble protein fractions. R. W. LINTON and B. N. MITRA (Indian J. Med. Res., 1934, 22, 295—308; cf. this vol., 787).—Two acid-sol.

protein substances, A and B, were extracted from a no. of vibrios. A was extracted by $0.025N\text{-HCl-EtOH}$; amide-N was double, and humin-N half, that of the total protein. A occurred in the pseudo- and eu-globulin fractions of the protein, and appeared to increase when the whole protein was kept in H_2O at 10° for 2 weeks; it was destroyed by attempted extraction with $0.125N\text{-HCl}$. B was extracted after the removal of A by boiling in 75% EtOH , dilution with 0.9% NaCl , and making $0.05N$ with HCl . B was present in greater amount in the euglobulin fraction, and did not increase in H_2O at 10° . Neither fraction showed any dependence on the strain of the vibrio. B was chemically similar to the residual protein and the whole protein.

R. N. C.

Structure of cholera and cholera-like vibrios. R. W. LINTON, D. L. SHRIVASTAVA, and B. N. MITRA (Indian J. Med. Res., 1934, 22, 309—312; cf. this vol., 786).—Elementary analytical figures are given for a no. of vibrios. The polysaccharide of *Vibrio* W880 contains arabinose (I) and an aldobionic acid complex of galactose (II) and glycuronic acid. In cholera vibrios (I) is replaced by (II).

R. N. C.

Scarlet fever. II. Toxins produced by hæmolytic streptococci of scarlatinal origin. S. B. HOOKER and E. M. FOLLENSBY (J. Immunol., 1934, 27, 177—193).—Two toxins are demonstrated. These may be distinguished by immunological and chemical criteria. A single toxigenic strain of organisms may produce either toxin, both, or neither.

CH. ABS. (p)

Respiratory mechanism of the *Streptococci*. M. A. FARREL (J. Bact., 1935, 29, 411—435).—*Streptococci* contain no catalase, but a heat-stable peroxidase (differing from plant-peroxidase) is intimately associated with the dehydrase mechanism of the cell. Cytochrome and indophenol-oxidase could not be detected in the organism. The ability of *Streptococci* to activate a large no. of org. substances is examined.

A. G. P.

Formation of precipitin for the group A specific carbohydrate of *Streptococcus hæmolyticus* in rabbits injected intravenously and subcutaneously. D. SEEGAL, M. HEIDELBERGER, and E. L. JOST (J. Immunol., 1934, 27, 211—214).—Rabbits injected intravenously with heat-killed *S. hæmolyticus* rapidly developed precipitin for the bacterial nucleoprotein (I) and the group A-sp. carbohydrate (II). Subcutaneous injection produced the precipitin for (I) in all cases, but that for (II) was less often obtained. Animals failing to produce the (II) precipitin after subcutaneous injection developed the antibody after intravenous injection.

CH. ABS. (p)

Amino-acids and *Staphylococcus* toxin. O. GENGOU (Ann. Inst. Pasteur, 1935, 55, 129—147).—*Staphylococcus* in culture media containing peptone utilises the protein of the medium in the development of its toxin. The toxin is still produced when certain NH_2 -acids replace the peptone, but only with arginine (I) is the development of the toxin immediate. The toxin produced in a medium containing (I) is identical with that formed in a bouillon-peptone medium.

E. A. H. R.

Crystal-violet-agar as a differential medium for *Staphylococci*. G. H. CHAPMAN and C. BERENS (J. Bact., 1935, 29, 437—448).—The colour of the growths on this medium differentiates the organisms with the same order of accuracy as the hæmolytic and coagulase tests and animal inoculations.

A. G. P.

Plurality of antigens of *Clostridium welchii*. A. SORDELLI and J. FERRARI (Folia biol., 1931, 10—12).—Extracts of high fixative val. are obtained from suspensions of *C. welchii* at p_H 7.0. The antigen is not destroyed by boiling at p_H 8.6. Addition of 10% Na_2SO_4 to the boiling antigen causes pptn. Antigenic activity is destroyed by EtOH or CO_2Me_2 . Differentiation between fixation antigen and precipitinogen is described.

CH. ABS. (p)

Prozone phenomenon in specific bacterial agglutination. F. S. JONES and M. ORCUTT (J. Immunol., 1934, 27, 215—233).—When suitable proportions of agglutination-inhibitory sera [sp. to *Br. abortus*] are added to a strong *Br. abortus* agglutinin, agglutination is inhibited or a prozone developed. Failure to agglutinate is attributed to the deposition on the surface of the globulin film of a substance which interferes with the cohesive properties of specifically sensitised organisms.

CH. ABS. (p)

Factors influencing the rate of thermal destruction of the tetanus antitoxin of antitetanic horse plasma at 60—66°. T. D. GERLOUGH and W. WHITE (J. Immunol., 1934, 27, 367—377).—Destruction of the antitoxin is accelerated by addition of neutral salts, up to a max. corresponding with an ionic concn. of 0.6—0.9. Further additions decrease the effect. The p_H of max. stability is at or near neutrality. The rate of destruction is markedly increased by PhOH, the increase being $\propto [PhOH]^2$.

CH. ABS. (p)

Comparative value of fresh and aged tetanus toxoid as an immunising agent. H. L. WILCOX (J. Immunol., 1934, 27, 195—198).—Fresh toxoid has approx. 50% higher antigenic val. than that stored for 3 years.

CH. ABS. (p)

Decomposition of organic matter in sea-water by bacteria. I. Bacterial multiplication in stored sea-water. II. Influence of addition of organic substances on bacterial activities. S. A. WAKSMAN and C. L. CAREY (J. Bact., 1935, 29, 531—543, 545—561).—I. The $[O_2]$ of the H_2O has an important influence on bacterial activities. With a reduced $[O_2]$ org. matter is attacked with considerable difficulty. A close parallelism exists between bacterial multiplication, O_2 consumption, and the liberation of N in an available form. Sea- H_2O contains sufficient dissolved org. matter to support an extensive bacterial population.

II. The bacterial population developing in sea- H_2O varies with the nature and quantity of org. matter present. The decomp. of N-free org. matter, e.g., glucose (I), added to the H_2O is controlled by the amount of available N. The latter may be determined directly (as NH_3) or indirectly by the amount of (I) decomposed.

A. G. P.

***Escherichia-Aerobacter* intermediates. I. Cultural characteristics.** R. P. TITSLER and L. A.

SANDHOLZER (J. Bact., 1935, 29, 349—361).—The heterogeneity of this group of organisms is demonstrated by the varied ability of different members to ferment carbohydrates, notably cellobiose and α -methylglucoside, and other materials. A system of classification is described.

A. G. P.

Fermentation of α -methylglucoside by bacteria. R. P. TITSLER and L. A. SANDHOLZER (J. Bact., 1935, 29, 363—368).—Relatively few species characterise the glucoside. The use of this substance in characterising certain species of the *Escherichia-Aerobacter* group is considered (see preceding abstract).

A. G. P.

Specificity of hexosidases. Comparison of activity of *E. coli* and *E. communior*. M. HOTCHKISS (J. Bact., 1935, 29, 391—398).—All preps. of *E. coli* contained maltase but not invertase. In a no. of cultures of *E. communior*, either or both enzymes appeared.

A. G. P.

Growth of *B. coli* on alanine. E. AUBEL and K. SOETERS (Compt. rend. Soc. Biol., 1935, 119, 1035—1036).—*B. coli* grown in a medium containing alanine decolorises methylene-blue, Nile-blue, or cresyl-violet, the last also being decolorised in a medium containing $AcCO_2H$.

R. N. C.

Lipoid hapten of aqueous extracts of living tubercle bacilli. G. SANDOR and C. NINNI (Ann. Inst. Pasteur, 1935, 55, 38—45).—Aq. extracts of tubercle bacilli yield a lipid hapten sol. in EtOH and then insol. in H_2O which is responsible for its power of absorbing complement in presence of antiserum. Its presence in the aq. extract is apparently due to its forming loose combinations with the proteins and allied substances.

W. O. K.

Residual antigens of *B. tuberculosis*. G. SANDOR and W. SCHAEFER (Ann. Inst. Pasteur, 1935, 55, 163—174).—Polysaccharides (I) and proteins pptd. from filtrates of *B. tuberculosis* cultures by $(NH_4)_2SO_4$ have the same antigenic effect on anti-BCG horse-serum. A very active hapten-like fraction is obtained by fractional pptn. of (I) with MeOH. This fraction has a very variable chemical constitution and the hapten-like substance can be present only in very small concn.

E. A. H. R.

Chemistry of tubercle bacilli. Presence in the "smooth" variety of a precipitation hapten that does not exist in the "rough" variety. M. A. MACHEBOEUF and J. DIERYCK (Compt. rend. Soc. Biol., 1935, 119, 917—919).—EtOH extracts of "smooth" tubercle bacilli, shaken, after removal of EtOH, with H_2O and Et_2O , give a three-phase mixture, a thick opaque emulsion-like layer appearing between the H_2O and Et_2O phases; extracts of the "rough" bacilli do not give this substance. The emulsion is purified by repeated pptn. from tepid EtOH solution with H_2O (the last pptn. at 0°), followed by pptn. with Et_2O . The ppt. contains no P or N, and is hydrolysed by acid or alkali into an Et_2O -sol. fraction containing sp. fatty acids, and a H_2O -sol. fraction, which is not a reducing sugar. It is pptd. by "anti-smooth," but not by "anti-rough," sera. It does not fix alexin, and is hence a pptn. hapten.

R. N. C.

Development of precipitins for protein, lipin, and carbohydrate fractions of *S* and *R* forms of tubercle bacilli. C. E. RICE (J. Immunol., 1935, 28, 19—30).—Precipitin tests show small differences in the proteins (I) and carbohydrates (II) of *S* and *R* types. Lipin fractions show no type-specificity. During immunisation with killed *S* bacilli there is an increase in precipitins for (I) and (II) from *S* organisms over that of precipitins for (I) and (II) of *R* forms. *S*-antisera reacted more strongly with purified globulin and polysaccharide preps. from virulent cultures of human types than did *R*-antisera. The latter were the more reactive toward purified albumin.

CH. ABS. (p)

Properties of the tuberculin extracted from bacilli by serum and organic liquors. A. BOQUET and R. LAPORTE (Compt. rend. Soc. Biol., 1935, 119, 1038—1040).

R. N. C.

Action of dilute heavy water on tubercle bacilli. M. ITOH, K. INOSHITA, and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 260).—The growth of tubercle bacilli of types *bobinus* and *Kamike* in Long's medium is increased both by decrease of $[H^+]$ from p_H 5.83 to 7.25 and by increase of D_2O from 0.08% to 2.24% [D].

F. R. G.

Metabolism of residual nitrogen and curves of elimination of glycine in rabbits inoculated with BCG. F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, 119, 964—966).—The metabolism of residual N is scarcely affected by injection of BCG. The elimination curves of residual N after injection of glycine are slightly disturbed, becoming normal again 4 weeks after the BCG-inoculation.

R. N. C.

Cultural requirements of bacteria. IV. Quantitative determination of bacterial growth. J. H. MUELLER (J. Bact., 1935, 29, 383—387).—Micro-determinations of bacterial N serve as a measure of growth. The cells are separated and subsequently washed (centrifuge) with dil. AcOH.

A. G. P.

Micro-method for determining the utilisation of carbohydrates and polyhydric alcohols by micro-organisms. F. H. JOHNSON (Science, 1935, 81, 620—621).—The change in colour of phenol-red to yellow is the basis of the method.

L. S. T.

Agar. II. Physico-chemical properties of agar and their influence on the growth of micro-organisms. A. ITANO and Y. TSUJI (Ber. Ohara Inst. landw. Forsch., 1935, 6, 575—586; cf. B., 1934, 475).—Good-quality agar is more sol. and contains less total N than other grades. Grade III agar is more efficient than grade I for the growth of *B. subtilis*, *Azotobacter chroococcum*, and *Saccharomyces cerevisiae*. Grade I agar has a lower p_H .

P. G. M.

Inactivation of bacteriophage by oxidation. I. LOMINSKI (Compt. rend. Soc. Biol., 1935, 119, 952—954).—Bacteriophage is inactivated by $KMnO_4$ at relatively low concns. The min. concn. for inactivation is \propto the reducing power of the medium, and inversely \propto the temp., suggesting that the inactivation is due to oxidation.

R. N. C.

Comparative sensitivity of bacteriophages and homologous bacteria to oxidation. I. LOMINSKI

(Compt. rend. Soc. Biol., 1935, 119, 1090—1092).—Bacteriophages are more sensitive to oxidation by $KMnO_4$ than the homologous bacteria, which is in contrast to their behaviour with most physical and chemical agents. The fact permits the removal of bacteriophages from cultures containing them. $KMnO_4$ appears to act only on the extracellular bacteriophages.

R. N. C.

Antibacteriophagic properties of human sera. R. BIGLIERI and A. FISCHER (Folia biol., 1931, 21—24).—Certain human and rabbit (but not horse or guinea-pig) sera possessed marked antibacteriophagic properties in presence of *Staphylococcus* of human origin.

CH. ABS. (p)

Bactericidal action of water exposed to the combined action of metallic silver and electrolysis. N. METALNIKOV (Compt. rend., 1935, 201, 411—412).—Marked bactericidal activity (\propto area of anode and *I* and not destroyed by boiling) in H_2O is produced by mild electrolysis (e.g., 3—4 milliamp. at 1.5—4.5 volts) with Ag anode and C cathode. The product is not toxic to mice.

F. O. H.

Gonococcicidal action of mallophen in urine. R. D. HERROLD (J. Lab. Clin. Med., 1934, 20, 53—55).—Mallophen (I) in urines (1:2000—3000) at p_H 4.9—7.0 kills gonococci. At dilutions of 1:4000 (I) is not effective in nearly neutral urines, but prevents growth in acid samples. All urines having $p_H < 5.4$ have some gonococcicidal action.

CH. ABS. (p)

Bactericidal power of blood. R. OTTENBERG (J. Lab. Clin. Med., 1934, 20, 70—74).—The bactericidal power of blood is not decreased by presence of Na citrate. Disappearance of streptococci during incubation with blood is more marked when the latter is drawn from patients infected with homologous strains. Defibrination removes large nos. of bacteria from serum.

CH. ABS. (p)

Action of X-rays on certain bacteria. A. T. PUGSLEY, T. H. ODDIE, and C. E. EDDY (Proc. Roy. Soc., 1935, B, 118, 276—298).—*Sarcina lutea*, *B. coli*, and *Phytomonas medicaginis* are killed by X-rays, the ratio of sensitivities being 0.3:1:3. For equal doses, the longer λ are more effective and it appears that the medium is affected similarly to the production of a toxin. After consideration of the survival rate of bacteria singly and in colonies, the one-quantum-hit-to-kill theory of Crowther is considered the most satisfactory explanation of the mode of killing.

H. G. R.

Hormones. O. RIDDLE (Endocrinol., 1935, 19, 1—13).—An address.

R. N. C.

Biological effects of thymus extract (Hanson). L. G. ROWNTREE, J. H. CLARK, and A. STEINBERG (Arch. Int. Med., 1935, 56, 1—29).—A detailed account of work already noted (A., 1934, 1266).

Determination of thyroxine in thyroid substance. N. F. BLAU (J. Biol. Chem., 1935, 110, 351—363).—Greater yields of thyroxine (I) are obtained by acidification of the tissue hydrolysate to p_H 5 before extraction with BuOH; the time of hydrolysis with NaOH may be shortened by this treatment.

Only 4% loss is sustained by boiling (I) with $\text{Ba}(\text{OH})_2$ for 6 hr.; this is increased to 10% if proteins are present. The method of determining (I) described earlier (A., 1933, 1209) is modified accordingly.

H. D.

Determination of thyroxine-iodine by hydrazine. H. PAAL and G. MOTZ (Biochem. Z., 1935, 279, 106—107).—Aq. preps. (equiv. to 1—2 mg. of thyroxine) are refluxed with N_2H_4 (1—2 drops) and $N\text{-NaOH}$ (1—2 c.c.) for 1 hr. and the liberated I is pptd. as AgI and determined electrochemically.

F. O. H.

Thyroxine and tissue metabolism. A. H. SCOTT (Amer. J. Physiol., 1935, 111, 107—117).—Thyroxine (I) *in vivo* accelerates metabolism in the blood of the alligator. Glucose consumption and lactic acid (II) production are increased, and intermediate products other than (II) decreased; the R.Q. is lowered *in vivo* and *in vitro*. Metabolism increases in early summer. (I) *in vivo* produces an initial acidosis followed by a progressive alkalosis, due probably to increased CO_2 production and increase of the buffering power of the blood. (I) is destroyed only slowly; increased metabolism persisting after 6 months. (I) *in vitro* increases O_2 consumption in some cases, but does not increase CO_2 production.

R. N. C.

Compounds that affect basal metabolism in man. W. O. THOMPSON, P. K. THOMPSON, S. G. TAYLOR, S. B. NADLER, and L. F. N. DICKIE (Endocrinol., 1935, 19, 14—20).—Thyroxine (I) is more active calorigenically than any other known compound. Basal metabolism is also affected by N -acetylthyroxine, adrenaline, di-iodothyronine (II), $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$ (III), and di-iodotyrosine, in decreasing order of activity; thyronine is apparently inert. The activity of (I) is greatly reduced by slight changes in the mol., the $(\text{C}_6\text{H}_5)_2\text{O}$ and NH_2 and all four I being important. The calorogenic response to (II) is of shorter duration than that to (I); the response to (III) lasts only a few days as compared with 70—90 days for (I). Attempts to determine the (I) content of desiccated thyroid have resulted in the destruction of most of its calorogenic activity. Peptic digestion of thyroid produces an acid-insol. I fraction, the activity of which per mg. I is $>$ that of the whole gland, and an acid-sol. fraction, the activity of which per mg. I is $<$ that of the whole gland. Subcutaneous injection of pituitary growth-hormone and of "phy-one" to cases of various types has produced in many of them a definite increase of basal metabolism.

R. N. C.

Action of diuresis and thyroxine on protein metabolism. G. SCOZ (Boll. Soc. Ital. Biol. sperim., 1933, 8, 1718—1720; Chem. Zentr. 1935, i, 917).—Total N excretion is temporarily increased by thyroxine; a longer retention period follows for N and S. Diuresis appears through increase of urea- NH_3 and NH_2 -acids, whilst allantoin, creatine, and creatinine fall. Hence thyroxine increases exogenous, and lowers endogenous, protein metabolism.

R. N. C.

Phospholipin content of liver, skeletal muscle, and whole blood, as affected by thyroxine injections. L. H. SCHMIDT (Amer. J. Physiol., 1935,

111, 138—144).—Injection of thyroxine in rabbits produces decrease of phospholipin fatty acids and increase of non-phospholipin fatty acids in liver, whilst in skeletal muscle the former are increased and the latter are decreased. Both are increased in blood.

R. N. C.

Inhibition of thyroid activity by animal blood. EITEL and LOESER (Klin. Woch., 1934, 13, 1742—1744).

G. H. F.

Biochemical basis of thyroid function. C. R. HARRINGTON (Lancet, 1935, 228, 1199—1204, 1261—1266).—Lectures.

L. S. T.

Use of rabbits in the standardisation of para-thyroid hormone. F. J. DYER (Quart. J. Pharm., 1935, 8, 197—212).—The method of Hamilton and Schwartz has been modified, using groups of rabbits and analysing the average blood samples. The variations in the normal val. and in those after injection admit of qual. work only.

H. G. R.

Vasopressin content of the pituitary of the normal guinea-pig, and after injections of folliculin or thyroxine. J. A. SCHOCKAERT and A. LEJEUNE (Compt. rend. Soc. Biol., 1935, 119, 1197—1199).—The vasopressin content of the posterior pituitary of the male guinea-pig is remarkably const., and is not affected by folliculin or thyroxine.

R. N. C.

Presence of a substance antagonistic to vasopressin in the serum of pregnant women. J. A. SCHOCKAERT and J. LAMBILLON (Compt. rend. Soc. Biol., 1935, 119, 1194—1197).—The effect of vasopressin in cats is reduced by simultaneous injection of pregnancy serum, but not by normal serum.

R. N. C.

Effect of the pituitary growth-hormone on mice with hereditary dwarf growth. T. KEMP (Klin. Woch., 1934, 13, 1854—1855).—Injection of ox anterior pituitary into dwarf mice with hereditary anterior pituitary defect (lack of eosinophils) resulted in harmonious growth of all organs. There was excessive growth of the thymus (3—4 times normal wt.).

G. H. F.

Maternal behaviour in male rats. M. McQUEEN-WILLIAMS (Science, 1935, 82, 67—68).—Such behaviour can be induced in male rats by chronic administration of bovine pituitary implants or by complete thyroidectomy. In both cases the pituitaries are considerably enlarged. No mammary development occurs in the latter case.

L. S. T.

Action of the anterior pituitary-like substance of urine on the metabolism of dogs. O. H. GAEBLER (Endocrinol., 1935, 19, 63—68).—Metabolism is not affected by large doses of the anterior pituitary-like substance of pregnancy urine. In some cases H_2O and N storage occurs similar to that produced by growth-hormone preps.

R. N. C.

Effect of antuitrin-S on the male lizard, *Anolis carolinensis*. L. T. EVANS (Anat. Rec., 1935, 62, 213—221).

R. N. C.

Response of the isolated gall-bladder to cholecystokin. F. T. JUNG and H. GREENGARD (Amer. J. Physiol., 1933, 103, 275—278).—Chole-

cystokinin caused contraction of the gall-bladder of the guinea-pig, was active between pH 5.0 and 8.5, and was destroyed by alkali and heat. It still produced contraction, after atropine had rendered both pilocarpine and acetylcholine ineffective.

CH. ABS. (p)

Effect of incretin on the glycogen reserve of the liver in the rabbit. J. LA BARRE and G. HOUSSA (Compt. rend. Soc. Biol., 1935, 119, 1179—1181).—Intravenous injection of small quantities of incretin in young rabbits produces an increase in liver-glycogen. The hypoglycæmic effect of duodenal extracts is probably due to this action.

R. N. C.

Plant secretions. J. SKUJA (Skand. arch. Physiol., 1934, 70, 126—132; Chem. Zentr., 1935, i, 912).—By the method previously described (A., 1933, 319) secretins were detected in fresh tomato sap, in fermenting cabbage, sour cucumbers, silage, and in spontaneously soured milk.

A. G. P.

Action of the pancreatropic hormone of anterior pituitary origin on blood-sugar. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1935, 119, 1174—1177).—Intravenous injection of pancreatropic hormone in dogs produces a fall of blood-sugar by stimulating insulin secretion. Thyroidectomy does not affect the action.

R. N. C.

Influence of various hormones on intestinal absorption. III. Amino-acid. S. ISAWA (J. Chosen Med. Assoc., 1934, 24, 1332—1342; cf. this vol., 540).—Absorption of 0.5% glycine solution (in 0.9% NaCl) was accelerated by insulin, retarded by pituglandol and adrenaline, and unaffected by thyroxine.

CH. ABS. (p)

Insulin-inhibiting agency in the duodenum. A. B. MACALLUM (Nature, 1935, 136, 32).—Extracts from the duodenum of rabbits contain a component antagonistic to insulin.

L. S. T.

Influence of adrenaline and insulin on carbohydrate metabolism of snails (*Helix pomatia*, L.). G. WOLF-HEIDEGGER (Biochem. Z., 1935, 279, 55—63).—The blood-sugar of snails in summer is $0.022 \pm 0.008\%$, this val. being reduced by approx. 50% in winter. Adrenaline produces a depigmentation but neither adrenaline nor insulin has any apparent effect on the carbohydrate metabolism (blood-sugar and glycogen levels).

F. O. H.

Increase in insulin secretion following injections of adrenaline and its relation to the high liver-glycogen values obtained. J. L. CHIDSEY and J. A. DYE (Amer. J. Physiol., 1935, 114, 223—229).—Adrenaline (I) is more effective in raising the blood-sugar of a depancreatized dog given sufficient insulin (II) to keep the blood-sugar normal, than that of a normal dog. Glycogen (III) is high in the liver and low in the muscles of a normal dog several hr. after (I) administration, but low in both liver and muscles in the depancreatized dog given (II). (I) stimulates (II) secretion in normal dogs, the increase being responsible both for the slower rise in blood-sugar and the high (III) vals.

R. N. C.

Effects of adrenaline injection in moderate work. D. B. DILL, H. T. EDWARDS, and R. H. DE

MEIO (Amer. J. Physiol., 1935, 111, 9—20).—A fasting man expends 5000 kg.-cal. of energy in 24 hr., about 1.5% of which is derived from protein, and about 50% of the total from carbohydrate in the early stages, but < 10% in the last 2 hr. Adrenaline (I) does not affect protein metabolism, but increases carbohydrate utilisation. Excretion of ketones always falls after (I), showing that carbohydrate oxidation in moderate activity is facilitated. The effects of (I) on blood-sugar resemble those in resting subjects.

R. N. C.

Continuous injection of adrenaline and adrenaline secretion. J. MALMEJAC, V. DONNET, and E. DESANTI (Compt. rend. Soc. Biol., 1935, 119, 1152—1154).—Continuous injection of small quantities of adrenaline in the dog reduces adrenaline secretion for the period of injection, the reduction being sufficient to cause a considerable fall of blood-sugar.

R. N. C.

A mechanism by which continuous injection of adrenaline reduces adrenaline secretion. J. MALMEJAC, V. DONNET, and E. DESANTI (Compt. rend. Soc. Biol., 1935, 119, 1155—1157).—Adrenaline (I) secretion is not reduced by continuous injection of (I) in the dog if the depressors have been cut. Perfusion of a vascularly isolated carotid sinus with Ringer's solution containing (I) reduces (I) secretion; hence this action is one of the mechanisms by which (I) secretion is reduced.

R. N. C.

Modifications in distribution of phosphorus in rabbit livers by changes in blood-sugar and liver-glycogen. T. TAKAHISA (Japan. J. Med. Sci., IV, 1934, 8, 117—119).—Subcutaneous injection of adrenaline hydrochloride (0.2 mg. per kg.) increased the blood-sugar and decreased liver-glycogen (I). Inorg. PO_4''' was slightly increased, but other constituents were scarcely affected. Administration of insulin (1 unit per kg.) caused hypoglycæmia and a slight increase in (I). Inorg. P, phosphagen, N, and total phosphates increased. Intravenous injection of phloridzin (300 mg. per kg.) produced no change in blood-sugar, but increased (I) and lactacidogen phosphate. Oral administration of glucose (10 g. per kg.) increased inorg., phosphagen-, and lactacidogen-phosphate.

CH. ABS. (p)

Influence of amino-acids on the action of adrenaline. K. TERAI (Japan. J. Med. Sci., IV, 1933, 7, 111—112).—Adrenaline inactivated by storage in darkness at pH 8.0 became active (perfusion through rabbit ears) on addition of NH_2 -acids (histidine, lysine, etc.). The degree of action was paralleled by the amount of acid added.

CH. ABS. (p)

Adrenaline-sensitising action of alanine. M. KATÔ (Japan. J. Med. Sci., IV, 1934, 8, 130).—The action of *d*- was > that of *l*-alanine in sensitising the constrictor action of adrenaline on the isolated rabbit ear.

CH. ABS. (p)

Influence of dihydroxyphenylalanine on adrenaline glycogenolysis. J. HORIMI (Japan. J. Med. Sci., IV, 1933, 7, 112).—Dihydroxyphenylalanine (I) exhibited a glycogenolytic action on toad liver resembling that of adrenaline (II). (I) potentiated the action of (II).

CH. ABS. (p)

Effect of sympathol and adrenalone on the action of adrenaline. M. KATÔ and S. AIBARA (Japan. J. Med. Sci., IV, 1933, 7, 113).—Administration of sympathol or adrenaline (1–2 mg. per kg.) increased the pressor action of adrenaline (I) on rabbits and also the depressant action on intestinal motility. Larger doses weakened the action of (I). CH. ABS. (p)

Effect of adrenaline on blood-sugar and lactic acid. T. ASADA (Japan. J. Med. Sci., IV, 1934, 8, 119–120).—Injection of adrenalone (I) increased blood-sugar and lactic acid to extents \propto the dosage. (I) was less effective than adrenaline and its action was partly antagonised by pituitrin or CaCl_2 . CH. ABS. (p)

Some factors affecting adrenal insufficiency in the rat. F. J. AGATE, jun., and R. L. ZWEMER (Amer. J. Physiol., 1935, 111, 1–8). R. N. C.

Adrenal cortex and vitamin-A content of the blood. J. MALMEJAC, A. CHEVALLIER, and Y. CHORON (Compt. rend. Soc. Biol., 1935, 119, 1158–1160).—Splanchnic excitation in the dog increases blood-vitamin-A by stimulation of the adrenal cortex. R. N. C.

Adrenaline content of adrenal glands of grown rats. H. ENDO (Japan. J. Med. Sci., IV, 7; Proc. Japan. Pharmacol. Soc., 1933, 82–83).—Monthly determinations are recorded. The average val. for the year was 0.09 g. per kg. body-wt. Subcutaneous administration of adrenaline lowered the amount in the gland. CH. ABS. (p)

Specificity of the Viale reaction for detecting adrenaline in the urine. F. DOMENICI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 53–55).—The reaction is sp. for adrenaline. R. N. C.

Effect of ultra-violet light on some sympathomimetic substances. P. L. EWING (J. Lab. Clin. Med., 1934, 20, 16–33).—The normal physiological activity of adrenaline is destroyed by exposure to ultra-violet light. The decomp. products, which have no pressor action, are similar to those formed by the action of H_2O_2 . The activity of synephrine (I) salts and of *p*-hydroxyphenylpropanolamine is increased by moderate and destroyed by excessive irradiation. The free (I) base is unaffected. CH. ABS. (p)

Padutin. R. SIVÓ and E. VON DOBOZY (Klin. Woch., 1934, 13, 1602–1605; Chem. Zentr., 1935, i, 917).—Padutin (callicrein), injected intramuscularly, abolishes the cyanosis and gangrene of the comb produced by ergotin in cocks. It also neutralises the constrictor effect of adrenaline (I) in the Lawen-Trendelenburg frog prep. It does not antagonise the midriatic effect of (I) on the enucleated frog's eye, but inhibits its hyperglycæmic action in normal man, without affecting the blood-sugar *per se*. R. N. C.

Effect of the circulation hormone padutin on the resorption of intracutaneous sodium chloride wheals. H. FRENKEL (Klin. Woch., 1934, 13, 1749–1751; Chem. Zentr., 1935, i, 917–918).—The rate of resorption of NaCl injected into the skin of rabbits is increased by intravenous injection of

padutin (I). The same effect appears in human patients, and COMe_2 and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ disappear from the urine. Intramuscular injection of (I) also accelerates resorption. (I) probably causes dilatation and increased permeability of the intradermal vessels. R. N. C.

Chemistry of œstrogenic substances. E. FRIEDMANN (Nature, 1935, 136, 108).—A criticism (cf. this vol., 1033). L. S. T.

Nature of the œstrogenic substance in human male urine and bull testis. R. I. DORFMAN, T. F. GALLAGHER, and F. C. KOCH (Endocrinol., 1935, 19, 33–41).—Theelol (I) is more effective than theelin (II) in causing vaginal introitus in the rat, whilst (II) is more effective in causing uterine hypertrophy. The œstrogenic substance in the total C_6H_6 extract of normal male urine does not cause either of these effects; that in the alkali-sol. fraction of the C_6H_6 extract is biologically identical with (II). The alkali-insol. fraction probably contains a substance that enhances the action of (II) on the uterus and vagina, but is neither (I) nor (II). R. N. C.

Effect of œstrin injections on the developing ova of mice and rabbits. H. O. BURDICK and G. PINCUS (Amer. J. Physiol., 1935, 111, 201–208).—Daily injections of œstrin from the day of mating result in retention of the ova in the Fallopian tubes, followed by degeneration from the fourth day. R. N. C.

Prolonged administration of theelin and theelol to male and female rats and its bearing on reproduction. N. J. WADE and E. A. DOISY (Endocrinol., 1935, 19, 77–87).—Prolonged administration of theelin or theelol (I) to male rats lowers body-wt. and the wts. of the testes, prostates, and Cowper's glands; fertility is somewhat reduced. Female rats given (I) show reproduction < normal and an interference with lactation. R. N. C.

Structural and functional features of rabbits' uteri following prolonged œstrin administration. S. R. M. REYNOLDS (Anat. Rec., 1935, 62, 269–277).—The uterus loses its motility and the endometrium undergoes progressive involution. The uterus is still responsive to progesterin, and hence the involution is not due to the development of an anti-hormone against œstrin. R. N. C.

Effect of œstrin and male hormone injected separately and simultaneously on the smooth muscle and epithelium of the seminal vesicle in the albino rat. M. D. OVERHOLSER and W. O. NELSON (Anat. Rec., 1935, 62, 247–267).—Prolonged administration of œstrin to normal or castrated rats stimulates the growth of the smooth muscle of the seminal vesicle, and also the seminal vesicle epithelium in castrated animals. Œstrin and the male hormone act synergistically on the smooth muscle and the epithelium when administered simultaneously. R. N. C.

Destruction of folliculin in the animal body. B. ZONDEK (Skand. Arch. Physiol., 1934, 70, 1933–1967).—When α -folliculin (I) is injected into male and female rats even in excessive doses, only about 0.2% can be recovered from the urine. In man (male

and female) approx. 3% is recovered. On extraction of whole rats < 2%, and after acid hydrolysis up to 20%, can be recovered. Loss of the remainder is due to inactivation in the liver. 95% of (I) is destroyed *in vitro* by liver extract. Folliculin benzoate is not thus inactivated. The enzyme action probably results in esterification, attacking the phenolic OH (the action being partly reversible by acid hydrolysis); in the benzoate mol., this position is already occupied by the Bz. (I) is adsorbed by striped muscle-tissue. G. H. F.

Hormones from cases of toxæmias of pregnancy. K. HEIM (Klin. Woch., 1934, 13, 1614).—The folliculin and prolan contents of urine in cases of toxæmias of pregnancy are much > normal and are comparable with those in cases of hydatidiform mole and chorioepithelioma. Increased secretion of folliculin in twin pregnancies is in agreement with the known relationship between multiple births and eclampsia. G. H. F.

Experimental production of hermaphrodites by injecting folliculin into chicken embryos. E. WOLFF and A. GINGLINGER (Compt. rend., 1935, 200, 2118–2120).—Folliculin injected into chicken embryos prior to the 7th day of incubation inhibits the development of males. After the 7th day, hermaphrodite tendencies are lessened. J. L. D.

Comparative luteinising capacity of the urine of pregnancy and of the menopause. A. LIPSCHUTZ (Endocrinol., 1935, 19, 42–50).—The coeff. of luteinisation in the infantile rat of the urine of pregnancy tends to diminish as the quantity of urine injected is increased. In the urine of the menopause it is relatively low. R. N. C.

Luteinising hormone and cholesterolaemia. L. CIOGLIA and D. TORE (Boll. Soc. Ital. Biol. sperim., 1935, 10, 75–77).—Injection of progesterin (I) in rabbits provokes an increase of blood-cholesterol (II). (I) combined with folliculin (III) provokes a smaller and less prolonged fall of (II) than (III) alone. (I) and antelobin (IV) combined do not affect (II). Hence (I) antagonises (III) and (IV). R. N. C.

Steric inversion of carbon 3 of sterols and male sexual hormones.—See this vol., 1125.

Sexual hormones. V, VI.—See this vol., 1125.

[Preparation of the male sexual hormone.] B. FRATTINI and M. M. MAINO (Ber., 1934, 68, [B], 677–679, 1264–1265). K. TSCHERNING (*ibid.*, 679–681).—A further discussion regarding priority (cf. A., 1930, 505; 1931, 398; 1934, 731).

Biological activity of derivatives of the male hormone androsterone. R. K. CALLOW and R. DEANESLY (Lancet, 1935, ii, 77–78).—Dihydroandrosterone produces normal growth of the accessory glands of the pre-puberally castrated rat; the seminal vesicles grow equally with prostate. Androsterone benzoate is inactive with respect to castrated rats, probably owing to its slow rate of hydrolysis. L. S. T.

Assay of crystalline male sexual hormone (androsterone). V. KORENCHESKY and M. DENNISON (Biochem. J., 1935, 29, 1720–1731; cf. A.,

1934, 1269).—Using castrated rats and doses of 200–900 × 10⁻⁶ g. in olive oil solution the dose of synthetic androsterone (I) ∝ % increase in wt. of prostate or prostate vesicles. For higher doses the increase is less. The relation between the average activity of (I) and the rat unit is determined; 1 rat unit of comb-growth activity = 162–169 and of whole male sexual activity is 165–172 × 10⁻⁶ g. The effects of (I) on the wt. of penis and preputial glands are not so regular. H. D.

Water retention and vitamin-A. G. DOMINICI and G. OLIVERA (Deut. med. Woch., 1934, 60, 1955).—Administration of vitamin-A increased the daily output of urine in cases of cirrhosis of liver, and slightly increased output in precirrhosis; it had no effect on normals, or on a cancer case with liver metastases. G. H. F.

Hypervitaminosis-A. K. STRAUSS (Beitr. path. Anat., 1934, 94, 345–352; Chem. Zentr., 1935, i, 1260).—White rats fed with large excess of vitamin-A show symptoms of poisoning after 4 weeks, even though the amount of vitamin-D given is < the toxic limit. R. N. C.

Histology of avitaminosis-A. I, II. T. H. DE RUYTER (Acta Brev. neerl. Physiol., 1934, 4, 122–124, 124–126; Chem. Zentr., 1935, i, 1260–1261).—I. The metaplastic epithelium of rats cured of avitaminosis-A is compensated, the lymphatic and recticular apparatus and the thymus recover, and glycogen reappears in the liver. There is no indication of a relation between vitamin-A deficiency and tumour formation.

II. Avitaminosis-A reduces the resistance of rats to spontaneous lung infections. Fat resorption is more rapid than in normal animals. There is no difference in the lipin-P of the blood. R. N. C.

Antagonism of vitamin-A and -C. H. WENDT and H. SCHROEDER (Z. Vitaminforsch., 1935, 4, 206–212).—Administration of vitamin-C to guinea-pigs or rats inhibits the symptoms of hypervitaminosis, growth retardation, and hepatic storage of vitamin-A due to excessive doses of -A. F. O. H.

Influence of vitamins on growth of normal and tumour tissue. T. GORDONOFF and T. LUDWIG (Z. Vitaminforsch., 1935, 4, 213–223).—The growth of embryonic heart fibroblasts and tumour transplants in plasma from rats suffering from avitaminosis-A is < that in normal plasma which, in turn, is < that in plasma from rats receiving excess of vitamin-A. The same technique indicates that vitamin-D has no influence, and -C a retarding action, on growth. F. O. H.

Plural nature of vitamin-B. A. G. HOGAN and L. R. RICHARDSON (Nature, 1935, 136, 186).—EtOH extracts of rice, wheat-germ oil, and flavins differ in their ability to cure dietary deficiencies in rats, and provide additional evidence for the plural nature of vitamin-B. L. S. T.

"Oryzotoxin" and experimental beri-beri in the pigeon. G. SOLARINO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 11–14).—Intramuscular or oral administration of EtOH extracts of rice, autoclaved grain, or starch to starved pigeons produces poly-

neuritis leading to death. In birds fed with maize, larger doses and longer treatment are necessary. The extracted rice or autoclaved grain also provokes beri-beri, the toxic action being > that of the unextracted material. Et_2O extracts a further quantity of "oryzotoxin" from the residue, but does not lessen the toxic action. R. N. C.

Avitaminosis. Toxic substance extracted from polished rice. L. TOCCO and S. BRUNO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 67—68).—A substance producing polyneuritis in pigeons is extracted from polished rice with slightly acid H_2O and pptd. from the extract by neutralisation with NH_3 .

R. N. C.

Growth factors. Influence of vitamin- B_1 and wheat-germ oil on *Mucorineae*. W. H. SCHOPFER (Z. Vitaminforsch., 1935, 4, 187—206).—Various genera of *Mucorineae* do not grow in a synthetic medium free ($< 1 \times 10^{-6}$ g.) from vitamin- B_1 . Wheat-germ extracts contain a similar growth factor which is not identical with vitamin- B_1 (cf. this vol., 544, 663).

F. O. H.

Crystalline vitamin- B_1 as growth-hormone for micro-organisms (*Phycomyces*). W. H. SCHOPFER (Arch. Mikrobiol., 1935, 6, 139—140).—Effects previously ascribed (this vol., 534) to vitamin- B_2 are now recorded as due to certain impurities, probably B_1 .

A. G. P.

Vitamin- B_1 . I. Solubility as present in the international standard preparation. II. Isoelectric point as determined by electrophoresis of solutions made from the international standard preparation. G. SANKARAN and N. K. DE (Indian J. Med. Res., 1934, 22, 215—232, 233—247).—I. The solubility of vitamin- B_1 is min. at p_H 3.5; the rate of increase as p_H rises is > as p_H falls. The relation between p_H and $\lambda_{\text{max. abs.}}$ is linear, λ increasing with p_H . The prep. of standard solutions at all p_H vals. is described.

II. Vitamin- B_1 behaves as an amphoteric electrolyte in electrophoresis, migration being bipolar over a range of two p_H units. The isoelectric point is approx. 3.0.

R. N. C.

Electrical transference of vitamin- B_1 in aqueous solution. B. N. GHOSH and B. C. GUHA (Current Sci., 1935, 3, 554).—Electrodialytic migration of vitamin- B_1 to the cathode (A., 1931, 1338) is confirmed at p_H 8.2, in refutation of the criticisms of Sankaran and De (see above).

E. W. W.

Oryzanin "antineuritic vitamin." IV. Activity and thermostability of oryzanin hydrochloride. S. ODAKE and T. YAMAGISHI (Bull. Agric. Chem. Soc. Japan, 1935, 11, 51—61).—The yield of oryzanin hydrochloride (I) from rice polishings and yeast has been improved. 0.001 mg. is the min. dose for curing young rats of vitamin- B_1 deficiency and for maintaining normal growth. The activity of (I) is destroyed by heating the aq. solution for 1 hr. at 140° , or by heating the crystals for 1 hr. at 180° .

J. N. A.

Growth-promoting action of synthetic flavins. P. GYÖRGY (Z. Vitaminforsch., 1935, 4, 223—226).—The identity of synthetic 6 : 7-dimethyl-9-d-1'-ribityl-

isoalloxazine (A., 1934, 1233; this vol., 359, 631, 760) (and the non-identity of the corresponding arabino-flavin) with lactoflavin from milk is confirmed by growth-promoting experiments on rats.

F. O. H.

Photochemical phenomena involved in vitamin- B_2 studies. G. C. SUPPLEE, S. ANSBACHER, and R. C. BENDER (J. Biol. Chem., 1935, 110, 365—374).—Vitamin- B_2 (I), prepared by a slight modification of Kuhn's method (A., 1933, 847), is subjected to irradiation with various λ and its growth-promoting power assayed. Exposure to light produces a progressive change in the fluorescence from yellow-green to blue-green, running parallel with decreases in (I) activity; light of $> 310 \text{ m}\mu$ is responsible for the change.

H. D.

Effect of administration to children of extra vitamin- B_2 . M. ISHII (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 608—617).—Addition of the vitamin to the diet of children receiving typical Japanese food had only a very slight favourable effect on the normal gain in body-wt.

W. McC.

Avitaminosis- B_2 and pellagra in rats. Biological investigation of vitamins. W. VON DRIGALSKI (Z. Vitaminforsch., 1935, 4, 177—187).—Diets deficient in vitamin- B_2 produce pellagra-like skin lesions in rats, the effect not being influenced by natural or artificial irradiation. No antagonism exists between B_1 and B_2 (cf. A., 1934, 208). Considerable storage of B_2 occurs in healthy rats. A basal diet supplemented with all the known vitamins produces growth < that with a diet of bread, milk, and kitchen scraps.

F. O. H.

Occurrence of cataract in rats fed on diets deficient in vitamin- B_2 . M. C. BOURNE and M. A. PYKE (Biochem. J., 1935, 29, 1865—1871).—Only 20—31% of young rats, fed on a vitamin- B_2 (I)-deficient diet, developed cataract; on the diet + cystine and on one containing caseinogen, salts, and maize-starch no cataract developed. Dermatitis is a better characteristic of (I) deficiency than cataract.

H. D.

Effect of the growth-promoting, appetite-stimulating, or "physin" factor on the live-weight increase of swine. G. DUNLOP (J. Agric. Sci., 1935, 25, 445—459).—Physin has a stimulative effect on the growth of pigs and customary rations are deficient in this factor. It stimulates appetite and general growth without enhancing the net energy val. of the ration. The physin content of foodstuffs is in the descending order, liver, liver meal, dried whole milk, whey, green food, fish meal, meat meal, soya-bean meal.

A. G. P.

Discovery, isolation, and synthesis of vitamin-C. K. TAUFEL (Z. Unters. Lebensm., 1935, 70, 7—16).—A lecture.

Galacturonic acid as a precursor of ascorbic acid. R. JOHNSTIN and K. S. POTTER (J. Biol. Chem., 1935, 110, 279—284).—Guinea-pigs on a vitamin-C-deficient diet given *d*-galacturonic acid (I) orally, subcutaneously, and intraperitoneally show no differences from those on the diet without (I).

H. D.

Vitamin-C and thiosulphate in the urine. M. VAN EEKELLEN (*Acta Brev. neerl. Physiol.*, 1934, 4, 137—139; *Chem. Zentr.*, 1935, i, 1262).—Normal human urine, after pptn. with $\text{Hg}(\text{OAc})_2$, shows only half of its original reducing power against dichlorophenol-indophenol, which corresponds with its vitamin-C (I) content; the ppt. contains other reducing substances. Administration of (I) in large quantities increases urinary (I). The reducing action of urine is increased by hydrolysis with 5% H_2SO_4 in CO_2 ; the effect is possibly due to reduction of dehydroascorbic acid or formation of reductic acid from glycuronic acid. A reducing substance, probably $\text{Na}_2\text{S}_2\text{O}_3$, is found in the urine of diabetics, cats, and dogs, and in normal human urine in small quantities.

R. N. C.

Ascorbic and dehydroascorbic acids in the urine of normal and scorbutic guinea-pigs. E. MARTINI and F. PINOTTI (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 58—60).—The scorbutic index of the urine of scorbutic guinea-pigs rises to 5 times the normal val. Injection of dehydroascorbic acid produces a fall of the scorbutic index.

R. N. C.

Ascorbic and dehydroascorbic acids in the aqueous humour under the action of light. A. BONSIGNORE (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 62—65).—Illumination of the normal eye causes a lowering of the dehydroascorbic/ascorbic acid ratio of the aqueous humour. In the atropinised eye the ratio rises.

R. N. C.

Behaviour of the ascorbic acid of the tissues in inanition. E. MARTINI and A. BONSIGNORE (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 60—62).—The scorbutic index of the adrenals of guinea-pigs is not affected in starvation, but rises in scurvy.

R. N. C.

Ascorbic acid and adrenaline. A. BONSIGNORE and F. PINOTTI (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 55—58).—Oxidised adrenaline is reduced by ascorbic acid to a physiologically inactive compound.

R. N. C.

Depigmenting effect of vitamin-C. F. TECHNER (*Klin. Woch.*, 1934, 13, 1614).—Pigmentation occurring in a pregnant woman was not diminished by feeding lemon-juice; pigment faded naturally after delivery. Animal experiments have shown that vitamin-C is ineffective in reducing pigmentation caused by ovarian substances.

G. H. F.

Influence of vitamin-C on pigmentation. H. A. SCHADE (*Klin. Woch.*, 1935, 14, 60—61).—Administration of vitamin-C to man inhibited both the erythema and pigmentation caused by artificial sun rays. Vitamin-C also caused leucopenia and lymphocytosis, but was without effect on the oxidase reaction of leucocytes.

G. H. F.

Distribution of vitamin-C in organs of the fox. G. BOURNE (*Austral. J. Exp. Biol.*, 1935, 13, 113—125).—Reduction of AgNO_3 (in dil. AcOH) indicates the presence of vitamin-C (I) in almost every tissue of foxes. The high concns. of (I) in the anterior lobe of the pituitary gland, adrenals, corpus luteum, and interstitial cells of the gonads indicate the possibility of (I) being concerned in the production of the respective hormones.

F. O. H.

Formation, origin, and distribution of vitamin-C in plant tissues. R. STROHECKER (*Z. Unters. Lebensm.*, 1935, 70, 76—81).—The reduction of 2:6-dichlorophenol-indophenol by extracts of fruits and leaves is not due to vitamin-C (I). (I) is formed in germinating barley and in birch leaves at the beginning of development, whilst the reducing power of hawthorn berries is at a max. when the red pigment appears. Birch and robinia leaves are rich in (I). The glands of the former contain a reducing substance.

E. C. S.

Vitamin-C content of cucumbers and fruits of *Ziziphus sativa* and *Sorbus domestica*. E. CASERIO (*Z. Vitaminforsch.*, 1935, 4, 173—177).—In each case the amount in mature or immature fruit is \approx approx. 20% of that of lemon-juice.

F. O. H.

Vitamin-C in lower organisms. G. BOURNE and R. ALLEN (*Nature*, 1935, 136, 185—186).—Staining with AcOH-AgNO_3 reveals small black granules scattered in the protoplasm in the cells of protozoa, bacteria, moulds, lichens, and algæ. This reducing agent is possibly vitamin-C, which may be essential for the existence of living protoplasm, probably as an integral part of an oxidation-reduction system.

L. S. T.

Determination of ascorbic acid by titration. M. VAN EEKELLEN (*Nature*, 1935, 136, 144—145).—Data for the amount of vitamin-C (I) extracted from the potato under various conditions indicate that the increase in (I) recorded by McHenry and Graham (this vol., 903) is due to the destruction by cooking of an oxidase present in some vegetables, and not to the liberation of more (I) from an ester. The oxidase can be activated in 3% $\text{CCl}_3\text{-CO}_2\text{H}$ solution. In determining (I) in blood, reduction with H_2S must follow the $\text{Hg}(\text{OAc})_2$ pptn., since, in presence of erythrocytes, (I) is reversibly oxidised when blood is pptd. by $\text{CCl}_3\text{-CO}_2\text{H}$.

L. S. T.

Constitution of calciferol (vitamin-D).—See this vol., 1120.

Properties and physiological significance of biosterol. IX. Condensation of biosterol with maleic and citraconic anhydrides. Z. NAKAMIYA (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 584—607).—Biosterol (I) from *Stereolepis ischinagi* is accompanied by a triacontane ("stereolepisane"), $\text{C}_{30}\text{H}_{62}$, m.p. 65°. (I) with citraconic anhydride gives biosterol-citraconic acid, $\text{C}_{25}\text{H}_{34}\text{O}_4$, m.p. 207° (perhydro-derivative, $\text{C}_{25}\text{H}_{42}\text{O}_4$, m.p. 65—66°; bromide, $\text{C}_{25}\text{H}_{34}\text{O}_4\text{Br}_2$, m.p. 186—188°; hydrochloride, $\text{C}_{25}\text{H}_{34}\text{O}_4\text{HCl}$), and with maleic anhydride gives the substance (II), $\text{C}_{27}\text{H}_{36}\text{O}_8$, m.p. 247°, which with AcCl in $\text{C}_5\text{H}_5\text{N}$ yields an isomeride, m.p. 227°. Bromination of crude (II) in CHCl_3 followed by fractional pptn. with MeOH yields the compounds $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_3$, m.p. 247.5°, $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_4$, m.p. 230°, $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_5$, m.p. 215°, and $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_6$, m.p. 160—170°. W. McC.

Biochemical standardisation of vitamin-D or irradiated ergosterol. N. K. BASU (*Indian J. Med. Res.*, 1934, 22, 199—202).—The standard vitamin dose is the min. quantity that can raise $[\text{Ca}] \times [^{\text{P}}]$ in the blood of rabbits from 27 to 40 mg. in 7—10 days, or to 60 mg. in 15—18 days.

R. N. C.

Calcium and phosphorus contents of the offspring after feeding vitamin-D to the mother rat. W. W. SWANSON and L. V. IOB (Amer. J. Dis. Children, 1935, 49, 43—46).—Administration of cod-liver oil or viosterol to the mother increased the Ca and P contents of the young. CH. ABS. (p)

Prevention of injury from excess vitamin-D by feeding vitamin-A. C. GROSS-SELBECK (Klin. Woch., 1935, 14, 61—62).—Harmful effects of overdoses of vitamin-D on growth and condition of growing rats were prevented by feeding large amounts of -A. G. H. F.

Carr-Price reaction of the fatty acids of cod-liver oil after vigorous saponification. A. EMERIE (Nature, 1935, 136, 183—184).—The effect on the Carr-Price reaction of the saponification of the fatty acids of cod-liver oil and the method of concn. of the substance responsible for the reaction are described. L. S. T.

Vitamin-E. II. Eutrophic action and vitamin-E activity of rice-husk oil. III. Influence on fertility. L. SCHIOPPA (Z. Vitaminforsch., 1935, 4, 162—167, 167—173).—II. Wheat- and rice-germ oil have a marked eutrophic action in rats fed on a vitamin-E-deficient diet (this vol., 670).

III. Addition of small amounts of vitamin-E to a diet of bread, green vegetables, and mineral salts increases the fertility and the size and viability of the young of rats. F. O. H.

Chlorophyll and hæmoglobin—two natural pyrrole pigments. E. M. DIETZ (J. Chem. Educ., 1935, 12, 208—216).—A review. L. S. T.

Chlorophyll derivatives. L. MARCHLEWSKI and W. URBANCZYK (Bull. Acad. Polonaise, 1935, A, 146—155).—Blood-hæmatin and α - and β -phyllhæmatin (formed by dissolution of the respective hæmins in NaOH) have similar absorption curves, as have the corresponding hæms (formed by action of H_2S on the hæmatin) and the hæmatochromogens (produced by action of $N_2H_4 \cdot H_2O$ on the hæm). J. W. S.

Variations in chlorophyll content of leaves. N. T. DELEANO and J. DICK (Biochem. Z., 1935, 279, 49—54).—Determinations of Mg (A., 1934, 465, 1044) in leaves of *Salix fragilis* and *Populus alba* indicate that storage of chlorophyll continues for approx. 70 and 40 days, respectively. The content increases during growth, remains const. during the assimilation period (110—120 days), and decreases rapidly during the last 20—25 days; small amounts occur in the yellowed leaves. Florescence and fructification do not influence storage. F. O. H.

Causes of the irregular course of photosynthesis during the day. Diurnal course of respiration in sugar-beet leaves. A. KURSANOV and P. UGRUMOV (Bull. Soc. nat. Moscow, Sect. biol., 1934, 43, 159—166).—Physical causes, e.g., variation in the absorptive capacity of living tissue for CO_2 , may operate to cause fluctuations. CH. ABS. (p)

Influence of deuterium oxide on the rate of photosynthesis. J. CURRY and S. F. TRELEASE (Science, 1935, 82, 18).—Measurements of the rate of O_2 evolution at 25.7° by *Chlorella* suspended in

$CO_3^{--}HCO_3'$ buffer show that the rate of photosynthesis with 99.9% D_2O is approx. 0.41 of that with H_2O . L. S. T.

Assimilation of carbon dioxide by plants. P. KLASON (Svensk Pappers-Tidn., 1934, 37, 572—573; Chem. Zentr., 1935, i, 1077).—Assimilated CO_2 is converted directly into sugars and only to a minor extent into CH_2O . Lignin is produced exothermically from xylose (I) independently of O_2 . The mol. ratio (I) : hexoses is 1 : 1 in conifers and becomes 3 : 2 in broad-leaved plants if to the (I) content is added a further amount of (I) corresponding with the lignin present. A. G. P.

[Chlorophyll fluorescence and assimilation of carbonic acid.] H. KAUTSKY (Naturwiss., 1935, 23, 389).—The contention of Franck (cf. this vol., 681, 794) that his theory of the mechanism of CO_2 assimilation is supported by the author's experimental data (cf. *ibid.*, 263) is refuted. F. O. H.

[Chlorophyll fluorescence and assimilation of carbonic acid.] J. FRANCK (Naturwiss., 1935, 23, 389—390).—A reply to the above. F. O. H.

Carbon dioxide storage. VIII. Chemical changes in potato tubers resulting from exposure to carbon dioxide. N. C. THORNTON (Contr. Boyce Thompson Inst., 1935, 7, 113—118).—Exposure of tubers to atm. containing 20% O_2 and varying proportions of CO_2 resulted in increased respiratory activity, increased sp. conductivity of tissue leachings, and higher catalase activity, p_n , sucrose, and reducing sugar contents in the extracted juice. A. G. P.

Physiology of development and ripening in the strawberry. C. W. CULPEPPER, J. S. CALDWELL, and H. H. MOON (J. Agric. Res., 1935, 50, 645—696).—Fruit at the petal-fall stage shows max. total and insol. solids and "total astringency" ($KMnO_4$ -reducing power). Titratable acidity and sol. solids are high but < max. Of the sol. solids, 30—40% is sugar, 60—99% of which comprises reducing sugars. In the stage of rapid development the H_2O content increases markedly. The corresponding decline in total solids occurs principally in the insol. fraction. The sugar val. remains practically unchanged, acidity increases, and astringency declines. With the approach of the "whitening" stage changes in acidity, total solids, and sugars are small. In the "whitening" period H_2O contents and acidity reach max., and sol. solids increase, mainly as a result of sugar formation. Insol. solids and astringency decrease less rapidly. The transition to full ripeness is marked by a further increase in total solids, the rate of sugar formation being > the decline in insol. matter. From 70 to 80% of the sol. solids is now represented by sugars (mainly reducing). Titratable acidity decreases rapidly and astringency more slowly. Varieties are grouped according to chemical characteristics, which are discussed in relation to adaptability to different methods of preservation. A. G. P.

Trend of organic food reserves in lucerne roots as affected by cutting practices. C. O. GRANFIELD (J. Agric. Res., 1935, 50, 697—709).—The carbohydrate and N contents of roots decline

rapidly during early spring growth and after each cutting, min. vals. being reached approx. 20 days after each cut. Max. vals. occur at the full-bloom stage. Early and frequent cutting tends somewhat to lower the winter reserves of carbohydrate and N. The extent of winter accumulation is largely influenced by the amount of growth permitted after the final cutting. Spring growth is improved by permitting the aftermath to remain during winter. A. G. P.

Nutrient intake and transport in the leaves of *Drosera capensis*, L. J. OUDMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 650—662).—Plants developed normally in nutrients containing sufficient N. In N-free media N was assimilated from compounds [e.g., asparagine (I)] applied to the leaves or from insects. The intake of (I) occurred through tentacles or through the underside of leaves, and increased with rising temp. or with increasing concn. applied. The influence of temp. and concn. was most marked > 6 hr. after treatment. Assimilation of caffeine was > that of (I). Glands of the outer tentacles facilitated N absorption. Synthesis of protein from (I) in leaves was very small. N thus absorbed was probably utilised in other organs of the plant. A. G. P.

Effect of temperature on growth anatomy and metabolism of apple and peach roots. G. T. NIGHTINGALE (Bot. Gaz., 1935, 96, 581—639).—Growth responses at different temp. are examined in relation to the p_H of the tissues and to carbohydrate and N metabolism. The absorption of NO_3^- was limited to current roots in both species and was but little affected by the temp. of the medium. The reduction of NO_3^- to NH_4^+ and the production of NH_2 -acids increased, within limits, with rising temp. Max. root growth is associated with max. abs. reduction of NO_3^- at 18.3°. The distribution of carbohydrates in the various tissues is examined in relation to differences in temp. A. G. P.

Physiological significance of ammonium salts in relation to the composition changes of nutrient solutions. I. G. DIKUSAR (Lenin Acad. Agric. Sci. Ged. Inst. Fert., 1934, No. 3, 67—76).—In sand cultures of sugar-beet, cabbage, and flax, NH_4^+ gave somewhat better yields at p_H 7.0 and NO_3^- was the more effective at p_H 5.0. The response of flax to NH_4Cl was favoured by increasing the proportions of Ca, Mg, and K in the nutrient. An increase in Mg in place of Ca decreased the yield and prevented seed formation. The cation content (especially K) of plants was decreased and the PO_4^{3-} content increased by NH_4^+ , whereas NO_3^- favoured the reverse changes. Toxic effects of Al in media may be counteracted by increasing the concn. of Ca, Mg, and K. CH. ABS. (p)

Effect of a controlled nitrogen supply with different temperatures and photo-periods on the development of the potato plant. H. O. WERNER (Nebraska Agric. Exp. Sta. Res. Bull., 1934, No. 75, 132 pp.).—Carbohydrates (I) accumulated (with tuber formation) in conditions in which N assimilation was inhibited, viz., low temp., short days, deficient N supply. With high temp. excessive respiration

prevented the accumulation of (I). Reverse conditions favoured vegetative growth. The effect of various growth conditions and of different levels of N supply on the distribution of N and of (I) in the plant system, and on the collateral morphological and physiological responses of the plant, is examined.

Effect of potassium on the respiration of plants. G. ROHDE (Z. Pflanz. Düng., 1935, 39, 159—170).—The action of K in facilitating aerobic and retarding anaerobic (intermol.) respiration is related to its ability to improve the distribution of Fe within the plant. A. G. P.

Effect of the rate of flow of air on assimilation and of fluids on other natural fluids. A. H. BURGESS (Ann. Bot., 1935, 49, 567—578).—The effect of the rate of air-flow on the drying of hops, on the absorption of CO_2 by alkalis, and on the rate of absorption of CO_2 by plant leaves during photosynthesis depends on the same principles as the effect of the rate of flow of H_2O on the dissolution of Na_2CO_3 , CuSO_4 , and rock-salt crystals. The rates $\propto v^{0.39}$ (v =velocity of fluid-flow). Hence the thickness of the "stagnant film" of fluid at the boundary surface $\propto 1/v^{0.39}$. A. G. P.

Changes in hydrogen-ion concentration of culture solutions containing nitrate- and ammonium-nitrogen. S. F. TRELEASE and H. M. TRELEASE (Amer. J. Bot., 1935, 22, 520—542).—The growth of plants tended rapidly to decrease the p_H of media (initial p_H 4.3—6.0) having a low $\text{NO}_3^- : \text{NH}_4^+$ ratio and to increase the p_H of those having a high ratio. The extreme vals. approached were p_H 3.0 and 6.5, respectively. By suitable adjustment of NO_3^- and NH_4^+ , media may be obtained the p_H of which remain substantially const. during 8 days' growth. The ability of plants to change the reaction of media varied with age. A. G. P.

Influence of light on certain plant processes. P. P. LAZAREV and L. N. FORMOZOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 414—418, 419—421).—A mathematical relationship is derived expressing the variation in H_2O content of pea plants with light intensity. No significant differences in H_2O content could be attributed to the use of various light filters. Lighting did not affect the amount of sol. minerals in the plants. A. G. P.

Metabolism of calcareous algæ. II. Seasonal variation in certain metabolic products of *Corallina squamata*, Ellis. P. HAAS, T. G. HILL, and W. K. H. KARSTENS (Ann. Bot., 1935, 49, 609—619; cf. A., 1934, 121).—The incrustation of *C. squamata* consists of CaCO_3 and MgCO_3 and shows seasonal variations in amount (max. in winter, min. in spring). The ratio of the bases also varies, Ca being max. in January and July, and Mg max. in November and min. in March. The N fractions fluctuate considerably with season. Floridoside (I) contents are high in May and low in January. A reciprocity between (I) and $\text{NH}_2\text{-N}$ is apparent during the active growth season, thus supporting the view that the presence of peptides results from a lack of balance between C and N metabolism. A. G. P.

Production of ethylene by plant-tissue as indicated by the epinastic response of leaves. F. E. DENNY and L. P. MILLER (Contr. Boyce Thompson Inst., 1935, 7, 97—102).—Emanations from various fruits and other plant-tissues caused epinasty in young potato plants, probably due to the presence of C_2H_4 . A. G. P.

Wood. I. The cell-wall. II. Water content of certain Canadian trees and changes in the water-gas system during seasoning and flotation. III. Physiology of the tree with special reference to the ascent of sap and the movement of water before and after death. R. D. GIBBS (Canad. J. Res., 1935, 12, 715—726, 727—760, 761—787).—I. A review of lit. on the nature of the cell-wall and a description of attempts to separate lignin (I) and cellulose (II) by the use of solvents. For (I) lactic acid containing 0.1% HCl and for (II) 72% aq. H_2SO_4 and $CCl_3 \cdot CO_2H$ are effective except for the material of the torus, pit membrane, and bordered pits, which are more resistant.

II. Diurnal and seasonal variations in the H_2O content of paper birch, poplar, jack pine, white spruce, and balsam fir trees are studied. H_2O decreases during the morning and increases later in the day, whilst in hard woods a max. is reached in spring and a min. in summer. No seasonal variation in the H_2O content of soft wood occurs. The distribution of H_2O and the seasonal changes in corresponding parts of the tree vary from year to year, but are const. for each species. The effects of girdling on H_2O content and the changes in the rate of penetration of H_2O into logs due to differences in length, barking, and painting are described. Whilst H_2O penetration is chiefly through the ends, gas escape is in a radial direction, so that seasoning followed by end-painting leads to slow H_2O entry.

III. The seasonal and diurnal variations in the H_2O and gas content of trees are in accordance with the demands of the tension hypothesis for the ascent of sap. The reasons for the observed differences in the H_2O content of the various species and the problem of log flotation are discussed. A. L.

Catalase activity as a measure of viability of tree seeds. H. I. BALDWIN (Amer. J. Bot., 1935, 22, 635—644).—Conifer seed of high germinative capacity showed a marked increase in catalase activity due to stimulation in the germinator. The quotient, O_2 evolved by stimulated seed O_2 evolved by resting seed was > 1 in nearly all cases of high viability. A. G. P.

Distribution of enzymes in dormant and germinating wheat seeds. I. Dipeptidase and protease. II. Lipase. L. B. PETT (Biochem. J., 1935, 29, 1898—1904).—I. Dipeptidase (I) and protease (II) activity decrease on drying the seed; the optimum p_H was 7.5 and 5.0, respectively. The small quantities of (I) and (II) in the hull and endosperm are not increased on germination, whereas those in the scutellum and embryo increased greatly. After 12 hr. germination the embryo enzymes decrease and only after 36 hr. do those in the scutellum also.

II. Lipase occurs chiefly in the scutellum and decreases rapidly on germination. The lipase in the

endosperm and embryo passes through a max. 12 hr. after germination. H. D.

Action at a distance of metals on germinating seeds. G. A. NADSON and C. STERN (Compt. rend., 1935, 201, 159—161).—At short distances small metal discs retard the germination of white mustard seeds in the dark. The effect is almost independent of the thickness of the discs, but increases with increasing at. no. of the metal and with increasing surface of the disc, large discs having an effect at greater distances. The effect depends strongly on the radio-activity of the surrounding air, being considerably increased when this contains radon. The radio-activity of the air is regarded as producing a secondary radiation (chiefly β -electrons) from the discs and this retards the growth of the seeds. H. G. M.

Influence of the micro-elements on the distribution of calcium, magnesium, and phosphates in plants. A. P. SCHTSCHERBAKOV (Z. Pflanz. Düng., 1935, 39, 129—140).—Flax grown in cultures to which the micro-elements (B, F, I, Mn, Zn, Al, Cu) were added produced greater growth, higher chlorophyll accumulation, and less leaf dry matter per unit length of stem than when these elements were omitted. Addition of micro-elements increased the % of Ca and Mg in the dry matter of leaves and decreased that in stems. The intake of Mg and PO_4''' per plant was lowered. Differences in distribution of Ca and Mg corresponding with presence or absence of micro-elements are attributable to differences in the form of combination of the bases within the plant, org. compounds predominating when micro-elements are supplied, and inorg. compounds when they are omitted. A. G. P.

Kinetics of penetration. X. Guanidine. A. G. JACQUES (Proc. Nat. Acad. Sci., 1935, 21, 488—492).—Similarly to NH_3 (cf. this vol., 671) guanidine enters *Valonia* cells in combination with an acidic constituent of the sap. H. G. R.

Spectrographic determination of calcium in plant ashes. K. WAY and J. M. ARTHUR (Contr. Boyce Thompson Inst., 1935, 7, 103—112).—Apparatus and technique are described. Accuracy within 5% of that of chemical methods is attainable. A. G. P.

Phosphorus content of marine algæ. P. HAAS and B. RUSSELL-WELLS (Biochem. J., 1935, 29, 1915—1917).—Data for total P of the plant and of aq. extracts are given for *Chondrus crispus*, *Polysiphonia fastigiata*, and *Dilsea edulis*. With aq. extracts, P occurs mainly as esters of H_3PO_4 and varies slightly with the month of collection. F. O. H.

Determination of molybdenum in plants and soils. K. E. STANFIELD (Ind. Eng. Chem. [Anal.], 1935, 7, 273—274).—When > 5 mg. Mo is present it is determined gravimetrically as Pb molybdate by pptn. with $Pb(OAc)_2$ in presence of AcOH and NH_4OAc . For smaller amounts of Mo a colorimetric method is described, based on extraction of the red-coloured Mo thiocyanate by BuOAc. E. S. H.

Gold in Zea mays. B. NĚMEC (Ber. deut. bot. Ges., 1935, 53, 560—562).—Plants from W. Czechoslovakia contain about 0.0001% of Au and As equiv.

to about 0.7% of As_2O_3 . Beans (*Vicia faba*) grown in the same district contain no Au. W. McC.

Chemical composition of the loquat (*Eriobotrya japonica*). C. G. CHURCH and D. G. SORBER (Fruit Products J., 1935, 14, 335—340).—Analyses of loquats (Japanese medlar) are compared with those made by other authors and with analyses of apples.

E. B. H.

Constituents of the bark of *Nerium odorum*, Soland. G. P. PENDSE and S. DUTT (Bull. Acad. Sci. Allahabad, 1934, 3, 209—214).—The dried bark does not contain alkaloids but yields 13.5% of ash (78% of H_2O -sol., 22% of H_2O -insol.). An EtOH extract deposits a white ppt. which, recrystallised from EtOH, has m.p. 97° (carnaubyl coccerate?). Concn. of the EtOH filtrates yielded an essential oil, a tannin, m.p. 240° (decomp.), a phlobaphen, m.p. 120—122°, and a red amorphous pigment. From the mother-liquors after pptn. with EtOH-Pb(OAc)₂, there were obtained *neriodorin*, $\text{C}_{22}\text{H}_{32}\text{O}_7$, m.p. 86—87° (sol. in EtOAc), and *neriodorein*, $\text{C}_{23}\text{H}_{34}\text{O}_{11}$, m.p. 106—107° (insol. in EtOAc), glucosides of which the aglucosones have, respectively, m.p. 68° and 70°. P. G. M.

Surface composition of certain latex particles. L. S. MOYER (Amer. J. Bot., 1935, 22, 609—627).—Latex particles from various plant species varied widely in their resistance to wetting by oil. In *Euphorbia* a protein surface of the latex is associated with high resistance to passage through an oil interface. The phenomena of wetting is discussed in relation to the chemical nature of the particle surface.

A. G. P.

Composition of the latex of *Asclepias cornuti* (Syriaca, L.). I. K. MATZUREVITSCH (J. Appl. Chem. Russ., 1935, 8, 476—487).—The latex contains rubber, inorg. salts, reducing substances (not sugars), esters of aliphatic (AcOH, PrCO_2H , palmitic, cerotic, and erucic acids) and OH-acids with unidentified alcohols ($\text{C}_{20}\text{H}_{35}\text{OH}$, m.p. 137°; $\text{C}_{25}\text{H}_{43}\text{OH}$, m.p. 158—160°; $\text{C}_{28}\text{H}_{47}\text{OH}$, m.p. 180—181°), lecithin, and α - and β -myrrin.

R. T.

Components of Shaohsing-Chiu. Y. WANG (Bull. Agric. Chem. Soc. Japan, 1935, 11, 70).—Formic, acetic, lactic, and succinic acids and histidine have been obtained.

J. N. A.

Seeds of *Plantago ovata* (Isabghol). G. P. PENDSE and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 133—140).—The seeds (5% ash) are free from enzymes and alkaloids and contain 5% of a semi-drying oil having d 0.9212, n_D^{25} 1.4737, sap. val. 181.8, Ac val. 37.7, I val. 116 [oleic acid, 37%; linoleic, 48%; linolenic, trace; saturated acids, 12.5%; unsaponifiable fraction (containing sitosterol), 1.8—2.0%].

F. O. H.

Seed kernels of *Cesalpinia bonducella*. N. GHATAK (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 141—146).—The kernels are free from alkaloids and contain oil (23.9%), amylase, starch, sucrose, a substance, m.p. 107—109°, a bitter principle ("bonducin"), $\text{C}_{20}\text{H}_{28}\text{O}_8$, m.p. 119—120°, $[\alpha] +25.6^\circ$ in EtOH, which is hydrolysed to glucose and a non-bitter substance, m.p. 127—128°.

F. O. H.

Presence of sterols in vesicular cryptogams. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1219).—Sterols are obtained from *Equisetum arvense* and, in small amounts, from *Scolopendrium officinale*, L., and *Cetraria Islandica*.

R. S. C.

Non-heptane constituents of digger pine (*Pinus sabinana*). A. H. UHL (J. Amer. Pharm. Assoc., 1935, 24, 380—382).—*n*-Oct., *n*-non., *n*-dec., and *n*-myrist-aldehydes have been isolated. The presence of *n*-lauric and other aldehydes is indicated.

M. T.

Separation of *n*-nonacosane from myrrh. F. TROST and B. DORO (Annali Chim. Appl., 1935, 25, 227—229).—0.14% of *n*-nonacosane may be obtained by distilling the Et₂O extract in a current of superheated steam.

T. H. P.

Carotenoid content of peaty soils. O. BAUDISCH and H. VON EULER (Arkiv Kemi, Min., Geol., 1935, 11, A, No. 21, 10 pp.).—The exhaustive extraction of various peaty soils with org. solvents is described. Chalk-containing layers adsorb xanthophyll specifically, whilst carotene (0.6 mg. per g. of org. material) is almost exclusively found in other layers.

E. A. H. R.

Pigmentation of the ripening gourd blossom (*Cucurbita pepo*). L. ZECHMEISTER, T. BERES, and E. UJHELYI (Ber., 1935, 68, [B], 1321—1323).—Ripening of the blossoms is accompanied by increase in carotenes and, particularly, in polyene alcohols. The amount of lutein (I) is greatly diminished and that of zeaxanthin (II) is very greatly increased. The isolation of (I), (II), and cryptoxanthin is described.

H. W.

Substance with a blue fluorescence from carrots. F. H. COHEN (Chem. Weekblad, 1935, 32, 441—442).—The aq. extract of carrots containing lactoflavin (I) is acidified (3% HCl) and adsorbed twice on franconite. The second adsorbate when extracted with H_2O -EtOH- $\text{C}_5\text{H}_5\text{N}$ (4:1:1) affords a substance (II) with a strong blue fluorescence, especially in alkaline solution, destroyed reversibly by $\text{Na}_2\text{S}_2\text{O}_4$ and irreversibly by 0.1*N*-NaOH (24 hr.) but not by heating to 60°, which is not due to quinine, α -esculin, or salicylic acid. (II) gives no ppt. with $\text{Pb}(\text{OAc})_2$ or KI-HgI_2 and is not a decomp. product of (I).

S. C.

Yellow colouring matter from the wood of *Adina cordifolia*, Hook.—See this vol., 1129.

Gum of the lemon tree. E. PARISI (Annali Chim. Appl., 1935, 25, 230—236).—Hydrolysis of the gum yields arabinose, galactose, small amounts of a methylpentose, and a uronic acid, but no glucose or xylose.

T. H. P.

Mucilage of *Scaphium affine*, Pierre. H. NAKAHARA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 77—78).—Autoclaving of the mucilage (1.5 hr., 130°) rendered it completely sol. and addition of 95% EtOH pptd. a Ca-Mg salt of pectic acid. Hydrolysis of the free acid with H_2SO_4 yielded galactose, arabinose, and galacturonic and acetic acids. No tetragalacturonic acid was obtained.

J. N. A.

Soluble sugars in *Mercurialis perennis*, L. II. M. BOUILLENNE and R. BOUILLENNE (Bull. Acad.

roy. Belg., 1935, [v], 21, 642—659; cf. A., 1933, 1342).—The sucrose and maltose content of the male plants is greater during the period of growth, but lower during the flowering period, than that of the female plants. F. R. G.

Decomposition in potatoes. III. Ascorbic acid, glutathione, and sugar. E. PFANKUCH (Biochem. Z., 1935, 279, 115—130).—Press juice from normal potatoes contains 0.002—0.005% of glutathione and 0.015—0.020% of ascorbic acid; approx. the same vals. are obtained with diseased potatoes, the increased reducing power being therefore due to increased dehydrogenase activity. Enzymic hydrogenation of dehydroascorbic acid by press juice indicates the function of vitamin-C as an O_2 -carrier. With virus-diseased tubers the ratio sucrose:reducing sugar is increased due to enzymic activity. F. O. H.

Mono-amino-acids of soya-bean protein. S. SASAKI (Bull. Agric. Chem. Soc. Japan, 1935, 11, 78).—The following NH_2 -acids, expressed as wt.-% of protein, have been obtained: glycine (0.23), alanine (4.12), valine (2.56), leucine (10.02), isoleucine (2.38), proline (3.94), phenylalanine (5.21), tyrosine (3.82), aspartic (15.09), glutamic (16.50), and β -hydroxyglutamic (13.20) acids. J. N. A.

Proteins of Indian foodstuffs. VI. Globulins of the cowpea (*Vigna catianga*). K. BHAGOAT (J. Indian Inst. Sci., 1935, 18, A, 39—47).—Determinations of N distribution in four preps. of the globulins of cowpea obtained by dialysis and by $(NH_4)_2SO_4$ pptn. indicate the presence of two cystine-rich fractions. Fractionation of the globulins by $(NH_4)_2SO_4$ pptn. and heat-coagulation is described. A. L.

***Butea frondosa* flowers. Isolation of a crystalline glucoside of butin.** J. B. LAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 262—267).—In addition to a phlobaphen, m.p. 115° (Proc. C.S., 1903, 19, 133), and butein (*ibid.*, 134; J.C.S., 1904, 85, 1463), a diglucoside, butrin (I), $C_{27}H_{32}O_{15} \cdot 2H_2O$, m.p. 193.5°, has been extracted from the dried flowers. (I) loses $2H_2O$ at 120° and is hydrolysed (dil. H_2SO_4) to glucose and butin (*loc. cit.*). (I) is a flavanone derivative. H. G. M.

Isomerisation of cyanogenic heterosides.—See this vol., 1083.

Amygdonitrile glucoside and amygdaloid in plants. V. PLOUVIER (Compt. rend., 1935, 200, 2120—2122).—The glucosides are isolated and characterised by their glucose:HCN ratios. J. L. D.

Hydrocyanic acid in *Pyrocydonia winkleri*. L. D. M. CORNIER (Compt. rend., 1935, 200, 2031—2032).—HCN (0.09%) is extracted from the fresh leaves with H_2O ; *Cydonia vulgaris* contains 0.0116%. After 15 days' growth, the HCN content is 0.0421 and 0.0059%, respectively. J. L. D.

Reaction for *Helvella esculenta* [distinction from other fungi]. G. REIF (Z. Unters. Lebensm., 1935, 69, 585—586).—*H. esculenta* reacts with H_2SeO_3 in H_2SO_4 to give a red colloidal solution of Se, and eventually a red ppt. The substance responsible is present in both pileus and stalk, and is sol. in H_2O .

Of 13 other species of fungi examined, including 3 species of morel, none gave the reaction. E. C. S.

Sex reversal of *Melandrium album* by a fungus. H. ERLÉNMEYER and M. GEIGER-HUBER (Helv. Chim. Acta, 1935, 18, 921—923).—Male sexual hormone could not be detected in the extract from a culture of *Ustilago violacea* although this is able to reverse the sex of female *M. album*. F. R. G.

Biochemical factors of disease-resistance in plants. A. V. V. IYENGAR (Current Sci., 1935, 4, 47—50).—A review.

Pathological and physiological effects of *Erwinia tracheiphila*. E. F. Smith, on species of *Cucurbitaceae*. T. F. YU (Nanking J., 1933, 3, 47—128; Coll. Agric. and Forestry Univ. Nanking, Bull. 5, 82 pp.).—The organism produced acid but no gas from glucose, fructose, galactose, mannose, mannitol, sucrose, glycerol, dextrin, and, feebly, from inulin, starch, lactose, and raffinose. Xylose and arabinose were unattacked. The C but not the N of tyrosine, phenylalanine, and asparagine was utilised. Growth was optimum at p_H 6.75—7.60 and ceased in old cultures at approx. 5.7. No artificial medium was as favourable as those prepared from plant or animal extracts. In beef broth the inhibitory action of NaCl was counteracted by additions of KH_2PO_4 and $MgSO_4$. Neither alone was effective. No evidence was obtained of toxic substances produced by the organism in media or in diseased plants. The latter showed abnormally low transpiration rates and characteristic variations in osmotic pressure in leaves. CH. ABS. (p)

Biochemistry of the spike disease of *Vinca rosea*. A. V. V. IYENGAR (J. Indian Inst. Sci., 1935, 18, A, 61—67).—The stem and leaf-tissue of spiked *V. rosea* compared with that of healthy plants show reduced ash, Ca, and protein contents and increased NH_4^+ , starch, and sugar contents and diastatic activity. The roots of the diseased plants have a reduced N and an increased Ca content. These findings are similar to those obtained in the case of spiked *Z. anoplia* and sandal. A. L.

Changes in tobacco leaves due to "wild-fire" disease. H. LEGATU and L. MAUME (Compt. rend., 1935, 201, 374—376).—The disease produces a decrease in mineral content ($N+P_2O_5+K_2O$), $K_2O:N$ ratio, and K_2O content, whilst the CaO level increases. F. O. H.

Isolation of a crystalline protein possessing the properties of tobacco mosaic virus. W. M. STANLEY (Science, 1935, 81, 644—645).—The cryst. protein, practically insol. in H_2O but sol. in dil. acid, alkali, or salt solutions, has been pptd. by 0.4-saturated $(NH_4)_2SO_4$, by saturated $MgSO_4$, or by safranine, $EtOH$, $COMe_2$, $CCl_3 \cdot CO_2H$, tannic acid, phosphotungstic acid, and $Pb(OAc)_2$ from the juice of infected tobacco plants. The mol. wt. of the protein is of the order of a few millions. 1 c.c. of a 1 to 10^9 dilution of the crystals is usually infectious. Injection of solutions of the crystals into animals causes the production of a precipitin which is active for solutions of the crystals and the juice of infected but not normal plants. Tobacco mosaic virus is regarded

as an autocatalytic protein which, for the present, may be assumed to require the presence of living cells for multiplication. L. S. T.

Filtration of tobacco mosaic virus. H. H. THORNBERRY (Phytopath., 1935, 25, 601—617).—Filtration through Berkefeld "W" candles depended on the p_H of the suspension, being complete at 8.5 and negligible at 1.5. The virus in acid media is adsorbed by the filter and after the filter surface is saturated the filtrate is as infectious as the original material. Such adsorbed virus is eluted by PO_4^{3-} buffer solutions at p_H 8.5. Filtration of virus at p_H 8.5 increased its infectivity by 66%. A. G. P.

Effect of phosphate buffers on infectivity of tobacco mosaic virus. H. H. THORNBERRY (Phytopath., 1935, 25, 618—627).—Infectivity was greatly increased by dibasic phosphates in 0.1M solution. The valency of anion or cation of salts examined was without influence. Optimum activity occurred at p_H 7.0—8.5. Complete inactivation took place in suspensions at p_H 10.6 in 4 hr. and at p_H 11.2 in 5 min. The presence of $Al_2(SO_4)_3$ reduced infection, but adjustment of the reaction to p_H 8.5 restored full activity. A. G. P.

Serological estimate of the absolute concentration of tobacco mosaic virus. K. S. CHESTER (Science, 1935, 82, 17).—It is estimated that the concn. of virus in expressed virus sap is < 0.1 — 1.0 mg. per c.c. Assuming a mol. wt. of 10^5 for tobacco mosaic virus, 1 c.c. of virus sap will contain 6.06×10^{14} — 6.06×10^{15} mols. of virus, and a single min. infective dose on *Nicotiana glutinosa* corresponds with 6 — 60×10^7 mols. of virus antigen. L. S. T.

Rapid combined fixing and staining method for plant chromosome counts. E. BACKMAN (Stain Tech., 1935, 10, 83—86).—Smears, made by Taylor's method, are fixed and stained with Bouin's solution in which picric acid is replaced by anthraquinone and alizarin-red S, with a metallic salt as mordant, is present. The smears are then dehydrated with concns. of aq. EtOH rising to 95%, differentiated in 95% EtOH saturated with picric acid and containing 0.5% H_2SO_4 , washed, cleared, and mounted in xylene-balsam. Root-tips fixed in the above solution may be dehydrated in dioxan, infiltrated, embedded, and sectioned in the ordinary manner. H. W. D.

Syringe hydrogen electrode.—See this vol., 1097.

Determination of bromine in biological material. L. OLSZYCKA (Bull. Soc. Chim. biol., 1935, 17, 852—873).—A review of the methods for the determination of Br and a summary of recent literature on the metabolism of Br. A. L.

Determination of iodine in biological material. V. TREVORROW and G. J. FASHENA (J. Biol. Chem., 1935, 110, 29—38).—Biological material is digested with $K_2Cr_2O_7$, $Ce_2(SO_4)_3$, and $K_2Cr_2O_7$ — H_2SO_4 , the IO_3^- formed is converted into I by H_3PO_3 , and the I is steam-distilled into K_2CO_3 . To the K_2CO_3 —KI solution $NaHSO_3$ and Me-orange are added and H_2SO_4

until just acid after boiling. Br is added and the solution is conc.; KI and starch are added and the free I is titrated with $Na_2S_2O_3$. The method has an error of approx. 10%. H. D.

Determination of iodine in biological substances. C. O. HARVEY (Med. Res. Coun., Spec. Rept. 201, 43 pp.).—A modification of Hurlley's method (Chem. and Ind., 1929, 1246; A., 1932, 1272) is described. The conditions for the destruction of the org. matter with KOH, extraction of the iodide from the ash with EtOH, destruction of nitrite with N_3H , oxidation with $Br-H_2O$, removal of Br, and titration of the I with $Na_2S_2O_3$ solution have been studied and standardised. E. H. S.

Conditions for precipitation of lead chromate in forensic analysis. K. HÖLL (Z. anal. Chem., 1935, 102, 4—7).—Org. matter is destroyed by conc. HNO_3 , excess of acid evaporated off, H_2O added, and H_2S passed in presence of $Cu(NO_3)_2$. The ppt. is dissolved in HNO_3 and treated with $NaOAc$, dil. AcOH, and $K_2Cr_2O_7$. The $PbCrO_4$ is centrifuged off and determined iodometrically. The necessary conditions are: the Pb^{++} solution must be added to the $K_2Cr_2O_7$ and not *vice versa*, and must then be kept for 2 hr. with const. shaking; the concn. of $NaOAc$ or $AcOH$ may not exceed 5%, whilst that of $K_2Cr_2O_7$ must be $< 3\%$. 0.02 mg. of Pb in 15 c.c. of solution can then be satisfactorily determined. S. J. G.

Specific micro-determination of mercury in biological media. M. RANGIER and H. RABUSIER (Compt. rend. Soc. Biol., 1935, 119, 1052—1054).—After destruction of org. matter with $HCl-HNO_3$ and $KClO_3$, $Ca_3(PO_4)_2$ is added if not already present, and the Hg pptd. with NaOH, dissolved in dil. HCl , and, after addition of $CdSO_4$, pptd. with H_2S . The HgS — CdS ppt. is dissolved in dil. $HCl-HNO_3$, nearly neutralised with NaOH, excess of KI is added, and NaOH till alkaline. After removal of $Cd(OH)_2$, Hg is determined colorimetrically with NH_3 . R. N. C.

Spectro-analytically detected elements adsorbed on ferromagnetic colloidal γ -ferric oxide as biological indicators. O. BAUDISCH (Naturwiss., 1935, 23, 512).— γ - Fe_2O_3 retains its ferromagnetic properties in the colloidal state, and may be used as a biological indicator, and for the magnetic separation of living cells of the reticulo-endothelial system. By adding spectrally pure $(C_5H_5N)_4FeCl_2$ to solutions of $Cu(NO_3)_2$, $Zn(OAc)_2$, $BeCl_2$, and $MnSO_4$, colloidal γ - Fe_2O_3 with adsorbed Cu, Zn, Be, and Mn, respectively, is obtained. The use of these enables their location in tissues or isolated cells to be determined spectro-analytically. A. J. M.

Determination of very small quantities of ethyl bromide in biological systems. F. L. HAHN (Compt. rend., 1935, 201, 296—298).—EtBr in animal tissues is determined to within 5% by passing air and H_2O vapour through the heated system and then through a red-hot quartz tube; HBr in the condensate is neutralised, and Br liberated by NH_2Cl is determined colorimetrically (fluorescein). The method can also be applied to Pr^+Br and Pr^+Br . E. W. W.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1935.

General, Physical, and Inorganic Chemistry.

Mathematical representation of the energy levels of the secondary spectrum of hydrogen. II, III. I. SANDEMAN (Proc. Roy. Soc. Edin., 1934—1935, 55, 49—61, 72—84).—II. Analyses of the $1s2s^3\Sigma$ and $1s2p^1\Sigma$ states and vals. of the structural consts. calc. on Dunham's solution of the Schrodinger equation are given (cf. Physical Rev., 1932, [ii], 41, 713). There is little evidence of l -uncoupling for these states. Potential functions are obtained and indicate that the Morse function is not applicable to the two states.

III. On the above basis the mol. consts. of the ground state, $1s1s^1\Sigma$, of H_2 are determined together with those of the ground state, $1s^2\Sigma$, of H_2^+ for comparison. N. M. B.

Gross intensities in electronic bands, with special reference to C_2 (Swan) and N_2 (second positive) systems. N. R. TAWDE (Proc. Indian Acad. Sci., 1935, 2, A, 67—81).—A general survey is given. The Swan systems of C_2 and N_2 are considered relative to conditions of excitation. The probabilities of transition, the temp., and the "centres of intensity" are discussed. Explanations are suggested for unusual intensity features of bands excited in different sources, especially in A. N. M. B.

Theory of $^3\Sigma^+ - ^3\Sigma^-$ transitions in band spectra. R. D. PRESENT (Physical Rev., 1935, [ii], 48, 140—148).—Mathematical. The interpretation of certain faint absorption bands in O_2 , showing Q but not P and R branches, is examined. N. M. B.

Spectrum of aluminium vapour distilled by a tungsten coil in vacuum. E. GAVIOLA and J. STRONG (Physical Rev., 1935, [ii], 48, 136—137).—A W coil, charged with Al, and brought to incandescence in vac. of 10^{-5} mm. Hg, evaporates a cloud of metal which emits a violet-blue light found to be mainly a line spectrum containing Al I, II, W, and impurity lines. The excitation is produced by collisions with electrons from the filament and accelerated by the potential drop across it. λ 3443.6 behaves as an Al arc and not as an Al II line. N. M. B.

Rotational analysis of the S_2 bands. E. W. VAN DIJK and A. T. LAMERIS (Physica, 1935, 2, 785—786).—An analysis of the S_2 bands is given, which disagrees with those of Naude and Christy (A., 1931, 540) and Badger (Physical Rev., 1934, [ii], 46, 1025). The wave functions of the S_2 mol. are symmetrical in the nuclei; the nuclear distance in the final state is 1.73 Å. T. G. P.

Polarisation of resonance radiation of calcium and the effect of weak magnetic fields. A. STEINHAUSER (Z. Physik, 1935, 95, 669—686).—Depolarisation of the 4227 Å. line gives a mean life of 2.2×10^{-8} sec. for the excited level. A. B. D. C.

Infra-red arc spectrum of chromium. C. C. KIESS (J. Res. Nat. Bur. Stand., 1935, 15, 79—85).—The arc spectrum of Cr has been photographed between 7720 and 11,610 Å., about 200 lines being recorded and classified. J. W. S.

Spectrum of molybdenum v. M. W. TRAWICK (Physical Rev., 1935, [ii], 48, 223—225).—The spectrum was excited in a vac. spark and photographed. About 90 lines in the region 2100—400 Å. are tabulated and classified. N. M. B.

Hyperfine structure in silver. H. HILL (Physical Rev., 1935, [ii], 48, 233—237).—Using a hollow cathode source and Fabry-Perot interferometers, 20 lines in the visible region were found to be simple, λ 7688 in the infra-red was very broad, and the resonance lines λ 3383 and 3281 were each double, with the weaker component on the longer- λ side. The average separations were 0.055 in λ 3383 and 0.056 cm^{-1} in λ 3281. The doubling is attributed to a splitting of the 5S level because of nuclear spin, which is probably 3/2. N. M. B.

Spectrum of AgD. P. G. KOONTZ (Physical Rev., 1935, [ii], 48, 138—140).—A quantum analysis is tabulated for the 0,0 and 1,1 bands photographed at high dispersion from a Ag arc in D_2 . B_e is 3.2595 for the lower state. From the corresponding val. for AgH the ratio B_e^H/B_e for the two isotopic mols. is 0.50511, the ratio of the reduced masses being 0.50497. N. M. B.

Spectrum of ionised tellurium, Te III. S. G. KRISHNAMURTY (Proc. Roy. Soc., 1935, A, 151, 178—188).—The 5p, 6p, 5d, and 6s terms in the structure of the Te III spectrum have been identified. The spectrum agrees in its general features with that of Se III, but exhibits marked deviations from the usual interval and intensity rules. The calc. third ionisation potential of Te is approx. 30.5 volts. L. L. B.

Spectrum of trebly-ionised cerium. R. J. LANG (Canad. J. Res., 1935, 13, A, 1—4).—The principal multiplets of the Ce IV spark spectrum are reported. The ionisation potential is 33.3 volts. Further data relating to the ultra-violet spectrum of La III are given. R. S.

Hyperfine structure of the mercury triplet 6^3P_{012} — 7^3S_1 in optical excitation. (MISS) E. E. BOGGS and H. W. WEBB (Physical Rev., 1935, [ii], 48, 226—232).—The relative intensities of the hyperfine structure components of $\lambda\lambda$ 5461, 4358, and 4047 were calc. and checked experimentally. Since the excitation in optically excited Hg vapour is in two steps, the ratio of the intensities of the components due to the less abundant isotopes is $<$ in the normal low-pressure arc. N. M. B.

High-frequency spectrum of mercury vapour. N. B. BHATT (Proc. Indian Acad. Sci., 1935, 1, A, 891—904).—Simple circuits are given, and the spectrum is mapped. A. B. D. C.

Hyperfine structure in bands of mercury hydride. S. MROZOWSKI (Z. Physik, 1935, 95, 524—538). A. B. D. C.

Relation between the electron field emission and the work function of liquid mercury. L. R. QUARLES (Physical Rev., 1935, [ii], 48, 260—264).—The variation in the field necessary to initiate a vac. discharge between a Hg cathode and a Mo anode and the accompanying variation in the work function of the cathode were measured. Results show a more pronounced variation of the field with work function than is required by the Fowler-Nordheim theory. For a change of work function of 1 volt the field required to initiate the discharge varied from 375 to 575 kv. per cm. N. M. B.

Anomalous dispersion in thallium vapour. G. S. KVATER (Physikal. Z. Sovietunion, 1935, 7, 226—244).—The Tl lines 5350, 3775, 3529, and 3519 Å. have been investigated. The doublet 3519, 3529 Å. obeys Dorgelo's rule and $h/k = 4.67 \times 10^{-11}$. R. S.

Interferometer measurements of the hyperfine structure of some lines of singly ionised bismuth. S. SMITH and J. S. BEGGS (Canad. J. Res., 1935, 12, 690—698).—The hyperfine structures of the 6808, 6600, 5719, 5270, 5209, 5144, 4392, 4272, and 4259 Å. lines of Bi II and the 4561 Å. line of Bi III have been examined using quartz and glass Lummer plates. The separation factors of the $6p_15f_{31}14_4$ and $6p_16d_{31}8_1^0$ terms are deduced and the interaction consts. of the $5f_{21}$, $5f_{31}$, and $6d_{21}$ electrons calc. J. W. S.

Transparency of the air between 1100 and 1300 Å. T. LYMAN (Physical Rev., 1935, [ii], 48, 149—151).—The transparency is demonstrated by means of a thermoluminescent screen, the selective sensitivity of the screen and the nature of the Entladungsstrahlen are examined, and a simple method of testing the transparency of LiF crystals is described. N. M. B.

Initiation of the high-frequency discharge [in hydrogen]. J. THOMSON (Nature, 1935, 136, 300). L. S. T.

Gas discharges with an electrolyte as cathode. A. KLEMENC (Z. Physik, 1935, 95, 799—800).—Polemical, against Braunbek (A., 1934, 1281). A. B. D. C.

Gas discharges with an electrolyte as cathode. W. BRAUNBEK (Z. Physik, 1935, 95, 800).—A reply to the above. A. B. D. C.

Discharge processes in gases before breakdown. E. FLEGLER and H. RAETHER (Naturwiss., 1935, 23, 591).—Cloud chamber experiments show that the discharge in gases before breakdown takes place along canals whether the field be homogeneous or inhomogeneous. A. J. M.

Faraday dark space. K. G. EMELEUS (Proc. Roy. Irish Acad., 1935, 42, A, 31—36; cf. this vol., 556).—Qual. evidence is given that the Faraday dark space need not be traversed by fast electrons, and that diffusion in a combined electric field and concn. gradient can account for part of the conductivity, but that, in some cases, effects due to short- λ resonance radiation reaching the dark space from the negative glow, and propagated rectilinearly and not by diffusion, may be of importance electrically and optically. N. M. B.

Intensities of satellites of $K\alpha$. (MISS) A. W. PEARSALE (Physical Rev., 1935, [ii], 48, 133—135).—Intensities of $K\alpha_1$ satellites were measured and plotted for elements of the at. no. range 16—29; they are, in general, $<$ for $L\beta_2$ satellites. N. M. B.

K Series X-ray emission lines of manganese in several compounds. S. TANAKA and G. OKUNO (Japan. J. Physics, 1935, 10, 45—48).—The effect of chemical combination on the $K\alpha_1$, α_2 , β_1 , β' lines of Mn was studied with MnO , $MnCO_3$, $KMnO_4$, $Mn(OAc)_2$, and $MnSO_4$. Appreciable shifts were found for the $K\beta_1$ and $K\beta'$ lines, but scarcely any effect for the $K\alpha$ doublet. N. M. B.

Absorption and scattering of X-rays. D. BLOCHINZEV and F. HALPERIN (Physikal. Z. Sovietunion, 1935, 7, 175—188).—The absorption coeff. calc. for the K electron level in metals is in agreement with experimental data. The scattering coeffs. of Ca, Ni, and Al in the region of shorter $\lambda\lambda$ have been derived and increase with the at. no. R. S.

Excitation potential of the X-ray satellites in the L series. D. COSTER, H. H. KUIPERS, and W. J. HUIZINGA (Physica, 1935, 2, 870—878).—The doubly ionised state $L_{III}M_{IV,v}$ responsible for the satellites on the short- λ side of the $L\alpha_1$ line is mainly due to the radiationless transition $L_{II} \rightarrow L_{III}$ with the ejection of an M-electron. T. G. P.

Lines of the M series of niobium to silver. H. KIESSIG (Z. Physik, 1935, 95, 555—573). A. B. D. C.

Double electron transitions in X-ray spectra. F. BLOCH (Physical Rev., 1935, [ii], 48, 187—192).—Elementary processes are examined in which simultaneous transitions of an inner and an outer at. electron result in the emission of one light quantum. Assuming the nuclear distance of the inner electron to be small compared with that of the outer electron, expressions are developed for the probability of double transitions by dipole radiation. The Cu $K\alpha_2$ satellite illustrates the case where the inner transition alone occurs by dipole emission. N. M. B.

Calculation of X-ray terms according to Heisenberg's theory on electron holes. G. ARAKI (Sci. Rep. Tokyo Bunrika Daigaku, 1935, A, 2, 189—216).—The numerical vals. of K -terms and their screening consts., calc. for all atoms, are in good agreement with experiment. N. M. B.

Ionisation of a gas at different pressures by photon and corpuscular radiation. J. CLAY (Physica, 1935, 2, 811—816).—Quant. relationships between incident radiation, pressure, and ionisation are developed which satisfy the experimental results (this vol., 426). T. G. P.

Ionisation potentials calculated with the Thomas-Fermi equation and Dirac exchange correction. L. HULTHÉN (Z. Physik, 1935, 95, 789—795). A. B. D. C.

Molecular orientation and the probability of dissociation of molecules by electron impact. N. SASAKI and T. NAKAO (Nature, 1935, 136, 260).—The probability of the dissociation of H_2 mols. increases rapidly as the mol. axis approaches from the perpendicular position that parallel to the electron beam. A diagram of the apparatus used in measuring the angular distribution of resulting ions is given. L. S. T.

Elastic scattering of electrons in krypton. A. L. HUGHES and S. BILINSKY (Physical Rev., 1935, [ii], 48, 155—160; cf. this vol., 557).—The calc. scattering coeffs. agree satisfactorily with experiment for electron energies 250, 350, and 510 volts, and less so for those of 780 and 950 volts. N. M. B.

Collision efficiency of slow electrons and inert gas atoms. H. MAIER-LEIBNITZ (Z. Physik, 1935, 95, 499—523).—Measurements of collision efficiency, accurate to within 20%, have been obtained for He, Ne, and A. A. B. D. C.

Production and focussing of intense positive-ion beams. M. A. TUVE, O. DAHL, and L. R. HAFSTAD (Physical Rev., 1935, [ii], 48, 241—256).—A high-intensity source of positive ions using a gaseous low-voltage arc constricted by a metal capillary, and the focussing of weak and intense beams by various electrostatic lens arrangements are described and quantitatively examined. N. M. B.

Platinum isotopes and their nuclear spin. B. VENKATESACHAR (Proc. Indian Acad. Sci., 1935, 1, A, 955—960).—The isotopes of Pt are 196, 195, 194, and 192. The nuclear spin of the odd isotope is $1/2$. A. B. D. C.

Isotope abundance in platinum. B. VENKATESACHAR and L. SIBAIYA (Proc. Indian Acad. Sci., 1935, 2, A, 101—103).—The relative abundance is estimated from an analysis of the microphotograms of the structure pattern of Pt λ 3408.13. Assuming a positive isotope shift the results are: Pt^{196, 195, 194, 192}, abundances 16, 13, 10, ~ 2 , respectively. At. wt. divergences are discussed. N. M. B.

Periodic system of the stable isotopes and the relation of the mass and charge of the nuclei. J. SELNOV (Physikal. Z. Sovietunion, 1935, 7, 82—98).—Empirical formulæ are proposed for the relation between the mass no. (A), at. no. (N), and no.

of neutrons (n) for stable isotopes, the nuclei of which are considered to consist entirely of neutrons and protons. For odd elements, $A=3N-2\alpha+\beta$ (approx.), $n=2(N-\alpha)+\beta$, where α =no. of single isotopes, and β is the pleiade no., and =0 or 2. For even elements $A=3N-2\alpha+1+\beta$ (approx.), and $n=2(N-\alpha)+1+\beta$, where $\beta=\pm 0, 1, 2, 3, 4, 5, 6, 7$, for A and $\pm 0, 1, 3, 5, 7$, for n . A system of isotopes exhibiting periodicity (perhaps due to a shell structure of the nucleus) is built up from these formulæ. In agreement, the mass defect curve, calc. according to the formula (mass of protons and neutrons—at. wt.)/at. no., is periodic. On dividing the mass defect by $N+n/2$ a curve is obtained on which isotopes of a single element are represented as a single point, with a step-like character the periodicity of which coincides with that of the calc. isotopic system. New isotopes, and the no. of single isotopes, may be predicted, and isotopes not included have been found to be radioactive. R. S. B.

Deuterium. I. D. MACGILLAVRY (Chem. Weekblad, 1935, 32, 490—493).—A review. D. R. D.

Radioactivity of the earth's crust and its influence on cosmic-ray electroscope observations made near ground level. R. D. EVANS and R. W. RAITT (Physical Rev., 1935, [ii], 48, 171—176).—Ra analyses of 23 rock specimens from the scene of cosmic-ray observations show a linear relation between the average Ra content and the local γ -ray ionisation in the cosmic-ray electroscope; this indicates that ionisation due to γ -rays arising from impact or reflexion of cosmic rays by the earth's crust is negligible, and the Th/U ratio is approx. const. An expression is found for the γ -ray ionisation above a radioactive surface. N. M. B.

Radioactivity of potassium. K. SITTE (Nature, 1935, 136, 334—335).—The existence of a rare isotope, ^{43}K , which is transformed into ^{40}Ca , is the only assumption which agrees with the available evidence. The radiation of K shows no track of positively-charged particles in a cloud chamber. L. S. T.

Half-lives of potassium, rubidium, neodymium, and samarium. A. RUARK and K. H. FUSSLER (Physical Rev., 1935, [ii], 48, 151—154).—The suggestion that the long apparent half-lives of K, Rb, and Nd are due to isotopes of small abundance having half-lives small in comparison with the apparent ones is examined. Using data on the relative abundance of the elements it is shown that the half-life of the active fraction of K is $>10^7$ years, and, correspondingly for Rb, Nd, and Sm, $>10^8$ years. The activities may be due to small radioactive fractions of well-known isotopes. N. M. B.

Absence of natural β -ray radioactivity from beryllium. E. FRIEDLANDER (Compt. rend., 1935, 201, 337—339).—Carefully purified Be salts show no β - or γ -ray activity. This is in agreement with Aston's measurements of the masses of light nuclei and with the results of artificial transmutation, which indicate that the energy of disintegration of the Be atom is of the order of 10^6 e.v. J. W. S.

Ionisation currents produced by radon, Ra-A, and Ra-C' in cylindrical ionisation chambers. R. D. EVANS (Physical Rev., 1935, [ii], 48, 177—186).—An expression is derived for the ionisation produced in cylindrical ionisation chambers by Rn and its decay products, and is confirmed experimentally. Equations are also derived for α -ray ionisation above a plane surface due to a homogeneous radioactive substance below the plane, a radioactive substance uniformly distributed on a wire normal to the plane, and for the ionisation outside a dihedral angle enclosing the radioactive substance. N. M. B.

Radiative capture of protons by carbon. G. BREIT and F. L. YOST (Physical Rev., 1935, [ii], 48, 203—210).—Mathematical. The theoretical yield in the reaction $C^{12} + H^1 \rightarrow N^{13} + \gamma$ is $>$ that observed by a factor approx. 1000. Modifications of the calculation are examined. The γ -ray yield expected in the bombardment of Be⁹ by protons is calc. N. M. B.

Yield of α -particles from lithium films bombarded by protons. R. G. HERB, D. B. PARKINSON, and D. W. KERST (Physical Rev., 1935, [ii], 48, 118—124).—Abs. yields from a thick Li target were determined for proton energies up to 400 kv. For thin films the yield increases linearly in the voltage range 180—400 kv.; there is no indication of resonance levels. N. M. B.

Transformation of chemical elements by bombardment with hydrogen nuclei. F. KIRCHNER (Chem.-Ztg., 1935, 59, 713—716).—A review. A. J. M.

Cloud-chamber studies of the γ -radiation from lithium bombarded with protons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 48, 125—133).—The spectrum, investigated by a cloud chamber operating in a magnetic field of 2000 gauss, consists of at least 11 lines, the highest of which is 16 me.v. The voltage excitation curve max. for the γ -radiation is at 650 kv. proton energy. The division of energy between the members of electron pairs arising from absorption, the ratio of positive to negative electrons, and an interpretation of results are examined. N. M. B.

Lower limit of the nuclear photo-effect in beryllium. L. ARZIMOVITSCH and P. PALIBIN (Physikal. Z. Sovietunion, 1935, 7, 245—254).—Neutrons could not be produced from Be⁹ by γ -radiation from an X-ray tube using tensions $>$ 1350 kv. This is contrary to the results of Gentner (this vol., 141). R. S.

Secondary γ -rays excited by the passage of neutrons through matter. D. E. LEA (Proc. Roy. Soc., 1935, A, 150, 637—668).—When neutrons pass through matter, γ -rays are produced. The quantum energies of the radiation are $3\text{--}4 \times 10^6$ volts for H₂, and 1.5×10^6 volts for Pb and Fe. The origin of the radiation is discussed; nuclear excitation appears to be the most plausible explanation in most cases. L. L. B.

Slowing down of neutrons in various substances containing hydrogen. T. BJERGE and C. H. WESTCOTT (Proc. Roy. Soc., 1935, A, 150, 709—728).—Measurements have been made of the

effect of slowing down neutrons in various substances containing H, and of the scattering and absorption of slow neutrons by various nuclei. The results indicate that the majority of the neutrons slowed down in H₂O or paraffin oil have acquired gas-kinetic velocities. The cross-sections for scattering of such slow neutrons are 3×10^{-23} cm.² for the H nucleus, and about 3×10^{-24} cm.² for C and O₂. The cross-sections for absorption are 1.2×10^{-21} cm.² for B, $< 2 \times 10^{-24}$ cm.² for N₂, about 4×10^{-25} cm.² for O₂ and C, and about 2×10^{-25} cm.² for H₂. L. L. B.

Interaction of neutrons with matter. J. R. DUNNING, G. B. PEGRAM, G. A. FINK, and D. P. MITCHELL (Physical Rev., 1935, [ii], 48, 265—280).—The interaction of fast and slow neutrons with matter was investigated. The anomalous effects of slow neutrons were not observed with the lowest-energy neutrons detectable through projected electrons. A Cd shutter with Li ion-chamber permits separation of fast and slow neutron effects. The production of slow by collisions of fast neutrons with H nuclei was studied by using paraffin, H₂O, and D₂O. H₂O is about 5.5 times as effective as D₂O in producing slow neutrons. Investigation of the thermal equilibrium of slow neutrons showed that, in the range 95—373° abs., the change in the no. of disintegrations of Li and in the absorption of Cd was small. Neutron-nucleus collision cross-sections for fast neutrons plotted against at. wt. give a smooth curve indicating increasing nuclear radii with at. wt. Neutron-nucleus collision cross-sections for slow neutrons are tabulated for a large no. of elements. Investigation of elastic scattering of slow neutrons shows that the large neutron-nucleus cross-sections are due to neutron capture and not to elastic scattering. N. M. B.

Induced radioactivity of fluorine and calcium. O. R. FRISCH (Nature, 1935, 136, 220).—Bombardment of NaF and LiF with α -rays gives a radioelement, probably Na²², of half-period $>$ 6 months, emitting positrons of approx. 2×10^5 e.v. mean energy. Ca gives a radio-element, probably Sc⁴³, with a half-period of 4.4 ± 0.4 hr., emitting positrons with an Al half-val. thickness of approx. 0.06 g. per cm.² No short-period activity, corresponding with the intermediate formation of Ti⁴³, could be detected. L. S. T.

β -Ray spectra of artificially-produced radioactive elements. A. I. ALICHANOV, A. I. ALICHANIAN, and B. S. DŽELEPOV (Nature, 1935, 136, 257—258).—The half-life periods and the max. energy of the electrons emitted by 14 radioactive elements obtained by neutron bombardment are recorded. The results do not agree with Fermi's theory of β -ray decay nor do they fit Sargent's diagram. L. S. T.

Beta processes and nuclear stability. G. BECK (Nature, 1935, 136, 257).—A discussion. L. S. T.

Velocity of "slow neutrons." O. R. FRISCH and E. T. SØRENSEN (Nature, 1935, 136, 258).—Many of the neutrons from a Be+Rn source probably have velocities of the order of 2×10^5 cm. per sec. after passage through paraffin wax. The main part

of those slow neutrons which are strongly absorbed in Cd have very nearly thermal velocities. L. S. T.

Coincidence method for investigating nuclear processes. H. J. VON BAERER (Z. Physik, 1935, 95, 417—439). A. B. D. C.

Nature of cosmic rays. J. CLAY (Proc. Roy. Soc., 1935, A, 151, 202—210).—Theoretical. Evidence is adduced that one or more intermediate photon radiations exist between the primary radiation, which is wholly corpuscular, and most of the corpuscles observed in ionisation chambers, or in counters, or in the Wilson chamber. L. L. B.

Cosmic ray ions and the shower producing radiation. F. H. NEWMAN and H. J. WATKINS (Phil. Mag., 1935, [vii], 20, 263—266). A. J. M.

Sommerfeld's fine structure constant. H. ERTL (Z. Physik, 1935, 95, 775—777).—Theoretical. A. B. D. C.

Formation of electron-positron pairs by internal conversion of γ -radiation. M. E. ROSE and G. E. UHLENBECK (Physical Rev., 1935, [ii], 48, 211—223).—Mathematical. The probability of production of an electron and positron by the spherical γ -wave emitted from a nucleus is examined by approximation methods. N. M. B.

Calculation of pair creation by fast charged particles and the effect of screening. H. J. BHABHA (Proc. Camb. Phil. Soc., 1935, 31, 394—406).—Mathematical. W. R. A.

Properties of dipole and quadrupole radiation from nuclei. H. M. TAYLOR (Proc. Camb. Phil. Soc., 1935, 31, 407—415).—The types of radiation emitted by a quantum-mechanical system when a spinless radiating particle changes its azimuthal quantum no. by 2, 1, or 0 have been examined mathematically. W. R. A.

Diamagnetism of the Dirac electron. II. T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 109—115; cf. A., 1934, 1054).—Mathematical. J. W. S.

Elements of the quantum theory. III. Problems of potential barriers. S. DUSHMAN (J. Chem. Educ., 1935, 12, 326—336; cf. this vol., 1050). L. S. T.

Difference in inner pressure of the condensed hydrogen isotopes. H. CLUSIUS and E. BARTHOLOME (Z. Elektrochem., 1935, 41, 487—488; cf. this vol., 155). T. G. P.

Hydrogen atom and non-Euclidian geometry. V. FOCK (Bull. Acad. Sci. U.R.S.S., 1935, 169—188).—Mathematical. J. W. S.

Transport phenomena and quantum mechanics. A. GANGULI and P. MITRA (Current Sci., 1935, 4, 22—23).—A wave-mechanical treatment is applied to transport phenomena in various stars. W. R. A.

Exact solutions of the Schrodinger equation. M. F. MANNING (Physical Rev., 1935, [ii], 48, 161—164).—Mathematical. N. M. B.

Matrix elements for alkali metals. A. THOMAS (Z. Physik, 1935, 95, 539—554).—Mathematical. A. B. D. C.

Alkali metals. P. GOMBAS (Z. Physik, 1935, 95, 687—691).—Lattice const., lattice energy, and compressibility are determined theoretically for the K lattice. A. B. D. C.

Quantum levels of neutrons in the nucleus. T. HIKOSAKA (Sci. Rep. Tohoku, 1935, 24, 208—221).—The energy vals. of the quantum states of neutrons, deduced from a simplified nuclear model, are in accord with observed vals. The theory explains periodicity in nuclear structure. J. W. S.

Neutrino theory of light. II. R. DE L. KRONIG (Physica, 1935, 2, 854—860).—Theoretical discussion. A. J. M.

Calculations of atomic wave functions. IV. Results for F', Al^{III}, and Rb'. D. R. HARTREE (Proc. Roy. Soc., 1935, A, 151, 96—105).—A continuation of previous work (A., 1933, 1101). L. L. B.

Electron conductivity and lattice stability of binary crystals. T. NEUGEBAUER (Z. Physik, 1935, 95, 717—733).—Theoretical. Polarisation energies are calc. A. B. D. C.

Molecular emission spectra of some metallic salts. P. MESNAGE (Compt. rend., 1935, 201, 389—391; cf. this vol., 1051).—The majority of the bands in the spectra of CoCl₂, CrCl₃, FeCl₂, and FeCl₃ may be attributed to diat. mols. CoCl, CrCl, and FeCl, but a series of ultra-violet bands of FeCl₂ and FeCl₃ may be due to FeCl₂ mols. J. W. S.

Representation of statistical distributions by continuous spectra. T. H. HAZLEHURST, jun., and W. H. KELLEY, jun. (J. Chem. Educ., 1935, 12, 309—313).—The method elaborated has been applied to the representation of Maxwellian distribution of mol. velocities, electron density in the H atom, black-body radiation, phase space for a unidimensional gas, and particle density in the classical and quantised linear harmonic oscillator. L. S. T.

New interpretation of the structure of band spectra. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 92—100).—A suggested process of electronic excitation of mols. leads to a new interpretation of band structure. Calc. and observed oscillation frequencies are in good agreement. N. M. B.

Band spectra of calcium hydride. III. B. GRUNDSTROM (Z. Physik, 1935, 95, 574—587). A. B. D. C.

Absorption and fluorescence measurements of cadmium and zinc halides in the vapour phase. E. OESER (Z. Physik, 1935, 95, 699—716).—CdI₂ shows five, ZnI₂ three, and CdBr₂ two absorption max., and CdCl₂, ZnBr₂, and ZnCl₂ show only continuous absorption. The iodides and CdBr₂ show fluorescence, but the others do not, in agreement with all these halide mols. being atom mols. A. B. D. C.

Absorption spectrum of stannous sulphide. G. D. ROCHESTER (Proc. Roy. Soc., 1935, A, 150, 668—684).—The absorption spectrum of SnS has been analysed up to 1200°. The analysis is consistent with the assumption that the absorbing mol. is the chemical mol. SnS, and there is no evidence that any of the bands are due to the oxidation products of

SnS or to S₂. Evidence relating to Sn isotope effects is discussed. L. L. B.

Near ultra-violet absorption bands of SO₂. R. K. ASUNDI and R. SAMUEL (Proc. Indian Acad. Sci., 1935, 2, A, 30—45).—Additional data and classifications of bands are tabulated. Provisional analyses, with the help of Raman and infra-red data, are given. N. M. B.

Fine structure analysis of the red bands of magnesium oxide and isotope effect. P. C. MAHANTI (Indian J. Physics, 1935, 9, 455—486).—Measurements of the structure lines in the (0,1), (0,0), (1,0), and (2,0) bands and combination differences are tabulated. Each band has two strong *P* and *R* branches associated with Mg²⁴O, usually accompanied by fainter components due to Mg²⁵O and Mg²⁶O. The *P* and *R* branches are single; the system is due to a ¹Σ→¹Σ transition. The principal mol. consts. evaluated from rotational term differences are given. N. M. B.

Band spectra of AgO and CuO. F. W. LOOMIS and T. F. WATSON (Physical Rev., 1935, [ii], 48, 280—282).—The spectra obtained by arcing between metal electrodes in O₂ at reduced pressure were photographed. Data and a vibrational analysis are given for the ultra-violet and blue system of AgO; a system in the far red was too faint for measurement. The red system of CuO is discussed. N. M. B.

Scandium oxide bands in the spectra of cold stars. (MLLE.) E. BODSON (Bull. Acad. roy. Belg., 1935, [v], 21, 535—541).—Interpretation of the bands by Russell's method (Astrophys. J., 1933, 77, 345) is in satisfactory agreement with the results of Swing's (cf. A., 1934, 125). N. M. B.

Pleochroism of crystals of rare-earth salts as evidence of the non-rotation of certain electronic orbits. E. E. JELLEY (Nature, 1935, 136, 335—336).—The absorption spectra for various vibration directions in crystals of Nd, Pr, Sm, and Ce NH₄ sulphates have been determined. With Nd and Pr sulphates, light of certain λλ is not absorbed when its plane of direction is in certain sp. directions, indicating that the orbits of at least some of the *N* electrons are fixed in relation to the crystal structure. Probably the metal ions as a whole are incapable of free rotation. L. S. T.

Theory of co-ordinate linking. VII. Absorption spectra of some complex ions. R. SAMUEL, M. ZAMAN, and A. W. ZUBAIRY (Indian J. Physics, 1935, 9, 491—505; cf. this vol., 427).—Data and deductions from curves for absorption spectra of some complex salts in solutions containing KCl, KBr, NaCl, Na₂CO₃, HCl, and HBr are: K₄[Cr(CN)₆], deformation of mol.; K₂[Pd(CN)₄], mol. Stark effect only, due to positive ion; K[Cu(CN)₂], probably the same; H₂PtCl₆, true complex salt. Data and curves are also given for aq. solutions of [Co(NH₃)₄CO₃]Br, [Co(NH₃)₄(NO₂)₂]Cl, [Co(NH₃)₄(NO₂)₂](NO₃), [Co(NH₃)₄CO₃](NO₃).0.5H₂O, [Co(NH₃)₅Cl]SeO₄, K₂Pd(CN)₄, KCu(CN)₂, and K₄Cr(CN)₆, the three last-named in solutions of NaCl, KCl, and Na₂CO₃. Deductions are discussed. N. M. B.

Perturbation and predissociation in the b³Σ term of the CO band spectrum. L. GERO (Z. Physik, 1935, 95, 747—751). A. B. D. C.

Electronic structures of polyatomic molecules. VII. Ammonia and water type molecules and their derivatives. VIII. Ionisation potentials. IX. Methane, ethane, ethylene, and acetylene. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 506—514, 514—517, 517—528).—VII. From spectroscopic and ionisation potential data electron configurations in terms of mol. orbitals are obtained for NH₃, PH₃, H₂O, H₂S, and their derivatives. The longest-λ ultra-violet spectra and min. ionisation potential are ascribed in NH₃ derivatives to excitation of a nearly non-linking electron of the N atom, and in H₂O and H₂S derivatives to excitation of a non-linking O or S atom electron.

VIII. The differences between observed and predicted vals. for ionisation potentials of non-linking electrons are due mainly to charge-transfer effects.

IX. Observed ionisation potentials are interpreted with the aid of the electron configurations for the normal states of C₂H₆, C₂H₄, and C₂H₂. Excited orbitals are discussed. R. C.

Absorption spectra of hydrogen cyanide, hydrazine, ethylene, and ammonia in the Schumann region, and of hydrazine in the quartz ultra-violet. H. J. HILGENDORFF (Z. Physik, 1935, 95, 781—788).—HCN shows bands between 2000 and 1790 Å., C₂H₄ predissociation bands near 1800 Å. with a heat of dissociation of 158.6 kg.-cal. per mol., and N₂H₄ continuous absorption. The ultra-violet measurements on N₂H₄ give heat of dissociation of 122.4 kg.-cal. per mol. A. B. D. C.

Absorption spectrum of methyl iodide. N. S. BAYLISS (Nature, 1935, 136, 264).—No bands were found in the spectrum through 6.6 m. of gaseous MeI at 220 mm. Continuous absorption extends to 3600 Å., but a band system is possible. The absorption limits in equiv. columns of gaseous and liquid MeI (6.6 m. at 220 mm. and 0.6 cm., respectively) occur at approx. the same λ. The determination of absorption limits by extrapolation from results obtained with short columns of gas may lead to erroneous vals., which have no thermochemical significance. L. S. T.

Absorption spectra of some polyatomic molecules containing methyl and ethyl radicals. H. W. THOMPSON (Proc. Roy. Soc., 1935, A, 150, 603—614; cf. A., 1934, 828).—Measurements have been made of the absorption spectra of ZnMe₂, ZnEt₂, HgEt₂, PbEt₄, GeMe₄, NMe₃, NEt₃, PEt₃, Et₃S, Me₂O, Et₂O, and EtSH. Most of the mols. examined show continuous absorption in the ultra-violet region, but ZnEt₂ and HgEt₂ have diffuse bands. An attempt is made to analyse these. L. L. B.

Electron affinity of free radicals. VIII. Diphenylanisylmethyl and the colour of its sodium addition compound. H. E. BENT and M. DORFMAN. IX. Pentaphenylethyl and triphenyldiphenyl-ethyl. M. DORFMAN (J. Amer. Chem. Soc., 1935, 57, 1452—1455, 1455—1459; cf. this vol., 1058).—VIII. The extinction coeff. of solutions of diphenylanisyl-

methyl (*R*) and the val. of ΔF for the reaction of *R* with Na have been determined. The results are consistent with the reactions $R + Na = NaR$ and $NaR + R = NaR_2$. The second reaction is somewhat erratic.

IX. ΔF for the addition of Na to pentaphenylethyl and triphenyldiphenylethyl in Et_2O solution has been determined. E. S. H.

Absorption spectra of α - and β -carotenes and lycopene. E. S. MILLER, G. MACKINNEY, and F. P. ZSCHEILE, jun. (Plant Physiol., 1935, 10, 375—386).—Curves showing absorption over the range 3900—5300 Å. are given. Carotenes from different localities separated on different adsorbents [MgO and $Ca(OH)_2$] yielded identical products. A. G. P.

Spectroscopy of an enzyme reaction. K. G. STERN (Nature, 1935, 136, 335).—When EtH peroxide is added to an active prep. of liver catalase at pH 7, the enzyme spectrum immediately disappears and two new green absorption bands appear. After a few min. these bands decrease in intensity and the original spectrum simultaneously reappears. The cycle can be repeated by addition of fresh substrate. At 4° , the time required for the cycle is 4 times that at 24° . The reappearance of the enzyme spectrum is accompanied by the disappearance of titratable peroxide O from the system. No gas is evolved in this reaction. The spectrum of the intermediate compound is attributed to a combination of enzyme with substrate, 5×10^5 mols. of substituted peroxide per enzyme mol. being required to complete the transformation into the intermediate compound. With H_2O_2 as substrate, no apparent change of the enzyme spectrum is observed. L. S. T.

Significance of the isotope effect in the analysis of the vibration spectra of organic molecules. E. BARTHOLOMÉ and H. SACHSSE (Z. Elektrochem., 1935, 41, 521—522).—The isotope effects resulting from the substitution of H by D in a mol. allows important conclusions to be reached concerning the particular portions of the mol. responsible for the vibrational spectrum concerned, even when the mol. is too complicated to permit a quant. interpretation. Results obtained by substituting D in MeOH and C_2H_6 are discussed. T. G. P.

Optical investigations of the constitution of glasses. Transformation point and boric acid anomaly. W. WEYL (Z. Elektrochem., 1935, 41, 472—476).—Absorption spectra show that the transformation point is not a true "transition point." Ni and Co have been used as indicators in the spectroscopic investigation of the chemical effects resulting from the addition of B_2O_3 to a Na borosilicate glass. The influence of B_2O_3 on the physical properties of glasses is discussed. T. G. P.

Investigations in the infra-red. I. Absorption spectrum and molecular structure of borates. M. K. SEN and A. K. S. GUPTA (Indian J. Physics, 1935, 9, 433—443).—Results of investigations on the borates of Li, K, Ca, Mn, Cu, and Pb in the range 5 — 15μ agree with the predictions of Cassie (cf. this vol., 281). The val. of the true force const. of the radical compared with that of CO_3 and NO_3 shows that the linking is not localised as in BCl_3 ; the plane

configuration is not due to repulsion of the O ions alone and follows the central quantisation more closely than NO_3 or CO_3 . N. M. B.

Quantitative studies of the infra-red absorption of organic compounds containing NH and OH groups. O. R. WULF and U. LIDDEL (J. Amer. Chem. Soc., 1935, 57, 1464—1473).—Results in the region 1.65 — 1.35μ are given for many org. compounds, containing NH, NH_2 , and OH groups, in CCl_4 solution. The origin of the spectra and the applicability to the detection of particular groups and the determination of some types of org. mols. are discussed. E. S. H.

Far ultra-violet absorption spectra and ionisation potentials of benzene and deuterobenzene. W. C. PRICE and R. W. WOOD (J. Chem. Physics, 1935, 3, 439—444).—The spectra of both substances, measured at 2000 — 1000 Å., are similar, strong continuous absorption at 1840 — 1600 Å. being followed by sharp bands down to about 1360 Å. An ionisation potential of 9.190 ± 0.005 volts is deduced for C_6H_6 , and that of C_6D_6 is about 3×10^{-4} volt greater. All the electronic states are split up into patterns believed to be due to true electronic multiplicity. From more diffuse bands below 1360 Å. the second ionisation potential of C_6H_6 is estimated at 11.7 ± 0.3 volts. R. C.

Near infra-red spectrum of deuterobenzene. R. B. BARNES and R. R. BRATTAIN (J. Chem. Physics, 1935, 3, 446—449).—The transmission spectrum has been examined from 1 to 13.25μ . The shifts of the infra-red active vibrations agree with a plane hexagon model for C_6H_6 (cf. A., 1934, 928). The transmission spectra of C_6H_6 and thiophen from 1 to 15μ have been observed. R. C.

Raman spectrum of deuterobenzene. R. W. WOOD (J. Chem. Physics, 1935, 3, 444—445).—The Raman spectrum of C_6D_6 and new lines in that of C_6H_6 have been observed. The shifts of the lines are discussed. R. C.

Linking energies from Raman frequencies and thermochemical data. K. S. G. DOSS and M. P. V. IYER (Current Sci., 1935, 4, 25—26).—Discrepancies between the linking energy val. calc. from Raman and thermochemical data for Se_2O and S_2O are discussed. From the Raman frequencies of $SeO_4^{''}$, $SeO_3^{''}$, $SO_4^{''}$, and $SO_3^{''}$ the heat of formation of $H_{(aq)}$ is calc., but the vals. are not concordant, and it is therefore suggested that Raman data can be employed to calculate heat of formation of mols., but not of ions. W. R. A.

Raman spectra of arsenic trichloride and of its mixtures. A. E. BRODSKII and A. M. SACK (J. Chem. Physics, 1935, 3, 449—451).—The Raman frequencies of C_6H_6 , CCl_4 , MeOH, or EtOH are unchanged on admixture with $AsCl_3$, but those of $AsCl_3$ decrease in presence of MeOH or EtOH. It is suggested that for the frequencies of one component of a mixture to be shifted by the other the latter must have a considerable dipole moment, and in the former the linking between the parts of the mol. participating in active vibrations, here As—Cl, must be weak. The

const. of the AsCl_3 mol. have been calc. and agree with electron-diffraction data. R. C.

Raman spectra. II. Raman spectra of perchloric acid and nitrosyl perchlorate. W. R. ANGUS and A. H. LECKIE (Proc. Roy. Soc., 1935, A, 150, 615—618).—Raman spectra of 60% HClO_4 , solid NOClO_4 , and solutions of NOClO_4 in HClO_4 of varying concn. have been obtained. The spectrum of NOClO_4 is similar to that of HClO_4 , with the addition of a strong displacement at 2329 cm^{-1} assigned to the NO^+ group. This confirms the val. previously found for this group in $(\text{NO})_2\text{SO}_4$ (cf. this vol., 1056). L. L. B.

Raman spectrum of carbon disulphide. A. V. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 46—53).—A detailed investigation of the intensity and polarisation characters of the Raman lines is described. The Q branch of the principal vibration line 656 cm^{-1} cannot be separated from the PP and RR branches; in these the intensity distribution is similar to that in the wings accompanying the Rayleigh lines in liquids. When excited by $\lambda\ 4358$ the depolarisation of the line is 0.15, increasing to 0.2 if excited by $\lambda\ 4046$. The ratio of intensities of the peaks of 656 and 796 Raman lines is 9.2. N. M. B.

Carbon isotope in Raman scattering. I. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 86—91).—The principal Raman lines in C_6H_6 , cyclopropane, and C_3H_6 of frequency shifts 992, 1188, and 993 have feeble companion lines of shifts 985, 1175, and 974, respectively. These are attributed to C^{13} isotope replacements, i.e., $\text{C}^{12}_5\text{C}^{13}\text{H}_6$, $\text{C}^{12}_2\text{C}^{13}\text{H}_6$, and $\text{C}^{12}\text{H}^{13}\text{H}_6$, respectively. This is deduced from positions and relative intensities. N. M. B.

Diffusion spectra (Raman effect) and infra-red absorption spectra of saturated aliphatic alcohols and ethylenic hydrocarbons. A. ANDANT, P. LAMBERT, and J. LECOMTE (Compt. rend., 1935, 201, 391—393).—The Raman spectra and infra-red absorption spectra (between 500 and 1600 cm^{-1}) of 8 saturated alcohols and the 8 ethylenic hydrocarbons produced by their dehydration have been measured. The very strong 1600 cm^{-1} Raman line characteristic of the double linking does not appear in absorption. *tert.*-Alcohols are characterised by a very strong infra-red band at 1140 cm^{-1} and a weak band at 1240 cm^{-1} , neither of which has a direct equiv. in Raman spectra. The max. due to the C chains do not occur in the same positions in the two series. The combined data permit distinction between successive homologues and isomerides. Ethylenic hydrocarbons have spectra distinct from those of the alcohols from which they are derived, suggesting that the ethylenic linking disturbs the true vibrations of the C chains. J. W. S.

Raman effect. XLIII. Raman effect and free rotation. II. K. W. F. KOHLRAUSCH and (GROSS-PRINZ) YPSILANTI. XLIV. Raman effect and free rotation. III. K. W. F. KOHLRAUSCH and W. STOCKMAIR (Z. physikal. Chem., 1935, B, 29, 274—291, 292—298; cf. this vol., 914).—XLIII. The Raman spectra of $\text{OMe}\cdot\text{CH}_2\cdot\text{CN}$, $\text{CH}_3\text{Cl}\cdot\text{OMe}$, and substituted ethanes, $\text{CH}_2\text{X}\cdot\text{CH}_2\text{Y}$, have been

determined. Taking into account infra-red and polarisation data and utilising models (*ibid.*, 432), the Raman spectra of $\text{CH}_2\text{X}\cdot\text{CH}_2\text{Y}$ indicate that in the liquid state these are equilibrium mixtures of plane *cis*- and *trans*-forms, the latter predominating at room temp. The time of sojourn in either configuration is long compared with the time of vibration, but so short compared with that of chemical attack that chemical separation is impossible. Trumpy's deductions (*ibid.*, 565) are criticised.

XLV. From the Raman spectra of allyl derivatives, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{X}$, it is concluded that these are mixtures in the liquid state of plane *cis*- and *trans*-forms. $\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3$ is apparently wholly *trans*. R. C.

Raman effect in solutions of some amino-acids. N. WRIGHT and W. C. LEE (Nature, 1935, 136, 300).—Raman frequencies and estimated relative intensities are recorded for solutions of glycine, tyrosine, alanine, and cystine. L. S. T.

Decay time of fluorescence measured with an improved fluorometer. W. SZYMANOWSKI (Z. Physik, 1935, 95, 440—449).—Accuracy attained is $0.2\text{--}0.3 \times 10^{-9}$ sec. A. B. D. C.

Duration of luminosity and decay law for fluorescence radiation. W. SZYMANOWSKI (Z. Physik, 1935, 95, 450—459).—The exponential law holds for decay of fluorescence of fluorescein in H_2O . A. B. D. C.

Variation of fluorescence decay time with concentration of dye and viscosity of solvent. W. SZYMANOWSKI (Z. Physik, 1935, 95, 460—465).—Collisions of the second kind cannot directly explain extinction processes, as revealed by decay of fluorescence of fluorescein in H_2O , EtOH , Bu^nOH , and glycerol. A. B. D. C.

Molecular rotation and measurements of decay time of fluorescence. W. SZYMANOWSKI (Z. Physik, 1935, 95, 466—473).—The rate of decay of the radiation excited by polarised light depends on the orientation of the fluorescent radiation relative to the plane of polarisation. A. B. D. C.

Excitation spectra of the luminescence of solid solutions of rhoduline. S. I. GOLOUB (Physikal. Z. Sovietunion, 1935, 7, 49—57).—The excitation spectra of fluorescence and phosphorescence of solid solutions of rhoduline in sucrose have been examined and shown to be identical, indicating identical mechanisms of excitation in the case of passage to a temporary or prolonged excited state. R. S. B.

Distribution of intensity in the Rayleigh lines of compressed gases. I. Experiments with carbon dioxide. J. WEINER (Ann. Physik, 1935, [v], 23, 493—506).—The distribution of intensity of the Rayleigh lines of CO_2 at 10—80 atm. and in the neighbourhood of the crit. temp. was determined for Hg line 4047 \AA . The variation of the intensity (I) in the middle of the line with pressure was determined. $I \propto$ change of density, d , of the gas. In the middle part of the wings $I \propto d$. At high pressures an additional radiation is observed, which is connected with the inner mol. state of the compressed gas. A. J. M.

Hindered rotation and oscillation of molecules in liquids and in crystals. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 63—66).—The extended portion of rotation wings in liquids and the separate lines which take their place in the corresponding solids are explained as due to small mol. oscillations or incomplete rotations, the motion being properly quantised in solids, and imperfectly so in liquids. N. M. B.

Experiments with two thin metallic layers pressed together. A. DEUBNER (Naturwiss., 1935, 23, 557).—The conductivity and light absorption of thin metallic layers made by vaporisation do not vary directly with the amount of substance vaporised. That this behaviour is not due to some anomalous variation of the thickness of the layer with the amount of substance vaporised is shown by pressing together two equally thin layers of Ag ($1-2 \times 10^6$ cm.). The properties of the two layers are not additive. It is shown that the light absorption should vary with the square of the thickness. A. J. M.

Contact phenomena in carborundum resistances. I. V. KURTSCHATOV, T. Z. KOSTINA, and L. I. RUSINOV (Physikal. Z. Sovietunion, 1935, 7, 129—154).—Existing theories of self-regulating carborundum resistances are rejected. It is suggested that the phenomenon is governed by the transference of electrons at the points of contact of the CSi particles through the operation of the wave-mechanical tunnel effect. Results agree with experimental data. R. S.

Photo-electric effect in a layer of silver deposited on nickel. N. FEDENEV (Physikal. Z. Sovietunion, 1935, 7, 58—65).—The photo-electric current has been studied with films of Ag sublimed on Ni. The work function rises from 3.7 to 4.2 volts as the film thickness increases from 0 to 3.5 Å., and then decreases, becoming const. at 3.9 volts (val. for pure Ag) at $>$ approx. 12 Å. R. S. B.

Photo-electric cells with an artificially deposited insulating layer. W. C. VAN GEEL and J. H. DE BOER (Physica, 1935, 2, 892—900).—“Sperrschicht” cells with Se as semi-conductor, and CaF_2 , SiO_2 , MgO , and a cresol- CH_2O resin as insulating layers are described. The photo-electric effect is observed with such cells, although the insulating layer itself can give rise to no inner photo-effect. The photo-conduction of the insulating layer is not, therefore, a necessary factor in a “sperrschicht” cell. The connexion between photo-current (i) and intensity of light (L) is given by $i-AL^{\frac{1}{2}}$ (A const.). The inner photo-effect of the Se used obeyed the relationship $i-BL^{\frac{1}{2}}$ (B const.). A. J. M.

Selective photo-effect. P. I. LUKIRSKI and J. L. HURGIN (Physikal. Z. Sovietunion, 1935, 7, 99—107).—The photo-electric effect for pure metals is shown to be purely optical in origin, and is correlated with a variation in the electromagnetic field depending on λ and degree of polarisation. R. S. B.

Spectral photo-electric sensitivity of composite photo-cathodes on variation of the supporting metal and alkali metal. W. KLUGE (Z. Physik, 1935, 95, 734—746).—Cathodes of Ag, Au, Ni, and

Cu supporting Na, K, Rb, and Cs all show a long-wave max. in the visible, and two short-wave max. in the ultra-violet. A. B. D. C.

Light distribution and the external photo-effect. F. HLUCKA (Z. Physik, 1935, 95, 486—498).—Available data are critically reviewed. A. B. D. C.

Temperature dependence of the photo-electric effect. K. MITCHELL (Proc. Camb. Phil. Soc., 1935, 31, 416—428).—The temp. dependence of the photo-electric effect with the image field agrees with Fowler's T^2 law near the threshold. Fowler's $T^{3/2}$ law rests on a mistake in the normalisation of the free wave functions. The methods of Fowler and Du Bridge for analysing experimental results are discussed; Du Bridge's method should give more trustworthy results. W. R. A.

Electrostatic potential of a crystal of the cuprite type. T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 1, A, 905—914).—Theoretical. A. B. D. C.

Dielectric loss in anisotropic liquids. V. FREDERIKS, G. MICHAÏLOV, and D. BENESCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 469—473).—A repetition of the work of Ornstein *et al.* (A., 1933, 338) on *p*-azoxyanisole gave results in disagreement with Kast's. W. R. A.

Molecular polarisation and association. W. HEROLD (Z. physikal. Chem., 1935, B, 29, 259—273).—The calculation from the variation of mol. polarisation with concn. of orientation polarisation and concn. of double mols. when only double mols. are present in addition to single mols. is described; the method is also applicable on certain assumptions to more complex systems. Application to Parts' data for C_6H_6 solutions of Bu halides (A., 1930, 667) shows that at the concns. examined only double mols. and single mols. are present, and that the former consist of complexes with parallel and antiparallel orientations, respectively, of the moments of the components. The heat of formation of the two types of complex has been calc.; it becomes increasingly positive with increasing steric shielding of the C-halogen groups. The association is not a simple function of the shielding. R. C.

Influence of nuclear substituents on side-chain reactions. IV. Reconsideration of the quantitative relationship between energies of activation and dipole moments. D. P. EVANS, V. G. MORGAN, and H. B. WATSON (J.C.S., 1935, 1174—1178).—In three cases where energies of activation have been determined for a given reaction of a series of *m*- or *p*-substituted aromatic compounds, their relationships with the dipole moments of the corresponding substituted benzenes is given generally by $E-E_0 \pm C(\mu+au^2)$. It represents a slight modification of Nathan and Watson's original formula. The same relationship is found in eleven other reactions, on the assumption that, throughout a series of nuclear-substituted compounds, all factors other than the energy of activation are const. It is suggested that both the constancy of factors other than E and the relationship between E and μ may persist, with

reservations, throughout a large no. of side-chain processes. H. W.

Rotating polar groups in organic molecules. W. ALTAR (J. Chem. Physics, 1935, 3, 460—472).—The variation with temp. of the dipole moment of mols. with rotating polar groups may be quantitatively explained in terms of intramol. forces opposing free rotation. Application to $(\text{CH}_2\text{Cl})_2$ of considerations derived from a discussion of the statistical wt. to be assigned to a configuration and the approximation of the periodic potential function by its first and second Fourier component indicates the presence of repulsive forces between the two Cl atoms at distances as large as 4 Å. The *cis*- and *trans*-forms of $(\text{CHCl})_2$ probably both have approx. the same heat of formation. An explanation of the observed equilibrium ratio of the two forms is offered. R. C.

Dielectric constant of hydrogen at pressures up to 1425 atm., and at temperatures of 25° and 100°. A. MICHELS, P. SANDERS, and A. SCHIPPER (Physica, 1935, 2, 753—756; cf. A., 1933, 447).—The dielectric const. has been measured up to 1425 atm. The Clausius-Mosotti expression $P = (\epsilon - 1)/(\epsilon + 2)d$ is fulfilled. T. G. P.

Magnetic variation of the dielectric constant of liquids. A. PIEKARA and M. SCHERER (Compt. rend., 1935, 201, 335—337).—The increase of the dielectric const. (ϵ) of a liquid under the action of a magnetic field follows the law $\Delta\epsilon = AH^2 + BH^4$, where A and B are consts. characteristic of the liquid. The increase for C_6H_6 and CHCl_3 under a field of 50 k. gauss is independent of λ between 500 and 1500 m. The sign of the change is the same whatever the orientation of magnetic to electric fields. For C_6H_6 the effect is about twice as great for perpendicular fields as for parallel fields. The results can be explained by mol. deformation. J. W. S.

Electric moments of alkyl borates and substituted boric acids. M. M. OTTO (J. Amer. Chem. Soc., 1935, 57, 1476—1478).—The electric moments of Bu borate, methyl borate, phenyl-, *n*-amyl-, and *n*-butyl-boric acids in C_6H_6 and dioxan solutions have been determined. The acids are not associated in C_6H_6 , and no compounds are formed with dioxan. E. S. H.

Dielectric properties of some vegetable oils. G. R. PARANJPE and P. Y. DESHPANDE (Proc. Indian Acad. Sci., 1935, 1, A, 880—886).— d , n , and dielectric const. at 30 m. have been determined at 26° for castor, olive, sesame, and coconut oils in C_6H_6 , and give the electric moments as 3.68, 3.03, 2.91, and 2.82×10^{-18} , respectively. A. B. D. C.

Specific rotatory power and stereochemistry of the cinchona alkaloids.—See this vol., 1256.

Solvent action. X. Rotatory powers of dimethylene tartrate, methylenetartaric acid, and its dimethyl ester in the presence of added solvents and salts. H. G. RULE and J. P. CUNNINGHAM. XI. Influence of solvent, concentration, and temperature on the rotatory powers of *l*-menthyl *o*-substituted benzoic esters. H. G. RULE and A. DUNBAR (J.C.S., 1935, 1038—1043,

1043—1049).—X. $[M]_{5461}^{20}$ has been determined for dimethylene tartrate (I), methylenetartaric acid (II), and Me_2 methylenetartrate (III) in various solvents. The characteristic rotatory powers of (I) and (III) in solution rise in magnitude as the dipole moment of the solvent increases. The rotatory power of the strongly-associated (II), on the other hand, varies irregularly with the solvent, and the observed changes may be interpreted on the assumption that solute-solvent and solute-solute association both raise the rotation. In agreement with the demands of the association hypothesis, the optical rotation of (III) dissolved in a non-polar solvent increases with the concn. of the ester and the rotatory powers of solutions in a highly polar and in a non-polar solvent approach one another as the temp. rises. The cationic effects produced by the addition of metallic chlorides to aq. solutions of the above esters are identical with those found for optically active acids and their salts. Such effects must therefore be transmissible through the dipoles as well as through ionised groupings contained in the active solute.

XI. $[M]^{20}_1$ has been observed for *l*-menthyl *o*-substituted benzoates (substituent NO_2 , CO_2H , H, OH, Cl, OMe) in various solvents. The effect of concn. on $[M]^{20}_{5461}$ for the esters in C_6H_6 and the behaviour of *l*-menthyl *o*-nitrobenzoate (IV) at various concns. in mixtures of solvents have been investigated. The influence of temp. on $[M]_{5461}$ of the esters in PhNO_2 , PhBr, decahydronaphthalene, and PhCN has been observed. With the more polar NO_2 ester and H phthalate, the rotations fall as the polarity of the solvent increases or as the concn. of these esters in a non-polar solvent rises. In each case the temp.-rotation curves for the ester in polar and in non-polar solvents converge as the temp. rises. These changes are explained on the theory of dipoles by assuming varying degrees of solute-solute or solute-solvent association in accordance with experimental conditions. For the remaining esters the observed changes are irregular. In general, solvents of exceptionally high refractive index tend to yield solutions of abnormally high rotatory power with each of the six esters examined, thus showing the existence of a minor effect due to the refractivity of the solvent. In *n*- C_6H_{14} the rotatory powers of *l*-menthyl salicylate exhibit an exaltation between the concns. $c=35$ and $c=65$. H. W.

Rotatory dispersion of α -iodopropionic acid and β -octyl iodide. W. KUHN and H. BILLER (Z. physikal. Chem., 1935, B, 29, 256—258).—The absorption and rotatory dispersion of β -octyl iodide and Me α -iodopropionate and the rotatory dispersion of α -iodopropiondimethylamide have been measured. The results confirm the view that (+)-iodopropionic acid corresponds with *d*(-)-lactic acid. Levene and Rothen's methods (A., 1934, 476) are criticised. R. C.

Electro-optical Kerr effect in ammonia, nitrogen, and oxygen. W. M. BREAZEALE (Physical Rev., 1935, [ii], 48, 237—240).—The following abs. vals. for the Kerr const. were obtained: anhyd. NH_3 at 6500 and 5750 Å., 13—30 atm., and 40—80° $62.3 \pm 1.8 \times 10^{-12}$; N_2 and O_2 at 6500 Å., approx.

100 atm., and $20-65^\circ$ 4.64 ± 0.10 and $6.94 \pm 0.30 \times 10^{-12}$, respectively. N. M. B.

Geometrical structure of the N_3H molecule. G. HERZBERG, F. PATAT, and H. VERLEGER (Z. Elektrochem., 1935, 41, 522-524).—The infra-red rotation-vibration spectrum of gaseous N_3H consists of an intense band at 1.045μ and a weaker one at 0.808μ . The fine structures indicate that the N atoms lie in a straight line. In most of the mols. the H is not in this line, but a linear modification probably exists. T. G. P.

Rotation and vibration of the methane molecule. H. A. JAHN (Ann. Physik, 1935, [v], 23, 529-556).—Mathematical, employing a group theory method. A. J. M.

Character of binding in the carbon monoxide molecule. R. J. JAANUS and J. A. SHUR (Physikal. Z. Sovietunion, 1935, 7, 19-25).—The val. $-118 \pm 6 \times 10^{-7}$ has been determined for the mol. magnetic susceptibility (χ) of CO by a modification of Lehrer's method (A., 1926, 1086). Since Pascal's additivity law, with a C:O linking, gives $\chi = -42.5 \times 10^{-7}$, it is inferred that the val. of χ implies a triple or even quadruple linking. R. S. B.

Dissociation of the carbon monoxide molecule. B. ROSEN (Nature, 1935, 136, 226).—A correction (cf. this vol., 925). L. S. T.

Theory of ionic recombination. W. R. HARPER (Proc. Camb. Phil. Soc., 1935, 31, 429-430).—The correction of a numerical error in a previous paper (A., 1932, 554) gives better agreement with experimental data. W. R. A.

Statistical theory of superlattices. H. A. BETHE (Proc. Roy. Soc., 1935, A, 150, 552-575).—Assuming interaction between nearest neighbouring atoms only, the order in an alloy containing two sorts of atoms in equal proportions is calc. statistically. At high temp. the state of the crystal as regards order is rather similar to a liquid, but at low temp. the crystal as a whole is ordered, and the structure is "solid-like." The long-distance order and energy as functions of temp. are discussed qualitatively and calc. The theory of Bragg and Williams (A., 1934, 954) gives a fair approximation. L. L. B.

Molecular constants and potential energy curves for diatomic molecules. M. L. HUGGINS (J. Chem. Physics, 1935, 3, 473-479).—Using a modified Morse equation for the potential energy of a diat. mol., in which the repulsive term is the same for all electronic states of a particular mol., $U = ce^{-a(r-r_0)} - C'e^{-a'(r-r_0)}$, and putting $a = 6.0 \times 10^8 \text{ cm.}^{-1}$, r_{12} vals. calc. from the band spectrum consts. are approx. const. at 1.46 \AA. for all except highly excited states of all diat. mols. containing only elements in the first period of the periodic scheme and with ≤ 12 electrons. This indicates that the repulsive term is nearly const., and permits calculation from the vals. of two mol. consts. of those of others. The calc. vals. of $\omega_e y_e$ and $\omega_e z_e$ are small, but $\neq 0$. To obtain the observed dissociation energy a must be taken as $4.0 \times 10^8 \text{ cm.}^{-1}$ R. C.

Surface tension and its variation with temperature. A. GANGULI and P. MITRA (Current Sci., 1935, 4, 23-24).—London's (A., 1931, 149) quantum-mechanical expression of van der Waals force requires modification for liquids and solids. A further modification for absorption phenomena is suggested. W. R. A.

Possibility of faulty explanations in X-ray diascopy due to neglecting the selective absorption of X-rays. F. REGLER (Physikal. Z., 1935, 36, 530-535).—Errors can easily arise in dealing with X-ray diagrams when the K-absorption edge of the substance which is being irradiated lies in the λ range of the X-rays used. Such errors occur particularly in the investigation of metals in solutions of salts which have approx. the same degree of absorption as the metal. The contrast of the X-ray photograph obtained with regard to selective absorption, and methods of increasing it, are considered. A. J. M.

Crystal and slit systems for X-ray monochromatisation and spectroscopy. G. I. HARPER (Proc. Roy. Soc., 1935, A, 151, 118-141).—A quant. theory of the use of crystal and slit systems in X-ray physics for the production of monochromatised beams and for the analysis of composite radiations is developed. L. L. B.

X-Ray source in a single crystal. G. BORRMANN (Naturwiss., 1935, 23, 591-592).—Secondary X-rays produced by the irradiated single crystal interfere and give a Laue pattern. A. J. M.

Direct method for the determination of the components of interatomic distances in crystals. A. L. PATTERSON (Z. Krist., 1935, 90, 517-542).—Mathematical: a new method of application of Fourier analysis to crystal structures. B. W. R.

Tabulated data for the seventeen plane groups. A. L. PATTERSON (Z. Krist., 1935, 90, 543-554).—Tables necessary for the application of the preceding paper are given. B. W. R.

Technique of structure determination. A. HETTICH (Z. Krist., 1935, 90, 473-492).—Summarised or improved ideas under the following heads are given: (a) allotting of indices to Weissenberg (moving-film) photographs; (b) adjustment of the specimen on the goniometer by X-rays, when visible faces are not available; (c) varying effective exposure time in photometric work, due to the location of poles of planes at varying angles from the equator; (d) the "Eigen" diagram, a new concept in X-ray Fourier treatment of groups of atoms; (e) optical methods of synthesis of Fourier components in the final determination of crystal structure. B. W. R.

Detection and evaluation of residual distortion in crystals, with special reference to electric steel. G. L. CLARK and M. M. BECKWITH (Z. Krist., 1935, 90, 392-398).—4% Si steel after cold-working and heat-treatment gives an X-ray photograph intermediate between a Laue and a powder diagram; an arbitrary modulus depending on distortion and position of the spots is found to measure quantitatively the degree of residual distortion, and to correspond with the magnetic properties. B. W. R.

Determination of the distortion axis of bent crystals from Laue diagrams. W. BOAS and H. EKSTEIN (*Z. Krist.*, 1935, **90**, 408—414).—A mathematical treatment, applied in particular to a Zn crystal. B. W. R.

Polished layer of metals. M. MRWA (*Sci. Rep. Tôhoku*, 1935, **24**, 222—239).—The diffraction patterns of Cr, Fe, Co, Ni, Cu, Zn, and Ag become blurred as the surfaces are polished, certain lines becoming more weakened than others until finally they yield two diffuse lines, the spacing of which indicates that the surface becomes an amorphous liquid-like layer (cf. Beilby). The results with Cd, Sn, and Sb indicate that their polished surfaces consist of minute pseudocrystals, whilst polished surfaces of Si, Mn, and Bi, owing to their brittleness, are cryst. J. W. S.

Grain changes in polymorphic transformation. G. TAMMANN and W. BOEHME (*Z. anorg. Chem.*, 1935, **223**, 365—368).—When polymorphic transformation occurs in a cryst. melt, the boundaries of the original grains may, or may not, be overstepped, depending mainly on whether the original crystallisation occurred as dendrites and spherulites or as crystallites, respectively. KNO_3 , NH_4NO_3 , AgI , AgNO_3 , and TlNO_3 crystallised as dendrites, S and resorcinol as spherulites. A small, irregularly oriented grain is favourable for the strength of Fe and alloy steels; the δ - γ transition gives much smaller grains, the γ - β smaller still, but as the orientation of β and γ grains is identical, this gives no technical improvement of Fe. The β - α transition is accompanied by no change of size or orientation of grains. The effect of certain admixtures on the Fe transitions is briefly discussed. S. J. G.

Amorphous antimony. J. A. PRINS (*Nature*, 1935, **136**, 299).—Changes in the electron diffraction patterns of amorphous Sb obtained by distillation in vac. (A., 1933, 657) show that crystallites oriented at random are formed at 120—150° according to the thinness of the film. The patterns of explosive Sb are identical with those of the amorphous films. The diamagnetic susceptibility increases markedly when explosive Sb changes to the ordinary form. This and the heat of crystallisation suggest that explosive Sb is in the supercooled liquid state. L. S. T.

Recrystallisation of pure aluminium. J. CALVET, J. J. TRILLAT, and M. PAÏÇ (*Compt. rend.*, 1935, **201**, 426—428).—The rate of recrystallisation of very pure cold-rolled Al was high, being complete in 32—48 hr. at 40°, and in < 1 min. at 100°. J. S. A.

Transformation of magnetite at low temperature. H. SHOJI (*Sci. Rep. Tôhoku*, 1935, **24**, 250—253).—Comparison of the X-ray diffraction patterns of magnetite at room temp. and at -190° indicates no lattice transformation between these temp. Hence the transformation found at -162° by thermal, dilatometric, electric, and magnetic methods is probably a change either in the state of the electrons or in the orientation of the atoms. J. W. S.

Fine structure of X-ray absorption edges of alloys. II. CuBe, NiO, and AuCu₃ (statistic and ordered phases). R. SMOLUCHOWSKI (*Z.*

Physik, 1935, **95**, 588—598; cf. this vol., 812).—The character of the linkings throughout the lattice affects the position of the edges, but not their fine structure. The fine structures of β -brass and CuBe, similar lattices, are totally different, due to change of at. no. from Zn to Be. A. B. D. C.

Crystal structure and composition of rhombic cobalt silicide. B. BOREN, S. STAHL, and A. WESTGREN (*Z. physikal. Chem.*, 1935, **B**, **29**, 231—235; cf. A., 1934, 482).— Co_2Si has the space-group V_6^{16} . The Si atoms form zigzag chains in the direction of the c axis, the at. arrangement being similar to that in FeB, CoB, and Cr_3C_2 . R. C.

Crystal structure of aluminium orthophosphate AlPO_4 . H. F. HUTTENLOCHER (*Z. Krist.*, 1935, **90**, 508—516).—The prep., morphology, and X-ray examination of AlPO_4 are described; the crystal is hexagonal, a 4.93, c 2×5.47 Å. The similarity to quartz and AlAsO_4 is indicated. B. W. R.

Diffraction of X-rays by a linear crystal grating of AgCN. C. D. WEST (*Z. Krist.*, 1935, **90**, 555—558).—AgCN cryst. from aq. NH_3 solution has a structure in which $\cdot\text{Ag}\cdot\text{C}\cdot\text{N}\cdot\text{C}\cdot\text{Ag}\cdot$ chains are extended along the c axis in regular hexagonal packing with other similar chains. Photographs are described which correspond with diffraction from this lattice, if random translation along the length of the chain is assumed. B. W. R.

Symmetry alterations of etch figures due to optically active impurities. J. NOVAK (*Z. Krist.*, 1935, **90**, 385—391).—Small concns. of malic acid (active) in AcOH (inactive) produce considerable changes in the symmetry of etch-figures on the cleavage plane of CaCO_3 . Various concns. of sucrose had no such effect. B. W. R.

Mineral carbonates. K. SCHOKLITSCH (*Z. Krist.*, 1935, **90**, 433—445).—Lattice consts. and various physical data for a series of mineral carbonates (dolomite, magnesite, siderite, etc.) are determined and collated with the chemical composition. B. W. R.

X-Ray analysis of the structure of iridescent shells. S. RAMASWAMY (*Proc. Indian Acad. Sci.*, 1935, **1**, A, 871—879).—X-Ray diffraction patterns of the nacreous layer show it to consist of aragonite crystals with their c axes normal to the surface, and the ab planes variously distributed depending on the species examined. A. B. D. C.

Crystal structure of cyanuric triazide. (Miss) I. E. KNAGGS (*Proc. Roy. Soc.*, 1935, **A**, **150**, 576—602).—Crystals of $(\text{C}_3\text{N}_3)(\text{N}_3)_3$ have been examined by X-rays and subjected to a Fourier analysis about the zone parallel to the hexagonal axis. The mol. is planar and has a 3-fold axis of symmetry, and the 2 mols. of the unit cell are situated on planes separated along the c axis by half its length. The configuration of the mol. has been determined, and the following interat. distances are given: C—N outside the C_3N_3 ring, 1.38 Å.; C—N in the C_3N_3 ring, 1.38 Å.; C=N in the C_3N_3 ring, 1.31 Å.; N=N, 1.26 Å.; N=N, 1.11 Å. The N_3 group is linear, and is linked to a C only of the C_3N_3 ring. The latter is a 6-membered ring having trigonal symmetry and alternate double

and single linkings. There is no oscillating double linking as in C_6H_6 . The mols. are arranged in sheets 2.98 Å. apart. L. L. B.

Study of the crystal structures of *s*-di-iodoethane and *s*-di-iodoethylene. H. P. KLUG (Z. Krist., 1935, 90, 495—507).— $(CH_2I)_2$ and *s-trans*- $C_2H_2I_2$ are isomorphous, monoclinic, space-group C_{2h}^2 , a_0 7.582, b_0 12.897, c_0 5.810 Å., β 90° 12', and a_0 7.280, b_0 13.310, c_0 5.553 Å., β 90°, respectively. The pseudorhombic cell is used as the basis for discussion; the I parameters are fixed from intensity measurements. B. W. R.

Crystallography of pentaerythritol tetraphenyl ether. J. BEINTEMA, P. TERPSTRA, and W. J. VAN WEERDEN (Rec. trav. chim., 1935, 44, 627—630).—Pentaerythritol Ph_4 ether crystallises in the tetragonal bisphenoidal class, $a : c = 1 : 0.6843$. The crystals are built on a body-centred lattice; space-group S_6^3 , 2 mols. in unit cell of dimensions $12.32 \times 12.32 \times 8.43$ Å. The mol. possesses fourfold alternating axis of symmetry. A structure is suggested in which the planes of the Ph are parallel to {110} and the aliphatic C show considerable departures from the ideal angle between the valencies. H. W.

Crystalline structure of the sugars. I. Simple sugars and glycosides. E. G. COX, T. H. GOODWIN, and (MISS) A. I. WAGSTAFF (J.C.S., 1935, 978—982).—The cell dimensions and space-groups of sorbose, α -galactose, α -methylgalactoside, α -fucose, α -methylgalactoside-6-bromohydrin, β -methylarabinoside, and α -methylfucoside are recorded. The accepted configurations of the groups attached to C1 are confirmed. F. R. G.

Crystal structure of methylene-blue. W. H. TAYLOR (Chem. and Ind., 1935, 732—734).—X-Ray data are given for the chloride, bromide, iodides I and II of methylene-blue, and also for Se methylene-blue bromide. The mols. of all these compounds (excepting the iodide II) are probably lath-shaped, parallel to the b axis with flat faces perpendicular to the c axis, separated by about 3.5 Å.; in the special case of the iodide I the I can be located with more certainty. Evidence supports the p - rather than the o -quinonoid structure. B. W. R.

Crystallographic and refractometric researches on the natural and synthetic corpus luteum hormone. A. NEUHAUS (Z. Krist., 1935, 90, 415—432).—Luteosterone C and D from natural sources are examined crystallographically and optically; the etch-figures, piezoelectric behaviour, d , and mol. refractivity are also observed. No difference is found between the natural and the synthetic product. The D compound will change into the C, but the reverse transformation has not been observed. B. W. R.

X-Ray studies of the structures of hair, wool, and related fibres. III. Configuration of the keratin molecule and its orientation in the biological cell. W. T. ASTBURY and W. A. SISSON (Proc. Roy. Soc., 1935, A, 150, 533—551).—It is shown by direct measurement that the "backbone spacing" (4.65 Å.) and the "side-chain spacing" (9.8 Å.) of the

keratin "grid" are those of planes at right angles, as proposed previously from indirect evidence (A., 1934, 352). The significance of this fact in the study of proteins and the structure of the biological cell is pointed out. The method used was to destroy the axial symmetry of the keratin-fibre structure by lateral compression in the presence of steam; after such compression the keratin grids are found to be so oriented that the "side-chain spacing" stands normal to the plane of flattening, whilst the "backbone spacing" lies in this plane. The crystallites of β -keratin are broader in the direction of the backbone spacing than in that of the side-chain spacing. The biological cells in keratinous structures are in general flat, and laid down with their flat sides roughly parallel to the natural surface of the specimen. L. L. B.

Measurements of previously unknown large interplanar spacings in natural materials. G. L. CLARK, E. A. PARKER, J. A. SCHAAD, and W. J. WARREN (J. Amer. Chem. Soc., 1935, 57, 1509).—Modifications of X-ray technique permit large interplanar spacings to be detected. Preliminary results obtained with living nerve, collagen, gelatin, keratin, gel rubber, and cellulose are reported. E. S. H.

Scattering of fast electrons by crystals. N. PISARENKO (Physikal. Z. Sovietunion, 1935, 7, 26—42).—Theoretical. It is shown that the inelastic scattering of fast electrons by a dielectric lattice is not influenced by the crystal structure. The influence of heat oscillations of the crystal atoms corresponds with only a small part of the background intensity of electron diffraction diagrams. R. S. B.

Dilatations in Rochelle salt. I. VIGNESS (Physical Rev., 1935, [ii], 48, 198—202; cf. A., 1934, 1163).—The inverse piezoelectric effect was studied by means of mechanical dilatometers. The dilatation of a crystal in a given direction varied with the field direction, indicating a permanent electric polarisation within the crystal. Prolonged application of voltage slowly changes this polarisation, giving rise to an inverse piezoelectric fatigue effect. N. M. B.

Magnetostriction of bismuth single crystals. D. SHOENBERG (Proc. Roy. Soc., 1935, A, 150, 619—637).—Measurements of the transverse magnetostriction of Bi single crystals confirm the general features of the phenomenon found by Kapitza in large fields (A., 1932, 565) for the region of much lower fields ($\sim 15,000$ gauss) available in an electromagnet. A new magnification method for measuring the extremely small changes of length involved ($\sim 5 \times 10^{-7}$ cm.) is described. L. L. B.

Size and arrangement of bismuth microcrystals formed from vapour. C. T. LANE (Physical Rev., 1935, [ii], 48, 193—198).—The magneto-resistance R of Bi films deposited on glass and mica was measured at -180° and 20° for various angles between the film normal and the magnetic field ($H=16,000$). The ratio R_{-180}/R_{20} rises steeply for thicknesses 0.1—0.4 μ and then gradually to 4 μ ; the thermal coeff. of resistance shows no such anomaly. X-Rays show all the films composed mainly of small crystals with (111) parallel to the backing. R varies

with the direction of H ; the current direction in the film is const. The relation of results to film structure is discussed. N. M. B.

Ferromagnetism for small variations of field. R. GANS and H. WITKE (Ann. Physik, 1935, [v], 23, 459—464).—The work of Jordan on ferromagnetic losses in weak alternating fields (this vol., 149) is criticised. A. J. M.

Magnetic after-effect. H. WITKE (Ann. Physik, 1935, [v], 23, 442—458).—The magnetic after-effect is a property dependent on the material only, and not on the variation of the field strength with time. A. J. M.

Formation and magnetic properties of some ferrites. D. P. RAYCHAUDHURI (Indian J. Physics, 1935, 9, 425—432).—The magnetic properties of ferrites depend largely on the method of their prep.; for the dry method the main factors are duration of heating and temp. Effects of time and temp. are given for the ferrites of Co and Zn, eliminating discrepancies in previous reports. Data for Curie point, susceptibility, and X-ray structure are given for 15 ferrites. N. M. B.

Propagation of the magnetic reversal wave. D. S. STEINBERG (Physikal. Z. Sovietunion, 1935, 7, 155—174).—The magnetisation wave in stretched Fe-Ni wires has been studied. The wave is initiated only when a crit. field strength is attained at any given point and continues only so long as the frontal field preceding the wave + the impressed field = the crit. field. R. S.

Change in the resistance of magnetite in a magnetic field at low temperature. P. A. CHALILEEV (Physikal. Z. Sovietunion, 1935, 7, 108—114).—The electrical resistance (ρ) of magnetite has been studied at 80—120° abs. in fields of 3000, 7000, and 8750 gauss. ρ decreases in the field, with a max. decrease (8—10% with 8750 gauss) at 111.4° abs. It is considered that at 111° abs. magnetite undergoes a change similar to that of a ferromagnetic body at the Curie point. R. S. B.

Influence of temperature on the electrical conductivity of quartz. R. RADMANECHE (Compt. rend., 1935, 201, 448—449).—For SiO_2 plates cut perpendicular to the optic axis, at -64° to 3000° , $\log i = a/T + b$, where i = current at const. p.d. and a and b are consts. At $< -64^\circ$ i is immeasurable. R. S. B.

Condition of electrons in superconductors. J. STARK (Physikal. Z., 1935, 36, 515—516).—Free electrons, in consequence of an axial structure of their electric fields, exert mutual directional forces on each other, and by arranging their axes parallel to each other an ordered arrangement is produced, which may be called an electron crystal. In superconduction it is supposed that the electron crystal moves as a whole through the metal. It is to be expected that forces which distort the electron crystal will alter the conditions under which superconduction occurs. Such forces are thermal agitation (hence the appearance of superconduction below a certain temp.), magnetic forces (variation of transition point in a magnetic field), and inter-at. forces (unique transition point for each metal). It is to be expected that the size

of crystallites in a metal will affect the transition point, and that the transference of the electron crystal through a straight wire will take place more readily than through a kinked one. A. J. M.

Effect of size of crystallite on the occurrence of superconduction. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 516—519).—According to the theory of Stark (see preceding abstract) the transition temp. from the ordinary to the superconducting state should vary with crystallite size, being the lower the larger is the crystallite. In a polycryst. wire the transition should take place over a range of temp. The transition temp. was determined for Sn wires which had been subjected to various tempering processes, and of which the crystallite size had been determined. Displacements of the transition temp. were found in the direction required by Stark's theory. The effect of strains due to plastic deformation was found to be negligible. A. J. M.

Effect of kinks in wires on the occurrence of superconductivity. W. MEISSNER, K. STEINER, and P. GRASSMANN (Physikal. Z., 1935, 36, 519—520).—The curve of transition temp. between ordinary and super-conduction is displaced to lower temp. when Sn wire and foil or In and Ta wire is kinked. Control experiments show that the displacement is not due to variation of the magnetic field in the neighbourhood of the kinks (see preceding abstract). A. J. M.

Properties of rotating superconducting loops in a magnetic field. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 520—524).—The interaction between a closed, superconducting, freely rotating loop and an external magnetic field, and the effect of self-induction on the current distribution of a parallel superconductor have been investigated. A. J. M.

Current distribution in parallel smooth and kinked wires at the commencement of superconduction. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 524—525).—Two Sn wires of equal length, one kinked, the other straight, were arranged parallel to, and connected with, each other. A current is started in them before the onset of superconduction. When the latter takes place, the magnetic moment of the smooth loop is $>$ that of the kinked. Superconduction begins at a higher temp. in the smooth than in the kinked loop, as required by Stark's theory. A. J. M.

Upper limit to the ohmic resistance of superconductors. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 525—527).—The variation with time of currents in superconducting Sn, Pb, In, Sn+In, and Sn+Pb has been determined. The resistance of kinked wires in the superconducting state is immeasurably small. A. J. M.

Upper limit of the thermo-electric power between superconductors. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 527—528).—The thermo-electric coeff. between superconducting Pb and Sn is $< 5 \times 10^{-14}$ volt per degree, and that between Sn and In $< 3 \times 10^{-15}$. A. J. M.

Variation with magnetic field and temperature of the thermoelectric properties of ferromagnetics. F. E. LOWANCE and F. W. CONSTANT

Physical Rev., 1935, [ii], 48, 257—260).—Measurements on Fe, Ni, Co, and permalloy from room temp.

above the Curie point indicate that the e.m.f. produced by a magnetic field in these thermocouples is conditioned by the crystal structure, the change in direction of the resulting spins, or intrinsic magnetisation in separate crystal regions, and that this effect is related to the change in length on magnetisation.

N. M. B.

Diamagnetism of the Thomas-Fermi ion. T. IRONE (Sci. Rep. Tôhoku, 1935, 24, 264—267).—On the basis of the Thomas-Fermi model of a metallic ion, a relationship is developed expressing diamagnetic susceptibility of ions as a function of at. no. and valency. The theory is in closer accord with experimental data for alkali and alkaline-earth metals than Sommerfeld's (Z. Physik, 1932, 78, 283).

J. W. S.

Diamagnetism of thallium single crystals. R. RAO and K. C. SUBRAMANIAM (Nature, 1935, 136, 336—337).—At 30°, the diamagnetic susceptibility parallel to the hexagonal axis of a single Tl crystal is 0.407×10^{-6} unit and perpendicular to it, -0.163×10^{-6} unit, giving a magnetic anisotropy, 50, > the corresponding vals. for similar metals. The calc. mean val. for polycryst. Tl is 0.244×10^{-6} unit. The susceptibilities remain const. up to 35°, the transition temp. to the cubic form, when the mean val. decreases to 0.170×10^{-6} and remains the same for all orientations of the crystal in the magnetic field. The hexagonal structure of Tl is due to the 6 valency electrons (6s and 6p), whilst in the cubic form only the single valency electron (6p) is active. The single valency electron apparently contributes a paramagnetic susceptibility of +4 per g.-atom, a val. of the same order as those for Cu, Ag, and Au.

L. S. T.

Magnetic susceptibility of ice. L. SIBAIYA (Current Sci., 1935, 4, 41; cf. this vol., 689).—Shiawara's results (A., 1915, ii, 141) are discussed.

W. R. A.

Magneto-chemical investigations. XV. Magnetic behaviour of a number of sulphides with pyrites structure. H. HARALDSEN and W. KLEMM (Z. anorg. Chem., 1935, 223, 409—416).—Two lattice structures are possible for metallic disulphides MS_2 , (a) pyrites lattice, M^{++} and S_2^{--} , and (b) layer lattice, S_2 groups indistinguishable and ions M^{++++} and S^{--} . The difference in magnetic properties between M^{++} and M^{++++} enables a distinction to be made between the two lattices. Determinations of the permeabilities and susceptibilities of MnS_2 , FeS_2 , NiS_2 , and CoS_2 show they possess the "ideal" pyrites lattice. CoS_2 is anomalous in being ferromagnetic at -183° , the susceptibility falling rapidly with rising temp., explained by postulating parallel spin vectors in place of the more usual antiparallelism.

S. J. G.

Molecular susceptibilities of some diamagnetic compounds in different solvents. O. E. FRIVOLD and H. SOGN (Ann. Physik, 1935, [v], 23, 413—424).—The mol. susceptibilities of LiCl , LiBr , NaClO_4 , CaCl_2 , CaBr_2 , $\text{Ca}(\text{NO}_3)_2$, SrBr_2 , and $\text{Ba}(\text{ClO}_4)_2$ were determined in H_2O , EtOH , and (in some cases) in

COMe_3 . The mol. susceptibilities of the salts in aq. solution were, in general, > in non-aq. solution. Magnetic properties of substances in solution are not, therefore, strictly additive.

A. J. M.

Diamagnetic properties of inorganic compounds in aqueous solution and in the solid state. M. FLORDAL and O. E. FRIVOLD (Ann. Physik, 1935, [v], 23, 425—430).—The mol. susceptibilities of LiCl , LiBr , NaCl , KF , KCl , KBr , KI , CaCl_2 , CaBr_2 , ZnCl_2 , SrCl_2 , CdBr_2 , BaCl_2 , and $\text{K}_4\text{Fe}(\text{CN})_6$ were determined in the solid state and in aq. solution. In the case of uni-univalent salts the difference between the two vals. of the mol. susceptibility is within the experimental error, but it is > for bi-univalent salts.

A. J. M.

Magnetometric measurement of susceptibility of ferromagnetic powders. D. P. RAYCHAUDHURI (Indian J. Physics, 1935, 9, 417—424).—An improved method is described. Data are given for Fe_2O_3 , Fe_3O_4 , and the ferrites of Mn, Co, Cu, Ni, and Zn. In certain cases magnetic viscosity is observed for NiO , Fe_2O_3 .

N. M. B.

Velocity of sound in low-temperature liquids at ultrasonic frequencies. A. PITT and W. J. JACKSON (Canad. J. Res., 1935, 12, 686—689).—The velocity of ultrasonic waves of 427 kilocycles per sec. is 912 m. per sec. in liquid O_2 at -182.9° and 1127 m. per sec. in H_2 at -252.7° .

J. W. S.

Kinetic theory of gases. I. Absorption of sound. II. General equations of motion and heat conductivity and their application to gliding and temperature jumps. K. F. HERZFELD (Ann. Physik, 1935, [v], 23, 465—475, 476—492).—Theoretical.

A. J. M.

Melting curve of oxygen. J. H. C. LISMAN and W. H. KEESOM (Physica, 1935, 2, 839).—The m.p. of O_2 has been determined at pressures between 48 and 168 kg. per sq. cm.

T. G. P.

Bakerian lecture. Anomalous specific heats of crystals, with special reference to the contribution of molecular rotations. R. H. FOWLER (Proc. Roy. Soc., 1935, A, 151, 1—22).—The present state of the theory of the partition functions of solids and their success or failure in describing the observed facts are discussed. The various types of anomaly in the sp. heat curves not provided for by the simpler versions of the theory are dealt with, and an account is given of a theory of the contribution that mol. rotations may make to the sp. heats, and in general to the equilibrium properties of crystals (cf. this vol., 683).

L. L. B.

Second virial coefficient and specific heats of oxygen. J. A. VAN LAMMEREN (Physica, 1935, 2, 833—839).—The second virial coeff. is recalcd. by a modified method from previous data supplemented by redeterminations at liquid C_2H_4 temp. in order to obtain better fitting to the S curve in this region. Vals. of C_p and C_v at liquid O_2 temp. are recorded.

T. G. P.

Heat capacity of oxygen at high temperatures from ozone explosions and the energy of the $^1\Delta$ level of the neutral oxygen molecule: correction for the temperature gradient in explosions.

B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1935, 57, 1399—1401).—Previous determinations (cf. A., 1933, 343) have been corr. for the temp. gradient existing in the exploded gases at max. pressure. The new vals. agree with those calc. from band spectroscopic data. The O level is determined as 0.85 volt. E. S. H.

Thermal properties of deuterium oxide and their interpretation. R. S. BROWN, W. H. BARNES, and O. MAASS (Canad. J. Res., 1935, 12, 699—701).—The heat capacities of D_2O between initial temp. of 4° to -78.5° and a final temp. of 25° have been determined. The average sp. heat of D_2O between 4° and 25° is 1.028 g.-cal. and the latent heat of fusion 74.2 ± 0.2 g.-cal. The sp. heat of solid D_2O is $>$ that of H_2O at the same temp. and varies from 0.579 at 0° to 0.391 at -70° . The results accord with the view that liquid D_2O is more highly associated than H_2O . J. W. S.

Anomaly in the specific heat of anhydrous ferrous chloride. O. N. TRAPEZNIKOVA and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1935, 7, 66—81).—The sp. heat of powdered $FeCl_2$ has been determined at 16 — 120° abs. A sharp max. (7.22 g.-cal. per mol.) occurs at 23.5° abs., and is discussed in comparison with similar magnetic phenomena. R. S. B.

Anomaly of the specific heat of anhydrous chromium trichloride. O. N. TRAPEZNIKOVA and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1935, 7, 255—256).—The sp. heat-temp. curve of $CrCl_3$ has been determined up to 50° abs. There is a sharp max. at 16.8° abs. and two broad max., none of which coincides with the Curie point, in contradistinction to $FeCl_2$ (cf. A., 1934, 1164). R. S.

Theory of liquids. IV. T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 1—9; cf. this vol., 1058).—Mathematical. Equations are deduced for the forces on a particle vibrating in a spherical space under attractive and repulsive forces between it and uniformly distributed matter outside the space. N. M. B.

Properties of real gases according to the thermodynamic equation of state. VIII. The inversion line of the Joule-Thomson effect for helium. W. JACYNA (Z. Physik, 1935, 95, 692—697; cf. this vol., 1064). A. B. D. C.

Vapour pressure of hexadeuterobenzene. C. L. WILSON (Nature, 1935, 136, 301).—The v.p. of C_6D_6 is $>$ that of C_6H_6 over the range 0 — 80° . The b.p. at 760 mm. is 0.8° lower (cf. this vol., 967). L. S. T.

Entropy of manganous ammonium sulphate at temperatures close to absolute zero, in relation to the magnetic anisotropy of the salt at room temperatures. K. S. KRISHNAN and S. BANERJEE (Proc. Indian Acad. Sci., 1935, 2, A, 82—85).—The entropy-temp. curve close to 0° abs. can be predicted from magnetic anisotropy measurements at room temp. N. M. B.

Calculation of entropies from X-ray data. F. S. LEI (J. Chinese Chem. Soc., 1935, 3, 199—205).—The rotational entropy at 25° of C_6H_6 calc. from

mol. dimensions by the approx. formula (A., 1933, 218) agrees with the val. calc. by the exact equation. J. G. A. G.

Influence of magnetic field on the coefficient of viscosity of liquids. P. K. RAHA and S. D. CHATTERJEE (Indian J. Physics, 1935, 9, 445—454).—Long-chain aliphatic liquids, $COMe_2$ and $PrOH$, show diminution of viscosity in a magnetic field; aromatic liquids, $PhNO_2$, $PhMe$, and an alcohol with side chains, isoamyl alcohol, show an increase; CCl_4 , H_2O , and aq. $Ce(NO_3)_3$ show no change. For $PhNO_2$, increases linearly with rise of temp., with no indication of saturation. The thermal variation of $d\eta/\eta$ for $PhNO_2$ is given. N. M. B.

Influence of a magnetic field on the viscosity of p-azoxyanisole. M. MIĘSOWICZ (Nature, 1935, 136, 261).—The viscosity of p-azoxyanisole at 125° , measured by the damping effect on an oscillating plate, is increased approx. 3.5 times by a magnetic field of 2400 gauss. The effect disappears after transition to the isotropic liquid phase. L. S. T.

X-Ray study of copper-silver alloys. E. A. OWEN and J. ROGERS (J. Inst. Metals, 1935, 57, Advance copy, 173—184).—Parameter measurements, with the precision X-ray camera, on Ag-Cu alloys show that the solubilities of Cu in Ag and of Ag in Cu are 8.5 and 8.4%, respectively, at 778° , 1.8 and 1.4% at 500° , 0.2 and 0.1% at 200° , and, by extrapolation, practically zero at room temp. A. R. P.

Gold-copper alloys. M. LE BLANC and G. WEHNER (Ann. Physik, 1935, [v], 23, 570).—Variations in the results of different workers on Au-Cu alloys are due to insufficient tempering, and consequent non-attainment of equilibrium conditions. The work of Broniewski and Wesolowski (cf. A., 1934, 248; B., 1934, 364) is criticised. A. J. M.

X-Ray investigation of certain copper-tin alloys. E. A. OWEN and J. IBALL (J. Inst. Metals, 1935, 57, Advance copy, 185—204).—The solubility of Sn in Cu increases from 14.6% at 750° to a max. of 16.2% at 550 — 520° and then decreases again with fall in temp. to 9.9% at 300° . The γ -phase at 480° has a 17.917 Å. in alloys with 79.6—68.1% Cu and a 17.924 Å. in alloys with 68—66% Cu. The ϵ -phase is a solid solution extending over a range of about 1.5% around the composition Cu_3Sn ; at 380° the at. vol. of ϵ saturated with Cu is 14.124 Å. and of ϵ saturated with Sn 14.177 Å. The transformation of γ into $\alpha + \epsilon$ occurs at slightly above 300° and the boundary of the Cu-saturated ϵ -phase slopes slightly towards the Sn side between 380° and 300° . A. R. P.

Constitution and structure of the alloys of silver and calcium. C. DEGARD (Z. Krist., 1935, 90, 399—407).—Thermal measurements have suggested the existence of a number of Ag-Ca compounds. When the alloys are melted in vac. and examined by X-rays, the only compounds indicated are $AgCa$ (face-centred cubic, a_0 9.07 Å.) and Ag_3Ca (tetragonal, c/a 0.88). There is no evidence for $AgCa_2$, Ag_4Ca , and Ag_5Ca . B. W. R.

Determination of certain phase boundaries in the silver-zinc thermal diagram by X-ray ana-

lysis. E. A. OWEN and I. G. EDMUNDS (*J. Inst. Metals*, 1935, 57, Advance copy, 321—330).—The γ -(γ + δ) boundary lies at 48.6% Ag between 20° and 530° and then bends towards the Zn side, reaching 47.8% Ag at 608°. The (γ + δ)- δ boundary lies at 44.5% Ag up to 530° and then bends towards 43.2% Ag at 608°; the δ -(δ + η) boundary lies at 21.3% Ag up to 300° and is continued by the δ -(δ + ϵ) boundary which bends towards the Zn side and reaches 20.5% Ag at 408°. The (δ + ϵ)- ϵ boundary slopes from 6.2% Ag at 343° to 9.0% Ag at 408°. A. R. P.

Alloys of magnesium. III. Constitution of the magnesium-rich alloys containing aluminum and cadmium. J. L. HAUGHTON and R. J. M. PAYNE (*J. Inst. Metals*, 1935, 57, Advance copy, 369—380).—Addition of Cd to Mg-Al alloys depresses the liquidus slightly, 20% Cd lowering that of the 80 : 20 Mg-Al alloy by 50°, but has little effect on the eutectic temp. of the Al-Mg system, 20% Cd depressing this temp. by only 5°. The solubility of Al in Mg rises almost linearly from 4% at 200° to about 10% at 400°; addition of 20% Cd depresses these vals. to 1.5% and 6%, respectively. Binary alloys of Al and Mg containing 5—10% Cd if slowly cooled from within the solid solution range may be obtained with the pptd. Al_3Mg_2 in a pearlitic condition; a larger amount of Cd prevents this behaviour. A spheroidising treatment can also be given to the alloys. A. R. P.

X-Ray investigation of iron-nickel alloys. F. MARSCHAK and D. STEPANOV (*Z. Elektrochem.*, 1935, 41, 599—602).—Examination of Fe-Ni alloy electrodeposits shows that they consist of solid solutions, although there is evidence of slight heterogeneity at 30—50% Ni. E. S. H.

Dissolution of electrodeposits of iron-nickel alloys. D. STEPANOV, F. MARSCHAK, N. BALASCHOVA, and V. KABANOVA (*Z. Elektrochem.*, 1935, 41, 597—599).—The loss of wt. of Fe-Ni alloys immersed in sea- H_2O , 2—25N- H_2SO_4 , and 0.01N-lactic acid, respectively, has been determined as a function of composition of the alloy. The anodic behaviour of the alloys in the same electrolytes has also been examined. The results support the view that Fe and Ni form an unbroken series of solid solutions. E. S. H.

Kinetics of the breakdown of the solid solution Al-Mg. M. I. ZACHAROVA and V. K. TSCHIKIN (*Z. Physik*, 1935, 95, 769—774).—The limiting solubility of Al in Mg has been determined by X-rays at 150°, 218°, and 300°. The kinetics of breakdown of the solid solution vary greatly with the thermal treatment of the alloy. A. B. D. C.

Two-component system iron-tantalum. W. JELLINGHAUS (*Z. anorg. Chem.*, 1935, 223, 362—364).—Equilibrium data for the range 0—50 at.-% Ti are recorded, together with X-ray and magnetic data. The compound FeTi is indicated. S. J. G.

Magnetic properties of some nickel alloys. D. P. RAY-CHAUDHURY and P. N. SEN GUPTA (*Sci. and Cult.*, 1935, 1, 114).—The magnetic susceptibilities of alloys with Al, As, and Cr have been examined with reference to the influence of temp. C. W. G.

Diagram of state and magnetic properties of platinum-iron alloys. L. GRAF and A. KUSSMANN (*Physikal. Z.*, 1935, 36, 544—551).—The variation of magnetic properties of Pt-Fe alloys with composition and the concn. range in which intermediate phases are present have been investigated by micrographic, X-ray, and magnetic methods. The connexion between cryst. structure and magnetic properties has also been studied. The addition of Pt to Fe at first results in an increase of the saturation magnetism up to 10% > that of α -Fe; the val. then decreases with the formation of face-centred cubic γ -crystals. At room temp., in the neighbourhood of 26 at.-% Pt, the alloys consist almost entirely of γ -crystals, and are not ferromagnetic. Between 30 and 70 at.-% Pt the alloys are again strongly ferromagnetic (Curie point up to 450°). The ferromagnetic carriers are face-centred cubic γ -mixed crystals which are transformed below 1200° into ferromagnetic FePt (space-centred cubic, a 2.88 Å., without superstructure), with Curie point about 100° > that of mixed crystals of the same composition. Between 30 and 70 at.-% Pt, the hysteresis loop is very wide, giving a coercivity of 1800 gauss with a retentivity of 3000—4000 c.g.s. The width of the hysteresis loop is, in part, due to the distortion of the lattice on transition from mixed crystal to compound. A. J. M.

Special state of matter in certain alloys in relation to the volume. W. BILTZ and F. WEIBKE (*Z. anorg. Chem.*, 1935, 223, 321—361).—In the case of intermetallic compounds, the increment (contribution made per g.-atom by an element to the mol. vol. of the alloy) of a metal remains fairly const., independent of the nature and quantity of the partner. For a high degree of constancy the proportions should be < definite limits, and the two partners should lie far apart in the electrochemical series. The increments are somewhat < the at. vols., so that a contraction occurs when intermetallic compounds are formed; the contraction is a max. for the light and easily compressible metals. The vol. of mixed-crystal alloys is also an additive function of const. increments; the increment for a given element in a mixed crystal is usually slightly different from its val. in a compound. The connexion between the increment vals. and the lattice types of metals and alloys is discussed. In accordance with the electron theory of metals it is found that the contraction depends on the difference in nobility of the two metals and on their relative amounts. Metals in alloys behave like the free metals under pressure, and as a result the compressibility of alloys should be < for metals in the free state, since in alloys the metals are already compressed. This is found experimentally. Existing data and new results are discussed. S. J. G.

Criterion for ordered atomic distributions in series of metallic mixed crystals. H. J. SEEMANN (*Z. Physik*, 1935, 95, 796—798).—Mixed crystals with unordered at. distribution will give an ordered distribution if the lattice const. of the unordered mixed crystal is > that corresponding with linear variation of the const. from one pure metal to the other. A. B. D. C.

Special type of unstable mixed crystals with anomalous lattice constants. G. NATTA (Naturwiss., 1935, 23, 527—528).—The structure of films obtained by depositing metals on plates of other metals and then treating with dil. HNO_3 has been examined by the method of electron diffraction. The composition and structure of the film depend on the ratio of the at. radius of the pptd. metal to that of the pptg. metal. Films obtained by pptn. of Pt, Pd, or Ag on a metal of smaller at. radius, e.g., Cu, are solid solutions of Pt, Pd, or Ag in the Cu lattice, with const. between those of Cu and the pptd. metal. The val. of the lattice const. depends on the thickness of the film, the $[\text{HNO}_3]$, and the conditions of prep. of the film. The structure of films of Cu—Pt containing 30—70% Pt attains lower symmetry on heating. If Pt is deposited on a metal of greater at. radius, e.g., Ag, the lattice const. of the freshly prepared film is that of Ag. The film is insol. in 30% HNO_3 . On keeping for some days, or more rapidly on heating to 700° , the lattice const. becomes smaller. The film consists of unstable mixed crystals with the lattice const. of the foundation metal. A colour change often accompanies the contraction of the lattice.

A. J. M.

Perfect ternary solid solutions. H. SELTZ (J. Chem. Physics, 1935, 3, 503—505).—Equations for the solidus and liquidus surfaces for systems in which there is complete miscibility in the solid state and both liquid and solid solutions are perfect have been derived from fugacities (cf. A., 1934, 365). The system Au—Cu—Ni deviates markedly from ideality at low mol. fractions of Au.

R. C.

Specific heats of isobutyric acid—water mixtures at 15° . D. G. DAVIES (J.C.S., 1935, 1166—1167).—A sudden increase of sp. heat occurs at a concn. of about 22% of acid, above which two liquid layers exist.

E. S. H.

Molecular clustering in binary liquid mixtures. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 1, A, 915—927).—Depolarisation of light in different states of polarisation has been determined for scattering by the binary mixtures CS_2 —MeOH, MeOH—*n*-hexane, H_2O — $\text{Pr}^n\text{CO}_2\text{H}$, NH_2Ph —*cyclohexane*, PhNO_2 —*n*-hexane, NH_2Ph —*n*-hexane, PhOH — H_2O , H_2O — NMe_3 ; the results indicate presence of clusters from the crit. solution temp. to considerably higher temp.

A. B. D. C.

Optical investigations on the constitution of solutions and glasses. W. WEYL (Angew. Chem., 1935, 48, 573—575).—The optical properties of aq. and org. solutions are compared with those of glasses.

E. S. H.

Solubility of a mixture of hydrogen and nitrogen in water at 25° in the pressure range 50—1000 atmospheres. R. WIEBE and V. L. GADDY (J. Amer. Chem. Soc., 1935, 57, 1487—1488).—Data are recorded for the mixture $3\text{H}_2 : 1\text{N}_2$. The solubility of the mixture can be calc. within a few % from the vals. for the pure components.

E. S. H.

Diffusion of hydrogen and deuterium in palladium. I. W. JOST and A. WIDMANN (Z. physikal. Chem., 1935, B, 29, 247—255).—At 192 — 302.5° the

diffusion coeff. for $\text{H} = 5.95 \times 10^{-3} e^{-5720/RT}$ (sq. cm.; sec.). At 302.5° that for D is $1/1.35$ times the H val., which agrees with the ratio of the thermal velocities of H and D.

R. C.

Connexion between adsorptivity and physico-chemical properties of substances. S. S. URAZOVSKI and S. S. SCHARASCHENIDZE (Ukrain. Chem. J., 1935, 10, 152—160).—In homologous series the adsorptivity by C varies linearly with the dielectric const. and with the surface tension.

R. T.

Adsorption of atmospheric ions by active charcoal. W. ZIMMERSCHIED (Kolloid-Z., 1935, 72, 135—151).—Adsorption measurements in the ionised atm. provided by a Bunsen flame have been carried out, using three kinds of charcoal, each in three different states of division. The lighter ions are the more easily adsorbed; the amount of adsorption is \propto the ion density, and increases with decreasing particle size of the adsorbent. Little difference was observed in the behaviour of the different kinds of C. Adsorption probably occurs at the outer surface of the C, not at inner surfaces such as pores.

E. S. H.

Ion adsorption and exchange. E. J. W. VERWEY (Kolloid-Z., 1935, 72, 187—192).—Theoretical. Electrolyte adsorption is discussed in terms of the processes: (1) adsorption of ions which determine the potential, (2) exchange of the oppositely-charged ion, (3) pure adsorption of the electrolyte.

E. S. H.

Surface activity of silica gel treated with lime. A. MAFFEI and A. BATTAGLIA (Annali Chim. Appl., 1935, 25, 309—318).—Absorption of CaO by SiO_2 gel diminishes progressively as the temp. to which the gel has been previously heated rises. Especially with gels heated at low temp., the absorptive power is decreased by quenching the heated gel in H_2O at 20° . Velocity of dehydration curves, which express variations in the v.p., show that CaO increases the surface and adsorbent activity of the gel.

T. H. P.

Influence of surface tension of the intermicellar liquid on the structure formation of silica gel. V. S. VESSELOVSKI and I. A. SELAJEV (Kolloid-Z., 1935, 72, 197—202).—The formation of xerogels of SiO_2 by drying the hydrogel in air, and in air saturated with the vapours of xylene, PrOH , *iso*amyl alcohol, $\text{Bu}^n\text{CO}_2\text{H}$, PhOH , and EtOH , respectively, has been studied. The sorption properties of the resulting xerogels are influenced strongly by the surface tension of the intermicellar liquid. Other factors, such as concn. of SiO_2 in the hydrogel, ageing, etc., are of less importance. Alkaline hydrogels provide xerogels which are richer in pores than those derived from acid hydrogels.

E. S. H.

Capillary systems. XVII. (1) Regular logarithmic sphere-spirals and sphere-screws. E. MANEGOLD and H. LINDEMANN (Kolloid-Z., 1935, 72, 151—164; cf. this vol., 443).—Mathematical.

E. S. H.

Transparency of thin metallic films in the ultra-violet. H. H. HARTZLER (J. Opt. Soc. Amer., 1934, 24, 339—341).—A method for the production of thin metallic films is described. The observations, which extend from 4300 to 1600 \AA , have

afforded no evidence of any well-defined regions of transparency in Cu, Ag, Au, Mg, Al, Sn, Pb, As, Sb, and Bi. J. L.

Interference colours in oil films on water. K. B. BLODGETT (*J. Opt. Soc. Amer.*, 1934, **24**, 313—315).—A high-grade motor lubricating oil, oxidised by heat (or by exposure to light), is most suitable for the production of thin films; the more the oil is oxidised, the thinner is the film obtained. Films showing any required spectral colour are obtained by progressive dilution with an unoxidised oil or by altering the thickness of the films by compressing them in a confined area with the use of movable wax-coated barriers. J. L.

Physical properties of surfaces. II. Viscous flow of liquid films. Range of action of surface forces. S. H. BASTOW and F. P. BOWDEN (*Proc. Roy. Soc.*, 1935, **A**, 151, 220—233).—Films of a dil. solution of a liquid crystal shows a pronounced rigidity, but thin films of H_2O , cyclohexane, EtOH, AcOH, Et palmitate, and LiCl solution behave as perfect fluids even when cooled to within 0.1° of the f.p. The viscosity of the film is the same as that of the liquid in bulk, and there is no evidence for rigid oriented chains of mols. extending from the surface to a distance of 1500—50,000 Å. as reported. If such chains exist, their length is certainly < 1000 Å. L. L. B.

Expansion of films of myosin on potassium lactate. S. A. MOSS, jun., E. K. RIDEAL, and E. C. B. SMITH (*Nature*, 1935, **136**, 260).—At p_H 7, unimol. layers of myosin (I) expand on 0.5*M*-K lactate $>$ on equiv. solutions of KCl or other neutral salts. The extension occurs to a smaller degree with tartrates, but not with acetates or propionates. With lactate it increases with a rise in p_H . The effect appears to be sp. for (I). Lactate may facilitate relaxation of fibrils during muscle recovery. L. S. T.

Mechanism of flotation. IV. Oriented coagulation in non-polar and in aqueous media. Z. V. VOLKOVA (*Kolloid-Z.*, 1935, **72**, 229—233; cf. this vol., 820, 1071).—The oriented coagulation of asbestos fibres and $BaSO_4$ particles is described, and discussed as a condition for flotation. E. S. H.

Theory of flotation. WO. OSTWALD (*Z. physikal. Chem.*, 1935, **173**, 393—400).—A defence of the linear theory (cf. this vol., 931). R. C.

Effect of flotation reagents on the charge of suspensions of mineral particles. M. TICHONOV (*Bull. Acad. Sci. U.R.S.S.*, 1935, 239—254).—Alkaline solutions of peat-tar and oleic acid do not recharge an apatite suspension, probably because they affect the particles chemically. Both $Ca(OH)_2$ and oleic acid change the sign of the charge on quartz. Quartz particles adsorb oleic acid and $Ca(OH)_2$ coagulates colloidal muds. K ethylxanthate does not change the sign of oxidised pyrites which has not been treated with strong acids, but it is adsorbed by purified pyrites, changing the sign of the charge. Colloidal quartz muds, treated with $Ca(OH)_2$, change the sign of their charge and are adsorbed by pyrites

grains. Electric charges are an important factor, but do not wholly explain the phenomena of flotation. J. W. S.

Osmotic theory. K. WOHL (*Physikal. Z.*, 1935, **36**, 566).—The theory of Fredenhagen (*A.*, 1934, 252, 728) according to which the v.p. of a solution is \propto no. of free mols. of solvent per unit vol., is shown to give results which are thermodynamically impossible. A. J. M.

[Osmotic theory.] K. FREDENHAGEN (*Physikal. Z.*, 1935, **36**, 566—567).—A reply to Wohl (preceding abstract). A. J. M.

[Osmotic theory.] K. WOHL (*Physikal. Z.*, 1935, **36**, 567).—A reply to the above. A. J. M.

Kinetic significance of osmotic pressure. M. VON STACKELBERG (*Z. Elektrochem.*, 1935, **41**, 615 617).—Theoretical. E. S. H.

Study of solvation and measurement of thickness of the solvate sheath. N. S. SCHEINKER (*Kolloid-Z.*, 1935, **72**, 192—197).—Measurements of diffusion and η have shown that malachite-green is solvated in EtOH- H_2O solutions and that desolvation occurs on adding light petroleum or C_6H_6 . The thickness of the solvate sheath is 1.2—1.3 Å. E. S. H.

Density of aqueous solutions of lanthanum, cerous, praseodymium, and neodymium chlorides at 25° . C. M. MASON and H. L. LELAND (*J. Amer. Chem. Soc.*, 1935, **57**, 1507—1508).—Data are recorded with an estimated accuracy of ± 0.0002 g. per c.c. E. S. H.

Compressibility of strong electrolytes. H. FALKENHAGEN and C. BACHEM (*Z. Elektrochem.*, 1935, **41**, 570—575; cf. this vol., 820).—The adiabatic compressibilities of NaCl, KBr, $BaCl_2$, Na_2CO_3 , $MgSO_4$, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ at concns. < 1 mol. per litre have been derived from optical measurements of ultrasonic wave velocities. The apparent mol. compressibility is $\propto c^{1/2}$ for strong electrolytes, and $\propto c$ for non-electrolytes. T. G. P.

Determination of refractive index of aqueous solutions of electrolytes with free electric waves. A. DEMBER (*Ann. Physik*, 1935, [v], **23**, 507—528).—The method involves the use of free electric waves (λ 92.5 cm.). The positions of resonance were determined by setting up a stationary wave in the solution between a parabolic reflector and a plane mirror, thus giving the wave-length in the liquid. Solutions of HCl (0.0024*M*), NaCl (0.0084*M*), and $MgSO_4$ (0.0112*M*) have the same n , and therefore the same dielectric const. The calc. conductivity ratio for high and low frequencies shows a considerable increase (11%) due to dispersion in the case of the $MgSO_4$ solution. The results agree with the Debye-Onsager-Falkenhagen theory. Solutions of $CO(NH_2)_2$ show a molar increase of dielectric const. of 2.85 ± 0.4 , whilst 0.22*M*- $HgCl_2$ shows a decrease of 1.25 ± 0.4 , due to the admixture of symmetrical, non-polar $HgCl_2$ mols. with H_2O dipoles. A. J. M.

Effect of change of temperature on the constitution of water in solutions of electrolytes. C. S. S. RAO (*Proc. Roy. Soc.*, 1935, **A**, 151, 167—178; cf. this vol., 295).—The effect of a rise in temp. on

the constitution of H_2O in the pure liquid and in 8*N* solutions of LiCl , NaNO_3 , and H_2SO_4 has been investigated by a study of the Raman H_2O band. With rise of temp. (1) the position of the intensity max., as well as that of the lower-frequency portion, shifts towards higher frequency; (2) the part of the intensity curve on the lower-frequency side becomes less convex, whilst that on the higher-frequency side remains more or less unaltered in position and shape; (3) the band gets sharper, except in H_2SO_4 at 95°, which shows an increased broadening at this temp. These results are explained as being due to a simplification of the more complex H_2O mols. into simpler types, and by a change in the water of hydration of the ions of the solute. The peculiar result in H_2SO_4 at 95° is interpreted as being due to a breakdown of the hydrates present in solution into free ions and single H_2O mols. L. L. B.

Hydrogen-ion concentrations in, and absorption spectra of, aqueous solutions of chromium amines. I. T. UEMURA and H. SUÉDA (Bull. Chem. Soc. Japan, 1935, 10, 267—289).—The spectra at a series of p_{H} vals. for a no. of Cr amines are used to follow the changes in constitution of the amines with changing p_{H} . Cr amines which do not contain OH within the complex react acid in aq. solution, giving p_{H} 3—4 at concns. 0.003—0.002*M*. On increasing to p_{H} 4.5 approx., OH enters the complex except with $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Both H_2O of constitution and Cl if present alongside H_2O in the complex are easily replaceable by OH. S. J. G.

Liesegang rings. E. B. HUGHES (Kolloid-Z., 1935, 72, 212—216).—The theory formerly developed (cf. this vol., 702) is amplified and supported by measurements of ring distances. E. S. H.

Periodic precipitates (Liesegang rings). L. MAY (Kolloid-Z., 1935, 72, 217—221).—The formation of periodic diffusion structures, which conform with the conditions of Wo. Ostwald's diffusion-wave theory, is described. The theory is amplified by extending the concept of reversibility to include many physical changes, and is thus applied to the formation of periodic structures involving no chemical change. E. S. H.

Formation of platinum sols. I. W. PAULI and T. SCHILD (Kolloid-Z., 1935, 72, 165—178).—The concn. and purification by electro-decantation of Pt sols, prepared by electro-dispersion in dil. HCl, is described. The composition, properties, and reactions of the sols have been investigated. Determinations of the ratio $\text{H}^+ : \text{Cl}^-$ support the view that the charging complex is of the type $[\text{PtCl}_2(\text{OH})_n]\text{H}_2$. Analogies with Au sols are pointed out. E. S. H.

Electrical properties of colloidal solutions. V. J. N. MUKHERJEE and S. MUKHERJEE (Kolloid-Z., 1935, 72, 178—186).—A reply to criticism (cf. A., 1934, 488). E. S. H.

Effect of aggregation on the cataphoretic velocity of colloidal particles. J. N. MUKHERJEE and S. G. CHAUDHURY (Sci. and Cult., 1935, 1, 111—112).—A summary. C. W. G.

Deformation of swollen cellulose ester. O. KRATKY, G. SAITO, and V. BIERSTEIN (Z. Elektrochem.,

1935, 41, 518—519).—When a film of cellulose acetate is increased 20—30% in vol. by swelling in aq. dioxan and then stretched, the extension-double refraction curve indicates a net-like behaviour and saturation is reached at 100% extension. When the swelling is 45—55% the curve indicates that the micelles are carried along by the movement of the swelling agent. When the swelling is still greater the curve is linear up to an extension of 280%, and the double refraction then increases rapidly to saturation; the micelles appear to have an independent (Brownian) movement. A. G.

Diffusion of fatty acids in presence of cholate. O. FURTH and H. HERRMANN (Biochem. Z., 1935, 279, 326—337; cf. A., 1934, 961).—The rate of diffusion of iodobenzoic acid into gelatin in presence of Na glycocholate (I) is scarcely affected by changes in degree of acidity, presence of sugar, proteins, or blood-serum, or age of the gelatin, and not much by changes in the concn. of (I) or in the degree of dispersion of the gelatin. Inorg. ions greatly reduce the rate of diffusion. The colloidal condition of the gelatin and the degree of dispersion of the acid have no predominating influence on this rate. Ionic effects, depending on the electric charges, may be the decisive factors. The diffusion proceeds in accordance with Stefan's law (diffusion coeff. 0.006—0.010). The diffusion of the acid, in presence of (I), through porous glass plates into H_2O also follows the law, but (I) diffuses more rapidly than does the acid and retards its diffusion. W. McC.

Humic acids. K. ZEILE (Kolloid-Z., 1935, 72, 211—212).—The diffusion coeff. of humic acid, prepared by extracting peat with $(\text{CH}_3)_6\text{N}_4$ or $\text{CO}(\text{NH}_2)_2$ solutions, is 0.1345—0.1075 sq. cm. per day. The calc. particle wt. is 1060—1650. E. S. H.

Isoelectric point of gelatin. R. A. DULITZKAJA (Kolloid-Z., 1935, 72, 205—211).—The isoelectric points of three kinds of gelatin have been determined by electrophoretic, nephelometric, and viscosimetric experiments. The mean results are 4.87, 5.09, and 5.65—6.08 for the three gelatins. Potentiometric titrations with acid and alkali have also been carried out. A review of the results, together with published data, suggests that natural, unchanged collagen has a higher isoelectric point than gelatin, and that the variable vals. found for gelatin are due to different degrees of hydrolysis. E. S. H.

Heat capacity measurements on gelatin gels. III. W. R. HORN and J. H. MENNIE (Canad. J. Res., 1935, 12, 702—706).—The heat capacity of gelatin gels between 0° and 25° is > the sum of the heat capacities of the H_2O and gelatin. For gels containing >0.9 g. of H_2O per g. of gelatin the discrepancy is 6.7 g.-cal. per g. of dry gelatin. There is a sharp discontinuity in the heat capacity-concn. curve at 0.52 g. of H_2O per g. of gelatin, and it is inferred that this amount of H_2O is closely bound at 0°, whilst at higher temp. there is less bound H_2O or it is less firmly bound. J. W. S.

Physical chemistry of lipins. II. Protective power of lipins. M. SPIEGEL-ADOLF (J. Amer.

Chem. Soc., 1935, 57, 1431—1433; cf. A., 1932, 1089).—Kephalin (I) (prep. described) protects colloidal Au against flocculation 3—4 times as efficiently as does brain-lecithin (II), whilst egg-lecithin (III) is still less effective. Unlike (III), (I) is not flocculated by serum-albumin (IV) and only aged (I) is rendered cloudy by high pseudoglobulin concns. One part of (I) prevents heat-coagulation of 2 (not 3) parts of (IV) in H₂O and pptn. of 10 parts of (II) by proteins. (I) and (II) protect cholesterol sol against pptn. by salts or proteins, but (I) is 10 times the more effective. The protective power of (I) for Au is unimpaired by boiling, but that for cholesterol sols is largely destroyed by ultra-violet light. Irradiated (I), however, does not ppt. Au sol nor does it haemolyse erythrocytes. R. S. C.

Colloid chemistry of edestin. I. K. HOLWERDA (Biochem. Z., 1935, 279, 353—380).—The separation of edestin (18.4% N, 0.03% ash, isoelectric point about p_H 7.0) from sols (obtained by peptisation with salt solutions) by addition of H₂O is a form of coacervation, the separation and peptisation being colloidal processes. The effect of addition of salts on the acidity and peptisation of the sols and the effect of protein concn. and acidity on the viscosity of the sols have been measured. Denaturation by salts is usually not appreciable if the p_H is >5.2. During peptisation lyotropic influences, especially those of anions, are pronounced. W. McC.

Dissociation constants of weak and moderately strong electrolytes. II. **Dissociation constant and solubility of 2:4-dinitrophenol in salt solutions.** H. VON HALBAN, G. KORTUM, and M. SELER (Z. physikal. Chem., 1935, 173, 449—465; cf. this vol., 34).—The optical determination of the dissociation const., K_c , has been extended to NaClO₄ and BaCl₂ solutions and the solubility in NaCl, KCl, KClO₄, NaClO₄, and BaCl₂ solutions of concn. 0.01—1M at 25° determined. The considerable differences between the K_c -concn. curves for the various salt solutions are due principally to the activity coeff. of the undissociated acid; the variations in the mean activity coeff. of the acid ions are smaller. Theories of salting in and salting out so far proposed are inadequate; in addition to hydration, sp. properties of the ion which are influenced by the oppositely charged partner appear to be involved. R. C.

Dissociation constants of acids in light and heavy water. O. HALPERN (J. Chem. Physics, 1935, 3, 456—457).—The ratio of the consts. for an acid in H₂O and D₂O is the larger the weaker is the acid, owing to the differences in zero-point energy of the proton (deuteron) when combined with the anion and in the dissociated hydrated state. R. C.

Determination of the second dissociation constant of carbonic acid. O. WEIDER (Ber., 1935, 68, [B], 1423—1430).—The method depends on the extrapolation of the concn.-dissociation const. (K_2) of the given solutions first to vals. in pure NaCl solution with the same [Na⁺] and then to vals. in pure H₂O. If the actual dissociation const. is K_2 , then $K_2^- = [H^+][CO_3^{2-}]/[HCO_3^-]$ and $K_2^0 = {}^aH^+{}^aCO_3^{2-}/{}^aHCO_3^-$. K_2^0 is the val. of K_2 at infinite dilution. Determinations

are based on electrochemical measurements, using the chain, Pt, H₂, [x], 3.5N-KCl|0.1N-KCl, HgCl|Hg, and the measured potential is expressed $E - E_0 + E_D + (RT/F \log e) \log a_{H^+}$, in which E_0 is a const. and E_D the diffusion potential. The uncertainty in the val. of E_0 is overcome by an adaptation of the method of Bjerrum and Unmack. At 0° and 18° the vals. of K_2 are 2.29×10^{-11} and 4.01×10^{-11} , respectively. H. W.

Multivalent amino-acids and peptides. IV. **Apparent dissociation constants of α -aminotri-carballic acid and of glycyl- α -aminotricarballic acid.** J. P. GREENSTEIN and N. R. JOSEPH (J. Biol. Chem., 1935, 110, 619—624).—Measurements at 25° show that the dissociation range of the peptide is narrower than that of the NH₂-acid. F. A. A.

Hydrogen-ion concentration of lead solutions. D. N. MEHTA and S. K. K. JATKAR (J. Indian Inst. Sci., 1935, 18, A, 75—83).— p_H vals. of solutions of PbO and Sb₂O₃ agree with those calc. from solubility data. C. W. G.

Heavy-metal compounds as neutral constituents of complex cations. E. HAYEK (Z. anorg. Chem., 1935, 223, 382—386).—The undissociated mol. of a compound in solution may become attached to a cation. This cation (best derived from its perchlorate, since perchlorates are highly dissociated) should be very small (e.g., Be) or strongly polarising (e.g., Ag⁺, Hg²⁺, Pb²⁺, Tl⁺); the neutral mol. which is to become attached should be a sparingly sol. compound, composed of a strongly polarising cation and an easily polarisable anion, since these show small dissociation (e.g., halides of Ag, Hg, Pb, Tl). Solubility experiments along these lines gave the following results: halides of Ag and Hg dissolve in solutions of corresponding perchlorates with increasing ease as at. wt., and therefore polarisability of the halogen, increases; PbI₂ dissolves in perchlorates of Ag and Hg, but not of Pb. Among oxides, PbO being amphoteric dissolves readily in its salt solution; Ag₂O and HgO, less amphoteric, dissolve slightly in conc. AgClO₄, although HgO is insol. in Hg(ClO₄)₂. Ag₂S and Ag₂Se are sol. in AgClO₄. Certain results were confirmed by transference experiments. The following compounds were isolated by dissolving the neutral constituent in hot conc. solution of the corresponding perchlorate and cooling: [Hg(HgI₂)](ClO₄)₂; [Hg(HgI₂)₂](ClO₄)₂; [Hg(AgBr)₂](ClO₄)₂; 2AgClO₄.AgI; [Hg(HgO)₂](ClO₄)₂. S. J. G.

Vapour pressures of aqueous potassium chloride solutions, and their thermodynamic utilisation. Z. SHIBATA and K. NIWA (Z. physikal. Chem., 1935, 173, 415—426).—The v.p. and v.-p. depressions have been measured from 0—10° from 0.2736M to saturation. The product of the entire heat of dissolution and concn., in mol. per litre, of the saturated solution at 0—25° is —17,811 g.-cal. From the results there have been calc. differential and last heats of dissolution, and the activity in each solution of the H₂O at 0—25° and the KCl at 25°. R. C.

Determination of thermodynamic properties of solutions of mineral salts during evaporation and crystallisation. G. I. VOINLOVITSCH, L. K.

ACHRAP, and L. S. MAI (J. Appl. Chem. Russ., 1935, 8, 589—597).—Formulæ are derived which connect the v.p. with the heats of evaporation and dilution of aq. solutions, and with the heats of dissolution of various salts. R. T.

Free energy of sulphur dioxide. A. R. GORDON (J. Chem. Physics, 1935, 3, 336—337).—Vals. of $(F^\circ - E^\circ)/T$ are calc. from spectroscopic data. The heat of formation of SO_2 from S_2 and O_2 is calc. from the heats of formation of SO_2 and H_2S , and from the dissociation energy of H_2S . Equilibrium const. for the reactions $\frac{1}{2}\text{S}_2(g) + \text{O}_2 = \text{SO}_2$ and $\text{SO} + \frac{1}{2}\text{O}_2 = \text{SO}_2$ are tabulated for the range 298.1—2800° abs.

N. M. B.

Heat of formation of azoimide. P. GUNTHER and R. MEYER (Z. Elektrochem., 1935, 41, 541).—From the explosion of gaseous HN_3 at 60—100 mm., the heat of formation from its elements is found to be 70.9 ± 0.5 kg.-cal. at const. vol. T. G. P.

Heat content and lattice structure of active ferric oxide. II. Amorphous ferric oxide hydrate as initial material. R. FRICKE and L. KLENK (Z. Elektrochem., 1935, 41, 617—622; cf. A., 1934, 1083).—The heat of dissolution of amorphous $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, after dehydration at 250°, in HF has been determined and the influence of the duration of dehydration investigated. The vals. obtained decrease as the duration of heating increases; the max. difference, 13,000 g.-cal. per mol. Fe_2O_3 , is regarded as a lower limit for the heat of crystallisation in the change amorphous $\text{Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$.

E. S. H.

Apparent molal heat capacities of amino-acids and other organic compounds. J. T. EDSALL (J. Amer. Chem. Soc., 1935, 57, 1506—1507).—Comparison of published data for the mol. heat capacities of org. compounds in dil. aq. solution and in the pure state shows that the presence of a hydrocarbon chain tends to produce a positive deviation from the ideal solution law, whilst substances which contain many polar groups behave more nearly like ideal solutes in H_2O .

E. S. H.

Thermodynamic problem. R. EMDEN (Z. Elektrochem., 1935, 41, 622—623).—A discussion (cf. this vol., 301, 446).

E. S. H.

System $\text{HgCl}_2\text{--PbCl}_2$. M. VAN DRIEL (Z. anorg. Chem., 1935, 223, 318—320).—Two liquid phases coexist between 6 and 44 mol.-% PbCl_2 ; the three-phase temp. $[L_1 + L_2 + S_{\text{PbCl}_2}]$ is 414°. The eutectic point lies very close to the m.p. of HgCl_2 . S. J. G.

Oxygen pressures of liquid $\text{FeO--Fe}_2\text{O}_3$ melts. W. KRINGS and H. SCHACKMANN (Z. Elektrochem., 1935, 41, 479—487).— O_2 pressures of molten $\text{FeO--Fe}_2\text{O}_3$ mixtures, with or without added SiO_2 or CaO , have been measured between 1550° and 1600° and 5 and 500 mm., and the dependence on temp. and composition has been determined. T. G. P.

System calcium carbide-lime. G. FLUSIN and C. AALL (Compt. rend., 1935, 201, 451—453).—The f.-p. diagram of the system $\text{CaC}_2\text{--CaO}$ in presence of traces of SiO_2 , Fe_2O_3 , Al_2O_3 , MgO , C, and SO_3 has eutectics at 68% of CaC_2 (1750°) and at 35.6% of

CaC_2 (1800°), with a max. at 52.5% of CaC_2 (1980°) corresponding with the compound $\text{CaC}_2\text{,CaO}$.

R. S. B.

Decomposition pressures of nitrates and sulphates. III. Anhydrous copper nitrate. B. NEUMANN and A. SONNTAG (Z. Elektrochem., 1935, 41, 611—615; cf. A., 1933, 45, 1246).—Decomp. pressures of $\text{Cu(NO}_3)_2$ at different temp. are recorded and the heats of formation calc. The thermal decomp. involves the intermediate formation of $4\text{CuO,3N}_2\text{O}_5$.

E. S. H.

Critical points of transformation of difficultly fusible oxides, and of their hydrates, at high temperatures. P. N. LASCHTSCHENKO and D. I. KOMPANSKI (J. Appl. Chem. Russ., 1935, 8, 628—653).—Cooling curves suggest the hydrates $\text{ZnO, H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 0.5, 1, 2$, and $3\text{H}_2\text{O}$, $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{SnO}_2 \cdot 0.5$ and $1\text{H}_2\text{O}$, $\text{TiO}_2 \cdot 0.5$ and $1\text{H}_2\text{O}$. The transformation points recorded are: ZnO 570°, Al_2O_3 940°, bauxite 950°, kaolin 860°, obsidian 850°, SnO_2 400—420°, cassiterite 425—435°, TiO_2 650°, and brookite 760—790°.

R. T.

Active oxides. XCI. Active states occurring during the chemical combination of two metallic oxides. G. F. HUTTIG (Z. Elektrochem., 1935, 41, 527—538; cf. this vol., 930).—A comprehensive survey of recorded results. New data are given for the systems $\text{MgO--Fe}_2\text{O}_3$, $\text{ZnO--Fe}_2\text{O}_3$, $\text{CaO--Fe}_2\text{O}_3$, $\text{CuO--Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--CuO}$, $\text{CdO--Fe}_2\text{O}_3$, $\text{Cr}_2\text{O}_3\text{--Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3\text{--CuO}$, $\text{SiO}_2\text{--Fe}_2\text{O}_3$, $\text{SiO}_2\text{--Cr}_2\text{O}_3$, $\text{TiO}_2\text{--Fe}_2\text{O}_3$, $\text{TiO}_2\text{--Cr}_2\text{O}_3$. T. G. P.

Stabilities of aluminates. H. ZUR STRASSEN (Z. Elektrochem., 1935, 41, 476—478).—The affinities for Al_2O_3 of the oxides of Ca, Cd, Zn, Mg, Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , and Bi have been compared by studying the equilibria $\text{M}^{\text{II}}\text{O} + \text{M}^{\text{II}}\text{O,Al}_2\text{O}_3 \rightleftharpoons \text{M}^{\text{II}}\text{O} + \text{M}^{\text{II}}\text{O,Al}_2\text{O}_3$. Three reaction types are indicated: (a) the oxides and aluminates exist in four separate phases, (b) the oxides and the aluminates form mixed crystals, and (c) the aluminates are completely, but the oxides incompletely, miscible. The stability of the aluminates generally increases with decreasing lattice energy of the bivalent oxide. Aluminates of the spinel type are divisible into two groups on the basis of their reaction with gehlenite ($2\text{CaO,Al}_2\text{O}_3\text{,SiO}_2$): $\text{MgO,Al}_2\text{O}_3$ and $\text{ZnO,Al}_2\text{O}_3$ are more stable, and the rest less stable, than is gehlenite.

T. G. P.

System ultramarine-sulphur. E. GRUNER (Z. Elektrochem., 1935, 41, 478—479).—Chemical and X-ray examination of the thermal desulphurisation of ultramarine, and its reaction with KCN, show that a part of the S is linked to the free alkali of the fundamental lattice unit, since the sulphide-S cannot be removed without loss of alkali, although the lattice is not thereby affected.

T. G. P.

Equilibrium $\text{NaCl--HCl--H}_2\text{O}$ at 18°. R. FRICKE and F. BRUMMER (Z. anorg. Chem., 1935, 223, 397—398).—The solubility of NaCl in 0—5M-HCl has been determined at 18°.

S. J. G.

Matter-current-work relationships in ideal electrochemical polyphase systems. Faraday's law of electrolysis in ideal galvanic cells. E.

LANGE and K. NAGEL (Z. Elektrochem., 1935, 41, 575—582).—Theoretical. T. G. P.

Electrolytic transport of carbon in solid steel. W. SEITH and O. KUBASCHOWSKI (Z. Elektrochem., 1935, 41, 551—558).—Diffusion of C along a steel wire heated to 1000° has been studied photomicrographically and by conductivity measurements. The "mobility" of C towards the cathode determined by independent methods is 1.6 and 2.2×10^{-5} (sq. cm. sec. volt), whilst an evaluation from the diffusion const. gives 0.8×10^{-5} on the assumption that univalent C is involved. Diffusion also occurs towards the anode, but much more slowly. T. G. P.

Reaction of borax-glycerol-water solutions. P. VAN DER WIELEN (Pharm. Weekblad, 1935, 72, 875—877).—The p_H varies with the composition of the solvent. Solutions containing 20% of glycerol are neutral. S. C.

E.m.f. of the quinhydrone electrode in heavy water. Acidic dissociation of deuterioquinone. V. K. LA MER and S. KORMAN (J. Amer. Chem. Soc., 1935, 57, 1511).— $E_D - E_H = 0.0345$ volt. The ratio of the acid dissociation consts. is given by $K_H/K_D = 3.84$. E. S. H.

Theory of galvanic potentials. I. P. GROSS and O. HALPERN (J. Chem. Physics, 1935, 3, 458—460).—Thermodynamic considerations show that differences in normal electrode potentials can be expressed by the difference between a group of quantities which refer only to the properties of the substances forming the electrode and are independent of the solvent, e.g., heat of vaporisation of the neutral electrode atom, and another group relating to the free energy liberated when a gaseous ion of the substance forming the electrode is dissolved in the solvent. There is no general theoretical evidence of the equivalence of voltaic and galvanic potentials. R. C.

Polarographic studies with the dropping mercury cathode. II. Electroreduction of unsaturated acids. L. SCHWAER (Coll. Czech. Chem. Comm., 1935, 7, 326—335).—There is a sharp rise in the current-voltage curve at the potential, v , at which the unsaturated acid (I) is reduced ($2F$ per mol.), and the saturation current $\propto [(I)]$. In $N\text{-HCl}$, only undissociated mols. of (I) are reduced, and the vals. of v with respect to the $N\text{-Hg}_2\text{Cl}_2$ electrode are pyruvic (-0.2 volt) $<$ acetylenedicarboxylic $<$ fumaric (II) and maleic (III) $<$ aconitic $<$ mesaconic (IV) and citraconic (V) $<$ cinnamic acid (-0.96). The anions of these acids and the sorbate ion in neutral and alkaline solutions have sp. vals. of v between -1.2 and -2.1 which depend on the [neutral salt]. Bi- and ter-valent cations decrease the magnitude of v . The *cis*- and *trans*-forms of an acid have the same v in acid solution, but in neutral and alkaline solution, the magnitude of v for (II) is $<$ (III) and (IV) is $<$ (V) in $4N\text{-Li}_2\text{SO}_4$; an excess of NH_4^+ , primary, *sec.*-, and *tert.*-amine ions reverses the relative orders of magnitude, probably owing to buffer action. Crotonic, itaconic, and lævulic acids are not reduced. The nature of the system of double linkings which are

reducible is discussed, and the polarographic determination of unsaturated acids in mixtures is indicated. J. G. A. G.

Asymmetry of the ferrous iron-dichromate titration curve. P. K. WINTER and H. V. MOYER (J. Amer. Chem. Soc., 1935, 57, 1402—1403).—A symmetrical curve is obtained when a sufficiently long time is allowed for the potential to approach equilibrium after the end-point is passed. The abnormal asymmetry is due to the fact that the dichromate-chromic electrode potential is not strictly reversible. E. S. H.

Simultaneous cathodic and anodic direct-current polarisation of electrodes. I. Electrodes of platinum, palladium, and gold. P. S. TUTUNDŽIĆ (Z. Elektrochem., 1935, 41, 602—611).—The influence of a superimposed d.c. on the potential of cathodes of Pt, Pd, and Au in $2N\text{-H}_2\text{SO}_4$ at room temp. and on the decomp. potential has been studied, with reference to direction of current, p.d., and c.d. The depolarising effect obtained in the one direction is $<$ that obtained by the use of oxidising agents in the solution. When the opposite polarisations are equal, the electrode attains a const. end val. of $+0.927 \pm 0.005$ volt, which is regarded as the true potential of formation of H_2O . E. S. H.

Processes [occurring] on the anode during the electrolysis of picrates in non-aqueous solvents. E. HERTEL and F. KRUGER (Z. Elektrochem., 1935, 41, 564—569).—The dependence of the anode potential on the nature of the solvent, concn., stirring, anode surface, and temp. has been determined in an endeavour to explain the peculiar relationship which exists between anodic and applied potential during electrolysis. T. G. P.

Absolute rate of reactions in condensed phases. W. F. K. WYNN-JONES and H. EYRING (J. Chem. Physics, 1935, 3, 492—502).—The activated complex theory (this vol., 586) shows the rate of a reaction of any order in any phase where the slow process is the surmounting of a potential energy barrier to be equal to the product of a transmission coeff., a universal frequency, an equilibrium const. between an activated complex and the reactants, and an activity coeff. factor. The theory is successfully applied to numerous unimol. and bimol. reactions, including those having velocities anomalous from the point of view of the collision theory, and to acid-base catalysis. Brönsted's, Lewis', and other earlier theories of reaction rate are special cases of the present theory. The latter reduces velocity problems to the thermodynamic calculation of an equilibrium const. for the activated complex and the calculation of a transmission coeff. which often ≈ 1 . R. C.

Entropy and the absolute rate of chemical reactions. II. Unimolecular reactions. O. K. RICE and H. GERSHINOWITZ (J. Chem. Physics, 1935, 3, 479—489).—The considerations previously advanced (this vol., 306) are further developed and correlated with Eyring's theory (*ibid.*, 586). The rates of numerous unimol. reactions may be accounted for either by examining the extent to which rotational degrees of freedom must be frozen out for the reverse

bimol. or termol. association to occur or by Eyring's method. R. C.

Statistical mechanical treatment of the activated complex in chemical reactions. L. S. KASSEL (J. Chem. Physics, 1935, 3, 399—400).—A crit. discussion of Eyring's method of computing abs. reaction rates (this vol., 586). H. J. E.

Mechanism of polymerisation reactions. I. H. DOSTAL and H. MARK (Z. physikal. Chem., 1935, B, 29, 299—314).—Theoretical. Kinetic formulæ are derived assuming that polymerisation to chains consists in nucleus formation followed by growth, the relative rates of the two processes determining the course of the reaction (cf. A., 1934, 607). R. C.

Activation energy of unimolecular reactions. II. O. K. RICE and H. GERSHINOWITZ (J. Chem. Physics, 1935, 3, 490—492).—The theory previously developed (A., 1934, 846) is revised, and related to Kassel's quantum theory of unimol. reactions (A., 1928, 960). The connexion between observed activation energy and the energy required to break the linking is discussed. R. C.

Mechanism of chemical reactions. C. N. HINSHELWOOD (J.C.S., 1935, 1111—1115).—Theoretical. Two classes of activated mols. are distinguished: (i) preactivated mols. which have received so much energy that they can decompose after a certain internal redistribution of energy, and (ii) critically activated mols. which possess sufficient energy in sp. linkings to ensure decomp. within the next vibration period. These conceptions lead to a general interpretation of the wide variations in the vals. of the probability factor P found when the equation rate = $PZe^{E/RT}$ is applied to catalysed and uncatalysed unimol. and bimol. reactions. Factors greatly affecting the magnitude of P for bimol. reactions are mol. orientation, the short time available for appropriate redistribution of energy during the life of the collision complex, and entities facilitating sp. energy transfers. The relation between P and the energy of activation, E , in series of related reactions is discussed. J. G. A. G.

Thermodynamic theory of detonation. R. L. SCORAH (J. Chem. Physics, 1935, 3, 425—430).—Theoretical. The speed at which detonation is stable is determined from considerations of available energy. Agreement with experimental vals. was obtained for a H_2 - O_2 mixture. H. J. E.

Thermal decomposition of ozone. M. RITCHIE (Nature, 1935, 136, 221).—A reply to criticism (cf. this vol. 1080). L. S. T.

Thermal reactions of gaseous hydrocarbons. Paraffins, olefines, acetylenes, and cycloparaffins. G. EGLOFF and E. WILSON (Ind. Eng. Chem., 1935, 27, 917—933).—A survey is given of published work on the mechanism of the thermal reactions of gaseous hydrocarbons. The reaction products may be accounted for by (1) polymerisation, (2) hydrogenation to C_2H_6 , (3) scission of one C—H, (4) scission of the double linking, (5) dehydrogenation to C_2H_2 . For gaseous paraffins and higher olefines, the reactions occurring at $< 750^\circ$ must be considered in addition to the reactions of C_2H_4 . The nature of the products

is dependent on temp., pressure, and contact time and the energy of activation is an important guide to possible reactions at a given temp. C. C.

Pyrolysis of propane in presence of water vapour.—See this vol., 1221.

Flash points and explosion limits of ethyl alcohol-trichloroethylene mixtures. K. R. DIE-TRICH and H. GRASSMANN (Z. Spiritusind., 1935, 58, 251—252).—The flash point of EtOH is raised by additions of $> 50\%$ C_2HCl_3 , being 22° and 50° for mixtures containing 80% and 90% C_2HCl_3 , respectively. The explosion region for EtOH- C_2HCl_3 -air mixtures gradually narrows for vapours arising from liquid EtOH- C_2HCl_3 mixtures containing $> 40\%$ C_2HCl_3 , whilst mixtures containing $< 72\%$ C_2HCl_3 give non-explosive vapours. S. J. G.

H-atom concentration and mechanism of the thermal decomposition of some organic molecules. H. SACHSSE [with F. PATAT] (Z. Elektrochem., 1935, 41, 493—494).—From measurements of the stationary concn. of H atoms during the decomp. of $COMe_2$, $MeCHO$, $EtCHO$, CH_2O , and C_2H_4 , using para-H, as indicator, the authors assess the relative merits of Rice and Herzfeld's (A., 1934, 369) and Fletcher and Hinshelwood's (A., 1933, 910) theories of the thermal dissociation of org. mols. T. G. P.

Equilibrium and kinetics of bromine chloride ($BrCl$). G. BRAUER and E. VICTOR (Z. Elektrochem., 1935, 41, 508—509; cf. A., 1934, 984).—Reaction between Br and Cl_2 has been examined spectro-photometrically. The bimol. dark reaction is a chain process strongly influenced by the walls. The heat of reaction is 310 ± 30 g.-cal., and $K = 0.144 \pm 0.003$. The photo-reaction is affected equally by light in the continuous or banded regions, and is a chain process of quantum yield $1-2 \times 10^3$. T. G. P.

Limits of inflammability of diethyl ether and ethylene in air and oxygen. G. W. JONES, W. P. YANT, W. E. MILLER, and R. E. KENNEDY (U.S. Bur. Mines Rep. Invest., 1935, No. 3278, 1—5).—The following vals. indicate the lower and upper limits, respectively. In air: Et_2O 1.85, 36.50%, C_2H_4 2.75, 28.60%; in O_2 : Et_2O 2.10, 82.00%, C_2H_4 2.90, 79.90%. E. S. H.

Reactions of oxides of nitrogen with atomic oxygen and nitrogen. M. L. SPEALMAN and W. H. RODEBUSH (J. Amer. Chem. Soc., 1935, 57, 1474—1476).—The reaction $NO_2 + O = NO + O_2$ is estimated to have a probability 10^{-5} per collision at 40° . The reactions $N + NO_2 = 2NO$ and $N + NO = N_2 + O$ are fairly rapid. The reaction $NO + O = NO_2$ appears to take place by triple collision and is accompanied by the O afterglow. E. S. H.

Reactivity of atoms and groups in organic compounds. XVI. Relative effect of substituents on the rates at which aryl and alkyl chlorides react with ethyl alcohol. J. F. NORRIS, E. V. FASCE, and C. J. STAUP. XVII. Effect of change in reactant and of temperature on the relative reactivities of substitution products of benzoyl chloride. J. F. NORRIS and H. H. YOUNG, jun. XVII. Effect of the solvent on the rate of

reaction between benzoyl chloride and ethyl alcohol. J. F. NORRIS and E. C. HAINES (J. Amer. Chem. Soc., 1935, 57, 1415—1420, 1420—1424, 1425—1427; cf. this vol., 487).—XVI. k for the first-order reaction of $C_6H_5X \cdot COCl$ with an excess of EtOH at 0°, Pr^oOH at 25°, and H₂O in COMe₂ at 0° and of $C_6H_5X \cdot CHPhCl$ with EtOH at 25° and H₂O in COMe₂ at 60° are determined by measurement of Δ . With EtOH the effect of substituents is > with Pr^oOH. BzCl reacts 6 times as fast with H₂O as with EtOH at 0°, but the effect of substitution, except by Me, in the EtOH is > in the H₂O series. The relative effects of substitution, except by *p*-Me, are opposite with BzCl and CHPh₂Cl. The relative k for $C_6H_5X \cdot COCl$ -EtOH at 0° are X=*o*-2.2, *m*-20.5, and *p*-NO₂ 21.6, *o*-3.7, *m*-0.85, and *p*-Me 0.78, *o*-29, *m*-1.1, and *p*-OMe 0.81, *o*-3.5, *m*-5.6, and *p*-Cl 1.9, and *o*-2.9, *m*-4.1, and *p*-I 1.9.

XVII. Changes of k for the reaction of $C_6H_5X \cdot COCl$ with MeOH and EtOH with change of X are in the same order except for the pair, X=*o*-Me and *m*-Cl. Heat of reaction, measured by k , with EtOH at 0° and 25°, bears no relation to the abs. val. of k , but is controlled by the nature and position of X. 2:4:6-Tri-nitro- and -bromo-benzoyl chloride react very slowly with MeOH; 2:4:6-*C*₆H₂Me₃·COCl reacts very fast.

XVIII. k for the second-order reaction of BzOH with EtOH at 25° in 17 solvents is measured. R. S. C.

Oxidation of silicon hydrides. I. H. J. EMELEUS and K. STEWART (J.C.S., 1935, 1182—1189; cf. this vol., 451).—At the lower crit. oxidation pressure, P_i , of SiH₄-O₂ mixtures at 15°, there is a sp. approx. hyperbolic relation between p_{O_2} and p_{SiH_4} , depending on the diameter, D , of the tube (p_{O_2} is much < p_{SiH_4}). P_i is depressed by adding N₂ and by increasing D . Induction periods were observed. The upper crit. oxidation pressure, P_u , at 100° is raised slightly by adding N₂ and He, but $P_{O_2} + P_{SiH_4}$ is diminished. P_u is depressed by SO₂, C₂H₄, C₆H₆, EtI, CHCl₃, COMe₂, and EtOH. There is very little reaction at pressures > P_u , and the effect of temp. on P_u has been investigated. A branched-chain mechanism is proposed which, with the data for P_u , leads to a chain length of 2 and a probability of branching of 1 in 6. J. G. A. G.

Kinetics of the reaction between carbonyl sulphide and water. H. W. THOMPSON, C. F. KEARTON, and S. A. LAMB (J.C.S., 1935, 1033—1037).—The reaction between COS and H₂O (i) in aq. solution at 15.5—47.4°, (ii) in EtOH at 60—75°, and (iii) in the gas phase at 244—382° has been investigated. The reaction between the vapours is partly heterogeneous, and the very slow reaction between EtOH and COS, probably COS+EtOH→CO₂+EtSH, does not interfere with (ii). The velocities of the bimol. reactions in (ii) and (iii) are several powers of 10 < the vals. calc. by means of the observed energies of activation, 15,000 and 25,700 g.-cal., respectively. The velocity coeff. in (i) is $k=5 \times 10^{16} e^{-26,260/RT}$, corresponding with a collision frequency slightly > the calc. val., and is diminished by added AcOH and HCl. The results suggest that, in general, the reaction between COS and H₂O is "slow" and becomes "normal" only in an ionic atm. J. G. A. G.

Kinetic medium and salt effects in reactions between ions of unlike sign. Reaction between ammonium ion and cyanate ion. J. C. WARNER and E. L. WARRICK (J. Amer. Chem. Soc., 1935, 57, 1491—1495).—The rate of conversion of NH₄CNO into CO(NH₂)₂ has been studied at 50° in H₂O and in binary mixtures of H₂O with MeOH, EtOH, Pr^oOH, and 1:4-dioxan having dielectric consts. ranging from 65 to 40. The primary salt effect in each solvent mixture agrees well with that predicted by the Bronsted-Christiansen theory for a reaction between univalent ions of opposite charge. Differences in rate consts. at equal dielectric consts. are discussed.

E. S. H.

Kinetics of the Friedel-Crafts ketone and hydrocarbon syntheses. H. ULICH and G. HEYNE (Z. Elektrochem., 1935, 41, 509—514).—The progress of the reactions between (I) BzCl and C₆H₆ and (II) Pr^oCl and C₆H₆ in CS₂ solution in presence of (a) AlCl₃ and of (b) GaCl₃ have been studied by measuring the vol. of HCl evolved. (I) is unimol., and proceeds by way of MCl₃-BzCl complexes. The resulting COPh₂ forms more stable complexes with AlCl₃ than does BzCl, and thus deactivates the catalyst. (II) proceeds by way of MCl₃-Pr^oCl complexes which are in equilibrium with similar complexes formed by C₆H₆ and by the reaction products. The changes in equilibrium concn. of the complexes caused by the reaction result in dissolution of AlCl₃ in the early stages of (IIa) with an increase in reaction velocity, whereas in (IIb) the catalyst is dissolved from the start. GaCl₃ is a better catalyst than AlCl₃ for reaction (II). T. G. P.

Kinetics of the reaction between hydrogen peroxide and the sodium salt of *p*-toluenesulphon-chloroamide (chloramine-T). J. COULL, H. B. HOPE, and B. GOUQUELL (J. Amer. Chem. Soc., 1935, 57, 1489—1490).—A differential equation expressing the rate of reaction at const. [H⁺] and [Cl⁻] has been developed. E. S. H.

Relation between the rates of reactions and oxidation-reduction potentials. I. Oxidation of formate ion by halogens in the dark. II. Oxidation of oxalate by halogens in the dark. B. F. CHOW (J. Amer. Chem. Soc., 1935, 57, 1437—1440, 1440—1443).—I. The empirical relation previously reported for the oxidation of oleic acid and linseed oil (A., 1934, 607) holds also for the oxidation of HCO₂⁻ by I or Br.

II. The same relation is applicable to the oxidation of C₂O₄²⁻ by Cl₂, Br, or I. E. S. H.

Rates of reaction of brominated malonic and succinic acid salts with the thiosulphate ion at two temperatures. M. H. BEDFORD, R. J. AUSTIN, and W. L. WEBB (J. Amer. Chem. Soc., 1935, 57, 1408—1411).—Reaction velocities have been determined over a range of concn. and temp. The results cannot be explained by the Bronsted theory, but are explicable in terms of the orientation hypothesis of La Mer and Kamner. E. S. H.

Study of enzyme action by thermal analysis of reaction velocity. I. Action of invertase.—See this vol., 1278.

Factors determining the velocity of reactions in solution. Formation of quaternary ammonium salts in benzene solution. C. A. WINKLER and C. N. HINSHELWOOD (J.C.S., 1935, 1147—1151).—The activation energies, E , of twelve reactions between alkyl halides and C_5H_5N , quinoline, NMe_3 , and NEt_3 are calc. from velocity measurements at 4—140°. The probability factor P , in the equation $k = PZe^{-E/RT}$, is of the order 10^{-6} — 10^{-8} . The vals. of k , the velocity coeff., for $MeI > EtI > Pr^iI$, are related chiefly to increases of E , but P decreases in the series $EtI(Br) > Pr^iI(Br)$. Orientation effects account for the vals. of P ; $NMe_3 > NEt_3$ and $C_5H_5N > \text{quinoline}$. k and P increase in the series alkyl $Br < \text{alkyl } I$, possibly owing to the ability of I to facilitate crit. activation (cf. this vol., 1206). J. G. A. G.

Rate of transformation into methylcarbamide of methylammonium cyanate dissolved in ethyl alcohol. (Miss) C. C. MILLER (Proc. Roy. Soc., 1935, A, 151, 188—201).—The rate of transformation of $NH_3Me \cdot CNO$ into $NHMe \cdot CO \cdot NH_2$ over the concn. range 0.04—0.0002*M* at 0° and 10° in EtOH containing 1.91 wt.-% of H_2O was determined. The rate in EtOH was 500 times that in H_2O at infinite dilution and the same temp. The rate in EtOH solutions was represented by $v = k_0 C^2 F$, where the concns. of the ions were involved, and the reaction kinetic factor F had the significance attached to it by Brønsted. Assuming that $F = f^2$, the distances between the centres of reacting ions were calc. at 0° and 10°. The vals. found differed by 25% at the two temp., contrary to the almost const. vals. which have been obtained by others from e.m.f. data. The increased rate of reaction in EtOH compared with aq. solutions was associated with changes in the crit. increment of the reaction, the dielectric const. of the solvent, and the distance between the centres of the reacting ions. Kinetic activities are similar to, but not identical with, thermodynamic activities. L. L. B.

Kinetics of absorption of oxides of nitrogen by 78% sulphuric acid. A. N. TZEITLIN (Ukrain. Chem. J., 1935, 10, 242—261).—The velocity of absorption varies linearly with the concn. of N oxides in the gas, whilst the velocity coeff. attains a max. val. when the gas contains 40% of $NO + NO_2$. The application of these findings to factory practice is discussed. R. T.

Kinetics of formation of silver sulphide from silver and sulphur or hydrogen sulphide. H. REINHOLD and H. SEIDEL (Z. Elektrochem., 1935, 41, 499—507).—Reaction velocities have been measured for (I) $2Ag + S_{liq.} = \beta\text{-}Ag_2S$, (II) $2Ag + S_{liq.} = \alpha\text{-}Ag_2S$, (III) $2Ag + S_{gas} = \beta\text{-}Ag_2S$, (IV) $2Ag + S_{gas} = \alpha\text{-}Ag_2S$, (V) $2Ag + H_2S = \beta\text{-}Ag_2S + H_2$, (VI) $2Ag + H_2S = \alpha\text{-}Ag_2S + H_2$, (VII) $Ag + \frac{1}{2}I_2 = \alpha\text{-}AgI$, (VIII) $2Ag + Te = \alpha\text{-}Ag_2Te$. The velocities are determined by the slowest of the reactions occurring in or between the phases M, M+MX, MX, MX+X, X. The velocities of (I), (II), (III), and (VII) are determined by the rate of diffusion in the reaction zone, and are \propto its thickness. The velocities of (V) and (VI) are determined by the velocity at the boundary MX-X, and are approx. \propto the partial pressure of

S in the H_2S equilibrium. The velocity of (IV) is identical with that of (II) at high temp.; at low temp. it is independent of the zone thickness, and \propto the v.p. of $S_{liq.}$, and thus determined by the reaction at the boundary MX-X. (VIII) is characterised by an induction period, and its velocity is determined by the reaction at the boundary M-MX. T. G. P.

Anomalous behaviour of nickel sulphide. W. H. CONE, M. M. RENFREW, and H. W. EDELBLUTE (J. Amer. Chem. Soc., 1935, 57, 1434—1436).—The initial rate of dissolution of NiS in HCl depends on $[H_2S]$ in the system and is increased by the presence of nascent H. H_2S is more strongly adsorbed by NiS than by PbS, CdS, or FeS, the amount increasing with increasing $[HCl]$. The Ni sulphide has the composition NiS_x , where x is < 1 and increases with increasing $[H_2S]$. E. S. H.

Corrosion of steel.—See B., 1935, 807.

Oxidation and reduction reactions of colloidal dissolved substances. III. Reduction of colloidal manganese dioxide. V. N. SKVORZOV (Kolloid-Z., 1935, 72, 203—205; cf. A., 1933, 916).—The rate of oxidation of $H_2C_2O_4$ by colloidal MnO_2 in acid solution has been investigated and an equation developed. E. S. H.

Autoxidation of *n*-hexadecane. G. ARDITTI (Compt. rend., 1935, 201, 396—398; cf. B., 1931, 661; 1932, 7).—There is an induction period in the absorption of O_2 by $n\text{-}C_{16}H_{34}$ which is the shorter the higher is the temp. After this induction period the velocity of absorption increases rapidly to a max., then diminishing and tending slowly towards zero. In the absence of unsaturated compounds this absorption \propto the amounts of H_2O , CO_2 , CO , H_2 , and CH_4 formed. The first stages of the oxidation are accompanied by the production of a preponderance of CO , formation of CO_2 occurring later. The amount of $H_2 + CH_4$ formed \propto the O_2 absorbed. The loss of O_2 is $>$ the O evolved in gaseous products, so it is concluded that some products remain in solution. J. W. S.

Theory of the catalysis of the ortho-para-transformation by paramagnetic gases. F. KALCKAR and E. TELLER (Proc. Roy. Soc., 1935, A, 150, 520—533).—The reaction velocity depends not only on the interaction energy between the nuclear moment and the magnetic field, but also on the nuclear spin. The reaction can be used to determine the ratio of the magnetic moments of the proton and the deuteron. L. L. B.

Catalysis of acetylene polymerisation in ultra-violet light by mercury vapour. W. KEMULA (Coll. Czech. Chem. Comm., 1935, 7, 319—320; cf. A., 1934, 168).—Polemical (cf. *ibid.*, 852). J. G. A. G.

Polarographic studies with the dropping mercury cathode. L. Secondary or catalytic effects in heavy water. O. H. MULLER (Coll. Czech. Chem. Comm., 1935, 7, 321—325).—The evolution of H_2 at the dropping Hg cathode catalysed by cysteine in buffered Co^{++} solutions (cf. A., 1933, 964) and by Mg and, to a smaller extent, by Ca deposited from aq. Cl^- solutions (*ibid.*, 131) is that of D_2 from D_2O .

The height of the max. in the current-voltage curve decreases as $[D_2O]$ in the aq. solutions is increased. These differences are not observed with aq. Tl^+ , Ni^{++} , Co^{++} , and Ba^{++} , and electrolytic separation of D_2O may be due to a difference between the rates at which D_2O and H_2O react at the cathode either directly or by secondary reactions, and not to a difference between the overpotentials of D^+ and H^+ .
J. G. A. G.

Effect of addition agents on deposition of tin from alkaline stannate baths.—See B., 1935, 809.

Influence of nuclear substituents on side-chain reactions. II. Factors controlling the velocities of acid-catalysed prototropy of nuclear-substituted acetophenones. D. P. EVANS, V. G. MORGAN, and H. B. WATSON. **III. Base-catalysed prototropy of substituted acetophenones.** V. G. MORGAN and H. B. WATSON (J.C.S., 1935, 1167—1173, 1173—1174; cf. A., 1933, 1124).—II. The velocity of bromination of eleven *p*- and *m*-derivatives of $COPhMe$, using 0.1*M* solutions in 75% $AcOH$ in the presence of 0.5*M*- HCl , has been determined at 15—45° and the energy of activation, E , calc. In agreement with theory (this vol., 569) the velocities for the halogen and NO_2 -derivatives are $>$ and for *m*- $C_6H_4Me-COMe$ is $<$ the calc. vals. (cf. A., 1933, 505, 890). The factor causing the deviations is independent of temp., and it is not necessary to assume variations in the proportion of fruitful collisions between activated ketone mols. and catalyst, since the observed rates are not necessarily a true measure of the relative speeds of the initial reaction which determines E . Apparent changes in a probability factor may originate in a subsequent stage of the process. Similar considerations apply to other reactions.

III. The velocity of bromination of 0.1*M* solutions of *m*- and *p*-derivatives of $COPhMe$ in 75% $AcOH$ in presence of 2% wt./vol. of cryst. $NaOAc$ at 35° is $NO_2 > F, I > Cl, Br > H$, in general agreement with the theory.
J. G. A. G.

Reactions catalysed by aluminium chloride. XI.—See this vol., 1221.

Catalytic action of monoses on the formaldehyde condensation. II.—See this vol., 1224.

Esterification of hydroxy-acids and polyhydric alcohols.—See this vol., 1223.

Acid catalysis in non-aqueous solvents. II. Rearrangement of *N*-bromoacetanilide in chlorobenzene catalysed by trichloroacetic acid. R. P. BELL and (SIR) R. V. H. LEVINGE (Proc. Roy. Soc., 1935, A, 151, 211—219).—The velocity of rearrangement of $NBrAcPh$ (I) in $PhCl$ catalysed by CCl_3CO_2H has been measured at 35°, 45°, 50°, and 65°. The catalytic const. is independent of acid concn., and decreases with increasing concns. of (I) and *p*- $C_6H_4Br.NHAc$. The mol. statistics of the unretarded reaction were investigated. Only about 1 in every 10^4 of collisions possessing the necessary energy leads to reaction. This factor is interpreted as due to purely spatial effect.
L. L. B.

Heterogeneous catalysis. II. Graphite and diamond as adsorbents and catalysts. E. STOR-

FER (Z. Elektrochem., 1935, 41, 540—541; cf. this vol., 696).—A discussion.
T. G. P.

Mechanism of the catalysis of hydrogen peroxide by platinum. V. A. ROITER (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 49—53).—It is suggested that O adsorbed at the active centres is reduced electrolytically by H_2O_2 on the inactive surface. The theory is discussed in connexion with experimental data.
R. S.

Influence of sorbed gas on the catalytic activity of hydrogen peroxide decomposition catalysts. II. V. A. ROITER and I. G. SCHAFFRAN (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 29—33; cf. A., 1930, 1531).—The activity of Pt is increased by evacuation at 0.1 mm. The original activity is restored on exposure to the atm., and it is concluded that the whole surface is involved in the decomp. reaction. An irreversible poisoning effect due to diffusion of the P_2O_5 drying agent occurs at 10^{-6} mm.
R. S.

Mechanism of the catalytic combustion of ammonia. M. BODENSTEIN (Z. Elektrochem., 1935, 41, 466—468).—Intermediate products from the combustion of NH_3 at 0.01 mm. on an electrically heated Pt surface were isolated at mean free path distances on a surface cooled with liquid air. NH_2OH , HNO_2 , and a little HNO_3 were found, but no N_2H_4 . The effluent gases, principally N_2 with a little N_2O , contained no NO . A mechanism is suggested.
T. G. P.

(A) Activation of chromium catalysts by barium oxide. (B) Poisoning of chromium catalysts by arsenic and other catalyst poisons. I. E. ADADUROV and D. V. GERNET (J. Appl. Chem. Russ., 1935, 8, 606—611, 612—627).—(A) The activity of a catalyst containing BaO 0.1, SnO_2 1, and Cr_2O_3 1 mol. is little $<$ that of Pt ; the stability and cheapness of the catalyst render it eminently suitable for the H_2SO_4 industry.

(B) As_2O_3 inactivates the above catalyst at 450—475°, but not at 550°; inactivation is due to occlusion of the active surface by adsorbed As_2O_3 , and may be reversed by heating in a stream of CO . The use of $CO-H_2$ mixtures for regeneration leads to inactivation, due to reduction of SnO_2 to Sn ; at the same time H_2S is evolved, pointing to production of S from SO_2 as one of the stages of catalytic oxidation to SO_3 . The catalyst is not inactivated by H_2O or HCl in the reaction gas, but moist HCl reversibly inactivates it.
R. T.

Effect of adding oxides of different metals on the activity of tin-chromium catalysts. D. V. GERNET and A. CHITUN (J. Appl. Chem. Russ., 1935, 8, 598—605).—The activity of $Cr_2O_3-SnO_2$ catalyst is reduced by admixture of oxides of Ca , Mg , Sr , Zn , Al , Bi , Mn , Ni , or Cu , but is increased by BaO or Fe_2O_3 . In general, the inactivating effect varies inversely with the at. radius of the added element, and is greater for elements of even than of odd at. no.; the effect is ascribed to deformation of the field of the original catalyst.
R. T.

Activity and activation energy in heterogeneous catalysis of gas reactions. H. H. STORCH

(J. Amer. Chem. Soc., 1935, 57, 1395—1398).—Theoretical. The relation $A = C_0 e^{cE}$ between the activity, A , and energy of activation, E , for contact catalytic reactions is not due entirely to a probability distribution of active centres. Other factors discussed are: (1) that the frequency of energy exchange in the adsorbed phase may be reduced markedly when multiple adsorption occurs, and hence be a function of the spacing of the catalyst atoms; (2) that in reactions involving H_2 and having a relatively low activation energy a considerable fraction of the rate is to be ascribed to a quantum-mechanical leakage through the energy barrier.

E. S. H.

Influence of manganese on the corrosion of magnesium.—See B., 1935, 808.

Mechanism of the promoter action of iron ammonia catalysts.—See B., 1935, 801.

Catalysts for ammonia synthesis.—See B., 1935, 801.

Rapid oxidation of organic substances with sulphuric acid. J. MILBAUER (Z. Elektrochem., 1935, 41, 594—595).—The reaction $CO + H_2SO_4 = CO_2 + SO_2 + H_2O$ is catalysed markedly by mixtures of Pd with Ag_2SO_4 or $HgSO_4$, and by $SeO_2 + HgSO_4$. Addition of SeO_2 reduces the activity of Pd.

E. S. H.

Catalytic dehydration of ethyl alcohol by alumina. I. Effect of the water content of the catalyst. L. A. MUNRO and W. R. HORN (Canad. J. Res., 1935, 12, 707—710).—The catalytic activity of Al_2O_3 in the dehydration of EtOH vapour to yield Et_2O is a max. when the catalyst contains 5.5% H_2O . Al_2O_3 containing > 13.8% H_2O does not effect the reaction. The relative decrease in efficiency by poisoning during the course of the reaction is the greatest for the catalysts which are the most efficient initially.

J. W. S.

Structure and genesis of methyl alcohol catalysts.—See B., 1935, 795.

[Catalytic] hydrogenation of naphthalene.—See B., 1935, 795.

Activity of nickel catalysts [for dehydrogenation of hydrocarbons].—See B., 1935, 802.

Catalytic dehydration of formic acid.—See B., 1935, 795.

Energetics of catalysis. V. Temperature coefficient of hydrogenation processes. E. B. MAXTED and C. H. MOON (J.C.S., 1935, 1190—1192).—The rates of hydrogenation with a Pt-black catalyst of crotonic (I) and maleic (II) acids in AcOH and in stearic acid (cf. this vol., 589) have max. vals. at 80—90° (I) and 65° (II). The mol. heats of adsorption on the Pt are: (I) 15,500 and (II) 15,000 g.-cal. The apparent activation energies of hydrogenation are, in AcOH, (I) 6800 and (II) 9000, and (I) in stearic acid 10,000, leading to the true heats of activation (cf. A., 1934, 974) 23,000, 25,000, and 26,000, respectively.

J. G. A. G.

Electrolytic separation of the hydrogen isotopes. O. HALPERN and P. GROSS (J. Chem. Physics, 1935, 3, 452—456).—Assuming that the rate of production of gas on electrolysis is determined by the

speed of recombination of gas atoms on the electrode, an equation is deduced giving the separation coeff., α , in terms of thermodynamic consts. of H and D and the frequencies of thermal vibration of the atoms when bound to the electrode. The calc. vals. of α agree with experiment. With rise of temp. α should fall. A relation between the normal electrode potentials of H and D has been established.

R. C.

Critical voltage for formation of ozone by alternating-current discharge. M. SENKUS and A. C. GRUBB (J. Chem. Physics, 1935, 3, 529).—For each pressure and velocity of O_2 in the apparatus used there is a crit. voltage above which the discharge becomes greenish-yellow and O_3 ceases to be formed.

R. C.

Oxidation of graphite in electrolytic melts. V. SIHVONEN (Suomen Kem., 1935, 8, B, 29—30).—The oxidation of a graphite anode during the electrolysis of fused $NaOH + KOH$ at 200—550°, using a Ag cathode, and of fused $Na_2CO_3 + K_2CO_3 + Li_2CO_3$ at 400—900°, using a graphite cathode, has been studied. With the carbonates pure CO_2 is evolved at the anode at 400°, but at 500° there is a little CO , the % of which increases with rise of temp. No O_2 is evolved, even with a c.d. of 6 amp. per sq. cm. With rising temp. the p.d. between the graphite anode and Ag cathode increases uniformly. The p.d.-c.d. curves show no irregularities. The CO_3^{2-} ions probably react with the C atoms (C_x) of the graphite surface giving keto-groups: $C_x + CO_3^{2-} = C_xO + CO_2 + 2e$; the keto-groups are then further oxidised by CO_3^{2-} . With the alkalis, $C_x + 2OH^- = C_xO + H_2O + 2e$, and $C_x + H_2O = C_xO + H_2$. At 400—550° the p.d. and max. c.d. are > for the carbonates. No formation of O_2 , CO , formate, and oxalate occurs, and no gas is evolved at the anode, the primary product being CO_2 , which dissolves in the melt.

R. S. B.

Electrolytic preparation of fluorine.—See B., 1935, 802.

Action of alcoholic ammonium acetate in electroanalytical processes. H. FUCHSHUBER (Chem.-Ztg., 1935, 59, 676).—To prevent a spongy cathode deposit during the electrolysis of HNO_3 solutions of Cu, 10—15 c.c. of a saturated solution of NH_4OAc in EtOH are added to the electrolyte. Similarly, the anodic deposition of Mn-free Pb from solutions containing both elements is facilitated.

A. G. P.

Chemical reactions in the lead storage battery.—See B., 1935, 773.

Anodic oxidation of aluminium by superimposing three-phase a.c. on d.c. A. MIYATA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 651—678).—Electrolysis with superimposed three-phase a.c. on d.c. is simpler and better than the use of other polyphase a.c. for anodic oxidation of Al in $H_2C_2O_4$ solution. A stout hard film is obtained; the anode current during electrolysis reverses little, even when appreciable negative voltage is applied to the anode in each cycle; the energy efficiency of the film formation is higher than by other methods; the a.c. component introduced in the d.c. generator circuit that menaces the commutation of the machine is

suppressed; and pitting of the anode during electrolysis is avoided completely. J. W. S.

Oxidation-reduction process at the surface of a diaphragm (of kaolin) interposed in a copper solution during electrolysis. Factors determining its speed of appearance. (MME.) L. GUASTALLA (Compt. rend., 1935, 201, 268—270; cf. A., 1934, 739).—The time of appearance of Cu_2O and Cu, as reduction products of Cu salts, on the anodic face of a kaolin diaphragm during electrolysis, is independent, for the same anion, of the thickness of the diaphragm, decreases with increasing p_{H} , and increases with the dilution. R. S. B.

Electrochemical oxidation of mesitylene.—See this vol., 1229.

Electrolytic reduction of aliphatic ketones to hydrocarbons.—See this vol., 1224.

X-Ray photolysis of hydrogen peroxide. D. DEN HOED and C. W. F. SPIERS (Z. physikal. Chem., 1935, 173, 412—414; cf. A., 1928, 970).—The amount of photolysis of 0.02—0.05M aq. H_2O_2 by X-rays of λ 0.06—0.5 Å., 100—200 kv., depends on the energy absorbed, not on the voltage. R. C.

Occurrence of a metastable, active oxygen molecule in sensitised photo-oxidations. J. WEISS (Naturwiss., 1935, 23, 610).—The extinction of fluorescence of various dyes (eosin, uranin, trypan-flavin) by SO_3'' is considered. The dye may be dissociated photochemically into H atoms (or another radical) and then may take place either (1) the recombination of the H atoms or radicals, possibly with chemiluminescence, or (2) combination of H atoms with O_2 forming HO_2 which reacts with the acceptor. The HO_2 mol. takes the place of the metastable activated O_2 mol. in Kautsky's theory. A. J. M.

Solarisation at low intensity. A. J. REARDON and H. P. GRIGGS (J. Opt. Soc. Amer., 1934, 24, 331—338).—By prolonged exposure the characteristic curve of a photographic emulsion has been extended beyond the known second reversal, and contains a series of max. and min. points, up to 16 reversals having been obtained with exposures up to 1759 hr. The depth of reversal gradually decreases, and the time between two successive max. or min. increases. Ageing of the emulsion decreases D_{max} , and the degree of solarisation obtainable. J. L.

Photophysical changes in silver-silver chloride systems. A. E. CAMERON and A. M. TAYLOR (J. Opt. Soc. Amer., 1934, 24, 316—330).—Photo-anisotropy (emulsions red-sensitised by exposure to ultra-violet light, and then exposed to red polarised light) is shown to depend on a Ag-AgCl system alone; the same results were produced in suspensions in the absence of gelatin, and also in a single crystal of pure AgCl. The amount of free Ag does not change on production of the dichroism. Fixing the plates shifts the max. of the absorption, dichroism, and birefringence curves towards shorter λ , both for the ultra-violet-exposed plate and for the red-exposed plate. The effects are therefore due to the Ag particles. Measurements of the dichroism in the dry and wet (swollen) fixed plate, and further theoretical considerations lead to the theory that the photo-adapted image formation is

due to optical resonance, and orientation of the Ag particles. Red light causes a decrease in size and an increase in no. of the Ag resonators present. It is postulated that electrons are ejected, re-forming Ag from Ag^+ at another point, only correctly dimensioned and oriented particles responding to the incident polarised light. J. L.

Photochemical formation of carbonyl chloride from chloroform, chlorine, and oxygen, and its inhibition by added substances. H. J. SCHUMACHER and D. SUNDHOFF (Z. Elektrochem., 1935, 41, 499).—The duration of inhibition of the reaction between CHCl_3 , Cl_2 , and $\text{O}_2 \propto$ the quantity of MeOH, EtOH, or NH_3 added. Inhibition occurs through the removal of Cl atoms, for if the inhibitors are first chlorinated, they cease to affect the reaction. T. G. P.

Photochemical dissociation of methyl and ethyl alcohols. F. PATAT [with H. HOCH] (Z. Elektrochem., 1935, 41, 494—498).—MeOH and EtOH dissociate in light between 1800 and 2000 Å. into H_2 , CO, and CH_2O , and H_2 and MeCHO, respectively, with quantum yields between 1 and 2. Mechanisms are discussed. T. G. P.

Free radicals and atoms in primary photochemical processes. II. Photo-dissociation of aliphatic aldehydes and ketones. T. G. PEARSON and R. H. PURCELL (J.C.S., 1935, 1151—1156; cf. this vol., 48).—The identification of minute quantities of free radicals in presence of a larger amount of condensable vapour has been investigated. The radicals from the photolysis of COMe_2 and COEt_2 are proved to be free Me and Et, respectively, by identifying the products of interaction with Te, Hg, and As. The products from the photolysis of MeCHO do not remove cold metallic mirrors owing to a protective film of polymerised MeCHO, but free Me has been detected by the action on warm metallic mirrors. Approx. six times as many radicals participate in the photo-dissociation at 100° of COMe_2 as in that of an equiv. of MeCHO under identical conditions. These results confirm that there is a fundamental difference between the mechanisms of photolysis of aldehydes and ketones and that free radicals take some part in the photolysis of aldehydes also (cf. A., 1933, 682; 1934, 976). J. G. A. G.

Free *n*-propyl radical.—See this vol., 1221.

Photochemical oxidation of mandelic acid by methylene-blue with uranyl nitrate as photosensitiser. J. C. GHOSH, D. S. NARAYANMURTHI, and N. K. ROY (Z. physikal. Chem., 1935, B, 29, 236—246).—The reaction has been studied for monochromatic radiation of λ 254—436 m μ . The mechanism $\text{UO}_2^{++} + h\nu \rightarrow \text{UO}_2^{+*}$, $\text{UO}_2^{+*} \rightarrow \text{UO}_2^{+} + \text{fluorescence}$, $\text{UO}_2^{+*} + \text{UO}_2^{++} \rightarrow 2\text{UO}_2^{+}$, $\text{UO}_2^{+*} + \text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H} \rightarrow \text{UO}^{+} + \text{PhCHO} + \text{H}_2\text{O}$, $\text{UO}^{+} + \text{methylene-blue} + \text{H}_2\text{O} \rightarrow \text{UO}_2^{+} + \text{leuco-base}$ leads to $-d[\text{methylene-blue}]/dt = I_{\text{abs. by UO}_2^{++}}[k_1[\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}]/\{N h\nu(k_2 + k_3[\text{UO}_2^{+*}] + k_4[\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}])\}]$, which, utilising Vavilov's data (cf. A., 1928, 1072), represents the course of the reaction satisfactorily. R. C.

Use of the hydrolysis of monochloroacetic acid for absolute actinometric measurements. B. J.

DAIN and E. S. PUSENKIN (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 75—81).—The photodecomp. of H_2O_2 has been studied using $\text{CH}_2\text{Cl}-\text{CO}_2\text{H}$ in an actinometer arranged symmetrically with respect to the arc. The relation $\gamma \propto I^{1/2}$ (cf. A., 1930, 715) has been confirmed. R. S.

Rate of photosynthesis. W. O. JAMES (Nature, 1935, 136, 220—221).—A crit. discussion. L. S. T.

Effect of X-rays on glutathione. V. E. KINSEY (J. Biol. Chem., 1935, 110, 551—558).—A linear relation was observed between the destruction of glutathione (I) in aq. solution and the dose of X-rays. The effect increases linearly with concn. of (I) up to 0.01% and then again linearly but at a smaller rate, the energy efficiency increasing with the concn. Increase of p_{H} also augments destruction. H. G. R.

Attempts to produce helium 3 in quantity. F. A. PANETH and G. P. THOMSON (Nature, 1935, 136, 334).—During the bombardment of heavy H with positive rays measurable amounts of $\text{He}+\text{Ne}$ were obtained. This gas is considered as derived from the walls of the discharge vessel and not He^3 produced by at. transmutation. L. S. T.

Possibility of the ignition of electrolytic gas by fast electrons. A. E. MALINOVSKI and J. A. SKRINNIKOV (Physikal. Z. Sovietunion, 1935, 7, 43—48).—An electron beam of 2.5×10^{-7} amp. was passed for 10—60 sec. through a mixture of 7.5% of C_2H_2 and air at 15—76 cm., and beams of 2.24×10^{-6} and 2.5×10^{-7} amp. through electrolytic gas at 10—64 cm. No explosions occurred. R. S. B.

Action of "Erdstrahlen" on the diving rod. II. M. TRENEL (Angew. Chem., 1935, 48, 575—578; cf. this vol., 600).—The results previously reported are confirmed. E. S. H.

Cryogenic laboratory of the California Institute of Technology. I. A. GOETZ (Rev. Sci. Instr., 1935, [ii], 6, 217—229).—The purification and liquefaction of H_2 are described. C. W. G.

Concentration of heavy isotopes in carbohydrates. T. TITANI and M. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 261—263).—Samples of H_2O were prepared by destructive distillation of cane molasses, refined cane sugar, beet sugar, grape- and milk-sugar, sol. starch, potato starch, rice flour, wheat flour, dextrin, and agar-agar. All were denser by 4—6 p.p.m. than Osaka town H_2O . Consequently the carbohydrates must contain enhanced concn. of the heavy isotope of either O or more probably H. It is considered probable that the enhanced concn. of D is located in the OH groups. S. J. G.

Quantitative isotopic exchange reactions in the carbohydrate group. W. H. HAMILL and W. FREUDENBERG (J. Amer. Chem. Soc., 1935, 57, 1427—1430).—Quant. isotopic exchange reactions have been carried out with free hexoses, their methylglycosides, and other derivatives in 11—30% and 80—96% D_2O . The exchange no. for 21 samples agrees closely with the no. of OH groups in the sample. E. S. H.

Cupric ammonium compounds and cupric acid ammonium compounds. H. BRINTZINGER and H.

OSSWALD (Z. anorg. Chem., 1935, 223, 393—396).—The compounds formed by the action of aq. NH_3 on solutions of Cu^{II} salts were investigated by a dialysis method with $\text{S}_2\text{O}_3^{2-}$ as reference ion using a membrane of Cuprophane. With $\text{Cu}(\text{NO}_3)_2$, CuCl_2 , and $\text{Cu}(\text{CNS})_2$, the ion present was probably $[\text{Cu}(\text{NH}_3)_4]^{2+}$, and with $\text{Cu}(\text{OAc})_2$, some other unknown ion; with CuSO_4 , CuSeO_4 , and $\text{Cu}_3(\text{PO}_4)_2$ undissociated compounds appear to be formed, viz., $[\text{Cu}(\text{NH}_3)_4\text{SO}_4]$, $[\text{Cu}(\text{NH}_3)_4\text{SeO}_4]$, and $[\text{Cu}_3(\text{NH}_3)_4(\text{PO}_4)_2]$. The earlier assumption that a $\text{Cu}(\text{NH}_3)_4$ ion is formed in all cases of dissolution of a Cu salt in aq. NH_3 , independently of the nature of the anion, appears therefore to be unjustified. S. J. G.

Precipitation of copper and of silver by the action of the latter. A. P. SERGUEEV and A. A. KOCHOVCHOVSKI (Ann. Chim. Analyt., 1935, [iii], 17, 231—232).—When Ag powder is heated in a solution of CuSO_4 containing KCl or NaCl in excess (or in an EtOH solution of anhyd. CuCl_2), Cu is deposited on the Ag and the solution or dilution yields a ppt. of AgCl. Similar treatment with NaCl solution free from Cu produces no ppt. of Ag. If Ag is enclosed in a thin paper sachet and after treatment with CuSO_4 -NaCl is dipped in aq. AgNO_3 , Ag is deposited on the sachet and Cu on the Ag within. By dipping a sachet containing Ag in conc. aq. KCl, washing, and then placing in aq. AgNO_3 , a Ag deposit is obtained on the sachet. Similar but less effective results are obtained with KNO_3 solutions, and a small but distinct deposit is obtained by use of H_2O in place of the salt solution. The $[\text{Ag}^+]$ of the solution remains unchanged. Conditions comparable with those of a concn. cell are attained when the wetted sachet is dipped into aq. AgNO_3 . KCl intensifies the action by modifying the character of the Ag surface. A. G. P.

Action of nitrosyl chloride on some salts of silver. R. PERROT (Compt. rend., 1935, 201, 275—277).—Three types of reaction are observed between NOCl and anhyd. Ag salts at room temp. (a) Formation of nitrosyl derivatives by double decomp.; e.g., AgNO_3 rapidly forms pure NO_2 , and AgClO_4 slowly forms a compact residue containing NOClO_4 (which hydrolyses to HNO_2 with H_2O). (b) Formation of NO and liberation of anion of salt. With salts of oxyacids the reaction is complicated by the transitory formation of NO_2 ; e.g., AgCNS gives a quant. yield of NO and a yellow polymeride of cyanogen sulphide. AgI gives I, but AgBr reacts only partly, even at 200° . AgNO_3 gives a mixture of NO and NO_2 . Ag_2CO_3 reacts: $2\text{Ag}_2\text{CO}_3 + 3\text{NOCl} \rightarrow 3\text{AgCl} + \text{AgNO}_3 + 2\text{NO} + 2\text{CO}_2$; a little AgNO_2 is also formed. Ag_2SO_3 gives nitrosyl pyrosulphate: $3\text{Ag}_2\text{SO}_3 + 6\text{NOCl} \rightarrow 4\text{NO} + \text{SO}_2 + \text{S}_2\text{N}_2\text{O}_9 + 6\text{AgCl}$. $\text{Ag}_2\text{N}_2\text{O}_9$ rapidly forms N_2 with a little NO. (c) Oxidation of the salt and reduction of NOCl to N_2 or NO; e.g., $\text{Ag}_2\text{C}_2\text{O}_4$ gives CO_2 and NO, AgCNO gives N_2 , Ag_2CN_2 inflames, but AgCN and Ag dicyanoimide require heating to 150° . R. S. B.

Action of sulphur on silver. R. DUBRISAY (Compt. rend., 1935, 201, 425—426).—The direct union of Ag with S at room temp. is shown by the blackening of Ag by S vapour in vac. Substances

readily adsorbed on the Ag surface retard or inhibit the action.

J. S. A.

Action of carbonic acid on calcium phosphates.

W. FISCHER and K. BRUNGER (Z. anorg. Chem., 1935, 223, 422—426).—The action of $\text{H}_2\text{O} + \text{CO}_2$ on Ca phosphates at 15°, 120°, and 170° up to 50 atm. (as measured by the quantity of phosphate, sol. in citric acid, formed) was negligible even in presence of K and NH_4 salts.

S. J. G.

Perchlorates. III. Barium ammine perchlorates. C. SMEETS (Natuurwetensch. Tijds., 1935, 17, 83—90).—Isotherms for the system $\text{Ba}(\text{ClO}_4)_2\text{--NH}_3$ at temp. from -79° to 80° indicate the existence of compounds with 2, five, 6, and nine NH_3 . Dissociation pressure curves are given.

D. R. D.

Peroxide compounds. R. SCHWARZ and F. HEINRICH (Z. anorg. Chem., 1935, 223, 387—392).—Using Liebafsky's test (this vol., 173) the following are found to be peroxide compounds: $\text{Ti}(\text{OH})_3\text{O}_2\text{H}$; $\text{K}_2[\text{TiO}_2(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$; $\text{Zr}(\text{OH})_3\text{O}_2\text{H}$; $\text{Zr}_2\text{O}_6\text{SO}_4 \cdot 8\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{Cr}_2\text{O}_{12} \cdot 2\text{H}_2\text{O}$; and the following are additive compounds: $\text{K}_2\text{TiO}_4 \cdot 4\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$; $\text{ThO}_2 \cdot 3\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$; $\text{K}_2\text{GeO}_5 \cdot 2\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$; whilst $\text{K}_4\text{UO}_6 \cdot 6\text{H}_2\text{O}_2 \cdot x\text{H}_2\text{O}$ is a mixed compound.

S. J. G.

Lead chlorite: double and basic salts. G. R. LEVI and G. PEYRONEL (Atti R. Accad. Lincei, 1935, [vi], 21, 381—384).—The double salts $\text{PbCl}_2 \cdot \text{Pb}(\text{ClO}_2)_2$ and $\text{PbBr}_2 \cdot \text{Pb}(\text{ClO}_2)_2$ may be crystallised from aq. solution. A basic salt, probably $\text{Pb}(\text{ClO}_2)_2 \cdot \text{Pb}(\text{OH})_2$ or $\text{Pb}(\text{ClO}_2)_2 \cdot 2\text{Pb}(\text{OH})_2$, may be obtained by addition of aq. NaOH to $\text{Pb}(\text{ClO}_2)_2$ suspended in H_2O . No chemical or X-ray evidence could be obtained for the existence of Schiel's $\text{PbCl}_2 \cdot 2\text{Pb}(\text{ClO}_2)_2$ and $4\text{PbCl}_2 \cdot 6\text{Pb}(\text{ClO}_2)_2 \cdot \text{PbO}$.

D. R. D.

Chemical reactions with active nitrogen. E. TIEDE [with H. KNOBLAUCH] (Z. Elektrochem., 1935, 41, 526).—N atoms react with Hg to yield Hg_3N , which decomposes quietly at 100° , and gives NH_3 with NaOH. Ga gives a substance which is not GaN . Na-rich amalgams and molten alkali metal alloys yield azides.

T. G. P.

Action of hydrogen peroxide on nitrous acid.

Pernitrous acid. II. K. GLEU and R. HUBOLD (Z. anorg. Chem., 1935, 223, 305—317; cf. A., 1929, 523).—The oxidising substance obtained by action of H_2O_2 or NaNO_2 in acid solution, previously believed to be pernitric acid, is shown to be pernitrous acid. It is identical with the product of ozonisation of NaNO_3 and is prepared as follows: 1 mol. of NaNO_2 is mixed with slightly > 1 mol. of H_2O_2 , treated with much ice, and 1 mol. of $M\text{--H}_2\text{SO}_4$ added. Excess of NaOH is added after 2 sec., yielding an intense yellow solution containing approx. 0.1 mol. of $\text{NaNO}_2 \cdot \text{O}$. To determine H_2O_2 , NaNO_2 , and $\text{NaNO}_2 \cdot \text{O}$ when present together the H_2O_2 is titrated with 0.1N-NaOCl in alkaline solution in presence of 10 drops of 0.1N-KI until the colour of Ru-red indicator ($2\text{RuOHCl}_2 \cdot 7\text{NH}_3 \cdot 3\text{H}_2\text{O}$; A., 1893, ii, 172) is discharged. Excess of 0.1N- As_2O_3 is immediately added and back-titrated with NaOCl (same indicator), to determine active O of the pernitrite. NO_2' is determined by reducing with VOSO_4 to NH_3 and distill-

ing into 0.1N-HCl, nitrate being unaffected. The ratio active O : NO_2' is always 1 : 1, proving the presence of pernitrite and absence of pernitrate.

S. J. G.

Nitrous oxide as an oxidising agent in the gaseous state. E. W. R. STEACIE and R. D. McDONALD (Canad. J. Res., 1935, 12, 711—714).— N_2O reacts with MeOH, C_2H_4 , MeCHO, PH_3 , or CS, only at temp. where its decomp. becomes appreciable, and it is a much less efficient oxidising agent than mol. O_2 . It is concluded that in general N_2O does not itself act as an oxidising agent in the gaseous state, but acts merely as a reservoir of at. O when the temp. is sufficiently high.

J. W. S.

Existence of a series of ammonium orthophosphates and orthoarsenates. A. DE PASSILLE (Compt. rend., 1935, 201, 344—345).—By progressive withdrawal of NH_3 from $(\text{NH}_4)_6\text{P}_2\text{O}_8$ and $(\text{NH}_4)_6\text{As}_2\text{O}_8$ equilibria have been obtained corresponding with the compounds $(\text{NH}_4)_5\text{HP}_2\text{O}_8$, $(\text{NH}_4)_4\text{H}_2\text{P}_2\text{O}_8$, $(\text{NH}_4)_3\text{H}_3\text{P}_2\text{O}_8$, $(\text{NH}_4)_2\text{H}_4\text{P}_2\text{O}_8$, $(\text{NH}_4)_5\text{HAS}_2\text{O}_8$, $(\text{NH}_4)_4\text{H}_2\text{As}_2\text{O}_8$, $(\text{NH}_4)_3\text{H}_3\text{As}_2\text{O}_8$, $(\text{NH}_4)_2\text{H}_4\text{As}_2\text{O}_8$, $\text{NH}_4\text{H}_5\text{As}_2\text{O}_8$. The heat changes of equilibria are recorded.

J. W. S.

Salts of hexafluoroantimonic acid, HSbF_6 . W. LANGE and K. ASKITOPOULOS (Z. anorg. Chem., 1935, 223, 369—381).— KSbF_6 and NaSbF_6 were prepared by evaporating the pyroantimonates with excess of 40% HF; the NH_4 and Rb salts by dissolving Sb_2O_5 in HF and evaporating with the calc. amount of NH_4F or RbF . The alkali salts are readily sol. in H_2O , and are stable if dry but hydrolysed in moist air or solution: $[\text{SbF}_6]^- \rightleftharpoons [\text{SbF}_x(\text{OH})_{6-x}]^- \rightleftharpoons [\text{Sb}(\text{OH})_6]^-$. A no. of intermediate products of hydrolysis have been isolated, e.g., $\text{SbOF}_3 \cdot \text{NaF} \cdot \text{H}_2\text{O}$. The less sol. salts were prepared by pptg. HSbF_6 with sol. salts of the base. NMe_4 , strychnine, brucine, cocaine, nitron, and diphenylene-4 : 4'-bisdiazonium salts were prepared thus. They resemble the corresponding P compounds but are more sol. The aryldiazonium salts are readily sol. in H_2O , stable if dry, and not decomposed by detonation; when heated they decompose thus: $[\text{ArN}_2][\text{SbF}_6] \rightarrow \text{ArF} + \text{SbF}_5 + \text{N}_2$. The salts of heavy and alkaline-earth metals are in time completely hydrolysed in solution owing to insolubility of the fluoride formed. $[\text{SbF}_6]^-$ is quickly and completely hydrolysed by not too dil. alkali, in contrast to $[\text{PF}_6]^-$, which is unaffected; and in general $[\text{SbF}_6]^-$ is more reactive than $[\text{PF}_6]^-$. The salts of $[\text{HSbF}_6]$ are rhombohedral, those of $[\text{HPF}_6]$ regular.

S. J. G.

Ammonium compounds of bismuth halides. R. SCHWARZ and H. STRIEBIG (Z. anorg. Chem., 1935, 223, 399—408).—Halides of non-metals are ammonolysed by NH_3 , whereas metal halides add on NH_3 . This can occur in two ways. (a) NH_3 mols. may enter the structure of the halide mol., surrounding the cation with a dielectric shell and displacing the anion into the outer sphere. The result is an "enclosure compound" (Einlagerungsverbindung), characterised by an ionic lattice, solubility in liquid NH_3 , and a definite NH_3 dissociation pressure. (b) An "attachment compound" (Anlagerungsverbindung) may be formed, which is the first stage towards

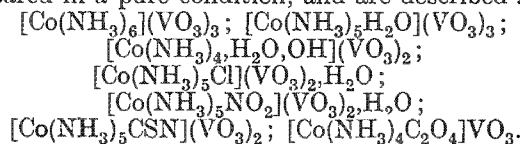
ammonolysis. No separation of the central atom and its halogen atoms occurs, the latter merely undergoing electric deformation, which leads to intense coloration. Such compounds are insol. in liquid NH_3 , give no NH_3 pressure, and can be distilled without decomp. The action of NH_3 on BiCl_3 , BiBr_3 , and BiI_3 has been investigated in the light of the above classification. None of them undergoes ammonolysis even after 50-fold treatment with liquid NH_3 . The following were formed: (a) $\text{BiCl}_3 \cdot 12.5\text{NH}_3$; BiBr_3 with 18.5, 14, and 3NH_3 ; BiI_3 with 22, 12.5, 12, 4, 3, and 2NH_3 ; (b) $\text{BiCl}_3 \cdot \text{NH}_3$, $\text{BiCl}_3 \cdot 0.5\text{NH}_3$, $\text{BiBr}_3 \cdot 1.5\text{NH}_3$, $\text{BiBr}_3 \cdot 0.5\text{NH}_3$. The physical and chemical properties of the compounds are elucidated with the aid of spatial models. S. J. G.

Yields in the preparation of protoactinium. A. VON GROSSE (Ber., 1935, 68, [B], 1511—1512; cf. this vol., 460).—A reply to Hahn (this vol., 593)

H. W.

Constitution and formation of bleaching powder. C. W. BUNN, L. M. CLARK, and I. L. CLIFFORD (Proc. Roy. Soc., 1935, A, 151, 141—167).—As a result of phase-rule studies, all the pure compounds which could be isolated under equilibrium conditions from the system $\text{CaO}-\text{CaCl}_2-\text{Ca}(\text{OCl})_2-\text{H}_2\text{O}$ below 40° have been defined, and used as a basis for comparison with the solid phases present in bleaching powder, by means of microscopic and X-ray methods. Samples taken at intervals during the reaction of Cl_2 with $\text{Ca}(\text{OH})_2$ have been examined by the same methods. The first stage in the reaction is the formation of $\text{Ca}(\text{OCl})_2 \cdot 2\text{Ca}(\text{OH})_2$ (I) and $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (II). On further chlorination the former is converted into a mixed crystal of which the chief constituent is $\text{Ca}(\text{OCl})_2$. Ordinary bleaching powder (35% available Cl) is a mixture of this mixed crystal with (II). On further chlorination (II) is partly converted into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, whilst the hypochlorite mixed crystal persists, with gradually changing properties. The non-deliquescent nature of bleaching powder and the difficulty of introducing >35% of available Cl into the solid are due to the presence of the very stable compound (II). The unit cell dimensions of (I) (hexagonal) and $\text{Ca}(\text{OCl})_2 \cdot 3\text{H}_2\text{O}$ (tetragonal), and the refractivities of the OCl^- ion parallel and perpendicular to its axis have been deduced. L. L. B.

Vanadates of some cobaltammine complex salts. E. NEUSSER (Z. anorg. Chem., 1935, 223, 417—421).—The following compounds have been prepared in a pure condition, and are described:



S. J. G.

Novel type of isomerism among complex metallic salts. F. G. MANN and D. PURDIE (Chem. and Ind., 1935, 814—815).—Compounds of the type $[(\text{R}_2\text{S})_2\text{PdCl}_2]$, $[(\text{R}_3\text{P})_2\text{PdCl}_2]$, and $[(\text{R}_3\text{As})_2\text{PdCl}_2]$ have been prepared and derivatives are described of the type $[\text{Bu}^n\text{PPdCl}_2]_2$ (I), deep orange crystals, m.p. 144° . It is shown that in (I) both R_3P are coordinated to the same Pd. (I) has been converted

into an isomeric form in which the R_3P are attached to different Pd. This gives pale yellow crystals, m.p. 71° , and dissociates in solution forming $[\text{R}_3\text{PPdCl}_2]$.

R. S.

Quantitative spectral analysis.—See B., 1935, 788.

Application of Delaunay's theory of the basic parallelepipeds of crystal cell structure to determination of crystalline substances. V. LINITZKI (Ukrain. Chem. J., 1935, 10, 161—175).—Theoretical.

R. T.

End-point of potentiometric titration of weak acids and bases. S. KILPI (Z. physikal. Chem., 1935, 173, 427—448; cf. this vol., 1091).—For a weak acid (base) to be titratable with a strong base (acid) K_c must be $> 27K_w$, where c is the concn. of the acid (base) calc. on the final vol. The titration is more exact than when the strong is titrated with the weak component. In the titration of a weak acid with a weak base, $K_{HA}K_{BOH}$ must be $< 28K_w$, and the end-point and equiv. point coincide only if $K_{HA}K_{BOH} > 10^{-10}$. These theoretical deductions have been verified by study of the titration of H_2CO_3 in the second stage. KCl shifts the end-point towards the equiv. point. In the titration of HCO_3^- with NaOH or of a mixed solution of NaOH and Na_2CO_3 with HCl the end-point is on the acid side of the equiv. point, and the more so the lower is the concn.

R. C.

Determination of traces of bromine in presence of chlorine. S. GILDE (Ann. Chim., 1935, [xi], 4, 224—269).— Br^- cannot be determined satisfactorily in presence of Cl^- by pptn. methods. The method based on liberation of Br followed by distillation is also inaccurate. Colorimetric methods detect 0.1×10^{-6} g. Br , but the potentiometric method described is equally sensitive for determination of $[\text{Br}^-]$ of 0.2—2% and is independent of lighting conditions and colour-sensitivity of the operator. Irregularities in a Hg_2Cl_2 electrode potential may arise through traces of KBr in the KCl .

J. W. S.

Determination of hydrobromic acid in presence of hydrochloric acid. G. G. LONGINESCU and E. I. PRUNDEANU (Bull. Sci. Acad. Roumaine, 1935, 17, No. 3—4, 1—4).— H_2O_2 under certain conditions oxidises HBr but not HCl . 10 c.c. of KBr and KCl solution, 100 c.c. of light petroleum, 5—6 c.c. of conc. H_2SO_4 , and 2—3 c.c. of H_2O_2 are mixed and shaken vigorously at intervals for 30 min. The petroleum layer (a) is then separated from the aq. layer (b); to (a) 40 c.c. of amyl alcohol + 2 g. Na are added little by little to reduce the Br to NaBr ; this is extracted by H_2O , the reduction and extraction being repeated twice more. The combined aq. extracts are cautiously acidified with HNO_3 , and the Br^- is determined gravimetrically by pptn. as AgBr in the usual way. The HCl in aq. layer (b) is similarly determined after warming to destroy H_2O_2 .

S. J. G.

Does azoimide disturb micro-iodometric determinations by Winkler's method? J. F. REITH and J. DE BEUS (Biochem. Z., 1935, 279, 203—204).— HN_3 does not interfere.

P. W. C.

Detection and determination of fluorine in natural waters.—See B., 1935, 832.

Determination of dissolved oxygen in de-aerated water by Winkler's method.—See B., 1935, 832.

Atmospheric sulphur and arable soils. G. BERTRAND (Compt. rend., 1935, 201, 309—312).—In the determination of S in rain- H_2O an error is introduced during evaporation due to the absorption of S from the gas flame. H. D.

Potentiometric determination of S'' , CNS' , and Cl' ions in presence of one another. A. J. BURSUK and A. M. ZANKO (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 83—88).—The mixture is titrated potentiometrically with AgNO_3 in presence of $\text{Ba}(\text{NO}_3)_2$. S'' is determined in presence of NH_3 , after which the solution is acidified with HNO_3 and the CNS' and Cl' equivalence points are obtained, in good agreement with the calc. vals. R. S.

Determination of oxides of nitrogen, excluding nitrous oxide.—See B., 1935, 766.

Sensitive test for phosphorus. Modification of Mitscherlich's procedure. R. GROS (J. Pharm. Chim., 1935, [viii], 22, 211—215).—Material containing white P is distilled with H_2O in the dark under a pressure of 15 mm. and the glow of P is observed. 0.002 mg. of P can be detected in 200 g. of sample. R. S.

Volumetric determination of phosphate. H. SEMMICH (Angew. Chem., 1935, 48, 566).—In the determination of PO_4''' by the method of Sanfourche and Focet (A., 1934, 43) < 3.5 equivs. of AgNO_3 must be employed. Bromothymol-blue is the most suitable indicator. J. S. A.

Zinc pellets for generation of arsine in the Gutzeit method. P. A. MILLS (J. Assoc. Off. Agric. Chem., 1935, 18, 506).—Zn cast in a porcelain mould in the form of pellets 9×12.5 mm. gives a const. and uniform supply of H_2 . E. C. S.

α -Naphthoflavone, a new indicator for bromatometry. E. SCHULEK (Z. anal. Chem., 1935, 102, 111—113).—The disadvantages of the usual indicators employed in the titration of As and Sb solutions with KBrO_3 solutions are discussed. The author's method is to add 10 c.c. of 50% H_2SO_4 to the As^{III} or Sb^{III} solution, dissolve 0.2 g. of KBr in the mixture, and add 2 drops of a 0.5% solution of naphthoflavone in 96% EtOH . The solution is titrated with 0.1N- or 0.01N- KBrO_3 solution until the greenish opalescence of the solution is replaced by a reddish-brown colour. With Sb^{III} it is advantageous to add 0.5 g. of tartaric acid to keep the Sb in solution. J. W. S.

Rapid photometric determination of silicon in light metals.—See B., 1935, 771.

Chemical analysis of volcanic rocks. A. M. DE JESUS (Rev. Chim. Pura Appl., 1932, [iii], 7, 115—119).—In the determination of SiO_2 , a second evaporation to dryness appears to be unnecessary as the amount so recovered is negligible; the rather larger ppt. so recovered in the case of basic rocks consists largely of TiO_2 . In the Lawrence Smith method for the determination of alkalis, it is essential to heat to about 750° , as no decomp. occurs at about 375° .

4 M

The Schlösing-Wende perchlorate method for the separation of K and Na is recommended. E. L.

Conditions of titration of silicofluorides, and their application to the determination of silica in silicates. A. BABKO (Ukrain. Chem. J., 1935, 10, 133—147).—0.1 g. of silicate is fused with 1 g. of KNaCO_3 , the melt is boiled with H_2O and aq. HCl , the solution is diluted to 25 ml., approx. neutralised with NaOH (Me-orange), boiled, and 12—15 ml. of 5% aq. NaF are added. The solution is then made acid with HCl , 6—10 g. of CaCl_2 are introduced, and N-NaOH is added to an alkaline reaction (phenolphthalein). The solution is then made exactly neutral with HCl , diluted to 150 ml., and titrated at 90° with 0.1N- NaOH to a faint red coloration. The method involves a mean error of 1%, and requires 1 hr. R. T.

Helium. XI. Spectro-analytical detection of traces of hydrogen and neon in helium. P. L. GUNTHER and F. A. PANETH (Z. physikal. Chem., 1935, 173, 401—411).—By a method similar to that previously described (A., 1928, 858) as little as 0.1% H_2 or 0.002% Ne can be detected in 10^{-7} c.c. of He . The air near the ground contains $< 2 \times 10^{-4}\%$ H_2 . The determination of small amounts of He is described. R. C.

Microchemical colorimetric determination of sodium. A. ELIAS (Anal. Asoc. Quím. Argentina, 1935, 23, 1—3).—The triple acetate of U, Mg, and Na described by Kahane (A., 1933, 1024) dissolved in H_2O gives an orange-yellow solution which is used in the colorimetric determination of small amounts of Na. F. R. G.

Determination of sodium as sodium magnesium uranyl acetate. F. KOGLER (Angew. Chem., 1935, 18, 561—565).—The substance is dissolved in H_2O , and evaporated with HClO_4 to remove K. The filtrate and alcoholic washings are neutralised with NH_3 and evaporated to dryness. The residue is dissolved in 5 c.c. of H_2O , and Na is pptd. at 20° with Kahane's reagent (A., 1930, 726). Ba and Sr, but not Ca, interfere, and may be removed by pptn. with $(\text{NH}_4)_2\text{CO}_3$. SO_4'' if present is removed as BaSO_4 before pptg. the K. PO_4''' if present may then be pptd. by making strongly alkaline with NH_3 (tropæolin O as indicator). In absence of SO_4'' , PO_4''' may be pptd. with CaCl_2 . Na should be pptd. at the temp. at which Kahane's reagent is kept saturated. J. S. A.

Determination of caesium as caesium bismuth iodide. R. W. FELDMANN (Z. anal. Chem., 1935, 102, 102—108).—The method of Tananaev and Harmasch (A., 1932, 1010) does not give accurate results when Cs is pptd. from pure solutions of its salts or from solutions containing Cs and Rb. J. W. S.

Determination of small quantities of radium in minerals. J. A. BOTTEMA (Chem. Weekblad, 1935, 32, 482—486).—To determine the age of U minerals in which the proportion of U is too small for direct determination, the latter is deduced from the Ra content, which is measured by an ionisation chamber method. D. R. D.

Beryllium. I. I. IITAKA, Y. AOKI, and T. YAMANOBE (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 741—748).—Be may be determined with fair accuracy by pptg. $\text{Be}(\text{OH})_2$ with aq. NH_3 and NH_4Cl , or KI and KIO_3 , and igniting to BeO . The colorimetric titration method using quinalizarin indicator is also satisfactory, and is unaffected by the presence of Cu or Al. In presence of Mg the Be must be separated with aq. NH_3 and NH_4Cl , after which the $\text{Be}(\text{OH})_2$ may be redissolved in HCl and titrated. J. W. S.

Volumetric determination of magnesium. W. DAUBNER (Angew. Chem., 1935, 48, 551).—To the solution of MgCl_2 , free from metals other than the alkalis, is added a slightly acid solution of Na_2HAsO_4 together with NH_4Cl . Aq. NH_3 is added dropwise with stirring until cryst. $\text{MgNH}_4\text{AsO}_4$ is pptd. The solution is then kept for 4—5 hr. The As solution used must contain $> 0.3\%$ As_2O_5 , and under these conditions the composition of the ppt. is const. The ppt. is collected, washed with EtOH, dissolved in HCl, reduced with SO_2 , and the As_2O_3 content determined volumetrically. Results appear to be accurate to $\pm 0.3\%$ on the Mg content. C. I.

Determination of small amounts of zinc in commercial nickel.—See B., 1935, 771.

New reagent for the gravimetric determination of certain metals. II. Macro- and micro-determination of cadmium. G. SPACU and M. KURAŠ (Z. anal. Chem., 1935, 102, 108—110; cf. this vol., 1094).—The solution containing Cd is treated with NH_3 until a clear solution is obtained and then a solution of thiolbenzthiazole (I) and NH_3 added. The Cd is pptd. as $\text{Cd}(\text{C}_6\text{H}_4\text{NS})_2 \cdot 2\text{NH}_3$, which at 110—120° yields $\text{Cd}(\text{C}_6\text{H}_4\text{NS})_2$. Cu and Cd can be determined in the same solution by pptg. Cu only with (I) in neutral solution and then adding NH_3 in excess to ppt. Cd. J. W. S.

Iodometric determination of copper. Determination of copper in white metal. H. A. J. PIETERS (Chem. Weekblad, 1935, 32, 509—510).—Foote and Vance's method (this vol., 837) gave excellent results. D. R. D.

Use of 8-hydroxyquinoline in determinations of aluminium, beryllium, and magnesium. H. B. KNOWLES (J. Res. Nat. Bur. Stand., 1935, 15, 87—96).—The solution containing Al and Be is freed from Cu, Pb, Bi, etc. with H_2S , from Mn, Mg, alkaline earths, and moderate amounts of Ni, Co, and Zn by pptn. with aq. NH_3 , or from Fe, Ti, Zr, etc. by pptn. with excess of NaOH. To 200 c.c. of acid solution containing > 0.1 g. Al and 10 c.c. of HCl are added 15 c.c. of NH_4OAc solution (30 g. NH_4OAc to 75 c.c. H_2O) and 8—10 drops of 0.04% solution of bromocresol-purple. Dil. aq. NH_3 is added until the solution turns purple, and an AcOH solution of 8-hydroxyquinoline (I) (15—25% excess) added slowly during stirring. The solution is heated to the b.p. for 1 min., cooled to 60°, filtered, and the ppt. washed with 100 c.c. of cool H_2O , dried, and weighed as $\text{Al}(\text{C}_8\text{H}_6\text{ON})_3$ or determined volumetrically by dissolving in HCl, adding a slight excess of standard KBrO_3 in KBr, and determining the excess by treatment with KI

and titration with $\text{Na}_2\text{S}_2\text{O}_3$. Be can be determined in the filtrate from the (I) pptn. by pptg. $\text{Be}(\text{OH})_2$ from the cold solution with NaOH and subsequent ignition to BeO . In absence of Be, tartaric acid (5 times wt. of Al) can be added to the Al solution, followed by rapid addition of the (I). Both methods give slightly high results, the reasons for which are discussed. J. W. S.

Separation of iron and aluminium from alkaline-earth elements by means of ammonia. M. FERRICH (Bull. Soc. Chim. Yougoslav., 1935, 6, 27—50).—25 c.c. of solution, containing Fe^{III} and Al, are poured in a thin stream into 75 c.c. of a solution of 5 g. of NH_4NO_3 , and 2—3 c.c. of aq. NH_3 in 75 c.c. of H_2O at 85—90°, with const. stirring, and the ppt. is collected after 20 min., washed with 0.2% aq. NH_4NO_3 , dried, ignited at 1200° for 20 min., and weighed. Should Mg, Ca, Sr, and Ba be present, freshly distilled aq. NH_3 , not containing traces of SiO_2 or CO_2 , should be used, and the ppt. should be washed with < 400 —500 c.c. of solution. R. T.

Determination of chromium by the liquid amalgam method. P. G. POPOV and M. A. NECHAMKINA (Ukrain. Chem. J., 1935, 10, 187—192).—The solution, containing Cr^{III} or $\text{Cr}_2\text{O}_7^{II}$, is reduced by Zn-Hg in 6N- H_2SO_4 , and Cr^{II} is titrated with KMnO_4 . R. T.

Infra-red photographs of chromium compounds. J. RZYMKOWSKI (Naturwiss., 1935, 23, 610).—The great majority of Cr compounds of all types reflect infra-red radiation in the range 720—880 μ . The use of this for the detection of Cr compounds on paintings is mentioned. A. J. M.

Determination of chromium in stainless steel.—See B., 1935, 807.

Electrolytic determination of titanium, zirconium, or aluminium in chromium steels and alloys.—See B., 1935, 807.

Analysis of very small amounts of monazite. F. HECHT and E. KROUPA (Z. anal. Chem., 1935, 102, 81—99).—The mineral is extracted with H_2SO_4 and then with HCl, the residue being weighed and subsequently treated with HF to determine SiO_2 . The solution is treated with $(\text{NH}_4)_2\text{MoO}_4$ to ppt. P, excess of Mo being removed as MoS_3 . Fe, Al, rare earths, Mn, U, Ca, and Mg are then determined by the usual methods. Pb is determined separately as PbSO_4 . J. W. S.

Determination of small amounts of vanadium in uranium preparations. N. I. TSCHERVJAKOV and E. A. OSTROUMOV (Z. anal. Chem., 1935, 102, 181—186).—V and Fe^{III} give with $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-NH}_2$ (I) in slightly acid solution a red to violet coloration stable in presence of excess of EtOH. For analysis, U preps. are converted into UO_2Cl_2 . To a solution of 0.2—0.5 g. in a colorimeter tube, HCl + 0.5 c.c. of H_3PO_4 are added, and then 4 vols. of EtOH. 3—4 c.c. of glycerol are added to bind the Fe as a glycerophosphate complex, and finally 1 c.c. of 0.5% aq. (I) hydrochloride. The colour is matched against that produced from V-free U_3O_8 in a solution of identical acidity, to which standard V_2O_5 solution is added.

Determination of antimony in lead [by electrical resistance measurement].—See B., 1935, 808.

Determination of antimony in alloys by means of permanganate.—See B., 1935, 808.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXIX. Separation of tungsten from titanium, niobium, tantalum, and zirconium. A. R. POWELL, W. R. SCHOELLER, and C. JAHN (*Analyst*, 1935, 60, 506—514; cf. A., 1934, 503).—W and Ti cannot be separated by fusion of the mixed oxides with $K_2S_2O_7$ and extraction with H_2O or dil. acid, nor by fusion with Na_2CO_3 and extraction with H_2O , but they may be quantitatively separated by extraction of the Na_2CO_3 melt with 10% aq. NaOH. The only procedure found to separate W from Ti and Nb, with or without Ta and Zr, consists in fusing the mixed oxides with K_2CO_3 , and treating the aq. extract of the melt with a slightly ammoniacal aq. Mg salt, whereby the earths are pptd. For accurate work the procedure should be repeated. ZrO_2 may be separated from WO_3 by fusion with Na_2CO_3 and extraction with H_2O . The applicability of the methods available for the separation of W from the individual or mixed earths is discussed. Ta and Nb may be approx. determined by titration of the alkali in the NaCl ppt. of the mixed earth acids. E. C. S.

Thermodynamic temperature scale below 1° abs. W. H. KEESOM (*Physica*, 1935, 2, 805—806).—A previous method (cf. A., 1934, 1061) of establishing the thermodynamic temp. scale is modified.

T. G. P.

Electric heater designed to prevent losses from creeping in the evaporation of concentrated salt solutions preliminary to mineral analysis. G. M. GUEST and E. LEVA (*J. Biol. Chem.*, 1935, 110, 777—779).—The liquid to be evaporated is heated by an electrically heated coil well above the surface of the liquid and fitting closely around the brim of the vessel. J. N. A.

Hot plate. L. C. KREIDER (*J. Chem. Educ.*, 1935, 12, 336—337).—A 100-watt lamp gives temp. from 30° to 70° in the arrangement described. L. S. T.

Thyatron control for incubators and water-baths. J. W. MAJOR and E. W. THATCHER (*Science*, 1935, 82, 201—202). L. S. T.

Outfit for photomicrography. H. WRIGHTON (*J. Roy. Microscop. Soc.*, 1935, [iii], 55, 79—82).—Crit. vertical illumination for metal specimens is provided. C. W. G.

Technique for X-ray studies of substances under high pressures. L. K. FREVEL (*Rev. Sci. Instr.*, 1935, [ii], 6, 214—215).—The substance is sealed up in a cooled tube containing PhMe and the pressure is raised by warming the tube. C. W. G.

Preparation of photon counters for visible light. A. KOLIN (*Rev. Sci. Instr.*, 1935, [ii], 6, 230—231).—A small piece of alkali metal attached to an Fe or Ni rider is heated on the anode wire of a Geiger-Müller counter to obtain a deposit of metal on the cathode. The rider and unused metal can be removed by means of a magnet. C. W. G.

Arrangement for microscopical work at low temperatures. S. ERK (*Z. Elektrochem.*, 1935, 41, 521).—Condensation of H_2O on the objective etc. is prevented by a stream of evaporated liquid air. Observations may be made down to -120° .

T. G. P.

Colour measurement with the leukometer.—See B., 1935, 785.

Thin cell for use in determining the refractive indices of crystal grains. C. P. SAYLOR (*J. Res. Nat. Bur. Stand.*, 1935, 15, 97—98). J. W. S.

Counting-field finder [for microscope]. T. E. WALLIS (*Analyst*, 1935, 60, 520—521). E. C. S.

Vacuum monochromator and spectrograph with quartz and fluorite optical systems for the regions 0.700—0.160 μ (quartz) and 0.700—0.130 (fluorite). C. LEISS (*Z. Physik*, 1935, 95, 778—780). A. B. D. C.

Investigations in the ultra-soft X-ray region. I. Spectrograph for relative measurements. E. A. W. MULLER (*Z. Physik*, 1935, 95, 763—768).

A. B. D. C.

Measurement of quantity of light by the photoelectric cell. D. V. GOGATE and D. S. KOTHARI (*Indian J. Physics*, 1935, 9, 487—489).—Relations are deduced for calculating quantity of light from the use of the cell and galvanometer and are verified experimentally. N. M. B.

Measurement of radium emanation implants. P. A. MACDONALD and E. M. CAMPBELL (*Rev. Sci. Instr.*, 1935, [ii], 6, 212—214).—The change of current in an ionisation chamber produced by movement of the emanation container is amplified as though it were a half wave of a.c. Rn implants can be measured to 2%. C. W. G.

Ionising particle counters. J. R. DUNNING and S. M. SKINNER (*Rev. Sci. Instr.*, 1935, [ii], 6, 243—246).—Improvements in point and tube counters are described. C. W. G.

Amplification of photo-currents through emission of secondary electrons. F. M. PENNING and A. A. KRUTHOF (*Physica*, 1935, 2, 793—804).—The current from the cathode of a vac. or gas-filled photocell may be considerably amplified by secondary emission from a third electrode of the same material as the cathode. Evacuated secondary emission cells show a practically const. dynamic response to light variations up to ≈ 20 kilocycles. T. G. P.

Determination of the dielectric constants of solids by the method of mixtures. E. KLEINKE (*Physikal. Z.*, 1935, 36, 565—566).—The application of Stark's method to substances with high dielectric consts., and to insulators containing conducting inclusions, is described. A. J. M.

Significance and principles of electrostatic e.m.f. measurements with the help of electron tubes. F. MULLER and W. DURICHEN (*Z. Elektrochem.*, 1935, 41, 559—563; cf. this vol., 1097).—The utility of the method and recent developments in apparatus and technique are discussed.

T. G. P.

Mechanism of action of solid electron rectifiers.

V. P. JOUSE (Physikal. Z. Sovietunion, 1935, 7, 1—18).—A new Cu_2O rectifier has been prepared, with an artificial "blocking layer" consisting of a wedge of SiO_2 , B_2O_3 , NaCl , S , glass, or bakelite, 10^{-6} – 5×10^{-4} cm. thick, attached to the Cu_2O plate and confined between Au electrodes. Current-p.d. curves have been measured at -100° to 50° . The rectifying coeff. is a max. with a blocking layer thickness of 2×10^{-6} – 10^{-5} cm., and may reach 100 at 1 volt. R. S. B.

Hydrogen electrode for p_{H} determinations.

H. C. LOCKWOOD (J.S.C.I., 1935, 54, 295–296T).—The electrode consists essentially of a U-shaped vessel down one limb of which slides a glass tube carrying a sealed-in Pt wire. The end of the wire is arranged directly above a jet through which the H_2 bubbles. Each bubble impinges on the end of the Pt wire and, being pierced, travels up the whole length. The liquid is made to circulate by means of a suitable inlet and outlet in the U-tube. The electrode is very economical with H_2 and 40 ml. per min. is ample. Before using the electrode, the Pt wire is cleaned on fine emery cloth and recoated with a min. deposit of Pt-black. The electrode takes 0.5–5 min. to reach equilibrium. Two modified types have been designed whereby the containing vessels are incorporated and they work on 1 mm. or 5 mm., respectively.

Technique of glass electrode. H. A. BROMLEY (Analyst, 1935, 60, 533–536).—A modification of Harrison's circuit is described. E. C. S.

Degree of accuracy of the glass electrode in alkaline solutions. I. D. BURTON and J. BATESON (J. Soc. Leather Trades Chem., 1935, 19, 306–313).—The results obtained by the glass electrode are < those given by the H electrode at $p_{\text{H}} > 11.35$; for other vals. the agreement is good. D. W.

Antimony electrode. D. N. MEHTA and S. K. K. JATKAR (J. Indian Inst. Sci., 1935, 18A, 85–100).—Best results were obtained with freshly polished cast electrodes. $E = -0.0293 + 0.0591 p_{\text{H}}$ at 25° . C. W. G.

Antimony[–air] electrode for p_{H} measurements. Mechanism of potential formation and the practical application of the electrode. P. WULFF, W. KORDATZKI, and W. EHRENBERG (Z. Elektrochem., 1935, 41, 542–551).—Measurements have been made which indicate that the p_{H} -dependent potential of the Sb electrode in presence of air is not determined by the Sb^{+++} activity of the solution, but by the irreversible oxidation process and by the diffusion velocity of the reaction products on the electrode surface. For practical use the Sb electrode must be in contact with a well-stirred solution saturated with air, the deposit on its surface must be continuously removed, and it must be calibrated under the experimental conditions. A suitable arrangement is described. T. G. P.

Micro-quinhydrone electrode: its application to the determination of the p_{H} of glomerular urine of *Necturus*. J. A. PIERCE and H. MONTGOMERY (J. Biol. Chem., 1935, 110, 763–775).—The prep.

of a micro-quinhydrone electrode which can be used for the trustworthy determination of the p_{H} of 10^{-4} c.c. of liquid is described. It can be inserted through or into tissues without contamination, and its accuracy is the same as that of the ordinary quinhydrone electrode. The p_{H} of glomerular urine from *Necturus* ranged from 7.07 to 7.63. The difference between these vals. and those obtained colorimetrically is a physiological one. J. N. A.

Micro-quinhydrone-silver chloride cell for precision e.m.f. studies on heavy water. V. K. LA MER and M. H. ARMBRUSTER (J. Amer. Chem. Soc., 1935, 57, 1510–1511). E. S. H.

Pipette for storage of air-free reagents used in gasometric analysis. G. M. GUEST and F. E. HOLMES (J. Biol. Chem., 1935, 110, 781–783).—A pipette having a capacity of approx. 25 c.c. is described. The reagent is not in contact with the stop-cock, and the pipette is considerably less fragile than the Hempel pipette. J. N. A.

Microburette with interchangeable jets. J. KHOURI (Bull. Soc. Chim. biol., 1935, 17, 1077). A. L.

Micropyknometer method for density determinations. G. R. CLEMO and A. MCQUILLEN (J.C.S., 1935, 1220).—The micropyknometer holds approx. 2 mg. and is made by drawing out each end of a short piece of capillary tube. $d^{17.2}$ are: C_6H_6 0.879 and C_6D_6 0.954. J. G. A. G.

Casting molybdenum buttons in brass, for water-cooled targets in X-ray tubes. F. H. TRIMBLE (Rev. Sci. Instr., 1935, [ii], 6, 216).—Small pieces of brass placed on top of a Mo disc are heated in a small arc furnace. Good contact between the Mo and the brass is obtained without the use of a flux. C. W. G.

Mercury cistern. R. M. BOWIE (Rev. Sci. Instr., 1935, [ii], 6, 242).—The Hg of a McLeod gauge is released from a cistern through a ground valve operated by a hand lever, permitting large or small rates of flow. C. W. G.

Introducing oxygen into evacuated systems. J. B. TAYLOR (Rev. Sci. Instr., 1935, [ii], 6, 243).— O_2 diffuses through hot Ag. C. W. G.

Mechanical properties of stretched and unstretched sulphur threads and their changes with time. K. SAKURADA and H. ERBRING (Kolloid-Z., 1935, 72, 129–135).—Apparatus and technique for obtaining amorphous S threads of definite cross-section and length are described. The breaking strength of the threads depends on the temp. from which the S is cooled; it reaches a max. at 300° . The breaking strength also varies with ageing, passing through a max. after a few days; the position of this max. also depends on the temp. The elongation increases with rising temp. of prep. The breaking strength of permanently deformed S threads (extension 800–900%) is very high (11 kg. per sq. mm.). E. S. H.

Middle piece of the Soxhlet extractor and the simple extraction tube. A problem of standardisation. The cold extractor. F. W. NEUMANN (Chem. Fabr., 1935, 8, 326–327).—The Soxhlet

extractor is critically compared with simpler types. An apparatus in which the solvent vapour is condensed and allowed to pass through the material at any desired temp. below the b.p. is described. R. S.

Determination of absorption coefficients of sound for different materials. L. P. VARMA (Proc. Acad. Sci. Agra and Oudh, 1935, 4, 301—315).—A very sensitive method is described. C. W. G.

Device for aerating and circulating aquarium water. P. L. VARNEY (Science, 1935, 82, 136).

Glass manometer for laboratory use. T. E. PHIPPS, M. L. SPEALMAN, and T. G. COOKE (J. Chem. Educ., 1935, 12, 321—323).

Measurement of the elastic constant of isotropic transparent solids. E. HIEDEMANN (Nature, 1935, 136, 337).—The elastic consts. of glass have been calc. from measurements of the velocity of ultrasonic compression waves.

Applications of pervaporation. L. FARBER (Science, 1935, 82, 158).—The apparatus described can be used for the concn. of aq. glycerol solutions of enzymes, of dil. protein solutions with simultaneous removal of salts, and the rapid evaporation of large vols. of H_2O at room temp.

Sucking gases out of fume cupboards. W. F. BON (Chem. Weekblad, 1935, 32, 510).—A vac. pump is used to remove gases, in place of the usual flame or fan.

Highly polymerised compounds. CXIV. Comparison of the osmometrically and viscosimetrically determined mol. wts. of mixtures of polymeric homologues. W. KERN (Ber., 1935, 68, [B], 1439—1443).—It is shown mathematically that the mean mol. wt. of a given mixture of polymeric homologues is greater when determined by viscosimetric than by osmotic methods. With very carefully fractionated mixtures the two methods give not very dissimilar results.

Nomogram for the Hagenbach correction for the suspended level viscosimeter. L. UBBELOHDE (Oel u. Kohle, 1935, 11, 578—579).

Construction of a cartesian nomogram for the law of mass action. F. C. McLEAN (Science, 1935, 82, 104—105).

Ancient Chinese treatise on alchemy. J. R. PARTINGTON (Nature, 1935, 136, 287—288).

Geochemistry.

Presence of inert gases in certain mineral spring gases in Japan. I. SUGANUMA and K. KITAOKA (Bull. Chem. Soc. Japan, 1935, 10, 289—296).—Gases escaping from certain springs in Japan, some radioactive and some inactive, have been examined spectroscopically. In all cases Ne, and sometimes A, were found in addition to He. This appears to disprove the view that the He is exclusively radioactive in origin; it is more likely that the inert gases arise from the primordial air originally entrapped in the earth, the O_2 and N_2 having been long ago lost by chemical action.

Isotope composition of rain and snow water. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 263—266).—Samples of rain collected at the beginning of a rainfall were somewhat denser (about 2 p.p.m.) and those at the end lighter (about 2 p.p.m.) than standard town H_2O . Samples of snow collected in 1934 and 1935 were all lighter (0.5—3.3 p.p.m.) than standard. Ice collected in a gully 2257 m. above sea level was also lighter (2.2 p.p.m.), whereas according to Emeleus *et al.* (A., 1934, 1062) the fractional crystallisation should make it heavier. An explanation is offered.

Analysis of water of the Velika thermal spring. S. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1935, 6, 51—60).—Analytical data are recorded.

The p_H of the mineral springs of Bagneres-de-Bigorre. F. L. YDRAC (Bull. Soc. Ramond, 1933—1934, 68—69, 39—41).—Vals. of the p_H of 20 springs lie between 6.9 and 7.7, and the p_H of Labassere is 10.

Chemical and chemico-physical analysis of the mineral water of the Valleverde Spring (Abruzzo). D. MAROTTA and E. SORRENTINO (Annali Chim. Appl., 1935, 25, 324—350).—This H_2O gives 0.27 g. of fixed residue (at 110°) per litre, and contains chiefly $Ca(HCO_3)_2$; SiO_2 is relatively high and traces of Ag are present.

Plankton production and the nitrate nitrogen and phosphate cycles in the Pacific Ocean off New South Wales. W. J. DAKIN and A. N. COLEFAX (Nature, 1935, 136, 339).— NO_3' and PO_4''' are reduced to a trace or even zero in the surface waters on certain occasions which always follow a spring max. in diatom production. In summer $[NO_3']$ is low, but the $[PO_4''']$ is quickly regenerated; in winter, $[PO_4''']$ for surface waters ranges from 20 to 30 mg. of P_2O_5 per cu. m. and $[NO_3']$ from 20 to 35 mg. per cu. m.

Phosphate in the western basin of the North Atlantic. H. R. SEIWEILL (Nature, 1935, 136, 206—208).—The vertical distribution, its variation and mechanism are described. There is probably a significant eddy transfer from the PO_4''' -rich mid-strata to impoverished surface layers. The bearing of this factor on biological fertility is discussed.

Origin of petroleum water. N. TAGEEVA (Petroleum, 1935, 31, No. 32, 15—23).—There is a marked similarity between the analyses of oil-field waters from different fields. All are saline and contain only small amounts of sulphate and carbonate. The ratio Na : Cl is approx. const., averaging 0.79. Further similarity is shown on the Na : Cl

basis with a number of sea-waters of different origin, and it is suggested that the typical oil-field waters may originate from sea-waters. This hypothesis is supported by other geochemical properties of oil-field waters. The fact that the Mg:Ca ratio for the latter (< 1) differs from that of sea-water, whilst Ca+Mg closely corresponds with the Mg combined with Cl in sea-water, can be explained by geochemical changes. A brief discussion is given of the geological features with which petroleum is usually associated and their bearing on the composition of oil-field waters. The geochemical significance of such constituents as Li, Sr, Ba, B, and Br in oil-field waters has yet to be elucidated. C. C.

Correlation of pre-Cambrian granites by means of heavy mineral analysis. J. T. STARK and F. F. BARNES (Geol. Mag., 1935, 72, 341—350).—Heavy mineral analyses for various localities of the Pikes Peak and Silver Plume granites of pre-Cambrian age in the Sawatch Range, Colorado, are recorded and discussed. Although the % of constituents vary widely in different specimens of a given batholith, there is a general tendency towards uniformity in the relative abundance of certain minerals, especially zircon and titanite, and a sufficiently large no. of analyses might lead to a successful correlation.

L. S. T.

Spessartite in the Cambrian manganese ore of Merionethshire. A. W. WOODLAND (Geol. Mag., 1935, 72, 384).—The silicate constituent of the ore is mainly, if not entirely, in the form of minute crystals of garnet conforming in colour and composition to pure spessartite.

L. S. T.

Exogenous contact-zone at Ben Bullen, New South Wales. (Miss) G. A. JOPLIN (Geol. Mag., 1935, 72, 385—400).—The exogenous contact consists of a series of cordierite-hornfels and of magnesian and non-magnesian marbles (petrography described). The marbles show an apparent increase in SiO_2 content, and the development of certain index minerals, viz., brucite (I), forsterite, and diopside, but this is actually due to a decreasing MgO content. Thermal metamorphism among the limestones has given rise to dolomite coronas about (I) and dactylitic intergrowths between calcite and dolomite. In the contact of the magnesian marbles the metasomatising solutions are usually Fe- and SiO_2 -bearing and there is some migration of solutions derived from the marbles themselves. In the zone of the non-magnesian marbles, Fe-, SiO_2 -, and Al_2O_3 -bearing solutions play a prominent part. L. S. T.

Mechanical composition of the London Tertiaries in the neighbourhood of Harrow-on-the-Hill. W. H. BARRETT (Geol. Mag., 1935, 72, 337—341).—Mechanical analyses for sand, silt, and clay of three exposures are recorded. L. S. T.

Alkaline quartz-dolerites, from Bijawar, and their chemical relationships. M. P. BAJPAI (Current Sci., 1935, 4, 39—41).—The chemical composition of several quartz-dolerites from Bijawar was compared with that of Deccan basalt and spilite; approx. agreement in the amounts of all constituents,

except Na_2O , was found. A further comparison was made with Gwalior and Singhbhum dolerites.

W. R. A.

Pre-Cambrian granites in the Canadian Shield. R. T. CHAMBERLIN (Science, 1935, 82, 126—127).—A reply to criticism. The view that there are < 3 granites of widely different age in the Canadian Shield is maintained. L. S. T.

Comparative study of the weathering of rocks under different climatic conditions. E. BLANCK and R. THEMLITZ (Chem. Erde, 1935, 9, 529—539; cf. A., 1928, 612).—Further analyses of samples of limestone and sandstone which had been exposed to the weather for 12 years at Göttingen and on the summit of the Brocken are recorded. L. J. S.

Microscopical study of copper ore from Niedermarsberg, Westphalia. F. SCHWAKE (Chem. Erde, 1935, 9, 486—528).—The several minerals (pyrite, marcasite, chalcocine, bornite, chalcopyrite, covellite, native Cu, etc.) are described and their origin is discussed. L. J. S.

Chemical structure of clay minerals and of corresponding silicates of tervalent and bivalent metals. J. HOLZNER (Chem. Erde, 1935, 9, 464—485).—A recalculation of old analyses to fit them in with theories of structure types as determined by X-rays. L. J. S.

Chemical and optical interrelations of the brittle mica group. G. KOCH (Chem. Erde, 1935, 9, 453—463).—Ten new analyses with optical data are given of margarite, clintonite, and chloritoid. These are tabulated and plotted with other data from the lit. to show the variation of the optical properties with the chemical composition. In margarite ($\text{H}_2\text{CaAl}_4\text{Si}_2\text{O}_{12}$) with replacement of Ca by Na_2 there is a linear decrease in n and optic axial angle and an increase in the birefringence. Clintonite (including xanthophyllite and brandisite) has the formula $\text{H}_2\text{CaMg}_3\text{Al}_2\text{Si}_2\text{O}_{12}$, equiv. to that of margarite with Mg replacing some Al. L. J. S.

Chemical weathering and soil formation in Siam. E. BLANCK, W. CREDNER, and E. VON OLDERSHAUSEN (Chem. Erde, 1935, 9, 419—452).—Analyses of rocks and soils are given from different districts, ranging from the moist tropical Malay peninsula to the northern uplands. The main types are the grey soils of the flood plains, and the yellow, brown, and red soils of the uplands. L. J. S.

Anemousite in essexite. F. F. OSBORNE (Canad. J. Res., 1935, 12, 668—675).—Anemousite (undersaturated feldspar) has been found in some Monteregian essexites. J. W. S.

"Mercallite," a new mineral among the products of the fumarolic activity of Vesuvius during 1933. G. CAROBBI (Atti R. Accad. Lincei, 1935, [vi], 21, 385—393).—Mercallite consists of KHSO_4 identical in cryst. form and d with KHSO_4 crystallised from aq. solutions containing about 4% Na and 4% SO_4 . D. R. D.

Trieuite, a new cobalt mineral. L. DE LEENHEER (Natuurwetensch. Tijds., 1935, 17, 91—95).—The name trieuite is proposed for the mineral described by Schoep (A., 1921, ii, 649). Its composition is $2\text{Co}_2\text{O}_3, \text{CuO}, 6\text{H}_2\text{O}$. D. R. D.

Chemical and physico-chemical properties of Dniepropetrovsk glauconites. A. J. MIKEI (Ukrain. Chem. J., 1935, 10, 262—265).—The dehydrated glauconite has pronounced permutitic activity. Analytical data are recorded. R. T.

Organic Chemistry.

Free *n*-propyl radical. T. G. PEARSON and R. H. PURCELL (Nature, 1935, 136, 221).— COPr^a_2 is decomposed in the light from a quartz-Hg vapour arc with the formation of free Pr^a . L. S. T.

Pyrolysis of propane in presence of water vapour. J. W. LANG and J. J. MORGAN (Ind. Eng. Chem., 1935, 27, 937—941).—The products of the pyrolysis of C_3H_8 at 600—700° and low partial pressures in presence of steam (which is practically inert under the prevailing conditions) have been analysed. Changes in pressure affect the products (e.g., the proportion of C_3H_6 to C_2H_4 in the unsaturated hydrocarbons is increased at higher pressures). A bimol. reaction must occur to some extent. Temp. has no effect on the proportion of primary products obtained from C_3H_8 over the temp. range normally used in this connexion; they may be accounted for by the reactions: $\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2$, $\text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4$, $2\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_6 + \text{CH}_4$. It is considered that the mechanism of hydrocarbon pyrolysis is best explained by Nef's dissociation hypothesis which postulates "active" and "inert" mols. C. C.

Reactions catalysed by aluminium chloride. XI. Branching of the carbon chain during the treatment of saturated hydrocarbons with acetyl chloride in presence of aluminium chloride. C. D. NENITZESCU and I. CHICOS (Ber., 1935, 68, [B], 1584—1587).—The action of AcCl on $n\text{-C}_6\text{H}_{12}$ in presence of AlCl_3 at 15—16° leads to $\gamma\delta$ -dimethylpentan- β -one with smaller amounts of $\gamma\delta$ -dimethyl- Δ^7 -penten- β -one according to the scheme: $n\text{-C}_5\text{H}_{12} \xrightarrow{\text{Pr}^a\text{Et}} \text{CMe}_2\text{CHCH}_2 \rightarrow \text{CMe}_2\text{CHMeAc} \rightarrow \text{CMe}_2\text{CMeAc}$ or CHMePr^aAc . Similarly $n\text{-C}_6\text{H}_{14}$ yields δ -methyl- γ -ethylpentan- β -one and δ -methyl- γ -ethyl- Δ^7 -penten- β -one. The rate of reaction of paraffins of medium mol. wt. with AcCl is of the same order of magnitude as that of cyclopentane and cyclohexane; the separation of these classes in petroleum in this manner is impossible. H. W.

Nitrous oxide as an oxidising agent in the gaseous state.—See this vol., 1213.

Autoxidation of *n*-hexadecane.—See this vol., 1208.

Thermal reactions of gaseous hydrocarbons.—See this vol., 1206.

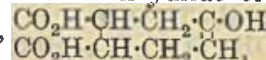
Application of Raman spectrography to the study of the ethylenic linking. L. PLAUX (Ann. Chim., 1935, [xi], 4, 147—223).—A summary and discussion of results reported previously (cf. A., 1933, 553; 1934, 583, 943). J. W. S.

Synthetic rubber "sovprene" [chloroprene]. A. L. KLEBANSKI, L. G. ZURICH, I. M. DOLGOPOLSKI, et al. (Bull. Acad. Sci. U.R.S.S., 1935, 189—226).—

Low-temp. continuous polymerisation of C_2H_2 in a slightly acid aq. solution of $\text{CuCl}, \text{NH}_4\text{Cl}$ gives $\text{CH}_2\text{C}(\text{CH})\text{CH}_2$ (I) in 75—80% yield (on the C_2H_2) and 25—30% of trimerides and higher polymerides of C_2H_2 . About 40% of the C_2H_2 is converted in a single passage of the gas. The continuous prep. of chloroprene from (I) and from mixtures of (I) and C_2H_2 is described, and the conditions for converting the chloroprene into its α -polymerides, with a min. formation of balata-like polymerides which harden, are defined. Ozonisation of α - and ω -polymerides of chloroprene yields $(\text{CH}_2\text{CO}_2\text{H})_2$ in almost quant. amount; HNO_3 gives $(\text{CH}_2\text{CO}_2\text{H})_2$ and $\text{H}_2\text{C}_2\text{O}_4$. A new trimeride of C_2H_2 , acetylenyldivinyl, $\text{CH}_2\text{CH}(\text{CH})\text{CH}(\text{CH})\text{CH}_2$, b.p. 30—32°/100 mm., gives CH_4 when treated with MgMeI , forms a *Cu* derivative, $\text{C}_6\text{H}_5\text{Cu}$, and combines with HCl to form the compound, $\text{CH}_2\text{CH}(\text{CH})\text{CH}(\text{CH})\text{CClCH}_2$, b.p. 40—41°/25 mm., which polymerises rapidly in air. A tetrameride of C_2H_2 , b.p. 44°/20 mm., 51°/30 mm., was obtained. Polymerisation of the trimeride and higher polymerides of C_2H_2 yields, under some conditions, products useful in the prep. of artificial lacquers and varnishes.

The action of EtOH-KOH on $\beta\delta$ -dichloro- Δ^8 -butene yields β -chloro- δ -ethoxy- Δ^8 -butene, b.p. 143°, 62—64°/40 mm.; the corresponding alcohol, b.p. 92°/50 mm., forms a xanthate. Di- γ -chloro- Δ^8 -butenyl ether has b.p. 142°/50 mm. The action of NaOCl on (I) gives α -chloro- β -vinylacetylene, which combines with HCl in presence of $\text{CuCl}, \text{NH}_4\text{Cl}$ to give $\alpha\beta$ -dichloro- $\Delta^{\gamma\gamma}$ -butadiene, b.p. 60—65°/40 mm. In presence of KOH at 150°, (I) combines with MeOH to give β -methoxy- $\Delta^{\gamma\gamma}$ -butadiene, b.p. 33°/27 mm., 97°/760 mm.; in absence of KOH , styrene is formed in large proportion. With KOH and EtOH at 150°, (I) gives β -ethoxy- $\Delta^{\gamma\gamma}$ -butadiene, b.p. 113.4°, which yields $\text{H}_2\text{C}_2\text{O}_4$ and HCO_2H on oxidation with KMnO_4 or O_3 , and Et sec-Bu ether on hydrogenation.

In presence of HgSO_4 or of $\text{HgO} + \text{BF}_3$, (I) condenses with: (1) HCO_2H to give formoprene (II), $\text{CH}_2\text{CH}(\text{C}(\text{OCHO})\text{CH}_2)$, b.p. 42°/40 mm., which, like chloroprene, spontaneously polymerises in the air in 10 days, giving a rubber-like, plastic polymeride; with maleic anhydride, (II) condenses to give cyclohexan-1-one-3:4-dicarboxylic acid (III), m.p. 161—162° [semicarbazone, m.p. 199° (decomp.)], (2) AcOH to give β -acetoxy- $\Delta^{\gamma\gamma}$ -butadiene, b.p. 50—52°/25 mm.; this condenses with maleic anhydride to form the unstable compound,



which undergoes isomerisation to (III). Hydrogenation of (I) in presence of colloidal Pd on starch in EtOAc , or Ni , yields butadiene. T. H. P.

Application of Raman spectrography to the study of the acetylenic linking. (MILLE.) B. GREDY (Ann. Chim., 1935, [xi], 4, 5—82).—A detailed

account of work already reviewed (cf. A., 1933, 553, 886; 1934, 239, 943; this vol., 73).

Active hydrogen in chloroform and the co-ordination formulæ proposed by Urbain and Tchakirian. E. V. ZAPPI and H. DEGIORGI (Anal. Asoc. Quím. Argentina, 1935, 23, 14—21).—0.001 mol. of CHCl_3 in $\text{C}_5\text{H}_5\text{N}$ with MgMeI in diamyl ether gives 24.4 c.c. of gas indicating 105% of active H. Similarly CHBr_3 and CHI_3 contain 50% and 3%, respectively, of active H. These results support the formula $[\text{CX}_3]\text{H}$ proposed by Tchakirian *et al.* (A., 1932, 901). F. R. G.

Refraction equivalents of the triple carbon linking. K. VON AUWERS (Ber., 1935, 68, [B], 1635—1638).—Examination of recorded data for 12 Δ^a -alkines gives the val. 2.325 for $\bar{\nu}$ in $\text{CR}:\text{CH}$ and 2.573 in $\text{CR}:\text{CR}$. In acetylenic alcohols the corresponding vals. are 2.308 and 2.673. In conjugation a greater difference is observed between the Δ^a and Δ^b linkings. For H_a , H_β - H_a , and H_γ - H_a the respective vals., 2.329, 0.124, 0.149, and 2.543, 0.143, 0.186 are calc. for the series $\text{CR}:\text{CH}$ and $\text{CR}:\text{CR}$. H. W.

Structure of partly substituted sorbitols. F. MICHEEL and K. HASSE (Ber., 1935, 68, [B], 1582—1584).—Treatment of the benzylidenesorbitol (I) of von Vargha (this vol., 325) with CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ affords a compound $\text{C}_{51}\text{H}_{46}\text{O}_6$, m.p. 100—103°, $[\alpha]_D^{20} +20^\circ$ in CHCl_3 , which is very little affected by $\text{Pb}(\text{OAc})_4$ in AcOH or C_6H_6 and hence is $\alpha\zeta$ -ditriphenylmethyl- $\beta\delta$ -benzylidenesorbitol. The diacetate has m.p. 106—108°. (I) is therefore $\beta\delta$ -benzylidenesorbitol (cf. von Vargha, this vol., 325). H. W.

Alkyl peroxides. XI. Peroxides of formaldehyde. Hydroxymethyl hydrogen peroxide. A. RIECHE and R. MEISTER (Ber., 1935, 68, [B], 1465—1473).— Et_2O solutions of CH_2O obtained by extraction of aq. CH_2O are shown by their absorption spectrum to contain the solute as hydrate, thus explaining their inability to react with H_2O_2 . *Me H peroxide* is obtained as a relatively stable liquid by the action of H_2O_2 on the solution obtained by passing gaseous CH_2O into well-cooled Et_2O . (In this solution CH_2O rapidly polymerises to polyoxymethylenes, whereas the "extracted" solution is stable.) The product affords 94% of active O. The possibility that it is a mixture of $(\text{OH}\cdot\text{CH}_2)_2\text{O}_2$ and H_2O_2 is discounted by its unusual sensitiveness to heat and by its conversion by P_2O_5 into polymeric methylene peroxide, whereas $(\text{OH}\cdot\text{CH}_2)_2\text{O}_2$ gives tetrahydroxymethylene diperoxide. In contact with alkali $\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H}$ affords HCO_2H (97%) with H_2 and O_2 (2:1), reaction occurring to the extent of 73% and 27%, respectively, according to the schemes: $2\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H} \rightarrow 2\text{HCO}_2\text{H} + \text{H}_2 + 0.5\text{O}_2$ and $\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H} \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O}$. The liberated H is mol., since it does not decolorise methylene-blue. $\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H}$ and FeSO_4 immediately yield 50% of HCO_2H and 50% of CH_2O . The change is $\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}_2$, $\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H} + \text{CH}_2\text{O} \rightarrow (\text{OH}\cdot\text{CH}_2\cdot\text{O})_2 \rightarrow \text{HCO}_2\text{H} + \text{CH}_2\text{O} + \text{H}_2\text{O}$; the H_2O_2 formed is partly used in the oxidation of Fe^{2+} to

Fe^{3+} and partly catalytically decomposed under the influence of Fe^{2+} . $\text{OH}\cdot\text{CH}_2\cdot\text{O}_2\text{H}$ does not cause benzidine to become blue, but the addition of CH_2O gives an active solution when freshly made. MeO_2H behaves similarly, but reaction does not occur with Alk_2O_2 . Apparently a labile additive product of peroxide and aldehyde is a particularly active H acceptor. H. W.

Sodium tri-iodomethanesulphonate. A. BINZ and B. HUGHES (Ber., 1935, 68, [B], 1513—1520).—Treatment of $\text{CHI}_3\cdot\text{SO}_3\text{Na}$ with pptd. HgO in boiling H_2O affords *Na di-iodohydroxymercurimethanesulphonate* (I), $\text{OH}\cdot\text{Hg}\cdot\text{Cl}_2\cdot\text{SO}_3\text{Na}$, converted by I in warm $\text{MeOH}-\text{H}_2\text{O}$ into $\text{Cl}_3\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$ (II), also obtained without isolation of (I). Solutions of (II) in H_2O or EtOH free from air are neutral and stable for a protracted period in absence of light. In aq. solution under the influence of light (II) is hydrolysed to acid (mainly HI and H_2SO_4 or NaHSO_4). O_2 in presence or absence of light causes oxidation of (II) with liberation of I and acid, particularly rapidly and quantitatively in EtOH . Photohydrolysis occurs mainly according to $(\text{II}) + 3\text{H}_2\text{O} = 3\text{HI} + \text{NaHSO}_4 + \text{HCO}_2\text{H}$ and to a smaller extent according to $(\text{II}) + 3\text{H}_2\text{O} = 3\text{HI} + \text{NaHSO}_4 + \text{H}_2\text{CO}_2$. (II) is very slowly oxidised by the O of the blood. H. W.

Hypohalogenites of carboxylic acids. W. BOCKEMULLER and F. W. HOFFMANN (Annalen, 1935, 519, 165—192).—The equilibrium reaction $\text{R}\cdot\text{CO}_2\text{H} + \text{Hal}_2 \rightleftharpoons \text{R}\cdot\text{CO}_2\text{Hal} + \text{HHal}$ can most readily be caused to pass to completion by use of the requisite Ag salt in an indifferent medium such as CCl_4 in which $\text{R}\cdot\text{CO}_2\text{Ag}$ and AgHal are insol. In PhNO_2 reaction proceeds more slowly, whereas the more rapid change in CHCl_3 or CH_2Cl_2 is accompanied by halogenation of the solvent. The oxidising power of the acyl hypohalogenites is equal to that of the halogen used in the prep. and the halogen content is half as great; generally by reason of their instability the oxidising action falls somewhat short of that expected. Decomp. of acyl hypohalogenites occurs mainly according to $\text{R}\cdot\text{CO}_2\text{Hal} \rightarrow \text{R}\cdot\text{Hal} + \text{CO}_2$ and frequently affords a useful method of degrading acids. Reaction is not homogeneous and is certainly not unimol. Its rate increases rapidly with rise in temp. and exposure to light. The halogenating action of acyl hypobromites $\text{RH} + \text{R}'\cdot\text{CO}_2\text{Hal} \rightarrow \text{R}\cdot\text{Hal} + \text{R}'\cdot\text{CO}_2\text{H}$ is mainly evident with solvents containing replaceable H, but autohalogenation may occur. Treatment of acyl hypohalogenites with a moderate amount of H_2O causes hydrolysis $\text{R}\cdot\text{CO}_2\text{Hal} + \text{H}_2\text{O} \rightarrow \text{R}\cdot\text{CO}_2\text{H} + \text{HHal}$ leading ultimately to a solution of halogen and HHalO_3 , but if very little H_2O is used an unstable, unexplained olive-green colour is developed. Acyl hypohalogenites add to the C:C linking, $\text{R}\cdot\text{CO}_2\text{Hal} + >\text{C}:\text{C}< \rightarrow >\text{C}(\text{O}\cdot\text{COR})\cdot\text{CHal}<$. The rates of decomp. of AcOCl in AcOH in the dark at 23°, of AcOBr in AcOH and CCl_4 , of $\text{Pr}\cdot\text{CO}_2\text{Br}$ in CCl_4 , and of BzOBr in CCl_4 have been measured. Details are recorded of the degradation of AcOH , $\text{Pr}\cdot\text{CO}_2\text{H}$, stearic and adipic acids, and BzOH . $\beta\gamma$ -Dichloropropyl acetate, b.p. 83—84°, a by-product of the addition of AcO_2Cl to allyl chloride, 2-bromocyclohexenyl butyrate, b.p. 145°/14 mm., from $\text{Pr}\cdot\text{CO}_2\text{Br}$

and cyclohexene, and 2-bromocyclohexenyl benzoate, m.p. 66°, from BzOBr and cyclohexene, appear new.

H. W.

Mechanism of the thermal decomposition of diacyl peroxides. J. BÖSEKEN and P. H. HERMANS (Annalen, 1935, 519, 133—139).—The initial step in the thermal decomp. of diacyl peroxides in the presence of solvent is expressed $\text{COR}\cdot\text{O}_2\cdot\text{COR} + \text{R}'\text{H} \rightarrow \text{COR}\cdot\text{O}_2\cdot\text{COR}'$ (I) + RH and $\rightarrow \text{COR}\cdot\text{O}_2\cdot\text{COH}$ (II) + RR'. (II) immediately yields CO_2 and $\text{R}\cdot\text{CO}_2\text{H}$. (I) may then undergo further group exchange with R'H or may suffer thermal decomp., according to one or more of the schemes: (I) $\rightarrow \text{RR}' + 2\text{CO}_2$; (I) $\rightarrow \text{R}\cdot\text{CO}_2\text{R}' + \text{CO}_2$ (particularly in the case of mixed aliphatic-aromatic peroxides) or $\text{COPh}\cdot\text{O}_2\cdot\text{COR}' \rightarrow \text{C}_6\text{H}_4\text{R}'\cdot\text{CO}_2\text{H} + \text{CO}_2$ (particularly with Bz alkoyl peroxides).

H. W.

Unusual case of racemisation. E. BERGMANN and R. HARTROTT (J.C.S., 1935, 1218).—Me *l*- α -methyl-*n*-valerate (cf. A., 1926, 1226) with warm MgPhBr gives dl- α -diphenyl- β -methyl-*n*-amyl alcohol, b.p. 195—197°/14 mm. (also formed from the dl-ester and MgPhBr), the K derivative of which with MeI in xylene gives α -methoxy- α -diphenyl- β -methylpentane, b.p. 174—176°/13 mm., converted by Na in Et₂O during 3 months at room temp. into α -diphenyl- β -methylpentane, b.p. 163—164°/13 mm. The dl-alcohol is formed probably as a result of the spontaneous reversible dehydration of the optically active form.

J. L. D.

Addition of hydrogen bromide to non-terminal double linkings. *iso*Undecenoic acid. P. L. HARRIS and J. C. SMITH (J.C.S., 1935, 1108—1111).—Undecolic acid with HI in AcOH affords a mixture of I-compounds, which with Zn in boiling PrOH (cf. A., 1901, i, 115) gives *iso*undecenoic acid. Reaction with HBr in C₆H₆ or ligroin (cf. A., 1934, 631, 1200) in oxidising and anti-oxidising conditions always affords a product containing about 43% of the *l*-Br-acid (cf. A., 1925, i, 770; 1934, 753) which indicates the non-participation of catalysts in the reaction (cf. A., 1933, 805).

J. L. D.

Highly unsaturated acids of sardine oil. V. **Constitution of eicosatetraenoic acid.** VI. **Constitution of eicosapentaenoic acid.** Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 296—300, 301—304).—V. Ozonolysis of the amyl ester of eicosatetraenoic acid (I) (cf. this vol., 1105) gives $\text{Pr}^n\text{CO}_2\text{H}$, Pr^nCHO , $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, and amyl H succinate (II); the presence of $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CHO}$ (III), $(\cdot\text{CH}_2\cdot\text{CHO})_2$, and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{C}_5\text{H}_{11}$ (IV) is indicated. Minor amounts of CO_2 and MeCHO are ascribed to the presence of small quantities of another acid. (I) is given the structure $\Delta^{7,10}$ -eicosatetraenoic acid.

VI. The conc. acid fraction (cf. this vol., 1105), contains 68.44% of eicosapentaenoic acid (V). Ozonolysis of the amyl ester gives (II), (III), (IV), CO_2 , AcOH, and MeCHO; a higher aldehyde is probably present. (V) is provisionally given the structure $\Delta^{7,10,13}$ -eicosapentaenoic acid.

P. G. C.

Pyrolysis. III. Pyrolysis of carbonic and sulphurous esters. P. D. RITCHIE (J.C.S., 1935, 1054—1061; cf. this vol., 960).—36% of $\text{CO}(\text{OMe})_2$ is

“cracked” at 600°, whereas 66% of $\text{CO}(\text{OEt})_2$ is decomposed at 500°. COCl_2 with Me lactate in C₅H₅N at 100° affords α -carbomethoxyethyl carbonate, b.p. 172°/32 mm., which at 420—430° is mostly converted into $\text{CH}_3\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ and Me lactate. Similarly, $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Me}$ affords Me α -chloroisobutyrate, b.p. 133—135°/760 mm., and α -carbomethoxyisopropyl carbonate, m.p. 66—67°, converted entirely at 445—455° into Me methylacrylate and $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Me}$. α -Cyanoethyl, m.p. 44—44.5°, and α -cyanoisopropyl carbonate, m.p. 76—77°, which are prepared similarly, are converted at 460—480° into $\text{CH}_2\cdot\text{CH}\cdot\text{CN}$ and at 430—450° into α -methylacrylonitrile, respectively. ClCO_2Me with Me lactate in C₅H₅N at 100° gives Me α -carbomethoxyethyl carbonate, b.p. 91.5—92°/12 mm.; Me α -cyanoethyl carbonate, b.p. 80.5°/10 mm., is similarly prepared. These substances are pyrolysed to give $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CN}$, which indicates that one of the two possible decomp. mechanisms predominates. $\text{OEt}\cdot\text{CO}\cdot\text{OBu}^n$ is decomposed at 500—510° into EtOH and BuⁿOH; both decomp. mechanisms are operative, but EtOH is formed principally. $\text{OEt}\cdot\text{CO}\cdot\text{OPh}$ at 500—520° gives PhOH (85%), whereas $\text{CO}(\text{OPh})_2$ at 640—670° affords some CO_2 , C₆H₆, and PhOH, indicating that loss of CO_2 preceded pyrolysis of Ph₂O (cf. A., 1913, i, 259). SOCl_2 with Et lactate in C₅H₅N at 100° gives α -carbomethoxyethyl sulphite, b.p. 158—160°/4 mm., which is pyrolysed at 390—420° to give Et lactate and $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$.

J. L. D.

Esterification of hydroxy-acids and polyhydric alcohols. B. CIOCCA and A. SEMPRONI (Annali Chim. Appl., 1935, 25, 319—323).—In the prep. of Et lactate, tartrate, citrate, and ricinoleate, glycol distearate, and glycerol tristearate, increased yields are obtained by using sulphonic acids as catalysts. The reaction mixture is kept anhyd. by passing it continuously over CaC₂ in a Soxhlet apparatus. T. H. P.

Determination of pyruvic acid. C. FROMAGEOT and P. DESNUELLE (Biochem. Z., 1935, 279, 174—183).—A simple method is described for macro- and micro-determination of AcCO_2H (I) depending on the reduction in acid medium of Ce^{++++} by (I) with determination of the Ce^{++} by titration. The reaction is fairly sp. for α -keto-acids and is not given by HCO_2H , AcOH, EtCO_2H , CH_2O , MeCHO, EtCHO, MeOH, EtOH, PrOH, glycerol, sugars, glycine, and alanine.

P. W. C.

Lactone of γ -hydroxyvinylacrylic acid, protoanemonin. F. B. KIPPING (J.C.S., 1935, 1145—1147).—Protoanemonin from *Ranunculus hirsutus* or *R. bulbosus* with Pt-H₂ in EtOH gives *n*-valeric acid, γ -valerolactone, and tetrahydroanemonin, and with NaOH at 60° is converted into $\text{CHAc}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, and thence by reduction (Pt-H₂) into lævulic acid, thereby confirming the structure assigned to it by Asahina *et al.* (cf. A., 1922, i, 946). γ -Dibromo- Δ^2 -pentenoic acid when distilled affords, contrary to Muskat *et al.* (cf. A., 1930, 321, 451), a substance, m.p. 151—152° (re-solidifying at about 175—185°), mol. wt. 215, which is converted by HI into dilævulic acid, and is identical with anemonin.

J. L. D.

Trihydroxybutyric acids. J. W. E. GLATTFELD and R. E. HOEN (J. Amer. Chem. Soc., 1935,

57, 1405—1407).— $\text{CH}_2\text{:CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ (improved prep. from $\text{CH}_2\text{:CH}\cdot\text{CHO}$; Zn salt), AgClO_3 , and OsO_4 in absence of light give *dl*-erythrolactone (20%) (phenylhydrazide of the acid, m.p. 147.5°) and *dl*-threonic acid (7% yield; phenylhydrazide, m.p. 167.5°). R. S. C.

Rotatory powers of dimethylene tartrate, methylenetartaric acid and its dimethyl ester.—See this vol., 1192.

Constitution of glauconic acids. III. H. SUTTER and N. WIJSMAN (Annalen, 1935, 519, 97—110; cf. A., 1933, 1143).—It is proposed to retain the name glauconic acid (I) for the acid $\text{C}_{18}\text{H}_{20}\text{O}_7$, and to designate the acid II $\text{C}_{18}\text{H}_{20}\text{O}_6$ glaucanic acid. (I) has $[\alpha]_D^{20} -42.6^\circ$ in COMeEt . It is reduced by Zn dust in boiling AcOH to *dihydroglauconic acid*, m.p. 235° [*Me* ester, m.p. (indef.) 200°], which cannot be acetylated and is unchanged by boiling conc. HNO_3 . Thermal fission of (I) affords α -ethyl- Δ^2 -pentenal and *glauconin* (II) (*Ag* salt). Ozonisation of (II) at low temp. in EtOAc and fission of the ozonide by hydrogenation (Pd-C) gives AcCO_2H in such yield that two sources thereof in the mol. of (II) are indicated, $\text{H}_2\text{C}_6\text{O}_4$, HCO_2H , and $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in addition to an unidentified $\alpha\beta$ -dicarbonyl compound. When heated with HCl (II) affords CO_2 and a substance (III), $\text{C}_9\text{H}_{12}\text{O}_4$, m.p. 144°; the residue after treatment with AcCl yields two compounds $\text{C}_9\text{H}_{12}\text{O}_4$, m.p. 116° (IV) and m.p. 126° (V), respectively. All these compounds react with 2KOH and, after acidification of the solution, (III) and (V) yield an acid (VI), $\text{C}_{19}\text{H}_{14}\text{O}_5$, m.p. 140°, whereas (IV) affords an isomeric acid (VII), m.p. 127°. The behaviour of the compounds towards AcCl therefore resembles that of hydrochelidonic acid (VIII), and the relationship is further established by comparison of the absorption spectra of (VIII) and (VI) whereby also the structure $\text{CO}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})$ of (VIII) is established. Further, like (VIII), (VI) gives a *diphenylhydrazide*, m.p. 275—280° (decomp.), and a *mono-2:4-dinitrophenylhydrazide*, m.p. 230° (decomp.). Oxidation of (VI) or (VII) with HNO_3 gives AcCO_2H in excellent yield. Comparison of the absorption spectra of (VI) and (VIII) in conjunction with the known effect of the substituent Me on ketones suggests that (VI) has the structure $\text{CO}(\text{CH}_2\text{CHMeCO}_2\text{H})_2$. This is confirmed by the condensation of $\text{CO}(\text{CH}_2\text{CO}_2\text{Et})_2$ with $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ and treatment of the product with boiling 20% HCl , whereby (III), (IV), and (V) are obtained. (VI) and (VII) are therefore the *r*- and *meso*-forms, respectively. H. W.

Acetoacetic condensation. X. Condensation of ethyl α -carbethoxy- α' -ethyladipate. E. R. MEINCKE and S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1443—1445; cf. this vol., 83).—*Et_2 \alpha*-carbethoxy- α' -ethyladipate (I) (which has only 1 H α to CO_2Et) and NaOEt at 100°/200 mm. give EtOH (1.25 mols.) and *Et_2* 2-ethylcyclopentanone-2:5-dicarboxylate (22%), thus confirming the author's views on the acetoacetic condensation. $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{CEt}(\text{CO}_2\text{Et})_2$ and boiling 36% aq. NaOH give 88% of α -ethylbutyrolactone, b.p. 213—216°/740 mm., which with EtOH-HCl affords *Et \gamma*-hydroxy- α -ethylbutyrate, b.p. 78—80°/3 mm., converted by PBr_3

into the γ -*Br*-ester (78% yield), b.p. 90—93°/8 mm.; this with $\text{CH}_2(\text{CO}_2\text{Et})_2$ yields (I) (47%), b.p. 170—172°/8 mm. R. S. C.

Tautomerism of the system, thiocoumarindiol-thiochromonediol and of ascorbic acid.—See this vol., 1248.

Catalytic action of monoses on the formaldehyde condensation. II. A. KUSIN (Ber., 1935, 68, [B], 1494—1499; cf. this vol., 733).—The accelerating action of saccharates on the condensation of CH_2O to sugars is attributed to enol formation with 2 OH at the double linking. Since the main portion of the sugar is present in the cyclic form and only a part is enolised, $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$, which is incapable of cyclic formation, should be a more powerful catalyst than fructose or glucose (I); this is shown to be the case. In harmony with this view 1:2-isopropylideneglucosufuranose and 1:2-isopropylidene-3:5:6-trimethylglucose have no accelerating action, whereas 3:5:6-trimethylglucose is somewhat more active than (I). Benzoin has about the same activity as (I), whereas benzil is inert. Acetoin is somewhat less effective than (I). $\text{OEt}\cdot\text{CH}_2\cdot\text{CHO}$ is as active as (I), whereas $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and COMe_2 are inactive. Apparently two hydroxyl O attached to the double linking are essential to activity. H. W.

Condensation of halogen-substituted aldehydes with nitromethane. F. D. CHATTAWAY and P. WITHERINGTON (J.C.S., 1935, 1178—1179; cf. A., 1895, i, 637).—Equimol. amounts of $\text{CCl}_3\cdot\text{CHO}$, H_2O and NO_2Me in aq. Na_2SO_3 at 60° give $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane, b.p. 119°/3 mm. (which does not react further with $\text{CCl}_3\cdot\text{CHO}$) (*Ac* derivative, m.p. 61—62°). The Br_3 -analogue has m.p. 78° (*Ac* derivative, m.p. 70°). Butylchloral hydrate with NO_2Me similarly affords $\gamma\gamma\delta$ -trichloro- α -nitro- β -hydroxypentane, b.p. 156°/4 mm. (*Ac* derivative, b.p. 168°/4 mm.). J. L. D.

Free radicals and atoms in primary photochemical processes. II. Photodissociation of aliphatic aldehydes and ketones.—See this vol., 1211.

Electrolytic reduction of ketones in glacial acetic acid. II. Reduction of aliphatic ketones to hydrocarbons. S. SWANN, jun., L. F. DEDITUS, and W. A. PYHRR (Trans. Electrochem. Soc., 1935, 68, 89—95; cf. A., 1933, 1127).—The yields of $n\text{-C}_5\text{H}_{12}$ obtained by the electrolytic reduction of COMePr^a in AcOH at cathodes of Cd, Sn, Pb, Hg, Al, Zn, Ni, Cu, and Fe correspond with the H_2 overvoltages of the cathodes. The best yield is obtained with a Cd cathode in aq. solution. E. S. H.

Identification of arabinose in presence of other pentoses. E. VOTOČEK and L. SGARZI (Coll. Czech. Chem. Comm., 1935, 7, 355—358).—Arabinose (in quantity > 0.1 g.) is identified by addition of HCN , hydrolysis to a mixture of glucono- and mannono-lactone, reduction with Na-Hg , and conversion into glucosphenylosazone, which separates in the hot, whereas from xylose a phenylosazone is obtained sol. in the hot. Hexoses (particularly galactose) may interfere unless they are first removed by fermentation. P. G. C.

Conversion of derivatives of glucose into derivatives of altrose by simple optical inversions. G. J. ROBERTSON and C. F. GRIFFITH (J.C.S., 1935, 1193—1201).—2:3-Di-*p*-toluenesulphonyl-4:6-benzylidene- α -methylglucoside (I) with boiling MeOH-NaOMe affords 4:6-benzylidene-2:3-anhydro- α -methylaltroside (II), m.p. 199—200°, $[\alpha]_D^{25} +140.4^\circ$ in CHCl₃ [this, or (V), on prolonged treatment with 5% KOH under pressure gives 4:6-benzylidene- α -methylaltroside, m.p. 169—170°, which is methylated to give (IV), and is hydrolysed (COMe₂-HCl) to α -methylaltroside, a glass], and 4:6-benzylidene-2-methyl- α -methylaltroside (III), m.p. 98—99°, $[\alpha]_D^{25} +102.7^\circ$ in CHCl₃ [3-*p*-toluenesulphonyl, m.p. 166—167°, and 3-Bz derivative, m.p. 135—136°], in succession, the latter being methylated (Purdie's reagents) to 4:6-benzylidene-2:3-dimethyl- α -methylaltroside (IV), m.p. 83—85°, hydrolysed (boiling COMe₂-H₂O-HCl) to 2-methyl- α -methylaltroside, m.p. 81—83°, and its structure determined by the non-identity of its derivatives with the corresponding compounds from glucose, and by converting it into altrosazone. When (I) is impure, 4:6-benzylidene-2:3-anhydro- α -methylmannoside (V), m.p. 146—147° [converted by NaOH-NaOMe at 100° under pressure, after a Walden inversion at C3, into 4:6-benzylidene-3-methyl- α -methylaltroside (VI), m.p. 131—133° (cf. ease of hydrolysis of the isomeric altroside), which is methylated (Purdie's reagents) to (IV) and hydrolysed to 3-methyl- α -methylaltroside, a glass, which affords 3-methylaltrosazone, m.p. 168—169°], is also formed. 4:6-Benzylidene- α -methylglucoside with BzCl in C₅H₅N gives a mixture of Bz₁ and Bz₂ compounds, which with *p*-C₆H₄Me-SO₂Cl followed by hydrolysis (MeOH-NaOMe) affords 2-benzoyl-3-*p*-toluenesulphonyl-4:6-benzylidene- α -methylglucoside, m.p. 184—186°, further hydrolysed to (II). Similarly with *p*-C₆H₄Me-SO₂Cl in C₅H₅N, it affords 2-*p*-toluenesulphonyl-4:6-benzylidene- α -methylglucoside, m.p. 153—154° [3-Bz derivative (VII), m.p. 212—213°, hydrolysed (MeOH-NaOMe) to (V) because optical inversion occurs at the C bearing the *p*-C₆H₄Me-SO₂ (cf. J.C.S., 1923, 123, 44; A., 1925, i, 507)], and some 2:3-di-*p*-toluenesulphonate. (IV) with boiling COMe₂-aq. HCl affords 2:3-dimethyl- α -methylaltroside, methylated to 2:3:4:6-tetramethyl- α -methylaltroside, a syrup, which is hydrolysed (HCl) to 2:3:4:6-tetramethylaltrose, a syrup (cf. A., 1933, 1037), oxidised (cf. A., 1926, 385) to *l*-dimethoxysuccinic acid and *d*-trimethoxyaraboglutaric acid, which proves that (III), (IV), and (VI) have the altrose configuration. Hydrolysis (2*N*-HCl) of the methyl- α -methylaltrosides gives solutions containing anhydro-compounds (cf. A., 1923, i, 445; 1926, 601) in equilibrium with reducing sugar.

J. L. D.

New reaction of the dichloroacetyl group in derivatives of glucose. D. J. BELL (J.C.S., 1935, 1180—1182).—The following are prepared by interaction of the appropriate glucoside with CHCl₂·COCl in dry C₅H₅N-C₆H₆ below -10°: 2:3-bisdichloroacetyl-4:6-benzylidene-, m.p. 120—122°, 4:6-bisdichloroacetyl-2:3-dibenzoyl- (I), a glass, 6-dichloroacetyl-2:3:4-tribenzoyl- (II), a glass, and 6-dichloroacetyl-2:3-dibenzoyl-4-*p*-toluenesulphonyl- α -methylglucoside

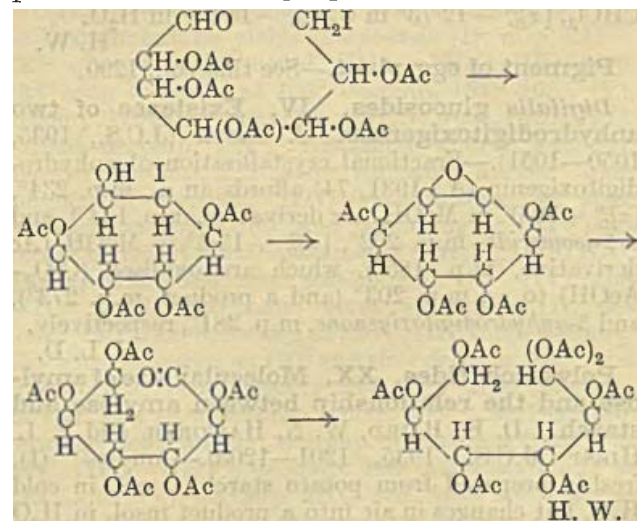
(III), m.p. 140—142°. 2:3-Bisdichloroacetyl-4:6-benzylidene-, m.p. 154—155°, 2:3:6-triacetyl-4-dichloroacetyl-, m.p. 78—79.5°, and 6-dichloroacetyl-2:3:4-tri-*p*-toluenesulphonyl- β -methylglucoside (IV), m.p. 169—171°, which is obtained from 2:3:4-tri-*p*-toluenesulphonyl- β -methylglucoside, m.p. 188—189° [obtained by reduction (Zn-Fe-AcOH) of its 6-nitrate (cf. A., 1932, 254)]. The above substances when treated with AgOAc in COMe₂-H₂O revert to the original compounds except (I) and (II), which suffer some racemisation; (IV) is converted into a Cl-free compound, m.p. 164°, and (III) remains unchanged.

J. L. D.

Osazones. I. Anhydro-osazones. O. DIELS and R. MEYER (Annalen, 1935, 519, 157—164).—The conversion of *d*-glucosazone into 3:6-anhydro-*d*-glucosazone (I), m.p. 180°, $[\alpha]_D^{20} -181^\circ$ in MeOH, is effected in varying yield by HCO₂H at room temp., by NH₂Me, HCl, or MgSO₄ in boiling Pr^oOH, but, most certainly, by boiling with MeOH or EtOH containing a little 20% H₂SO₄. Anhydro-*d*-galactosazone, m.p. 220° (slight decomp.), $[\alpha]_D^{20} +70.5^\circ$ in MeOH, anhydro-*d*-lactosazone, m.p. 230° (slight decomp.), $[\alpha]_D^{20} -138^\circ$ in MeOH, and anhydromaltosazone, m.p. 209—210°, $[\alpha]_D^{20} -10^\circ$ in MeOH, are similarly obtained. Treatment of quercitol with Br and of the product with NHPH·NH₂ affords an osazone, C₁₈H₂₀O₃N₄, m.p. 220° (decomp.). The well-defined m.p. of the anhydro-osazones render them very suitable for the identification of sugars.

H. W.

Transformation of hexoses into inositol. F. MICHEEL, H. RUKKOPF, and F. SUCKFULL (Ber., 1935, 68, [B], 1523—1527).—The main product of the action of ZnCl₂ in Ac₂O at 100° on 6-iodo-*al*-*d*-galactose 2:3:4:5-tetra-acetate (I) is *dl*-galactose hepta-acetate (II), m.p. 132°, $[\alpha]_D^{20} \pm 0^\circ$, hydrolysed (Zemplen) to *dl*-galactose, m.p. 141—142°. *al*-*d*-Galactose penta-acetate is transformed similarly into *al*-*d*-galactose hepta-acetate, m.p. 103°, $[\alpha]_D^{20} +9.8^\circ$ in EtOH. The conversion of (I) into (II) cannot be attributed to simple racemisation and the intermediate production of a 6-C ring is postulated, thus:



H. W.

Constitution of isosucrose. (SIR) J. C. IRVINE and D. ROUTLEDGE (J. Amer. Chem. Soc., 1935, 57, 1411—1414).—*iso*Sucrose (modified prep.; no sucrose formed) with Ag_2O -MeI or Me_2SO_4 or both successively gives a mixture of Me_7 ethers, which with K-MeI in liquid NH_3 gives the Me_8 ether, b.p. 180—185°/3 mm., hydrolysed by hot 0.01N-HCl to tetramethyl-glucose and γ -fructose, the separation of which is modified.

R. S. C.

Cellulose. LIV. Acetolysis of cellulose. VI. Cellotriose and its derivatives. K. HESS and K. DZIENGEL (Ber., 1935, 68, [B], 1594—1605).—Short acetolysis of linters under relatively mild conditions is followed by pptn. of a product practically free from glucose and poor in cellobiose which is hydrolysed (Zemplén) and separated into a H_2O -insol. portion, mainly hydrocellulose (I) which serves for the prep. of limit dextrins, and a H_2O -sol. portion which contains almost all the cellotriose (II), which is isolated by fractional pptn. with EtOH. The latter process falls into two stages, the second of which is continued until the properties of the material remaining in solution agree in all respects with those of the main fraction. Thus obtained, (II) has m.p. about 203° after softening at about 200°, decomp. about 214°, $[\alpha]_D^{20} + 32.0^\circ$ to $+23.2^\circ$ in H_2O . The X-ray diagram is sp. and quite distinct from that of (I). Treatment of (II) with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at $> 40^\circ$ yields α -cellotriose hendeca-acetate, m.p. 219—220° (corr.), $[\alpha]_D^{20} + 22.4^\circ$ in CHCl_3 , $[\alpha]_D^{25} - 6.5^\circ$ in C_6H_6 , $[\alpha]_D^{25} + 39.9^\circ$ in COMe_2 , whilst the corresponding β -compound, m.p. 219—220° (corr.), $[\alpha]_D^{20} - 6.5^\circ$ in AcOH , -13.7° in MeOH , -18.2° in CHCl_3 , -43.2° in C_6H_6 , -6.6° in COMe_2 , -17.5° in $\text{C}_2\text{H}_2\text{Cl}_4$, -30.1° in $\text{C}_5\text{H}_5\text{N}$, is isolated with difficulty from the mother-liquors and is best obtained by the addition of small successive quantities of (II) to a mixture of Ac_2O , AcOH , and KOAc at 120° . Cellobiose hendeca-acetate (mainly β -form) is transformed by Me_2SO_4 and 30% NaOH in COMe_2 and then in C_6H_6 into β -hendecamethylcellotriose, m.p. 116.5—117°, $[\alpha]_D^{20} - 15.42^\circ$ in MeOH , -11.06° in CHCl_3 , -14.62° in H_2O , $[\alpha]_D^{20} - 13.97^\circ$ in C_6H_6 . Cellobiose octa-acetate is transformed similarly into β -octamethylcellobiose, m.p. 86—87°, $[\alpha]_D^{20} - 16.16^\circ$ in MeOH , -14.88° in CHCl_3 , $[\alpha]_D^{20} - 12.73^\circ$ in C_6H_6 , -15.28° in H_2O .

H. W.

Pigment of egg-plant.—See this vol., 1290.

Digitalis glucosides. IV. Existence of two anhydrodigitoxigenins. S. SMITH (J.C.S., 1935, 1050—1051).—Fractional crystallisation of anhydro-digitoxigenin (A., 1931, 74) affords an α -, m.p. 234°, $[\alpha]_D^{20} + 39.0^\circ$ in MeOH (*Ac* derivative, m.p. 144°), and a β -isomeride, m.p. 202°, $[\alpha]_D^{20} - 13.3^\circ$ in MeOH (*Ac* derivative, m.p. 185°), which are oxidised (CrO_3 - AcOH) to α -, m.p. 203° (and a product, m.p. 273°), and β -anhydrodigitoxigenone, m.p. 281°, respectively.

J. L. D.

Polysaccharides. XX. Molecular size of amylose and the relationship between amylose and starch. D. K. BAIRD, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1935, 1201—1205).—Amylose (I), freshly prepared from potato starch, is sol. in cold H_2O , but changes in air into a product insol. in H_2O

and representing a higher state of aggregation of the mol. Repeated treatment of (I) with Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 50° affords a product (mol. wt. 21,000) [easily de-acetylated, but methylated only with difficulty to yield a product similar to (II) (below)] which, determined viscosimetrically, has a chain of about 73 glucose units. Further acetylation with Cl_2 and SO_2 as catalysts gives a substance (mol. wt. 35,000) with a chain-length of about 120 glucose units. Products similar to (I) are obtained by hydrolysis; the P content is unchanged throughout. Acetylation of (I) using Cl_2 and SO_2 as catalysts gives an acetate (mol. wt. 12,000) which with Me_2SO_4 in 30% KOH - COMe_2 at 55° affords a methylated amylose (II), $[\alpha]_D^{20} + 215^\circ$ in CHCl_3 , mol. wt. 4000—5000 (25 glucose units; confirmed by gravimetric determinations), which is the figure obtained for all other known methylated starches, and indicates that disaggregation of the mols. to yield a form which approximates to the chemical mol. of starch has occurred.

J. L. D.

Polysaccharides. XXI. Constitution and chain-length of some starch dextrins. W. N. HAWORTH, E. L. HIRST, and (MISS) M. M. T. PLANT (J.C.S., 1935, 1214—1217).—Potato starch with glycerol at 190 — 200° gives a dextrin, converted by Ac_2O - $\text{C}_5\text{H}_5\text{N}$ at 70° into an acetate, which gives no colour with I, and is separated into fractions (I) and (II) by pptn. from CHCl_3 . Repeated treatment of (I) with Me_2SO_4 -30% NaOH in hot COMe_2 affords a methylated dextrin, hydrolysed by conc. HCl at -15° to a mixture of sugars from which tri- and tetra-methylmethylglucoside (9.4%, which corresponds with a mean chain-length of 12 α -glucopyranose units; cf. A., 1932, 1022) are isolated after treatment with MeOH -dry HCl . Similarly determined, (II) has a mean chain-length of 8 units. The hexose residues of (I) and (II) are probably united exclusively by α -glucosidic linkings, as $[\alpha]$ is in agreement in each case with the calc. val. (cf. A., 1933, 211), and the chain-lengths derived by other methods agree with the vals. obtained above. The mols. of smaller mol. wt. show no tendency to undergo aggregation.

J. L. D.

Highly polymerised compounds. CXV. Transformation of cellulose into polymeric-analogous cellulose triacetates. H. STAUDINGER and H. EILERS (Ber., 1935, 68, [B], 1611—1618).—Further examples are cited of the conversion of cellulose into polymeric-analogous compounds, showing that changes of these macro-mols. can be effected without altering the C skeleton, as is also the case with compounds of lower mol. wt. Contrary to Hess *et al.* (B., 1928, 705), the triacetates obtained from Cu- (I) or viscose-silk (II) by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ are sol. in CHCl_3 , $\text{C}_2\text{H}_2\text{Cl}_4$, HCO_2H , and warm *m*-cresol; the mean degree of polymerisation is 150—300 and they have the same solubility relationships as the triacetates of similar mean mol. wt. obtained from cotton by cautious treatment with Ac_2O and H_2SO_4 or ZnCl_2 . The triacetates from linters are more complex and insol. in the media named above. (I), (II), and a degraded technical cellulose are converted by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ into their triacetates, the mol. wt. of which does not depend on the duration of the action,

thus showing that a change in the chain does not occur. The degree of polymerisation of the celluloses determined by measurement of the viscosity of their solutions in *m*-cresol is identical with that of the crude or reppd. triacetates. H. W.

Kinetics of benzooylation of cellulose. A. L. BERNOULLI, M. SCHENK, and F. ROHNER (Helv. Chim. Acta, 1935, 18, 1008; cf. A., 1934, 1314).—The authors' process (*loc. cit.*) is described in the patent lit. F. R. G.

Direct transformation of the skeleton substance of straw into an acetylated carbohydrate. R. S. HILPERT and O. PETERS (Ber., 1935, 68, [B], 1575—1578).—The high C content of straw is reconcilable with the absence of lignin if the presence of cellulose anhydrides is assumed. Attempts to verify the hypothesis by the direct acetylation of straw were unsuccessful, since complete reaction could not be secured, probably by reason of the slowness of the primary swelling. Preliminary treatment of the straw with alkali at low temp. causes reproducible dissolution of 20—30% of the material with production of a partly methylated cellulose anhydride. Acetylation of the product unexpectedly leads to a cellulose triacetate, thus establishing a primary fission of the anhydride. Pentosans do not disappear during acetylation, so that it must be assumed either that the present conception of OH in cellulose cannot be extended to them or that their determination is inaccurate. OMe present in the straw treated with alkali is present also in the acetate. The proportion of apparent lignin in the acetate is the same as in the original material, confirming the hypothesis that the materials separated by acids are solely reaction products of carbohydrates. The ready oxidisability of straw is evidence against the view that the main substance is carbohydrate. This property is lost in the acetate, which does not readily react with Cl_2 or OCl and is indifferent towards alkaline KMnO_4 . The properties of straw must be ascribed to the carbohydrates themselves and their mutual union.

H. W.

Quantitative isotopic exchange reactions in the carbohydrate group.—See this vol., 1212.

Preparation of diaminobutanes. IV. Gold diamine compounds. E. STRACK and H. SCHWANE-BERG (Ber., 1935, 68, [B], 1638—1651).—The following types of Au salts are obtained from diaminobutanes and, apparently, from all bases containing at least two NH_2 groups. Normal Au salts (I), $\text{C}_4\text{H}_{12}\text{N}_2 \cdot 2\text{HAuCl}_4$, obtained by use of 10—15% HCl with an excess of HAuCl_4 ; their solubility in H_2O appears to increase with increasing proximity of the NH_2 and their ease of transition into non-typical salts also increases with their solubility. Monoaurichlorides (II), $\text{C}_4\text{H}_{12}\text{N}_2 \cdot \text{HCl} \cdot \text{HAuCl}_4$, which are derived only from diamines which give freely sol. salts (I); they are obtained from conc. solution in 25% HCl by use of the theoretical amount of AuCl_3 ; they are freely sol. in H_2O and EtOH and pass readily into other non-typical products; they can be crystallised unchanged from conc. HCl. Derivatives (III), $\text{C}_4\text{H}_{12}\text{N}_2 \cdot 2\text{AuCl}_3$, obtained by warming (I) with much H_2O or by diminishing the acidity of the dil. solution until it is

just acid to Congo-red; all derivatives (III) are less freely sol. in H_2O than compounds (I) and are formed with increasing ease as the difference in solubility increases. Compounds (IV), $\text{C}_4\text{H}_{11}\text{N}_2\text{Au}_2\text{Cl}_5$, obtained pure when compounds (III) are warmed with much H_2O or, more completely, but with enclosed AcOH, when solutions of salts (I) are treated with NaOAc; they are very sparingly sol. in H_2O , freely in COMe_2 , variously in EtOH; they can be crystallised unchanged from $\text{COMe}_2 \cdot \text{Et}_2\text{O}$; they appear to be formed with loss of H from NH_2 . Derivatives (V), $\text{C}_4\text{H}_{10}\text{N}_2\text{Au}_2\text{Cl}_4$, apparently derived by loss of 2 H from NH_2 ; (IV) and (V) pass completely into (I) when heated with conc. HCl. Compounds (VI) in which Au salts have lost more HCl than in (V), obtained from (I) by treatment with NaHCO_3 and insol. in all org. media. Compounds (IV) unite with Et_2O , COMe_2 , and, particularly, with dioxan, so that a method is afforded of detecting small amounts of Au salt and dioxan which is very firmly retained. $\alpha\beta$ -Diaminobutane gives salts (I), (II), decomp. 204° after softening at 197° , (III), (IV) also $+1\text{C}_4\text{H}_8\text{O}_2$, decomp. 174° , and (VI). $\alpha\beta$ -Diamino- β -methylpropane affords compounds (I), (II), m.p. 227° after softening at 217° , (III), (IV) $+2\text{H}_2\text{O}$, decomp. 190 — 191° after softening at 158° ; $+ \text{C}_4\text{H}_8\text{O}_2$, decomp. 173 — 175° after softening at 170° . *r*- $\beta\gamma$ -Diaminobutane affords salts (I), (II) $+ \text{H}_2\text{O}$, (III), decomp. 235 — 237° , (IV), decomp. 217° after darkening at 200° and softening at 210° , also $+1\text{C}_4\text{H}_8\text{O}_2$, decomp. 215 — 217° after softening and darkening at about 190° . The optically active $\beta\gamma$ -diaminobutanes give salts (I), (II) $+1\text{H}_2\text{O}$, decomp. 222 — 223° after softening at 217° , (III) decomp. 235 — 237° , (IV) $+1\text{H}_2\text{O}$, decomp. about 220° after darkening and softening at 210 — 215° , $+1\text{C}_4\text{H}_8\text{O}_2$, decomp. 215 — 217° after softening at 190° . *meso*- $\beta\gamma$ -Diaminobutane yields compounds (I), (III), decomp. 225 — 227° after softening at 217° , (IV) $+1\text{H}_2\text{O}$, decomp. 197° ; $+1.5\text{C}_4\text{H}_8\text{O}_2$, slow decomp. above 130° . $\alpha\gamma$ -Diaminobutane affords salts (I), (III) $+1\text{H}_2\text{O}$, decomp. 180 — 181° after softening at 176° , (IV), decomp. 158 — 159° after softening at 150° , $+1\text{C}_4\text{H}_8\text{O}_2$, decomp. 148 — 150° after softening at 145° . $\alpha\gamma$ -Diamino- β -methylpropane gives substances (I), (III), decomp. 188 — 189° , and (IV), decomp. 196° after softening at 190° and, $+ \text{C}_4\text{H}_8\text{O}_2$, decomp. about 185° after softening at 175° . $\alpha\delta$ -Diaminobutane yields compounds (I), m.p. 231 — 232° when rapidly heated, (III) $+1\text{H}_2\text{O}$, (IV), m.p. 158° after softening at 155° , decomp. 164 — 165° , (V), decomp. 170 — 172° , and (VI), $\text{C}_4\text{H}_8\text{N}_2 \cdot \text{AuCl} \cdot \text{AuOH} \cdot \text{H}_2\text{O}$, violent decomp. 139° . Histamine affords salts (I), marked decomp. 222° after softening at 205° and, incipient decomp. 212° , (III), decomp. 200 — 202° after softening at about 190° and liquefying at 195° , converted by EtOH into the compound $\text{C}_5\text{H}_9\text{N}_3 \cdot \text{AuCl}_3 \cdot \text{H}_2\text{O}$, decomp. 175 — 180° after softening at 150° , (IV), and (VI). $\alpha\beta$ -Diaminoethane gives substances (I), decomp. 240° after softening at 230° , (III), rapid decomp. 235° after softening at 190° and slow decomp. 220° , and (IV) $+1\text{H}_2\text{O}$, rapid decomp. 217 — 220° after softening at 185° and slow decomp. about 205° . $\alpha\beta$ -Diaminopropane yields salts (I), decomp. 234° after softening at 228° , (III) $+1\text{H}_2\text{O}$, decomp. 220° after softening at 215° , and (IV), decomp. 220 — 225° after softening at about 195° . $\alpha\gamma$ -Diaminopropane gives salts (I)

+H₂O, decomp. 235° after softening at 230°, (III), decomp. about 205° after softening at 180°, and (IV), decomp. 170° after softening at 165°. α , δ -Diamino- β -methylbutane gives compounds (I) and (V), decomp. 165° after softening at 145°. H. W.

$\beta\beta'\beta''$ -Trichlorotriethylamine. H. McCOMBIE and D. PURDIE (J.C.S., 1935, 1217—1218).—The prep. from $\beta\beta'\beta''$ -trihydroxytriethylamine is described, and also that of some of its derivatives. J. L. D.

Derivatives of carbamylcholine. A. ERCOLI (Annali Chim. Appl., 1935, 25, 263—273).—The following compounds and their pharmacological actions are described: β -chloroethyl acetylcarbamate, m.p. 73—74°; acetylcarbamylcholine chloride; β -chloroethyl methylenedicarbamate, m.p. 148°; methylenedicarbamylcholine dichloride (I) (PtCl₄ compound + 2H₂O, m.p. 230°); β -chloroethyl anhydroformaldehydecarbamate; anhydroformaldehydecarbamylcholine chloride; β -chloroethyl phenylmethylcarbamate, b.p. 165°/12 mm.; phenylmethylcarbamylcholine chloride [AuCl₃ compound, m.p. 190°; PtCl₄ compound, m.p. 222° (decomp.)]; di- β -chloroethyl iminodicarboxylate, m.p. 202°; iminodicarboxylcholine dichloride [AuCl₃ compound, m.p. 240° (decomp.)]; PtCl₄ compound, decomp. 248°; dimethylcarbamylcholine chloride methochloride [AuCl₃ compound, m.p. 273° (decomp.)]. For (I), the ratio active dose:dose tolerated is > for carbamylcholine. T. H. P.

Configuration of norleucine and glucosamine. P. KARRER and V. ITSCHNER (Helv. Chim. Acta, 1935, 18, 782—790).—CHMe:CH·CH₂Br with Et phthalimidomalonate and NaOEt in EtOH yields Et phthalimido- Δ^{β} -butenylmalonate, m.p. 48°, which with conc. NaOH in EtOH-H₂O gives the cryst. Na₃ salt of o-carboxybenzamido- Δ^{β} -butenylmalonic acid; this with warm H₂O gives the hydrochloride, cryst., of dl- Δ^{β} -butenylglycine (I), m.p. 260—270° (decomp.) (Cu salt, cryst.), which with BzCl yields dl- Δ^{β} -butenylhippuric acid, m.p. 157°, oxidised (KMnO₄) to dl-benzoylaspartic acid, m.p. 174° [Fischer (A., 1899, i, 888) gives m.p. 162°], and with yeast gives d- Δ^{β} -butenylglycine, decomp. 260—270°, $[\alpha]_D^{25} +52.5^\circ$ in H₂O, reduced (H₂, Pt) to d-norleucine, decomp. 270—280°, $[\alpha]_D^{25} -23.1^\circ$ in aq. HCl, and benzoylated to d- Δ^{β} -butenylhippuric acid, m.p. 122°, $[\alpha]_D^{25} -66.0^\circ$ in C₆H₆, which by oxidation (KMnO₄) gives d-benzoylaspartic acid, $[\alpha]_D^{25} -36.4^\circ$ in aq. NaOH. F. R. G.

Action of erepsin and trypsin on polypeptides containing ψ -leucine. E. ABDERHALDEN and W. FAUST (Fermentforsch., 1935, 14, 407—412; cf. A., 1934, 516; this vol., 71).—The N-carbobenzyl-oxy-derivative of l- ψ -leucine (I) with PCl₅ yields the substance $\begin{matrix} \text{CO}\cdot\text{NH} \\ | \\ \text{O}-\text{CO} \end{matrix} > \text{CHBu}^\nu$, m.p. 132°. (I) with PCl₅ and AcCl yields the hydrochloride, m.p. 180° (decomp.), of l- ψ -leucyl chloride, which with the Et ester of l-tyrosine in C₅H₅N gives rise to l- ψ -leucyl-l-tyrosine (II), m.p. 245—250° (decomp.) (p-toluenesulphonate, m.p. about 180°, $[\alpha]_D^{25} -7.81^\circ$ in EtOH). Similarly from the hydrochloride, m.p. 185° (decomp.), of d- ψ -leucyl chloride d- ψ -leucyl-l-tyrosine (III), m.p. about 245° (p-toluenesulphonate, $[\alpha]_D^{25} +27.3^\circ$ in EtOH), is

obtained. (II) [but not (III)] is hydrolysed by erepsin: (II) and (III) are not hydrolysed by trypsin.

W. McC.

Walden inversion. II. E. OTT [with R. DEMME and V. BARTH]. III. E. OTT and K. KRAMER (Ber., 1935, 68, [B], 1651—1654, 1655—1658; cf. A., 1931, 1049).—II. Interaction of l(+)-asparagine with HNO₂ in H₂O proceeds slowly, is accompanied by little racemisation, and yields l(−)-malic acid; Walden inversion does not occur. In AcOH reaction is more rapid and is accompanied by much racemisation, whilst similar treatment of Et aspartate in EtOH is accompanied by Walden inversion. In explanation, it is pointed out that r-malic acid has a higher free energy content than either of its optical antipodes and, consequently, if reaction is sufficiently slow NH₂ is replaced by OH without inversion. With increasing rate of change the formation of the energy-richer r-compound becomes more pronounced, and ultimately becomes the general change. Inversion occurring when the reaction is still more rapid is explained in the same manner as the production of C₂H₆ compounds from C₂H₂ compounds by very rapid hydrogenation, whereby in the limiting case C₂H₄ compounds were not formed as intermediates.

III. Replacement of Cl by H in optically active CClPhMe·CO₂H by rapid catalytic treatment with H₂ affords CHPhMe·CO₂H with reversed sign of rotation, whereas the slower replacement by Zn dust and AcOH takes place without change of sign. In these changes racemisation is the main process. Catalytic hydrogenation with Pd-C occurs more rapidly in AcOH than in Et₂O. r-OH·CPhMe·CO₂H reacts much more rapidly than either of the optically active forms with SOCl₂, whereas even in dil. solution replacement of Cl by H takes place much more slowly with r-CClMePh·CO₂H than with the active forms.

H. W.

Effect of X-rays on glutathione.—See this vol., 1212.

Ethylenic nitriles. R. VANDEWYER (Bull. Soc. chim. Belg., 1935, 44, 376—386).—Forms (I), b.p. 127.5—127.7°/766.5 mm. and 144.5—144.7°/756 mm., respectively, of Δ^2 -pentenenitrile, separable by distillation, are obtained from Me·[CH₂]₂·CHBr·CN and quinoline (II) at 110°. Alternatively, Me·[CH₂]₂·CHCl·CN and C₅H₅N or Me·[CH₂]₂·CH(OH)·CN and P₂O₅ give a mixture of (I), which with 66% H₂SO₄ at 0° gives forms, m.p. 151.3—152° and 68.4—69°, respectively, of Δ^2 -pentenoamide, which with P₂O₅ give pure (I). Forms, b.p. 165.8—166°/759.2 mm. and 149.6—149.8°/745 mm., respectively, of Δ^2 -hexenenitrile (III) are obtained from Me·[CH₂]₃·CHBr·CN (modified prep.), b.p. 82—82.5°/10 mm., and (II) at 130° or from the amides, m.p. 124.6—125.3° and 67.4—68°, respectively, which are best obtained from (III) and H₂SO₄ (2—3 days at room temp. and then 100 hr. at 40—50°). C₆H₁₃·CHBr·CN gives similarly two forms of Δ^2 -octenenitrile, of which that of b.p. 78—78.2°/12.5 mm. gives an amide, m.p. 66.1—66.5°, whence it is regenerated by H₂SO₄. Physical data are given. R. S. C.

Racemisation in the preparation of the Grignard reagent. C. W. PORTER (J. Amer. Chem. Soc.,

1935, 57, 1436).— β -Bromo-*n*-octane, $[\alpha]_D +22.7^\circ$ and -20.7° (prep. without racemisation from the alcohol by PBr_3), and optically active CHMePhBr were racemised during prep. of the Grignard reagent by Mg and a trace of I in Et_2O under dry N_2 . R. S. C.

Plato- and plati-diammines containing methylamine. H. D. K. DREW and H. J. TRESS (J.C.S., 1935, 1212—1214).— K_2PtBr_4 with aq. NH_2Me at 0° affords $[\text{Pt}(\text{NH}_2\text{Me})_4]\text{PtBr}_4$, β -di(methylamino)platinous bromide (I) [converted (AgNO_3) through the nitrate into (HCl) the β -chloride, which is obtained in only small yield from K_2PtCl_4 and NH_2Me], and $[\text{Pt}(\text{NH}_2\text{Me})_4]\text{Br}_2$, which with conc. HBr gives the α -isomeride of (I) and thence the α -chloride. Similarly are obtained β -di(ethylamino)platinous bromide, the β -chloride, and α -bromide, the nitrate of which is converted into the α -nitrite, -thiocyanate, and -chloride by the action of NaNO_2 , KCNS , and HCl , respectively. The appropriate Pt^{II} salts with H_2O_2 and HCl afford α - and β -di(methylamino)platinic chloride, the corresponding thiocyanates, and the *Et* analogues of these compounds. The β -series do not react with phenox-tellurine dibisulphate nor afford salts of Cossa's type with boiling HCl , which indicates a structure similar to that of Pt enCl_2 (cf. A., 1933, 1282; 1934, 284; this vol., 100). J. L. D.

Formation of alicyclic hydrocarbons from free radicals. F. O. RICE and O. L. POLLY (Ind. Eng. Chem., 1935, 27, 915—916).— Hg di-*n*-heptyl (I) in CO_2 at 350° gives cyclohexane (II), $n\text{-C}_7\text{H}_{16}$, $n\text{-C}_{14}\text{H}_{30}$, and a cyclic hydrocarbon, b.p. $145\text{--}155^\circ$, $n_D^{20} 1.4260$. The formation of (II) is attributed to polymerisation of C_2H_4 formed during the decomp. of (I). F. R. G.

Influence of nuclear substituents on side-chain reactions.—See this vol., 1191.

1:3:5-Fluorodinitrobenzene. A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1935, 23, 4—7).—The diazonium solution from 3:5-dinitroaniline and NaNO_2 in aq. HCl with 40% HBF_4 gives 3:5-dinitrobenzenediazonium borofluoride, decomp. 203° , which when heated gives 1:3:5-fluorodinitrobenzene, m.p. 43° . F. R. G.

Halogenation. X. Iodination of xylenes and iodoxylenes. P. S. VARMA and K. S. V. RAMAN (J. Indian Chem. Soc., 1935, 12, 343—344; cf. this vol., 1114).—Addition of fuming HNO_3 -nitrosulphonic acid mixture to *o*-, *m*-, or *p*-xylene and I in hot AcOH and subsequent heating for 20 min. gives good yields of 4-iodo-*o*-, 4-iodo-*m*-, and 2-iodo-*p*-xylene (I), respectively, with a little nitroxylene. Heating for 5.5 hr. yields (? 4:5-)di-iodo-*o*-xylene, m.p. 73° , 4:6-di-iodo-*m*-xylene, m.p. 72° , and (? 2:5-)di-iodo-*p*-xylene (II), m.p. 104° , also obtained similarly from the I_2 -compounds. (I) and conc. H_2SO_4 at room temp. slowly form (II). R. S. C.

Electrochemical oxidation of benzene homologues. VI. Mesitylene. F. FICHTER and O. MULLER (Helv. Chim. Acta, 1935, 18, 831—840; cf. A., 1927, 348).—Electrochemical oxidation of 1:3:5- $\text{C}_6\text{H}_3\text{Me}_3$ (I) in 0.5*N*- H_2SO_4 emulsified with Nekal B.X. using a Pb anode and a Zn cathode gives 1:3:5- $\text{C}_6\text{H}_3\text{Me}_2\text{CHO}$ (II) (0.2%), 1:3:5-

$\text{C}_6\text{H}_3\text{Me}_2\text{CO}_2\text{H}$ (III), and 2:1:3:5- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}_2\text{CO}_2\text{H}$ (IV) (3%), 1:3:5- $\text{C}_6\text{H}_3\text{Me}(\text{CO}_2\text{H})_2$ (V) (1%), 1:3:5:2- $\text{C}_6\text{H}_2\text{Me}_2\text{OH}$ (VI) (7%), 1:3:2:5- $\text{C}_6\text{H}_2\text{Me}_2(\text{OH})_2$ (0.64%) (Ac_2 derivative, m.p. 97°), some 1:3-dimethylbenzoquinone (VII), a quantity of resin, AcOH , HCO_2H , and CO_2 . 79% of (I) was recovered unchanged. Electrochemical oxidation of (I) using a PbO_2 anode and a diaphragm yields 13% of (II), 0.8% of (III) and (IV), 0.33% of (V), 0.33% of (VI), 0.03% of (VII), and 75% of unchanged (I). Oxidation of (I) (Pt anode and diaphragm) gives lower yields of the same products, whilst addition of conc. HNO_3 and AcOH increases the yield of (III) to 6.6%. Electrochemical oxidation of (I) in presence of 1:3:5:2- $\text{C}_6\text{H}_3\text{Me}_3\text{SO}_3\text{H}$ gives smaller quantities of oxidation products; (V) and (VII) (PbO_2 anode) give in each case CO_2 , AcOH , and HCO_2H . Oxidation of PhMe in aq. H_2SO_4 (PbO_2 anode without diaphragm) gives in addition to *p*-cresol (0.9%) and toluquinone (1.8%) (cf. A., 1914, i, 946), PhCHO (0.08%) and BzOH (0.4%).

F. R. G.

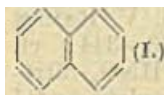
Highly polymerised compounds. CXVI. Polystyrenes with limited swelling power. H. STAUDINGER and E. HUSEMANN (Ber., 1935, 68, [B], 1618—1634; cf. A., 1934, 879).—Divinylbenzene (I) becomes polymerised much more readily than styrene (II), forming a hard, glassy mass, very brittle and insol. in all org. media. It is incompletely depolymerised with difficulty. The properties of the polymerisate are in harmony with its structure from three-dimensional mols. (I) yields sol. polymerides when heated in C_6H_6 or PhMe at 100° or with SnCl_4 in C_6H_6 or CCl_4 . Polymerisation of mixtures of (I) and (II) gives a non-homogeneous product, (I) undergoing change more rapidly and being followed by a mixture of (I) and (II). If (II) is in large excess, polymerisation of (I) does not occur and a homogeneous mixed polymeride is obtained. The amount of (I) necessary for the union of the threads of (II) is not directly \propto the length of the thread mols. With eucolloidal polystyrenes the quantity of (I) requisite to produce an insol. polystyrene is extraordinarily minute, and the viscosity of a sol. colloid can be very greatly modified by a small addition of a molecule-binding material. Mixed polymerisates of limited swelling powers yield sol. polystyrenes to suitable solvents; the η_{sp}/c vals. of these are $<$ those of pure polystyrenes prepared under like conditions. Further, the proportion of sol. material is greatest when least (I) is used and the extracted portions are more viscous than those derived from a more strongly bonded material. In the polystyrenes of limited swelling power the three-dimensional mols. of the mixed polymeride are greatly interwoven with the simple thread mols. of polystyrene. Experiments on the swelling of the insol. mixed polymerisates in C_6H_6 show that the ability to swell depends only on the no. of points of union by (I) bridges and is independent of the chain-length of the polystyrenes. The thread mols. must therefore be regarded as rigid, elastic structures which cannot be deformed at will. Swelling is at a max. in solvents which cause complete solvation of the polystyrene mols. and is much less marked in those of small power of solvation. H. W.

Walden inversion reactions of *d*- β -butyl, *d*- β -octyl, and *d*- β -benzylmethylcarbonyl *p*-toluenesulphonates. J. KENYON, H. PHILLIPS, and (MISS) V. P. PITTMAN (J.C.S., 1935, 1072—1084).—*d*-(+) β -Butanol with *p*-C₆H₄Me·SO₂Cl (cf. J.C.S., 1910, 97, 2585) in C₅H₅N below 0° affords *d*-(+) β -butyl *dl*-*p*-toluenesulphinatide, b.p. 98—100°/0.1 mm., which with KMnO₄ in aq. COMe₂ at 0° containing MgSO₄ gives *d*-(+) β -butyl *dl*-*p*-toluenesulphonate (I), b.p. 95°/0.1 mm., [α]_D²⁰ +7.00° in EtOH, which with boiling EtOH containing the appropriate Na or K salt gives (–) β -butyl thiocyanate [hydrolysed (KOH–EtOH) to the (–)disulphide, b.p. 95—97°/14 mm., and converted by hot HNO₃ into (+) β -butanesulphonic acid, b.p. 125°/0.1 mm.; the disulphide is reduced (Sn–HCl–AcOH) to the (–)thiol, b.p. 83—85°], (–)selenocyanate, b.p. 83—84°/16 mm. [the (+)selenocyanate, prepared from *l*-(–) β -butyl *dl*-*p*-toluenesulphonate, with boiling KOH–EtOH gives (+) β -butyl diselenide, b.p. 130°/16 mm.], (–)acetate [(+) β -butyl acetate is similarly obtained], (–)benzoate [the (+)benzoate is obtained similarly], (–)cyanide [hydrolysed to (–)methylacetic acid], and (–)iodide. Resolution of *dl*-methylacetic acid (cf. A., 1899, i, 477; 1896, i, 203) gives the (+)acid, which is converted successively through the chloride, b.p. 119—120°, and amide, m.p. 156°, into (+) β -butyl cyanide, b.p. 125—126°. (I) with boiling EtOH–K₂CO₃ affords (–)Et β -butyl ether, b.p. 82—83°. (–) β -Butyl *n*-butyl, b.p. 130—131°, and (–)Ph β -butyl ether, b.p. 92—93°/20 mm., are prepared similarly. (I) with piperidine at 100° gives (–)N- β -butylpiperidine, b.p. 75—76°/25 mm. (platinichloride, m.p. 197—198°), also formed from (–) β -butylamine and pentamethylene bromide in boiling Et₂O, thereby establishing its configuration. *dl*-N- β -Butylpiperidine, b.p. 70°/21 mm., and (–) β -butyl-*p*-toluidine, b.p. 136—138°/25 mm., are prepared similarly. (I) with NH₃ (*d* 0.88) under pressure at 100° affords a low yield of (–) β -butylamine [(–)Bz derivative, m.p. 88—89°]. (I) with MgPhBr in Et₂O at 0° affords (–) β -butylbenzene (cf. A., 1926, 509), C₆H₆, and Ph₂, whereas with MgEtBr it gives (–) β -butyl bromide, b.p. 90—91° (cf. A., 1925, i, 802); the latter is also obtained, together with *p*-C₆H₄Me·SO₂Br, from *d*- β -butyl *p*-toluenesulphinatide and Br in CHCl₃ (cf. A., 1929, 1164). Conversion of (–) β -butanol into β -butyl bromide is accompanied by inversion (cf. A., 1932, 251). *d*- β -Butanol and quinoline with COCl₂ in Et₂O afford *d*-(+) β -butyl chloroformate, b.p. 24—25°/13 mm., which when heated alone or with MgCl₂ or HgCl₂ gives (+) β -butyl chloride, but in C₅H₅N the (–)isomeride is formed (cf. A., 1930, 61; 1932, 251). The following are prepared by methods analogous to those used in the Bu series except where stated. (–)N- β -octylpiperidine, b.p. 125—126°/13 mm., and *p*-toluidine, b.p. 163—164°/15 mm.; (–) β -octyl thiocyanate, b.p. 119—120°/15 mm. [(+) β -octanesulphonic acid (Ba salt, m.p. >320°)]; (–) β -bromo-octane, b.p. 78—79°/18 mm., and (–)Ph β -octyl ether, b.p. 144—145°/20 mm. *d*-(+) β -Octyl *p*-toluenesulphonate (A., 1926, 159) with KSH in boiling EtOH gives (–) β -octylthiol, b.p. 78—80°/22 mm. [converted by Me₂SO₄ and Et₂SO₄ into (–)Me, b.p. 90—91°/18 mm., and (–)Et β -octyl sulphide, b.p. 99—100°/17

mm.], and probably some (–)*di*- β -octyl sulphide, b.p. 135°/2 mm. The *l*-(–)*p*-toluenesulphonate with PhSNa in EtOH gives (+)Ph β -octyl sulphide, b.p. 178°/20 mm. The relationship between [α] of the thiol and of its Me and Et ethers and λ indicates that the optically active thio-ethers show no complex rotatory dispersion (cf. A., 1924, i, 934). The following are prepared from *d*-(+)-benzylmethylcarbonyl *p*-toluenesulphonate (II) (J.C.S., 1923, 123, 44) by methods similar to those used in the Bu series, except where stated. (–) β -Piperidino-, b.p. 142—143°/11 mm., (–) β -*p*-toluidino-, b.p. 183—184°/11 mm., (+) β -amino-, b.p. 102°/16 mm., and (–) β -thiocyano- α -phenylpropane, b.p. 158°/16 mm., and (–) β -phenylisopropyl disulphide, b.p. 144°/0.1 mm. (II) with boiling MeCN–H₂O and NaCN gives (–) β -cyano- α -phenylpropane, b.p. 117°/17 mm., hydrolysed to the (–)acid (J.C.S., 1903, 83, 1005). (II) with NaSPh in EtOH gives (–)Ph α -phenyl- β -propyl sulphide, b.p. 177—178°/11 mm.; (–) α -phenyl- β -propylthiol, b.p. 105—110°/16 mm., is obtained by reducing the disulphide. (II) with LiCl in boiling EtOH gives (–) β -chloro- α -phenylpropane, b.p. 94°/17 mm., also obtained from (II) with MgEtCl in Et₂O. The *l*-(–)*p*-toluenesulphonate with NaBr in EtOH gives (+) β -bromo- α -phenylpropane, b.p. 121°/17 mm., and with boiling EtOH containing Na₂S affords *di*-(α -benzylethyl) sulphide, b.p. 209°/16 mm. The vals. of [α] for these compounds bear out the finding of Rule (A., 1930, 1095), whose views are used as criteria in establishing the configuration of substances the directions of rotation of which have altered as a result of chemical reaction. A change of rotatory sign is unaccompanied by change in configuration if the asymmetric atom takes no part in the reaction (cf. A., 1924, i, 940).

J. L. D.

Structure of naphthalene. L. F. FIESER and W. C. LOTHIROP (J. Amer. Chem. Soc., 1935, 57, 1459—1464).—Existing evidence in favour of a static 1:2-ethylenic linking in C₁₀H₈ is reviewed and supported by the facts that alkyl at 3, 6, or 7 increase the rate of methylation of β -C₁₀H₇·OH by *p*-C₆H₄Me·SO₃Me, whereas groups at 1 decrease it, and that halogen at 3 or 6 decreases it < does halogen at 1. The static formula (I) is indicated by the facts that 2:6-C₁₀H₆(OH)₂ (II) couples in the 1 and 8 positions, whereas 2:6-dihydroxy-1:5-dialkyl-naphthalenes do not couple, and that 2:6-dialkyl-naphthalenes rearrange only if the 1 and 5 positions are not substituted. 2:6-C₁₀H₆(OAc)₂ gives (Friedel-Crafts) 2:6-dihydroxy-1:5-diacetonaphthalene, m.p. 263° (Me₂ ether, m.p. 216°; with NaOEt–EtOH at 170° gives probably 2:6-dihydroxynaphthalene Me Et ether, m.p. 155°), the diacetate, m.p. 189°, of which is reduced by H₂–Cu chromite in EtOH at 170° to a product, which with HBr–AcOH in N₂ gives 2:6-dihydroxy-1:5-diethylnaphthalene, m.p. 262° (not obtained by other methods; Me₂ ether, m.p. 186°). The diallyl ether, m.p. 112°, of (II), obtained by the K₂CO₃–COMe₂ method, rapidly rearranges at 190° in N₂ to give 2:6-dihydroxy-1:5-diallylnaphthalene, m.p. 168° (dicoumarone derivative, m.p. 172°; Me₂, m.p. 113°, and diallyl ether, m.p. 100°). (II) and CH₂PhCl, best (70%) with Na in hot PhMe, give 2:6-dihydroxy-1:5-



dibenzyl-naphthalene (III), $+x\text{EtOH}$, m.p. 191° (Ac_2 derivative, m.p. 226°), converted by Zn dust into C_{10}H_8 only. 2:6- $\text{C}_{10}\text{H}_6(\text{OMe})_2$ and $\text{AlCl}_3\text{-BzCl}$ at room temp. give 2:6-dihydroxy-1:5-dibenzoyl-naphthalene, m.p. 282° [lit. 275° ; does not give a vat dye with AlCl_3 (cf. lit.)], from which a poor yield of (III) was obtained by hydrogenation (Cu chromite). Hydrogenation (Cu chromite) of 1:6-dihydroxy-12-pleiadone (IV) gives probably 2:7-dihydroxy-1-o-methylbenzyl-naphthalene, m.p. $235\text{--}236^\circ$, but the Me_2 ether of (IV) gives 1:6-dimethoxydihydropleiadene, m.p. 163° , demethylated by HBr-AcOH to the 1:6-(OH) $_2$ -compound, m.p. 217° , the diallyl ether, m.p. 93° , of which does not rearrange. R. S. C.

Selenium dioxide, a new oxidising agent. V. Some further oxidations. S. ASTIN, L. DE V. MOULDS, and H. L. RILEY (J.C.S., 1935, 901—904).—The varied reactivity of SeO_2 with org. compounds cannot be explained on a theory of intermediate compound formation. The property of SeO_2 of giving the same spectrum when many substances are burnt in its vapour (A., 1933, 685) suggests that it may have the capacity for providing O atoms in a very low energy state, and that this capacity may be effective in sp. oxidations at lower temp. The first stage in these may be removal of activated H atoms, which may or may not be followed by addition of O in a low energy state. Et acetonedicarboxylate is oxidised by SeO_2 to Et $\alpha\beta$ -diketobutyrate (probably through Et $\alpha\beta$ -diketoglutarate), with $\text{H}_2\text{C}_2\text{O}_4$ and organoselenium compounds. Et *dl*-malate gives Et diketosuccinate and fumarate, or, with excess of SeO_2 , $\text{H}_2\text{C}_2\text{O}_4$, malic acid, Et *H* malate, b.p. $240^\circ/35\text{ mm.}$, and Et *H* mesoxalate; organoselenium compounds are again also formed. Et β -phenylpropionate yields Et cinnamate and β -phenylpropionic acid. Dibenzyl gives benzil and stilbene; the last also gives benzil. Et mandelate is oxidised to BzCO_2Et , also formed, less readily, from $\text{CH}_2\text{Ph-CO}_2\text{Et}$. Anthracene yields anthraquinone; phenanthrene is less readily oxidised. NH_2Ph and SeO_2 in MeOH combine to an unstable compound, $\text{C}_7\text{H}_{11}\text{O}_3\text{NSe}$, m.p. 56° ; *p*-toluidine yields a compound, m.p. 67° . These results suggested combination of SeO_2 with MeOH, and these give in fact *Me H selenite* or *methylselenonic acid*, MeHSO_3 , m.p. 42° . Since the NH_2Ph compound does not furnish MeOH when treated with aq. NaOH, it is suggested that it is the NH_2Ph salt of methylselenonic acid, and not of *Me H* selenite. E. W. W.

Derivatives of 3:5-dihalogen-substituted anilines. F. D. CHATTAWAY and G. D. PARKES (J.C.S., 1935, 1005—1008).—The following are prepared: 3:5-dibromo-, m.p. 142° , and 2:3:4:5:6-pentabromo-diacetanilide, m.p. 198° ; 2:3:4:5-tetrachloro-, m.p. 165° , and 3:4:5:6-tetrabromo-acetanilide, m.p. 264° ; 3:5-dichloro-o-, m.p. 202° , -m-, m.p. 195° , and -p-, m.p. 221° , and 3:5-dibromo-o-, m.p. 228° , -m-, m.p. 220° , and -p-nitrobenzanilide, m.p. 240° . 3:5-Dichlorobenzeneazo-2'- and -4'-phenol, m.p. 142° and 138° ; 3:5-dibromobenzeneazo-2'- and -4'-phenol, m.p. 161° and 162° ; 3:5:3':5'-tetrachloro- and 3:5:3':5'-tetrabromo-2:4-bisbenzeneazo-phenol, m.p. 236° and 274° ; 3:5-dichloro-, m.p. 203° ,

2:3:4:5-tetrachloro-, m.p. 252° , and 3:5-dibromobenzeneazo- β -naphthol, m.p. 235° .

Benzaldehyde- and nitrobenzaldehyde-3:5-dichloro- and 3:5-dibromo-phenylhydrazones etc. are halogenated to the following: ω -chloro-o-, -m-, and -p-nitrobenzaldehydepentachlorophenylhydrazone, m.p. 137° , 198° , and 208° ; ω -bromobenzaldehyde-, m.p. 190° , and ω -bromo-o-, -m-, and -p-nitrobenzaldehyde-2:3:4:5-tetrabromophenylhydrazone, m.p. 161° , 242° , and 268° ; ω -bromobenzaldehyde-, m.p. 179° , and ω -bromo-o-, -m-, and -p-nitrobenzaldehyde-pentabromophenylhydrazone, m.p. 240° , 255° , and 265° ; m- and p-nitrobenzaldehydepentachlorophenylhydrazidine, m.p. 210° and 217° ; benzaldehyde-, m.p. 171° , and m- and p-nitrobenzaldehyde-2:3:4:5-tetrabromophenylhydrazidine, m.p. 218° and 248° ; benzaldehyde-, m.p. 106° , and m- and p-nitrobenzaldehyde-pentabromophenylhydrazidine, m.p. 227° and 248° . Nitrosocycloazipentachlorobenztriazone, $\begin{array}{c} \text{CO}-\text{N} \\ | \quad | \\ \text{C}_6\text{H}_4-\text{NO} \end{array} \text{N}\cdot\text{C}_6\text{Cl}_5$, explodes 128° , and the -tetrabromo-, explodes 155° , and -pentabromo-, explodes 157° , analogues are prepared.

3:5-Dichlorobenzene diazonium chloride and similar salts combine readily with Et acetoacetate. The following Et esters are prepared: 3:5-dichloro-, m.p. 106° , 3:5-dichloro-4-bromo-, m.p. 127° , 3:5-dibromo-, m.p. 96° , and 3:4:5-tribromo-benzeneazoacetoacetate, m.p. 146° ; α -bromoglyoxylate-3:5-dichloro-4-bromo-, m.p. 176° , -3:4:5-tribromo-, m.p. 129° , α -chloroglyoxylate-2:3:4:5-tetrachloro-, m.p. 128° ; α -aminoglyoxylate-3:5-dichloro-4-bromo-, m.p. 180° , and -2:3:4:5-tetrachloro-phenylhydrazone, m.p. 148° ; 3:5-dichlorobenzeneazo- γ -bromo-, m.p. 110° , and - $\gamma\gamma$ -dibromo-, m.p. 126° , 3:5-dichloro-4-bromobenzeneazo- γ -bromo-, m.p. 146° , and - $\gamma\gamma'$ -dibromo-, m.p. 125° , and 3:5-dibromobenzeneazo- γ -bromo-, m.p. 134° , and - $\gamma\gamma'$ -dibromo-acetoacetate, m.p. 123° .

$\beta\omega$ -Tribromo- α -ketopropaldehyde-3:5-dichloro-2:4-dibromophenylhydrazone, $\text{CHBr}_2\cdot\text{CO}\cdot\text{CBr}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{HCl}_2\text{Br}_2$, has m.p. 223° . 4-Hydroxy-, m.p. 154° , and 5-bromo-4-hydroxy-, m.p. 156° , -3-carbethoxy-1-(3':5'-dichlorophenyl)pyrazole, and 4-hydroxy-3-carbethoxy-1-(3':5'-dibromophenyl)pyrazole, m.p. 154° , are prepared; the acetates of these three compounds have m.p. 123° , 101° , and 125° , respectively. E. W. W.

N-Benzhydryl-N'-arylformamidines. L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1935, 1219—1220).—When heated with ArNH_2 , benzhydrylformamide (I) gives N'-benzhydryl-N'-arylformamidines; the following are obtained from (I) and the appropriate base: N-benzhydryl-N'-phenylformamide (II), m.p. 126.5° ; N-benzhydryl-N'-p-tolylformamide, m.p. 131° ; N-benzhydryl-N'-p-chlorophenylformamide, m.p. 124° ; N-benzhydryl-N'-p-anisylformamide, m.p. 137° ; N-benzhydryl-N'-2-naphthylformamide, m.p. 115° . Boiling 4N-HCl converts (II) into (I) and $\text{NH}_2\text{Ph}\cdot\text{HCl}$; the other compounds of the same class behave similarly. At $150\text{--}160^\circ$ (II) with $\text{CH}_2\text{Ph-CN}$ affords β -benzhydrylamino- α -phenylacrylonitrile, m.p. 141° . From (II) and $\text{CH}_2(\text{CO}_2\text{Et})_2$ at $145\text{--}150^\circ$, Et benzhydrylamino-methylenemalonanilide, m.p. 145° , is obtained, and

similarly $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ gives *benzhydrylaminomethyl-eneacetoacetanilide*, m.p. 154° . P. G. C.

Effect of substituents on reactivity of functional groups. E. HERTEL and J. DRESSEL (Z. physikal. Chem., 1935, B, 29, 178—191).—This influence can be determined only by observation of the reactivity of these groups in simple addition reactions, or intramol. changes within the groups. Kinetic measurements show that the ability of the NMe_2 group in the substances $\text{C}_6\text{H}_4\text{X}\cdot\text{NMe}_2$ to take up a third Me by adding trinitroanisole increases as X is varied in the order NO_2 , CN, Br, H, Me, OMe, NMe_2 . From electro-metric titration of the base with HClO_4 in AcOH it appears that the affinity of the NMe_2 in NPhMe_2 for H^+ increases as X changes in the order NO_2 , CN, Br, H. The additive power of the bases for picric acid has also been examined. R. C.

Action of acetic anhydride on N-nitrosophenylglycine and some of its derivatives. J. C. EARL and A. W. MACKNEY (J.C.S., 1935, 899—900).—When N-nitrosophenylglycine (new prep. by treating a solution of phenylglycine in aq. NaNO_2 with HCl) is treated with Ac_2O , the product, $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$, m.p. 134 — 134.5° , is best formulated $\text{NPh}\langle\begin{smallmatrix} \text{N} \\ \text{CH}\cdot\text{CO} \end{smallmatrix}\rangle$. It is

decomposed by HCl to $\text{NHPh}\cdot\text{NH}_2\text{Cl}$ and HCO_2H , and by NaOH to N-nitrosophenylglycine. N-Nitroso- α -anilinopropionic acid, decomp. 80 — 81° (prepared from α -anilinopropionic acid), similarly gives a substance, $\text{C}_9\text{H}_8\text{O}_2\text{N}_2$, m.p. 98 — 99° , decomposed by HCl to $\text{NHPh}\cdot\text{NH}_2\text{Cl}$ and AcOH, and by NaOH to its starting material. The N-NO-derivative, decomp. 117° , of α -anilinosobutyric acid (best obtained from the nitrile by way of the amide) is unchanged by Ac_2O . E. W. W.

β -Substituted ethylamines. I. Preparation of β -phenylethylamines from ω -nitrostyrenes. O. SCHALES (Ber., 1935, 68, [B], 1579—1581).— β -Phenylethylamines are obtained in good yield by slow addition of ω -nitrostyrenes in AcOH to the Adams catalyst in $\text{AcOH}\text{--}\text{H}_2\text{SO}_4$ in presence of H_2 . The prep. of homopiperonylamine and β -3-aminophenylethylamine is described. H. W.

Ammines from cyclic diamines and metallic salts.—See this vol., 1087, 1089.

Oxidation-reduction indicators. I. Diphenylbenzidinesulphonic acid.—See this vol., 1092.

Mechanism of diazotisation. J. REILLY and P. J. DRUMM (J.C.S., 1935, 871—873).—On the Hantzsch-Schumann view of diazotisation as reaction between ArNH_3^+ and undissociated HNO_2 , amines should, in absence of excess of mineral acid, diazotise faster the greater is their basicity, and the rate should not be appreciably affected by excess of acid over that required to prevent hydrolysis of the amine salt. This is confirmed by experiment. Of the amines $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{Cl}$ (I), $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_2\text{Cl}$ (II), and $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{NMe}_2\text{Cl}$ (III), the effect of the positive ($\cdot\text{NMe}_2$) pole in attracting unshared electrons and thus reducing basicity will be least in (III), and greatest in (I), and the basicity will be in the order (III) > (II) > (I); it is found that the velocity

coeffs. of diazotisation (at 1° and 0.001N solution), without excess of HCl, are less in the same order. Confirming the second deduction, the rate for any of the three is approx. the same whether 2 or 4 mols. excess of HCl are present. (II) is obtained by reducing dimethyl-p-nitrobenzylamine, b.p. $150^\circ/20$ mm. (picrate, m.p. 151°), to the p- NH_2 -compound (azo- β -naphthol derivative, m.p. 129.5°), converting the p-NHAc-compound, m.p. 103° , into trimethyl-p-acetamidobenzylammonium iodide, m.p. 232° , and this (AgCl, HCl) into trimethyl-p-aminobenzylammonium chloride hydrochloride, m.p. 194 — 196° , decomp. 270° . (III) is obtained by converting trimethyl- β -p-nitrophenylethylammonium picrate (A., 1927, 236) into the hydrochloride and reducing to trimethyl- β -n-aminophenylethylammonium chloride hydrochloride, m.p. 283° . E. W. W.

Electrolytic reduction of m-halogenonitrobenzenes to the azo-compounds. T. Y. CHANG and D. S. WANG (J. Chinese Chem. Soc., 1935, 3, 218—222).—3:3'-Dichloro-, -dibromo-, and -diiodo-azobenzene are prepared electrolytically from the NO_2 -compounds, using a rotatory Ni cathode and 75% EtOH (without NaOAc) as solvent.

E. W. W.

Fat-soluble azo-dyes. II. Dyes from palmitic acid. O. ROUTALA and E. PULLINEN (Suomen Kem., 1935, 8, B, 29).—Palmitic acid and $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ condense to form palmit- β -naphthylamide, m.p. 110 — 111° , which is converted into the NO_2 -, m.p. 87 — 88° , and NH_2 -, m.p. 160 — 162° , -derivatives, and thence, by diazotisation and coupling, into α - and β -naphthylamineazopalmit- β -naphthylamide, m.p. 155 — 158° and 134 — 139° , respectively, red dyes sol. in fats and fatty acids. Palmit- α -naphthylamide has m.p. 112 — 113° .

E. W. W.

Azo dyes [from N-sulphato-ethyl- or -propyl-anilines].—See B., 1935, 797.

Carvacrol. III. H. JOHN and P. BEETZ (J. pr. Chem., 1935, [ii], 143, 253—258).—Mainly a correction to previous work (A., 1933, 827). Owing to the presence of thymol in the sample of carvacrol previously used the compound there described as 5-acetocarvacrol is actually 6-acetothymol, its NO_2 -derivative is the 2-compound (I) (2-nitro-3-hydroxy-6-acetyl-1-methyl-4-isopropylbenzene), and the $(\text{NO}_2)_2$ -derivative is the 2:5-compound, all other derivatives requiring corresponding correction. The compound described as 3-acetocarvacrol is actually 5-acetocarvacrol (II), and its NO_2 -derivative is the 3-compound (III), thus necessitating appropriate correction to all derivatives. Pure carvacrol, b.p. 237.5° , m.p. 1° , with $\text{AlCl}_3\text{--AcCl}$ in PhNO_2 , gives (II), m.p. 101° . Condensation of 6-acetothymol with p- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ affords 4'-nitro-2-hydroxy-5-acetyl-6-methyl-3-isopropylazobenzene, m.p. 206° , reduced (alkaline $\text{Na}_2\text{S}_2\text{O}_4$) to 2-amino-6-acetylthymol, m.p. 100° , identical with the compound (loc. cit.) obtained by reduction of (I). (II) and p- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ similarly afford 4'-nitro-2-hydroxy-5-acetyl-3-methyl-6-isopropylazobenzene, m.p. 194° , reduced to 3-amino-5-acetylcarvacrol, m.p. 117° , identical with the compound previously obtained by reduction of (III).

Therapeutic substances derived from unsymmetrical diphenyl compounds. III. **Arylesters of hydroxydiphenyls.** S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 553—557).—The following were prepared, but have no val. as urinary disinfectants: *benzoates* of *o*-(I), m.p. 75—76°, *m*-, m.p. 57—58°, and *p*-C₆H₄Ph·OH, m.p. 148.5—149.5°, 6- (II), m.p. 86—87°, and 4-chloro-, m.p. 88.5°, 4-bromo-, an oil, and 4-*n*-propyl-2-hydroxydiphenyl (III), m.p. 96°, *α*-chloro-3-, an oil, and 2-chloro-4-hydroxydiphenyl, m.p. 110—111°, and 5:7-dichloro-8-hydroxyquinoline, m.p. 129—130.5°; *salicylates* of (I), m.p. 91—92°, and (II), m.p. 107°; *cinnamates* of (I), m.p. 103—104°, (II), m.p. 74.5—75°, and (III), m.p. 72.5°; *β-resorcylate*, m.p. 185—186°, and *acetylsalicylate*, m.p. 71.5—72.5°, of (I); *K sulphate* of (II), decomp. 225—230°, and (III), decomp. 180—190°. The *p_H* of rabbits' urine is variable; that with *p_H* > 7.5 or < 6.5 is very often germicidal. R. S. C.

Anionotropic and prototropic changes in cyclic systems. V. **System derived from 1-hydroxyindene.** H. BURTON and C. W. SHOPPEE (J.C.S., 1935, 1156—1161).—1-Hydroxy-1-phenyl-2-methylindene (I), b.p. 157°/0.6 mm., m.p. 59°, with Ac₂O (7 hr.; reflux) affords, by anionotropic change, 1-acetoxy-3-phenyl-2-methylindene (II) (two forms, m.p. 75—76° to a turbid liquid clearing at 90—91°; β, m.p. 90—91°), which undergoes with EtOH—KOH prototropic change to 3-phenyl-2-methylhydrindanone. With SOCl₂ (I) affords 1-chloro-3-phenyl-2-methylindene, m.p. 47°, converted by AgOAc—AcOH into (II). 2:3-Dimethylindenone, m.p. 80° [2:4-dinitrophenylhydrazones, m.p. 273—274° (decomp.); semicarbazone, m.p. 197°], is obtained directly from Et β-hydroxy-β-phenyl-α-methylbutyrate, or by ring-closure of *cis*-+*trans*-α-β-dimethylcinnamic acid (prep. methods of A., 1914, i, 281 are confirmed; cf. A., 1927, 257). With MgPhBr it gives 1-hydroxy-1-phenyl-2:3-dimethylindene, b.p. 175°/0.4 mm., converted into resins when treated with Ac₂O or Ac₂O—H₂SO₄; neither resin gives CH₂O on ozonolysis. P. G. C.

4-Hydroxy-1:2-benzpyrene. L. F. FIESER, E. B. HERSHBERG, and M. S. NEWMAN (J. Amer. Chem. Soc., 1935, 57, 1509—1510).—4'-Keto-1':2':3':4'-tetrahydro-1:2-benzpyrene with Se (1 atom; 310—320°; 2 hr.) gives a poor and with S (220—230°; 75 min.) a 19% yield of 4'-hydroxy-1:2-benzpyrene, m.p. 218—219° (acetate, m.p. 194—195°; benzoate, m.p. 191—192°; Me ether, m.p. 183—184°; CO₂Me-derivative, m.p. 239—240°; red colour in conc. H₂SO₄ with 1 drop of HNO₃ turns blue by way of green). M.p. are corr. R. S. C.

Dissociable organic oxides. Reversible oxidisability of the anthracene structure: dissociable oxide of 9:10-diphenylanthracene. C. DUFRASSE and A. ÉTIENNE (Compt. rend., 1935, 201, 280—282).—On theoretical grounds, 9:10-diphenylanthracene should be reversibly oxidisable, and it does in fact absorb O₂ when insolated in solution, forming a *photo-oxide*, which dissociates at 200°. E. W. W.

2-Amino-3:4-dimethoxytoluene. E. LEHMANN and W. PAASCHE (Ber., 1935, 68, [B], 1520—

1523).—2-Nitroveratraldehyde (I) is converted by PCl₅ into 2-nitro-3:4-dimethoxybenzylidene chloride, m.p. 43°, which could not be satisfactorily reduced catalytically. (I) is reduced by FeSO₄—NH₃ to 2-aminoveratraldehyde, m.p. 38° (*oxime*, m.p. 124°), converted by Zn—Hg and 6*N*-HCl into 2-amino-3:4-dimethoxytoluene (III), b.p. 137°/15 mm. (*hydrochloride*, m.p. 233°; Bz derivative, m.p. 142°), better obtained similarly and directly from (I). (III) is diazotised and transformed by CuCN into 2-cyano-3:4-dimethoxytoluene, b.p. 154—157°/15 mm., m.p. 34°, which cannot be hydrolysed by acid or alkali, but is transformed by prolonged boiling with KOH in amyl alcohol into 2-cyano-4-hydroxy-3-methoxytoluene, m.p. 114°. H. W.

Preparation of 2- and 4-allylresorcinol and their transformation into hydroxy-1-chloromercurimethyl-1:2-dihydrobenzofurans. A. N. NESMEJANOV and T. S. SAREVITSCH (Ber., 1935, 68, [B], 1476—1479).—Gradual addition of CH₂:CH·CH₂Cl to a solution of resorcinol and Na in MeOH gives the allyl ether, which becomes isomerised during distillation to 4-allylresorcinol (I), b.p. 144—146°/10 mm., m.p. 67°, catalytically reduced to 4-propylresorcinol, m.p. 77°. β-Methylumbelliferone is converted by NaOMe and CH₂:CH·CH₂Cl in MeOH into the allyl ether, m.p. 102.5—103°, which is isomerised at 235° to methylallylumbelliferone, m.p. 195—196°, converted by boiling aq. NaOH into 2-allylresorcinol (II), m.p. 52°. (II) is hydrogenated to 2-propylresorcinol, m.p. 99—101°, and transformed by HgCl₂ in H₂O into 3-hydroxy-1-chloromercurimethyl-1:2-dihydrobenzofuran, m.p. 151—152°. (I) similarly affords 5-hydroxy-1-chloromercurimethyl-1:2-dihydrobenzofuran, m.p. 148—149°. H. W.

Bromination of resorcinol monobenzoate and nitration of 4:6-dibromoresorcinol 3-benzoate. Example of group migration. H. H. HODGSON and (in part) R. J. H. DYSON (J.C.S., 1935, 946—948).—In dry CHCl₃, resorcinol 3-benzoate (I) is brominated in three stages, in the 6, 4, and 2 positions. Its activated structure is therefore formulated as BzO·C<CH=C(OH)>CH. The first product (obtained only when the CHCl₃ is dry) is 6-bromoresorcinol 3-benzoate, m.p. 169°, which with Me₂SO₄ gives 6-bromoanisyl 3-benzoate, m.p. 140°, hydrolysed to 6-bromo-3-hydroxyanisole, which with NaNO₂ forms 4-bromo-6-nitroresorcinol 3-Me ether, m.p. 114°, identified by prep. from 6-nitroresorcinol 3-Me ether and Br in CHCl₃; further bromination (NaOBr) gives 2:4-dibromo-6-nitroresorcinol 3-Me ether, m.p. 128°. For comparison, 4-bromoanisyl 3-benzoate, m.p. 65°, is prepared by converting 3-nitro-*p*-anisidine (Sandmeyer) into 4-bromo-3-nitroanisole, m.p. 32°, reducing to 4-bromo-*m*-anisidine (*hydrochloride*, m.p. 186°), and benzoylating the 4-bromo-3-hydroxyanisole thence obtained. Dibromination of (I) gives 4:6-dibromoresorcinol 3-benzoate, m.p. 155°, hydrolysed to 4:6-dibromoresorcinol; both these with BzCl yield the dibenzoate, m.p. 164°. 4:6-Dibromoresorcinol mixed with K₂CO₃ and treated with Me₂SO₄ gives 4:6-dibromoresorcinol Me₂ ether, m.p. 65°;

in aq. Na_2CO_3 , 4:6-dibromoanisyl 3-benzoate, m.p. 95° , is formed. By nitration in AcOH , 2:4-dibromo-6-nitroresorcinol 3-benzoate, m.p. 141° , is obtained (scarlet *Na* salt), hydrolysed to 2:4-dibromo-6-nitroresorcinol; nitration by diacetylorthonitric acid in Ac_2O gives a product, m.p. 130° , hydrolysed to a mixture of red and yellow crystals, m.p. 145° , apparently 4:6-dibromo-2-nitro- and 2:4-dibromo-6-nitroresorcinol. By tribromination, 2:4:6-tribromo-resorcinol 3-benzoate, m.p. 120° , is formed. Resorcinol or its Me_1 ether dissolved in AcOH and treated first with oleum, then with HNO_3 , yields respectively 2-nitroresorcinol, m.p. 85° , and 6-nitroresorcinol 3-*Me* ether, m.p. 95° ; the former with Br in AcOH gives 4:6-dibromo-2-nitroresorcinol. E. W. W.

Oxidation of quinol solutions. III.—See this vol., 1083.

Lichen substances. LIV. Constitution of physodic acid. III. Y. ASAHINA and H. NOGAMI (Ber., 1935, 58, [B], 1500—1503; cf. this vol., 490).—Et 3:5-dimethoxybenzoylacetate is transformed by NaOEt and Pr^{I} in EtOH into Et α -3:5-dimethoxybenzoyl-*n*-valerate, m.p. 44 — 45° , which with 6% H_2SO_4 at 195° affords 3:5-dimethoxyvalerophenone (I), m.p. 42 — 43° (semicarbazone, m.p. 204°). Reduction of (I) with Zn-Hg and HCl proceeds unsatisfactorily, whereas treatment with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and of the product with KOH at 220 — 245° affords 3:5-dimethoxy-1-*n*-amylbenzene (olivetol Me_2 ether), b.p. $114^\circ/2$ mm. (Br_2 -derivative, m.p. 74.5 — 75.5°), in good yield, converted by HI into olivetol (II). Treatment of (II) with Br (0.5 mol.) in AcOH yields bromo- (+ $2\text{H}_2\text{O}$) m.p. 61° , and dibromo-olivetol. Bromo-olivetol Me_3 ether, Cu-bronze, and the K derivative of orcinol at 180 — 220° afford protophysodon Me_3 ether, the Br_3 -derivative of which is identical with that derived from physodic acid. H. W.

Interaction of organomagnesium compounds with naphthalene- and phenanthrene-carboxylic esters. G. DARZENS and A. LEVY (Compt. rend., 1935, 201, 152—154).—Me 1-methyl-3-naphthoate (A., 1926, 1239) and MgMeBr in Et_2O afford 1-methyl-3-naphthyltrimethylcarbinol, which loses H_2O above 125° yielding 1-methyl-3-isopropenyl-naphthalene, b.p. $154^\circ/12$ mm. (picrate, m.p. 81 — 81.5°). This readily polymerises to a high-melting compound, and is reduced by EtOH-Na to 1-methyl-3-isopropyl-naphthalene (I), b.p. $150^\circ/11$ mm. (picrate, m.p. 84° ; styphnate, m.p. 119°). Similarly Me 1-methyl-1:2:3:4-tetrahydronaphthalene-3-carboxylate (*loc. cit.*) and MgMeBr afford 1-methyl-1:2:3:4-tetrahydro-3-naphthyltrimethylcarbinol, b.p. 159 — $161^\circ/10$ mm., dehydrated by KHSO_4 at 150° to a mixture of unsaturated compounds, b.p. 139 — $141^\circ/15$ mm. This mixture is reduced by boiling Na-EtOH to 1-methyl-3-isopropyl-1:2:3:4-tetrahydronaphthalene, b.p. 138 — $139^\circ/16$ mm., dehydrogenated by S and by Se to (I). Me 1-methylphenanthrene-3-carboxylate, m.p. 123° (cf. this vol., 975), and MgMeBr afford 1-methyl-3-phenanthryltrimethylcarbinol, m.p. 115° , dehydrated to 1-methyl-3-isopropenylphenanthrene, b.p. $192^\circ/2$ mm., which readily polymerises. It is readily reduced by Na-EtOH to 1-methyl-3-isopropylphenanthrene (II), m.p. 79° , b.p. $18^\circ/1.5$ mm. (picrate, m.p.

150° ; styphnate, m.p. 155° ; the corresponding quinone has m.p. 167 — 168°). Me 1-methyl-1:2:3:4-tetrahydronaphthalene-3-carboxylate (*cf. loc. cit.*) and MgMeBr afford 1-methyl-1:2:3:4-tetrahydronaphthyltrimethylcarbinol, b.p. $189^\circ/2$ mm., dehydrated by KHSO_4 to a mixture of unsaturated compounds, b.p. $210^\circ/2.5$ mm. This is reduced to 1-methyl-3-isopropyl-1:2:3:4-tetrahydronaphthalene, b.p. $208^\circ/23$ mm. (picrate, m.p. 67° ; styphnate, m.p. 128°), dehydrogenated by S and by Se to (II). H. G. M.

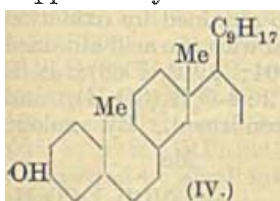
Optically active diphenylhydroxyethylamines and isohydrobenzoins. VI. Di-*o*-methoxyphenylhydroxyethylamines and related substances. N. A. B. WILSON and J. READ (J.C.S., 1935, 1120—1123).—The prep. of NH_2 -alcohols, $\text{Ar}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{Ar}$ (from $\text{Ar}\cdot\text{CHO}$, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and alkali; A., 1905, i, 131), fails with α - and β - $\text{C}_{10}\text{H}_7\cdot\text{CHO}$, heptaldehyde, and the following benzaldehydes: *m*-OMe-, *o*- and *m*- NO_2 -, *p*-NMe₂-, *o*-OBz-, and 3:4-(OMe)₂-. *o*-OMe- $\text{C}_6\text{H}_4\cdot\text{CHO}$ affords dl-isodi-*o*-methoxyphenylhydroxyethylamine (I), m.p. 136° (*Ac* derivative, m.p. 180° , does not react with HNO_2 ; benzylidene derivative, m.p. 131°). (I) with *d*-tartaric or *d*-camphor-10-sulphonic acid gives l-isodi-*o*-methoxyphenylhydroxyethylamine (II), m.p. 111° , $[\alpha]_D -52.7^\circ$ in EtOH (*Ac*₂ derivative, m.p. 170° ; salicylidene derivative, m.p. 106° , $[\alpha]_D -24.0^\circ$ in EtOH). (I) gives cis- $\alpha\beta$ -di-*o*-methoxyphenylethyl-ethylene oxide, m.p. 127 — 128° [also obtainable from (II)], when converted into dl-isodi-*o*-methoxyphenylhydroxyethyltrimethylammonium iodide, m.p. 183 — 184° , and heated with $\text{Ag}_2\text{O-H}_2\text{O}$. A dil. H_2SO_4 solution of (II) affords with HNO_2 an oil (optically inactive, *Ac* val. 7.4), probably a mixture of 30% of di-*o*-methoxyhydrobenzoin, 34% of di-*o*-methoxyphenylacetaldehyde (III) (semicarbazone, m.p. 204°), and 36% of unidentified material. Di-*o*-methoxydeoxybenzoinsemicarbazone, m.p. 196° , is prepared from the oil obtained by Zn-dust distillation of di-*o*-methoxybenzoin; the last-named with Na-Hg affords di-*o*-methoxyhydrobenzoin, converted by hot 20% H_2SO_4 into di-*o*-methoxyhydrobenzoin anhydride, m.p. 175.5° , and (III). From di-*o*-methoxybenzoinoxime and Na-EtOH, 1-di-*o*-methoxyphenylhydroxyamine *H* d-tartrate, m.p. 160° , $[\alpha]_D -66.0^\circ$ in H_2O , is obtained. The mother-liquors contain dl- α -aminodi-*o*-methoxydibenzyl, m.p. 60° (*Ac* derivative, m.p. 156° ; salicylidene derivative, m.p. 83.5°). dl-isoDi-*o*-chlorophenylhydroxyethylamine, m.p. 151.5° (*Ac* derivative, m.p. 160° ; *Ac*₂ derivative, m.p. 184° ; benzylidene derivative, m.p. 146.5° ; salicylidene derivative, m.p. 130.5°), is not resolved by *d*-tartaric acid or *l*-menthyloxyacetic acid, or by way of the methylenecamphor route, but a specimen of the base regenerated from the *d*-camphor-10-sulphonate had m.p. 152 — 152.5° , $[\alpha]_D +3.5^\circ$ in EtOH .

Electrolytic reduction of the following aldehydes is mentioned (products in parentheses): PhCHO (hydro-+isohydro-benzoin), anisaldehyde (hydro-+isohydro-anisoin), *m*-OMe- $\text{C}_6\text{H}_4\cdot\text{CHO}$ (*m*-methoxybenzyl alcohol; 3:5-dinitrobenzoate, m.p. 124°), *o*- and *m*-nitro- and *p*-dimethylamino-benzaldehyde (resins), 1- $\text{C}_{10}\text{H}_7\cdot\text{CHO}$ (1- $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$), *o*-OMe- $\text{C}_6\text{H}_4\cdot\text{CHO}$ (corresponding alcohol and acid). P. G. C.

Solubility of cholesterol in certain acyclic amines. M. VILLARET, L. JUSTIN-BESANÇON, and M. DRILHON (Compt. rend. Soc. Biol., 1935, 119, 1317—1319).—Dissolution of cholesterol (I) in NMe_3 is accompanied by a loss of some of the titratable alkalinity of the latter, which is \propto the amount of (I).

H. G. R.

Chemistry of some irradiation products of ergosterol. I. M. HEILBRON and F. S. SPRING (Chem. and Ind., 1935, 795—797).—In reply to Rosenheim *et al.* (this vol., 1120) it is pointed out that ring scission during the changes ergosterol \rightarrow lumisterol (I) \rightarrow tachysterol (II) \rightarrow calciferol (III) occurs during the transition (I) \rightarrow (II). A definite allocation of the second nuclear ethenoid linking of (I) is not yet possible. It is fair to assume that (II) and (III) possess the same ring structure and differ in the position of their ethenoid linkings. Since the change (I) \rightarrow (II) is accompanied by ring opening, the seat of this change is the unsaturated ring B, a point which is supported by the non-formation of $\text{C}_6\text{HMe}_4\cdot\text{CO}_2\text{H}$ on



oxidation of (III) with HNO_3 . The six possible ring systems of (II) and (III) depending on the mode of scission of the unsaturated ring B of (I) are considered, all of which are eliminated except (IV) by the formation of the aldehyde

$\text{C}_{20}\text{H}_{33}\cdot\text{CHO}$ by mild oxidation of (III) or its acetate (this vol., 1036).

H. W.

Sterol group. XX. Partial reduction of fucosterol. D. H. COFFEY, I. M. HEILBRON, F. S. SPRING, and H. R. WRIGHT (J.C.S., 1935, 1205—1207).—Fucosteryl acetate is hydrogenated (Pd) to a mixture of α -dihydrofucosteryl acetate (I), m.p. 133—134°, $[\alpha]_D^{20} -43.53^\circ$, and the β -form (II), m.p. 121—122°, $[\alpha]_D^{20} -38.7^\circ$. Hydrolysis of (I) with EtOH-KOH gives α -dihydrofucosterol (III), m.p. 136—137°, $[\alpha]_D -38.43^\circ$, which contains 1 double linking (BzO_2H titration) and is converted by H_2 and Adams' PtO_2 catalyst into stigmastanol (IV), oxidised to stigmastanone (V). (II) on hydrolysis gives β -dihydrofucosterol (VI), m.p. 132—133°, $[\alpha]_D^{20} -30.36^\circ$, which also contains 1 double linking and gives (IV) on hydrogenation. CrO_3 oxidation of (III) affords α -fucostenone, m.p. 158° (2:4-dinitrophenylhydrazine, m.p. 272°), and similarly (VI) affords β -fucostenone (VII), m.p. 135—136° (2:4-dinitrophenylhydrazine, m.p. 185°). Reduction of fucosterol with Na-amyl alcohol affords epi- β -dihydrofucosterol (VIII), m.p. 159°, $[\alpha]_D^{20} +12.2^\circ$ (Ac derivative, m.p. 86°; dibromide, m.p. 139°), hydrogenated to epifucostanol, m.p. 173.5—174.5°. The latter is converted by $\text{CrO}_3\text{-AcOH}$ into (V); the same reagent oxidises (VIII) to (VII). All vals. of $[\alpha]$ are in CHCl_3 .

P. G. C.

Interaction of thionyl chloride with *m*- and *p*-aminobenzoic acids. P. CARRE and D. LIBERMANN (Compt. rend., 1935, 201, 147—149).—Contrary to the conclusions of Michaelis *et al.* (A., 1893, i, 515), $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (I) and SOCl_2 in C_6H_6 afford the diamide $\text{C}_6\text{H}_4\langle\text{NH}\cdot\text{CO}\rangle\text{C}_6\text{H}_4$ (II) (cf. A., 1883, 999).

Contrary to the conclusions of McMaster *et al.* (A., 1928, 271), (I) when heated with 6 mols. of SOCl_2 affords *m*-thionylaminobenzoyl chloride, $m\text{-COCl}\cdot\text{C}_6\text{H}_4\cdot\text{NSO}$ (decomp. on distillation in vac.). With H_2O this yields mainly (II) (and some polymeride), HCl , and SO_2 , and with EtOH it yields (II), HCl , $\text{SO}(\text{OEt})_2$, and a little Et *m*-thionylaminobenzoate (cf. A., 1893, i, 515). Similarly $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (III) with excess of SOCl_2 affords *p*-thionylaminobenzoyl chloride, b.p. 147—150°/27 mm. (decomp.). With H_2O this yields HCl , SO_2 , and an insol. substance, m.p. 325°, hydrolysed by alkalis to (III) and considered to be the diamide corresponding with (II).

H. G. M.

Anthracene series. X. E. DE B. BARNETT, N. F. GOODWAY, and E. V. WEEKES (J.C.S., 1935, 1102—1104).—Anthracene (I), when boiled during 8 hr. in $o\text{-C}_6\text{H}_4\text{Cl}_2$ with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II), yields $\alpha\beta$ -endo-9:10-dihydroanthraquinyl-9:10- β -propionic acid, m.p. 186°. The corresponding compounds prepared from (II) and 1:4-dimethyl-, 9:10-dichloro-, and 9:10-dibromo-anthracene have m.p. 250°, 245°, and 252°, respectively, and show no visible fluorescence. The last two products gave no ionised halogen when boiled for 40 min. with 10% NaOH-EtOH . $\alpha\beta$ -endo-9:10-Dihydroanthraquinyl-9:10- β -phenylpropionic acid (III), m.p. 248°, is obtained when HCl is passed during 12 hr. into a solution of (I) and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in boiling $o\text{-C}_6\text{H}_4\text{Cl}_2$. The following compounds were obtained by boiling (II) in $o\text{-C}_6\text{H}_4\text{Cl}_2$ with the appropriate anthrone during 8 hr. When the latter contains a substituent *peri* to the CO, an anthronylpropionic acid is formed, otherwise the product is an anthronylidenedipropionic acid: anthronylidenedipropionic acid, m.p. 248—250° (decomp.); 2:3-dimethylanthronylidenedipropionic acid, m.p. 298°; 1:5-dichloro-, m.p. 163°; 1:8-dichloro-, m.p. 204°; 4:5-dichloro-, m.p. 174°; 1:4-dimethyl-anthronylpropionic acid, m.p. 168°. This last is reduced by boiling with Zn (activated by CuSO_4) and 2*N*- NaOH for 4 hr. to 1:4-dimethylanthranlylpropionic acid, m.p. 205°, neutral and alkaline solutions of which are strongly fluorescent. Reduction of the other anthronylpropionic acids gave uncrystallisable products, sol. in alkali. β -Phenyl- β -anthronylpropionic acid, m.p. 197° [obtained by passing HCl during 15 hr. through a boiling solution of anthrone (IV) and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in $o\text{-C}_6\text{H}_4\text{Cl}_2$], is reduced by $\text{Zn-NaOH-H}_2\text{O}$ to β -phenyl- β -anthranlylpropionic acid, m.p. 225° (strongly fluorescent in neutral and alkaline solution). This and its isomeride (III) are not interconvertible. (IV) with $\text{CHCl}_2\cdot\text{CO}_2\text{H}$, KOH , and boiling H_2O yields a little anthronylideneacetic acid, m.p. 205° (non-fluorescent). (IV) and (I) did not, however, condense with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ with (IV) gave only resinous products, but when boiled with 1:5-dichloroanthrone, KOH , and H_2O yields 1:5-dichloro-10-cinnamylanthrone, m.p. 148°, oxidised by $\text{CrO}_3\text{-AcOH-H}_2\text{O}$ at the b.p. to 1:5-dichloroanthronylacetic acid, m.p. 218°. An acid, m.p. 132°, is not formed by condensation of (II) with phenanthrene (cf. B.P. 303,389; B., 1929, 237), and commercial pyrene can be recovered, colourless but unattacked, after treatment with (II) (cf. A., 1932, 1131).

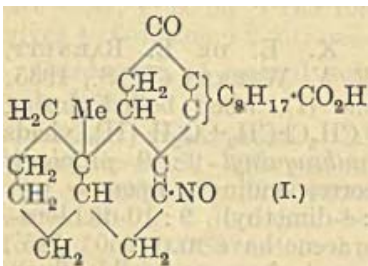
H. G. M.

Influence of solvent, concentration, and temperature on rotatory powers of *l*-menthyl α -substituted benzoic esters.—See this vol., 1192.

Structure of betaine.—See this vol., 1064.

Rates of racemisation of acids of the type $\text{CHRR}'\text{CO}_2\text{H}$.—See this vol., 1083.

Bile acids. XLVI. Behaviour of the nitroso-compound $\text{C}_{24}\text{H}_{33}\text{O}_8\text{N}$ (isobilianic acid series) and of the dioxime of 7:12-diketocholanic acid towards nitric acid. M. SCHENCK (Z. physiol. Chem., 1935, 235, 74—80).—Oxidation of the NO-compound, $\text{C}_{24}\text{H}_{33}\text{O}_8\text{N}$, obtained from the dioxime of isobilianic acid with 32.5% HNO_3 at 100° gives bilisoidanic acid. Treatment of the dioxime of 7:12-diketocholanic acid with HNO_3 affects the N·OH groups less readily than in analogous cases, and N is not



immediately evolved from the N·OH at 12. The blue product which separates spontaneously is a mixture of (I) and a second NO-compound, provisionally designated "2N-substance."

H. W.

Multiplanar cyclohexane rings. M. QUDRAT-KHUDA (Nature, 1935, 136, 301).—The four isomerides of 4-methylcyclohexane-1-carboxylic-1-acetic acid have again been isolated as a reply to criticism (this vol., 489).

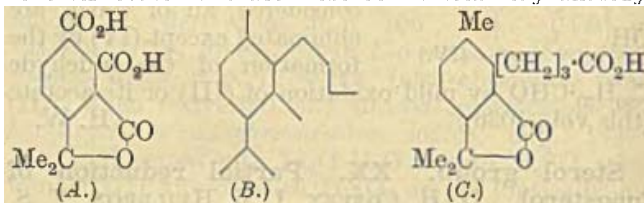
L. S. T.

ω -3-Amino-4-methoxy- and -ethoxy-benzoyl derivatives of propionic, butyric, and valeric acids. S. G. P. PLANT and (MISS) M. E. TOMLINSON (J.C.S., 1935, 1092—1093).—Adipic anhydride, PhOMe, CS_2 , and AlCl_3 when refluxed for 3 hr. afford $\alpha\delta$ -dianisoylbutane (I) and δ -anisoylvaleric acid (II) (cf. A., 1932, 63). With Zn-Hg and conc. HCl (I) yields α -di-*p*-anisylhexane, m.p. 69—71°, b.p. 250—260°/23 mm., and (II) yields ϵ -*p*-anisylhexoic acid, m.p. 47—49°, b.p. 208—210°/14 mm. (II) in H_2SO_4 at —5° to 0° and KNO_3 yield δ -3-nitro-4-methoxybenzoylvaleric acid, m.p. 107—109°, oxidised by boiling with HNO_3 (*d* 1.42) to 3-nitro-4-methoxybenzoic acid (III), and reduced by boiling with NH_3 - H_2O - FeSO_4 solution to δ -3-amino-4-methoxybenzoylvaleric acid (IV), m.p. 116°. The following substances were prepared by similar methods: $\alpha\delta$ -diphenetylbutane, m.p. 127°; δ -phenetylvaleric acid, m.p. 110°; α -di-*p*-phenetylhexane, m.p. 69—70°; ϵ -*p*-phenetylhexoic acid, m.p. 57°; δ -3-nitro-4-ethoxybenzoylvaleric acid, m.p. 110° [oxidised by HNO_3 (*d* 1.42) (steam-bath) to 3-nitro-4-ethoxybenzoic acid (V)]; δ -3-amino-4-ethoxybenzoylvaleric acid (VI), m.p. 102°; β -3-amino-4-methoxybenzoylpropionic acid, m.p. 138°, from the corresponding NO_2 -compound [oxidised by boiling HNO_3 (*d* 1.42) to (III)]; β -3-amino-4-ethoxybenzoylpropionic acid, m.p. 144—146°, from β -3-nitro-4-ethoxybenzoylpropionic acid, m.p. 153° [oxidised to (V)]; γ -3-nitro-4-methoxybenzoylbutyric acid, m.p. 145° [prepared by nitration of γ -anisoylbutyric acid (this vol., 961) and oxidised to (III)]; γ -amino-4-methoxybenzoylbutyric acid, m.p. 162—164°; γ -3-nitro-4-ethoxybenzoylbutyric acid, m.p.

127° [prepared by nitration of γ -phenetylbutyric acid (*loc. cit.*) and oxidised to (V)]; and γ -3-amino-4-ethoxybenzoylbutyric acid, m.p. 176—178°. Attempts to cyclise (IV) and (VI) through the *m*-position were unsuccessful; the stereochemical considerations (A., 1934, 189) according to which such ring-closure is possible have, however, been illustrated by the recent prep. of *m*-ring compounds (A., 1934, 894; this vol., 844).

H. G. M.

Picrotoxin. I. Constitution of picrotic acid and the C-skeleton of picrotoxinin and picrotin. D. MERCER, A. ROBERTSON, and (in part) R. S. CAHN (J.C.S., 1935, 997—1000).—The acid $\text{C}_{11}\text{H}_{10}\text{O}_4$, m.p. 202°, obtained by Hansen (A., 1933, 712) by oxidation of picrotoxinin and of picrotin with MnO_2 and H_2SO_4 (improved method described) and degradation of the resulting dibasic acid, $\text{C}_{12}\text{H}_{10}\text{O}_6$, is identified (comparison with synthetical specimen) as $\alpha\alpha$ -dimethylphthalide-4-carboxylic acid (cannabinolactonic acid). The intermediate NH_2 -acid has m.p. 183—200°, and is apparently a mixture of two isomerides. The dibasic acid, $\text{C}_{12}\text{H}_{10}\text{O}_6$, is also obtained by oxidation of picrotic acid, and is identical with the acid obtained by Angelico (A., 1911, i, 1004; 1913, i, 69); it is oxidised by HNO_3 to 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$, and the structure A is therefore confirmed. By analogy



with santonin and its related lactones, it is suggested that picrotin and picrotoxinin are related to the sesquiterpenes and have the skeleton B, and that picrotic acid has not the structure proposed by Angelico (A., 1924, i, 183), but the structure C. This is confirmed by the identification of Angelico's acid, $\text{C}_{12}\text{H}_{14}\text{O}_4$ (new m.p. 135—136°), obtained by hydrolytic fission of picrotic acid, as 3-carboxy- γ -o-tolyl-n-butyric acid, since its *Et* ester, b.p. 158—160°/1 mm., is converted by Na in PhMe into *Et* 5-methyl-1-keto-1:2:3:4-tetrahydronaphthalene-2-carboxylate, b.p. 152—155°/1 mm. (pyrazolone, m.p. 265°), and this by 20% H_2SO_4 into 5-methyl-1-keto-1:2:3:4-tetrahydronaphthalene (semicarbazone, m.p. 245—246°; 2:4-dinitrophenylhydrazone, m.p. 229—230°; unstable phenylhydrazone, m.p. 105°). This is synthesised by a new method (cf. A., 1930, 593), condensing *o*-toluoyl chloride with *Et* sodioacetacetate to give *o*-methylacetophenone (semicarbazone, new m.p. 210°), of which the ω -*Br*-derivative, b.p. 138—140°/16 mm. [converted into ω -acetoxy-*o*-methylacetophenone (semicarbazone, m.p. 174°)], reacts with *Et* sodiomalonate to form *Et* β -*o*-toluoylthane- $\alpha\alpha$ -dicarboxylate, b.p. 170°/1 mm. (2:4-dinitrophenylhydrazone, m.p. 136—137°). This keto-ester (also prepared from *o*-toluoyl chloride and CH_2N_2 , the product of which is converted by HCl into ω -chloro-*o*-methylacetophenone, and this treated with *Et* sodiomalonate) is reduced by Zn in *EtOH*-HCl to the acid, decomp. to γ -*o*-tolyl-n-butyric acid, m.p. 60—61°, from which the naphthalene is obtained (cf. *loc. cit.*).

E. W. W.

4-Methoxycinnamylidenepyruvic acid. E. FRIEDMANN (J.C.S., 1935, 1053).—4-Methoxycinnamylidenepyruvic acid, m.p. 137—138° (decomp.) [Na salt, +1.5H₂O; 2:4-dinitrophenylhydrazone, m.p. 201° (decomp.)], is obtained from *p*-OMe·C₆H₄·CH:CH·CHO and AcCO₂H in cold aq. EtOH–NaOH. R. S. C.

Stereoisomerism due to restricted rotation of single linking. I. Optical isomerism of 4:6:4':6'-tetrabromodiphenic acid. H. C. YUAN and T. T. HSU (J. Chinese Chem. Soc., 1935, 3, 206—212).—From the 2-NH₂-acid, 3:5-dibromo-2-iodobenzoic acid, m.p. 199°, is prepared, and its *Et* ester, m.p. 36—36.5°, is heated with Cu-bronze. After hydrolysis, 4:6:4':6'-tetrabromodiphenic acid, m.p. 271° (decomp.), is obtained, and thence the *brucine*, [α]_D²⁰ –76.6°, and *Na*, [α]_D²⁰ +47.28°, salts of the *d*-acid, m.p. 181°, [α]_D²⁰ +258.2°, and similar *l*-compounds (impure). The *d*-acid is racemised on heating in COMe₂ or AcOH, and the *l*-salt in aq. NaOH. E. W. W.

Fission of ketosulphidocarboxylic acids. O. BEHAGEL and E. SCHNEIDER (Ber., 1935, 68, [B], 1588—1593).—Desylthiolacetic acid, CHPhBz·S·CH₂·CO₂H, m.p. 105° (*oxime*, m.p. 123°; *semicarbazone*, m.p. 178°), obtained by the action of HCl on a mixture of benzoïn and SH·CH₂·CO₂H at 100°, or from CHPhBzCl and SH·CH₂·CO₂H at 100°, is converted by alkali into CH₂PhBz and OH·S·CH₂·CO₂H (whence H₂S, OH·CH₂·CO₂H, and H₂C₂O₄). Similarly, anisoïn is readily transformed into deoxyanisoïn, m.p. 110°, by condensation with SH·CH₂·CO₂H and treatment of the product with NaOH. CPhBz·CH₂Br and SH·CH₂·CO₂H afford benzoylmethylthiolacetic acid, m.p. 101° [*semicarbazone*, m.p. 201° (decomp.)], hydrolysed by NaOH to CPhBzMe and OH·S·CH₂·CO₂H. Benzoïn and SH·CH₂·CO₂H in presence of anhyd. ZnCl₂ at 100° yield αβ-diphenylethylenedithiolacetic acid, (CPh·S·CH₂·CO₂H)₂, m.p. 213° (*Me*₂ ester, m.p. 97—98°). Benzil and SH·CH₂·CO₂H in presence of HCl at 100° or chlorobenzil and SH·CH₂·CO₂H at 100° afford benzoylphenylmethylenedithiolacetic acid, CPhBz(S·CH₂·CO₂H)₂, m.p. 185°, converted by alkali partly into CH₂PhBz, mainly into benzyldenedithiolacetic acid and BzOH. *o*-Desylthiolbenzoic acid, m.p. 189°, is transformed by alkali exclusively into *o*-benzylthiolbenzoic acid and BzOH. H. W.

***n*-Propyl and *n*-butyl gallate.** R. M. HARRIS and J. C. SMITH (J.C.S., 1935, 1220).—The binary system of Pr^c and Bu^c gallates forms a continuous series of solid solutions with α max. m.p. 153.6°, corresponding with 57% of the former ester.

P. G. C.

Synthesis of α-naphthol-2:4-dicarboxylic acid. B. K. MENON (J.C.S., 1935, 1061—1063).—Treatment of CH₂Ph·CO₂Et with OEt·CH:C(CO₂Et)₂ and NaOEt–EtOH at 0° and then, after removal of EtOH, at 150° during 2 hr. affords *Et* α-naphthol-2:4-dicarboxylate, m.p. 98° (green coloration with FeCl₃), hydrolysed to the acid (I), m.p. 304° (decomp.) (gives blue fluorescence in EtOH and green coloration with FeCl₃). CO₂Et·CHPh·CH:C(CO₂Et)₂ is an intermediate compound in the condensation. When heated with NaOH–CaO (I) yields α-C₁₀H₇·OH. (I)

dissolved in NaHCO₃–H₂O and coupled with *p*-NO₂·C₆H₄·N₂Cl affords 4-*p*-nitrobenzeneazo-α-naphthol-2-carboxylic acid, m.p. 242° (J.C.S., 1907, 91, 1260), and a compound, m.p. 262°, which may be 2-*p*-nitrobenzeneazo-α-naphthol-4-carboxylic acid. With PhN₂Cl (I) yields a compound, m.p. 212°, which may be 2-benzeneazo-α-naphthol-4-carboxylic acid. (I) with Me₂SO₄ and NaOH affords 1-methoxynaphthalene-2:4-dicarboxylic acid, m.p. 252° (decomp.) [*amide*, m.p. 198° (decomp.); *anilide*, m.p. 262° (decomp.)]. H. G. M.

Dehydrogenation of phenols. VII. Coupling by dehydrogenation of guaiacol derivatives. H. ERDTMAN (Svensk Kem. Tidskr., 1935, 47, 223—230).—Ferulic acid (4-hydroxy-3-methoxycinnamic acid) gives with FeCl₃ dehydrodiferulic acid, m.p. 202—205°, having the properties of a lactone. Vanillic acid does not yield a cryst. compound with FeCl₃. *Me* vanillate gives with Na persulphate and Fe⁺⁺Me₂ dehydrodivanillate, m.p. 231—232°, hydrolysed to divanillic acid, which is methylated to Me₂ divertrate (I). The structure of (I) is confirmed by synthesis. Vanillin with I and KI in alkaline solution gives 5-iodovanillin, m.p. 180—181.5°, methylated to 5-iodoveratraldehyde, m.p. 73—74°, oxidised to 5-iodoveratric acid, m.p. 185—186° [*Me* ester (II), m.p. 106—107°]. Cu converts (II) into Me₂ 2:3:2':3'-tetramethoxydiphenyl-5:5'-dicarboxylate, identical with (I). Vanillinoxime is dehydrogenated by FeCl₃+Na persulphate to a product converted by Ac₂O into 5:5'-dicyano-2:2'-diacetoxy-3:3'-dimethoxydiphenyl, m.p. 220—221°, identical with the product obtained by the action of Ac₂O on the dehydrogenation product of vanillonitrile and on dehydrovanillin. All these products therefore form Ph₂ derivatives by dehydrogenation of the OH to O. Gallic acid, unlike *Me* gallate, is not oxidised by air in alkaline solution to ellagic acid. E. P.

Transformation of dehydrocholic acid into β-3-hydroxy-7:12-diketocholic acid in the organism of the toad. K. YAMASAKI and K. KYOGOKU (Z. physiol. Chem., 1935, 235, 43—46; cf. this vol., 749).—The isoreductodehydrocholic acid isolated from the urine or bile of toads to which Na dehydrocholate has been administered is transformed into the semicarbazone, which is converted by NaOEt in EtOH at 180° into β-lithocholic acid (I), m.p. 177—178° after softening at 176°, [α]_D²⁰ +25.29° in EtOH (*Me* ester, m.p. 115—116° after softening at 114°). Since (I) is oxidised by CrO₃ to dehydrolithocholic acid it is β-3-hydroxy-7:12-diketocholic acid.

H. W.

Synthesis of conjugated bile acids. I. Glycocholic acid. F. CORTESE and L. BAUMAN (J. Amer. Chem. Soc., 1935, 57, 1393—1395).—Cholic acid and HCO₂H (*d* 1:2) at 50—55° give trimethylcholic acid, m.p. 206—207°, which with SOCl₂ affords the chloride, decomp. about 147°, and thence the *amide*, m.p. 187° (hydrolysed by very dil. NaOH–EtOH to cholamide, +3H₂O and +H₂O, decomp. about 115° after softening at about 107°), and with glycine a 40—60% yield of glycocholic acid, +1.5H₂O, m.p. about 130°, [α]_D²⁰ (anhyd.) +32.5° in EtOH, converted by hot H₂O into impure paraglycocholic acid. Glycodeoxy-, tauro-,

and taurodeoxy-cholic acids have been similarly obtained.

R. S. C.

Lichen pigments of the pulvinic acid series.

III. Reduction of pinastric acid and vulpinic acid. IV. Constitution of calycin and its synthesis. M. ASANO and Y. KAMEDA (Ber., 1935, 68, [B], 1565—1567, 1568—1571; cf. A., 1934, 1352).—

III. The extraction of pinastric acid (I) and pulvinic acid (II) from *Cetraria juniperina* and *C. pinastri* is described. Reduction of (I) (Zn dust, AcOH; 100°) gives Me γ -keto- α -phenyl- δ -p-anisyl-*n*-valerate, m.p. 55—56° (semicarbazone, m.p. 144—145°), identical with that obtained from synthetic material (*loc. cit.*), and a dibasic acid, C₁₉H₁₆O₆, decomp. 218°, probably *p*-methoxydihdropulvinic acid,

$\text{CO}-\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})\text{CO}_2\text{H} > \text{C}\cdot\text{OH}$. Similar reduction of (II) yields Me hydrocornicularate, m.p. 144—145° (semicarbazone, decomp. 144—145°), converted into hydrocornicularic acid, m.p. 133—134° (semicarbazone, decomp. 177—178°), and an acid, C₁₉H₁₆O₅, m.p. about 90° after softening at about 50°, probably

dihydrovulpinic acid $\text{CO}-\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})\text{CPh} > \text{C}\cdot\text{OH}$.

IV. Extraction of the thalli of *Sticta aurata*, Ach., with warm Et₂O gives pulvinic anhydride, m.p. 222—224°, and calycin (III), C₁₈H₁₀O₅, m.p. 244—245° (*Ac* derivative, m.p. 177—179°). When warmed with 50% KOH (III) affords H₂C₂O₄, CH₂Ph·CO₂H, and *o*-OH·C₆H₄·CH₂·CO₂H, and hence is *o*-hydroxypulvinic anhydride, $\text{O}-\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\text{CO}_2\text{H} > \text{CO}$.

The synthesis of (III) is effected by condensing Et₂C₂O₄ with *o*-OMe·C₆H₄·CH₂·CN in presence of NaOEt to Et cyano-*o*-methoxyphenylpyruvate, m.p. 104—105°, which on further treatment with CH₃Ph·CN affords *o*-methoxydiphenylketipinodinitrile, CN·CHPh·CO·CO·CH(CN)·C₆H₄·OMe, m.p. 262° (decomp.) after becoming discoloured at 220°, transformed by HI (*d* 1.7) in AcOH into (III). If (I) is treated with HI in AcOH and the product with boiling Ac₂O *p*-hydroxypulvinic acid diacetate, m.p. 175—177°, is obtained. Hydrolysis of (I) with Ba(OH)₂ and treatment of the product with Ac₂O and finally with HI leads to *p*-hydroxypulvinic anhydride, m.p. 298° (acetate, m.p. 213—215°), not identical with (III).

H. W.

Lichen substances. LV. Endocrocin, a new hydroxyanthraquinone derivative. Y. ASAHINA and F. FUJIKAWA (Ber., 1935, 68, [B], 1558—1565).—Extraction of the air-dried thalli of *Nephromopsis endocrocea* with hot COMe₂ yields a fatty acid, a neutral, colourless compound, and endocrocin (I), C₁₆H₁₀O₇, m.p. about 318° (decomp.) (triacetate, m.p. 212°; dibromide, m.p. 285°). Decarboxylation of (I) at 320° or in quinoline containing Cu chromite at 170—190° affords 1:6:8-trihydroxy-3-methylanthraquinone (frangula emodin), m.p. 256—257° (Br-, m.p. 278—279°, and Br₂-, m.p. 246—247°, -derivatives; triacetate, m.p. 197°; tribenzoate, m.p. 189—190°; emodic acid, decomp. about 300°, and its triacetate, m.p. 218°). Oxidation of emodin Me₃ ether (II) with CrO₃ in AcOH affords 3-methoxy-5-methyl-*o*-phthalic acid, m.p. 200° (Me₂ ester,

m.p. 86°; anhydride, m.p. 166—167°). (I) is converted by Me₂SO₄—10% NaOH into its Me₃ ether Me ester (III), m.p. 225—226°, whence endocrocin Me₃ ether, m.p. 240°, decarboxylated in quinoline containing Cu chromite to (II). Oxidation of (III) affords 3-methoxy-4-carbomethoxy-5-methyl-*o*-phthalic acid, m.p. 181° (bath preheated to 170°), converted by CH₂N₂ into Me₃ 3-methoxy-5-methylbenzene-1:2:4-tricarboxylate, m.p. 88°, hydrolysed to 3-methoxy-5-methylbenzene-1:2:4-tricarboxylic acid, m.p. 205° (bath pre-heated to 190°), which yields an anhydride, m.p. 180°. (I) is therefore 1:6:8-trihydroxy-3-methylanthraquinone-2-carboxylic acid. H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. III. Mixed halogeno- and halogenonitro-benzaldehydes. G. LOCK (Ber., 1935, 68, [B], 1505—1511; cf. A., 1934, 190).—Treatment of 2:6-C₆H₃MeBr₂ with Br at 180—200° slowly affords mainly 2:6-C₆H₃Br₂·CHBr₂, hydrolysed by H₂SO₄ (*d* 1.84) at 100° to 2:6-C₆H₃Br₂·CO₂H and 2:6-dibromobenzaldehyde, m.p. 90.5° [oxime, m.p. 153° (corr.)], which is converted by 50% KOH at 100° into *m*-C₆H₄Br₂ and HCO₂H. 2:3:6-NH₂·C₆H₃Cl₂·CHO (I) is transformed into 3:6-dichloro-2-iodobenzaldehyde, m.p. 108.5° (corr.) [oxime, m.p. 133° (corr.)], which is oxidised by Ag₂O to 3:6-dichloro-2-iodobenzoic acid, m.p. 147.5° (corr.), and converted by KOH into 2:5:1-C₆H₃Cl₃I and HCO₂H. (I) appears to be partly polymerised, but otherwise little affected by KOH, whereas 2:3:6-NO₂·C₆H₃Cl₂·CHO yields 2:5:1-C₆H₃Cl₃·NO₂ and HCO₂H. 3:2:6-NO₂·C₆H₃Cl₂·CHO is transformed by KOH into 2:4:1-C₆H₃Cl₂·NO₂. 6-Bromo-2-nitroveratraldehyde, m.p. 117.5° (corr.), from 6-bromo-2-nitrovanillin, NaHCO₃, and Me₂SO₄, is oxidised by KMnO₄ to 6-bromo-2-nitroveratric acid, m.p. 198° (corr.), and converted by 50% KOH into HCO₂H and 5-bromo-3-nitroveratrole. H. W.

Peroxide effect in the Cannizzaro reaction. M. S. KHARASCH and (MRS.) M. FOY (J. Amer. Chem. Soc., 1935, 57, 1510).—PhCHO, C₆H₄Me·CHO, and OMe·C₆H₄·CHO do not give the Cannizzaro reaction with 55% KOH with or without Fe⁺⁺⁺ unless peroxides are present or the solution is aerated. Peroxides, therefore, are the primary catalyst and the catalytic function of Fe⁺⁺⁺ is merely to hasten their formation.

R. S. C.

Chlorinated cinnamaldoximes and cinnamonitriles. K. VON AUWERS and R. HUGEL (J. pr. Chem., 1935, [ii], 143, 179—188; cf. A., 1932, 271).— α -Chloro-*cis*-cinnamaldehyde (I) (oxidised quantitatively to the *trans*-acid by AgNO₃—0.5*N*-NaOH) affords an oxime (II), m.p. 161—163° (Naar, A., 1891, 562, gives m.p. 157—159°) (*Ac* derivative, m.p. 74—76°), hydrolysed by HCl (1:1) to (I), but converted by PCl₅ in Et₂O, or by heating with Ac₂O, into α -chloro-*trans*-cinnamonitrile, identical with a specimen prepared from the *trans*-amide. With 10% KOH-EtOH (II) affords the known β -ethoxycinnamonitrile, b.p. 158—160°/12 mm. With HCl-AcOH, CPh₂·C·CHO affords β -chloro-*cis*-cinnamaldehyde, b.p. 125—126°/10 mm. (semicarbazone, m.p. 208°; phenylhydrazone, m.p. 148°; *p*-nitrophenylhydrazone, m.p. 197—199°) (oxidised to the *trans*-acid), the oxime

(III), m.p. 77–78°, of which is separated by dil. NaOH into the salt of the *cis*-anti-oxime, m.p. 107°, and (from the mother-liquor) the *cis*-syn-oxime, m.p. 94–96° after purification through its *Ac* derivative, m.p. 69.5–70.5° [(IV) is isolated from the acetylation mother-liquor]. (III) is converted by $\text{PCl}_5\text{-Et}_2\text{O}$ into β -chloro-trans-cinnamionitrile (IV), m.p. 31–33°, but hot Ac_2O affords a mixture of the *cis*- and *trans*-nitriles. With 10% KOH-EtOH (IV) gives a β -ethoxycinnamionitrile, b.p. 170°/22 mm. (configuration uncertain), converted by hot conc. HCl into $\text{COPh-CH}_2\text{-CN}$. J. W. B.

Nitration of methyl ether of salicylaldehyde. S. N. CHAKRAVARTI (Current Sci., 1935, 4, 26–28).—Nitration of $\text{o-OMe-C}_6\text{H}_4\text{-CHO}$ gives 5- and 3-nitro-2-methoxybenzaldehyde (20% yield); these are separated by crystallisation from C_6H_6 followed by fractional crystallisation of the mixed *p*-toluidides obtained from the mother-liquor. F. N. W.

Azoaldehydes. R. N. SEN and B. N. BANERJI (J. Indian Chem. Soc., 1935, 12, 293–299).—The following are prepared by the Reimer-Tiemann reaction, best with 23% NaOH and $\text{CHCl}_3\text{-EtOH}$ (1:4) (yields in parentheses below), and, in many cases, by coupling the requisite amines and aldehydes: benzeneazozaldehyde-resorcinol, m.p. 231°, *o*-cresol (4%), m.p. 76°, *thymol*, m.p. 178° (*phenylhydrazone*, m.p. 180°), and *carvacrol*, m.p. 135° (*phenylhydrazone*); benzeneazosalicylaldehyde, m.p. 127° (*phenylhydrazone*, m.p. 198°); *p*- (7%), m.p. 192–193° (*phenylhydrazone*, m.p. 235–240°), *o*- (4%), m.p. 141° (*phenylhydrazone*, m.p. 192°), and *m*-nitro- (5%), m.p. 163° (*semicarbazone*, m.p. 248°), *p*- (10%), m.p. 198° (*semicarbazone*, m.p. 300°), and *o*-chloro-benzeneazosalicylaldehyde (10%), m.p. 184° (*semicarbazone*, m.p. 259°); *p*- (8%), m.p. 147° (*semicarbazone*, m.p. 250°), and *o*-tolueneazosalicylaldehyde (8%), m.p. 120° (*semicarbazone*, m.p. 196°). Substitution depresses the yield in the Reimer-Tiemann reaction, which failed entirely with benzeneazo-*m*- and *o*-nitro- and *o*-chloro-phenol. The CHO in the products reacts only with difficulty and has little effect on the dyeing properties. Azotriphenylmethane and azopyronine dyes have been obtained from the above products. *Carvacrylaldehyde*, prepared by the Reimer-Tiemann reaction, has b.p. 237° (*semicarbazone*, m.p. 252°). R. S. C.

Bagasse. VI. Methyl and acetyl derivatives of bagasse lignin. H. HACHIYAMA and H. SAEGUSA (J. Soc. Chem. Ind. Japan, 1935, 38, 310B).—Bagasse lignin (I) on methylation ($\text{Me}_2\text{SO}_4\text{-10% NaOH}$) gives a compound with empirical formula $\text{C}_{60}\text{H}_{39}\text{O}_5(\text{OMe})_{12}$; and on acetylation ($\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$) the compound $\text{C}_{60}\text{H}_{39}\text{O}_5(\text{OAc})_5(\text{OH})(\text{OMe})_6$ is formed. The empirical formula of (I) is presumably $\text{C}_{60}\text{H}_{39}\text{O}_5(\text{OH})_6(\text{OMe})_6$. F. N. W.

Supposed isolation of a second form of $\beta\beta$ -dimethylcyclohexanone. Ring rearrangement during Clemmensen reduction. A. N. DEY and R. P. LINSTEAD (J.C.S., 1935, 1063–1065).—The reduction of dimethyldihydroresorcinol (I) by the method of Crossley *et al.* (J.C.S., 1907, 91, 63) to 3:3-dimethylcyclohexanone (II) (*semicarbazone*, m.p.

195°) and the oxidation of this to $\beta\beta$ -dimethyladipic acid have been confirmed. Clemmensen reduction of (I) affords a ketone (*semicarbazone*, m.p. 162°) isomeric with (II). Contrary to the conclusions of Khuda (A., 1933, 952), this ketone is not a second form of (II) corresponding with the other multiplanar (Sachse) form of the cyclohexane ring. It is shown to be 2:4:4-trimethylcyclopentanone (A., 1918, i, 442) by its properties and by oxidation by KMnO_4 to α -dimethylsuccinic acid, by HNO_3 to a mixture of this and $\alpha\alpha'$ -trimethylglutaric acid, and by Beckmann's mixture to γ -acetyl- $\beta\beta$ -dimethylbutyric acid identical with material synthesised (cf. A., 1929, 295) by addition of mesityl oxide to malonic ester and subsequent hydrolysis and decarboxylation of the product. The C skeleton of a diketone has therefore undergone rearrangement during Clemmensen reduction. H. G. M.

Fused carbon rings. V. Synthesis of reduced dicyclic systems. J. W. BARRETT, A. H. COOK, and R. P. LINSTEAD. VI. Optical activity connected with the presence of multiplanar rings. J. W. BARRETT and R. P. LINSTEAD (J.C.S., 1935, 1065–1069, 1069–1071; cf. this vol., 750).—V. Three methods have been examined. (a) (cf. A., 1934, 1002) Condensation of $\text{CN-CH}_2\text{-CO}_2\text{Et}$ with a cyclic ketone containing an α -aliphatic ester group, followed by reduction, hydrolysis, and cyclisation of the resulting dibasic acid. The primary condensation is inhibited by α - and α' -alkyl substituents. *Me cyclohexanone-2- β -propionate*, $\text{CN-CH}_2\text{-CO}_2\text{Me}$, and $\text{C}_5\text{H}_{11}\text{N}$ after 6 weeks at room temp. afford some cyanoacetopiperidine, m.p. 88–89°, b.p. 150–160°/1 mm., and *Me_2 cyclohexylidene-1-cyanoacetate-2- β -propionate*, b.p. 178–180°/1.5 mm., reduced by Al-Hg in moist Et_2O to *Me_2 cyclohexane-1-cyanoacetate-2- β -propionate*, b.p. 165°/1 mm., hydrolysed with conc. HCl to *cis-cyclohexane-1-acetic-2- β -propionic acid* (I) (A., 1925, i, 258) [dianilide, m.p. 165° (lit. 163°)] and a little *cis- β -decalone* [*semicarbazone*, m.p. 182–183° (decomp.) (lit., m.p. 182°)], also obtained by heating (I) at 280–300° with Ba(OH)_2 . *Et 2-methylcyclohexanone-2- and -6- β -propionates* and *Me 2-methylcyclopentanone-2- and -5- β -propionates* failed to condense with $\text{CN-CH}_2\text{-CO}_2\text{Et}$ in presence of $\text{C}_5\text{H}_{11}\text{N}$. By similar methods *Et 2-methylcyclopentanone-2-carboxylate* with $\text{CN-CH}_2\text{-CO}_2\text{Et}$ and $\text{C}_5\text{H}_{11}\text{N}$ affords a little of a condensation product, b.p. 150–157°/1 mm., reduced to the saturated CN-ester, b.p. 148–150°/1 mm., hydrolysed to *1-carboxy-1-methylcyclopentane-2-acetic acid* (probably *cis*-), m.p. 125–126°.

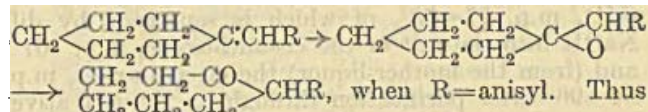
(b) Michael additions. Contrary to the statement of Kon *et al.* (A., 1927, 150), decalin-1:3-dione, m.p. 142° (cf. lit.), as prepared by them, is oxidised by NaOBr to *trans-cyclohexane-1-carboxy-2-acetic acid*, m.p. 156–157°. The oxidation by KMnO_4 to *trans-hexahydrophthalic acid* is confirmed. *Et Δ^1 -cyclopentenecarboxylate* with $\text{CH}_2\text{Ac-CO}_2\text{Et}$ and EtOH-NaOEt (steam-bath) affords *Et trans-cyclopentane-1-carboxylate-2-acetate*, b.p. 148°/16 mm. (cf. A., 1934, 1002), a little *Et trans-cyclopentane-1-carboxylate-2-acetoacetate*, b.p. 176°/16 mm., and a small amount of a solid, m.p. 64° (probably dicyclic; sol. in alkali). Similarly acetylcylohexene and

CHNaAc·CO₂Et yield *Et* trans-3-methyl-Δ²-octal-1-one-4-carboxylate b.p. 180°/9 mm. (unsaturated to KMnO₄; gives violet colour with FeCl₃), and trans-3-methyl-Δ²-octal-1-one, b.p. 110—111°/10 mm. (reduces neutral KMnO₄ immediately), reduced catalytically (Adams) to trans-3-methyl-α-decalone, b.p. 120°/8 mm. [semicarbazone (II), m.p. 203—205°], and some high-boiling auto-condensation products. (II), on distillation with KOH and a little Pd-BaSO₄, yields trans-2-methyldecalin, dehydrogenated by Se at 320—350° to 2-C₁₀H₁₆Me.

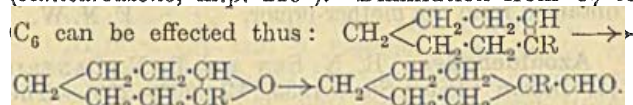
(c) cyclopentanone-2-β-propionic acid, when refluxed (6 hr.) with conc. HCl and Zn-Hg, affords cyclopentane-β-propionic acid, b.p. 131°/6 mm. [solidifies in ice; *Et* ester, b.p. 90°/9 mm.; acid chloride (III), b.p. 66°/1.5 mm.; anilide, m.p. 110°], which yielded no α-dicyclooctanone when distilled over P₂O₅. (III) and AlCl₃ in light petroleum gave only a waxy solid.

VI. *dl*-trans-cyclohexane-1:2-diacetic acid, m.p. 167°, has been resolved by means of its cinchonidine salt. The *d*-acid (IV) has m.p. 152° and [α]_D¹⁸₄₆₁ +54.9° in EtOH, and the *l*-acid (V), not quite optically pure, m.p. 148—149°, [α]_D¹⁸₄₆₁ -47.9° in EtOH. (IV) when heated at 290—300° with Ba(OH)₂, yields *l*-trans-β-hydrindanone (VI), b.p. 83°/10 mm., [α]_D¹⁸₄₆₁ -337.2° in light petroleum (b.p. 40—50°) [semicarbazone, m.p. 242—243° (decomp.), [α]_D¹⁸₄₆₁ -109.4° in AcOH, which does not depress the m.p. (243°) of the *dl*-semicarbazone]. Similarly (V) yielded *d*-trans-β-hydrindanone (semicarbazone, m.p. 241—242°, [α]_D¹⁸₄₆₁ +96.3° in AcOH). The small amounts of unchanged active acids were nearly optically pure. (VI) was reduced by Zn-Hg and AcOH-HCl by the method of Linstead *et al.* (A., 1934, 1002) to *l*-trans-hydrindane, b.p. 156°/747 mm., [α]_D¹⁹₄₆₁ -10.8° in light petroleum. *dl*-trans-cyclopentane-1:2-diacetic acid, m.p. 132°, has been resolved by means of its neutral *brucine* salt. The *l*-acid has m.p. 151°, [α]_D¹⁸₄₆₁ -63.5° in EtOH (neutral *brucine* salt, m.p. 105—108°), and the nearly pure *d*-acid has m.p. 150—151°, [α]_D¹⁹₄₆₁ +62.3° in EtOH. The former when heated at 330—350° with Ba(OH)₂ affords *d*-trans-β-0:3:3-dicyclooctanone, m.p. 41°, [α]_D¹⁸₄₆₁ +437° in light petroleum (semicarbazone, m.p. 249°, [α]_D¹⁸₄₆₁ +139.6° in AcOH, which did not depress the m.p. of the *dl*-semicarbazone). This was reduced with Zn-Hg and AcOH-HCl to trans-0:3:3-dicyclooctane (VII), m.p. -30° to -29° (alone or admixed with that prepared from the *dl*-ketone), which showed the expected absence of rotation. The m.p. recorded (this vol., 750) for (VII), *cis*-dicyclooctane, *cis*- and *trans*-β-dicyclooctanone are 5° too low. These results confirm the correctness of the configurations given by Hückel to the *cis*- and *trans*-decalins and -hydrindanes and those by Cook *et al.* (A., 1934, 1002) for the corresponding dicyclooctanes, and prove independently that both 5- and 6-membered rings can exist in multi-planar forms. H. G. M.

Molecular transpositions in cyclic hydrocarbon series. Extension and contraction of rings. M. Tiffeneau, P. Weill, J. Gutmann, and B. Tchoubar (Compt. rend., 1935, 201, 277—280).—Passage from a C₆ to a C₇ ring may be effected by the scheme:



when C₆H₁₁·MgBr and OMe·C₆H₄·CHO are combined to form cyclohexyl-*p*-anisylcarbinol, m.p. 89°, and this is dehydrated (Al₂O₃ at 280°), the resulting *p*-anisylidenecyclohexane (I), b.p. 172°/23 mm., can be converted through its epoxide, b.p. 175°/18 mm., by heating, into *p*-anisylcycloheptanone, m.p. 60° (semicarbazone, m.p. 145°). The iodohydrin derived from (I) is, on the other hand, when dehalogenated by HgO, transformed into *p*-anisylcyclohexyl-1-aldehyde (semicarbazone, m.p. 219°), which is oxidised to the -1-carboxylic acid, m.p. 178°. Benzylidenecyclohexane (A., 1934, 649) gives, however, either through its epoxide, b.p. 135°/15 mm., or through its iodohydrin, phenylcyclohexane-1-aldehyde, b.p. 144—145°/19 mm. (semicarbazone, m.p. 219°). Diminution from C₇ to



Thus phenylcycloheptene, b.p. 131—132°/16 mm., obtained from cycloheptanone and MgPhBr by way of the carbinol, forms an epoxide which when heated yields phenylcyclohexyl-1-aldehyde and phenylcycloheptanone (semicarbazone, m.p. 155°); similarly *p*-anisylcycloheptene, b.p. 170—175°/14 mm., forms an epoxide converted into *p*-anisylcyclohexyl-1-aldehyde and *p*-anisylcycloheptanone. E. W. W.

Cleavage of carbonyl compounds. I. De-oxybenzoin derivatives and phenacylsulphonic acid. T. Y. KAO and H. C. KUNG (J. Chinese Chem. Soc., 1935, 3, 213—217).—ω-Bromo- and ω-dibromo-ω-phenyl- and ω-bromo-ω-ω-diphenyl-acetophenone, and Na acetophenone-ω-sulphonate are all hydrolysed by NaOH in either EtOH or H₂O, with formation of BzOH. E. W. W.

Constitution of the methylionones. H. KOSTER (J. pr. Chem., 1935, [ii], 143, 249—252).—Fractional crystallisation of the semicarbazones of the mixture of methylionones obtained by cyclisation of methyl-β-ionone and regeneration of the ketones affords (1) α-methylionone, R·CH·CH·COEt, b.p. 125—126°/9 mm. (semicarbazone, m.p. 146°), (2) β-methylionone, R'·CH·CH·COEt, b.p. 133°/9 mm. (semicarbazone, m.p. 140°), (3) α-isomethylionone, R·CH·CMe·COMe, b.p. 121—122°/9 mm. (semicarbazone, m.p. 202°), and (4) β-isomethylionone, R'·CH·CMe·COMe, b.p. 124—125°/9 mm. (semicarbazone, m.p. 182°), where R=Δ²- and R'=Δ^{1,2}:6:6-trimethylcyclohexenyl. The structures are assigned because (1) and (2) are sol. and (3) and (4) are insol. in hot Na₂SO₃ solution, and only (3) and (4) give CHI₃ with I-NaOH.

7-Methyl-4-isopropyl-1-hydrindone. (Mrs.) O. BLUM-BERGMANN (J.C.S., 1935, 1030).—3-Bromo-*p*-cymene with activated Mg and CH(OEt)₃ in Et₂O gives 5-methyl-2-isopropylbenzaldehyde *Et*₂ acetal, b.p. 135—145°/15 mm., which is hydrolysed to the aldehyde and this condensed with CH₂(CO₂H)₂ to form 5-methyl-2-isopropylcinnamic acid, m.p. 145—146.5°. Na-Hg (4%) converts this into β-3-*p*-cymyl-

propionic acid, new m.p. 66—68.5° (cf. this vol., 75), from which the hydrindone is prepared. E. W. W.

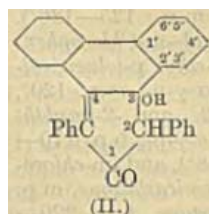
Imidochlorides. II. Condensation of benz-anilide imidochloride with substituted dialkyl-anilines in presence of anhydrous aluminium chloride. Synthesis of dialkylaminobenzo-phenones. R. C. SHAH and M. B. ICHAPORIA (J.C.S., 1935, 894—896; cf. A., 1932, 386).—In Et₂O at room temp., this condensation gives, from *m*- and *o*-C₆H₄Me·NMe₂, respectively, 4-dimethylamino-2-methyl-, b.p. 195—198°/2 mm. [oxime, m.p. 158—160°; methiodide, m.p. 163° (decomp.)], and -3-methyl-, m.p. 45°, b.p. 208—210°/12 mm. (oxime, m.p. 119°; methiodide, m.p. 184°), -benzophenone; the last is also prepared from 4-amino-3-methylbenzophenone. *p*-C₆H₄Me·NMe₂ yields 2-dimethylamino-5-methylbenzophenone, b.p. 176—178°/6 mm. (NO₂-derivative, m.p. 173—175°); *o*-C₆H₄Me·NEt₂, 4-diethylamino-3-methylbenzophenone, b.p. 214—216°/15 mm.; α -C₁₀H₇·NMe₂, 4-benzoyldimethyl- α -naphthylamine, m.p. 102—104°, b.p. 283—285°/40 mm. (oxime, m.p. 212—215°); and benzyl-methyl- and -ethyl-aniline, 4-benzyl-methyl-, m.p. 78—80°, and -ethyl-, b.p. 320—325°/40 mm. (oxime, m.p. 140—142°) -aminobenzo-phenone, respectively. E. W. W.

Abnormal reaction of an α -bromoketone. (Miss) S. N. MCGEOCH and T. S. STEVENS (J.C.S., 1935, 1032).—Ph α -bromo- β -phenylethyl ketone combines with NH₂Ph to form not only the expected Ph α -anilino- β -phenylethyl ketone, m.p. 106°, but also α -anilindibenzyl ketone, m.p. 125° (also prepared from α -bromodibenzyl ketone). The former is reduced (Zn and H₂SO₄) to CPh·CH₂·CH₂Ph, the latter to CO(CH₂Ph)₂. E. W. W.

Sulphur [compounds]. VII. Preparation and properties of some thioketones. R. W. BEST and B. O. CROSBY (J. Amer. Chem. Soc., 1935, 57, 1404—1405).—By a modification of the procedure of Staudinger *et al.* (A., 1928, 1010) are prepared Ph C₆H₄Ph, m.p. 125.7°, α -C₁₀H₇, m.p. 110°, and *p*-tolyl thioketone (I), m.p. 35°, which are monomeric and stable for 2 years, give salts with HgCl₂ and HgI₂, with hot 10% KOH-EtOH give the CO-compounds, and have absorption bands in EtOH at about 5900 Å. (I) alone gives a ppt. with SnCl₄ and is oxidised by 15% H₂O₂. R. S. C.

Unsaturated sulphur compounds. II. $\alpha\beta$ -Unsaturated ketosulphones. E. P. KOHLER and R. G. LARSEN (J. Amer. Chem. Soc., 1935, 57, 1448—1452; cf. this vol., 1115).—Ph β -benzoylvinyll sulphone (I) resembles (COPh·CH₂), in reactions and particularly in the stability of the isomerides. The stable, yellow trans-form, m.p. 114°, of (I) is changed in Et₂O in light into a colourless cis-form, m.p. 149°, from which it is re-formed by a trace of HCl in AcOH or NaOMe in MeOH; an equilibrium mixture is formed at 160°. Probably the SO₂, like CO, contributes to more complete conjugation. (I) is obtained in fair yield from CHBr₂·CH₂·COPh (1 mol.), pure PhSO₂Na (II) (1 mol.), and KOAc (slightly >1 mol.) in hot EtOH, but is better prepared by elimination of HBr, best (92%) by KOAc in MeOH at 40°, from Ph β -bromo- β -benzoyl ethyl sulphone (III), m.p. 71°, which is formed (a) slowly in 5% yield with some (I) from CH₂Br·CHBr·COPh and (II) in hot EtOH or (b) from Ph β -benzoyl ethyl sulphone (IV), m.p. 98°, and Br in CHCl₃. (IV) is prepared by adding PhSO₂H to CH₂·CH·COPh or, better (68% yield), from CH₂Cl·CH₂·COPh and (II) in hot EtOH; with warm 5% aq. KOH it yields PhSO₂H and an oil (? polymeride of COPhMe) and with NaOEt PhSO₂H and a polymeride, m.p. about 96°, of CH₂·CH·COPh. With warm Zn dust-aq. AcOH (I) gives (IV); with Br (1 mol.) in various solvents oily or solid (m.p. of an impure product 95—100°) mixtures of dibromides are formed, but successive action of Br and KOAc in AcOH yields Ph β -bromo- β -benzoylvinyll sulphone, yellow form, m.p. 105°, isomerised in Et₂O by light to a colourless form, m.p. 128°. With HBr in AcOH (I) gives at once Ph α -bromo- β -benzoyl ethyl sulphone, m.p. 135°; with KOH-MeOH at room temp. it gives Ph α -hydroxy- β -benzoyl ethyl sulphone (V), m.p. 95—100°, which dissolves with formation of a Na salt in aq. NaHCO₃, but is partly cleaved thereby to PhSO₂H and CH₂Bz·CHO, so that a NaHCO₃ solution of (V) gives the reactions of CH₂Bz·CHO and allows recovery of only 30—40% of (V) on acidification. (I) reacts with MgPhBr mainly by 1:4-addition to the CO·C·C, but some 1:2-addition also occurs; the primary product, OMgBr·CPh·CH·CHPh·SO₂Ph, however, is cleaved during reaction to CHBz·CHPh and PhSO₂·MgBr, which react further; the substances isolated are, therefore, CHPh₂·CH₂·COPh, Ph₂SO, Ph γ -hydroxy- $\gamma\gamma$ -diphenyl- Δ^2 -propenyl sulphone (VI), m.p. 193° with decomp. later, and Ph α -hydroxy- $\gamma\gamma$ -diphenylallyl sulphone (VII), m.p. 164° (decomp.). (VI) is the product of 1:2-addition to (I); (VII) is formed therefrom by allylic rearrangement, which is unusually facile; thus, in solvents an equilibrium mixture is formed from either (VI) or (VII), and (VI) is obtained by crystallisation from C₆H₆ or (VII) from MeOH or EtOH. The structures are proved thus. Hydrogenation (2 atm.; PtO₂) of (VI) in EtOAc yields Ph γ -hydroxy- $\gamma\gamma$ -diphenylpropyl sulphone, m.p. 206°, also obtained from (IV) and MgPhBr (83% yield). (VII) at 100° gives some $\gamma\gamma$ -diphenylacetaldehyde, m.p. 44° (phenylhydrazone, m.p. 173°), also obtained (53% yield) from CPh₂·CH·MgBr and CH(OEt)₃. PhSO₂H and MgPhBr are shown in a separate experiment to give Ph₂SO (and a little Ph₂S), as assumed above. R. S. C.

Heteropolarity. XXVII. Deep-coloured aromatic five-ring ketones. W. DILTHEY, I. TER HORST, and W. SCHOMMER (J. pr. Chem., 1935, [ii], 143, 189—210).—Condensation of phenanthraquinone (I) with CO(CH₂Ph)₂ and KOH-EtOH in the cold affords colourless 3-hydroxy-2:5-diphenyl-3:4-(2:2'-diphenylene)- Δ^4 -cyclopentenone (II), m.p. 226° [the compound, m.p. 102—103°, assigned this structure by Sen *et al.* (A., 1932, 272) could not be obtained] [Ac derivative, m.p. 250—251°, with decomp. to (III)], converted by hot KOH-EtOH into greenish-black 2:5-diphenyl-3:4-(2:2'-diphenylene)- Δ^2 :4-cyclopentadienone (III), m.p. 273°, which is



Δ^2 :4-cyclopentadienone (III), m.p. 273°, which is

thus the product when the initial condensation is effected with heating. When poured on ice a solution of (III) in conc. H_2SO_4 affords 2-hydroxy-2:5-diphenyl-3:4-(2:2'-diphenylene)- Δ^3 -cyclopentenone, m.p. 235—245° (decomp.), different from (II), since crystallisation from AcOH converts it into an Ac derivative, m.p. 255—256°. Addition of KOH-EtOH to a solution of (I) and $\text{CO}(\text{CH}_2\text{Ph})_2$ in boiling EtOH gives (III) and 2:5-diphenyl-3:4-(2:2'-diphenylene)- Δ^3 -cyclopentenone (IV), m.p. 314—315° (block), also obtained by reduction of (III) with red P-HI at 165°, or reduction of either (II) or (III) with Zn-AcOH. Substitution of (IV) by Br-boiling CHCl_3 or addition of $\text{Br}-\text{C}_6\text{H}_5$ to (III) affords a Br_2 -derivative (2:3- Δ^4 - or 2:5- Δ^3 -), m.p. 296—297° (decomp.). By similar types of condensation using substituted phenanthraquinones are obtained 3-hydroxy-2:5-diphenyl-3:4-(4'-nitro-2:2'-diphenylene)-, m.p. 275—276° (decomp.), -3:4-(6'-nitro-2:2'-diphenylene)-, m.p. 257—258° (decomp.), and -3:4-(4'-amino-2:2'-diphenylene)-, m.p. 254° (decomp.), - Δ^4 -cyclopentenone [all of type (II)], and (in the hot) 2:5-diphenyl-3:4-(4'-amino-2:2'-diphenylene)-, m.p. 284—285°, -3:4-(5'-amino-2:2'-diphenylene)-, m.p. 275°, and -3:4-(4'-methoxy-2:2'-diphenylene)-, m.p. 273—274°, - $\Delta^{2:4}$ -cyclopentadienone. All these compounds are halochromic and the constitution of the salts is discussed. All substituents in the phenanthraquinone nucleus have a very slight hypsochromic effect on the colour, but a definite hypsochromic effect on the H_2SO_4 -colours. Similar condensation of $\text{CO}(\text{CH}_2\text{Ph})_2$ with acenaphthenequinone gives, in the cold, 3-hydroxy-2:5-diphenyl-3:4-(1:8-naphthylene)- Δ^4 -cyclopentenone, m.p. 230—231° (slow heating), and, with hot KOH-EtOH, 2:5-diphenyl-3:4-(1:8-naphthylene)- $\Delta^{2:4}$ -cyclopentadienone, m.p. 289°, reduced by Zn-AcOH to a (?) H_2 - or H_4 -derivative, m.p. 229—230°. Similar condensation with aceanthrenequinone affords 2:5-diphenyl-3:4-(1:9-anthranylene)- $\Delta^{2:4}$ -cyclopentadienone, m.p. 284—285°. J. W. B.

Alkylation of acetoacetic ester by toluenesulphonic esters. C. N. NAIR and D. H. PEACOCK (J. Indian Chem. Soc., 1935, 12, 318—321).—*p*-Toluenesulphonic esters of alcohols $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ ($\text{R}=\text{aryl}$) (improved prep.) are used for alkylation of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$. The $\text{OPh}\cdot\text{C}_6\text{H}_4$ ester and $\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, best with NaI, in dry EtOH give a product, which (i) with KOH-EtOH leads to $\text{OPh}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ (I) and an acid, m.p. 156—157° (decomp.), or to (II), $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{H}$, and *Me* γ -phenoxypropyl ketone, m.p. 53—54° (semicarbazone, m.p. 144°; oxime, m.p. 78°), and (ii) with CH_2PhCl gives an ester, hydrolysed to γ -phenoxy- α -benzylbutyric acid, m.p. 77° (amide, m.p. 125—126°). β -p-, b.p. 178°/35 mm., m.p. 79°, and -*m*-Chlorophenoxy-, m.p. 57°, and β -2-naphthoxy-ethyl *p*-toluenesulphonate, m.p. 90°, lead similarly to γ -p-, m.p. 120°, and -*m*-chlorophenoxy-, m.p. 51—52°, and -2-naphthoxybutyric acid, m.p. 122°, and *Me* γ -p-, b.p. 170—195°/35 mm. (semicarbazone, m.p. 178°), and -*m*-chlorophenoxy-, b.p. 180—200°/35 mm. (semicarbazone, m.p. 146°), and γ -2-naphthoxypropyl ketone, b.p. 220—230°/25 mm. (semicarbazone, m.p. 174°). R. S. C.

Hydrolytic fission of aromatic ketones by acids. P. HILL and W. F. SHORT (J.C.S., 1935, 1123—1126).—The fission $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ is effected by boiling $\text{AcOH}\cdot\text{HBr}$ when an *o*-OH or -OMe is present in the Ph nucleus; it is facilitated by an *o*-Me in the Ph and retarded by NO_2 in the CH_2Ph nucleus. An *o*- or *p*-Me in the CH_2Ph accelerates decomp. 4-Hydroxy- and 4-methoxy-deoxybenzoin, 2'-methyldeoxybenzoin (from *o*-toluamide and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$), b.p. 172—173°/10 mm., m.p. about 18° (2:4-dinitrophenylhydrazones, m.p. 146—147°), 4-hydroxy-2-methyldebenzyl, and 4'-nitro-4-methoxy-2-methyldeoxybenzoin, m.p. 92—93° (from *m*-tolyl Me ether and 4-nitrophenylacetyl chloride; 4'-nitro-4-hydroxy-2-methyldeoxybenzoin, m.p. 128°, is obtained as a by-product), are stable to (or slightly decomposed by) $\text{AcOH}\cdot\text{HBr}$, which decomposes the following (%) fission in parentheses): 4-methoxy-2-methyldeoxybenzoin (semicarbazone, m.p. 165—165.5°) (100%), 4-methoxy-2:2'-dimethyldeoxybenzoin (2:4-dinitrophenylhydrazones, m.p. 188—189°) (100%), 4-methoxy-2:4'-dimethyldeoxybenzoin (2:4-dinitrophenylhydrazones, m.p. 154.5—155.5°) (100%), and 4-methoxy-2-methylacetophenone (79%). By thermal analysis of the derived xylyl alcohols, it is shown that 53% and 42%, respectively, of *o*-xylyl chloride is obtained together with the *p*-isomeride in the reaction between PhMe and $(\text{CH}_2\text{Cl})_2\text{O}$, or paraform and HCl. P. G. C.

(A) Preparation of dehydroandrosterone from cholesterol. (B) Oxidation and reduction of dehydroandrosterone. E. S. WALLIS and E. FERNHOLZ (J. Amer. Chem. Soc., 1935, 57, 1504—1506, 1511—1512; cf. this vol., 1125).—(A) Cholesteryl acetate dibromide and $\text{CrO}_3\cdot\text{AcOH}$ give dehydroandrosterone acetate (I), isolated as semicarbazone, m.p. 270° (decomp.), which with hot $\text{H}_2\text{SO}_4\cdot\text{EtOH}$ gives dehydroandrosterone (II) (benzoate, $[\alpha]_D^{20} + 26.1^\circ$ in CHCl_3), identical with the natural product. With (I) is formed 3-hydroxy- Δ^5 -cholenic acid, m.p. 236° (decomp.) [*Me* ester, m.p. 144° (*Ac* derivative, m.p. 156°, $[\alpha]_D^{20} - 18.7^\circ$ in CHCl_3), pptd. by digitonin], which is pptd. by digitonin and at 240° loses 0.5 H_2O .

(B) The testicular and corpus luteum hormones may be similarly constituted, since both are sensitive to alkali. The dibromide of (II) with CrO_3 gives Δ^4 - α -tiocholene-3:17-dione, m.p. 170° (uncorr.), $[\alpha]_D^{20} + 199^\circ$ in CHCl_3 . Hydrogenation of (II) in presence of Pd-black in EtOH gives 3-hydroxy α -tioallocholen-17-one, m.p. 172° (uncorr.), $[\alpha]_D^{20} + 88.6^\circ$ in MeOH, but in AcOH or in presence of Pt-black the CO is also reduced. R. S. C.

Sexual hormones and related substances. III. Constitution of cinchol; its transformation into 3-hydroxy α -tioallocholan-17-one. W. DIRSCHERL (Z. physiol. Chem., 1935, 235, 1—7).—Acetylation of cinchocerotin and crystallisation of the product from EtOH affords acetylcinchol (I), m.p. 132° (corr.), $[\alpha]_D^{20} - 38^\circ$ in CHCl_3 . Cinchol (II) can be pptd. by digitonin, showing that OH is attached to C-3 in the same steric arrangement as in cholesterol; recovered (II) has m.p. 140—141° (corr.). Titration of (I) with BzO_2H indicates the presence of one double linking and hydrogenation (Pd-sponge in EtOH or Et_2O) gives acetyldihydrocinchol (III), m.p. 135—136° (corr.),

$[\alpha]_D +17.8^\circ$ in CHCl_3 . Oxidation of (III) with CrO_3 affords 3-acetoxyætioallocholan-17-one, the semicarbazone, m.p. $261\text{--}262^\circ$ (corr.), of which is converted by AcOH-HCl followed by hydrolysis into 3-hydroxyætioallocholan-17-one, m.p. $176\text{--}177^\circ$ (corr.), $[\alpha]_D +88.8^\circ$ in EtOH . Dihydrocincholinol is therefore *trans-trans-trans-trans*-3-hydroxy-1'-decylætioallocholan; the suggested structure of the side-chain is $\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CHEtPr}^g$. H. W.

Benzoin reaction. II, III.—See this vol., 1084.

Manufacture of cyclic 1:2-aminoketones.—See B., 1935, 796.

Preparation of octoic acid derivatives of phenols [resorcinol].—See B., 1935, 761.

Action of diazomethane derivatives and of azides on 1:4- and 1:2-naphthaquinones. L. F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1935, 57, 1479—1482).—1:2-Naphthaquinones, unlike the 1:4-isomerides, do not react with CH_2N_2 or its derivatives, nor with azides. 1:4-Naphthaquinone and MeN_3 in $\text{EtOH-C}_6\text{H}_6$ at 105° give 1-methyl-*lm*-naphthatriazole-1:4-quinone and 1:4-naphthaquinol. 6-Bromo-1:2-naphthaquinone (I) [prep. from 1:6:2- $\text{C}_{10}\text{H}_5\text{Br}_2\cdot\text{OH}$ by way of the NO_2 -ketone or, less well, 6:2- $\text{C}_{10}\text{H}_5\text{Br}\cdot\text{OH}$, the 1-*p*-sulphobenzeneazo-dye, and 1:6:2- $\text{NH}_2\cdot\text{C}_{10}\text{H}_5\text{Br}\cdot\text{OH}$ (Ac_2 derivative, m.p. $120\text{--}121^\circ$)] with PhN_3 at 66° gives the dinaphthyldiquinhydrone, converted by reductive acetylation into 6:6'-dibromo-1:2:1':2'-tetra-acetoxy-4:4'-dinaphthyl, m.p. $226\text{--}226.5^\circ$ [also obtained directly from (I)]; it does not react with CH_2N_2 or $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ to give definite products. 1:2-Naphthaquinone behaves similarly. (I) with CPh_2N_2 in C_6H_6 at room temp. gives 6-bromo-1:2-dihydroxynaphthalene diphenylmethylene ether, m.p. $150.5\text{--}151^\circ$, and, in one experiment, a red substance, m.p. $210\text{--}210.5^\circ$. 4-Triphenylmethyl-1:2-benzoquinone and CPh_2N_2 , best in EtOH , afford similarly the corresponding diphenylmethylene ether, m.p. $258\text{--}259^\circ$, also obtained from 4-triphenylmethylpyrocatechol and CPh_2Cl_2 in C_6H_6 . 2-Diphenylmethyl-1:4-naphthaquinone does not exist in the *o*-quinonoid form, since with CH_2N_2 it affords the pyrazoline, $\text{o-C}_6\text{H}_4\text{--}\begin{matrix} \text{CO-C(CH}_2\text{Ph)}\cdot\text{N} \\ \text{CO-CH-CH}_2\text{--N} \end{matrix}$ which at the m.p., $167\text{--}168^\circ$, yields N_2 and 2-benzhydryl-3-methyl-1:4-naphthaquinone, m.p. $162\text{--}163^\circ$, reduced by Zn dust- AcOH to the quinol diacetate, m.p. $215\text{--}217^\circ$.

R. S. C.

Reaction of hydrazoic acid with naphthaquinones. L. F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1935, 57, 1482—1484).— HN_3 with 1:4- and 1:2-naphthaquinones gives the 2- and 4- NH_2 -derivatives, m.p. $204\text{--}205^\circ$ and $224\text{--}225^\circ$, respectively (cf. A., 1924, i, 1354), probably by way of the azidoquinols, which, however, cannot be isolated in this series owing to the high reducing power of naphthaquinols. Attempts to prove the mechanism failed. 2-Chloro-1:4-naphthaquinone and NaN_3 in EtOH give the 2-azide, m.p. 118° (decomp.), which is equally readily reduced at the N_3 and CO groups. *p*-Xyloquinone does not react with HN_3 , but toluquinone and *ar*-tetrahydro-1:4-naphthaquinone, like

benzoquinone, give azidoquinhydrones. 2-Methyl-1:4- and 4-methyl-1:2-naphthaquinone do not react, but 3-bromo-1:2-naphthaquinone gives the 3-bromo-4-aminoquinone.

R. S. C.

Tautomerism between diphenylmethyl-1:2-naphthaquinone and hydroxy- α -naphthafuchsone. L. F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1935, 57, 1484—1486).—1:2- $\text{C}_{10}\text{H}_6(\text{OH})_2$ (prep. from the quinone by SO_2 in hot H_2O), m.p. $(+\text{H}_2\text{O}) 56\text{--}60^\circ$, (anhyd.) $101\text{--}102^\circ$, adds CPh_2Cl_2 at 100° to yield 2-hydroxy-1:4-naphthafuchsone-I (I), m.p. $202\text{--}202.5^\circ$, which exists partly in this form, since it is sol. in NaOH and gives an acetate, m.p. $158\text{--}159^\circ$ (decomp.), *Me ether* (II) (by CH_2N_2), m.p. $177\text{--}178^\circ$, and *azine*, m.p. $263\text{--}264^\circ$, but also partly as 4-benzhydryl-1:2-naphthaquinone, since reduction gives an electromotively active system of the type characteristic of naphthaquinones. (I) and Zn-AcOH afford 1:2-dihydroxy-4-benzhydryl-naphthalene, m.p. $161\text{--}161.5^\circ$ (Ac_2 derivative, $+\text{AcOH}$, m.p. $159\text{--}161^\circ$, and anhyd., m.p. $163\text{--}164^\circ$; diphenylmethylene ether, m.p. $174\text{--}175^\circ$). (II) yields similarly 2-methoxy-4-benzhydryl-1-naphthol, m.p. $136\text{--}137.5^\circ$ (Ac derivative, m.p. $166\text{--}167^\circ$). 6:1:2- $\text{C}_{10}\text{H}_5\text{Br}(\text{OH})_2$, $+\text{H}_2\text{O}$, m.p. $88\text{--}88.5^\circ$ (Ac_2 derivative, m.p. $117\text{--}118^\circ$), yields similarly 6-bromo-2-hydroxynaphthafuchsone-1, m.p. $223\text{--}224^\circ$. α -Naphthafuchsone resembles a quinone only in its reduction products; additive reaction involving the 2:3-ethylenic linking do not occur.

R. S. C.

Degradation of naphthazarin and naphthazarin homologues by ozone. H. RAUDNITZ and F. BEHRENS (Ber., 1935, 68, [B], 1484—1487).—Ozonolysis of naphthazarin in AcOH and decomp. of the ozonide by H_2O leads to 3:6-dihydroxyphthalic acid. Similar treatment of methyl-naphthazarin (I) from methylquinol and maleic anhydride or quinol and citraconic anhydride affords 2:5-dihydroxy-6- α -diketopropylbenzoic acid, m.p. 84° ; (I) is therefore 1:4-dihydroxy-7-methyl-5:8-naphthaquinone. Dimethyl-naphthazarin analogously yields 3(?4)-methyl-6- α -diketopropylbenzoic acid, m.p. 165° . The anomalies observed in the ozonolysis of alkannin *Me* ether are due to the stable OMe.

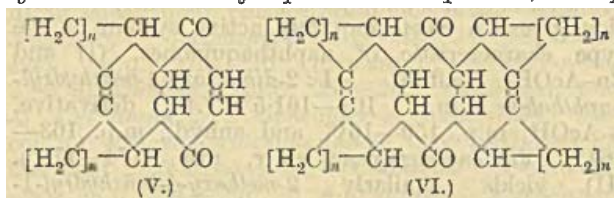
H. W.

Condensation of naphthalene with phthalic anhydride. E. DE B. BARNETT and N. R. CAMPBELL (J.C.S., 1935, 1031).—The product of this condensation (with AlCl_3 in $\text{C}_6\text{H}_2\text{Cl}_4$ at room temp.) contains *o*- β -naphthoylbenzoic acid, m.p. 166° , a powerful sternutator, which with H_3BO_3 in conc. H_2SO_4 gives 1:2-benzanthraquinone and other quinones, is reduced (Zn-Cu in alkali) to ω - β -naphthyl-*o*-toluic acid, m.p. 135° , and is readily decarboxylated by Cu chromite .

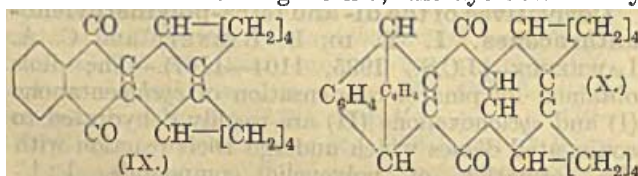
E. W. W.

Derivatives of the di- and tetra-polymethyleno-anthracenes. I. E. DE B. BARNETT and C. A. LAWRENCE (J.C.S., 1935, 1104—1107).—The diols obtained by pinacol condensation of cyclopentanone (I) and cyclohexanone (II) are readily dehydrated to conjugated dienes which undergo Diels reaction with the formation of polycyclic compounds. 1:1'-Dihydroxy-1:1'-dicyclopentyl [obtained in moderate yield by heating (water-bath) (I), Al , HgCl_2 , and C_6H_6

for 1 hr. and then for a further hr. after the addition of H_2O and more C_6H_6 (cf. lit.) when heated at $140\text{--}160^\circ$ with dehydrated alum affords crude *di- $\Delta^{1:1'}$ -cyclopentene* (III), b.p. 208° . This when warmed with maleic anhydride affords 1:2:3:6-tetrahydro-3:4:5:6-dicyclopentenophthalic anhydride, m.p. 104° , and when boiled during 1 hr. with benzoquinone (IV) and MeOH affords tetrahydro-5:6:7:8-dicyclopenteno-1:4-naphthaquinone (V, $n=3$), m.p. 124° , converted by boiling with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ into 5:8-dihydro-5:6:7:8-dicyclopentenonaphthaquinyl diacetate, m.p. 145° . (V, $n=3$) when heated with (III) affords octahydro-tetracyclopentenoanthraquinone (VI, $n=3$), m.p. 152° . (III) when boiled with α -naphthaquinone (VII) and EtOH during 1 hr. affords tetrahydro-1:2:3:4-dicyclopentenoanthraquinone, m.p.



134° , converted by boiling with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ during 3 hr. into 1:4-dihydro-1:2:3:4-dicyclopentenoanthraquinyl diacetate, m.p. 195° , and oxidised with the loss of 4H by passing air through a suspension in EtOH (+a little NaOH) to 1:2:3:4-dicyclopentenoanthraquinone, m.p. 253° . This when boiled with Zn, NaOH, NH_3 , EtOH, and H_2O during 6 hr. is reduced to 1:2:3:4-dicyclopentenoanthracene, m.p. 146° . By similar methods (II) is converted into *di- $\Delta^{1:1'}$ -cyclohexene* (VIII), m.p. 28° , b.p. $245\text{--}251^\circ$, which when heated with maleic anhydride affords dodecahydrophenanthrene-9:10-dicarboxylic anhydride, m.p. 122° , and when boiled with (IV) and EtOH during 5 hr. yields dodecahydro-5:6:7:8-dibenz-1:4-naphthaquinone (V, $n=4$), m.p. 114° , converted by boiling with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ during 2 hr. into decahydro-5:6:7:8-dibenzonaphthaquinyl diacetate, m.p. 161° . (VIII) when heated with (IV) alone yields eicositetrahydro-tetrabenzoanthraquinone (VI, $n=4$), m.p. 315° (decomp.). (VIII) when heated with (VII) affords dodecahydro-1:2:3:4-dibenzanthraquinone, m.p. 208° (decomp.), converted by boiling with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ during 2.5 hr. into decahydro-1:2:3:4-dibenzanthraquinyl diacetate, m.p. 228° , and oxidised with the loss of only 2H by passing air through a suspension in EtOH+alkali to decahydro-1:2:3:4-dibenzanthraquinone (IX), m.p. 254° . No pure product could be obtained from the interaction of (VIII) with naphthazarin, but 5:8-diacetoxydodecahydro-1:2:3:4-dibenzanthraquinone, m.p. 173° , is obtained when naphthazarin diacetate, (VIII), and PhMe are boiled during 2.5 hr.; the dye obtained by



subsequent hydrolysis and oxidation could not be purified. (V, $n=3$) when boiled with (VIII) yields

hexadecahydro-5:6:7:8-dicyclopenteno-1:2:3:4-dibenzanthraquinone, m.p. 222° . (VIII) when boiled during 1 hr. with endo-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone and xylene yields endo-9:10-*o*-phenylenetetradecahydro-1:2:3:4-dibenzonaphthacenequinone (X), m.p. $260\text{--}267^\circ$ (decomp.). Attempts to obtain purely aromatic hydrocarbons by Se dehydrogenation of some of the above derivatives of (VIII) were not successful.

By a method similar to that used for the prep. of (III), 1-ketotetrahydronaphthalene is converted into 1:1'-dihydroxy-1:2:3:4:1':2':3':4'-octahydro-1:1'-dinaphthyl, m.p. 191° , which when heated at $170\text{--}190^\circ$ with dehydrated alum yields 3:4:3':4'-tetrahydro-1:1'-dinaphthyl, m.p. 140° . This, however, did not react with (IV) or with (VII), and gave no pure product with maleic anhydride. H. G. M.

General reaction of halogen-tannins. F. ALLEGRI (Boll. Chim. Farm., 1935, 74, 555—556).—The violet-red colour given by a solution of I and tannin when poured into H_2O containing an electrolyte is not due to nascent I liberated by hydrolysis and oxidation of a labile iodotannin, as it is given also when the I is replaced by Cl or Br. T. H. P.

Chemistry of saponins. R. TSCHESCHE (Angew. Chem., 1935, 48, 569—573).—A review.

New sulphur-bacterium from thermal springs.—See this vol., 1281.

Echinone and pentaxanthin.—See this vol., 1145.

Red dye of the *Alkanna* root. K. BRAND and A. LOHMANN (Ber., 1935, 68, [B], 1487—1494).—Percolation of *Alkanna* root with light petroleum and removal of the solvent followed by extraction of the residue with abs. Et_2O gives, after removal of Et_2O , a dark red oil which is transformed by $\text{Cu}(\text{OAc})_2$ into the compound (I), $\text{C}_{21}\text{H}_{20}\text{O}_6\text{Cu}$ or $\text{C}_{20}\text{H}_{20}\text{O}_6\text{Cu}$. Treatment of (I) with 25% HCl and Et_2O affords a red oil (II) also obtained from alkannin "Merck" through the Ni compound (III) of Raudnitz *et al.* (this vol., 217). (I) and (III) are free from OMe (cf. this vol., 1254). Hydrolysis of (II) with KOH gives angelic acid in 27.5—27.8% yield. Alkannin therefore occurs in the root as a very unstable mono-ester. H. W.

Preparation of bixin. H. N. HOLMES and W. H. BROMUND (Science, 1935, 82, 202).—The prep. of cryst. bixin (I), m.p. 192° , by treatment of annatto seeds with COMe_2 is described. Traces of (I) give a blue solution with conc. H_2SO_4 . (I) is readily sol. in alkali. L. S. T.

Resinols of the latex of *Holarrhena anti-dysenterica*. J. C. CHOUDHURY and D. H. PEACOCK (J.C.S., 1935, 1129—1131).—This latex contains *lettoresinol-A* (I), $\text{C}_{28}\text{H}_{50}\text{O}_5$, m.p. $227\text{--}228^\circ$, $[\alpha]_D^{25} +68.6^\circ$ in CHCl_3 , and -B (II), $\text{C}_{32}\text{H}_{54}(\text{OH})_2$, m.p. $136\text{--}137^\circ$, $[\alpha]_D^{25} +61.1^\circ$ in CHCl_3 (Ac_2 derivative, m.p. 170° , $[\alpha]_D^{25} +71.2^\circ$ in CHCl_3), and much uncrystallisable gum. (I) is neutral, unchanged by hot KOH-EtOH, Ac_2O , or ketonic reagents, and contains no OMe. (II) is neutral and stable to hot KOH-EtOH. With CrO_3 (1—2 mols.) in AcOH (II) gives a *hydroxyketone*, $\text{C}_{32}\text{H}_{54}\text{O}_2$, m.p. 216° , isolated as *Ac* deriv-

ative, m.p. 208°, but with 3 mols. of CrO_3 a compound, $\text{CHO} \cdot \text{C}_{29}\text{H}_{49} \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix}$ or $\text{C}_{28}\text{H}_{47}\text{Ac} \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix}$, m.p. 265°, $[\alpha]_D^{25} + 90.6^\circ$ in CHCl_3 (disemicarbazone, m.p. 287°), and an acid, $\text{C}_{29}\text{H}_{49}\text{O}_2$ or $\text{C}_{28}\text{H}_{47}(\text{CO}_2\text{H})_2$, m.p. 174—175°, $[\alpha]_D^{25} + 25.3^\circ$ in CHCl_3 . R. S. C.

Bitter principles of the Colombo root. II. K. FEIST, E. KUNTZ, and R. BRACHVOGEL (Annalen, 1935, 519, 124—133; cf. this vol., 864).—Distillation of columbin (I) with Zn dust yields *o*-cresol and 1:2:5- $\text{C}_{10}\text{H}_5\text{Me}_3$. Dehydrogenation of hydrochasmanthic acid (II) with Se at 280° affords small amounts of readily volatile hydrocarbons which give cryst. derivatives with Br and a substance, $\text{C}_{15}\text{H}_{16}\text{O}_2$, m.p. 205°, also obtained similarly from hydro-*V*-columbin; at 320°, 1:2:5- $\text{C}_{10}\text{H}_5\text{Me}_3$ is produced. (I) and chasmanthin do not show absorption in the region 405—238 μ and therefore probably do not contain conjugated double linkings. (I) and KOH at 310° give 2:4- $\text{C}_6\text{H}_3\text{Me}_2\text{CO}_2\text{H}$. Oxidation of (I) or (II) with MnO_2 and H_2SO_4 yields 1:2:3- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ and 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$. *d*-Columbin, m.p. 194°, $[\alpha]_D^{25} + 37.9^\circ$ in COMe_2 , is isolated from the residue of the prep. of (I).

H. W.

1:5-endoMethylenecycloheptane-2:4-dione. P. C. GUHA and S. K. RANGANATHAN (Current Sci., 1935, 4, 26).—The *Me*, ester of cyclopentane-1:3-dicarboxylic acid, b.p. 156°/4 mm. (from *cis*-cyclopentane-1:3-dicarboxylic anhydride), with SOCl_2 gives the corresponding acid chloride, b.p. 109°/3 mm., converted by ZnMeI into *Me* 1-acetylcyclopentane-3-carboxylate, b.p. 100°/2 mm. (semicarbazone, m.p. 139°), which is hydrolysed to 1-acetylcyclopentane-3-carboxylic acid (I), b.p. 155°/5 mm. (lit. 175—205°/10 mm.) (semicarbazone, m.p. 169°), whilst reaction with $\text{NaOMe} \cdot \text{MeOH}$ gives a mixture of (I) and 1:5-endomethylenecycloheptane-2:4-dione (?), m.p. 123—5° (semicarbazone, m.p. 224°). F. N. W.

Dehydrocineoles. I. Preparation of 5-methyl-2-isopropylfuran and its condensation with maleic anhydride. L. W. BUTZ (J. Amer. Chem. Soc., 1935, 57, 1314—1315).—Oxidation (aq. KMnO_4 at about 6°) of methylheptenone gives β , γ -dihydroxy- β -methylheptan- γ -one, b.p. 138.5°/11 mm., converted by boiling 5% H_2SO_4 into β -methylheptane- γ , γ -dione, b.p. 90—92°/11 mm., which is dehydrated by conc. H_2SO_4 (at 50° and subsequent distillation) to 5-methyl-2-isopropylfuran, b.p. 135—137°/770 mm. This and maleic anhydride in cold Et_2O afford 2:3-dehydro-1:4-cineole-5:6-dicarboxylic anhydride [3:6-oxido-3-methyl-6-isopropyl- Δ^4 -tetrahydrophthalic anhydride], m.p. 77°. H. B.

Carvone series. III. Carvomenthols, l-isocarvomenthone, and l-isocarvomenthylamine. R. G. JOHNSTON and J. READ (J.C.S., 1935, 1138—1143; cf. A., 1934, 413).—Pure isomerides of this series are prepared for the first time. ≥ 2 isomerides are formed in each reaction, and these are separated before the next stage is undertaken. *d*-Carvomenthol (I), b.p. 101.8—102°/14 mm., $[\alpha]_D^{15} + 27.69^\circ$ [3:5-dinitro-, m.p. 107°, $[\alpha]_D^{15} + 52.8^\circ$, and *p*-nitrobenzoate, m.p. 60°, $[\alpha]_D^{17} + 51.7^\circ$; l-, $[\alpha]_D^{15} - 18.1^\circ$, and

d-menthoxyacetate, $[\alpha]_D^{15} + 93.4^\circ$ in CHCl_3 , oils; *d*-, a gum, $[\alpha]_D^{15} + 59.6^\circ$ in CHCl_3 , and *l*-camphor-10-sulphonate, m.p. 57—58°, $[\alpha]_D^{15} + 8.0^\circ$, decompose at 164—166° into *l*- Δ^1 -menthene (III) and the active camphor-10-sulphonic acid; $[\alpha]$ for these and other solids in CHCl_3 ; *H* phthalate, m.p. 90—91°, $[\alpha]_D^{15} + 57.8^\circ$ in EtOH , is obtained (1) from *d*-carvomenthylamine and HNO_2 (gives also a terpene fraction, b.p. 61—101°/16 mm., $\alpha_D + 0.32^\circ$), (2) as sole product of hydrogenation (colloidal Pd) of *d*-dihydrocarveol in H_2O , (3) with *l*-neoisocarvomenthol (III), $[\alpha]_D^{15} - 34.7^\circ$ (3:5-dinitro-, m.p. 71—72°, $[\alpha]_D^{15} - 16^\circ$, and *p*-nitrobenzoate, m.p. 54—55°, $[\alpha]_D^{15} - 23.7^\circ$), by hydrogenation (Pd- CaCO_3) of *d*-*cis*-carveol (IV) in MeOH , and (4) with *l*-neocarvomenthol (V) from *l*-carvomenthone (VI) and $\text{Al}(\text{OPr}^i)_3$. (V), b.p. 102°/18 mm., $[\alpha]_D^{15} - 41.70^\circ$ (*p*-nitro-, m.p. 95°, $[\alpha]_D^{15} - 22.8^\circ$, and 3:5-dinitrobenzoate, m.p. 129°, $[\alpha]_D^{15} - 22.6^\circ$; *H* phthalate, m.p. 123—124°, $[\alpha]_D^{15} - 48.7^\circ$ in EtOH), is obtained also (a) with (II) and (I) from *l*-neocarvomenthylamine (hydrochloride, $[\alpha]_D^{15} - 31.9^\circ$ in H_2O) and HNO_2 , (b) by hydrogenation (colloidal Pd) of *l*-neodihydrocarveol in H_2O , (c) with (II) by hydrogenation (colloidal Pd) of esters, best the acetate, $[\alpha]_D^{15} + 177.5^\circ$, of *d*-*trans*-carveol (VII) in Et_2O (the free alcohol gives mainly *p*-menthane with this catalyst), and (d) from (VII) with H_2 -Pd- CaCO_3 in MeOH . *dl*-*trans*-Carveol with Pd- CaCO_3 - H_2 (4 atm.) in aq. MeOH gives *dl*-neo-, an oil (*p*-nitro-, m.p. 91—92°, and 3:5-dinitrobenzoate, m.p. 101°), and *dl*-isocarvomenthol (VIII), b.p. 110°/20 mm. (3:5-dinitrobenzoate, m.p. 94.5°), and only a little hydrocarbon. Reaction (d) gives also *l*-isocarvomenthol, b.p. 106°/17 mm., $[\alpha]_D^{15} - 17.72^\circ$ (*p*-nitro-, m.p. 64.5°, $[\alpha]_D^{15} - 27.3^\circ$, and 3:5-dinitrobenzoate, m.p. 111°, $[\alpha]_D^{15} - 26.7^\circ$), further obtained from *l*-isocarvomenthylamine (IX) and HNO_2 with another alcohol, b.p. 98°/21 mm. (VIII) with Beckmann's reagent gives *l*-isocarvomenthone (cf. *loc. cit.*), $[\alpha]_D^{15} - 56.5^\circ$ [semicarbazone, m.p. 171—172°, $[\alpha]_D^{15} - 117^\circ$; with cold NaOEt is equilibrated to give 80% of (VI)], the oxime, an oil, $[\alpha]_D^{15} - 79.5^\circ$, of which with $\text{Na} \cdot \text{EtOH}$ gives (IX), b.p. 90°/15 mm., $[\alpha]_D^{15} - 14.7^\circ$ [*Bz*, m.p. 153° (lit. 151—152°), $[\alpha]_D^{15} - 40.7^\circ$, and *Ac* derivative, m.p. 96°, $[\alpha]_D^{15} - 57.4^\circ$; hydrochloride, $[\alpha]_D^{15} - 14.3^\circ$ in H_2O ; *H* *d*-tartrate, m.p. 179°, $[\alpha]_D^{15} + 5.3^\circ$ in H_2O], previously (*loc. cit.*) obtained impure by $\text{Na} \cdot \text{EtOH}$ reduction of the oxime of (VI). Oxidation (Beckmann) of (I) and (V) gives (VI). Reduction of carvone to a mixture of *cis*- and *trans*-carveol is effected better by $\text{Al}(\text{OBu}^i)_3 \cdot \text{Bu}^i\text{OH}$ than by $\text{Al}(\text{OPr}^i)_3 \cdot \text{Pr}^i\text{OH}$. Crude (VI), obtained by hydrogenation of *d*-carvone (X), is purified by treatment with NaOEt , oximation, reduction, benzylation, hydrolysis, and finally oxidation, which gives a product having b.p. 98.5°/18 mm. and $[\alpha]_D^{17} - 7.8^\circ$. The *p*-nitrobenzoates of (IV) and (VII), m.p. 28° and 77°, $[\alpha]_D^{15} - 57^\circ$ and 264° , respectively, form a const.-crystallising mixture, m.p. 84°, $[\alpha]_D^{15} + 85^\circ$. Hydrogenation of (X) with Rupe's Ni gives a mixture containing 62% of (VI). A 1:2-menthenediol, m.p. 112—114°, has been prepared. R. S. C.

Isomerisation of terpene oxides. I. Isomerisation of α -pinene oxide during Reformatsky's

reaction. B. ARBUSOV (Ber., 1935, 68, [B], 1430—1435).— α -Pinene oxide (I) is transformed by Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ into *Et* β -hydroxy- γ -2:2:3-trimethyl- Δ^3 -cyclopentenylbutyrate, b.p. 146—147°/4 mm., hydrolysed to β -hydroxy- γ -2:2:3-trimethyl- Δ^3 -cyclopentenylbutyric acid, m.p. 74—75°. The structure of the product follows from its formation from Zn, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and campholenaldehyde (II) obtained by the action of ZnBr_2 in C_6H_6 on (I). Oxidation of (II) with Ag_2O affords α -campholenic acid, b.p. 142—142.5°/10.5 mm., oxidised by KMnO_4 to dihydroxydihydrocampholenic acid, m.p. 143—144°. H. W.

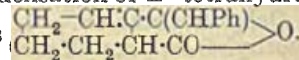
Anomalous mutarotation of salts of Reychler's acid. II. Ketimine formation from amine salts of *d*-camphor-10-sulphonic acid. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1445—1447; cf. this vol., 1118).—The salts of *d*-camphor-10-sulphonic acid (I) with NHMe_3 , m.p. 69—83°, $[\alpha] +34.6^\circ$, $+32.1^\circ$ (all $[\alpha]$ are $[\alpha]_D^{25}$ in CHCl_3 and MeOH , respectively), NMe_3 , m.p. 140—145°, $[\alpha] +33^\circ$, $+29.2^\circ$, NBu_3 , m.p. 128—138°, $[\alpha] +29.2^\circ$, $+22.8^\circ$, piperidine, m.p. 135—138°, $[\alpha] +33.3^\circ$, $+30^\circ$, NHPhMe , m.p. 113—115°, $[\alpha] +29.6^\circ$, $+29.2^\circ$, NPhMe , m.p. 137—139°, $[\alpha] +37.9^\circ$, $+27.5^\circ$, and $\text{C}_5\text{H}_5\text{N}$, m.p. 185—192°, $[\alpha] +45.8^\circ$, $+31.6^\circ$, do not mutarotate in abs. MeOH , EtOH , or CHCl_3 and are not dehydrated when heated, thus confirming their structure and the authors' views (*loc. cit.*) on the mutarotation of the salts of primary bases. The NH_2Me salt of (I), m.p. 167—168°, $[\alpha] +33.7^\circ$, $+34.6^\circ$, does not mutarotate and loses H_2O only at 180° to form the ketimine, m.p. 296—297° (block), $[\alpha]^{25} -136^\circ$ in EtOH (mutarotates slowly), but the $\text{NH}_2\cdot\text{CH}_2\text{Ph}$ salt mutarotates so rapidly that it cannot be obtained pure. 2-Benzyliminocamphane-10-sulphonic acid has m.p. 241—243°, $[\alpha] -107.5^\circ$, -112.5° . Imine formation makes a large laevo-contribution to α ; all imines, except camphoranil, m.p. 13.5°, $[\alpha] +11.5^\circ$, $+7.2^\circ$, are laevorotatory. The phenylhydrazone of (I) has $[\alpha]^{25} -185.3^\circ$ in $\text{CHCl}_3\text{-MeOH}$ (1:1). R. S. C.

Terpene compounds. II. Synthesis of homoapofenchocamphoric acid. J. C. BARDHAN, S. K. BANERJI, and M. K. BOSE (J.C.S., 1935, 1127—1129; cf. this vol., 756).—Preliminary steps in the synthesis of β -fenchocamphorone are recorded. *iso*Laurolic acid (modified prep.) and HNO_3 give α -dimethylglutaric acid, the Et_2 ester, b.p. 110—115°/9 mm., of which in $\text{Et}_2\text{O-EtOH}$ gives a K-derivative, converted by $\text{Et}_2\text{C}_2\text{O}_4$ into Et_3 γ -methylbutane- $\alpha\gamma$ -tricarboxylate, b.p. 145—148°/10 mm. This ester with Na and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ gives Et_4 β -methylpentane- $\beta\delta\epsilon$ -tetracarboxylate, b.p. 175—176°/9 mm., which with hot 19% HCl affords β -methylpentane- $\beta\delta\epsilon$ -tricarboxylic acid, m.p. 185—187°. The Et_3 ester, b.p. 159°/8 mm., thereof with "mol." Na in C_6H_6 yields Et_2 2:2-dimethylcyclopentanone-4:5-dicarboxylate, b.p. 147—149°/9 mm., affording with hot 8% H_2SO_4 2:2-dimethylcyclopentanone-4-carboxylic acid, m.p. 93°. The *Et* ester, b.p. 113°/9 mm., of the last-mentioned acid with Zn and a trace of I in C_6H_6 gives an impure OH-ester, converted by $\text{POCl}_3\text{-C}_6\text{H}_6$ into *Et* dehydrohomoapofenchocamphorate, b.p. 126—127°/4 mm., which is hydrogenated (PtO_2) in Et_2O to homo-

apofenchocamphoric acid, m.p. 246°, and a gummy acid. R. S. C.

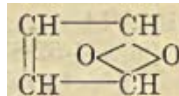
Action of acraldehyde and crotonaldehyde on alloocimene. B. ARBUSOV (Ber., 1935, 68, [B], 1435—1439).—*allo*Ocimene (I) and crotonaldehyde at 200° afford the additive product, $\text{C}_{14}\text{H}_{22}\text{O}$, b.p. 117.5—118.5°/3 mm., which with NaOEt and COMe_2 affords the substance, $\text{C}_{17}\text{H}_{26}\text{O}$, b.p. 148—150°/3 mm. Acraldehyde and (I) yield the aldehyde, $\text{C}_{13}\text{H}_{20}\text{O}$, b.p. 123—123.3°/10 mm. (*semicarbazone*, m.p. 200°), which condenses with COMe_2 to the compound, $\text{C}_{16}\text{H}_{24}\text{O}$, b.p. 144.5—146°/3.5 mm. H. W.

Hydrophthalides. VII. S. BERLINGOZZI and (SIGNA.) V. SENATORI (Gazzetta, 1935, 65, 424—440).—When benzylidenetetrahydrophthalide (I) is hydrolysed by conc. KOH , the resulting *o*-phenylacetyltetrahydrobenzoic acid (II) has m.p. 119° (A., 1932, 269). When, however, the hydrolysis is by dil. KOH in $\text{EtOH-H}_2\text{O}$, the product is an isomeride (III), m.p. 115° (*Ag* salt; *oxime*, m.p. 62°); this is a labile form, converted by conc. KOH into the stable (II). (III) is accompanied by a small quantity of 2-phenyl-1:3-diketotetrahydrohydrindene, m.p. 104°, readily prepared by action of NaOMe on (I). Oxidation (alkaline KMnO_4) of both (II) and (III) gives BzOH , with some PhCHO , and traces of $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$. Na-Hg in the cold, which is without action on (II), reduces (III) to *o*-phenylacetylhexahydrobenzoic acid (IV), m.p. 98° [*phenylhydrazone*, m.p. 50° (decomp.)], readily obtained from (II) or (III) by action of Zn and NaOH . Reduction of (II), (III), or (IV) by Na-Hg in dil. NaOH at the b.p. yields benzylhexahydrophthalide, m.p. 79°, and bis-(benzylhexahydrophthalide), $\text{C}_{30}\text{H}_{34}\text{O}_4$, m.p. 113°. From these reactions it is deduced that (III) is 2-phenylacetyl- Δ^2 -tetrahydrobenzoic acid, and (II) most probably 2-phenylacetyl- Δ^1 -tetrahydrobenzoic acid (or possibly the Δ^6 -compound). Benzylidenetetrahydrophthalide, obtained by condensation of Δ^2 -tetrahydrophthalic anhydride, is thus



E. W. W.

Catalytic oxidations. I. Oxidations in the furan series. N. A. MILAS and W. L. WALSH (J. Amer. Chem. Soc., 1935, 57, 1389—1393).—An apparatus is described whereby an easily resinified substance may be brought rapidly in a stream of gas in contact with a heated catalyst. The technique is used to investigate the effect of varying the ratio, *R*, furfuraldehyde (I): air or oxygen, H_2O content, temp., time of contact with the catalyst, and the nature of the catalyst [V_2O_5 (prep. described), Bi vanadate, $\text{Mo}_2\text{O}_3\text{-V}_2\text{O}_5$]. Only maleic acid (II) is isolated, the max. yield, 25%, being obtained at 320° with V_2O_5 and *R*—180:1 (air or oxygen, moist or dry). With V_2O_5 in dry air at 320° furan (III), furoic acid (IV), (I), and furfuryl alcohol give max. yields of 65, 48.4, 25, and 22.5% of (II) with *R*—130, 242, 180, and 180, respectively. Oxidation probably proceeds thus: (I)→(IV)→(III)→(V)→ $(\text{CH}\cdot\text{CHO})_2$ →(II).



(V.)

R. S. C.

Diphenylene oxide series. V. N. M. CULLINAN and H. J. H. PADFIELD (J.C.S., 1935, 1131—1134; cf. A., 1934, 779).—The following and other substitutions agree with an extension of Robinson's electronic mechanism for substitution of diphenylene oxide derivatives. 2-Nitrodiphenylene oxide is unchanged by SOCl_2 , but with Cl_2 in warm AcOH gives 6-chloro-2-nitrodiphenylene oxide (I). Diphenylene oxide (II) and Cl_2 (1 mol.) in AcOH give the 6-Cl- (III) and 3:6- Cl_2 -derivatives, but with 0.5 mol. of Cl_2 only (I) is formed. (III) and HNO_3 (*d* 1.5) in AcOH give (I). 2-Aminodiphenylene oxide (IV) gives (diazotization) the 2-Br-compound, which with Br in hot AcOH gives a Br_2 -derivative, m.p. 174°. Nitration of 2-chlorodiphenylene oxide gives probably 2-chloro-7-nitrodiphenylene oxide, m.p. 253°. Nitration of (IV) gives 3-nitro-2-aminodiphenylene oxide (previously considered to be the 1- NO_2 -compound), the structure of which is proved by conversion into 3-nitrodiphenylene oxide, m.p. 110°; this is reduced to the amine, which yields the known 3-Br- and 3- CO_2H -derivatives. (II) with Na-cyclohexanol or H_2 -Pt-black in AcOH gives the 1:2:3:4- H_4 -derivative (70 and 97% yield, respectively), b.p. 151°/20 mm., 270°/760 mm. (picrate, m.p. 91°), dehydrogenated to (II) by S or Se at 260° or by hot 5% KMnO_4 with or without MgSO_4 , but not by $\text{Hg}(\text{OAc})_2$. The H_2 -derivative of (II) could not be prepared by hydrogenation. PhSH and PbO at 160° give diphenylene disulphide and sulphide (thianthren), Ph_2S , and $(\text{PhS})_2$. R. S. C.

Constitution phenylbenzoxanthens and β -benzoxanthone. W. KNAPP (J. pr. Chem., 1935, [ii], 143, 210).—In an earlier thesis (1931) the author put forward views in agreement with those of Dilthey *et al.* (A., 1934, 1227). J. W. B.

Manufacture of quinones of [benznaphthofuran].—See B., 1935, 796.

β -Hydroxyethyl ethers of substituted phenols and related substances. D. C. MOTWANI and T. S. WHEELER (J.C.S., 1935, 1098—1101).—Attempts to synthesise dihydrofuranoflavones from a coumaran or a flavone were unsuccessful; numerous flavone derivatives obtained are described. Resacetophenone (I) with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, KOH, and H_2O (100°; 3 hr.) affords 2-hydroxy-4-(β -hydroxyethoxy)acetophenone (II), m.p. 106° [gives violet coloration with $\text{FeCl}_3\text{-EtOH}$; Ac_2 derivative, m.p. 70°; oxime, m.p. 144°; hydrazone, m.p. 123°; azine (III), melts at 253° to an opaque liquid becoming transparent at 263°; phenylhydrazone (IV), m.p. 148—149°; anil (V), m.p. 173°; benzidine condensation product, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CMe}\cdot\text{N}\cdot[\text{C}_6\text{H}_4]_2\cdot\text{NH}_2$, m.p. 283—290° (softens at 153°; gives a red dye when diazotised and coupled with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$); the corresponding 4-(β -acetoxyethoxy)-, m.p. 117°, and 4-(β -benzoyloxyethoxy)-, m.p. 100°, compounds give a violet coloration with $\text{FeCl}_3\text{-EtOH}$ and are sol. in alkali]. Only one OH of (I) reacts with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$. (II) is reduced by Zn-Hg-conc. HCl to 2-hydroxy-4-(β -hydroxyethoxy)ethylbenzene, m.p. 99—100°, b.p. 200—210°/5 mm. (gives blue-black coloration with $\text{FeCl}_3\text{-EtOH}$; Bz derivative, m.p. 109—110°, sol. in alkali), also obtained, together with some 2:4-di-(β -hydroxy-

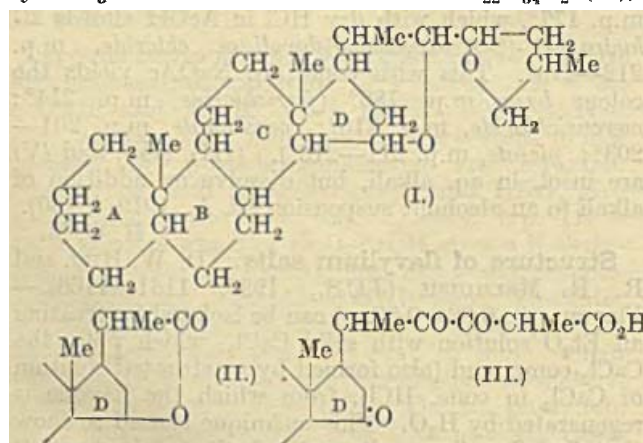
ethoxy)ethylbenzene, m.p. 66°, from the condensation of 4-ethylresorcinol with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$. Similarly *m*-methoxyphenol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, and KOH afford *m*-(β -hydroxyethoxy)anisole, b.p. 160°/2 mm. [Ac derivative, b.p. 140°/7 mm.; Bz derivative, m.p. 91—92°; chloro-ether, b.p. 130°/5 mm. (obtained on treatment with PCl_5)]. (II) with PhCHO, KOH, and EtOH affords 2-hydroxy-4-(β -hydroxyethoxy)-chalcone (VI), m.p. 123—124° [Ac_2 derivative (VII), m.p. 68°; the corresponding 4-(β -acetoxyethoxy)-chalcone has m.p. 139° (softens at 135°; violet coloration with $\text{FeCl}_3\text{-EtOH}$), which when refluxed with $\text{EtOH-H}_2\text{SO}_4$ yields 7-(β -hydroxyethoxy)flavanone, m.p. 113°. (VII) and Br in CS_2 give a Br_2 -derivative, m.p. 122°, which with NaOH-EtOH- H_2O affords 7-(β -hydroxyethoxy)flavone, m.p. 166° (Ac derivative, m.p. 130°); this when boiled with PhOH and HI (CO_2 atm.) affords 7-hydroxyflavone (cf. A., 1926, 1149). (VI) with Br in CHCl_3 yields *o*-bromo-2-hydroxy-4-(β -hydroxyethoxy)chalcone dibromide, m.p. 204° (efferv.), hydrolysed by NaOH-EtOH- H_2O to 6-bromo-7-(β -hydroxyethoxy)flavone, m.p. 206.5°, which when refluxed with PBr₅ in PhMe affords the corresponding 7-(β -bromoethoxy)flavone, m.p. 199°. (II) with *p*-anisaldehyde and KOH affords 2-hydroxy-4'-methoxy-4-(β -hydroxyethoxy)chalcone, m.p. 134° [Ac_1 derivative, m.p. 134—135° (sol. in alkali; gives violet coloration with $\text{FeCl}_3\text{-EtOH}$); Ac_2 derivative (VIII), m.p. 87—88°]. (VIII) with Br in CS_2 affords a Br_2 -compound, m.p. 105—107° (efferv.), hydrolysed to 4'-methoxy-7-(β -hydroxyethoxy)flavone, m.p. 155° [Ac derivative, m.p. 141° (efferv.)]. (II) when shaken with *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, KOH, and EtOH in an amber-coloured bottle affords 2'-nitro-2-hydroxy-4-(β -hydroxyethoxy)chalcone, m.p. 183° (turns green on exposure to light), the Ac_2 derivative, m.p. 155°, of which regenerates the original substance on hydrolysis, thus proving that the original substance is not the lactyl-ketone. Condensation of (II) with *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, KOH, and EtOH (60°; 24 hr.) affords 2:2'-dihydroxy-4-(β -hydroxyethoxy)chalcone, m.p. 177°, which with dry HCl in AcOH affords 2'-hydroxy-4'-(β -acetoxyethoxy)flavylum chloride, m.p. 212—213°. This with conc. aq. NaOAc yields the colour base, m.p. 180° (ferrichloride, m.p. 214°; mercurichloride, m.p. 215°; perchlorate, m.p. 201—203°; picrate, m.p. 211—213°). (III), (IV), and (V) are insol. in aq. alkali, but dissolve on addition of alkali to an alcoholic suspension (cf. A., 1919, i, 160).

H. G. M.

Structure of flavylum salts. D. W. HILL and R. R. MELHUSH (J.C.S., 1935, 1161—1166).—Flavones ($>0.02\text{--}0.03$ g.) can be isolated by treating an Et₂O solution with solid CaCl_2 , which ppts. the CaCl_2 -compound (also formed by a saturated solution of CaCl_2 in conc. HCl), from which the flavone is regenerated by H_2O . This technique is used to show that five flavylum salts not substituted in position 3 react with Na_2CO_3 or NaOH at room temp. to give 10% of flavones with some chalcone and (probably) a mixture of pyranols. The heteropolar atom of such flavylum salts is, therefore, C4. 3-Substituted flavylum salts, shown by H_2O_2 -oxidation to have C2 heteropolar, under similar conditions give only pyranols. 4-Flavonols from salts unsubstituted in

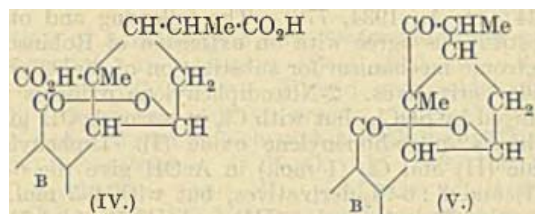
position 3 are highly unstable; they are isolated as Et ethers by NaOH-EtOH at low temp., but these ethers give salts with even a trace of acid and, although fairly stable in abs. EtOH, give chalkones quantitatively with hot aq. EtOH. 3-Substituted flavylum salts, however, give 2-flavonols by NaOAc or NaOH, and these give Et ethers with boiling EtOH; both these flavonols and their ethers are stable to hot aq. EtOH. 2-Phenyl-, m.p. 76°, and 2-anisyl-benzopyranol, m.p. 86°, 2-phenylnaphthapyranol, m.p. 131—133°, and 6- and 7-methoxy-2-phenylbenzopyranol 4-Et ethers, oils, are prepared from the corresponding flavylum chlorides and 3% NaOH in EtOH-H₂O (2:1) at room temp.; with HCl or AcOH and FeCl₃ or HClO₄ they give flavylum ferrichlorides or perchlorates, and with hot 50% EtOH the chalkones. 2-Hydroxynaphthylideneacetophenone, thus obtained, has m.p. 143—144°. 3-Methylflavylum chloride and KOH-EtOH give 2-phenyl-3-methylbenzopyranol 2-Et ether, m.p. 44°. 3-Phenylflavylum perchlorate and aq. NaOAc give 2:3-diphenylbenzo-2-pyranol, m.p. 125—126° (lit. 121—122°), converted by hot EtOH into the Et ether, m.p. 80°. 3-Methoxyflavylum perchlorate gives similarly 3-methoxy-2-phenylbenzo-2-pyranol, m.p. 122°, and its Et ether, m.p. 123°, stable to 50% aq. EtOH. Flavylum chloride, 6-, 7-, and 4'-methoxy-, and β-naphthylflavylum chloride with 10% NaOH, 5% Na₂CO₃, or (the 4'-OMe-compound) with H₂O give the corresponding flavones. 6'- and 4'-Methoxyflavone have m.p. 162° and 156°, respectively. R. S. C.

Sarsasapogenin. III. Deoxysarsasapogenin. Further degradations of sarsasapogenin. J. C. E. SIMPSON and W. A. JACOBS (J. Biol. Chem., 1935, 110, 565—573).—Sarsasapogenin in CHCl₃ is converted (with much by-product formation) by PCl₅ in CS₂ at 0° into sarsasapogenyl chloride, C₂₇H₄₃O₂Cl, m.p. 228—229°, reduced by Na and boiling C₅H₁₁·OH to deoxysarsasapogenin (I), m.p. 216—217°, oxidised by CrO₃-AcOH at 75° to a lactone C₂₂H₃₄O₂ (II),



m.p. 127—128° (hydrolysed by 0.5*N*-NaOH; lactone re-formed on acidification), which is very resistant to oxidation, and a mixture of acid products from which a cryst. Me ester is obtained with CH₂N₂. This affords, in small yield, a disemicarbazone, m.p. 239—240°, of a triketto-acid, C₂₇H₄₀O₅ (III), probably formed from (I) through the intermediate glycol.

Pyrolysis of the dibasic lactonic acid C₂₂H₃₂O₆ (IV) (this vol., 864; formula revised; the position of the



OH is probably C₁₅) at 300° (N₂) affords a ketolactone, C₂₁H₃₀O₃ (V), m.p. 200.5—202°. Hydrolysis of the CO₂Me at C₉ in the Me₂ ester of the dibasic acid C₂₇H₄₂O₆ (VI) (*loc. cit.*) is effected by 0.1*N*-NaOH-EtOH (but not by aq. alkali) to give the MeH ester, the second CO₂Me being resistant. The above side-chain structures are deduced on the basis of these new data. J. W. B.

2:4-Derivatives of thiophen. R. O. CINNEIDE (Proc. Roy. Irish Acad., 1935, 42, B, 359—363).—Thiophen-2-carboxylic acid (I) condenses with OH·CH₂·NH·CO·CH₂Cl in H₂SO₄ at 0—5° to give 4-*N*-chloroacetamidomethylthiophen-2-carboxylic acid, m.p. 153—156°, hydrolysed by boiling *N*-HCl to the hydrochloride (II), m.p. 242—245°, of 4-aminomethylthiophen-2-carboxylic acid, m.p. 292—295°, decomp. 302—305° [platinichloride, m.p. 205° (decomp.); aurichloride, m.p. 204—205°], converted by KNO₃ into the 4-hydroxymethyl acid, m.p. 115—117°. Oxidation of (II) with cold, alkaline KMnO₄ gives thiophen-2:4-dicarboxylic acid. Similar condensation of (I) with OH·CH₂·NHBz affords 4-*N*-benzamido-methylthiophen-2-carboxylic acid, m.p. 177.5—179.5° (Et ester, m.p. 90—96°), which also gives (II) when hydrolysed with HCl-EtOH at 100°. J. W. B.

Tautomerism of the system thiocoumarindiol-thiochromonediol and of ascorbic acid. F. ARNDT and B. EISTERT (Ber., 1935, 68, [B], 1572—1575).—Developments in the knowledge of the action of CH₂N₂ enable the chemistry of the thiochromonediols to be interpreted as follows. The solid diol as such is 3:4-dihydroxy-6-methyl-1-thiocoumarin (I), which, in solution, is in equilibrium with a small proportion of 2:3-dihydroxy-6-methylthiochromone (II), C₆H₃Me<CO·C(OH)S—C(OH). In (II) the 2-OH is much more acidic than OH in any other position. If sufficient time is allowed for (I) to become enolised during the action of CH₂N₂, the main product is therefore 3-hydroxy-2-methoxy-6-methylthiochromone; further methylation can then give rise only to 2:3-dimethoxy-6-methylthiochromone (III). The product obtained by partial hydrolysis of (III) or by the action of Me₂SO₄ on (I) is 4-hydroxy-3-methoxy-6-methylthiocoumarin, C₆H₃Me<C(OH)·C(OMe)S—CO, which in solution can become enolised to 2-hydroxy-3-methoxy-6-methylthiochromone, converted by CH₂N₂ predom-

inatingly into (III). If, however, (I) is introduced directly into excess of CH_2N_2 the formation of 3:4-dimethoxy-6-methyl-1-thiocoumarin is favoured. The analogy of the system with that of ascorbic acid is pointed out. Tautomerism between γ -keto- α -hydroxy- and α -keto- γ -hydroxy-forms appears restricted to systems with β -OH or β -OAlk. Thus, naphthapyronone, $\text{C}_{10}\text{H}_6\text{C}(\text{CO})\text{CH}_2$, under varied conditions is transformed by CH_2N_2 into a *Me ether*, m.p. 207—208°, also obtained by the action of MeI on the Ag salt and therefore formulated $\text{C}_{10}\text{H}_6\text{C}(\text{OMe})\text{CH}(\text{CO})$. Similarly 6-methylpyronone and CH_2N_2 afford only the ether $\text{O}(\text{CMe})\text{CH}(\text{CO})\text{C}(\text{OMe})$. H W

Sulphur compounds of technical interest.

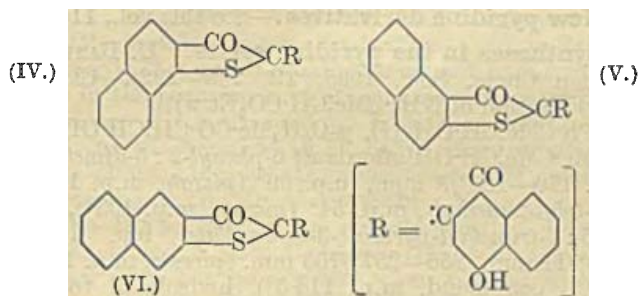
Isomeric thiophthens. F. CHALLENGER and J. B. HARRISON (J. Inst. Petroleum Tech., 1935, 21, 135—154).— C_2H_2 and S at 440° in CO_2 give CS_2 , thiophen, thionaphthen, thiopheno-2 : 3'-3 : 2-thiophen (I),

$\text{CH}(\text{CH}=\text{C}=\text{S})\text{CH}$, m.p. 56° [picrate, m.p. 145°; styphnate, m.p. 112—113°; Br_4 , m.p. 230—231°, and NO_2 -derivative (II), m.p. 124.5—125°], and a second, difficultly purifiable thiophthene (III), thiopheno-2' : 3'-2 : 3- (IV), $\text{CH}(\text{CH}=\text{C}=\text{S})\text{CH}$, or, less probably, -2' : 3'-3 : 4-thiophen, $\text{CH}(\text{CH}=\text{C}=\text{S})\text{CH}$ m.p. 6-25

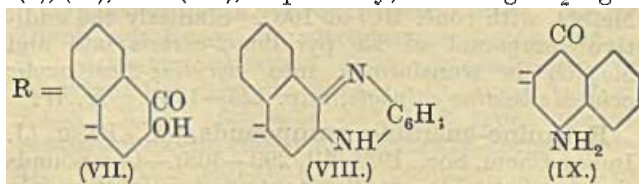
6.5°, b.p. 98°/13 mm. (picrate, m.p. 137—138°; styphnate, m.p. 127—128°; HgCl_2 , m.p. > 300°, Br_3 , m.p. 123—124°, and NO_2 -derivative, m.p. 125.5—126°). Citric acid and P_2S_3 afford (cf. A., 1886, 1032) a thiophthene (VI), m.p. 5.75—6°, b.p. 99—100°/12 mm. (picrate, m.p. 136—137°; styphnate, m.p. 129.5—130°; HgCl_2 , m.p. > 280°, Br_3 , m.p. 123—124°, and NO_2 -derivative, m.p. 122—123°; Hg dithiophthienyl, decomp. > 220°), and a ? hydroxythiophthene, $\text{C}_6\text{H}_4\text{OS}_2$, m.p. 86—87° (no picrate formed; properties of a phenol). (I) with Na-abs. EtOH affords 3-thiol-2-ethylthiophen, $\text{C}_6\text{H}_8\text{S}_2$, b.p. 195—197° (Hg salt, m.p. 75—76°), and (III) and (VI) also give mercaptans. (II) and SnCl_2 give the aminothiophthene (Ac derivative, m.p. 220.5—221.5°). (III) with AcCl and SnCl_4 in CS_2 yields thiophthienyl *Me ketone* (VII), m.p. 113° (p-nitro-, m.p. 246—247°, and 2 : 4-dinitro-phenylhydrazones, m.p. 267—268°; oxime, m.p. 172—173°), reduced (Clemmensen) to an ethylthiophthene, b.p. 120—125°/15 mm. (picrate, m.p. 70°). (VI) gives similarly a *Me ketone* (VIII), m.p. 115—116° (oxime, m.p. 160—161°; p-nitro-, m.p. 241—242°, and 2 : 4-dinitro-phenylhydrazones, m.p. 267—268°), and (I) forms the *Me ketone* (IX), m.p. 126—127° (oxime, m.p. 172—173°; p-nitro-, m.p. 246—247°, and 2 : 4-dinitro-phenylhydrazones, m.p. 267°), reduced to (? 2-) ethylthiophthene, b.p. 120°/15 mm. (impure picrate, m.p. 65°). The Grignard reagent from 2-bromothiophen and S in Et₂O give dithienyl sulphide, b.p. 155°/14.5 mm., oxidised by H_2O_2 to the sulphone, m.p. 130—131°. (IX) and its derivatives depress the m.p. of (VII) and (VIII) and their derivatives, but derivatives of (I), (III), and (VI) do not give depressions of the m.p. when mixed, nor do (VII) and (VIII)

and their derivatives. The structure of (I) is proved by its possession of a centre of symmetry (X-ray) and its zero dipole moment. The identity of (III) and (VI) is uncertain; (VI) has a dipole moment 1.16 and (III) 1.03 (possibly low owing to impurity), the former val. being in good agreement with that (1.17) calc. for (IV). R. S. C.

Indigoid dyes. VIII. P. C. DUTTA (Ber., 1935, 68, [B], 1447—1454).—In indigoid dyes ring formation with the chromophore CO in direct union with $>\text{C}:\text{C}<$ or with the auxochromes on the side remote from the ethylenic linking diminishes the chromophoric or auxochromic functions, since it somewhat diminishes the tension of the double linking of these C atoms the formation, stability, and strength of which are important factors in determining the colour. In compounds in which there scarcely exists the possibility of such ring formation from the $>\text{C}:\text{C}<$ group which would diminish the tension of the double linking of the ethylenic C atoms, or when the tension can be increased, the intensity of the colour is correspondingly increased. α -Naphthoquinone is converted by 1:2- (I), 2:1- (II), and 2:3-naphthoxythiophen (III) in EtOH containing Na_2CO_3 into 2-[1:2-naphthathiophen]- (IV), m.p. > 295°, 2-[2:1-naphthathiophen]- (V), m.p. 257°, and 2-[2:3-naphthathiophen]- (VI), m.p. 269° (Na salt), -2'-[4'-hydroxynaphthalene]indigotin. Similarly



β -naphthoquinone with (I), (II), and (III), respectively, affords 2-[1:2-naphthathiophen]-, m.p. 251—252°, 2-[2:1-naphthathiophen]-, m.p. 261°, and 2-[2:3-naphthathiophen]-, m.p. 261°, -1'-[3'-hydroxynaphthalene]indolignone (VII). Condensation of the indolignones with α - $\text{C}_6\text{H}_4(\text{NH}_2)_2$ gives the corresponding azines, $\text{C}_{28}\text{H}_{16}\text{ON}_2\text{S}$ (VIII), m.p. 268°, 264°, and 253° after softening at 244°, respectively. α -Naphtholazo-sulphanilic acid and (I), (II), and (III), respectively, in boiling EtOH- H_2O containing Na_2CO_3 give 2-[1:2-naphthathiophen]-, m.p. 261—262°, 2-[2:1-naphthathiophen]-, m.p. 235—237°, and 2-[2:3-naphthathiophen]-, m.p. > 295° after softening at 265°, -2'-[4'-amino-naphthalene]indigotin (IX). Anthraquinoneanil and (I), (II), and (III), respectively, in boiling Ac_2O give



2-[1:2-naphthathiophen]-, m.p. 241°, 2-[2:1-naphthathiophen]-, m.p. 225°, and 2-[2:3-naphthathiophen]-,

m.p. 248° after softening at 244°, -9'-anthraceneindolignone [as (IV), (V), and (VI) with $R = :C \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} CO]$.
H. W.

Action of ethylene dibromide on N-methylpiperidine. R. LUKES and O. GROSSMANN (Coll. Czech. Chem. Comm., 1935, 7, 344—354).—N-Methylpiperidine (I) heated with ethylene dibromide (II) for 2 hr. at 250° gave MeBr, NH₄Br, a portion (b.p. 110—270°) removed by steam-distillation, and a residue. The last was made alkaline and steam-distilled, the distillate converted into a mixture of hydrochlorides, from which a cryst. product, softens at 230°, m.p. 240.5°, was separated; the base with PhNCO gave N-phenyl-N'-piperidylcarbamide, m.p. 168.1°. The mother-liquors from the hydrochloride gave an impure base, b.p. chiefly 230°, which gave no well-defined salts, cryst. hydrate, nor a slightly-sol. platinichloride and did not give a satisfactory analysis (cf. Ladenburg, A., 1892, 1487). (I) and (II) heated at 45° for 5 days gave 1-methyl-1-β-bromoethylpiperidinium bromide (III), m.p. 218° (decomp.), picrate, m.p. 133°, and aurobromide, m.p. 167°. (III) heated at its decomp. point gave MeBr, piperidine, and tar; C₆H₂ and dipiperidylethane were not found. P. G. C.

Manufacture and application of reagents for the carbonyl group: hydrazidoacetpyridinium chloride.—See B., 1935, 840.

New pyridine derivatives.—See this vol., 1156.

Syntheses in the pyridine series. U. BASU (J. Indian Chem. Soc., 1935, 12, 289—292).—Claisen condensation of NH₂.CMe.CH.CO₂Et with CPh.CMe.CH.OH (I), p-C₆H₄.Me.CO.CH.CH.OH, or COMe.CMe.CH.OH affords Et 6-phenyl-2:5-dimethyl-, b.p. 170—185°/8 mm., m.p. 59° (picrate, m.p. 146°), 6-p-tolyl-2-methyl-, m.p. 54° (picrate, m.p. 133°), and 2:5:6-trimethyl-pyridine-3-carboxylate, b.p. 134—136°/11 mm., 256—257°/755 mm. (picrate, m.p. 187°; HgCl₂ compound, m.p. 118.5°), hydrolysed to the corresponding acids, m.p. 140° (decomp.), 207—208° (decomp.), and 217—218° (decomp.), respectively. Similarly, CPh.CH.CMe.NH₂ and (I) probably yield 3-benzoyl-6-p-tolyl-2-methylpyridine, an oil (picrate, m.p. 191°). R. S. C.

Methylation of pyridinecarboxylic acids. H. NIENBURG (Ber., 1935, 68, [B], 1474—1475).—The methylbetaine of 6-phenyl-2-methylpyridine-3-carboxylic acid, m.p. 240° (decomp.) after darkening (also +1H₂O) (sulphate, m.p. 223—224°; aurichloride, m.p. 160—161°), is not obtained by heating the acid with MeI and MeOH at 150° or 100°, with Me₂SO₄ at 100—130°, or by treatment of the alkaline solution of the acid with MeI or Me₂SO₄, but is readily prepared by hydrolysis of the adduct from its Et ester and Me₂SO₄ with conc. HCl at 100°. Similarly the additive compound of Et pyridine-2-carboxylate and Me₂SO₄ is transformed into pyridine-2-carboxylic acid Me betaine sulphate, m.p. 125—126°. H. W.

Ketimine-enamine compounds. U. BASU (J. Indian Chem. Soc., 1935, 12, 299—308).—Compounds showing ketimine-enamine tautomerism exist mainly in the latter form when molten or in solution, unless, in the latter case, ionisation is repressed. Thus,

CN.CH₂.CO₂Et (I) reacts with COR'.CH'.CR'.NH₂ to give COR'.CH'.CR'.NNa.CO.CH₂.CN (II) and thence an α-pyridone. Condensation with CN.CH₂.CO.NH₂ (III) or CH₂(CO.NH₂)₂ (IV) proceeds, however, by loss of NH₃ to yield COR'.CH₂.CR'.CX.CO.NH₂ (X=CN or CO.NH₂) and thence the α-pyridone. The two types of reaction yield in some cases isomeric products and the reaction mechanism of Knoevenagel *et al.* (A., 1902, i, 640) is thus disproved. NH₂.CMe.CH.COPh with (IV) at 175—180° gives 6-phenyl-4-methyl-2-pyridone-3-carboxylamide, m.p. 286—287° (hydrolysed by hot 80% H₂SO₄ to the known acid, m.p. 182°), and with (I) and NaOEt yields 3-cyano-4-phenyl-6-methyl-2-pyridone, m.p. 277°, but with CN.CH₂.CO.NHMe (V) at 150° affords 3-cyano-6-phenyl-1:4-dimethyl-2-pyridone and a little 3-cyano-6-phenyl-4-methyl-2-pyridone (VI), m.p. 310° [formed by reaction of some (V) with liberated NH₃ to yield (III) before condensation].

NH₂.CMe.CH.CO₂Et and (IV), when melted or heated in aq. EtOH with a little piperidine, give 6-hydroxy-4-methyl-2-pyridone-3-carboxylamide, m.p. 198° (decomp.), hydrolysed by fuming HCl at 150° to 2:6-dihydroxy-4-methylpyridine. Et cyclohexanone-2-carboxylate (VII), (IV), and a little piperidine in aq. EtOH or, less well, Et tetrahydroanthranilate [prep. from (VII) and NH₃] and (IV) at 190° afford 1-hydroxy-3-keto-2:3:5:6:7:8-hexahydroisoquinoline-4-carboxylamide, m.p. 183—184°, hydrolysed by HCl to 1:3-dihydroxy-Bz-tetrahydroisoquinoline. CPh.CH.CMe.NHMe does not react with (I) and NaOEt at 110° as a salt of type (II) cannot be formed, but with (III) at 125° gives (VI). R. S. C.

Preparation of histamine and its derivatives.—See B., 1935, 829.

Indole series. I. Derivatives of 2-phenylindole. N. CAMPBELL and R. C. COOPER (J.C.S., 1935, 1208—1211).—"Nitroso-2-phenylindole" (I), m.p. 280° (decomp.), is identical with 2-phenylindoloxime, is monomeric in camphor, resembles 3-methyloximino-2-phenylindolenine (II), but differs from 3-nitroso-2-phenyl-1-methylindole (III) in absorption spectrum, and thus has the oximino-structure. 2-Phenylindole (IV), therefore, reacts with HNO₂ in the indolenine form, although it reacts in the indole form with CPh₃.OH in boiling AcOH to give 2-phenyl-3-triphenylmethylindole, m.p. 212°. The general order of utility of Fischer's, Bischler's, and Madelung's indole syntheses is that given; *e.g.*, the yields of (IV) are 70, 16, and 4.5%, respectively, by these methods. Indoles are best characterised by the :N.OAc, :N.OBz-, or PhN₂-compounds, or by the :N.OH-compounds if specially purified (details given), but not well by the picrates or :CHPh derivatives. Reddelien's theory of Fischer's indole synthesis is untenable, since acetophenone-*p*- and -*o*-toluidine with NHPH.NH₂ give (IV) and not the 5- or 7-Me homologues. (I), NaOMe, and MeI in hot MeOH give (II), b.p. 193—194°/0.4 mm., m.p. 54°. 2-Phenyl-1-methylindole is obtained from distilled CPhMe.N.NPhMe, b.p. 186—192°/11 mm., m.p. 49—50°, and ZnCl₂ at 200° (2 min.), and with NaNO₂-AcOH gives (III), m.p. 144°. The following are pre-

pared. *Acetophenone-o*-, m.p. 101°, -*m*-, m.p. 81°, b.p. 214—223°/12 mm., and -*p*-tolylhydrazone, m.p. 125°. 2-*Phenyl-5*- (Fischer; 175°; 1.5 min.), m.p. 216° [*PhN*₂-, m.p. 193°, :*N*-OH-, m.p. 273° (decomp.), :*N*-OBz-, m.p. 159—160°, and :*N*-OAc-derivatives, m.p. 169.5°], -6- (Fischer, 78%, 280°, 0.5 min.; Bischler, 50%; Madelung 40%), m.p. 193° [*picrate*, m.p. 145.5°; *PhN*₂-, m.p. 177°, :*N*-OH-, m.p. 237° (decomp.), :*N*-OBz-, m.p. 142—143°, and :*N*-OAc-derivatives, m.p. 118—119°], -7- (Madelung, 40%), m.p. 117° (*PhN*₂-, m.p. 155°, :*N*-OH-, m.p. 244°, :*N*-OBz-, m.p. 163°, and :*N*-OAc-derivatives, m.p. 122.5°), and -4-methylindole (Madelung, 5.5%) [:*N*-OH-, m.p. 251° (decomp.), :*N*-OBz-, m.p. 145.5°, and :*N*-OAc-derivatives, m.p. 142°]. 3-Benzeneazo-2-phenylindole, *forms*, m.p. 137° and 165°, respectively. *Phenacyl-m-toluidine*, m.p. 110°. R. S. C.

Xanthurenic acid.—See this vol., 1268.

Manufacture of [bactericidal] azo-compounds [pyridines and quinolines].—See B., 1935, 829.

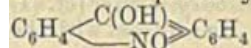
Attempts to find new antimalarials. XIII. Synthesis of ω -substituted derivatives of 8-methylquinoline. W. O. KERMACK, W. MUIR, and T. W. WRIGHT (J.C.S., 1935, 1143—1145; cf. A., 1934, 1368).—Basic derivatives of this type are prepared. 8-*Piperidinomethylquinoline*, an oil (*picrate*, m.p. 179°), is obtained from (a) *o*-aminobenzylpiperidine [Skraup, *o*-nitrobenzylpiperidine, glycerol, B(OH)₃, H₂SO₄, FeSO₄] and (b) 8-bromomethylquinoline and piperidine in hot C₆H₆. 6-*Piperidinomethylquinoline*, an oil [*picrate*, m.p. 195—196° (decomp.)], is obtained by method (a) from *p*-aminobenzylpiperidine. 8-*Diethylaminomethylquinoline*, an oil (*dihydrobromide*, m.p. 238—239°), could be obtained only by method (b), which gives also 8-*anilinomethylquinoline*, m.p. 71—73° (*dihydrobromide*), but with NH₄Et₂ and *p*-NH₂·C₆H₄·NHAc yields *di(quinolyl-8-methyl)ethylamine*, an oil (*trihydrobromide*, m.p. 202°), and *N-di(quinolyl-8-methyl)-p-aminoacetanilide*, m.p. 236—237°. R. S. C.

Quinoline derivatives. XLVI. Synthesis of 2-cyclohexylquinoline-4-carboxylic acid. LXVII. 2'- and 3'-Amino-2-phenylquinoline. H. JOHN and E. PIETSCH (J. pr. Chem., 1935, [ii], 143, 236—242, 243—248).—XLVI. Isatin when heated with cyclohexyl Me ketone (I) and aq. KOH affords 2-cyclohexylquinoline-4-carboxylic acid, m.p. 189° [*Me* (isolated as its *picrate*, m.p. 136°) and *Et* (*picrate*, m.p. 157°) esters; *hydrochloride*; *sulphate*; *nitrate*; *mercurichloride*], decarboxylated to 2-cyclohexylquinoline (*picrate*, m.p. 157°). Similar condensation of (I) with substituted isatins gives 6-*iodo-2-cyclohexyl*-, m.p. 227° (*nitrate*), and 2-cyclohexyl-6:8-dimethyl-, m.p. 206° (*hydrochloride*; *nitrate*; *sulphate*; *mercurichloride*; *ferrocyanide*), -*quinoline-4-carboxylic acid*. (I) and *o*-NH₂·C₆H₄·COMe (II) give 2-cyclohexyl-4-methylquinoline (*picrate*, m.p. 178°).

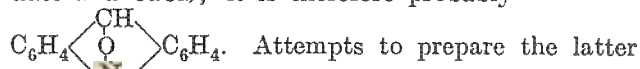
XLVII. 2'-Amino-2-phenylquinoline, m.p. 161° (*Ac*, m.p. 133°, *Ac*₂, m.p. 120°, and *carbamido*-, m.p. 210°, derivatives), is obtained by decarboxylation of its 4-carboxylic acid, m.p. 226° (*Me*, m.p. 82°, *Et*, m.p. 73°, and *Pr*^a, m.p. 87°, esters), obtained from isatin and (II). 3'-Amino-2-phenylquinoline, m.p. 122° (*Ac*₁,

m.p. 135°, *Ac*₂, m.p. 130°, and *benzylidene*, m.p. 68—70°, derivatives), and its 4-carboxylic acid, m.p. 228° (*Me*, m.p. 122°, and *Et*, m.p. 60—61°, esters), are similarly prepared. Many salts of each acid are briefly described. J. W. B.

Acridine. XII. *ms*-Acridine derivatives. III. Acridine-*N*-oxides and the "acridols." K. LEHMSTEDT (Ber., 1935, 68, [B], 1455—1464).—The product of the action of conc. H₂SO₄ on *o*-NO₂·C₆H₄·CHO in C₆H₆ has been regarded as 10-hydroxyacrid-5-one (I), but is now shown to be more probably 5-hydroxyacridine 10-oxide



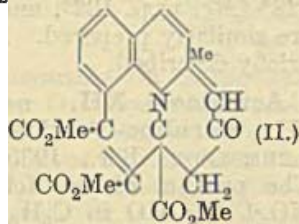
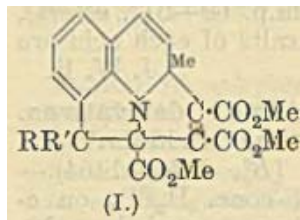
(cf. Tanasescu *et al.*, A., 1934, 1010). Thus when heated above 200° it decomposes into O₂ and acridone, a part of the gas causing further oxidation of the material. The possible linking of C and N by O is discounted by the behaviour of the material as a yellow acid dye towards cotton, by the brownish-red colour with FeCl₃, and by the production of a blue colour when it or certain of its derivatives is heated with NHPH₂ and H₂SO₄. It is remarkably stable to HCl in EtOH or HCl, whereas its *Me* or *Bz* derivative is readily transformed into 3-chloroacridone, identified by condensation with POCl₃ and NPhMe₂ to give 3-chloro-5-*p*-dimethylaminophenylacridine, m.p. 230° (1-chloro-5-*p*-dimethylaminophenylacridine has m.p. 279°). 5-Methoxyacridine (II) (+1H₂O), m.p. 103° (decomp.), anhyd. m.p. 63°, from the 5-Cl-compound and NaOMe, is stable towards Zn dust and CaCl₂ in EtOH-H₂O, so that it and its analogues cannot be intermediates in the conversion of (I) and its derivatives into acridone. (I) is oxidised by KMnO₄ in alkaline solution to the peroxide, C₂₆H₁₆O₄N₂, m.p. about 315° when plunged into a bath preheated to 220°, whereas the corresponding *Me* ether is stable. Reduction of (I) by Na-Hg at room temp. affords acridine, dihydroacridine, and a base C₁₃H₉ON (III) which gives a brown resin but no acridine when treated with Zn dust and CaCl₂; it is therefore probably



Attempts to prepare the latter substance or the acridine 10-oxide by oxidation of acridine with BzO₂H unexpectedly give the substance C₃₃H₂₂O₄N₂. On theoretical grounds it is suggested that 5-hydroxyacridine ("acridol") is incapable of existence. In this connexion it is shown that Marzin's "acridol" is discoloured acridone. Further, (II) is isomerised by heat to 10-methylacridone. NaHSO₄ is added to yield the *Na* 5-methoxy-5:10-dihydroacridine-5-sulphonate, hydrolysed to acridone. HCN transforms (II) quantitatively into 5-cyanoacridine. H. W.

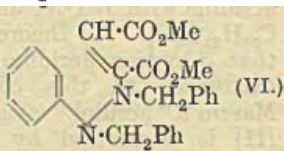
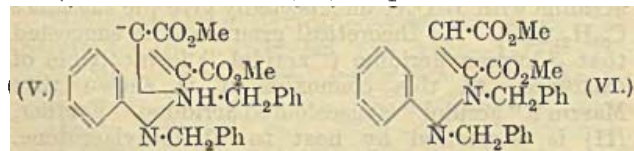
Syntheses in the hydroaromatic series. XXIV. Diene syntheses of nitrogenous hetero-rings. X. Adducts obtained from quinaldine and acetylenedicarboxylic esters. O. DIELS and H. KETCH. XXV. Adducts obtained from acetylenedicarboxylic esters and hydrazo-compounds. II. O. DIELS and J. REESE (Annalen, 1935, 519, 140—146, 147—157).—XXIV. The "stable adduct" (I) from 2-methylquinoline and (:C-CO₂Me)₂

(A., 1934, 782) is converted by nitrous fumes in AcOH into the *nitrate* of a NO_2 -compound [(I) $\text{R}=\text{NO}_2$;



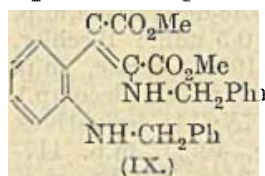
$\text{R}'=\text{CO}_2\text{Me}$], decomp. 162° , which passes under the action of H_2O into a *nitrotricarboxylic ester* [cf. (I) $\text{R}=\text{H}$; $\text{R}'=\text{NO}_2$], decomp. 224° . In contrast with the cases of $\text{C}_5\text{H}_5\text{N}$, quinoline, *isoquinoline*, and *stilbazole*, therefore, the formation of (I) is due to three-fold union of $(\text{:C}\cdot\text{CO}_2\text{Me})_2$ with the heterocyclic ring, thus explaining the differences in optical behaviour, and (I) has the structure (I) ($\text{R}=\text{H}$; $\text{R}'=\text{CO}_2\text{Me}$). The "oxidation product" of (I) has the constitution (I) ($\text{R}=\text{OH}$; $\text{R}'=\text{CO}_2\text{Me}$); it is transformed by CH_2N_2 into the *product* $\text{C}_{23}\text{H}_{23}\text{O}_9\text{N}_3$, decomp. about 167° , and an isomeric *substance*, decomp. about 157° . To the "colourless quinaldine adduct" the structure (II) is assigned. It yields a *hydrochloride*, m.p. 215° (slight decomp.), an enolic *Me ether*, m.p. 173° , and is transformed by excess of Br in CHCl_3 into the *derivative*, $\text{C}_{21}\text{H}_{16}\text{O}\cdot\text{NBr}$, decomp. 200° .

XXV (cf. A., 1934, 903). The ability to add acetylenedicarboxylic esters is a general property of hydrazo-compounds. The *adducts*, $\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_2$, m.p. 127° , from $\text{NHPh}\cdot\text{NHPh}$ and $(\text{:C}\cdot\text{CO}_2\text{Et})_2$, $\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_2$, m.p. 146° , from $(\text{:NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ and $(\text{:C}\cdot\text{CO}_2\text{Me})_2$, and $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_2$, m.p. 149° , from $\text{NHPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ and $(\text{:C}\cdot\text{CO}_2\text{Me})_2$, are described. $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NPh}\cdot\text{NH}_2$ and $(\text{:C}\cdot\text{CO}_2\text{Me})_2$ in MeOH at 0° afford the *adduct*, $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}_2$ (III), m.p. 72° , whereas when reaction occurs without cooling *Me*, 1-benzylindole-2 : 3-dicarboxylate (II), m.p. 102° [also obtained from (I) in boiling xylene], is produced. The *adducts*, $\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_2$, m.p. 87° , and $\text{C}_{27}\text{H}_{28}\text{O}_4\text{N}_2$, m.p. 158° , are derived from $(\text{:C}\cdot\text{CO}_2\text{Me})_2$ and $(\text{:NH}\cdot\text{CH}_2\text{Ph})_2$ and $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\text{Ph})_2$, respectively. $(\text{:C}\cdot\text{CO}_2\text{Me})_2$ and $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$ afford a yellow (V), m.p. 115° , and a colourless (VI), m.p. 157° , *adduct*. (V)



is readily transformed into (VI) by traces of acid. The constitutions are assigned by analogy with the corresponding compounds of the pyridine bases. Both isomerides pass when boiled in xylene into (IV), the constitution of which follows from its hydrolysis to 1-benzylindole-2 : 3-dicarboxylic acid, m.p. 198° (decomp.), decarboxylated successively to 1-benzylindole-2-carboxylic acid, decomp. 196° , and 1-benzylindole, m.p. 44° . In boiling $\text{C}_5\text{H}_5\text{N}$ (V) or (VI) passes into *Me* 2-keto-3-benzylamino-1-benzyl-1 : 2-dihydroquinoline-4-carboxylate, m.p. 191° , which is hydrolysed to the corresponding acid, m.p. 164° (decomp.) (also $+1\text{H}_2\text{O}$), decarboxylated to 2-keto-3-

benzylamino-1-benzyl-1 : 2-dihydroquinoline (VII), m.p. 174° . (VII) is transformed by boiling $\text{HBr}\cdot\text{AcOH}$ into 2-keto-3-benzylamino-1 : 2-dihydroxyquinoline, m.p. 190° , and by distillation with Zn dust



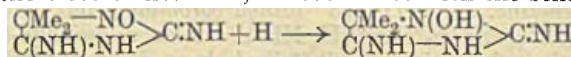
into quinoline. It is considered that the first change in these reactions is the isomerisation of (V) to (VI), followed by the formation of the (non-isolated) diamine (IX), which reacts mainly in the

cis-form to give the indole and in the *trans*-form to yield the quinoline.

H. W.

New metallic complexes of cyanogen compounds. J. V. DUBSKY, E. KRAMETZ, and J. TRTILEK (Coll. Czech. Chem. Comm., 1935, 7, 311—315; cf. A., 1933, 722).—Stable $\text{Fe}(\text{CNS})_3$, antipyrine, m.p. 185° approx., is pptd. by adding aq. FeCl_3 dropwise to cold aq. 1 : 1 (mol.) KCNS and antipyrine. $[\text{Fe}(\text{CN})_5\text{NO}]\text{Fe}(\text{OH})_4$, antipyrine is pptd. similarly from aq. 1 : 2 (mol.) $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ and antipyrine. J. G. A. G.

Redox potential of porphyraxide and porphyrindine. R. KUHN and W. FRANKE (Ber., 1935, 68, [B], 1528—1536).—Hydrogenation of porphyraxide (I) and porphyrindine (II) to their colourless leuco-compounds is instantaneously effected by *o*-, *m*-, or *p*- $\text{C}_6\text{H}_4(\text{OH})_2$, ascorbic acid, or cysteine in H_2O at $15\text{--}20^\circ$, by CH_2O , glucose, or fructose, but not mannitol or sucrose in warm solution containing Na_2CO_3 . HCO_2Na in warm solution containing Na_2CO_3 decolorises (II) but not (I), whereas $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na}$, $(\text{CH}_2\cdot\text{CO}_2\text{Na})_2$, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Na}$, and Na oleate are ineffective. Potentiometric titration of (I) using *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ over the investigated p_{H} region establishes the electron no. $n-1$, in accordance with the scheme :



Results for (II) are less decisive, but at $6.5\text{--}7.5$ n is approx. 1, increasing in the acid and diminishing in the alkaline region. The formation of a mono-radical appears very unlikely. The normal potential of (I) and (II) is much $>$ that of any org. dye hitherto examined, and they partly fill the gap between O and *p*-benzoquinone. Unless undefined catalytic influences are involved, NO appears a less active oxidising agent than either of the org. radicals. In the prep. of (I) the conversion of $\text{CMe}_2\text{N}\cdot\text{OH}$ into $\text{OH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CN}$, m.p. 99° , is best effected with 70% HCN . $\text{OH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{C}(\text{NH})\cdot\text{OEt}$, 2HCl , m.p. 200° (decomp.) [lit. m.p. 108° (decomp.)], is transformed into $\text{OH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HCl}$, gradual decomp. $140\text{--}240^\circ$ [lit., m.p. 154° (decomp.)], by excess of $\text{NH}_3\cdot\text{EtOH}$; this is oxidised by Cl_2 in $\text{HCl}\cdot\text{H}_2\text{O}$ to $\text{NO}\cdot\text{CMe}_2\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$ (VI). For the transformation of (III) into (I) by $\text{KCN}\cdot\text{H}_2\text{O}$ the temp. $55\text{--}60^\circ$ must be maintained.

H. W.

Manufacture of alkylated 5-phenyl-3-ethylhydantoins.—See B., 1935, 830.

1 : 1'-Dimethyl-2 : 3'-dipiperidyl. R. LUKEŠ and O. GROSSMANN (Coll. Czech. Chem. Comm., 1935, 7, 336—343).—Analysis of the mixed bases, b.p. $128.5\text{--}131^\circ/11.8$ mm., liberated by alkali from the

product of hydrogenation (PtO_2 and Ac_2O at $45\text{--}50^\circ/1.3$ atm.) of 2:3'-dipyridyl methosulphate indicated incomplete methylation. The mixture gave a picrate, m.p. 214° , in approx. 50% yield, incompletely converted into a mixture of mono- and di-benzoate, from which a base, b.p. $136^\circ/20$ mm., was obtained; analysis of its picrate, m.p. 191° , suggested that the base was *N*-methylpiperidyl. Methylation of its syrupy hydrochloride with paraformaldehyde gave 1:1'-dimethyl-2:3'-dipiperidyl, b.p. $159^\circ/20$ mm. [picrate, m.p. 210° ; platinichloride, m.p. $252\text{--}255^\circ$; aurichloride, m.p. 216° (decomp.), darkens 212°]. It is not identical with Ladenburg's dimethylpiperidyl (A., 1892, 1487), or the product obtained by electrolytic reduction of glutamethylimide (cf. A., 1933, 512).

P. G. C.

Synthesis of C-substituted pyridylpyrrole derivatives. E. OCHIAI, K. TSUDA, and S. IKUMA (Ber., 1935, 68, [B], 1551—1555).—Et 2-picolylacetate (I) and *p*-nitrophenylhydrazine in dil. AcOH afford 1-*p*-nitrophenyl-3:2'-pyridylpyrazolone, m.p. 169° . Condensation of (I) with CMeAc:N:OH proceeds with difficulty, and reduction of the mixture with Zn dust and 75% AcOH gives tetramethylpyrazine (II) and Et β -hydroxy- β -2-pyridylpropionate, b.p. $115\text{--}117^\circ/0.003$ mm., m.p. $35\text{--}37^\circ$. Condensation of (I) with $\text{NH}_2\text{CHMeCOMe.HCl}$ in 75% AcOH yields (II) and Et 5:2'-pyridyl-2:3-dimethylpyrrole-4-carboxylate, m.p. $76\text{--}77^\circ$ (picrate, m.p. 219°). The Na derivative of (I) is transformed by NaNO_2 in AcOH into Et α -oximino-2-picolylacetate (III), m.p. $142\text{--}143^\circ$, which is reduced by Zn dust and 75% AcOH in presence of $\text{CH}_2\text{Ac.CO}_2\text{Et}$ to Et, 4:2'-pyridyl-2-methylpyrrole-3:5-dicarboxylate, m.p. 129° (perchlorate, m.p. $212\text{--}213^\circ$; picrate, m.p. 165° ; styphnate, decomp. $210\text{--}211^\circ$), hydrolysed and decarboxylated by conc. H_2SO_4 at 100° to 4:2'-pyridyl-2-methylpyrrole, m.p. 93° (perchlorate, m.p. $191\text{--}192^\circ$). (III) and CH_2Ac_2 similarly afford Et 3-acetyl-4:2'-pyridyl-2-methylpyrrole-5-carboxylate ($+\text{H}_2\text{O}$), m.p. 117° after softening at about 113° (picrate, m.p. 201° ; perchlorate, m.p. 159° ; semicarbazone, decomp. 243°), hydrolysed to 3-acetyl-4:2'-pyridyl-2-methylpyrrole-5-carboxylic acid, decomp. 233° , whence 3-acetyl-4:2'-pyridyl-2-methylpyrrole, m.p. 198° (perchlorate, m.p. 171°).

H. W.

Piperazine. V. Compounds from *N*-phenylpiperazine and derivatives of chloroacetic acid. D. E. ADELSON and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1430—1431; cf. this vol., 1133).—*N*-Phenylpiperazine (I), $\text{CH}_2\text{Cl.CO}_2\text{R}$, and Na_2CO_3 in EtOH give 65—75% yields of *Me*, b.p. $175\text{--}177^\circ$ (dihydrochloride), Et (II), b.p. $194\text{--}195^\circ$ (sulphate; dihydrochloride), *Pr*, b.p. $185\text{--}186^\circ$ (dihydrochloride), and *Bu* *N*-phenylpiperazine-*N'*-acetate, b.p. $218\text{--}220^\circ$ (slight decomp.), m.p. $54\text{--}54.5^\circ$. (II) and conc. aq. NH_3 yield the *N'*-acetamide, m.p. $169\text{--}170^\circ$, also obtained from (I) and $\text{CH}_2\text{Cl.CO.NH}_2$. The *N'*-acetonitrile, m.p. $65\text{--}65.5^\circ$, is prepared from (I) by $\text{CH}_2(\text{OMe})_2$ and HCN (40% yield) or $\text{CH}_2\text{Cl.CN}$ and Na_2CO_3 in C_6H_{14} (70% yield). (II) with $\text{Na-Bu}^\circ\text{OH}$ gives the *N'*-OH- CH_2CH_2 derivative (35%), m.p. $82.5\text{--}83^\circ$, and the *Na N'*-acetate, cryst., also obtained quantitatively from (I), $\text{CH}_2\text{Cl.CO}_2\text{Na}$, and Na_2CO_3 in H_2O .

R. S. C.

Reaction of certain diazo-sulphonates from 2-naphthol-1-sulphonic acid. XII. Preparation of phthalazine, phthalazone, and phthalamidine derivatives of 2-bromo-4-nitroaniline. F. M. ROWE, G. B. JAMBUSERWALA, and H. W. PARTRIDGE (J.C.S., 1935, 1134—1137; cf. A., 1933, 1059).—The reactions described below show only minor differences from those usual in this series. 2-Bromo-4-nitroaniline (improved prep., also suitable for chloroxylenols; 90.2% yield), when diazotised and treated with Na β -naphthol-1-sulphonate, gives *H Na* 3-(2'-bromo-4'-nitrophenyl)-3:4-dihydrophthalazine-1-sulphonate-4-acetate, decomp. $234\text{--}236^\circ$, converted by hot HCl into 1-hydroxy-3-(2'-bromo-4'-nitrophenyl)-3:4-dihydrophthalazine-4-acetic acid (I), m.p. 235° (*Me*, m.p. 179° , and *Et* ester, m.p. 178° ; *Ac* derivative, m.p. 121° ; anilide, m.p. 207°). (I) affords 2'-bromo-4'-nitro-3-phenylphthalaz-1-one, m.p. 197° (decomp.) (gives only resins when methylated), and with $\text{K}_2\text{Cr}_2\text{O}_7$ in conc. H_2SO_4 yields 2'-bromo-4'-nitro-3-phenyl-4-methylphthalaz-1-one, m.p. 225° , which does not react with picric acid and gives oils when methylated. (I) is best reduced in acid solution (SnCl_2), giving the 4'- NH_2 -acid (II), m.p. $233\text{--}234^\circ$ (*Ac* derivative, m.p. 205°), the hydrochloride of which is so insol. in conc. HCl as to be unchanged even when boiled therein, but which is readily converted by hot aq. H_2SO_4 into 2'-bromo-4'-amino-3-phenylphthalaz-1-one (III), m.p. 242° . (III) with Zn dust and HCl gives according to the conditions poor yields of 2'-bromo-4'-amino-*N*-phenylphthalimidine, $+\text{EtOH}$, m.p. (anhyd.) 178° (also obtained from 2':6'-dibromo-4'-amino-3-phenylphthalaz-1-one), or 4'-amino-*N*-phenylphthalimidine, m.p. 198° , but in all cases fission predominates. 1-Keto-3-(2'-bromo-4'-nitrophenyl)-2-methyltetrahydrophthalazine-4-acetic acid has m.p. 229° (*Me* ester, m.p. $212\text{--}213^\circ$). Ring-closure of *o*-carboxyacetophenone-2'-bromo-4'-nitrophenylhydraz-1-one, m.p. $152\text{--}154^\circ$, does not occur in hot EtOH, AcOH, or PhNO_2 , but is effected by hot Ac_2O - $\text{C}_6\text{H}_5\text{N}$ and affords 2'-bromo-4'-nitro-3-phenyl-1-methylphthalaz-4-one, m.p. $200\text{--}202^\circ$. (II) with $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 , hot 10% KOH, or Na_2S yields 2'-bromo-4'-amino-3-phenyl-4-methylphthalaz-1-one, $+\text{EtOH}$, m.p. $279\text{--}280^\circ$, and $+\text{xEtOAc}$, which with Zn dust and HCl gives probably impure 1-keto-3-(2'-bromo-4'-aminophenyl)-4-methyltetrahydrophthalazine, m.p. $211\text{--}212^\circ$.

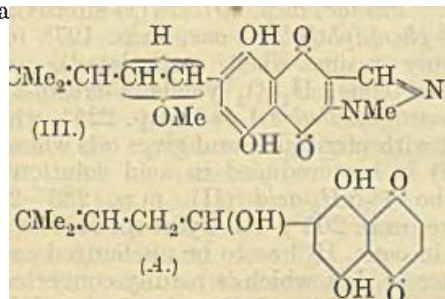
R. S. C.

Heteropolar compounds: complex salts of silver and mercury with 4-hydroxy-2-thion-1:2:3:4-tetrahydroquinazoline. C. GHEORGHIU and (MLLE.) L. MANOLESCU (Compt. rend., 1935, 201, 78—80; cf. this vol., 630).—4-Ethoxy-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline (I) with HgX_2 ($\text{X}=\text{Cl}$, Br , I) gives colourless complexes which yield yellow solutions when warmed, and at a high temp. lose EtOH to give insol. yellow compounds. (I) with AgNO_3 gives a colourless solution which is converted by HClO_4 and HCl into slightly coloured solutions, which when warmed to 100° give intensely coloured solutions. Structures are proposed for these coloured compounds.

F. R. G.

Addition of $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene and diazomethane to alkannin methyl ether; con-

stitution of alkannin. H. RAUDNITZ and W. STEIN (Ber., 1935, 68, [B], 1479—1484).—The product obtained by decomp. of the Ni salt of alkannin by HCl-MeOH (cf. this vol., 217) is now recognised as alkannin Me ether (I). Alkannin (II), m.p. 147°, is obtained if AcOH is used. Treatment of (II) with β - γ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene in boiling EtOH yields an *adduct*, $C_{23}H_{28}O_5$, m.p. 159°, oxidised by air in alkaline solution to a product which, by reason of elementary analysis, freedom from OMe, and spectroscopic behaviour, is regarded as 6:7-dimethyl-2- δ -methyl- $\Delta^{\alpha\gamma}$ -pentadienylquinizarin, m.p. 216°. (I) and excess of CH_3N_2 in MeOH slowly afford 5:8-dihydroxy-1-N-methyl-6(7)- α (β)-methoxy- δ -methyl- Δ^{γ} -pentenyl-lin-naphthaindazole-4:9-quinone (III), m.p. 139°. (II) has therefore the constitution (A) or the tautomeric formula



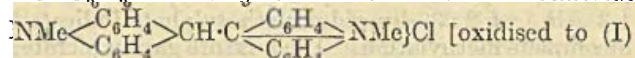
H. W.

Dianthraquinonylguanidines. M. BATTEGAY and E. RIESZ (Compt. rend., 1935, 200, 2019—2021).— β -Anthraquinonylguanidine with 1-chloroanthraquinone (I) in boiling $PhNO_2$ containing Na_2CO_3 or $NaOAc$ and some Cu gives a dianthraquinonylguanidine which cyclises to *py-C- β -anthraquinonylamino-1:9-pyrimidineanthrone*, m.p. about 340°. Similarly, *py-C- α -anthraquinonylamino-1:9-pyrimidineanthrone*. 2-Aminoanthraquinone with $CNBr$ in NO_2Ph at 170° gives *di- $\beta\beta'$ -anthraquinonylguanidine*, m.p. about 260° (*hydrobromide*; *sulphate*; *Bz* and *Bz*₃ derivatives) (which is converted by HNO_2 into a carbamide), and a polymerised *Br*-compound, m.p. about 215°. The I-isomeride reacts similarly, but forms more of the polymeride. J. L. D.

Diacridyl and its derived radicals and luminescent salts, luzigenin salts. H. DECKER and W. PETSCH (J. pr. Chem., 1935, [ii], 143, 211—235).—The chemiluminescent reactions of *NN'*-dimethyldiacridylium (now called luzigenin) salts (I) (Gleu *et al.*, this vol., 281), of its related compounds, and of the derived free radicals are described and discussed in relation to structure, and nomenclature (used below) is suggested. *NN'*-Dimethyldiacridylium nitrate (II) (A., 1909, i, 433) is converted by conc. aq. KBr into the *bromide* (III), which with KCN affords 9:9'-*dicyanodiacridane* (diacridane=9:10:9':10'-tetrahydrodiacridyl). By the action of Zn on (III) or by reduction (Zn-AcOH) of *N*-methylacridone (A., 1906, i, 901) is obtained *dimethyldiacridene*,

$NMe \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle C:$ (IV), m.p. 385°, decomp. 390° (corr.), which is stable to air or to reduction in acid or alkaline solution. (IV) is an en-onium conjugated pseudo-base converted (loss of fluorescence) by

$HCl-C_6H_6$ into *methylacridan-acridinium methochloride*



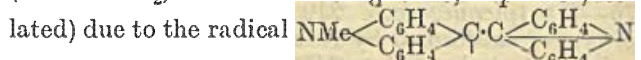
with chemiluminescence]. Its aq. solution shaken with C_6H_6 gives a rose coloration due to formation of the dimethyldiacridanyl radical

$NMe(C_6H_4)_2CH \cdot C(C_6H_4)_2NMe$. Addition of NaOH does not regenerate (IV) but gives the colourless carbinol base $NMe(C_6H_4)_2C(OH) \cdot CH(C_6H_4)_2NMe$; a *picrate*, m.p. 280°, decomp. 295°, was isolated from the C_6H_6 solution and the aq. NaOH is coloured violet due to the radical $NMe \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle \dot{C} \cdot C \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle NMe \rangle X$



(destroyed by O_2). Addition of Br to a C_6H_6 solution of (IV) gives (III). With Me_2SO_4 in hot $PhMe$ diacridyl (V) (*loc. cit.*) gives only the *monomethosulphate*, darkens 290°, m.p. > 350°, converted by aq. KBr into 10-N-methyldiacridylium bromide (VI), m.p. > 350° [with conversion into (V)] [*picrate*, m.p. 305° (decomp.); *iodide* (VII); *ferricyanide*, m.p. 250° (decomp.)]. With hot $K_3Fe(CN)_6$

(VI) gives a *substance*, m.p. 345°, probably an internal ether $(C_{27}H_{19}N_2)_2O$ of the carbinol base. When shaken with $Zn-C_6H_6$ (VI) gives a violet coloration (stable to O_2) in the solution (*picrate*, m.p. 220°, isolated) due to the radical



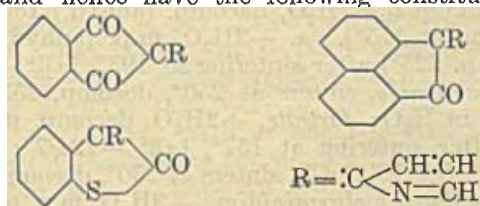
(VIII), but in $HCl-C_6H_6$ (exclusion of O_2) *monomethyldiacridine* [as (IV)] is obtained, and is readily oxidised by air to (VIII), and is converted by I into (VII). (V) is similarly converted into *diacridine*, m.p. 392°, which reacts in a similar manner to its methylated derivatives. (V) must be heated with Me_2SO_4 without solvent to give (I). The final product of the chemiluminescent reaction of $KOH-H_2O_2$ on (I) is *N*-methylacridone (isolated). J. W. B.

γ -Triazines. XXIX. Conversion of amino-thiol-alkyl-, aryl-, and arylalkyl-triazines into the corresponding aminohydroxy-derivatives. General considerations and description of two new homologues, aminohydroxy-ethyl- and -propyl-triazine. XXX. Some aminohydroxy-aryl-triazines. XXXI. Aminohydroxy-benzyl- and -styryl-triazines. A. OSTROGOVICH and V. GALEA (Gazzetta, 1935, 65, 349—356, 357—366, 367—370).—XXIX. H_2O_2 and an aminothioltriazine in aq. KOH give the aminohydroxytriazine. The following are prepared (each m.p. in this series is with decomp.): *aminohydroxy-ethyl*-, m.p. 277—278° (+2 or 3H₂O) (*hydrochloride*, m.p. 214—216°; *picrate*, m.p. 191—192°; *Ag* salt, m.p. 265—270°), and *n-propyl*-, m.p. 274—275° (*picrate*, m.p. 195—196°), γ -triazines.

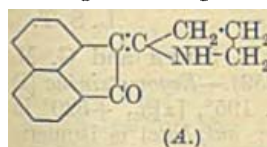
XXX. Aminohydroxyphenyltriazine (A., 1930, 1449) (*hydrochloride*, m.p. 295—296°; *sulphate*, m.p. 238—240°). *Aminohydroxy-o*-, m.p. 292—293° (*picrate*, m.p. 255—256°), *m*-, m.p. 217—219° (*picrate*, m.p. 292—293°), and *p*-, m.p. 333—334° (*hydrochloride*, m.p. 294—296°; *picrate*, m.p. 304—305°; *Ag* salt), *-tolyltriazines*. *Aminohydroxyanisyltriazine*, m.p. 327—328° (*hydrochloride*, m.p. 290—291°; *picrate*, m.p. 308—309°; *Ag* salt).

XXXI. Aminohydroxybenzyltriazine, new m.p. 277—278° (cf. Elzanowski, Diss., Freiburg, 1898) (hydrochloride, m.p. 220—222°; picrate, m.p. 208—210°; Ag salt). Aminohydroxystyryltriazine, m.p. 308—309° (picrate, m.p. 271—273°). E. W. W.

New colour reactions of pyrrolidine and proline. II. W. GRASSMANN and K. VON ARNIM (Annalen, 1935, 519, 192—208; cf. A., 1934, 665).—The final proof of the constitution of the dyes obtained from ninhydrin (I) or isatin (I) with proline (III), hydroxyproline (IV), or pyrrolidine (V) is given by the prep. of the dye $o\text{-C}_6\text{H}_4\text{<CR>NH}$ ($\text{R} = o\text{-C}_6\text{H}_4\text{<C>CO}$) from (II) and dihydroisoindole and by the observation that 3-methyl-4-ethyl- but not 2:4-dimethyl-3-ethyl-, 4:5-dimethyl-3-ethyl-, 2:4:5-trimethyl-3-ethyl-pyrrolidine, or 2-methylpyrrolidine condenses with (II). Dyes obtained from (III) and 5-iodo-, 5:7-dibromo-, 5-nitro-, 5-sulpho-, 1-methyl-, 1-acetyl-, and 1-benzoyl-isatin and from thionaphthenquinone, acenaphthenequinone (IV), α -naphthaisatin, β -naphthaquinone, and phenanthraquinone are prepared in AcOH. Analogous condensation products are derived in poorer yield from (IV). A red dye is obtained from (I) and piperidine-3-carboxylic acid and a green dye from piperidine and (VI). Pyrroline (VII) behaves similarly to (V) and its derivatives, yielding a cryst. blue dye with (II). The absorption spectra of the dyes from (IV) and (VII) are closely similar to one another and differ markedly from the differently constituted pyrrole-blue dyes. The condensation products from pyrrole, (I), (V), or thionaphthenquinone are similar to the known pyrrole dyes, and hence have the following constitutions:



(II) and (III) give a colourless intermediate product, too unstable to be isolated. If 1-methyl-, dibromo- or iodo-isatin is substituted for (II), cryst. compounds of the type $\text{NH<C}_6\text{H}_4\text{>C(CH<CH}_2\text{CH}_2\text{NH-CH}_2\text{)}_2$ are obtained which lose (V) and form the dyes when heated with Ac_2O . The golden-yellow intermediate product



from (I) and (III) (*loc. cit.*) has the structure (A). These monopyrrolidinylninhydrin compounds are characterised by enhanced condensing power, thus giving the possibility of the prep. of asymmetric dyes; the products from pyrrolidinylninhydrin and (II), phthalonic acid and mesoxalic esters, and from pyrrolidinylninhydrin and (II) or thionaphthenquinone are described. The following substances do not react with (III), (V), or their intermediate products: anthraquinone, α -naphthaquinone, 1:3-diketohydrindene, $\text{COPh}\cdot\text{COPh}$, phthalonic acid, phenylglyoxylanilide,

COMePh , COPh_2 , fluorenone, camphorquinone, phthalimide, glyoxal, $\text{COMe}\cdot\text{CHO}$, Ac_2 , dihydroxytartaric acid, and diketosuccinic ester. The presence of two vicinal CO groups in an aromatic ring system appears essential for the change. The colour reaction of proline peptides with (II) in AcOH is sp. to those containing terminal proline-N. The dyes obtained are identical with those derived from (III) and reaction therefore involves the separation of the proline residue from the remaining peptide. The micro-detection of (III) is effected by bringing the solution to p_{H} 7 by a phosphate buffer, immersing a few threads of acetate silk, adding a little (II), and boiling for a few min. In the presence of (III) the threads assume a pure blue colour. The test is less sensitive for (IV). H. W.

Production of therapeutically active tetrazole derivatives of terpene series.—See B., 1935, 830.

Oxidation of α tioporphyrin. M. DEŽELIĆ (Bull. Soc. Chim. Yougoslav., 1935, 6, 11—25).— α tioporphyrin (I) in $\text{CHCl}_3\text{-AcOH}$ and PbO_2 yield successively a green product (II), $\text{C}_{32}\text{H}_{38}\text{O}_8\text{N}_4$, m.p. $>250^\circ$, α tioxanthoporphyrinogen (III), and methylethylmaleimide (IV). Oxidation with CrO_3 yielded only (IV), whilst HIO_3 afforded a mixture of products containing I, yielding the substance $\text{C}_{32}\text{H}_{38}\text{O}_8\text{N}_4$, m.p. 140° , on hydrolysis with aq. Na_2CO_3 , and converted into (IV) on further oxidation. (I) and HCl and HIO_3 in AcOH give tetrachloro α tioporphyrin dihydrochloride (V), decomp. $>200^\circ$, oxidised to (III) by PbO_2 . (II), (III), and (V) regenerate (I) when reduced with Na-Hg . (I) and conc. HNO_3 afford a mixture of nitro α tioporphyrin (VI), not melting at 350° , and α tioporphyrin nitrate, m.p. 150° (decomp.), whilst fuming HNO_3 gives dinitro α tioporphyrin. The NO_2 of (VI) is replaced by SO_3H by the action of oleum.

R. T.

Pyocyaninium perchlorate. R. KUHN and K. SCHÖN (Ber., 1935, 68, [B], 1537—1539).—Leucopyocyanine is converted by Cl_2O_4 in Et_2O into pyocyaninium perchlorate (I), $\text{C}_{13}\text{H}_{12}\text{O}_5\text{N}_2\text{Cl}$, which is somewhat unstable. The semi-quinonoid nature of (I) is established by titration with Na_2SnO_2 and the radical nature by the paramagnetism. According to measurements of the rate of diffusion in H_2O and C_6H_6 pyocyanine is unimol. H. W.

Manufacture of derivatives of the anthraquinone series containing nitrogen and sulphur.—See B., 1935, 762.

Alkaloids of *Heliotropium lasiocarpum*. IV. Degradation of heliotridane to a pyrrole base. G. MENSCHIKOV (Ber., 1935, 68, [B], 1555—1558; cf. this vol., 995).—Heliotridane methiodide is converted by Ag_2O into de-N-methylheliotridane, b.p. $162.5\text{--}163^\circ$, $[\alpha]_{\text{D}} -36^\circ$ (picrate, m.p. $118.5\text{--}120^\circ$), which appears to polymerise readily when impure. It is hydrogenated (Adams) to dihydrode-N-methylheliotridane (I), b.p. $165\text{--}165.5^\circ$, $[\alpha]_{\text{D}} -1.5^\circ$ (methiodide, m.p. 144° after becoming turbid at $137\text{--}138^\circ$; picrate, m.p. $125\text{--}126^\circ$). Dehydrogenation of (I) over Pd-asbestos at $270\text{--}275^\circ$ affords 2H_2 and an optically inactive pyrrole base, $\text{C}_9\text{H}_{15}\text{N}$, b.p. $189\text{--}191^\circ$. Heliotridane therefore contains a pyrrolidine ring. H. W.

[Simplification of Pictet's synthesis of nicotine.] M. EHRENSTEIN (Ber., 1935, 68, [B], 1550).—A reply to Spath (this vol., 995). H. W.

Synthesis of *dl*-eserethole and bufotenine. Synthetical experiments on eserine. IV. T. HOSHINO, T. KOBAYASHI, and K. SHIMODAIRA (Proc. Imp. Acad. Tokyo, 1935, 41, 192—194; cf. this vol., 227, 499).—Hydrolysis of the *p*-toluenesulphonate of β -(5-hydroxy-3-indolyl)ethylmethylamine (norbufotenine) with HCl affords a gum, but the Et ether (I) is readily obtained from its *p*-toluenesulphonate. The Grignard derivative of (I) with MeI gives *isonorserethole*, m.p. 71—72° (cf. A., 1932, 952; 1933, 164) (*H* oxalate, m.p. 152—153°), the hydrochloride of which with MeI at 100° gives *dl*-eserethole, isolated as the picrate, m.p. 150—151° (lit., 155°; cf. this vol., 636). β -(2-Methyl-3-indolyl)ethyl bromide, readily obtained from the alcohol and PBr₃, when heated with aq. NH₃, NH₂Me, and NHMe₂ gives β -(2-methyl-3-indolyl)ethylamine, *-methylamine*, m.p. 82—83°, and *-dimethylamine*, m.p. 97—98°. Similarly, β -3-indolyethyl alcohol gives β -3-indolyethylamine, *-methylamine* (deoxynorbufotenine), and *-dimethylamine* (deoxybufotenine), m.p. 49—50°, and β -(5-ethoxy-3-indolyl)ethyl alcohol, m.p. 74—75°, gives β -(5-ethoxy-3-indolyl)ethylamine, (I), and bufotenine Et ether (*picrate*, m.p. 144—145°); the last-named with AlCl₃ in boiling C₆H₆ gives bufotenine identical with the natural product (cf. A., 1934, 1232). J. L. D.

Specific rotatory power of salts of quinine, quinidine, cinchonine, and cinchonidine. C. LAPP (Compt. rend., 1935, 201, 80—81; cf. A., 1933, 618).—Vals. of $[\alpha]$ for different λ are given for the bases, their hydrochlorides, and dihydrochlorides, whence the spatial configurations of the bases are deduced and the differences between their pharmacological properties explained. F. R. G.

Specific rotatory power and stereochemistry of the *Cinchona* alkaloids. C. LAPP (Bull. Soc. chim., 1935, [v], 2, 1407—1424).— $[\alpha]$ of quinine, quinidine, cinchonine, and cinchonidine in aq. solution and as a function of p_H has been determined. The graphs corresponding with the different λ in forms of a double S form a family and correspond with the saturation of the two basic junctions. The rotation due to each of the asymmetric C has been determined. It is concluded that C1 and C2 are fixed, whereas C3 and C4 are under the influence of ionisation. The $[\alpha]$ increases as the electric charges on the mol. due to dissociation increase. The results and the pharmacodynamic properties suggest that the OMe and vinyl chains are parallel in the levorotatory alkaloids and anti-parallel in the dextrorotatory compounds. H. W.

Modified *Cinchona* alkaloids. III. Chlorodi-hydro-bases. J. A. GOODSON (J.C.S., 1935, 1094—1097).—Addition of HCl to the vinyl groups in quinine (I), cinchonidine, cinchonine, or quinidine gives two isomerides. The Cl is, therefore, at the α -C. Names such as "hydrochloroquinine," "chlorocinchonide," etc. are replaced by the rational chlorodihydro-nomenclature, the isomeride with the higher $[\alpha]$ being given the prefix α and the other α' . CuCl₂ forms salts with

these bases and is, therefore, not a sp. reagent for the vinyl group in this series. The following are described, m.p. being corr. and $[\alpha]$ in *N*-HCl: α -, sinters at 203°, m.p. 210°, decomp. 215°, $[\alpha]_D^{20}$ -251° [*dinitrate*, m.p. 209°, decomp. 212°, $[\alpha]_D^{20}$ -196.6° in H₂O; *tartrate*, +7H₂O, m.p. (anhyd.) 187°, decomp. 198°, $[\alpha]_D^{20}$ -209.4°; *cuprichloride*, B, 2HCl, CuCl₂, decomp. 215° after sintering at 212°], and α' -chlorodihydroquinine, +x C₆H₆ and +x H₂O, m.p. (anhyd.) 194° (decomp. 225°) after sintering at 184°, $[\alpha]_D^{20}$ -163.1° [*dinitrate*, sinters at 219°, decomp. 223°, $[\alpha]_D^{20}$ -132.8° in H₂O; *tartrate*, +2H₂O, decomp. (anhyd.) 228° after sintering at 223°, $[\alpha]_D^{20}$ -132.3°; *cuprichloride*, 2B, 4HCl, CuCl₂, +3H₂O, decomp. (anhyd.) 198° after sintering at 190°], both about as active as (I) against bird malaria in doses of 5 mg. per 20 g. body-wt. α -, sinters at 233°, decomp. 236°, $[\alpha]_D^{20}$ +226° [*dihydrochloride*, sinters at 279°, decomp. 283°, $[\alpha]_D^{20}$ +196.7° in H₂O; *tartrate*, +2H₂O, decomp. (anhyd.) 204° after sintering at 196°, $[\alpha]_D^{20}$ +185.4°; *cuprichloride*, B, 2HCl, CuCl₂, +H₂O, decomp. (anhyd.) 234° after sintering at 228°], and α' -chlorodihydrocinchonine, sinters at 220°, decomp. 223°, $[\alpha]_D^{20}$ +176° [*dihydrochloride*, sinters at 273°, decomp. 276°, $[\alpha]_D^{20}$ +154° in H₂O; *tartrate*, +2H₂O, decomp. (anhyd.) 212° after sintering at 209°, $[\alpha]_D^{20}$ +142°; *cuprichloride*, B, 2HCl, CuCl₂, +H₂O, decomp. (anhyd.) 235° after sintering at 230°], both inactive against bird malaria. α -, sinters at 229°, decomp. 231°, $[\alpha]_D^{20}$ -135.6° (*cuprichloride*, B, 2HCl, CuCl₂, sinters at 218°, decomp. 220°), and α' -chlorodihydrocinchonidine, sinters at 244°, decomp. 246°, $[\alpha]_D^{20}$ -62.5° [*H* sulphate, +3H₂O, decomp. (anhyd.) 176° after sintering at 162°, $[\alpha]_D^{20}$ -59.5° in H₂O; *tartrate*, sinters at 210°, decomp. 212°, $[\alpha]_D^{20}$ -52.4°; *dihydrobromide*, sinters at 256°, decomp. 257°, $[\alpha]_D^{20}$ -50.4° in H₂O; *cuprichloride*, 2B, 4HCl, CuCl₂, +7H₂O, decomp. (anhyd.) 185° after sintering at 175°]. α -, +2H₂O, m.p. (anhyd.) 206°, (decomp. 225°) after sintering at 198°, $[\alpha]_D^{20}$ +276.3° [*dihydrobromide*, sinters at 250°, decomp. 253°, $[\alpha]_D^{20}$ +200° in H₂O; *tartrate*, +2H₂O, decomp. (anhyd.) 162° after sintering at 157°, $[\alpha]_D^{20}$ +224.7°; *cuprichloride*, B, 2HCl, CuCl₂, sinters at 230°, decomp. 233°], and α' -chlorodihydroquinidine, +3H₂O, m.p. (anhyd.) 200° (decomp. 229°) after sintering at 195°, $[\alpha]_D^{20}$ +240.7° [*tartrate*, +11H₂O, decomp. (anhyd.) 196° after sintering at 152°, $[\alpha]_D^{20}$ +203°; *cuprichloride*, B, 2HCl, CuCl₂, sinters at 230°, decomp. 236°].

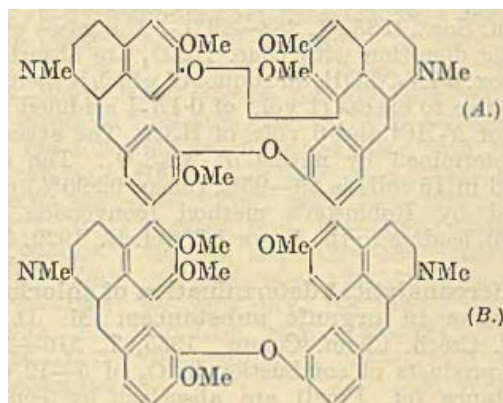
R. S. C.

New ergot alkaloid. H. H. DALE (Science, 1935, 82, 99—101).—Concerning nomenclature (cf. this vol., 1157). L. S. T.

New alkaloid of ergot. S. SMITH and G. M. TOMMIS (Nature, 1935, 136, 259).—*Ergometrine* (I) C₁₉H₂₃O₂N₃, decomp. approx. 195°, $[\alpha]_D^{20}$ +520° in CHCl₃ (*nitrate*; *hydrobromide*; *sulphate*) is isomeric with and convertible into *ergometrine* (II) (this vol., 655). Its aq. solutions are dextrorotatory. The relationship between (I) and (II) is apparently similar to that between ergotoxine-ergotinine and ergotamine-ergotaminine. L. S. T.

Constitution of phæanthine. H. KONDO and I. KEIMATSU (Ber., 1935, 68, [B], 1503—1505).—Elementary analyses and determination of OMe

establish the formula $C_{34}H_{30}O_2N_2(OMe)_4$ for phæanthine (I). Comparison of the properties of (I) and tetrandine shows them to be optical antipodes. (I) (A) or (B).



H. W.

Alkaloids of Hanfangchi. I. Hanfanchin A. C. F. HSÜ [with, in part, G. H. WANG and T. W. LU] (J. Chinese Chem. Soc., 1935, 3, 260—273).—Hanfangchi, a Chinese drug with diuretic and antipyretic properties, from the roots of plants of family Menispermaceæ, contains four alkaloids, *hanfanchin A* (see below), B, m.p. 241—242°, and C, amorphous, in the non-phenolic fraction, and the fourth in the phenolic fraction. The extract of Hanfangchi with boiling 90% EtOH is dissolved in dil. HCl, substances sol. in light petroleum are removed, and the base is liberated and taken up successively in $CHCl_3$, Et_2O , and $COMe_2$. *Hanfanchin B* is removed with C_6H_6 , and *hanfanchin A*, $C_{34}H_{30}O_2N_2$ or $C_{37}H_{34}O_2N_2$, m.p. 218—218.5°, $[\alpha]_D^{25} + 268.7^\circ$ in $CHCl_3$, is crystallised from $COMe_2$ (yield 0.6%). It forms a *picrate*, m.p. 247°, *phosphate*, m.p. 241—242.5°, *dimethiodide*, m.p. 259—260°, *aurichloride*, m.p. 185°, *platinichloride*, decomp. 225—228°, and an Ac_4 derivative, m.p. 100° (softening at 95°), $[\alpha]_D^{25} + 37.16^\circ$ in $CHCl_3$. It is probably a *tert.*-base, without phenolic OH, $N=NO$, O_2CH_2 , or $C=O$, containing two double linkings, 2 NMe and 4 OMe, and perhaps an O-bridge. Intraperitoneal injection of the *hydrochloride* into the albino rat (lethal dose, 220 mg. per kg. body-wt.) has no characteristic effect. The above properties show that *hanfanchin A* is different from tetrandine (cf. A., 1932, 1048).

E. W. W.

Alkaloids of *Anagyris foetida*. II. H. R. ING (J.C.S., 1935, 1053—1054; cf. A., 1933, 727).—The mother-liquors from the prep. of anagyrine and cytisine from the seeds of *A. foetida* yield *N*-methylcytisine and *d*-sparteine.

R. S. C.

Alkaloids of the Cactaceæ. L. RETI (Anal. Asoc. Quím. Argentina, 1935, 23, 26—40).—A lecture.

Configuration of heterocyclic compounds. II. Phenoxarsonium salts. M. S. LESSLIE and E. E. TURNER (J.C.S., 1935, 1051—1052; cf. A., 1934, 1118).—Two phenoxarsonium salts could not be resolved, thus supporting the theory previously proposed (*loc. cit.*) regarding the cause of the dissymmetry of phenox-

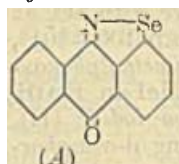
arsine compounds. 2-Methylphenoxarsinic acid and a trace of I in $CHCl_3$ and conc. HCl give with SO_3 at 50° 10-*chloro*-2-methylphenoxarsine (I), m.p. 100—101°, which with $MgMeI$ affords 2:10-dimethylphenoxarsine, b.p. 195°/17 mm.; this with MeI in EtOH gives 2:10:10-trimethylphenoxarsonium iodide (II), m.p. 205° (decomp.); the corresponding *d*-camphor-sulphonate, $+H_2O$, m.p. 275—276° (decomp.), $[\alpha]_D^{20} + 26.2^\circ$ in EtOH, and *d*- α -bromocamphor- π -sulphonate, $+H_2O$, m.p. 263—264° (decomp.), $[\alpha]_D^{20} + 67.1^\circ$ in EtOH, $+64.2^\circ$ in $CHCl_3$, are unchanged by crystallisation and give inactive (II). (I) and $MgPhBr$ give 10-phenyl-2-methylphenoxarsine, b.p. 250°/10 mm., m.p. 61—62°, which with MeI at 100° yields 10-phenyl-2:10-dimethylphenoxarsonium iodide (III), m.p. 179—180° (decomp.), the corresponding *d*- α -bromocamphor- π -sulphonate, $[\alpha]_D^{20} + 25.5^\circ$ in EtOH, being unchanged by crystallisation and giving inactive (III).

R. S. C.

Germicidal and antiseptic activity of some mercury compounds.—See this vol., 1161.

Aryl selenohalides. V. Hydrolysis of aryl selenomonohalides and selenenic acids of the benzene series. O. BEHAGEL and W. MÜLLER (Ber., 1935, 68, [B], 1540—1549; cf. A., 1934, 313).—The hypothesis that the hydrolysis of aryl selenohalides occurs according to $SeRHal + H_2O \rightarrow R-SeOH + HHal$ is strengthened by the isolation of a series of selenenic acids (cf. Foster, A., 1934, 539). The possibility of obtaining the latter compounds depends essentially on the stability of the monohalide, which increases with the negative nature of the aryl residue. *o*- $NO_2-C_6H_4-SeBr$ is converted by $AgOAc$ in boiling MeOH into *o*-nitrophenyl selenoacetate, m.p. 52°, and is hydrolysed by boiling H_2O to *o*-nitrophenylselenenic acid, $NO_2-C_6H_4-SeOH$, decomp. (indef.) 165—170°, and 2:2'-dinitrodiphenyl diselenide, m.p. 211°. *Se m*-nitrophenyl bromide, from the Br_3 -compound at 100°/diminished pressure, is converted by alcoholic alkali or $AgOAc$ in MeOH into (*m*- $NO_2-C_6H_4-Se$)₂. *Se p*-nitrophenyl bromide, m.p. 92°, is transformed into *p*-nitrophenyl selenoacetate, m.p. 62°. $[(NO_2)_2C_6H_3Se]_2$ and Br in $CHCl_3$ afford *Se* 2:4-dinitrophenyl bromide, m.p. 118°, whence 2:4-dinitrophenyl selenoacetate, m.p. 133°, and 2:4-dinitrophenylselenenic acid, decomp. $> 220^\circ$. (*o*- $NO_2-C_6H_4-Se$)₂ is reduced by $N_2H_4.H_2O$ in boiling EtOH to (*o*- $NH_2-C_6H_4-Se$)₂, m.p. 99°, whence 2:2'-dibenzamidodiphenyl diselenide, m.p. 146—147°, converted by Br in $CHCl_3$ into *Se* bromo-*o*-benzamidophenyl tribromide, which, with $AgOAc$ in boiling MeOH, yields bromo-*o*-benzamidophenylselenenic acid, m.p. 178° (decomp.). 2:2'-Dichlorodiphenyl diselenide has m.p. 74°. Naphthyl selenocyanide and Br in $CHCl_3$ yield *Se* tribromonaphthyl tribromide, m.p. 137°, converted by Zn dust in boiling PhMe into hexabromodinaphthyl diselenide, m.p. 162—164°. 2:4:6-Tribromophenyl selenocyanide m.p. 113—114°, and Br in $CHCl_3$ afford *Se* 2:4:6-tribromophenyl bromide, m.p. 99—100°, transformed by H_2O , alkali, or $AgOAc$ into 2:4:6:2':4':6'-hexabromodiphenyl diselenide, m.p. 212°. 1-Anthraquinonyl selenocyanide, from the bromide and KCN in boiling EtOH, is converted by conc. NH_3 at 130—140° into anthraquin-

onylselenazole (A), m.p. 208—209°. 1-Anthraquinonyl selenoacetate and 1-anthraquinonylselenolacetic acid, m.p. 245°, are described. Se 1-anthraquinonyl bromide is converted by the requisite amine into the corresponding amide, diethylamide, m.p. 107—108°, anilide, m.p. 192°, and *p*-diethylaminophenyl 1-anthraquinonyl selenide, m.p. > 300°. Hydrolysis of Se 1-anthraquinonyl trichloride gives 1-anthraquinonylseleninic acid, m.p. (indef.) 203°, after darkening.



H. W.
Organic derivatives of silicon. XLIX. Reduction of the tetranitrotetraphenylsilicane. F. S. KIPPING and J. C. BLACKBURN. L. Nitration of phenyltriethyl-, diphenyldiethyl-, and triphenylethyl-silicane. F. S. KIPPING and N. W. CUSA (J.C.S., 1935, 1085—1088, 1088—1091; cf. A., 1933, 1062).—XLIX. Tetra-*m*-aminotetraphenylsilicane (I), m.p. about 380° (decomp.), sublimes at about 350° (tetrahydrochloride; oxalate; picrate; platinichloride; sulphate; Ac_4 derivative, m.p. 300—301°), is obtained from the corresponding $(NO_2)_4$ -compound by $Zn-HCl-AcOH$ or PtO_2-H_2 (2—3 atm.) in $EtOAc$, but $Sn-HCl-COMe_2$ affords by condensation tetra-*m*-isopropylaminotetraphenylsilicane, m.p. 135° [tetrahydrochloride, m.p. 300° (decomp.)]. (I) is stable to hot $KOH-EtOH$ or aq. KOH and to conc. H_2SO_4 at 50—60°, does not eliminate NH_2Ph with Br , and, after diazotisation, couples with $\beta-C_{10}H_7-OH$. The mixture of tetranitrotetraphenylsilicane previously described (A., 1932, 1050) probably contains compounds other than the *s-m*- and *-p*-(NO_2)₄-derivatives; the presence of the *p*-compound is proved by liberation on reduction of 26% of NH_2Ph ; reduction led to (I), tri-*m*-aminotriphenylsilicol, amorphous (trihydrochloride, cryst.), and probably benzidine compounds.

L. The *p*- $Si-C_6H_4-NH_2$ linking is readily broken by acids, but the *m*-linking resists acids and alkalis. Both *p*- and *m*- $Si-C_6H_4-NO_2$ linkings are very stable to acids, but much less so to hot alkalis. The probable proportions of *p*- and *m*-nitration by HNO_3-Ac_2O are: $SiPhEt_3$ 83 and 17, $SiPh_2Et_2$ 70 and 30, $SiPh_3Et$ 40 and 60, and $SiPh_4$ 24 and 76%, respectively. *o*-Nitration does not occur. The products are not all *s*-substituted. $SiPhEt_3$ affords a NO_2 -compound, which with $Br-H_2O$ at 110° gives $(SiEt_3)_2O$ and $C_6H_4Br-NO_2$ (95%). $SiPh_2Cl_2$ and $MgEtI$ (3 mols.) afford diphenyldiethylsilicane, b.p. 295—298°, giving the *m*-(NO_2)₂-compound (III) (11%), m.p. 102—103°, and an oily mixture which on acid reduction yields much NH_2Ph and with $Br-H_2O$ at 110° gives $C_6H_4Br-NO_2$ (mixture; 97%). (II) with Br gives 98% of *m*- $C_6H_4Br-NO_2$ and with $Zn-HCl-AcOH$ or H_2-PtO_2 in $EtOAc$ di-*m*-aminodiphenyldiethylsilicane, m.p. 89—90° (Ac_4 derivative, m.p. 163—164°), stable to hot HCl and slowly decomposed by hot 10% KOH . The nitration product of $SiPh_3Et$ gives similar results with Br . Phenylcyclohexylethylsilicane has m.p. 52—53°.

R. S. C.

Correlation of the viscosities of protein solutions with their ability to crystallise.—See this vol., 1266.

Colloid chemistry of edestin.—See this vol., 1203.

Sodium hydroxide as a substitute for iodine in Robinson's sulphur dioxide method [for determining organic carbon]. C. K. LI (J. Chinese Chem. Soc., 1935, 3, 288—292).—The gases evolved during digestion with conc. H_2SO_4 are absorbed by approx. 0.7*N*- $NaOH$, an aliquot of which is then added dropwise to excess (1 vol.) of 0.1*N*- I acidified with 1 vol. of $N-HCl$ and 6 vols. of H_2O . The excess of I is determined by means of $Na_2S_2O_3$. The org. C found in 15 soils is 89—95% (mean 92.96%) of that found by Robinson's method (conversion factor 1.116), leading to the factor 1.20 (cf. B., 1929, 487).

J. G. A. G.

Microanalytical determination of chlorine and bromine in organic substances. M. JUREČEK (Coll. Czech. Chem. Comm., 1935, 7, 316—318).—The products of combustion in O_2 of 5—12 mg. of substance (cf. Pregl) are absorbed by conc. aq. Na_2CO_3 and Na_2SO_3 . After diluting to 30—40 ml., the SO_3'' is oxidised by heating with H_2O_2 and, when Br' is present, the excess of H_2O_2 is removed by heating with $N_2H_4.H_2SO_4$. After acidifying with 1 ml. of conc. HNO_3 , the Cl' or Br' is titrated with 0.01*N*- $Hg(NO_3)_2$ [indicator: $Na_2Fe(CN)_5NO$]. In general, calc. and observed % differ by ± 0.15 . J. G. A. G.

Determination of organic halogens. II. Stepanov method. C. L. TSENG, M. HU, and M. C. CHIANG (J. Chinese Chem. Soc., 1935, 3, 223—237).—Modified procedures for determining Cl , Br , and I are described, and the method is extended to the determination of org. F. After reaction with Na and $EtOH$, the F in the resulting solution is determined as CaF_2 , or volumetrically by the $Ca-H_2C_2O_4-KMnO_4$ method; the last is also applied to the Parr bomb method (this vol., 876).

E. W. W.

Rapid Kjeldahl determination of nitrogen. H. LUNDIN, J. ELLBURG, and H. RIEHM (Z. anal. Chem., 1935, 102, 161—172).—The substance is oxidised with a mixture of 3 vols. of $H_2SO_4 + 2$ vols. of H_3PO_4 + sufficient, but not a great excess of, 30% H_2O_2 , in presence of $Cu + HgSO_4$ as catalyst. Details are given of standardised apparatus and procedure for routine serial analysis. The time for a complete analysis is about 30 min.

J. S. A.

Determination of sulphur in organic substances. P. SAARINEN (Suomen Kem., 1935, 8, A, 57—61).—A claim of priority in the use of $HClO_4$ (cf. A., 1934, 910). Preliminary oxidation is effected by HNO_3 , and $HClO_4$ used only in the final stage. Loss of S in volatile form is avoided by using a long glass-bead reflux.

E. W. W.

Determination of sulphur in organic compounds by the semimicro-Carius method. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1935, 18, 476—477).—The procedure and apparatus are described.

E. C. S.

Micro-volumetric determination of sulphur in organic compounds containing halogen and nitrogen. D. T. GIBSON and T. H. CAULFIELD (Analyst, 1935, 60, 522—525).—Cowie and Gibson's method (A., 1934, 910) is improved by the incorporation of Vieböck's $Hg(OH)CN$ method (A., 1932,

529, 631) for the halogen determination. In presence of N, a method based on the use of BaCl_2 and K_2CrO_4 is employed. E. C. S.

2:4:6-Trinitrobenzoyl chloride as a reagent for the identification of alcohols. M. C. CHANG and C. H. KAO (J. Chinese Chem. Soc., 1935, **3**, 256—259).—This reagent has the advantage of giving esters of high m.p., and of being resistant to H_2O . The following are described: *Me*, m.p. 160—161°; *Et*, m.p. 156—157°; *Pr^a*, m.p. 145—146°; *Pr^β*, m.p. 154—155°; *Bu^a*, m.p. 125—126°; *Bu^β*, m.p. 127—128°; *n-amyl*, m.p. 124—125°; *isoamyl*, m.p. 134—135°; *n-hexyl*, m.p. 129—130°; *isohexyl*, m.p. 139—140°; *n-heptyl*, m.p. 127—128°; *n-octyl*, m.p. 125—126°; *sec-octyl*, m.p. 148—149°; *n-nonyl*, m.p. 124—125°; *n-decyl*, m.p. 123—124°; *allyl*, m.p. 146—147°; and *benzyl*, m.p. 176—177°; 2:4:6-trinitrobenzoates. E. W. W.

p-Nitrobenzhydrazide as reagent for the identification of aldehydes and ketones. P. CHEN (J. Chinese Chem. Soc., 1935, **3**, 251—255).—The following are described: *form*-, m.p. 229—230°; *acet*-, m.p. 199°; *prop*-, m.p. 165—166°; *n-but*-, m.p. 145—146°; *n-valer*-, m.p. 134—135°; *isovaler*-, m.p. 150°; *n-hex*-, m.p. 128—129°; *n-hept*-, m.p. 113—114°; *n-oct*-, m.p. 108—109°; *n-non*-, m.p. 103—104°; *benz*-, m.p. 252—253°; *m-nitrobenz*-, m.p. 277—278°; and *furfur*-, m.p. 249—250°; *-aldehyde-p-nitrobenzoylhydrazones*; *acetone*-, m.p. 162°; *Me Et ketone*-, m.p. 133°; *Me hexyl ketone*-, m.p. 90°; *acetophenone*-, m.p. 198—199°; *benzylideneacetone*-, m.p. 193—194°; and *-acetophenone*-, m.p. 153—154°; *p-methyl*-, m.p. 218—219°; *m-nitro*-, m.p. 231—232°; and *p-methoxy*-, m.p. 199—200°; *-acetophenone*-, *acetylacetone*-, m.p. 124°; and *Et acetoacetate*-, m.p. 105—106°; *-p-nitrobenzoylhydrazones*. E. W. W.

Semicarbazides. III. o-Tolylsemicarbazide as a reagent for the identification of aldehydes and ketones. H. H. LEI, P. P. T. SAH, and C. SHIH (J. Chinese Chem. Soc., 1935, **3**, 246—250).—The following are described: *acet*-, m.p. 143—145°; *prop*-, m.p. 129—130°; *n-but*-, m.p. 96—98°; *isobut*-, m.p. 113—115°; *n-valer*-, m.p. 131—132°; *n-hex*-, m.p. 111—113°; *n-hept*-, m.p. 122—123°; *n-oct*-, m.p. 125—126°; *n-non*-, m.p. 120—121°; *n-dec*-, m.p. 99—100°; *benz*-, m.p. 181—183°; *m*- and *p-nitrobenz*-, m.p. 213—215° and 229—230°; *p-homo-salicyl*-, m.p. 208—209°; and *furfur*-, m.p. 172—175°; *-aldehyde-o-tolylsemicarbazones*; *Me Et ketone*-, m.p. 168—170°; *Me hexyl ketone*-, m.p. 116—118°; *m-nitro*-, m.p. 215—217°; *p-methyl*-, m.p. 200—203°; and *p-methoxy-acetophenone*-, m.p. 182—184°; *benzophenone*-, m.p. 149—151°; *benzylideneacetone*-, m.p. 171—172°; *Et acetoacetate*-, m.p. 117—118°; *lævulic acid*-, m.p. 185—188° (*Et*, m.p. 111—113°, and CH_2Ph , m.p. 133—135°, esters); and *furylacetone*-, m.p. 176—178°, *-o-tolylsemicarbazones*. E. W. W.

Detection of citric acid. PESEZ (J. Pharm. Chim., 1935, [viii], **22**, 160—163).—A mixture of aq. citric acid (2 drops), $\text{Br-H}_2\text{O}$ (1 drop), conc. H_2SO_4 (2—3 drops), and saturated aq. KMnO_4 (1 drop) is boiled. Further addition of 2 c.c. of conc.

H_2SO_4 followed by warming causes any ppt. to dissolve; 0.1 c.c. of an EtOH solution of codeine followed by heating at 100° for 1—2 min. produces a bluish violet colour. Resorcinol, thymol, β -naphthol, salicylic acid and its Me ester can replace codeine with a modification of the colour produced. The reaction depends on the formation of glyoxal and can also be applied to the detection of the opium alkaloids.

P. G. M.

Gravimetric determination of ester derivatives of p-aminobenzoic acid, with special reference to anæsthesin and novocaine in presence of other substances. E. SCHULEK and I. FLÖDERER (Z. anal. Chem., 1935, **102**, 186—198).—The $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (I) derivative is dissolved in HCl , and then hydrolysed to free (I) by boiling with a small excess of 10% aq. NaOH . If other hydrolysable substances are present, the substance is first boiled with 1% HCl ; in presence of very H_2O -sol. or insol. substances (e.g., sugar or talc), the (I) derivative may first be isolated by extraction with org. solvents. After hydrolysis the solution is extracted with CHCl_3 , and the aq. residue is acidified, diluted, and boiled free from CHCl_3 . NaOH is added, and the solution evaporated to dryness. The residue is dissolved, acidified, and diazotised at 2—3° with 0.1N- NaNO_2 . Excess of HNO_3 is removed with $\text{CO}(\text{NH}_2)_2$, and the solution is diluted to contain >0.02 g. of (I) per 100 c.c. A fresh alkaline 0.5% solution of $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ is added, and β -naphtholazo-p-aminobenzoic acid is pptd. on acidifying. The ppt. is washed with H_2O and dried at 100°.

J. S. A.

Colorimetric determination of salicylic acid. J. E. HEESTERMAN (Chem. Weekblad, 1935, **32**, 463).—The violet colour obtained when Fe^{+++} is added to a solution of salicylic acid rapidly fades, but is permanent for 48 hr. when produced in 0.04N- AcOH .

S. C.

Thioglycollic acid, a reagent for lignin. P. KLASON (Svensk Kem. Tidskr., 1935, **47**, 220—223).—Holmberg's method (Ing. Vet. Akad. Handl., 1934, No. 131) is not satisfactory, because the presence of lignin of the type $\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ occurring in aquatic plants cannot be shown by means of thioglycollic acid (I), and the (I) compounds are not completely insol., hence lower results are obtained with pinewood. The H_2SO_4 method is less useful. In the sulphonic acid and (I) methods, but not on digestion with 66% H_2SO_4 , H_2O is evolved. E. P.

Quinidine thiocyanate. Gravimetric and volumetric determination of quinidine. R. MONNET (J. Pharm. Chim., 1935, [viii], **22**, 112—119).—The solution containing >0.2 g. of quinidine (I) is evaporated to 20 c.c., neutralised (litmus), and quinidine thiocyanate (II) pptd. with 3 g. of KCNS . The ppt. is filtered after 2 hr., washed with 2×2 c.c. of H_2O and with 8×2 c.c. of a saturated solution of (II), dried at 105—110°, and weighed. In the presence of quinine, cinchonine, and cinchonidine the ppt. is washed finally with 6×1 c.c. of 96% EtOH saturated with (II). Under neutral conditions KCNS also gives ppts. with emetine, papaverine, strychnine, vera-

trine, and berberine, but not with aconitine, atropine, brucine, caffeine, cocaine, codeine, conicine, eserine, hydrastine, hyoscyamine, morphine, ethylmorphine, heroin, narceine, narcotine, nicotine, pellerterine, pilocarpine, sparteine, thebaine, theobromine, yohimbine, digitalin, strophanthin, convallamarin, salicin, acetanilide, adrenaline, antipyrine, cryogenine, exalgine, novocaine, phenacetin, pyramidone, stovaine, carbamide, urethane, and veronal. In the absence of other alkaloids, (I) may be determined volumetrically by titrating excess of CNS' in the filtrate. S. C.

Determination of hydroxydimorphine. B. DREVON (J. Pharm. Chim., 1935, [viii], 22, 97—106).—5 c.c. of solution containing 0.04—0.1 mg. of hydroxydimorphine are treated with 5 drops of 5% silicotungstic acid and 0.03 g. of K_2CO_3 . The

ppt. is adsorbed on $BaSO_4$, centrifuged, dried, and dissolved in 2 c.c. of acetosulphuric acid (20 c.c. of H_2SO_4 , d 1.83, and 1 c.c. of Ac_2O) and the green coloration matched against a standard solution containing 1 c.c. of 15% $Cu(NO_3)_2$, 1 c.c. of 20% $Ni(NO_3)_2$, and 0.3 c.c. of 10% $Co(NO_3)_2$ solutions. The test is sp. and is accurate to 5%. S. C.

Specific reaction for yohimbine. PESEZ (J. Pharm. Chim., 1935, [viii], 22, 164—165).—To 3 c.c. of conc. H_2SO_4 are added 4 drops of a 20% solution of chloral, followed by 10 drops of an aq. yohimbine salt with shaking. On warming to 50—60° the rose-coloured solution rapidly turns a greenish-blue which is very stable and is not discharged by adding 3 c.c. of H_2O . 0.2 mg. of yohimbine hydrochloride can be detected. P. G. M.

Biochemistry.

Determination of oxygen capacity of blood at high altitude. F. ALMASY and A. KRUPSKI (Biochem. Z., 1935, 279, 433—435).—Errors due to the use of other methods are avoided and accurate results are obtained by means of a modification of the method of Sendroy (A., 1931, 753). W. McC.

Continuous photographic recording of volume changes of red corpuscles. Influence of temperature and importance of p_H on permeability to glycerol and urea. S. L. ØRSKOV (Biochem. Z., 1935, 279, 241—249).—Methods are described for the continuous photographic registration of the vol. of red corpuscles, and for the determination of the permeability velocity to various substances. The vol. changes on addition of urea, $EtCO\cdot NH_2$, glycol, and glycerol, and the influence of temp. on the permeability velocity with glycerol and thiourea are investigated. An influence of p_H on permeability to glycerol was detected. P. W. C.

Uric acid content of human blood corpuscles. J. HELLER (Biochem. Z., 1935, 279, 149—156).—Uric acid (I) is washed out of blood corpuscles much more slowly than is glucose (II) by hypertonic tungstate solutions. (I) also diffuses from the plasma into washed-out corpuscles much more slowly than (II). The (I) content of the corpuscles of human venous blood is 55% of that of the plasma. P. W. C.

Influence of carbonic acid and lead on the permeability of blood corpuscles to potassium and rubidium. S. L. ØRSKOV (Biochem. Z., 1935, 279, 250—261).—The increase brought about by CO_2 in the permeability of the rabbit's red blood-corpuscle membrane by amines and NH_4^+ is also obtained for Rb^+ and K^+ when Pb is present in minute amounts (4×10^{-8}), the optimum p_H for the Pb- CO_2 (I) action being 6.3—6.6. The migration of K^+ from the cells under the action of (I) is very rapid, 6/7 of the K^+ being separated in 10 min., the cell vol. decreased by 46%, and the resistance to hypotonic solutions greatly increased. The permeability of the membrane to glycerol is not affected by (I). Hg^{++} in rather large concns. also causes elimination of K^+ , but the effect

represents a far-reaching modification of the membrane, glucose, Na^+ , etc. being also lost. The cells of man and rat behave like those of rabbit, but no elimination of K^+ occurs with cells of goat, dog, or calf. The action of Pb is inhibited or abolished by the anions of certain acids, probably by pptn. of Pb. P. W. C.

Permeation of erythrocytes by cations. M. MAIZELS (Biochem. J., 1935, 29, 1970—1982).—The small changes in the K content of human erythrocytes suspended in KCl and NaCl solutions increase slightly with external concn., but are practically unaffected by temp., moderate changes in p_H , and duration of exposure. With $p_H > 9$ or < 5.6 and in solutions of high concn. (514 milliequivs.) increased permeation is due to cell damage, but at p_H 8.3—8.8 is probably due to physical causes. In glucose solutions the rate of loss of K from the cells increases with time, rise of temp., and p_H . CO_2 diffusing first out of the cell renders the external solution acid, but subsequent K^+ and HCO_3^- diffusion renders it faintly alkaline. Small amounts of electrolytes in the glucose solution retard loss of cell-K. E. A. H. R.

Electric impedance of hæmolysed suspensions of mammalian erythrocytes. H. FRICKE and H. J. CURTIS (J. Gen. Physiol., 1935, 18, 821—836).—Changes in the surface capacity and resistivity of the cells indicate that hæmolysis by H_2O is accompanied by increased permeability of the cell-membranes, whilst chemical lysis may also be accompanied by destruction of the membranes. Lysis by freezing and thawing differs from both the above. F. A. A.

Carb hæmoglobin of reduced hæmoglobin. G. GROSCURTH and R. HAVEMANN (Biochem. Z., 1935, 279, 300—313).—Using pure human hæmoglobin (I) solutions, systematically determined p_K vals. permit the calculation of the CO_2 directly bound with (I). (I) becomes saturated with CO_2 at pressures of 60—90 mm. A study of the relationship of CO_2 capacity and p_H leads to the view that the reaction between (I) and CO , may be stated as: $CO_2 + Hb\cdot NH_2 \rightleftharpoons Hb\cdot NH\cdot CO_2H \rightleftharpoons Hb\cdot NH\cdot CO_2' + H^+$. The dissoci-

ation const. of the NH_2CO_2 group is that
of the NH_2 9.04 ± 0.05 . P. W. C.

Dependence of the composition of the proteins of blood-serum and -plasma on the diet. (A) E. ABDERHALDEN. (B) E. ABDERHALDEN and H. SIEBEL (Fermentforsch., 1935, 14, 443—461, 462—482; cf. A., 1934, 1137).—(A) Seralbumin (I) from rabbits fed on bran and receiving injections of (I) from others also fed on bran gives the defence enzyme reaction, but if (I) from rabbits fed on green food is injected, the reaction is negative. Similar results are obtained when the food consists of oats and greens, but the reaction is not sufficiently sp. to decide whether or not the kind of food affects the fine structure of the proteins of plasma and serum.

(B) The variations in resistance to attack by *N*-alkali, trypsin, and gastric juice (dog) of albumin and globulin fractions from the blood-plasma and -serum of the horse, ox, and rabbit do not indicate any effect of the nature of the food on the composition of the proteins of the serum and plasma.

W. McC.

Effect of protein rations on the serum-protein concentration of the rat. A. L. BLOOMFIELD (J. Exp. Med., 1935, 61, 465—471).—When high-protein diets (20—100% of caseinogen) were fed to rats, the serum-protein concn. was 6.1—6.4%. On reducing the protein content of the diet the level was reduced to about 5.5% within 2 days, and remained approx. const. whether the diet contained 1, 5, or 10% of caseinogen. On changing from a protein-free or low-protein to a high-protein diet, the serum-protein rose to the higher level within 2 days. About one sixth of the serum-protein is labile; the remainder forms the "basic blood colloids," depletion of which seems to meet with resistance on the part of the body.

NUTR. ABS. (m)

Physico-chemical effect of some electrolytes on the myxoprotein of blood-serum. M. PIETTRE (Compt. rend., 1935, 201, 364—366).—Potentiometric and conductometric studies of serum-myxoprotein indicate that it has no buffering power. H. D.

Protein determination from acid-combining power. E. FREUDENBERG (Z. Kinderheilk., 1935, 57, 108—115).—A method for determining the total protein in 1 ml. of serum or plasma (fluoride), based on the acid-binding power of the protein, is described. Excess of $0.1N\text{-H}_2\text{C}_2\text{O}_4$ is added and the diluted fluid is titrated with $0.1N\text{-NaOH}$ before and after ultrafiltration. The method is inapplicable to fluids containing $< 0.5\%$ of protein.

NUTR. ABS. (m)

Stability of lipin-protein complexes in blood-serum. B. DELAGE (Bull. Soc. Chim. biol., 1935, 17, 927—937).—The extraction of lipins from blood-serum by mixtures of Et_2O and increasing quantities of EtOH , PrOH , BuOH , isomyl alcohol, glycol, MeCHO , or COMe_2 at room temp. follows the same course, the max. amount extracted being approx. the same in all cases. There is probably therefore an equilibrium between the free lipin and that combined with the serum-protein.

A. L.

Polypeptidæmia in disease. S. MARINO (Arch. Farm. sperim., 1935, 59, 274—283).—The blood-

polypeptide-N (normally 0.0016—0.0022%) increases markedly during fever, nephritis, and pulmonary diseases.

F. O. H.

Extraction of serum-lipins by cold ether-alcohol mixtures in health and disease. B. DELAGE (Bull. Soc. Chim. biol., 1935, 17, 938—943).—Heifers vaccinated with the Jenner virus, in contrast with healthy animals, have little or no serum-lipin extractable by Et_2O - EtOH at room temp.

Dissociation of the lipin-protein complex in serum by alcohol. Extraction of lipins, phosphoaminolipins, and cholesterol. A. GRIGAUT (Bull. Soc. Chim. biol., 1935, 17, 1031—1039).—The amount of EtOH required to be added to blood-serum to make possible the extraction of the total cholesterol by Et_2O is much $<$ that required for the extraction of the phosphoaminolipins (lecithin) and the total lipins.

A. L.

Extraction of cholesterol from blood-serum. I. J. DREKTER, A. BERNHARD, and J. S. LEOPOLD (J. Biol. Chem., 1935, 110, 541—549).—Cholesterol (I) linked to protein is extracted by boiling EtOH ; this is accompanied by denaturation of the protein, although preliminary heat-denaturation does not break the (I)-protein linking. A small proportion of (I) is present in either the absorbed or emulsified state and may be extracted with Et_2O . EtOH is the most efficient solvent for determination of the (I) in dried serum.

H. G. R.

Comparison of serum, heparinised plasma, and oxalated plasma in regard to cholesterol content. W. M. SPERRY and R. SCHOENHEIMER (J. Biol. Chem., 1935, 110, 655—658).—Oxalated plasma contains about 15% less cholesterol (I) than either serum or heparinised plasma from the same blood sample. Combined (I) and free (I) are reduced in the same proportion. (I) is not carried down with the CaC_2O_4 ppt.

F. A. A.

Blood-amino-acid level after resection of the colon. F. RABBONI (Riv. Patol. sper., 1935, 14, 177—201).—Following colectomy and intravenous injection of glycine there was some increase in blood- NH_2 -acid and a change from the normal type of curve. These modifications, which indicated a change in the deaminising function of the liver, tended to disappear after about 2 months.

NUTR. ABS. (m)

Suppression of renal function. X. Creatine and creatinine in blood. V. SCAFFIDI and P. GILBERTI (Riv. Patol. sper., 1935, 14, 59—69).—A marked increase in the blood-creatinine (I) and -creatinine (II) of dogs after bilateral nephrectomy indicates that formation of (II) from (I) takes place in the organism, and not exclusively in the kidney. In one dog 88 hr. after nephrectomy the blood contained 17 mg. of (I) and 8.4 mg. of (II) per 100 ml., as compared with 2.57 and 1.4 mg., respectively, before operation.

NUTR. ABS. (m)

Changes in sugar, lactic acid, and protein contents of lymph and blood. I. Effect of insulin. II. Effect of adrenaline and pituitrin. III. Lactic acid metabolism following experimental liver damage. T. KIKUTA (Tôhoku J. Exp. Med., 1935, 25, 148—168, 218—231, 232—

243).—I. In dogs fasted for 48 hr. and given morphine, the glucose content of the thoracic lymph was $>$ that of arterial blood; there was usually more lactic acid (I) in lymph than in blood. In the first period after injection of insulin there was an increase in the sugar of blood and lymph; later the fall of sugar level in the lymph was $>$ in the blood. The changes in (I) were not const., but were similar for blood and lymph. The protein content of blood and lymph changed to some extent, but the direction of the change was not const.

II. After intravenous injection of adrenaline (II), the increase in the sugar and (I) content in the lymph was $>$ in the blood. After intravenous injection of pituitrin there was a rise in the sugar level in blood and (less marked) in lymph. The (I) content increased, reaching a max. 30 min. after the injection. The changes in protein content of blood and lymph after injection of (II) or pituitrin were insignificant.

III. Ligation of the common bile duct or establishment of a duodenal ileus caused an increase in the (I) of the thoracic lymph, but not of the blood. Poisoning with P or tolylenediamine had a similar effect, often with a rise in blood-(I).

NUTR. ABS. (m)

Improvement of the apparatus for determination of blood-sugar by the Hagedorn-Jensen method. H. J. FUCHS and W. BUSS (Biochem. Z., 1935, 279, 314—317).—The method and apparatus are described.

P. W. C.

Determination of blood-sugar by the method of Crecelius and Seifert. H. ROSEGGGER (Klin. Woch., 1935, 14, 343—344).—The method gives satisfactory results. Accuracy in adding NaOH is most important. Rapid cooling is unnecessary and readings remain unchanged for 24 hr.

NUTR. ABS. (m)

Copper, blood-sugar, and adrenaline. H. HANDOVSKY (Arch. internat. Pharmacodyn., 1934, 49, 230—238).—Oral administration of Cu tyrosinate produced a decrease in blood-sugar several days after the first dose. Insulin had no effect on an animal previously treated with Cu, but there was a marked rise in blood-sugar when injection of adrenaline (I) followed treatment with Cu. Cu [through (I)] probably causes a hypersecretion of insulin, and aids the action of (I) by catalysing the decomp. of glycogen.

NUTR. ABS. (m)

Silica content in the blood-serum of cattle, sheep, goats, and pigs. E. PRIBYL (Klin. Spisy Skoly Zverol. Brno, 1934, 10, 1—21).—The SiO_2 content (mg. per 100 ml.) of the serum of healthy cattle was 0.948—2.172 (average 1.394); of sheep, 1.074—1.308 (average 1.219); of goats, 0.909—1.230 (average 1.044), and of pigs, 0.725—2.011 (average 1.327). The SiO_2 content of the serum of cows after calving was slightly reduced.

NUTR. ABS. (m)

Magnetic micro-determination of iron in blood. C. COURTY (Compt. rend., 1935, 201, 362—364).—A drop of blood is calcined and its magnetic power used as a measure of the Fe present. A calibrated Curie-Cheneveau magnetic balance is used.

H. D.

Variations in the calcium level of the blood of the domestic fowl. H. R. KNOWLES, E. B. HART, and J. G. HALPIN (Poultry Sci., 1935, 14, 83—89).—The blood-Ca level varies from one oviposition to another, being low during shell deposition and high when no formed egg is in the shell gland. Max. and min. vals. are not const. even for the same hen. A marked difference between vals. for the uterine artery and uterine vein is recorded during shell deposition. Chickens respond rapidly to subcutaneous injections of parathormone. A. G. P.

Determination of chlorine in blood. W. L. DULIERE (Rev. belge Sci. med., 1935, 7, 10—20).—Chlorine is determined directly in plasma by Volhard's method. Corpuscles are diluted with about 25 vols. of H_2O , the hæmoglobin is coagulated by the addition of cold HNO_3 and separated centrifugally. Cl' is then determined in the supernatant liquid by Volhard's method.

NUTR. ABS. (m)

Reducing substances and chloride in the blood of Orthoptera. R. M. MAY (Bull. Soc. Chim. Biol., 1935, 17, 1045—1053).—By the method of Baudouin and Lewin (A., 1927, 476) the reducing substance content (I) of the blood of normal and fasting adult males of *Locusta viridissima* was 0.075—0.178 and $>$ 0.092%, respectively. (I) for normal and fasting adult females of *Dixippus morosus* was 0.094—0.275 and 0.108%, respectively, and for fasting adult males of *Orphanidia denticauda*, 0.041—0.261%. The Cl' content of the blood of *D. morosus* varied little, however, being 0.310—0.352%.

A. L.

Vacate oxygen and oxidation quotient of serum. II. Effect of diet. W. ROMAN (Biochem. Z., 1935, 279, 381—386; cf. this vol., 508).—In 100 c.c. of rabbit serum the average val. for vacate O is 403 mg. Although there are wide individual variations the val. remains const. in the individual rabbit for long periods. Fasting causes decrease in vacate O, residual N, and oxidation quotient. Oral administration of glucose causes an increase, $>$ that corresponding with the blood-sugar increase, in the vacate O and a decrease in the residual N. Administration of peptone causes equal increase in vacate O and residual N, and that of olive oil causes slight increase in vacate O and decrease in residual N. The increase produced by peptone is $>$ that produced by glucose.

W. McC.

Physico-chemical study of blood-sera. J. ZOZAYA (J. Biol. Chem., 1935, 110, 599—617).—The relation between d , η , and other physico-chemical consts. and the blood-protein have been determined and also the standard error of determination.

H. G. R.

Hæmolytic power of the sera of different blood groups. R. D. DE LA RIVIERE, N. KOSOVITCH, and A. CYGLER (Compt. rend. Soc. Biol., 1935, 119, 1275—1276).—The hæmolytic power of the blood groups in order of decreasing activity is B, AB, A, O; that of male serum is $>$ that of female and of Bordet-Wassermann-negative $>$ -positive.

H. G. R.

Blood-coagulation. III. Constancy of hydrogen-ion concentration during the coagulation of fibrinogen by thrombin. H. EAGEE and J. P.

BAUMBERGER. IV. Nature of the clotting deficiency in hæmophilia. H. EAGLE (J. Gen. Physiol., 1935, 18, 809—812, 813—819).—III. The coagulation of fibrinogen by thrombin does not involve a significant shift in $[H^+]$ of the free fluid.

IV. In hæmophilic plasma, the prothrombin (I) content is normal, and hæmophilic platelets function normally. The delayed coagulation is due to a retarded conversion of (I) into thrombin; this may be brought to the normal rate by the addition of excess of normal, hæmophilic, or animal platelets, but not by kephalin. F. A. A.

Influence of compounds of the moranyl series on blood-coagulation. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 119, 1409—1412).—The anticoagulating power *in vitro* depends on the ability of these substances to modify the protein structure, whereas *in vivo* interaction with the modified protein may act as a complication. H. G. R.

Calcium metabolism in the first phase of blood-clotting. II. Change of state of combination of calcium during production of thrombin. H. SCHEURING (Biochem. Z., 1935, 279, 446—447; cf. this vol., 881).—Thrombokinas (I) added to blood-serum causes, parallel with the production of fresh thrombin (II), a conversion of Ca^{++} into negative Ca complex, the extent of conversion depending on the concn. of (I) and being greatest when that concn. is optimal. The optimal concn. of (I) is independent of the Ca content of the serum, but \propto the thrombogen (III) content. When the Ca content is increased the abs. amount of Ca complex increases, but the % amount decreases in parallel with the increase in Ca content. $>$ and $<$ a certain optimum $[Ca]$ (which is the physiological Ca content of the blood) production of (II), and parallel thereto conversion of Ca^{++} into Ca complex, become smaller. The optimum $[Ca]$ is independent of the (I) content, but indirectly \propto the (III) content of serum or plasma. Excess of (III) inhibits coagulation because it interferes with the conversion of Ca^{++} into Ca complex and the parallel production of (II). W. McC.

Nature of the agglutinogens of red corpuscles of different groups. R. D. DE LA RIVIERE and N. KOSOVITCH (Ann. Inst. Pasteur, 1935, 55, 331—339).—The agglutinogens may be conc. by successive treatment of the red cells with EtOH and Et_2O . They are not affected by heating to 100° or by ultra-violet light. They are adsorbed by kaolin and $Al(OH)_3$ and may be eluted with EtOH; agglutininogen-B is adsorbed by C, whereas agglutininogen-A is not. The agglutininogen is found in the phosphatide fraction of the stroma and does not contain protein or cholesterol. No differences were observed in the P content of the fractions from different blood-groups, but considerable variations were found in the I val. H. G. R.

Effect of repeated injections of phenol on the antibodies of normal rabbit serum. W. SCHAEFER (Compt. rend. Soc. Biol., 1935, 119, 1284—1286).—An increase in hæmolysins was observed, due probably to a modification in the organ concerned with the production of the antibodies. H. G. R.

Determination of abrin and anti-abrin by a specific flocculation reaction. G. RAMON and R. RICHOU (Compt. rend. Soc. Biol., 1935, 119, 1304—1306).—The antitoxic power of anti-abrin and antigenic power of abrin can be determined by a simple flocculation reaction. H. G. R.

Histochemistry of the adrenal gland. II. Quantitative distribution of lipolytic enzymes. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1935, 110, 575—582).—The distribution of esterase and lipase in the gland, the relative no. of cells in the various zones, and the lipolytic activity per cell have been determined. The presence of a tributyrinase and a less active esterase has been established. H. G. R.

Significance of water-soluble, diffusible substances for the production of rigidity by iodoacetic acid. F. LIPPAY and H. LONING (Pflüger's Archiv, 1935, 235, 448—452).—Spontaneous rigidity in $CH_2I \cdot CO_2H$ -poisoned frogs' sartorii in a moist chamber is $>$ in Ringer's solution; hence the rigidity is dependent on the presence of H_2O -sol. diffusible substances in the treated muscle. R. N. C.

Histochemical examination of the fatty granular cells of the lung. G. OUZOUNOV (Compt. rend. Soc. Biol., 1935, 119, 1342—1344).—The granules consist probably of a mixture of cholesterol and phosphatide. H. G. R.

Interaction between the alveolar epithelium of the lung and olive oil introduced by the trachea. G. OUZOUNOV and I. MINTCHEV (Compt. rend. Soc. Biol., 1935, 119, 1344—1345).—The fat penetrates certain alveoli which contain the fatty granular cells and is gradually absorbed, whilst others remain fat-free. H. G. R.

Phosphorus content and requirements of the flour beetle, *Tribolium confusum*, Duval, and its need for vitamin-D. J. W. NELSON and L. S. PALMER (J. Agric. Res., 1935, 50, 849—852).—Analyses of all stages of the insect are recorded. The time of pupation is related to the P content of the ration, the limiting val. being approx. 0.1%. The % of P in pupæ is const. irrespective of the amount of P supplied. Slow development and small nos. of *Tribolium* in certain prepared flours are probably related to their low P contents. No evidence of a need of vitamin-D was obtained. A. G. P.

Effect of parathyroid hormone and of tuberculosis on the serum- and tissue-calcium of guinea-pigs. G. C. LINDER (Biochem. J., 1935, 29, 2095—2100).—Parathyroid extract produced only a small increase of Ca in the serum of guinea-pigs, but with tuberculous animals there was a larger increase. No difference was found in the decalcification of bone in either series of animals. The extract probably increased the Ca content of the brain of tuberculous animals only, whilst the liver-Ca was increased by parathyroid extract and by tuberculous infection. J. N. A.

Iron store of newborn infants. K. UTHEIM-TOVERUD (Acta paediat., 1935, 17, Suppl., 136—140).—In newborn infants, the average Fe content per 100 g. of dry wt. was: full time, liver 200 mg.,

spleen 218 mg.; premature, liver 168 mg., spleen 183 mg. Close relationship was found between the Fe content of these organs and the age of the foetus. Premature infants of normal mothers contained 200 mg. of Fe. Fe deficiency in the mother results in a lower Fe store in the foetus.

NUTR. ABS. (m)

Cæsium tetraiodophenolphthalein, a new salt for gall-bladder visualisation. J. JOHNSON and L. H. HITZROT (J. Pharm. Exp. Ther., 1935, 54, 358—366).—The Cs salt is rather more efficient for X-ray gall-bladder visualisation than the Na compound.

H. D.

Lactic acid content of mammalian brain. B. F. AVERY, S. E. KERR, and M. GHANTUS (J. Biol. Chem., 1935, 110, 637—642).—Cat and dog brains, frozen *in situ* with liquid air to minimise *post-mortem* changes, have lactic acid (I) contents averaging 15.3 mg. and 22.3 mg. per 100 g., respectively. A technique for the determination of 0.1—0.5 mg. of (I) is described.

F. A. A.

Glycogen and lactic acid in cartilage. A. IKUTA (Fukuoka Acta med., 1935, 28, 25—26).—The glycogen (I) content of the epiphyseal cartilage decreased with the age of the animal. It was abnormally high in rickets. In normal rabbits the lactic acid (II) content of the cartilage was low, increasing rapidly *post mortem*, whilst in that of rachitic rabbits the initial (II) level was higher and the *post-mortem* increase slower. In rib cartilage, which is richer in (I) and (II) than epiphyseal cartilage, there was no demonstrable increase of (I) in rickets or of (II) *post mortem*.

NUTR. ABS. (m)

Histochemistry of the pituitary gland. Quantitative distribution of vitamin-C. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1935, 110, 583—588).—Pars intermedia contains 1.5 times the concn. of vitamin-C of the pars distalis or of the cortex and is the most potent source recorded. The concn. and the relative no. of cells in each portion and the vitamin content per cell are given.

H. G. R.

Effect of cold on the fat and carbohydrate contents of the liver. A. LANCZOS (Pflüger's Archiv, 1935, 235, 422—427).—The body-temp. of fasting mice rises on exposure to cold, and falls during recovery. Liver-carbohydrate increases during the recovery period, muscle-carbohydrate showing no corresponding decrease. Liver-fat is unaffected during either exposure or recovery.

R. N. C.

Chemical constitution of the fat of the subcutaneous connective tissue in man. I. Liquid and solid fatty acids in different periods of life. II. Liquid and solid fatty acids in patients affected with benignant and malignant neoplasm, and by cancerous cachexia. III. Cholesterol. IV. Acid and saponification values. V. Iodine value of the fat in different periods of life. VI. Iodine value of the fat in patients affected with benignant and malignant neoplasm, and by cancerous cachexia. G. STOLFI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 108—110, 110—111, 112—113, 113—115, 115—117, 117—118).—I. Unsaturated fatty acids (I) rise and saturated fatty acids fall in the sub-

cutaneous connective tissue in children during growth, both becoming steady at maturity.

II. (I) are decreased slightly in benignant neoplasm and increased slightly in malignant neoplasm; a greater increase occurs in cancerous cachexia.

III. Cholesterol shows no appreciable alteration with age. It is increased considerably in malignant neoplasm, and to a smaller extent in benignant neoplasm and cancerous cachexia.

IV. The acid val. of the tissue-fat is not altered by age, but the sap. val. falls slightly. Neither is altered by neoplasm or cachexia.

V, VI. The I val. of the tissue-fat increases with age in children, but remains steady when maturity is attained; it is unaffected in benignant neoplasm, but is increased in malignant neoplasm and cancerous cachexia.

R. N. C.

Absence of allocholesterol in the organism. R. SCHOENHEIMER, H. DAM, and K. VON GOTTBURG (J. Biol. Chem., 1935, 110, 659—665).—*allocholesterol* (I) is comparatively stable if high temp. and acid reaction are avoided, and may be determined in presence of cholesterol by the $\text{CCl}_3\text{-CO}_2\text{H}$ colour test. Animal sterols do not contain appreciable quantities of (I); sterols from hens' eggs appear to contain 1%.

F. A. A.

Absorbability of allocholesterol. R. SCHOENHEIMER, H. DAM, and K. VON GOTTBURG (J. Biol. Chem., 1935, 110, 667—671).—Experiments on mice, hens, and a dog show that *allocholesterol* (I) is little, if at all, absorbed in the alimentary tract, in contrast to cholesterol (II). (I) is partly changed into (II) in the stomach.

F. A. A.

Gadusene, an unsaturated hydrocarbon from animal and plant oils. Z. NAKAMIYA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 720—730).—From the unsaponifiable fractions of rice-embryo, soya, and fish-liver oils (e.g., *Gadus macrocephalus*, *Theragra chalcogramma*, *Stereolepis ischinagi*) an unsaturated hydrocarbon, *gadusene* (I), $\text{C}_{18}\text{H}_{32}$ (not identical with squalene), has been isolated. Catalytic hydrogenation yielded *gadusane*, $\text{C}_{18}\text{H}_{38}$. (I) may be identical with Drummond's hydrocarbon $\text{C}_{18}\text{H}_{32}$ from wheat-embryo oil and Tsujimoto's compound $\text{C}_{35}\text{H}_{60}$ from ishinagi-liver oil, since they have in common five characteristic absorption bands.

E. P.

Lipochrome content of human liver. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1934, 234, 241—244).—The livers examined (all from diseased subjects) contained ≥ 2.0 mg. of carotene and ≥ 0.5 mg. of lycopene and of xanthophyll per kg.

J. H. B.

Lipochrome metabolism of the horse. II. Selective absorption of carotenoids in the animal body. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1935, 234, 235—240; cf. A., 1934, 1251).—In the organism of the horse the only intact carotenoid found is carotene (I), which is selectively absorbed from the fodder. (I) is accompanied by unidentified degradation products, but plant polyene alcohols (II) are absent. (II) are not absorbed and subsequently destroyed by the liver, since they are not found even in the portal blood.

J. H. B.

Lipochromes of marine animals. VI. Carotenoids of salmon flesh. N. A. SÖRENSEN (Z. physiol. Chem., 1935, 235, 8—11).—Two salmon oils contained astacene (I) and small amounts of unidentified pigments: (I) is the main pigment in salmon. H. W.

Blue-fluorescing substance from corpus luteum. H. VON EULER and K. M. BRANDT (Naturwiss., 1935, 23, 544).—Treatment of COMe_2 -sol. substances of corpus luteum with Et_2O followed by EtOH and chromatographic adsorption yields preps. of a blue-fluorescing substance (I) (cf. A., 1934, 1382; this vol., 663) with max. fluorescence at approx. 420 μ and absorption max. at 260 and 345 μ ; it differs from lumichrome (A., 1934, 1233) in fluorescence acidity max. (p_H 2—6 for the latter). In contrast to the flavins, irradiation (Hg) of aq. solutions yields no CHCl_3 -extractable fluorescent product. Methylation (Me_2SO_4) yields a product with absorption bands (in CHCl_3) at 260—280 μ and a fluorescence band (in EtOH) between 380 and 500 μ . Acetylation affords a blue-fluorescing substance with absorption bands at 281 and 272 μ in CHCl_3 , aq. extraction yielding a purer product with bands at 255, 265, and 278 μ . The presence of a second substance occurring with (I) is therefore indicated. F. O. H.

Liver-glycogen. II. Acyl derivatives and "regenerated glycogens." D. J. BELL and H. KOSTERLITZ. **III. Molecular units of fish and rabbit glycogens.** D. J. BELL (Biochem. J., 1935, 29, 2027—2030, 2031—2035; cf. A., 1934, 914).—II. The glycogen (I) regenerated from its acyl derivatives is not significantly different from the original (I) in $[\alpha]$, rate of hydrolysis, or reducing power.

III. Rabbit- and fish-(I) gave similar products on exhaustive methylation. Hydrolysis of the products gave tetramethylglucopyranose, 2:3:6-trimethylglucose, and dimethylglucoses in each case, and it is concluded that the preps. are identical, being built up of unbranched chains of 12 glucose units. H. D.

Urea production in the human placenta. J. BOTELLA-LLUSIA (Arch. Gynakol., 1935, 159, 27—34).—The surviving human placenta converts NH_3 and NH_4 salts into urea, and can also produce it at the expense of some of its NH_2 -acids.

NUTR. ABS. (m)

Physiology of the skeletal muscle of mammals at different stages of their individual development. C. KOSCHTOJANZ and A. RJABINOWSKAJA (Pflüger's Archiv, 1935, 235, 416—421).—Creatine-phosphoric acid does not appear in rabbit muscle until after the 21st day of embryonal development. It rises from 4—5% to 60—70% in the first day after birth. R. N. C.

Phosphorus compounds of brain. I. Phosphocreatine. S. E. KERR (J. Biol. Chem., 1935, 110, 625—635).—Mammalian brain, frozen *in situ* with liquid air, yields a labile P compound, associated with 1 mol. equiv. of creatine. The properties of the compound and of a Ca salt, obtained cryst., agree with those of phosphocreatine from muscle. No significant differences are found between labile P contents of cerebrum and cerebellum. F. A. A.

Phosphatides. XII. Nature of the phosphatides and other lipins of the brain and liver in the Niemann-Pick disease. E. KLENK (Z. physiol. Chem., 1935, 235, 24—36; cf. this vol., 384).—The high sphingomyelin (I) content of the brain is in contrast with the almost complete absence of cerebrosides, although a material containing sugar is present which is possibly related to, although distinct from (I). The product in the liver is a mixture of lignocero-, nervo-, stearo-, and palmito-sphingomyelin, whereas that in the brain is almost homogeneous stearosphingomyelin, the absence of C_{24} acid derivatives being particularly characteristic. In the liver-phosphatides derivatives of the highly unsaturated C_{20} and C_{22} acids are easily identified, whereas they could not be detected with certainty in the brain. H. W.

Isolation of phosphocholine from ox liver. F. INUKAI and W. NAKAHARA (Proc. Imp. Acad. Tokyo, 1935, 11, 260—261).—60% MeOH containing H_2SO_4 extracts phosphocholine (picrate, m.p. 228° after softening at 225°), which is synthesised from choline chloride, P_2O_5 , and H_3PO_4 at 70°. J. L. D.

Water-soluble choline precursor in the human placenta. D. H. SMYTH (Biochem. J., 1935, 29, 2067—2070).—The method of Booth and Milroy (cf. below) for the extraction from the kidney of the H_2O -sol. choline precursor is applied to the placenta, and a substance (I) containing choline-N, NH_2 -N, and P in the ratio 1:1:1 is isolated in small amount. (I) is probably similar to the compound obtained by the above workers. A. L.

Water-soluble precursor of choline found in the kidney and other tissues. F. J. BOOTH (Biochem. J., 1935, 29, 2071—2076).—The method, involving repeated pptn. with HgCl_2 in EtOH solution, for the extraction of the H_2O -sol. choline precursor (I) from the kidney is described. The rate of hydrolysis of, and the N distribution in, (I) indicate that it is the choline ester of sphingosinephosphoric acid. (I) has no action on the eserinated rectus of the frog, but after acetylation, which causes decomp., the Ac derivative has the properties of acetylcholine. Compounds similar to (I) are present in the brain and the liver. A. L.

Transformation of dehydrocholic acid into β -3-hydroxy-7:12-diketocholanic acid.—See this vol., 1237.

Glutathione in hens' eggs. M. TALENTI (Arch. Farm. sperim., 1935, 59, 287—290).—Direct nitroprusside tests on yolk and white of sterile or fertilised eggs indicate the presence of reduced glutathione from the time of laying; aq. $\text{CCl}_3\text{CO}_2\text{H}$ extracts, however, give a zero titration with I (cf. A., 1933, 298). F. O. H.

Redox potential of glutathione. J. C. GHOSH and S. C. GANGULI (Biochem. Z., 1935, 279, 296—299).—A method for determination is described, the mean val. for E_0 being +0.068. P. W. C.

Physiological action of asterubin and of other sulphur-containing derivatives of guanidine. D. ACKERMANN and H. A. HEINSEN (Z. physiol. Chem., 1935, 235, 115—121; cf. this vol., 1004).—Taurine

(I), guanyltaurine (II), and asterubin (III) have no effect on blood-pressure in the dog. (I) and (II) cause decrease [preceded by increase in the case of (II)] and (III) causes increase in the sugar content of the blood. Cystamine (IV) and still more *di-guanylcystamine* (V) lower the blood-sugar level, but *tetramethylguanylcystamine* (VI) raises it greatly. The blood-pressure is lowered by (IV), (V), and (VI) [(VI) > (V) > (IV)]. (V) (*picrate*, decomp. 211–212°; *picrolonate*) is obtained by the interaction of cystamine (VII) and cyanamide and (VI) (*picrate*, m.p. 118°) by that of (VII) and dimethyleyanamide.

W. McC.

Guanidine nucleus in pseudomucin. H. FUCHS (Biochem. Z., 1935, 279, 413–416; cf. A., 1905, i, 104).—Guanidine (I), methylguanidine, creatine, creatinine, and arginine (II) resist, for short periods, hot acid oxidation by aq. NaMnO_4 . The amounts of arginine and (I) obtained from hydrolysed (30% H_2SO_4 for 12 hr.) pseudomucin by oxidation with aq. NaMnO_4 indicate that, after hydrolysis, pseudomucin contains no (I) nucleus other than that separated as (II).

W. McC.

Iodometric determination of muscle-guanine. A. DMOCHOWSKI, A. ZAJDENMAN, and A. RABANOWSKA (Biochem. Z., 1935, 279, 289–295).—A micro-method for determination of tissue-guanine (I) depends on purification of the tissue hydrolysate with tungstate, pptn. with Cu, repptn. with As, and final oxidation with NaOI . The (I) content of rabbits' muscle is 11–12 mg. per 100 g., or only about half of that as determined by the enzymic method. It is suggested that the muscle contains a new purine (aminohydroxypurine?).

P. W. C.

Extractives of dog and rabbit muscle. A. N. PARSCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 35–36).—Carnitine is absent.

E. P.

Nucleotides, nucleosides, and free purines of rabbit liver. G. DELL'ACQUA (Biochem. Z., 1935, 279, 403–412).—Sol. purines are irregularly distributed in the fresh liver, 100 g. of which contain an average of 44 mg. of N combined as nucleotides and 22 mg. as nucleosides and free purines. After autolysis for 24 hr. in unbuffered media there is an increase of 15% in the amount of sol. purines and the ratio nucleotide-N:nucleoside-N+free purine-N is reversed. Administration of adrenaline (I) frequently results in increase in the amount of sol. purines, nucleosides and free purines often increasing at the expense of nucleotides. Autolysis after (I) administration is more extensive, and sol. purines increase in amount by 33%. Insulin (II) produces no change in the amount of sol. purines or in the proportions of the three fractions, but autolysis is enormously increased after giving (II) and the amount of sol. purines increases by 66%. Poisoning with P causes 100% increase in the amount of sol. purines, but subsequent autolysis (24 hr.) causes no further increase.

W. McC.

Localisation of nucleic acids in the cell-nucleus. T. CASPERSSON (Naturwiss., 1935, 23, 527; cf. this vol., 375).—The powerful absorption of ultra-violet light by cell nuclei and chromosomes (*e.g.*, of salivary

glands of larvæ of *Diptera*) is due to the nucleic acids present. With thymonucleic acid the absorption exhibits a max. at 260 $\text{m}\mu$.

W. McC.

Boric acid reaction and the structure of nucleic acid. P. A. LEVENE and R. S. TIPSON (Z. physiol. Chem., 1935, 234, V).—Inosine and guanosine give a positive, thymidine gives a negative, boric acid reaction (cf. Makino, this vol., 772).

J. H. B.

Chemistry of chromosomes. I. H. HELLSTRÖM, D. BURSTROM, and H. VON EULER (Svensk Kem. Tidskr., 1935, 47, 207–211).—The salivary glands of the larvæ of *Drosophila virilis* are used as a source of chromosomes. The variation in intensity of absorption of these between 257 and 292 $\text{m}\mu$, as revealed by photomicrographs, suggests that they are related to the nucleic acids. Selective dissolution of chromosomes by appropriate fixing agents is also studied.

E. A. H. R.

Effect of heat and hot alcohol on liver-proteins. W. H. SEEGER and H. A. MATTILL (J. Biol. Chem., 1935, 110, 531–539).—The growth rate, biological val., and digestibility of the acid hydrolysates of dried whole liver, heated liver, and EtOH-extracted (130 hr.) liver are approx. the same. Heating at 120° for 72 hr. or EtOH-extraction for 130 hr. lowers the digestibility and thus the biological val. of the protein.

H. G. R.

Influence of hydrogen peroxide on the precipitability of proteins. P. RONDONI and L. POZZI (Z. physiol. Chem., 1935, 235, 81–90).—In all cases investigated pre-treatment with H_2O_2 increased the amount of proteins pptd. by $\text{CCl}_3\text{-CO}_2\text{H}$. Somewhat similar results are obtained when thermal pptn. is used, but not when sulphosalicylic acid is employed. The phenomenon is most pronounced in serum and other complex protein systems; increase is not observed with ovalbumin. The effect is not due to acidity of H_2O_2 .

H. W.

X-Ray reflexions of long spacing from tendon. R. W. G. WYCKOFF, R. B. COREY, and J. BISCOE (Science, 1935, 82, 175–176).—Long spacings observed in diffraction photographs of kangaroo tendon are recorded. Their existence shows that tendon cannot consist of parallel polypeptide chains bound together by irregularly repeated cross-linkings. Other possible structures are discussed.

L. S. T.

Fibre forms in animal hairs. H. J. WOODS (Nature, 1935, 136, 262).—The results described (this vol., 1144) for fibre forms of white fox guard hairs are compared with those obtained with merino wool.

L. S. T.

Correlation of the viscosities of protein solutions with their ability to crystallise. D. B. HAND (J. Gen. Physiol., 1935, 18, 847–852).—Proteins having viscosities in solution > serum-albumin are readily crystallised; those having viscosities < denatured ovalbumin have not yet been crystallised.

F. A. A.

Peroxidase reaction. LIII. Arakawa reaction and calcium content of human milk. Y. UGA (Tôhoku J. Exp. Med., 1935, 25, 169–185).—There is a more or less graded fall in Ca content when passing from a human milk with a strong positive

to one with a negative Arakawa reaction. Arakawa-positive milk is good milk. NUTR. ABS. (m)

Mechanism of the Umikoff reaction. M. POLO-NOVSKI and F. MORENO-MARTIN (Bull. Soc. Chim. biol., 1935, 17, 960—964).—The reaction of Umikoff given by human but not by cows' milk with aq. NH_3 at 60° is due to the difference in the buffering power, being given by milk above p_{H} 8. A. L.

Behaviour of caseinogenate sols: hysteresis-like phenomenon in the rennin coagulation of milk. M. E. POWELL and L. S. PALMER (J. Dairy Sci., 1935, 18, 401—414).—Heated Ca caseinogenate-colloidal Ca phosphate mixtures show a hysteresis-like effect when coagulated by rennin at different intervals after heating. Heating of either constituent alone prior to mixing does not induce this effect. A complex containing colloidal CaC_2O_4 has not this property. Heating increases the cataphoretic migration of the complex $>$ that of a Ca caseinogenate sol. A. G. P.

Components of gastric juice. P. NOPONEN (Acta med. scand., 1933, Suppl. 59, 386—394).—In human beings receiving fractional test meals histamine injection caused secretion of a very acid fluid, and pilocarpine injection secretion of a fluid rich in neutral chloride and N compounds but poor in acid. Normal gastric juice consists of these two secretions in varying amounts. NUTR. ABS. (m)

Gastric secretion and hypochloræmia. R. S. MACH (Schweiz. med. Woch., 1935, 65, 11—13).—Withdrawal of gastric juice before and at intervals during 4 hr. in which injections of histamine were given caused, in subjects suffering from gastric complaints, a slight decrease in cellular blood-Cl, but no distinct effect on plasma-Cl. NUTR. ABS.

Dependence of the amylolytic power of the intestinal juice on the type of diet. S. GEORGIEVSKI and S. ANDREEV (Pflüger's Archiv, 1935, 235, 428—437).—The amylolytic power of the intestinal juice in the dog is closely associated with the type of diet. The amylolytic index \propto the starch content of the diet. R. N. C.

Mucins and mucoids. G. BLIX, C. O. OLDFELDT, and O. KARLBERG (Z. physiol. Chem., 1935, 234, III—IV).—Very little H_2SO_4 was eliminated from various mucins on HCl hydrolysis, hence mucosulphuric acid is not the principal carbohydrate group. Submaxillary mucin (isoelectric point p_{H} 2.45) contains two carbohydrate complexes, one of which (5% in amount) is dimannose-glucosamine, the other (25%), a cryst. substance, $\text{C}_{14}\text{H}_{25}\text{O}_{11}\text{N}$ (?), containing glucosamine, 2 Ac groups, and probably a polyhydroxy-acid (not hexuronic acid). It gives a positive $\text{NMe}_2\text{C}_6\text{H}_4\text{CHO}$ reaction. J. H. B.

Composition of glomerular urine. XII. Reaction of glomerular urine of frogs and *Necturi*. H. MONTGOMERY (J. Biol. Chem. 1935, 110, 749—761).—A colorimetric method for determining the p_{H} of minute vols. of liquid is described. The error when applied to protein-free buffer solutions was $< 0.02 p_{\text{H}}$. The p_{H} of the glomerular urine from frogs and *Necturi* is the same as that of the plasma. J. N. A.

Micro-quinhydrone electrode: application to determination of the p_{H} of glomerular urine of *Necturus*.—See this vol., 1218.

Effect of tonsillary extract on diuresis and on elimination of sodium chloride. E. CHIAEPPE (Boll. Soc. Ital. Biol. speriment., 1935, 10, 157—159).—Injection of tonsillary extract in rabbits increases diuresis, which reaches its max. in 3 hr., and persists longer than in non-injected animals. NaCl elimination remains const. R. N. C.

Determination of neutral sulphur in urine. A. FREDERICH and F. MANDL (Z. physiol. Chem., 1935, 235, 174—180; cf. A., 1934, 1386).—The procedure is improved by boiling the urine (2 c.c.) for 30 min. with 5—6 drops of conc. HCl, removing org. matter from the diluted liquid (10 c.c.) by shaking with 0.5 g. of wood-C, and pptg. SO_4^{--} (from 5 c.c. of filtrate) with 20 c.c. of benzidine reagent. The vol. (≤ 0.6 c.c. for satisfactory results) of 0.02N-alkali used for titration is corr. by adding 0.15 c.c. If the amount of total SO_4^{--} is very low or if the urine has been too much diluted, 1 c.c. of 0.02N- H_2SO_4 is added before addition of benzidine and allowance made in calculation, the titration correction being now 0.18 c.c. W. McC.

Excretion of phosphates by the kidney. P. IVERSEN and E. JACOBSEN (Skand. Arch. Physiol., 1935, 71, 260—271).—The excretion coeff. of phosphate was determined under various experimental conditions by comparing the concn. indices of phosphate and creatinine (I), the concn. index being the ratio of the concn. in urine and plasma. The vals. found for women with healthy kidneys were 0.00—0.27, and showed no relationship with plasma-phosphate. If diuresis was increased by H_2O intake, there was a relative increase in phosphate excretion if the (I) concn. index was < 20 . With increasing blood-sugar an increase in phosphate excretion was observed, and with decreasing blood-sugar a decrease. Parathyroid or theophylline intake caused an increased, and salyrgan a decreased, excretion.

NUTR. ABS. (m)

Ammonia, urea, and p_{H} of urine in infants, healthy and with nutritional disturbances. V. ANGELINI (Riv. Clin. pediat., 1935, 32, 1310).—In infants, excretion of NH_3 occurs in relatively const. amounts, whilst that of urea shows variations apparently correlated with diet. In infants with nutritional disturbances, the increase in urinary NH_3 \propto the degree of acidosis; urea varies inversely. Neither in healthy nor in sick infants is there a const. inverse relationship between p_{H} and excretion of NH_3 . NUTR. ABS. (m)

"Free" ammonia in urine. Comparison of the Ronchese method with the so-called "micro-Schloesing" method. P. BALATRE (J. Pharm. Chim., 1935, [viii], 22, 107—112).—The Ronchese method (A., 1907, ii, 651) gives high results and the micro-Schloesing method (A., 1922, ii, 453; 1934, 1385) is preferred. S. C.

Occurrence of methylglyoxal in urine during vitamin-B₁ deficiency. J. LEHMANN (Skand. Arch. Physiol., 1935, 71, 157—165).—AcCHO occurs in the urine of rats on a basal diet with or without addition

of vitamin- B_1 or - B_2 . Hence the presence of AcCHO in the urine is not sp. for vitamin- B_1 deficiency. Most of the AcCHO disappears within 12 hr. when the urine is kept. NUTR. ABS. (m)

Micro-determination of ketones in urine. O. CANTONI (Biochem. Z., 1935, 279, 201—202).—The author's method (this vol., 104, 880) for determination of ketones in blood is adapted for use with urine. P. W. C.

Effect of diet on volatile reducing substances in urine. S. HOF LUND (Skand. Arch. Physiol., 1935, 71, 238—250).—After a meal the amount of reducing substances increases, reaching a max. after 2—3 hr. Carbohydrates and fats cause no appreciable increase, but proteins always do. Fried is more effective than boiled meat. NUTR. ABS. (m)

Excretion of glucose by the rabbit kidney. T. W. T. DILLON and R. O'DONNELL (Proc. Roy. Irish Acad., 1935, 42B, 365—405).—A method for determining the kidney threshold for glucose (I) in the rabbit is described. It is defined as the plasma-(I) level above which (I) appears in greater concn. in the urine than in the plasma. It is independent of the rate of secretion of urine and varies between 190 and 430 mg. of (I) per 100 c.c. Injections of NaCl do not raise the kidney threshold, but urea and Na_2SO_4 cause a sharp rise, whilst insulin probably lowers it slightly. The excretion of (I) is closely analogous to the excretion of Cl^- , and fulfils the requirements of the "diffusion-secretion" theory, but is incompatible with the Cushny theory. J. N. A.

Acidosis-producing substance (A.H.) of normal urine. C. FUNK, P. ZEFIROW, and I. C. FUNK (Arch. internat. Pharmacodyn., 1934, 49, 189—203).—Methods of prep. and assay of this hormone are described, and its effect on the utilisation of fats and carbohydrates is studied. It is similar to, but not identical with, the "fat metabolism" hormone of the anterior pituitary. The acidosis is not produced through the thyroid. NUTR. ABS. (m)

Determination of uric acid in urine. P. BALATRE (J. Pharm. Chim., 1935, [viii], 22, 120—123).—The method of determining uric acid by adding urine to I-KI solution containing CS_2 until the I is reduced is liable to serious errors on account of the presence of other reducing substances. S. C.

Xanthurenic acid. I. L. MUSAJO (Atti R. Accad. Lincei, 1935, [vi], 21, 368—371).—The reactions of the xanthurenic acid which imparts a green colour to the urine of albino rats fed on fibrin, ovalbumin, etc. indicate that it is a dihydroxyquinolinecarboxylic acid (cf. this vol., 1007). T. H. P.

Urinary phosphatase. W. KUTSCHER and H. WOLBERGS (Naturwiss., 1935, 23, 558—559).—The phosphatase (I) content of urine is high early in the morning, falls to a min. at midday, rises after a midday meal, and decreases gradually towards the evening. A high early-morning val. is also observed during fasting. Feeding of glucose after fasting leads to a decrease in the amount of (I) excreted corresponding with the rise in blood-sugar level. E. A. H. R.

Detection of defence enzymes in urine. E. ABDERHALDEN (Fermentforsch., 1935, 14, 502—521).—Dialysis is unnecessary and procedure is much simplified if the test is applied to suspensions (in 0.9% aq. NaCl) of the material pptd. from urine by COMe_2 instead of to blood-serum. W. McC.

Presence of the protective hormone in urine. A. DE BARBIERI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 153—154).—Injection of urine extract in guinea-pigs protects the animals against acute NH_4Cl poisoning; the Sato protective hormone of the liver is hence present in urine. R. N. C.

Detection of bile-pigments in urine by methylene-blue. P. BALATRE (J. Pharm. Chim., 1935, [viii], 22, 166—168).—The reaction is based on purely physical phenomena and is untrustworthy. P. G. M.

Perspiration and erythema. W. H. CAREW (Nature, 1935, 136, 340).—A film of human perspiration 1 mm. thick absorbs light slightly in the region of 330, appreciably at 290, and practically completely at 270 m μ . Uric acid may be the primary absorbing agent in sweat. L. S. T.

Ætiology of pernicious and related macrocytic anæmias. W. B. CASTLE (Science, 1935, 82, 159—164).—A lecture. L. S. T.

Colloidal dye effective in treating pernicious anæmia and evoking reticulocytosis in guinea-pigs. C. MERMOD and W. DOCK (Science, 1935, 82, 155—156).—The observation that repeated intravenous injection of Congo-red produces in primary anæmia effects similar to those of liver-extract has been confirmed. L. S. T.

Anæmia in the chronic rheumatic diseases. D. H. COLLINS (Lancet, 1935, 229, 548—550).—Anæmia due to diminished blood-hæmoglobin with a relatively insignificant fall in the red-cell count frequently accompanies chronic rheumatic conditions. The more severe degrees of anæmia practically only occur in atrophic arthritis. Anacidity is frequently found among females with atrophic arthritis, but deficient gastric secretion is not a const. factor in the production of anæmia in such cases. L. S. T.

Development of nutritional anæmia in dairy calves. C. E. KNOOP, W. E. KRAUSS, and R. G. WASHBURN (J. Dairy Sci., 1935, 18, 337—347).—Calves receiving exclusively a whole-milk diet developed nutritional anæmia. Supplementary feeding of Cu and Fe (40 and 400 mg. daily, respectively) prevented anæmia and markedly increased the Cu and Fe contents of livers. A. G. P.

Increase in blood-carbon monoxide in anæmia. M. LOEPER, E. BIOY, J. TONNET, and A. VARAY (Compt. rend. Soc. Biol., 1935, 119, 1319—1320).—Many types of anæmia are associated with an increase in blood-CO, although no relation between the quantity of CO and the extent of the anæmia is observed. H. G. R.

New cancer-producing hydrocarbons. A. A. MORTON, D. B. CLAPP, and C. F. BRANCH (Science, 1935, 82, 134).— $s\text{-C}_6\text{H}_5\text{Ph}_3$ and CPh_4 produce malignancy.

nant growths in mice, but more slowly than carcinogenic compounds containing a phenanthrene nucleus.

L. S. T.

Resistance of sarcomatous rats to insulin. M. PEREZ (Boll. Soc. Ital. Biol. sperim., 1935, **10**, 118—121).—The min. lethal dose of insulin in rats with sarcomatous tumours is $>$ in normal rats; both vals. fall as the fasting period increases, and the difference between them also decreases. The blood-sugar is unaltered by the presence of tumours, and is hence not associated with the increased resistance.

R. N. C.

Behaviour of serum in malign tumours, pregnancy, and gynaecological diseases. C. VERCESI and F. GUERCIO (Biochem. Z., 1935, **279**, 229—232).—The I val. of the material extracted with Et_2O from filter-paper on which serum of cases of pregnancy, uterus carcinoma, etc. had been dried was considerably higher in cases of malignant disease than in other diseases and pregnancy.

P. W. C.

Chemistry of cataract in the diabetic. H. N. CAREY and H. M. HUNT (New England J. Med., 1935, **212**, 463—468).—The cryst. lenses from 10 normal subjects contained approx. 400 mg. of cholesterol per 100 g., 9.5 mg. of Ca, and 16.5 mg. of P. Cataractous lenses contained on an average 522 mg. of cholesterol and 31.6 mg. of Ca. There were no marked differences in the Ca contents of diabetic and non-diabetic cataractous lenses, but the P content of the former was 6.2 mg. per 100 g., as compared with 19.7 mg. for the latter.

NUTR. ABS. (m).

Alkali reserve in induced hypoglycaemia in normal and diabetic subjects. M. TRIPODI (Políclinico, 1935, **42**, 111—127).—The effect of insulin on the alkali reserve was studied. Coincident with the appearance and to some extent \propto the degree of hypoglycaemia there was a const. fall in alkali reserve in normal and slightly diabetic subjects and in rabbits. In severe diabetes there was first a transient increase and then, when the blood-sugar fell below a certain level, a fall in alkali reserve which coincided with the disappearance of hypoglycaemia. Large doses of NaHCO_3 given intravenously when hypoglycaemia appeared had a favourable effect on slight, but none on severe, hypoglycaemia.

NUTR. ABS. (m)

Glucose and lactate usages of the diabetic heart and the influence of insulin thereon. C. L. EVANS, F. GRANDE, F. Y. HSU, D. H. K. LEE, and A. G. MULDER (Quart. J. Exp. Physiol., 1935, **24**, 365—376).—The glucose (I) and lactate (II) usages of the perfused diabetic dog's heart are about half the val. for the normal organ; although the (I) consumption is trebled by the addition of insulin, that of (II) is slightly decreased. It is of fundamental importance that the diabetic heart uses (II) at about the same rate as the hyperglycaemic normal heart.

NUTR. ABS. (m)

Hæmatic glycolysis *in vitro* in diabetes mellitus. I. Action of cortin. G. VIALE and A. CROCETTA (Boll. Soc. Ital. Biol. sperim., 1935, **10**, 143—145).—Cortin in any concn. inactivates hæmatic glycolysis in depancreatized dogs. In normal dogs and diabetic patients it activates glycolysis up to a given concn., above which it inhibits it completely.

Action of parathyroid extract on glycaemia in diabetes. J. OLMER, J. E. PAILLAS, and B. SICNASI (Compt. rend. Soc. Biol., 1935, **119**, 1264—1266).—Injection of parathormone causes a lowering of blood-sugar.

H. G. R.

Reducing substances in the blood in eclampsia. H. DIETEL (Arch. Gynäkol., 1935, **159**, 94—97).—Iodometric titration of blood, combined with separate determination of SH-compounds, indicates an excess of a non-SH reducing substance which is identified with ascorbic acid, and is much diminished in eclampsia. The redox processes of the cells are disturbed in this condition.

NUTR. ABS. (m)

Porphyrin excretion in hyperemesis gravidarum and its relationship to liver function. I. HEROLD (Arch. Gynäkol., 1935, **159**, 35—40).—The average daily urinary excretion of porphyrin in pregnancy was < 0.04 mg., the highest val. being 0.066 mg.

NUTR. ABS. (m)

Heat exchange of the rat in exogenous hyperthermia. K. SCHUECKER (Pflüger's Archiv, 1935, **235**, 490—513).

R. N. C.

Effect of tyrosine on the function of the thyroid gland. I. ABELIN (Naturwiss., 1935, **23**, 528—529).—Tyrosine administered together with thyroid preps. to animals suffering from experimental hyperthyroidism has a beneficial effect on the accompanying symptoms of disease and diminishes the metabolic action of the thyrotropic hormone.

W. McC.

Pathological physiology of infarct. II. Proteolytic activity of infarct tissue. G. BORGER and T. MAYR (Z. physiol. Chem., 1935, **234**, 245—253; cf. A., 1933, 852).—The proteolytic activity is much $<$ that of normal tissue. This appears to be due to destruction of enzyme in the infarct and not to the production of inhibitors.

J. H. B.

Lipæmia and uræmia. S. MARINO (Arch. Farm. sperim., 1935, **59**, 245—273).—Uræmia of some types of glomerular nephritis is accompanied by increased levels of blood-phosphatide (I), -cholesterol (II), and, occasionally, -fatty acids (III). (I) and (II) slowly diminish during uræmic coma, whilst (III) markedly increase. No correlation exists between the lipæmia and arterial pressure, albuminuria, or blood-N level. The increase in blood-lipins is a defensive reaction of the organism against the toxic effect of uræmia.

F. O. H.

Oxalic acid metabolism in nephritis. Determination of the acid in blood, food, urine, and faeces. R. RITTMANN and P. UNTERRICHTER (Arch. Verdauungs-Kr., 1935, **57**, 120—148).—The method of Bau (A., 1921, ii, 356), with slight modifications, is satisfactory for the determination of $\text{H}_2\text{C}_2\text{O}_4$ in urine, faeces, and foods, but not in blood. In kidney disease $\text{H}_2\text{C}_2\text{O}_4$ is probably retained in the blood.

NUTR. ABS. (m)

Nutritional œdema in the dog. I. Development of hypoproteinæmia on a diet deficient in protein. A. A. WEECH, E. GOETTSCH, and E. B. REEVES (J. Exp. Med., 1935, **61**, 299—317).—Dogs receiving a diet very low in protein showed first a rapid and then a slow decrease in serum-albumin and

total protein. The globulin, which showed wide individual variations, remained approx. const. There was a mean daily loss of 1.15 g. of N, only 3—4% of which was accounted for by the decrease in blood-protein. In one dog, a ten-day fast caused a rise of the serum-albumin to normal. When sufficient amounts of animal protein were given there was slow regeneration of blood-protein. NUTR. ABS. (m)

Acid-base balance in cows and ewes during and after pregnancy. Milk fever and acetonæmia. J. SAMPSON and C. E. HAYDEN (J. Amer. Vet. Med. Assoc., 1935, 86, 13—23).—In normal pregnant cows there was a slight lowering of CO₂ capacity and a slight rise in blood-ketones. In milk fever and acetonæmia, there was a further lowering of CO₂ capacity and raising of ketones, together with a marked lowering of serum-Ca. In other diseases the vals. were normal. In normal ewes there was little difference between the blood of pregnant and that of non-pregnant animals. In pregnancy disease there was a lowering of CO₂ capacity and rise in ketones with ketonuria. Serum-Ca was normal. In other diseases figures were normal. Acetonæmia in cows and pregnancy disease in ewes are possibly due to disturbance of carbohydrate metabolism.

NUTR. ABS. (m)

Calcium metabolism in pregnancy. W. VOGELER (Diss., Erlangen, 1933; Bied. Zentr., 1934, A, 5, 328).—The decline in total Ca of the blood in pregnancy is probably associated with an increase in % of dialysable Ca. The activity of internal secretion glands is closely related to Ca metabolism. The tendency toward caries in pregnancy is partly although not wholly dependent on Ca deficiency. A. G. P.

Iron metabolism during pregnancy. K. UTHEIM-TOVERUD (Acta paediat., 1935, 17, Suppl., 131—135).—In the last trimester of pregnancy, on Fe intakes varying from 7 to 28 mg. the daily retention in 8 cases out of 10 was < the foetal requirement of 4.7 mg., as calc. by Hugounenq. Including foetal requirements, the lowest intake with a positive balance was 13 mg.; in two cases a daily intake of 15 mg. gave a negative balance. 70 out of 181 mothers in the last trimester showed a hæmoglobin level < 70% (Sahli); in only 13 of these was hydræmia a possible explanation. Blood-Fe ranged from 40 to 59 mg. per 100 ml., figures < 45 mg. occurring in 28% of 114 women examined. Of 47 pregnant women, 28 showed hypo-acidity in the last trimester. A negative Fe balance may be due to an Fe intake below the min. needs, or to defective absorption, and leads to lowering of the blood-hæmoglobin and -Fe. NUTR. ABS. (m)

Intermediary fat metabolism in pregnancy. II. Dietary fat and blood-fat. O. BOKELMANN and A. BOCK (Arch. Gynakol., 1934, 158, 505—530).—The ketone contents of the blood and urine are somewhat higher and the blood-fatty acid content is considerably greater in pregnant than in non-pregnant women. After oral administration of large amounts of fat together with a correspondingly enriched carbohydrate diet, the blood-fatty acid and -ketone and the urinary ketone were increased, the increase being much greater in pregnant than in non-pregnant women.

NUTR. ABS. (m)

Thyroid action in pregnancy. Presence of the thyroid hormone in blood in pregnancy. K. J. ANSELMINO and F. HOFFMANN (Arch. Gynakol., 1935, 159, 84—93).—Experiments in which serum from pregnant (10 months) and non-pregnant (intermenstrual) women was fed to rats indicate that the amount of thyroid hormone in blood is increased in pregnancy. NUTR. ABS. (m)

Effect of the hen's diet on bone changes in rachitic chicks. B. E. KLINE, C. A. ELVEHJEM, and J. G. HALPIN (Poultry Sci., 1935, 14, 116—118).—Within the limits of practical feeding, the level of vitamin-D of hen's rations did not affect the % ash in the bones of chicks. A. G. P.

Blood-magnesium in Recklinghausen's disease. J. MARX (Orvosi Hetilap, 1935, 79, 351—353).—Parathyroid hormone injected into guinea-pigs caused a decrease in blood-Mg and an increase in blood-Ca. The decrease in the Ca in the bones was associated with an increase in Mg.

NUTR. ABS. (m)

Impregnation of the organism by dust. I. R. FABRE (J. Pharm. Chim., 1935, [viii], 22, 145—150).—A preliminary study of the problems involved in the physiology and pathology of silicosis, anthracosis, etc. P. G. M.

Modifications in the content of inorganic phosphorus in blood and urine in experimental scurvy. A. LEONE (Riv. Clin. Pediat., 1934, 32, 1185).—In experimental scurvy the P balance became sharply negative. The inorg. P of the blood fell and the urinary excretion increased, with a relative decrease just before death. The metabolism of carbohydrates and P, which rises with the formation of lactacidogen, possibly causes this change.

NUTR. ABS. (m)

Hypomagnesiæmia in equine transit tetany. H. H. GREEN, W. M. ALLCROFT, and R. F. MONTGOMERIE (J. Comp. Pathol., 1935, 48, 74—79).—The hypocalcæmia of equine transit tetany is associated with hypomagnesiæmia. There was a 50% decrease in serum-Mg as compared with vals. taken two weeks later.

NUTR. ABS. (m)

Etiology of grass tetany. V. Reduction of blood-calcium and -magnesium by a plant substance and by withdrawal of blood, fasting, and tissue necrosis. L. SEEKLES and B. SJOLLEMA (Arch. Tierheilk., 1935, 68, 386—396).—In rabbits serum-Ca was lowered by blood-sampling, fasting, or pathological change. Subcutaneous and oral administration of grass extracts (from meadows on which grass tetany had previously developed) and subcutaneous injection of earthnut extracts lowered the serum-Ca level. Some extracts produced a lowering of serum-Mg. Fractionation of the extracts did not yield a more highly active fraction.

NUTR. ABS. (m)

Vitamin-C and tubercular infection. G. DI BELLA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 141—142).—The resistance of guinea-pigs to tubercle bacilli is not increased by orange-juice or ascorbic acid. R. N. C.

Fat-tolerance tests and blood-sugar determinations on patients with peptic ulcer. Possible factors in the etiology of peptic ulcer. M. A. SCHNITKER and E. S. EMERY, jun. (Amer. J. Digest. Dis. Nutrit., 1935, 1, 834—840).—After ingestion of 100 g. of milk-fat, the blood-fat and -sugar level in patients suffering from peptic ulcer showed no significant variation from the levels in controls.

NUTR. ABS. (m)

Cod-liver oil treatment of wounds. J. P. STEEL (Lancet, 1935, 229, 290—292).—Crude cod-liver oil promotes rapid healing of burns with almost complete elimination of scar tissue. It is also useful with indolent ulcers and deep abrasions. L. S. T.

Relation between basal metabolism and endogenous nitrogen metabolism with particular reference to the determination of maintenance requirement of protein. D. B. SMUTS (J. Nutrition, 1935, 9, 403—433).—In the animals examined, adjustment to the post-adsorptive condition during fasting and to the endogenous level of urinary N excretion during sp. N starvation is more rapid in those of smaller body-size. Total endogenous N output is more closely related to body-surface than to body-wt. In a variety of animals the daily endogenous N loss approximates closely to 2 mg. of N per g.-cal. basal heat. This relationship forms a basis of calculation of the maintenance requirement of protein. Creatinine excretion bears a fairly const. proportionality to basal metabolism within a species, but in different species creatinine-N forms characteristically different % of the total endogenous N (the % decreases with body-size). A. G. P.

Liver and cerebral function. A. DE BARBIERI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 155—157).—Interference with the blood outflow from the liver in dogs affects central metabolism. Neither the protective hormone nor the antiperinicious principle of the liver is involved. R. N. C.

Hæmoglobin production in rats on diets containing bread. V. C. MYERS, D. G. REMP, and F. C. BING (Cereal Chem., 1935, 12, 372—376).—Some whole-wheat breads contain twice as much Fe and Cu as white bread, rye bread being intermediate. Both Cu and Fe in bread can be effectively utilised by anæmic rats for growth and hæmoglobin production. White bread forms a fair source of Cu, but a poor one of Fe. Whole-wheat bread is not an Fe-rich food, but consumed in liberal amounts it could supply a significant proportion of the daily requirements of normal adults; its Fe appears to be equiv. to inorg. Fe for hæmoglobin production, although only 50% is in this form. The utilisation of bread-Cu is < two thirds as effective as the utilisation of inorg. Cu. The better growth of rats receiving bread-Cu than those on CuSO_4 is probably due to the presence in bread of elements other than Cu. E. A. F.

Nutritional value of bread in diet of human subjects and experimental animals. K. EYERLY, C. OCLASSEN, and J. A. KILLIAN (Cereal Chem., 1935, 12, 377—389).—Varying the amount of white bread in the diet of rats from 50 to 70% produced no effect on their rate of growth; there were no excessive

gains in wt. with the higher levels of white bread (60 and 70%) in the diet. Under the conditions used, a large fraction of white bread in the diet does not produce any signs of inhibition of calcification in the young, nor of decalcification in the mature rats in successive generations. Studies on the effect of white bread and sugars (sucrose, glucose, and invert sugar) on human energy metabolism showed that the experimental subjects exhibited the min. tolerance for glucose and the max. tolerance for white-bread carbohydrates. White bread exhibited a higher sp. dynamic action than sugars, and effected a more uniform distribution of heat production between carbohydrate and fat. E. A. F.

Pigmentation in black-haired rats. M. H. HAYDAK (Science, 1935, 82, 107—108).—The changes in pigmentation which occur when young rats are fed solely on whole milk are described and discussed. L. S. T.

Photometric method for the determination of chromic oxide in digestibility research after the so-called quantitative indicator method. L. PALOHEIMO and I. PALOHEIMO (Suomen Kem., 1935, 8, B, 29).— Cr_2O_3 , which has been mixed with food as an insol. indicator of the extent of digestion, may be determined in the faeces by dissolution from the ash by means of Na_2O_2 . The concn. of Na_2CrO_4 is determined photometrically. R. S. B.

Effect of sudden severe anoxæmia on the function of the human kidney. R. A. MCCANCE (Lancet, 1935, 229, 370—372).—After overbreathing and accidental anoxæmia with unconsciousness the process of NH_3 excretion and the ability to concentrate H^+ were unaffected, the rates of excretion of creatinine and of SO_4^{--} were somewhat, and of urea, H_2O , Na^+ , K^+ , Cl^- , and P greatly, reduced. Recovery was apparently complete in 3 hr. L. S. T.

Determinism of the entry of the egg into maturation in some marine invertebrates. J. J. PASTEELS (Arch. Biol., 1935, 46, 229—262).— CaCl_2 induces maturation of oocytes in marine invertebrates, but the effect of KCl varies. The favourable effect of high p_{H} is due to its acceleration of the action of CaCl_2 . Maturation is unaffected by aerobic or anaerobic inhibition of respiration, but is inhibited by narcotics. The effect of CaCl_2 appears clearly in cases of species where the eggs are matured in sea-water before fertilisation, particularly where fertilisation takes place in the oocyte. The entry of the spermatozoon apparently accelerates maturation by an indirect route in which CaCl_2 plays an essential part. R. N. C.

Metabolism of the frog's egg in course of development. II. Respiration of the egg during fertilisation and mitosis. III. Respiratory metabolism and "organising centre" of the gastrula. J. BRACHET (Arch. Biol., 1935, 46, 1—24, 25—46; cf. A., 1934, 1390).—II. Eggs are not fertilised in absence of O_2 or presence of KCN, but can be activated by CHCl_3 under these conditions, indicating that the unfertilised egg is a facultative anaerobe, whilst the spermatozoon is an obligatory aerobe. Fertilisation does not immediately alter

O₂ consumption, which increases slowly during segmentation, without showing any parallelism with mitoses. O₂ consumption in polyspermic eggs is > in normal eggs. Eggs from the same female show equal O₂ consumptions when fertilised by spermatozoa from different males. Cyclic variations of O₂ consumption occur during mitoses. During segmentation anaerobic reactions occur, which liberate CO₂.

III. Destruction of the dorsal lip of the blastopore (organising centre) induces a fall in O₂ consumption > that induced by an equiv. lesion of an indifferent part of the organism; CO₂ evolution is correspondingly reduced. The isolated organising centre produces CO₂ more rapidly than the isolated marginal ventral zone. Hence the organising centre is also a centre of high respiratory metabolism. R. N. C.

Utilisation of protein concentrates by the growing chick. F. E. MUSSEHL and C. W. ACKERSON (Poultry Sci., 1935, 14, 119—121).—A considerable variety of protein sources does not necessarily enhance the biological val. of a concentrate when the basal ration contains ≤ 4 other sources of protein.

A. G. P.

Utilisation of gelatin, casein, and zein by adult rats. I. D. MASON and L. S. PALMER (J. Nutrition, 1935, 9, 489—505).—In N balance experiments the % retention (McCullum's method) averaged 74 for casein (I), 23 for gelatin (II), and 57 for zein (III). (I) and (II) were so well digested that there was no appreciable difference between % retention and biological val. (Mitchell). The digestibility of (III) was low and variable. A significant correlation exists between exogenous faecal N (expressed as % of N ingested) and exogenous urinary N (as % of N resorbed).

A. G. P.

Variation of the dietary protein without simultaneous variation of the urinary quotient. O. FRANKE (Biochem. Z., 1935, 279, 205—212).—With the same individual different metabolism levels are obtained with diets having the same cal. content but different % of protein; these levels are distinguished by the fact that considerable change in total food-protein can occur without significant change in urinary C:N and vacate O:N ratios. P. W. C.

Nutritive value of ishinagi- (*Stereolepis ishinagi*) and ox-liver. I. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 731—740).—Proteins of ishinagi- and ox-liver have a very high nutritive val. Diet containing 15% of liver-protein produced excellent growth in rats. Ishinagi-liver oil has a very high vitamin-A potency (about 900 cod-liver oil units); it contains a toxic substance, most of which can be removed with 90% MeOH; the residual oil yields vitamin-A on extraction with MeOH. 20 mg. of oil given orally to rats much retards the growth. Ox-liver oil contains nearly 10 times as much vitamin-A as commercial cod-liver oil, and is rich in -B₂, but poor in -B₁.

E. P.

Feeding experiments with decomposition products of proteins. IV. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1935, 11, 258—259; cf. A., 1933, 975).—White rats fail to grow on a basal diet con-

taining many NH₂-acids (enumerated) in place of protein, but respond immediately to α -amino- β -hydroxy-*n*-butyric acid (A., 1934, 638). J. L. D.

Oxidation of nucleic acid in tissues. I. Effect of the sodium salt on dehydrogenations. Y. TSUGE (Fermentforsch., 1935, 14, 422—429).—Fresh tissues (rabbit) contain nucleic acid dehydrogenase (I), the amount being greatest in the lower part of the small intestine. The decolorisation of methylene-blue (II) by (I) is more rapid when the concn. of (II) is low (1:105) than when it is high and the time of decolorisation \propto the concn. of (I). The optimum temp. for the action of (I) is 37°. W. McC.

Cystine metabolism: its rôle in nitrogen metabolism, intestinal absorption, and oxidation coefficient. E. F. TERROINE, M. MEZINCESCO, and S. VALLA (Ann. Physiol. Physicochim. biol., 1934, 10, 1059).—Addition of cystine (I) to a carbohydrate diet, on which min. N and S excretions have been established, improved N balance, although it remained negative, and gave a positive S balance. The reduction in N excretion was similar to that produced by non-essential NH₂-acids (glycine). Excretion of creatine and creatinine was not affected. Absorption of a large dose of (I) without other source of N was almost complete. Of the excess S excreted 85% was as SO₄".

NUTR. ABS. (m)

Value of non-essential amino-acids in covering endogenous nitrogen metabolism. M. MEZINCESCO (Ann. Physiol. Physicochim. biol., 1934, 10, 1011).—Addition of glycine, alanine, aspartic or glutamic acid to a carbohydrate diet on which min. endogenous N excretion has been attained improved the balance by about 30%, by supplying the α -NH₂ group. There is no change in excretion of creatinine or S. Synthetic formation of creatine from NH₂-acids without the guanidine grouping or the glyoxaline nucleus is unlikely. NUTR. ABS. (m)

Metabolism of amino-acids. V. Conversion of proline into glutamic acid in kidney. H. WEIL-MALHERBE and H. A. KREBS (Biochem. J., 1935, 29, 2077—2081).—Rabbit's kidney in presence of NH₄ salts oxidises proline (I) and hydroxyproline (II) to an acid amide which reacts like glutamine, and when the kidney is poisoned with As₂O₃, α -ketoglutaric acid is formed. The stages between (I) and glutamic acid are not known, but neither (II) nor pyrrolidonecarboxylic acid (III) is an intermediate in the oxidation, since (I) reacts more rapidly than (II), and (III) has no effect on the O₂ uptake.

J. N. A.

Metabolism of amino-acids. IV. Synthesis of glutamine from glutamic acid and ammonia, and the enzymic hydrolysis of glutamine in animal tissues. H. A. KREBS (Biochem. J., 1935, 29, 1951—1969).—Brain-cortex and retina of vertebrates and kidneys of rabbit and guinea-pig convert NH₄ glutamate (I) into glutamine (II). The energy for this endothermic synthesis is supplied either by respiration or, in retina, by anaerobic lactic acid fermentation. Tissues which synthesise (II) contain glutaminase (III), which hydrolyses (II) to (I). Both processes are inhibited by glutamic acid (IV). Mam-

malian liver also contains a (II)-splitting enzyme (V) which differs from (III) in its p_H optimum and is not inhibited by (IV). Both (III) and (V) are distinct from asparaginase. E. A. H. R.

Uric acid metabolism. D. JOFFE (Arch. Verdaunungskr., 1935, 57, 25—41).—The effect of fasting, and of ingestion of ordinary purine-free food, vegetable diet, and Na nucleinate on the uric acid content of the blood of persons on a basal purine-free diet was examined. On a purine-free diet the fasting level was 2—4 mg. per 100 ml. of blood. The fluctuations following a purine-free meal were variable. After feeding Na nucleinate the rise was in general greater. NUTR. ABS. (m)

Fat metabolism. VI. α -Lauro- β -triundecoin. P. E. VERKADE, J. VAN DER LEE, and K. HOLWERDA (Proc. K. Acad. Wetensch. Amsterdam, 1935, 38, 536—540, and Z. physiol. Chem., 1935, 234, 21—26).—The two fatty acids are liberated at the same rate from α -lauro- β -triundecoin as from the corresponding mixture of trilaurin and triundecoin. H. G. R.

Interrelations between water and fat metabolism in relation to disturbed liver function. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Lancet, 1935, 229, 297—298).—After partial hepatectomy of rats the liver remnants exhibit marked fatty changes if the animals are bled or injected with large amounts of saline, or if drinking- H_2O be withdrawn. The pituitary appears to be essential for the deposition of fat in the liver. L. S. T.

Fat formation from sucrose and glucose. S. FEYDER (J. Nutrition, 1935, 9, 457—468).—Rats fattened more rapidly on sucrose than on an equiv. supply of glucose. A. G. P.

Effect of blood-sugar concentration on the rate of absorption of sugar from the intestine. E. J. McDUGALL (Arb. ung. biol. Forsch.-Inst., 1934, 7, 217—222).—Hyperglycæmia was produced in anæsthetised rabbits by introducing 5—10% aq. glucose (I) or xylose (II) into the jugular vein at known rates and injecting aq. 11—14% sugar solution into the small intestine. Although the blood-sugar level was about doubled, the rate of absorption from the intestine was not decreased; in the case of (I) it was increased slightly. The rate of absorption of (I) was about twice that of an equimol. solution of (II). NUTR. ABS. (m)

Effects of lactose on growth and longevity. E. O. WHITTIER, C. A. CARY, and N. R. ELLIS (J. Nutrition, 1935, 9, 521—532).—Lactose (I) produced more rapid growth of young rats than did sucrose (II), but adult animals attained greater body-wt. on (II), when fed *ad lib*. Pigs stored more fat when supplied with (II). Rats receiving (I) lived longer. A. G. P.

Rates of absorption of and glycogenesis from various sugars. S. FEYDER and H. B. PIERCE (J. Nutrition, 1935, 9, 435—455).—Wide variations in the rates of absorption of glucose (I), sucrose (II), and maize-syrup, and in the total amounts absorbed, are recorded. Rates of glycogenesis from (I) and

(II) were similar in the 2 hr. following administration, but that from (I) declined subsequently. Rates for maize-syrup were lower and more const. A. G. P.

Effect of carbon dioxide on blood-sugar. Effect of change in acid-base equilibrium. Influence of the nervous system. D. CORDIER (Ann. Physiol. Physicochim. biol., 1934, 10, 1135).—In dogs anæsthetised with chloralose, inhalation of CO_2 caused progressive hyperglycæmia, but injection of $NaHCO_3$ or HCl (except in massive doses) had no effect on blood-sugar. The effect of CO_2 is attributed to its rapid diffusion into the liver cell. Experiments with section of the splanchnic nerves, removal of the adrenals, or section of the pneumogastries in the neck indicate that the effect of CO_2 on blood-sugar is due partly to sympathetic nervous action, direct and indirect, and partly to direct action on the liver-cells. There is no reflex action from the lung. NUTR. ABS. (m)

Glucose and lactate consumption of the dog's heart. C. L. EVANS, F. GRANDE, and F. Y. HSU (Quart. J. Exp. Physiol., 1935, 24, 347—364).—A perfused dog's heart utilises about three times as much lactic acid (I) as glucose (II). Addition of insulin increases the utilisation of (II), but not that of (I). NUTR. ABS. (m)

Formation of carbohydrate from glycerophosphate in the liver of the rat. C. F. CORI and W. M. SHINE (Science, 1935, 82, 134—135; cf. this vol., 523).—Inorg. PO_4''' increases and the PO_4''' fractions difficult to hydrolyse in *N*-HCl decrease when liver slices of rats are shaken for 3 hr. in oxygenated HCO_3' -Ringer's solution, indicating that glycerophosphate (I) may be a source of carbohydrate (II) in the liver. Addition of α - or β -(I) or of glycerol produces a larger increase in fermentable (II) than incubation of the liver without added substrate; under anaerobic conditions an increase does not occur. During incubation of liver slices with α -(I) more inorg. PO_4''' is liberated than during incubation without added substrate. The results emphasise the importance of the glycerol part of the lipin mol. as a source of (II) in the body, and do not support the view that fatty acids are converted into (II) in the mammalian liver. L. S. T.

Metabolism of lactic and pyruvic acids in normal and tumour tissues. II. Rat kidney and transplantable tumours. K. A. C. ELLIOTT, M. P. BENOY, and Z. BAKER (Biochem. J., 1935, 29, 1937—1950).—The cycle established by Elliott and Schroeder (A., 1934, 1394) for lactate (I) and pyruvate (II) metabolism is demonstrated more clearly with rat kidney, but does not occur in tumour. In tumour (I) is metabolised only slightly and succinate (III), fumarate (IV), and malate (V) not at all; (II) is oxidised as far as (III) and an equilibrium between (IV) and (V) can be established. The decomp. of oxalacetate to (II) is not catalysed by kidney. In the Clift and Cook determination of (II) (cf. A., 1933, 491) the solution should be cooled or Na_2HPO_4 added in place of $NaHCO_3$. E. A. H. R.

Ketogenesis—antiketogenesis. I. Influence of ammonium chloride on ketone formation in

liver. N. L. EDSON (Biochem. J., 1935, **29**, 2082—2094).— NH_4Cl increased the production of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ from AcCO_2H in liver, but in the absence of AcCO_2H there was an increased production only in a well-nourished liver, and no effect in a starved liver. Fatty acids with even and odd no. of C gave rise to β -keto-acids (I) during oxidation in liver slices, the yield being about 3 times as much with the even as with the odd. NH_4Cl accelerated the formation of (I) in the well-nourished liver. The effect of NH_3 was inhibited by glycerol. Micro-methods, suitable for tissue-slice work, for the determination of (I) and β -hydroxybutyric acid are described. J. N. A.

Dehydrogenating action of the liver on some phenylaliphatic acids. F. P. MAZZA (Boll. Soc. Ital. Biol. sperim., 1935, **10**, 138—140).— O_2 consumption by liver extract or perfused liver sections is increased by γ -phenyl- and γ -hydroxy- γ -phenylbutyric (I) acids; γ -phenylcrotonic acid (II) is effective in liver sections only, whilst γ -phenylisocrotonic and α -hydroxy- γ -phenylbutyric acids are without effect. The results confirm and demonstrate the Knoop theory *in vitro*, and suggest that (II) is transformed into (I) in the liver by an inextractable hydratase. R. N. C.

Alcohol injected intravenously: rate of disappearance from the blood-stream in man. H. W. NEWMAN and W. C. CUTTING (J. Pharm. Exp. Ther., 1935, **54**, 371—377).—EtOH injected intravenously is metabolised at a rate independent of its blood concn. H. D.

Central disturbance of sodium chloride metabolism. I. MOLNAR and Z. GRUBER (Orvosi Hetilap, 1935, **79**, 116—120).—Normal subjects and patients suffering from cerebral disease (acromegaly, tumour, etc.) were fed for a few days on a salt-poor diet, then 10 g. of NaCl were added daily. Healthy subjects retained 10—20 g. during the first two days of increased NaCl intake and were in equilibrium from the third day, but in most cases of cerebral disease more NaCl was retained and equilibrium was not reached until the fourth day. In some cases the NaCl output periodically exceeded the intake. NUTR. ABS. (m)

Metabolism of potassium and sodium. B. SJOLLEMA (Geneeskund. Bladen, 1934, **32**, 255).—A review. NUTR. ABS. (m)

Adult rats of low calcium content. H. L. CAMPBELL, O. A. BESSEY, and H. C. SHERMAN (J. Biol. Chem., 1935, **110**, 703—706).—A diet containing only 0.094% of Ca in the air-dried mixture when fed to 28-day-old rats sufficed for growth and health in the first but not in the second generation. Animals of the latter showed a low Ca content, were only about 75% of the normal size, failed to rear young, and were senile at the age of 1 year. J. N. A.

Growth of pigs. I. Lime and phosphate metabolism in young growing pigs. L. S. SPILDO (Beretn. Forsøgslab. Kopenhagen, 1933, No. 151; Bied. Zentr., 1935, **A**, 5, 327).—The P:Ca ratio of the food is more important than the abs. amounts supplied. High ratio causes ostitis fibrosa and tetany [and low serum-Ca. Low ratio induces

osteoporosis, and rickets with hypercalcaemia and hypophosphatemia. Addition of vitamin-D to a high-ratio ration improves the utilisation of Ca and favours growth. Similar addition to a low-ratio diet produces unfavourable effects. A. G. P.

Influence of phosphatic substances on calcium and phosphorus balances [of animals]. S. KOCH (Diss., Freiberg, 1933; Bied. Zentr., 1935, **A**, 5, 329).—Subcutaneous or intraperitoneal injection of P-containing substances into rats and guinea-pigs results in increased elimination of Ca and P and marked negative balances. Loss occurs in faeces during the injection period, and subsequently, to a considerable extent, in the urine. A. G. P.

Saliva tests. III. Detecting administration of some opium derivatives to horses. J. C. MUNCH (J. Amer. Pharm. Assoc., 1935, **24**, 557—560; cf. this vol., 397).—The administration or non-administration of opium derivatives to 37 horses was correctly diagnosed by the mouse test, but it was impossible to infer definitely what drug had been administered. R. S. C.

Pharmacological investigation of "Senso," a Chinese drug from the dried cutaneous secretion of the toad. IV. Action of ψ -bufotalin and ψ -bufotalin bromide. Y. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1935, **11**, 298—300).—The pharmacology of these substances is described. ψ -Bufotalin bromide is much less toxic than g -strophanthin, which it resembles; its lethal action is not cumulative. J. L. D.

Pharmacological properties of a new alkaloid from ergot of rye—ergobasine. E. ROTHLIN (Compt. rend. Soc. Biol., 1935, **119**, 1302—1304).—Ergobasine resembles ergotamine in its action on the uterus, but differs in that it does not produce gangrene when given to rats in toxic doses, and in its lack of sympathicolytic action. H. G. R.

Influence of the viscosity of blood on the depressor action of yohimbine. H. BUSQUET and C. V. VISCHNIAC (Compt. rend. Soc. Biol., 1935, **119**, 1376—1378).—In the dog, but not in the rabbit, the depressor action of yohimbine is decreased if the blood is made more viscous by the addition of gum and gelatin. The depressor action is then lost, but the sympathicolytic is not affected. H. G. R.

Elimination of hydrastinine in the bile and urine. J. BERNARDBEIG and F. CAUJOLLE (Compt. rend. Soc. Biol., 1935, **119**, 1299—1302).—Hydrastinine appears in the urine and in the bile of the dog after intravenous injection, the rate of elimination in the former depending on the rate in the latter. H. G. R.

Inhibitory action of eserine on choline-esterase *in vivo*. M. S. JONES and H. TOD (Biochem. J., 1935, **29**, 2242—2245).—Subcutaneous injection of eserine (I), but not of pilocarpine and adrenaline, inhibits the action of choline-esterase (II) on acetylcholine (III). This corroborates the theory that (I) acts on the parasympathetic by inhibiting (II) and thus prolonging the action of (III) present. E. A. H. R.

Cumulative poisoning by lanadigin, ouabain, and digitoxin in dogs. R. C. LI and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1935, 54, 415—425).—The lethal doses of ouabain, lanadigin (I), and digitoxin (II) are as 10 : 2 : 1 in the frog and 4 : 1 : 1 in the dog. (I) was the most effective cumulative poison; dogs tolerate repeated doses of (II) much better than cats. Repeated doses of tincture of digitalis were more lethal than those of (II). H. D.

Reduction of pitressin and pitocin with cysteine. R. R. SEALOCK and V. DU VIGNEAUD (J. Pharm. Exp. Ther., 1935, 54, 433—447).—Pitressin (I) and pitocin (II) are reduced by cysteine at pH 8 with no change in activity; treatment of the reduced products with CH_2PhCl or MeI inhibits their activity, whilst similar treatment of (I) and (II) is without effect. It is concluded that the mols. of (I) and (II) contain a S-S group which is directly associated with their activities. H. D.

Influence of hydrogen and hydroxyl ions on the anæsthetic action of propyl bromide on sticklebacks. M. TIFFENEAU and D. BROWN (Compt. rend. Soc. Biol., 1935, 119, 1382—1384).—Penetration of $PrBr$ into the brain is accelerated by acidosis (immersion in acid H_2O) and retarded by alkalosis. Little $PrBr$ is fixed by the gills. H. G. R.

Microdetermination of ethyl, propyl, and isopropyl bromides in the tissues of animals anæsthetised by these substances. M. TIFFENEAU and D. BROWN (Compt. rend., 1935, 201, 353—355).—The problem of hyper- and hypo-sensitivity to anæsthetics in relation to their concn. in the tissues is examined. With $EtBr$, Pr^aBr , and Pr^iBr the quantity of Br in the tissues varies with the speed of induction of the anæsthesia; the quantity in the hemispheres is in general < in the remaining parts of the brain. H. D.

Theories of narcosis of H. H. Meyer, Overton, K. H. Meyer, Traube, and Warburg. I. TRAUBE (Biochem. Z., 1935, 279, 166—173).—A reply to K. H. Meyer (this vol., 779, 893). The theories are critically discussed. P. W. C.

Chemical relationships between compounds of physiological importance having the phenanthrene nucleus. H. P. LUNDGREN (Science, 1935, 82, 130—133).—A summary. L. S. T.

"Anti-embryonic" sensitiser and lack of vitamin-A. L. NATTAN-LARRIER, L. GRIMARD, and S. NOUGUES (Compt. rend. Soc. Biol., 1935, 119, 1348—1350).—The sensitiser is present in rat-serum only when normal growth is retarded by deprivation of vitamin-A. H. G. R.

Effect of tyrosine on gaseous metabolism. L. BARBATO (Arch. Farm. sperim., 1935, 59, 291—304).—Injection of tyrosine into rats or pigeons has no significant effect on the O_2 consumption at normal or subnormal temp. F. O. H.

(A) Comparison of toxicity with concentration and time. (B) Quantitative relationship between the constitution and toxicity of some rotenone derivatives. W. A. GERSDORFF (J. Agric. Res., 1935, 50, 881—891, 892—898).—(A) Glaser's formula

best fits the author's data for the survival times of goldfish (2—2.5 g.) at 27° in solutions of rotenone (I) and its derivatives, but is inconvenient in use. The min. val. of $c \times t$, where c =concn. of poison and t =survival time of the fish, is suggested as criterion of toxicity. Published data give the following toxicities determined by the min. ct relative to (I)=1: rotenone hydrochloride 1.8, dihydrorotenone (II) 1.4, acetylrotenone (III) 0.55, toxicarol 0.55, deguelin 0.39, isorotenone 0.23, tephrosin 0.15, rotenolone (IV) 0.097.

(B) Relative toxicities to goldfish (2—2.5 g.) at 27° , as defined by min. ct , are determined as follows: (II) 1.4, (I) 1.0, acetyldihydorotenone 0.812, (III) 0.552, dihydrorotenolone 0.149, (IV) 0.0965, acetyldihydorotenolone 0.0819, acetylrotenolone 0.0546. Saturation of the ethylenic linking increases toxicity by 50%, but transformation into the OH-derivative decreases it by 90% and acetylation by 44%. The effect of > one such change is the product of the effect of each separately. R. S. C.

Photobiological sensitisation in the ultra-violet by compounds of the acridine and quinoline series. W. HAUSMANN and F. M. KUEN (Biochem. Z., 1935, 279, 387—392; cf. A., 1932, 1284; 1934, 94).—No relationship between constitution and photodynamic action in the ultra-violet of the compounds can be traced, since similarly constituted substances behave differently in many cases. Acridine hydrochloride, bistrypaflavine nitrate, yatren, flavophosphine, diamond-phosphine, sinflavine, 2-*p*-acetamidostyrylmethylquinoline methosulphate, and optoquin hydrochloride sensitise. Agar may be replaced by gelatin as medium without affecting the results. W. McC.

Photobiological desensitisation in the ultra-violet. Photobiological action of sodium sulphite on erythrocytes. F. M. KUEN (Biochem. Z., 1935, 279, 393—402).—Erythrocytes sensitised with hæmatoporphyrin are desensitised in different degrees by serum, glucose, fructose, pinacryptol, and neosalvarsan. Na_2SO_3 sensitises in presence of O_2 (not in its absence) in the region 365—248 $m\mu$, and since it acts at λ which its solutions do not absorb, the primary photochemical effect is then on the erythrocytes and not on the Na_2SO_3 . W. McC.

Aryl esters of hydroxydiphenyls.—See this vol., 1233.

Influence of dinitrophenol on carbohydrate metabolism. M. WISHNOFSKY, A. P. KANE, E. L. SHLEVIN, and C. S. BYRON (Arch. Int. Med., 1935, 56, 374—381).—In normal cases, $C_6H_3(NO_2)_2 \cdot OH$ causes glycaemia both during fasting and after ingestion of glucose (I). In diabetes mellitus, there is no change in the blood-sugar, but a reduction in glycosuria after administration of (I). H. G. R.

Metabolic response of white rats to continued administration of dinitrophenol. B. TERADA and M. L. TAINTER (J. Pharm. Exp. Ther., 1935, 54, 454—462).—Administration of 2:4- $C_6H_3(NO_2)_2 \cdot OH$ (I) to young rats produced little or no stimulation of metabolism. Adult rats show no tolerance to (I), which is absorbed intestinally

and excreted in the urine. Nephrectomy doubles the metabolic response. H. D.

Rigidity from iodoacetic acid in muscles of cold-blooded animals. F. LIPPAY and H. PATZL (Pflüger's Archiv, 1935, 235, 438—447).—The rigidity produced spontaneously in frogs' muscles treated with $\text{CH}_2\text{I}-\text{CO}_2\text{H}$ is distinct from that produced by electric excitation under similar conditions. R. N. C.

Acute carbon tetrachloride poisoning. E. R. LEHNHERR (Arch. Int. Med., 1935, 56, 98—104).—Data are given for a severe case of poisoning with CCl_4 . At first there was a decrease in the amounts of lipins in the plasma, and low vals. were obtained for total cholesterol (I) and for the ratio of ester (I) to total (I), which are typical of jaundice due to damage to the liver. There was an increase of urea, uric acid, and creatinine in the blood, which gradually returned to normal, but the NH_2 -acid-N was not altered. During the first 3 days, bile was visibly present in the urine. J. N. A.

Effect of cysteine on the toxicity of antimony. L. LAUNOY (Bull. Soc. Chim. biol., 1935, 17, 1022—1030; cf. A., 1934, 1256).—Cysteine has considerable antitoxic action towards Sb thiomalate (I) injected into mice infected with *T. brucei*. When injected simultaneously with moranyl and (I) into mice infected with *T. congolense*, however, the antitoxic action is greatly inhibited. A. L.

Inhibition of respiration by cyanide. W. E. VAN HEYNINGEN (Biochem. J., 1935, 29, 2036—2039).—The respiration of liver, kidney, and spleen slices is inhibited to 75—85% by 0.001*M*-HCN and to 80—90% by 0.01*M*-HCN. Lower vals. of other authors are attributed to differences in method, in particular, failure to prevent absorption of HCN by the CO_2 absorbent. H. D.

Cure of hydrocyanic acid poisoning by sodium tetrathionate. G. AURISICCHIO and G. DE NITO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 150).—HCN poisoning in animals is cured by successive injections of $\text{Na}_2\text{S}_4\text{O}_6$ and I solutions. R. N. C.

Opposite effects of hydrogen and hydroxyl ions on pharmacodynamical actions in the autonomic system. Action on uterine tonus. M. TIFFENEAU and D. BROWN (Compt. rend. Soc. Biol., 1935, 119, 1380—1382).—The tonic effects of adrenaline on the rabbit's uterus and of histamine and post-pituitary extract on the guinea-pig's uterus run parallel to $[\text{OH}^-]$. An increase in $[\text{OH}^-]$ suppresses or inverts the depressor effect of adrenaline on the guinea-pig's uterus. H. G. R.

Biochemistry of the heavy metals. T. BERSIN (Z. ges. Naturwiss., 1935, 1, 187—190).—A review and discussion of the role of heavy metals in biological processes. H. J. E.

Combined action of zinc and vitamins in animal nutrition. G. BERTRAND and R. C. BHATTACHERJEE (Ann. Inst. Pasteur, 1935, 55, 265—272).—Mice fed on a synthetic Zn-free diet supplemented with the vitamins do not survive, but good growth is obtained on the addition of 2 mg. of Zn per 100 g.

of food. Animals on a Zn diet contained 0.2 mg. more Zn than those on a Zn-free diet. H. G. R.

Biological effect of ionised air. C. T. CHASE and C. H. WILLEY (Science, 1935, 82, 157—158).—Exposure to ionised air induces coloration and subsequent death in the larvæ of *Drosophila melanogaster*. L. S. T.

Influence of a continuous electric current on the branchial permeability of some fresh-water fish. E. GRADINESCO and E. PORA (Bull. Soc. Chim. biol., 1935, 17, 1054—1057).—The branchial permeability of fresh-water fish is affected by the passage of electricity through the external H_2O medium. In most cases diffusion takes place from the fish. A. L.

Influence exercised by radioactivity on the localisation in the lung of cobalt administered in combination with pulmonary proteins. P. MASCHERPA and G. CAVALLI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 146—148).—Injection of Rn-treated Co-lung-protein complex in guinea-pigs produces a deposition of Co in the lungs > with untreated complex. No deposition of Co occurs with Rn-treated Co-serum-protein complex. R. N. C.

Possibility of conveying to an organ cobalt bound to the proteins of the same organ. P. MASCHERPA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 148—152).—A discourse. R. N. C.

Origin of the inhibition of cell division by X-rays. K. ERDMANN (Pflüger's Archiv, 1935, 235, 470—485).—Inhibition of yeast-cells by X-rays in solutions of $\text{NaCl}-\text{CaCl}_2$ or alkali chlorides at varying p_{H} follows the same laws as the effect of X-rays and ionic media on the shrinkage of proteins, suggesting that the origin of the inhibition of growth by X-rays is the reduction of the swelling power necessary for growth of living matter. R. N. C.

Determination of the effect of ultra-violet light on the proteins of skin and serum by means of the defence enzyme reaction. E. ABDERHALDEN and E. TETZNER (Fermentforsch., 1935, 14, 522—538; cf. A., 1934, 1137).—Proteins from the skin of rabbits which have been exposed to irradiation with the light can be distinguished, by means of the reaction, from those of the skins of non-irradiated rabbits. The degree of specificity of the reaction is low, but, in some cases at least, injection of the substrates is unnecessary. W. McC.

Cryolysis, diffusion, and particle size. Experiments on sodium oleate, ovalbumin, and polyacrylic acids. F. F. NORD and F. E. M. LANGE (Z. Elektrochem., 1935, 41, 519).—Previous results (cf. this vol., 932) are applied to the chemistry of enzymes. T. G. P.

Components of dehydrogenase systems. VI. Enzymic oxidation of hexoses in presence of adenosinetriphosphoric acid. H. VON EULER and E. ADLER. VII. Lactic acid dehydrogenase of yeast. E. ADLER and M. MICHAELIS. VIII. Activators. H. VON EULER and E. ADLER (Z. physiol. Chem., 1935, 235, 122—153, 154—163, 164—173; cf. this vol., 782).—VI. The hexose monophosphate dehydrogenase (I) system oxidises non-

phosphorylated hexoses (glucose, fructose) if adenosinetriphosphoric acid (II) is added. (II) cannot be replaced by adenylic acid, creatine, phosphagen, $\text{Na}_4\text{P}_2\text{O}_7$, or hexose diphosphate or mixtures of these. By adsorption on $\text{Al}(\text{OH})_3$ and elution with dil. aq. NH_3 the (I) is separated into the true (I) of the system and an enzyme, "heterophosphatase" (III), which, in presence of (II) and the system, attacks hexoses. (III) probably acts by transferring the labile P of (II) to the hexose (producing hexose monophosphate), the reaction being activated by Mg. The presence of a redox system is not essential. Sp. alcohol-(I) cannot replace (III), but Warburg's co-enzyme can replace cozymase in the system.

VII. The lactic acid-(I) of yeast, which requires no complement for anaerobic reaction and acts aerobically when an appropriate acceptor is added, differs from the flavin enzyme systems which act aerobically and anaerobically only when completed by addition of co-enzyme and flavin enzyme.

VIII. Purified cozymase activates the enzymic oxidation of EtOH, but not that of hexose monophosphate. Hence impure cozymase contains a second activator (not identical with Warburg's co-enzyme). This activator is dialysable and less stable to heat than is cozymase. Cozymase is indispensable for both oxidations and probably acts without the second activator in oxidation of EtOH. W. McC.

Dehydrogenase system of peas. A. FODOR and N. LICHTENSTEIN (Fermentforsch., 1935, 14, 413—421; cf. A., 1932, 651).—Macerates of pea-flour treated with kaolin contain a dehydrogenase system (optimum activity at p_{H} 6.5; after dialysis activity increases up to p_{H} 8) which is activated by boiled yeast juice and by purified co-enzyme. The system is damaged (but not destroyed) by boiling or ultra-filtration (removal of proteins) and its activity decreases continuously on keeping. The activity lost on boiling is partly restored by addition of HCO_2K , boiled yeast juice, or purified co-enzyme. Addition of NH_2 -acids (glycine, alanine, tyrosine, tryptophan) increases the activity if the macerates have been boiled, but decreases it if they have not. Boiled yeast juice with aldehyde and phosphate (but not with NH_2 -acid and phosphate) decolorises methylene-blue and activates the system NH_2 -acid-aldehyde-phosphate, but neither purified co-enzyme with NH_2 -acid or aldehyde and phosphate nor HCO_2K with NH_2 -acid or NH_2Me causes decolorisation. Neither purified co-enzyme nor HCO_2K nor both together activates the system aldehyde- NH_2 -acid-phosphate. Peas possibly contain also a non-enzymic dehydrogenating system (e.g., aldehyde- NH_2 -acid-phosphate). W. McC.

Action of poisons on the dehydrogenases and oxidases of muscle. R. LABES and K. KREBS (Fermentforsch., 1935, 14, 430—442).—The succinic dehydrogenase (I) (but not the *p*-phenylenediamine oxidase) of pig muscle is poisoned by low concns. (0.02%) of K_2TeO_3 , K_2SeO_3 , and $\text{Zn}(\text{OAc})_2$ and by PhOH (0.1—0.2%). Na_2HAsO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ (even in high concns.) have no toxic effect on (I) or the oxidase. $\text{Zn}(\text{OAc})_2$ also poisons the oxidase. Under certain conditions, however, the poisons have a stimulating effect. The toxicity of K_2TeO_3 and

K_2SeO_3 is due to their reduction to colloidal Te and Se. SH and alcoholic OH groups are not involved in the respiratory action of (I). W. McC.

Mechanism of the reaction of substrates with molecular oxygen. I, II. F. J. OGSTON and D. E. GREEN (Biochem. J., 1935, 29, 1983—2004, 2005—2012).—I. An investigation of the extent to which intermediary O_2 carriers determine the reaction of substrates with mol. O_2 . Cytochrome-c (I) acts as a carrier only for succinoxidase (II) and the lactate (III) dehydrogenase of yeast, yellow pigment (IV) for glucose- (V), hexose monophosphate- (VI), hexose diphosphate- (VII), and malate- (VIII) -dehydrogenases, and flavin for (VIII) only. Glutathione is reduced by the (V) and (VI) dehydrogenases and acts as a carrier for (VII). Its efficiency is limited by its rate of autoxidation. New methods are given for the prep. of (II) and the (III), (V), (VIII), and α -glycerophosphate dehydrogenases, and the use of a high-speed ball mill for extraction of enzymes from yeast is described. The identity of (VI) and (VII) dehydrogenases is doubtful.

II. The oxidation of substrates by respiring baker's yeast is almost completely inhibited by $M/600\text{-HCN}$, although *in vitro* the oxidation of (VI) and (VII) with (IV) as O_2 carrier is not CN'-sensitive. The low Q_{10} of bottom yeast is due to co-enzyme and intermediary carrier deficiency. The increase in respiration caused by pyocyanine suggests that *in vivo* the (IV) in bottom yeast is not concerned in the oxidations of (V), (VI), and (VII). The succinic-fumaric system cannot act as an intermediary link between (I) and dehydrogenases *in vitro*. Rat liver, heart, kidney, and brain have sufficient indophenol oxidase (IX) to account for most of their respiration. (IX) in heart muscle preps. is associated with fine particles from which it cannot be separated. There is no basis for ascribing enzymic properties to (IV). E. A. H. R.

Pure cytochrome-c. H. THEORELL (Biochem. Z., 1935, 279, 463—464; cf. A., 1932, 1054; this vol., 1024).—Purification of material from horse- or ox-heart (100 kg.) by extraction, dialysis, and pptn. is completed with the help of the cataphoresis apparatus (isoelectric point p_{H} 9.7) or by pptn. with picrolonic acid (yield 1 g.). The Fe content is the same as that of hæmo- and myo-globin and the N content is 14%. Reduced cytochrome-c is not converted into the oxidised form by H_2O_2 but is destroyed. The oxidised form, on reduction with $\text{H}_2 + \text{Pt}$, absorbs 0.5 H_2 per Fe. In the chain of enzymes involved in biological oxidation cytochrome-c is intermediate between the respiratory enzyme and the systems which supply H. W. McC.

Quantitative irradiation experiments with the yellow enzyme, flavinphosphoric acid, and lactoflavin. H. THEORELL (Biochem. Z., 1935, 279, 186—200).—Flavinphosphoric acid (I) is inactivated by light quantitatively in the same way as lactoflavin (II), esterification with H_3PO_4 having no effect on the reaction. Inactivation of (II) or (I) proceeds more quickly in air than in pure O_2 and still more quickly in total absence of O_2 . It is quicker in alkaline and slower in acid than in neutral solution. On irradiation in an atm. of A there is first formed deuteroleucoflavin

(-phosphoric acid) (III), which on prolonged irradiation is slowly broken down to 6:7-dimethylalloxazine. If O_2 is admitted during this period of irradiation, that portion of (III) not degraded is immediately converted into deuterioflavinphosphoric acid. On irradiation with light of λ 436 m μ in presence of O_2 , the catalytic activity decreases slowly in the same way as does the light absorption and at the same velocity as the decoloration of (II).
P. W. C.

Measurement of phenolase activity. R. SAMISCH (J. Biol. Chem., 1935, 110, 643—654).—Increase of the partial pressure of O_2 increases the rate of O_2 absorption by phenolase-substrate mixtures. Peach and apricot extracts show an optimum p_H of 4.9 with pyrocatechol as substrate, whilst apple extract has no optimum between p_H 3.7 and 6.4. An optimum concn. of substrate for different enzymes is found, at which the O_2 consumption \propto enzyme concn. Alkali halides have an inhibiting effect inversely \propto the at. no. of the halogen ion. The crit. temp., at which the enzyme is half destroyed in 1 hr., is for apricot-oxidase 38°. A proposed unit of phenolase activity is defined.
F. A. A.

Constitution of the prosthetic group of catalase. K. G. STERN (Nature, 1935, 136, 302).—The pure hæmin obtained from the catalase of horse liver yields on treatment with HI and AcOH a porphyrin with a spectrum identical with that of mesoporphyrin IX; the Me₂ esters are also identical (m.p., mixed m.p., and spectrum). The hæmatin group of catalase is thus a derivative of ætioporphyrin III and possesses a porphin skeleton with the same arrangement of the side-chains as occurs in proto-hæmatin IX.
L. S. T.

Reversible hydrolysis of liver-catalase. K. AGNER (Z. physiol. Chem., 1935, 235, II—III).—Catalase from horse liver on dialysis against 0.1N-HCl breaks down into a coloured constituent of low mol. wt. (possibly hæmin) which dialyses and a colourless non-dialysing constituent (protein) of high mol. wt., both constituents being without action on H_2O_2 . Activity is restored by re-combining the constituents.
W. McC.

Concentration and properties of two amylases of barley-malt. M. L. CALDWELL and S. E. DOEBELING (J. Biol. Chem., 1935, 110, 739—747).—Additional evidence is given for the presence of two distinct amylases in different fractions obtained from the same extract of barley-malt. Both amylases rapidly lose their activities when heated in H_2O . They are free from carbohydrate, but give a positive protein reaction. They catalyse the hydrolysis of amyloses in different manners. At 40° the saccharogenic action of both is favoured by a p_H of 4.3—4.6, and the amyloclastic action of the amylase with a preponderance of this activity is also favoured at p_H 4.3—4.7.
J. N. A.

Pancreas and diastase. H. J. DOHMEN (Deut. Z. Chirurg., 1935, 244, 620—630).—The blood of the pancreatic vein in dogs has a diastase (I) content > that of the ear vein. Since ligation of the pancreatic duct causes an increase, and removal of the pancreas a decrease, in blood-(I), (I) enters the blood-stream

directly from the pancreatic glands. There is no correlation between (I) concn. and sugar content of the blood.
NUTR. ABS. (m)

Study of enzyme action by thermal analysis of reaction velocity. I. Action of invertase. S. HORIBA and T. KOSAKI (Proc. Imp. Acad. Tokyo, 1935, 11, 232—234).—From observations of the rate of cooling it has been found that the early and later stages of the action of invertase can each be expressed by an empirical formula. On the assumption that the reaction is heterogeneous and that it occurs by way of the contact-catalytic action of the colloidal system of invertase, equations are derived which correspond with the two empirical ones.
P. G. C.

Cozymase. VIII. Action of adenylic acid deaminase on cozymase. K. MYRBACK and B. ÖRTENBLAD. IX. Oxidation and reduction. K. MYRBACK (Z. physiol. Chem., 1935, 234, 254—258, 259—266; cf. this vol., 782).—VIII. Neither active nor alkali-inactivated cozymase yields NH_3 with adenylic acid deaminase, indicating that adenylic acid is not liberated by the inactivation.

IX. On reduction with nascent H , cozymase is inactivated and the alkali-labile reducing group becomes stable. The OI' consumption is not much changed. After reduction no acid group is formed by treatment with alkali; the acid group probably arises from the labile reducing group.
J. H. B.

Activators of glycolysis. Cozymase and adenosinetriphosphoric acid. H. VON EULER and G. GUNTHER (Z. physiol. Chem., 1935, 235, 104—114).—The production, from added glycogen, of lactic acid (I) in muscle extracts (rat) inactivated by autolysis is greatly increased by addition of hexose diphosphate (II) with cozymase as activator. When adenylyl pyrophosphate is the activator addition of (II) is unnecessary. In extracts freed by dialysis from substances which suppress induction the addition of (II) or of another substance [e.g., $AcCO_2H$, creatine-phosphoric acid, but not adenosinetriphosphoric acid (III), ascorbic acid, glutathione, or flavin enzyme] having similar action is necessary if any (I) is to be produced from the glycogen. Cozymase, alone or with (III), has no effect. The action of cozymase inactivated by heat does not differ from that of fresh cozymase.
W. McC.

Linking of chemical changes in muscle extract. D. M. NEEDHAM and W. E. VAN HEYNINGEN (Biochem. J., 1935, 29, 2040—2050).—The nature of the coenzyme function of the adenylic compounds is investigated. Phosphoglyceric acid (I) is broken down to inorg. P by dialysed muscle extracts in the presence of adenylic acid (II) or adenylyl pyrophosphate (III); creatine (IV) does not assist the breakdown in the absence of (II) and (III); (IV) is converted into phosphocreatine (V) when present with (I) and (II) or (III). The synthesis of (V) involves the reactions: (I) + (II) \rightarrow (III) + $AcCO_2H$, and (III) + (IV) \rightarrow (V) + (II).
H. D.

Rôle of glutathione in muscle glycolysis. R. GADDIE and C. P. STEWART (Biochem. J., 1935, 29, 2101—2106).—In presence of Mg^{++} , adenylyl pyrophosphate (I), and reduced glutathione (II), more

lactic acid (III) is produced from glycogen (IV), glucose, and hexosediphosphoric acid by dialysed rabbit muscle extracts, than if (II) is absent. AcCHO tends to accumulate in absence of (II), but this can be prevented by addition of (II). Mg^{++} and (II) in absence of (I) cause production of (III) from (IV), but omission of (II) does not increase the amount of AcCHO . J. N. A.

— **Enzyme systems of sarcoma and muscle dealing with hexose phosphates.** F. H. SCHARES, M. D. BAKER, and W. T. SALTER (Biochem. J., 1935, 29, 1927—1936).—Tumour extract differs from skeletal muscle extract in being unaffected by F' in its ability to form lactic acid (I) or to liberate PO_4''' from hexose phosphates, in being much less susceptible to $\text{CH}_2\text{I}\cdot\text{CO}_2'$, in producing (I) from hexose monophosphate (II) after co-enzyme depletion, and in not esterifying PO_4''' with (II). This indicates that the path of carbohydrate breakdown in tumour and muscle extracts is different. Possible explanations of the inability of the former to produce (I) from glycogen are the formation of a different hexose phosphate and a lack of phosphatase. E. A. H. R.

Antiglyoxalase. R. STÖHR (Biochem. Z., 1935, 279, 184—195).—A reply to the criticisms of Girsavicius *et al.* (this vol., 122). P. W. C.

Acetylcholine-destroying action of blood. R. AMMON and G. VOSS (Pflüger's Archiv, 1935, 235, 393—400).—The choline-esterase (I) content of serum is < that of whole blood or hæmolysate in human, ox, or rabbit's blood, but greater in dog's or horse's. (I) in snail's blood is excessively high. Serum-(I) is not altered in labour, but is low in umbilical cord blood. (I) is the same in whole blood and hæmolysate in all types of blood examined. (I) in human serum is not appreciably altered in the course of many weeks, but oscillates considerably in rabbit's serum. The acetylcholine-destroying power of blood *in vivo* is inhibited by eserine. R. N. C.

Action of pepsin-hydrochloric acid on caseinogen and its degradation products produced by the action of hot anhydrous glycerol. A. FODOR and S. KUK (Fermentforsch., 1935, 14, 397—406; cf. A., 1933, 621).—The octapeptide D_1 is a double tetrapeptide. When first produced it exists as an association D_A , mol. wt. 3654, $[\alpha]_D^{20} -79.5^\circ$, of 4 mols. (less $2\text{H}_2\text{O}$) of D_1 and is accompanied by a substance D_{An} , $[\alpha]_D^{20} -86.8^\circ$, which is a mixture of (50%) with 2 double mols. of D_1 . Pepsin-HCl hydrolyses 4 $\text{CO}\cdot\text{NH}$ equivs. in 2.7 in D_{An} , and 2.45 in D_1 , and attacks caseinogen, eliminating and dissolving complexes identical with D_1 , D_A , and D_{An} . W. McC.

Intracellular proteinases. XIV. Activation and inhibition of papain by potassium ferricyanide. E. MASCHMANN and E. HELMERT. XV. **Inactivation of proteinases by iodoacetic acid.** E. MASCHMANN (Biochem. Z., 1935, 279, 213—224, 225—228).—XIV. The effect of $\text{K}_3\text{Fe}(\text{CN})_6$ (I) on the action of papain (cf. this vol., 897) is further examined. In acetate buffer the enzymic action with 4 samples of gelatin was increased by (I), but with one sample was decreased. In citrate buffer the results were inconsistent.

4 Q

XV. The inhibition of proteinases by $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ (II) is due to the reaction between an SH group of the enzyme and (II). P. W. C.

Fission of clupean by various trypsin preparations. H. HOLTER, M. KUNITZ, and J. H. NORTHROP (Z. physiol. Chem., 1935, 235, 19—23; cf. A., 1933, 94; Waldschmidt-Leitz *et al.*, this vol., 123).—Fission of clupean sulphate proceeded similarly with proteinase purified by adsorption and with various preps. of cryst. trypsin. H. W.

Action of erepsin and trypsin on polypeptides containing ψ -leucine.—See this vol., 1228.

Action of pepsin-hydrochloric acid and trypsin-kinase on *l*-, *d*-, and *dl*-leucylalbumin. Defence enzymes produced by injection of these substrates. E. ABDERHALDEN and E. KOELITZ (Fermentforsch., 1935, 14, 483—492).—The hydrolysis of *d*-, (*l*-, and *dl*-leucylalbumin [from plasma-albumin (horse) by treatment first with the corresponding α -bromoisohexoyl chlorides and then with aq. NH_3] by gastric juice (dog) and trypsin-kinase proceeds at a rate < that of the hydrolysis of the untreated albumin, and the rates for the different treated albumins also differ. Except with (I), which is most slowly attacked, the degree of hydrolysis eventually equals that of the untreated albumin. Sp. defence enzymes are produced when the leucyl-albumins are injected into rabbits. W. McC.

Purification of the active phosphatase in dog faeces. A. R. ARMSTRONG (Biochem. J., 1935, 29, 2020—2022).—Dog faeces are treated with H_2O , AcOH , and conc. aq. NH_3 and filtered at 0° . Protein material is pptd. with $(\text{NH}_4)_2\text{SO}_4$ and COMe_2 and on dissolution in aq. NH_3 is decolorised by charcoal and the active material is pptd. with COMe_2 . Activities varied from 130 to 185 ($\times 10^3$) units per g. of purified material. H. D.

Urinary phosphatase. I. W. KUTSCHER (Z. physiol. Chem., 1935, 235, 62—73).—The urine of adults invariably contains a phosphatase (I) which hydrolyses phenyl- and α - (II) and β - (III)-glycerophosphoric acids. Its max. activity occurs at p_H 4—5. At p_H 7.84 it is inactivated to the extent of 80% within 8 days, whilst at 8.32 inactivation takes place within 24 hr. It hydrolyses (III) more vigorously than (II). It is not activated by 0.01*M*- or 0.005*M*- Mg^{++} . In the urine there is also present a (I) with alkaline optimum and hydrolytic power comparable with those of the plasma-(I). Urinary (I) can be dialysed during 5—6 days without loss of activity. It is relatively stable and can be conc. in vac. at moderate temp.; at higher temp. it rapidly becomes inactive. H. W.

Effect of gangliary sympathectomy on the phosphatase content of bone. U. SACCHI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 100—103).—The phosphatase power of the bone increases in the first few days after gangliary sympathectomy, afterwards returning to normal. R. N. C.

Plasma-phosphatase in normal and rachitic children. O. ANDERSEN (Hospitalstidende, 1935, 78, 5—18).—In children 0—3 years old, without sign

of bone abnormality, plasma-phosphatase (I) was 0.14–0.34 unit per ml. (average 0.25). In normal children of 3–13 years, the val. was 0.06–0.26 (average 0.15). In rachitic children of 3–27 months, the val. was 0.42–1.41 (average 0.86). Following treatment with ultra-violet light and cod-liver oil, (I) decreased, in all cases, to < 0.30. Serum-Ca and -P always became normal before (I). (I) vals. > 0.40 are abnormal and those between 0.30 and 0.40 questionable. NUTR. ABS. (m)

Mechanism of the activation of intestinal phosphatase by magnesium. C. G. HOLMBERG (Biochem. Z., 1935, 279, 145–148).—A simple method for the prep. of phosphatase solutions practically free from mineral salts and proteins is described. The initial velocity of hydrolysis of glycerophosphoric acid by this prep. is not affected by Mg. An enzyme-Mg complex is formed which is not sensitive to the inhibitory action of small amounts of PO_4^{4-} .

P. W. C.

Bone-phosphatase and solar irradiation. U. SACCHI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 94–97).—The phosphatase content of rat bones is increased by exposure to solar radiation. R. N. C.

Phosphatases. V. Restriction of phosphatase by sulphur compounds. H. ALBERS (Ber., 1935, 68, [B], 1443–1447).—The fission of β -glycerophosphate by highly purified kidney-phosphatase (I) is notably restricted by very small amounts of glutathione and cysteine and to a smaller extent by cystine. KCN slowly reacts with (I) and causes marked restriction after prolonged action, whereas $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ has no influence. H. W.

Specificity of phosphatases. Hydrolysis of phospho-*l*-lactic acid by phosphatase. O. T. ROTINI and C. NEUBERG (Biochem. Z., 1935, 279, 453–458; cf. Wagner-Jauregg, this vol., 731).—Extract of rabbit muscle, top and bottom yeast, and the phosphatase of *Aspergillus oryzae* quantitatively convert phospho-*l*-lactic acid into *l*-lactic acid and H_3PO_4 only. W. McC.

Phosphatases in fungi. M. FRANCIOLI (Fermentforsch., 1935, 14, 493–501; cf. A., 1934, 1124).—Various fungi (e.g., *Amanita*, *Boletus*) contain lipase and one or more phosphatases. *Lycoperdon giganteum* at 37° (optimum p_H 5.5) liberates 81% of the H_3PO_4 of Na glycerophosphate in 140 hr. W. McC.

Phosphatases. IV. Phosphatases of yeast. H. ALBERS and E. ALBERS (Z. physiol. Chem., 1935, 235, 47–61).—Top yeast contains a single phosphatase “top yeast-phosphatase” (I) which causes vigorous fission of α - (II) and β -glycerophosphate (III). In the cell it is active between p_H 3 and 4.5 and after removal from the cell it hydrolyses (II) and (III) most readily at p_H 3.8–4.2 and hexose phosphate most readily at p_H 3.5. The ratio of fission for these substrates is 4 : 10 : 5.5. (I) is also largely present in bottom yeast, which also contains two phosphatases active near the neutral point, one of which hydrolyses (III), whereas the other is sp. towards (II). The behaviour of liberated (II), which appears enzymically homogeneous, is described. During dialysis it is suddenly and irreversibly in-

activated, probably by a dissociation into carrier and activating mols. Mg^{++} causes restriction of (I) independently of p_H . After liberation (I) is accompanied by a natural inhibitor which can be dialysed and is decomposed when the phosphate solutions are kept. Less pure cozymase solutions also contain an inhibitor. Adsorbates of (I) on $\text{Al}(\text{OH})_3$ -A or -C γ are completely active on the ppts.; elution by the reaction mixture does not occur. For preparative chemical purposes the adsorbates are particularly useful. The role of phosphatases during fermentation and the mode of hydrolysis of phosphoric esters by the yeast enzyme are discussed. H. W.

System sugar-amino-acid-yeast. F. LIEBEN and B. BAUMINGER (Biochem. Z., 1935, 279, 321–325; cf. Neuberg *et al.*, A., 1926, 1061).— NH_2 -acids (glycine, *l*-histidine, *dl*-alanine) added to glucose (I) in presence of yeast accelerate the degradation of (I) if conditions are such that CO_2 production is increased or if the mixture is agitated in O_2 , the total acidity of the mixture being increased because of production of increased amounts of AcCO_2H and lactic acid. The NH_2 -acids undergo no change and no NH_3 is produced. The interaction of (I) and NH_2 -acid involves no far-reaching change and the course of fermentation is only temporarily affected. W. McC.

Acid production in autolysis of yeast. II. Hydrolysis of the nucleic acid. H. HAEHN and H. LEOPOLD (Fermentforsch., 1935, 14, 539–548; cf. A., 1934, 451).—The H_3PO_4 liberated during the autolysis is derived from the nucleic acid, which is attacked successively (optimum effect at p_H 8) by polynucleotidase, nucleotidase (phosphatase), purine deaminase, and nucleosidase. Sugar (ribose) and NH_3 , in amounts (approx. equiv.) which increase with the extent of autolysis, are also liberated. The course of the degradation and the extent to which it proceeds are affected by the activators (e.g., H_3PO_4) and inhibitors (guanine, hypoxanthine) produced. W. McC.

Nature of the polysaccharides of yeast. M. G. SEVAG, C. CATTANEO, and L. MAIWEG (Annalen, 1935, 519, 111–124).—A thick suspension of *Saccharomyces cerevisiae* is triturated with COMe_2 and the residue is washed with Et_2O , dried, and ground. It is then subjected to prolonged agitation with a mixture of PhMe , CHCl_3 , and *isoamyl* alcohol (I) in presence of glass beads. The sediment is dried at 70°, triturated with H_2O , and treated repeatedly with liquid air. The residue is agitated with H_2O , CHCl_3 , and (I). The aq. solution is conc. at 37° and treated with MeOH , thereby affording the polysaccharide as a colourless powder, freely sol. in H_2O to a somewhat opalescent, viscous solution, sol. in 5*N*-HCl, *N*-NaOH, or 15% NaHCO_3 to solutions from which it is immediately pptd. by EtOH . It is partly pptd. by Fehling's solution. It has $[\alpha]_D^{20} +148.0^\circ$ in 5*N*-HCl and contains about 9% Ac . It is hydrolysed by boiling 3*N*-HCl to glucose. The extraction of acids, lipins, and polysaccharides from technical yeast is described. It appears probable that the “yeast-gum,” “yeast-cellulose,” and “yeast-glycogen” of Salkowski are not present as such in

the yeast, but are secondary products formed by the action of the alkali. Yeast-polysaccharide can be completely extracted by H_2O if the process is sufficiently prolonged; if extraction is incomplete it passes into an insol. form when subsequently treated with acid and alkali. Partial deacetylation probably occurs during treatment with H_2O . H. W.

Synthesis of reserve carbohydrate by yeast.
II. Effect of fluoride. R. A. McANALLY and I. S. MACLEAN (Biochem. J., 1935, 29, 2236—2241; see this vol., 1164).—Addition of NaF to yeast incubated in maltose (I) or glucose (II) solutions always strongly inhibited glycogen (III) storage. In (II)- PO_4''' media (III) storage is increased by low, and decreased by higher ($> 0.01\%$), [NaF], probably owing to the inhibitory effect of NaF on both synthesis and breakdown of (III). The rise in (III) storage was decreased when $[PO_4''']$ was doubled. In (I)- PO_4''' media, (III) storage is high; addition of 0.01% NaF may decrease it, but this effect was decreased with increased $[PO_4''']$. PO_4''' increases the amount of (II), but not of (I), fermented. Fermentation of (I) and (II) is inhibited by NaF, but this effect is largely counteracted by PO_4''' . The wet wt. of yeast appears to be connected with its total carbohydrate content. E. A. H. R.

Yeast gum. II. Gum content and its significance in yeast. F. STOCKHAUSEN and K. SILBEREISEN (Woch. Brau., 1935, 52, 257—259; cf. B., 1935, 649).—The gum (I) content of various yeasts varies according to the condition of growth, and no definite relationship was found between (I) content and the type of the yeast. (I) is not to be regarded as a reserve carbohydrate similar to glycogen. W. O. K.

Ecology of a salt-marsh. E. A. T. NICOL (J. Marine Biol. Assoc., 1935, 20, 203—261).—The fauna of the marsh are described. O_2 content of the H_2O varies between 40 and 200% saturation and pH between 6.8 and 9.6. The alkali reserve is high, varying between 0.0098 and 0.003N. H. G. R.

Organic metabolism of sea-water with special reference to the ultimate food cycle in the sea. A. KEYS, E. H. CHRISTENSEN, and A. KROGH (J. Marine Biol. Assoc., 1935, 20, 181—196).— O_2 consumption of sterile sea- H_2O remains practically const. when stored in the dark; for non-sterile H_2O it is approx. cc the bacterial multiplication, is max. immediately after collection, and gradually diminishes when 10—15% of the total dissolved org. matter is destroyed. These effects are decreased by filtration. H. G. R.

Plankton production and its control. H. W. HARVEY, L. H. N. COOPER, M. V. LEBOUR, and F. S. RUSSELL (J. Marine Biol. Assoc., 1935, 20, 407—441).—A quant. survey of zooplankton has been made and a close relation between the no. of diatoms and their pigment contents found. The relation between the plant and animal population is discussed. Much of the org. P in diatoms passes undigested through the animals. H. G. R.

Manganese in marine plankton. L. H. N. COOPER (J. Marine Biol. Assoc., 1935, 20, 201—202).—

The val. ($< 2 \times 10^{-6}$ g. per litre) was $<$ could be detected with certainty. H. G. R.

Rate of liberation of phosphate in sea-water by the breakdown of plankton organisms. L. H. N. COOPER (J. Marine Biol. Assoc., 1935, 20, 197—200).—Breakdown of zooplankton in sea- H_2O was very rapid, more PO_4''' being produced (from org. P in the H_2O) than was added as plankton. Breakdown of phytoplankton showed a time lag and only a part of the added P was set free. H. G. R.

Czapek's synthetic medium. B. S. NIGAM (Current Sci., 1935, 4, 29—30).—A discussion of the reactions between the inorg. salts in the Dox modification of Czapek's medium for culturing fungi. F. N. W.

Action of arsenic compounds on the spores of black rust disease in wheat. J. BODNAR, A. TERÉNYI, and J. PASKUJ (Biochem. Z., 1935, 279, 448—452; cf. A., 1927, 600).—The spores adsorb As from H_3AsO_4 and salvarsan (I) solutions (but not from solutions of other As compounds) and are thereby prevented from germinating, but are not killed. Part of the As of the H_3AsO_4 combines with proteins in the envelopes of the spores and cannot be washed out with H_2O . None of the As adsorbed from (I) can be so removed. Conc. solutions of K_3AsO_3 (but not of K_2HAsO_4) left in contact with the spores pass into their interior and kill them. W. McC.

Action of anemonin on micro-organisms. F. BOAS and R. STEUDE (Biochem. Z., 1935, 279, 417—423).—Anemonin (I) in concs. of 1 : 66,000 or less inhibits the growth of moulds (e.g., *Aspergillus niger*, *Mucor stolonifer*, *Saccharomyces cerevisiae*, *Oidium lactis*) in synthetic (poor in bios) and natural (rich in bios) media. In *Ranunculus* (I) acts antagonistically to the auxins also present. W. McC.

Bacteria on fresh fruit. M. M. JOHNSTON and M. J. KAAKE (Amer. J. Publ. Health, 1935, 25, 945—947).—No generally accepted pathogens of the colontyphoid-dysentery group held responsible for severe summer diarrhoea of children were found on fruit purchased in the open market. C. J.

New sulphur-bacterium from the thermal springs of Santa Rosalia, Mexico. O. BAUDISCH (Svensk Kem. Tidskr., 1935, 47, 191—204).—An unpigmented bacterium belonging to the group *Sulphomonas thio-oxidans* can produce $N-2N-H_2SO_4$ from S and can multiply in $N-H_2SO_2$. As (and to a small extent Sb), but not Fe and Cu, are essential for growth. The first stage in the oxidation of S appears to be the formation of H_2S or a SH-compound. A method of detecting such compounds is described depending on the reduction of $Na_2[Fe(CN)_5(H_2O)]$ to $Na_3[Fe(CN)_5(H_2O)]$, which then no longer gives a red coloration with reduced phenolphthalein. Cultures containing thymine glycol (I) develop a red colour in presence of mineral acid if the O_2 concn. is low and the solution kept in the dark. It is suggested that (I) first loses a mol. of H_2O to form $CO<\text{NH}\cdot\text{CH}(\text{OH})>\text{C}\cdot\text{CH}_2$ (II). Intramol. addition of 2 mols. of (II) gives $(CO<\text{NH}\cdot\text{CH}(\text{OH})>\text{C}\cdot\text{CH})_2$,

which is oxidised by O_2 to form the red dye $(CO \leftarrow N \text{---} C(OH) \rightarrow C \cdot Cl^+)_2$.

E. A. H. R.

Neutrality of flocculating staphylococcus toxin-antitoxin mixture. G. RAMON, P. NELIS, and R. RICHOU (Compt. rend. Soc. Biol., 1935, 119, 1306—1308).—The point of hæmolytic neutrality does not correspond with that of flocculation neutrality.

H. G. R.

A "growth substance." R. J. WILLIAMS and B. E. CHRISTENSEN (Science, 1935, 82, 178).—The organism isolated from a deep skin lesion grows very rapidly in a suitable medium. Apart from the ordinary nutrients used for yeast culture, it requires various NH_2 -acids and is stimulated by pantothenic acid and cryst. vitamin-B. For rapid growth a H_2O -sol. substance, abundant in liver, liver extract, kale, lucerne, and, to a smaller extent, in milk, is required. The "growth substance" concerned is probably of importance in the nutrition of animals as well as of the organism described. This nutritive tends to be associated with casein and ovalbumin; it is only partly destroyed by long autoclaving at 20 lb. pressure in 3—4N- H_2SO_4 or in 2N-Ba(OH) $_2$.

L. S. T.

Identification of asparagine as the substance stimulating the production of butyl alcohol by certain bacteria. E. L. TATUM, W. H. PETERSEN, and E. B. FRED (J. Bact., 1935, 29, 563—572).—*l*-Asparagine is the active material in potato extract which stimulates the bacterial conversion of starch into BuOH. *l*-Aspartic (I) and *d*-glutamic acids when supplemented with mol. equivs. of $(NH_4)_2SO_4$ produce a similar effect. NH_2 -acids and $(NH_4)_2SO_4$ alone were ineffective. NH_4 malate and to a smaller extent NH_4 succinate may be substituted for (I), but NH_4 tartrate has no effect. The transformation of starch into BuOH by certain butyric bacteria necessitates the presence of a 4- or 5-C dicarboxylic NH_2 -acid or a substance which can be converted into such an acid.

A. G. P.

Culture of anaerobic bacteria in non-regenerated media with the addition of extracts of embryonic cells. M. WEINBERG and A. GUELIN (Compt. rend. Soc. Biol., 1935, 119, 1364—1365).—Extracts of embryonic cells stimulate the growth of anaerobic bacteria under anaerobic conditions and, owing to their powerful reducing properties, allow growth in presence of air.

H. G. R.

Bacterial growth with automatic p_H control (A) Apparatus. (B) Acid production by *Lactobacillus acidophilus*. L. G. LONGSWORTH and D. A. MACINNES (J. Bact., 1935, 29, 595—607).—(A) The p_H of the media is determined by a glass electrode, and additions of alkali are controlled by a photo-electric relay actuated by the beam of light reflected from the mirror of the electrometer.

(B) Acid production by *L. acidophilus* is increased by maintaining a low p_H in the media. CO_2 is essential for the growth of the organism.

A. G. P.

Relationship between molecular structure, p_H , and the ability of bacteria to grow in solutions of salts of organic acids. W. F. BRUCE (J. Amer. Chem. Soc., 1935, 57, 1495—1503).—The approx.

relative rates of growth of 4 bacteria in solutions of the Na salts of 70 org. acids with p_H 4—9 are reported. The solutions become more alkaline when growth occurs. Growth is better on *cis*- than on *trans*-isomerides, on *n*-fatty acids with an even than those with an odd no. of C, on fatty acids of low than of high mol. wt., on OH- and NH_2 -acids with an odd than those with an even no. of C, and on acyclic than on cyclic acids. Substitution by Ph decreases greatly the rate of growth, but by Me may either increase or decrease it. Certain pairs of saturated and unsaturated acids of otherwise similar structure (e.g., succinic and fumaric acids) show great similarity, suggesting metabolic conversion of one into the other, e.g., by dehydrogenation.

R. S. C.

Anaerobic production of pyruvic acid from alanine. E. AUBEL and F. EGAMI (Compt. rend. Soc. Biol., 1935, 119, 1243).— $AcCO_2H$ is produced anaerobically from alanine using a medium containing KNO_3 inoculated with soil bacteria.

H. G. R.

Mechanism of the fermentation of glucose by *B. coli*. J. TIKKA (Biochem. Z., 1935, 279, 264—288).—The following scheme is suggested. Glucose is first converted into hexose diphosphate, which breaks down into 2 mols. of dihydroxyacetone-phosphoric acid (I) and on dismutation gives 1 mol. each of α -glycerophosphoric and phosphoglyceric acids. The former is converted into $EtOH + HCO_2H$ ($\rightarrow H_2 + CO_2$), whilst the latter undergoes dephosphorylation to $AcCO_2H$, which is in part reduced to lactic acid and in part split into 1 mol. each of $AcOH$ and HCO_2H ($\rightarrow H_2 + CO_2$). The formation of $AcCHO$ from hexose diphosphate by *B. coli* is detected and indicates the intermediate formation of (I). With *B. coli* the decarboxylation of $AcCO_2H$ (which occurs in yeast fermentation) does not occur. Instead, $AcCO_2H$ is partly reduced to lactic acid and partly degraded to $AcOH + HCO_2H$, the predominance of one or other reaction being largely determined by the p_H .

P. W. C.

Mechanism of the fermentation of dihydroxyacetone. A. I. VIRTANEN (Biochem. Z., 1935, 279, 262—263).—Attention is directed to the difference in mechanism according to the organism, $CO(CH_2OH)_2$ being fermented by yeast by way of hexose diphosphate, but by *B. coli* directly.

P. W. C.

Preparation of crystalline dihydroxyacetone by the biochemical method. C. NEUBERG and E. HOFMANN (Biochem. Z., 1935, 279, 318—320).—The details of the prep. using yeast- H_2O -glycerol and a culture of *Acetobacter suboxydans* are described, the yield of pure cryst. product representing 77% of that theoretically possible.

P. W. C.

Dismutation of *p*-tolylglyoxal. C. NEUBERG and C. OSTENDORF (Biochem. Z., 1935, 279, 459—462).—*B. coli*, *B. ascendens*, *B. lactis aerogenes*, *Termobacterium* Lindner, yeast, and pease-meal convert *p*-tolylglyoxal into *l-n*-methylmandelic acid.

W. McC.

Phosphatides of acid-fast bacteria. E. HECAT (Biochem. Z., 1935, 279, 157—165).—A method for the separation of the phosphatides of various acid-fast bacteria is described. Hydrolysis of the product

from human and bovine types of the tubercle bacillus gave an org. N base, very probably choline. Lecithin is therefore regarded as present. P. W. C.

Fixation of methylene-blue *in vivo* by leprosy bacilli. R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 119, 1326—1328).—There is no change in the oxidation-reduction potential of the tissue in leprosy. Methylene-blue is fixed on the bacilli by some substance sol. in cold EtOH. H. G. R.

Eosin-methylene-blue agar for rapid direct count of *E. coli*. H. W. GEHM and H. HEUKELEKIAN (Amer. J. Publ. Health, 1935, 25, 920—923).—Satisfactory counts are obtained, comparable with those from brilliant-green bile broth, by smears of heavily polluted H₂O on eosin-methylene-blue agar prepared by the standard method, but containing 2.0 instead of 1.5% of agar in order to give a firmer surface. C. J.

Inactivation of bacteriophage by oxidation and reactivation by ascorbic acid. I. LOMINSKI (Compt. rend. Soc. Biol., 1935, 119, 1345—1348).—Bacteriophages can be inactivated by I, H₂O₂, and O₂ and, in some cases, can be reactivated by ascorbic acid. H. G. R.

Trypanocidal action of certain styrylselenazole compounds. C. H. BROWNING, R. GULBRANSEN, and W. MCCARTNEY (J. Pharm. Exp. Ther., 1935, 54, 367—370).—2-(*p*-Acetamidostyryl)- (I) and 2-(*p*-dimethylaminostyryl)-selenazole (II) are tested for their trypanocidal action on *T. brucei* in mice. (I) has a marked but not permanent action; (II) has none, and sulphonation scarcely affects their activity. H. D.

Antiseptic action of carbazole-3-diazonium chloride and certain other diazonium compounds. Preparation of carbazole-3-diazonium chloride. C. H. BROWNING, R. GULBRANSEN, and S. H. TUCKER (J. Pharm. Exp. Ther., 1935, 54, 353—357).—Of a no. of diazonium salts the antiseptic action of carbazole-3-diazonium chloride to *S. aureus* and *B. coli* was by far the greatest, and was associated with the N₂ group, whilst with C₆H₆ and C₁₀H₈ derivatives the activity was not changed by decomp. H. D.

Rate of disappearance of certain intestinal bacteria in water. M. AITOFF and H. DOBKEVITCH (Compt. rend. Soc. Biol., 1935, 119, 1272—1274).—Filtered tap-H₂O is more bactericidal than either boiled or distilled H₂O, probably due to the presence of Pb and Ca salts, *p_H* having little effect. The bacteria live longer in filtered than in boiled rain-H₂O on account of the extra dissolved O₂. H. G. R.

Resistance of Stefansky's bacillus to ultra-violet light. R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 119, 1328—1330).—Irradiation for 1—2 min. with Hg-vapour lamps at 20 cm. inhibits the pathogenic action. H. G. R.

Incubator for biological laboratories. E. KRAUSS (Woch. Brau., 1935, 52, 261—262).—A large electrically-heated incubator suitable for industrial purposes is described. W. O. K.

Hormonal regulation of chlorine in children. G. TOROK and L. NEUFELD (Monatsschr. Kinderheilk., 1934, 61, 73—87).—Parathormone and extract of spleen increased retention of NaCl. Extracts of thymus, tonsils, liver, adrenal cortex, pineal gland, and insulin had no effect, whilst extracts of pituitary, ovary, and follicular hormone had variable effects.

NUTR. ABS. (m)

Site of action of acetylcholine and its significance. M. CATTELL and H. G. WOLFF (Science, 1935, 82, 106—107).—The action of acetylcholine on the iris of the cat is peripheral to the postganglionic fibres, and presumably a direct one on the radial muscles. L. S. T.

Adrenal denervation and adrenaline hyperglycemia. R. BERNARDINI (Riv. Patol. sper., 1935, 14, 15—23).—In rabbits the initial blood-sugar val. was 0.101—0.116% and the average vals. 5, 15, 30, and 60 min. after adrenaline (I) injection were 0.190, 0.175, 0.161, and 0.143%. After denervation of the adrenals the corresponding vals. were 0.140, 0.145, 0.129, and 0.113, and the hyperglycemia showed a retardation, the max. occurring after 15 instead of 5 min. Hence the adrenals normally intensify the direct hyperglycemic action of injected (I) and denervation interferes with the intensification.

NUTR. ABS. (m)

Interference of ascorbic acid in the determination of adrenaline in the adrenal gland. B. C. GUHA (Sci. and Cult., 1935, 1, 111).—Since the acid (I) occurs in adrenal glands and gives an intense bluish-violet colour with Folin's tungstic acid reagent (I) must be removed from adrenal extracts [e.g., by treatment with Pb(OAc)₂] before the adrenaline content is determined with that reagent. W. McC.

Cortical hormone and vagal excitability. A. DE BARBIERI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 152—153).—Cortin (I) increases vagal excitability in the dog. Hypovagotonia in adrenalectomised animals is due to both (I) and adrenaline deficiency.

R. N. C.

Adrenaltropic substance of the anterior pituitary. K. J. ANSELMINO, L. HEROLD, and F. HOFFMANN (Arch. Gynakol., 1934, 158, 531—543).—Injections of aq. extracts of anterior pituitary reduce the chromaffin reaction and produce vacuolisation of the cells of the suprarenal medulla. The substance responsible differs from those already known. Possibly increased medullary activity of this sort is the indirect cause of the blood-sugar-raising properties of the extracts. NUTR. ABS. (m)

Hormonal regulation of blood-sugar in infants. H. SCHONFELD (Monatsschr. Kinderheilk., 1934, 61, 241—248).—Infants fasted for 15—16 hr. were very sensitive to adrenaline injections, 0.3 ml. of 0.01% solution increasing the blood-sugar. Injections of anterior pituitary extract arrested the normal decrease in 8 out of 16 children who had previously fasted for 16 hr. In children fasted for 4 hr. the extract produced a slight increase in blood-sugar. Pituitrin caused an increase in blood-sugar in children fasted for 16 or 4 hr. NUTR. ABS. (m)

Thyrotropic hormone of the anterior pituitary. J. B. COLLIP and E. M. ANDERSON (J. Amer. Med.

Assoc., 1935, 104, 965—969).—Injection of purified thyrotropic hormone into rats causes a 28% rise in basal metabolic rate for the first week, a fall to pre-injection val. by the 2nd—3rd week, and a further fall to —29% (level in the untreated hypophysectomised rat) by the 5th week. The serum of injected animals contains an antithyrotropic substance which will inhibit the action of the hormone. This substance does not inhibit the action of thyroxine, but there is a given amount which will just prevent the rise in basal metabolic rate due to thyrotropic hormone without inhibiting thyroid hyperplasia. Severe hyperthyroidism develops in goitrous rats given the hormone. A possible hormone-antihormone balance is discussed.

NUTR. ABS. (m)

Determination of the thyrotropic action of anterior pituitary preparation and the unit of the hormone. J. G. HEYL and E. LAQUEUR (Arch. internat. Pharmacodyn., 1935, 49, 338—354).—There are three levels of activity in the thyroid gland of the young guinea-pig: an inner central zone, in a continual state of flux, a middle zone which reacts readily to the pure thyrotropic hormone, and a peripheral zone which is comparatively inactive. Changes which take place in the middle zone after injection into a young animal of thyrotropic hormone in known amounts, under standard conditions, may be used to standardise the prep. and serve as a basis for the definition of a unit. NUTR. ABS. (m)

Functional correlations between the anterior pituitary and the ovary. J. A. DUBOWIK (Pflüger's Archiv, 1935, 235, 412—415).—Maturation of the ovary of *Axolotl* is accelerated by stimulation of the anterior pituitary. Extirpation of the pituitary causes hypoplasia of the ovary. The anterior pituitary hormone induces maturation in hypophysectomised animals.

R. N. C.

Physico-chemical state of hormones in the blood. Diffusion of the oxytocic pituitary principle in dog- and ox-serum. D. BROWN and H. SCHEINER (Compt. rend. Soc. Biol., 1935, 119, 1379—1380).—The oxytocic hormone diffuses in serum in combination with a colloidal substance and becomes ultrafilterable only after treatment with acid or excess of CaCl_2 .

H. G. R.

Luteinising principle of the posterior lobe of the pituitary. A. MOSZKOWSKA (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 60—61).—Alkaline extracts of posterior lobes of ox pituitaries are without effect on the ovaries of immature guinea-pigs, but will produce cystic corpora atretica from follicles which are approaching maturity.

P. G. M.

Alkaline extracts of the posterior lobe of ox pituitary. A. MOSZKOWSKA (Compt. rend. Soc. Biol., 1935, 119, 1239—1240).—There is evidence of diffusion of the corticotropic and auxogenic hormones, but not of the thyrotropic or the crinogenic, from the anterior lobe.

H. G. R.

Gastric and pulmonary lesions following high doses of the vasopressor fraction of the posterior pituitary hormone. G. BERGAMI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 90—93).—The hæmorrhagic lesions produced by large quantities of vasopressin in

the stomach and lungs of rats and guinea-pigs occur in regions through which acid ions normally pass. Oxytocin does not produce lesions.

R. N. C.

Evaluation of gonadotropic hormone preparations on the basis of the rat-mouse ratio assay. W. O. NELSON and M. D. OVERHOLSER (J. Pharm. Exp. Ther., 1935, 54, 378—392).—The quantities of gonad-stimulating preps. corresponding with rat and mouse units are determined and shown to vary from a 5 : 1 rat : mouse ratio for pregnancy urine, to 1 : 3 for pituitary extract, and 2 : 1 for pregnant mare serum. Thus the ratio offers a method of differentiating between anterior pituitary and anterior pituitary-like gonadotropic complexes.

H. D.

Constitution of cinchol; its transformation into 3-hydroxyætiolallocholan-17-one.—See this vol., 1242.

Isolation of crystalline progesterin. W. M. ALLEN (Science, 1935, 82, 89—93).—A lecture.

L. S. T.

Crystalline progesterin and inhibition of uterine motility *in vivo*. W. M. ALLEN and S. R. M. REYNOLDS (Science, 1935, 82, 155).—Both cryst. forms of progesterin suppress uterine motility in rabbits. Inhibition of motility and progestational proliferation of the endometrium are produced by one and the same hormone.

L. S. T.

Nomenclature of the corpus luteum hormone. W. M. ALLEN, A. BUTENANDT, G. W. CORNER, and K. H. SLOTTA (Z. physiol. Chem., 1935, 235, I, and Nature, 1935, 136, 303).—The authors recommend the names α - and β -progesterone, respectively, for the high- and low-melting forms of the hormone of the corpus luteum (formerly progesterin or luteosterone).

W. McC.

Biological control of follicular and luteal preparations. Presence in the corpus luteum of a substance with action resembling that of insulin. Ovarian hormones and carbohydrate metabolism. B. BRUNELLI (Arch. internat. Pharmacodyn., 1934, 49, 212—221, 222—229, 243—258).—In ovariectomised rats, \approx 20 days after operation, injection of follicular hormone reduces, and of corpus luteum hormone increases, liver-glycogen (I). Treatment of fresh corpus luteum (non-pregnant cows) by methods for the extraction of insulin from pancreas gives a prep. which, injected into rabbits, reduces blood-sugar and increases (I) in rats. In adult female rats, folliculin injected daily from the beginning of pro-œstrus had a hyperglycæmic action and mobilised (I). Corpus luteum hormone injected in met-œstrus decreased blood-sugar and increased glycogen synthesis.

NUTR. ABS. (m)

Effect of prolactin on the œstrus cycle of non-parous mice. I. DRESEL (Science, 1935, 82, 173).—Prolactin suspends the œstrus cycle in mature, non-parous mice for approx. 3 weeks, after which, in spite of continued injections, a prolonged œstrus of 4—8 days sets in. The suspension of the œstrus cycle during lactation thus appears to be caused by the pituitary rather than by a corpus luteum hormone.

Administration of the oestrogenic substances in urine. A. GROLLMAN, H. B. SHUMACKER, jun., and E. HOWARD (*J. Pharm. Exp. Ther.*, 1935, **54**, 393—397).—The oestrogenic substances in urine may be adsorbed on to charcoal and administered orally; the adsorbed anterior pituitary-like substances are ineffective when administered in this way. H. D.

Regression of the histo-pathological modifications of the pituitary from castration, obtained with the new sex hormone extracted from male urine. A. MIGLIACCA (*Boll. Soc. Ital. Biol. sperim.*, 1935, **10**, 105—108).—Injection of the male hormone in castrated rats restores the histo-pathological picture of the anterior pituitary to normal in 3 weeks. The effective dose is equiv. to half the quantity of female hormone required. R. N. C.

Male sexual hormone in the female body. H. SIEBKE (*Z. ges. Naturwiss.*, 1935, **1**, 161—171).—A discussion. Curves are given showing the male and female hormone excreted in 3 months by a female subject. The former probably comes from the follicle. H. J. E.

Hormone content of the cock's comb. A. BERDNIKOFF and C. CHAMPY (*Compt. rend. Soc. Biol.*, 1935, **119**, 1314—1315).—Folliculin is present in the comb in the free state and the male hormone in an inactive form. H. G. R.

Activity of androstenedione on the sexual organs of the male rat. E. TSCHOPP (*Nature*, 1935, **136**, 258—259).—Androstenedione (I) is more active than androsterone (II), or the diol obtained by hydrogenation of (II), in increasing the wt. of the sexual organs of young castrated male rats. Its action on the capon's comb is less, however. The results support the view (this vol., 1125) that (I) or a similar unsaturated ketone may be identical with the less stable hormone of the testis. L. S. T.

Increased effectiveness of insulin when injected in equal doses at intervals of two to four hours. I. Use of insulin in divided doses in severe uncomplicated diabetes and in complicated medical cases. B. B. CLARK, R. B. GIBSON, and W. D. PAUL (*Arch. Int. Med.*, 1935, **56**, 360—373).—Insulin is most effective when given in equal doses at intervals of 2—4 hr. day and night. Under these conditions the daily requirement is less. H. G. R.

Influence of insulin on alcoholæmia in men. E. SERIANNI (*Atti R. Accad. Lincei*, 1935, [vi], **21**, 394—401).—The height of the blood-EtOH curve following ingestion of aq. EtOH is reduced (41—50%) by prior subcutaneous injection of insulin (20 units). F. O. H.

Effect of parathyroid extract on normal carbohydrate metabolism. A. FERRANNINI (*Policlin.*, 1935, **42**, 285—299).—Injection of 1 ml. of extract caused the blood-sugar to fall 13—56%; when injected simultaneously with 150 g. of glucose (I) given by mouth the degree of hyperglycæmia was < when (I) was given alone, and when injected simultaneously with 1 mg. of adrenaline, hyperglycæmia was in some cases reduced. NUTR. ABS. (m)

Role of the nervous system in the action of thyroxine on cell respiration. G. MANSFELD and G. HORVATH (*Pflüger's Archiv*, 1935, **235**, 520—521).—The increase of O₂ consumption in rabbit's kidney by thyroxine (I) is abolished by complete denervation of the kidneys. Excitation of the gastrocnemius nerve of the frog in Ringer's solution containing (I) produces an O₂ consumption > in absence of (I); unexcitable nerve shows no difference. Hence (I) is taken up by the nervous system and reaches the cells by the peripheral nerves, where it exerts its catalytic effect on anaerobic fermentation, and indirectly on cell oxidation. R. N. C.

Thyroglobulin studies. I. Thyroxine and iodine content of normal and goitrous human thyroglobulin. J. W. CAVETT, C. O. RICE, and J. F. MCCLENDON (*J. Biol. Chem.*, 1935, **110**, 673—683).—Thyroglobulin (I) from goitres contains less total I, and has a lower thyroxine I : total I ratio, than (I) from normal human thyroid glands. Administration of I to the patients does not restore the I content of (I) to normal. Widely different types of goitre give the same result. Vals. of the basal metabolic rates of the patients are given. F. A. A.

Effect of the thyroid on the formation of hen's egg. V. S. ASMUNDSON and P. PINSKY (*Poultry Sci.*, 1935, **14**, 99—104).—Feeding desiccated thyroid at the rate of 1 mg. of I per 1750 g. live-wt. resulted in a reduction in yolk-wt., a small increase in shell-wt., and a reduction in body-wt. and rate of growth of the ovum. A. G. P.

Relationship of the thyroid gland and the liver. H. DOETSCH (*Biochem. Z.*, 1935, **279**, 233—240).—The acceleration of metamorphosis of tadpoles by thyroxine is inhibited by the presence of the press-juice or pulp of liver, but not of kidney or muscle. P. W. C.

Effect of the duration in the solution on the action of thyroxine on tadpoles. P. ALPHONSE and G. BAUMANN (*Compt. rend. Soc. Biol.*, 1935, **119**, 1243—1245).—30 min. in 1 : 50,000 or 1 hr. in 1 : 400,000 thyroxine solution is sufficient to give a positive result. After immersion the animals are returned to H₂O and within 2—3 days the effect on the metamorphosis is noticeable. H. G. R.

Action of the plant hormones on the development of frog-spawn. R. M. DU PAN and M. RAMSEYER (*Compt. rend. Soc. Biol.*, 1935, **119**, 1236).—The growth hormones of plants increase the rate of development and cell division of frog-spawn. H. G. R.

Function of the corpus allatum of insects. V. B. WIGGLESWORTH (*Nature*, 1935, **136**, 338—339).—This gland secretes two and possibly three hormones regulating the growth of *Rhodnius*. L. S. T.

Effects of a deficiency of iodine and vitamin-A on the thyroid gland of the albino rat. H. M. COPLAN and M. M. SAMPSON (*J. Nutrition*, 1935, **9**, 468—487).—Deficiency of I causes initial hypertrophy of the thyroid in both sexes, but persisting longer in females. It is followed in both sexes by atrophy. Deficiency of vitamin-A produces hypertrophy in

females and atrophy in males. Deficiency of I and -A induces initial hypertrophy in both sexes followed by atrophy in males. A. G. P.

Internal energy relationships of organic substances. VIII. Formation of vitamin-A and the double linking rule. O. SCHMIDT (Ber., 1935, 68, [B], 1658—1662; cf. this vol., 852).—In accordance with the double linking rule the transformation of β -carotene into vitamin-A occurs according to the scheme: $\text{CMeR:CH:CH:CH:CH:CMeR} \rightarrow \text{CMeR:CH:CH}_2\text{:CH(OH):CH:CMeR} \rightarrow 2\text{CMeR:CH:CH}_2\text{:OH}$. The change is therefore similar to that of ergosterol into vitamin-D. With regard to the influence of Me and Cl on substitution in the C_6H_6 nucleus the dipole effect is regarded as of secondary consequence, and the valency activity of the B electrons not as an effluence of electrostatic forces, but as a quantum-mechanical resonance effect caused by the alternating direction of spin of the corresponding B electrons. It does not appear possible to explain electrostatically by dipole forces the author's double linking rule or the closely allied radical rule of Criegee. H. W.

Vitamins-A and -D of Suiyuan vegetable oils. T. Y. LO (Nutrit. Bull. B., No. 2, March, 1935, 22—33).—No evidence of the presence of vitamin-A or -D was found in linseed, mustard-seed, or hempseed oil. The oils, especially the hempseed, may contain toxic substances. NUTR. ABS. (m)

Effect of some yeast extract factors on the growth of rats on high-fat diet. C. Y. CHEN (Nutrit. Bull. B., No. 2, March, 1935, 43—51).—Rats fed on a basal diet containing peanut oil 65%, fish-protein 29%, McCollum's salt mixture 4%, and unsaponifiable matter from cod-liver oil 2% grew well only when given dried yeast, crude extract of yeast, or purified preps. of vitamin- B_1 and - B_2 , together with the residue of the extracted yeast. When receiving only the purified preps. of - B_1 , - B_2 , and - B_4 , the rats did not grow, although these supplements were sufficient to support growth on a diet containing only 5% of fat. NUTR. ABS. (m)

B-Vitamins as substitute for insulin. W. VON DRIGALSKI (Arch. Verdauungs-Kr., 1935, 57, 1—8).—Although there is a definite relation between carbohydrate metabolism and the vitamin-B complex, more particularly - B_1 , treatment of diabetic patients with yeast instead of insulin was unsuccessful, the complex, as present in yeast, having no effect on the glycosuria, blood-sugar level, acidosis, or insulin requirement of diabetics. NUTR. ABS. (m)

Crystalline fluorescent dehydrogenation product from vitamin- B_1 . G. BARGER, F. BERGEL, and A. R. TODD (Nature, 1935, 136, 259).—Alkaline $\text{K}_3\text{Fe(CN)}_6$ converts the vitamin hydrochloride into a pale yellow, S-containing compound, m.p. 221°, which, in neutral or alkaline solution, has an intense blue fluorescence. It possesses all the recorded properties of the "thiochrome" ($\text{C}_{12}\text{H}_{14}\text{ON}_4\text{S}$) of Kuhn *et al.* (this vol., 1026), including a similar absorption spectrum. L. S. T.

Vitamin- B_1 and - B_2 content of wheat products. A. F. MORGAN and M. J. HUNT (Cereal Chem., 1935,

12, 411—418).—The following vals., expressed as international units per 100 g., are given for wheat products. Vitamin- B_1 , whole wheat 125; wheat germ 758; whole wheat + 10% of germ 184; whole wheat + 20% of germ 242; whole-wheat bread 167—186. Vitamin- B_2 , whole wheat 100; germ 404; whole wheat + 20% of germ 124. E. A. F.

Antineuritic vitamin from yeast. H. RUHKOPF (Diss., Gottingen, 1933; Bied. Zentr., 1935, A, 5, 331).—The prep. of cryst. vitamin- B_1 from yeast is described. The free base, $\text{C}_{12}\text{H}_{16}\text{ON}_4\text{S}$, yields on hydrolysis with HCl $\text{C}_{12}\text{H}_{15}$ (or $17\text{O}_2\text{N}_3\text{S}$). A. G. P.

Growth-promoting action of synthetic d-riboflavin (6 : 7-dimethyl-9-[d-1-ribityl]isoalloxazine). P. KARRER, H. VON EULER, M. MALMBERG, K. SCHOPF, and F. BENZ (Svensk Kem. Tidskr., 1935, 47, 99—101).—Synthetic d-riboflavin, m.p. 282°, has a growth-promoting power equal to that of the purest samples of natural lactoflavin, with which it appears in other respects to be identical (cf. this vol., 359, 631). W. O. K.

Excretion and storage of vitamin-C in the human and animal body. I. Vitamin-C content of the urine of inhabitants of Sweden. H. VON EULER and M. MALMBERG (Biochem. Z., 1935, 279, 338—352).—No relationship could be traced between daily urinary excretion of vitamin-C (I) and physiological or pathological condition. The amount excreted in the urine of women is not increased during pregnancy. Although individual variations are very great, the (I) excretion of persons living (in N. Sweden) on a diet poor in (I) is much < that of persons living (in S. Sweden) on a diet richer in (I). W. McC.

Vitamin-C requirement of the guinea-pig. M. DANN and G. R. COWGILL (J. Nutrition, 1935, 9, 507—519).—Guinea-pigs require approx. 1 c.c. of lemon juice per 100 g. body-wt. No evidence was obtained of a relatively larger requirement for young rapidly-growing animals. Metabolic rate has no appreciable influence on the -C requirement. A. G. P.

Biochemical relationships between ascorbic acid and glutathione. T. BERSIN, H. KOSTER, and H. J. JUSATZ (Z. physiol. Chem., 1935, 235, 12—18).—A relationship is shown to exist between the ascorbic acid (I) and glutathione (II) contents of the kidney. The autoxidation of (I) at p_H 6.47 or 7.38 is considerably retarded by 10% of (II), whilst a solution of molar quantities of (I) and (II) at p_H 7.38 and 36° does not absorb O_2 , although separately the reactants do so. Solutions of (I) can be protected from atm. oxidation by addition of SH-compounds, the requisite amount of the latter being much less at p_H 7 than at p_H 4.5. The formation of a compound of (I) and (II) could not be established. H. W.

Vitamin-C content of brain after administration of the vitamin. M. MALMBERG and H. VON EULER (Z. physiol. Chem., 1935, 235, 97—103).—The vitamin-C (I) content of the brain of the guinea-pig is reduced to 20% of its normal val. by feeding (for 14—26 days) a diet free from (I). The (I) content of the rabbit brain is not decreased by feeding such diet or increased by giving enormous (I) excess. W. McC.

Distribution of vitamin-C in the brain-stem ganglia. F. PLAUT and K. STERN (Naturwiss., 1935, 23, 557—558).—Vals. are given for the vitamin-C contents of the globus pallidus (I), thalamus, caudate nucleus, and substantia nigra (II). (II) has a content significantly > (I). E. A. H. R.

Rheumatic heart disease and vitamin-C. C. B. PERRY (Lancet, 1935, 229, 426—427).—Determinations by the dichlorophenol-indophenol method of the ascorbic acid (I) excreted in the urine of children suffering from rheumatic carditis show that (I) deficiency is not an important causative factor, but that some degree of deficiency often occurs in such cases. L. S. T.

Antiscorbutic vitamin in horse-radish. K. P. KEDROV (Problems of Nutrition, U.S.S.R., 1934, 3, No. 5, 20—21).—Horse-radish is a good source of vitamin-C (I), since 20 g. daily would protect from scurvy a man on a diet otherwise lacking in (I).

NUTR. ABS. (m)

(A) Antiscorbutic properties of the turnip (*Brassica napus*). S. N. MATZKO. (B) Canned food enriched with vitamin-C by addition of fir-needle concentrate. N. S. JARUSOVA. (C) Antiscorbutic action of the concentrate from the sulphited black-currant, obtained in factory conditions. T. L. IZUMRUDOVA (Problems of Nutrition, U.S.S.R., 1935, 4, No. 1, 68—70, 70—72, 72—74).—(A) The turnip, yellow or white, is a comparatively poor source of vitamin-C.

(B) When an infusion of fir needles mixed with rice gruel was canned about half the vitamin-C activity of the infusion was lost.

(C) A juice, prepared from sulphited black-currants on a large scale and subsequently freed from sulphite by concn. at reduced pressure, showed a high vitamin-C activity.

NUTR. ABS. (m)

Ascorbic acid content of some plant fluids. H. N. BANERJEE (Current Sci., 1935, 4, 28—29).—The ascorbic acid (I) content of juices expressed from the following is in the decreasing order: coconut tree, Palmyra palm, pineapple, date-palm tree, and coconut. The (I) content of coconut decreases as the fruit ripens. F. N. W.

Enzymic determination of true vitamin-C. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1935, 110, 559—563).—The reducing substances are titrated both before and after removal of the ascorbic acid with ascorbic acid oxidase, after preliminary Hg(OAc)₂ treatment. H. G. R.

Determination of ascorbic acid by titration. E. W. MCHENRY and M. GRAHAM (Biochem. J., 1935, 29, 2013—2019; cf. this vol., 903).—The Harris titration of ascorbic acid (I) (A., 1933, 541) is modified by making up the indicator in HPO₄ buffer at p_H 7.2, using large dilutions, and extracting 3 times with CCl₃-CO₂H. Pigmented extracts are titrated under CHCl₃; with strawberries and red peppers the CCl₃-CO₂H extracts are washed with amyl alcohol. In the lettuce, cucumber, and turnip the concn. of (I) is greatest where photosynthesis occurs. The difference in (I) content between tetraploid and diploid tomatoes is probably due to the

difference in size. From the increases in (I) content of vegetables on cooking or treatment with H₂S the presence of a complex containing (I), insol. in CCl₃-CO₂H, is assumed. H. D.

Effect of feeding cacao shell to cows on the vitamin-D content of butter. S. K. KON and K. M. HENRY (Biochem. J., 1935, 29, 2051—2056).—The mean vitamin-D (I) content of cacao shell and cacao shell-fat determined by curative and protective methods on rats was 35 and 300 international units per g., respectively. The feeding of 2 lb. of the shell daily for 4 weeks to shorthorn cows under winter feeding conditions increased the (I) content of the butter to the summer level, i.e., from 0.20—0.25 to 0.50—0.60 international units per g. A. L.

Effect of vitamin-D on production and properties of eggs. H. W. TITUS and R. B. NESTLER (Poultry Sci., 1935, 14, 90—98).—Improvements in egg production, egg wt., and hatchability due to supplementary feeding of vitamin-D are recorded. The effect is dependent on the source as well as quantity of -D supplied. Large proportions produce deleterious results. The optimum quantity of cod-liver oil for confined birds is 1—2% of the diet. When viosterol is used 10—20 times the amount of -D is necessary. A. G. P.

Comparative vitamin-D requirements of growing chicks, turkeys, and pheasants. F. D. BAIRD and D. J. GREENE (Poultry Sci., 1935, 14, 70—82).—Min. requirements of vitamin-D are determined. The large demand of turkeys and pheasants may be met by feeding fortified cod-liver oil. A. G. P.

Vitamin-D in edible fungi. A. SCHEUNERT, M. SCHIEBLICH, and J. RESCHKE (Z. physiol. Chem., 1935, 235, 91—96).—The vitamin-D (I) contents (international units) of 1 g. of the fresh fungi are: *Boletus edulis* and *Cantharellus cibarius* 0.83, *Helvella esculenta* 1.25, *Agaricus s. Psalliota campestris* (grown in the dark) 0.21, (grown in the open) 0.63. *B. badius* and many (if not all) other fungi contain (I). The (I) content of the fungi is reduced if they are grown in the dark. W. McC.

Fat-soluble growth factor required by blow-fly larvae. II. Identity of the growth factor with cholesterol. R. P. HOBSON (Biochem. J., 1935, 29, 2023—2026; cf. this vol., 889).—Cholesterol from several sources had the same growth-promoting power for blow-fly larvae; sitosterol, ergosterol, and lanosterol had smaller effects. The fat-sol. growth factor is therefore a sterol. H. D.

Effect of calcium and phosphorus variations and source of experimental chicks on assay of vitamin-D carriers. W. B. GRIEM, M. J. KILLIAN, L. E. CLIFCORN, W. S. THOMPSON, and E. GUNDLACH (J. Assoc. Off. Agric. Chem., 1935, 18, 471—475).—Variation of Ca from 0.83 to 0.90% and of P from 0.48 to 0.78% produces no significant effect on the accuracy of assay by the A.O.A.C. tentative method. The origin of the white Leghorn chicks used has no effect on the result. E. C. S.

Vitamin-E. III. Evidence for the presence of a hydroxyl group. Biological utilisation of esters. Absorption spectrum. H. S. OLCOTT (J.

Biol. Chem., 1935, **110**, 695—701).—The presence of at least one OH in vitamin-*E* (I) is proved by the formation of ethers with MeI(EtI)-Ag₂O, and the formation of a urethane (II) with PhNCO. These processes destroy the activity of (I) (no litters from rats), but an active sample of (I) is regenerated by hydrolysis of (II) with KOH-EtOH. The activity of the Bz and Ac derivatives of (I) (A., 1934, 462) indicates that rats can utilise these esters, but not (II). Acetylation may destroy the antioxidant, but rancidity in the acetylated concentrate does not diminish its physiological activity. Hydrogenation (H₂-N₁ at 230°/250—280 atm.) neither destroys (I) nor saturates the concentrate (residual I val. 26). The conclusion (this vol., 129) that the band at 294 mμ is not due to (I) is confirmed by a lack of parallelism between its intensity and the activity of the sample. J. W. B.

Summation of [plant] cell e.m.f. H. F. ROSENF (Plant Physiol., 1935, **10**, 209—224).—The polarity of a region of the root tip (*Allium cepa*) is increased or decreased when an electrolyte solution (e.g., tap-H₂O) surrounds a segment of that region. Initial conditions are restored on removal of the solution. Evidence is advanced showing that the principle of algebraic summation of e.m.f. in polar cell systems applies to the polarity of roots.

A. G. P.

Material basis of the osmotic pressure in *Hedera helix* and *Ilex aquifolium*. G. PITTIUS (Bot. Archiv, 1935, **37**, 43—64).—The osmotically active constituents of the plant saps are sugars (glucose, fructose, sucrose), org. acids (malic), and K and Na salts (principally malate, PO₄^{'''}, SO₄^{'''}, Cl[']). Tannins and related compounds are unimportant as osmotic factors. Periodic fluctuations in osmotic pressure are controlled mainly by the sugars, except in the period of shoot formation, when the rapid decline in sugar content is partly counteracted by an increase in org. acid and salts.

A. G. P.

Effect of frost on wheat at progressive stages of maturity. II. Composition and biochemical properties of grain and flour. A. G. MCCALLA and R. NEWTON (Canad. J. Res., 1935, **13**, C, 1—31; cf. B., 1934, 596).—The rate of increase in dry matter of the kernels was high for approx. 14 days after flowering, decreasing subsequently to zero at a crit. stage 24 days later. During this period, the total N content increased to a max., the salt-sol. N declined steadily, and NH₃-N increased at first and subsequently fell to a negligible amount. The ratio of N to non-N materials translocated to the endosperm during active development remained approx. const. Frost did not affect the ash or invert sugar contents of the grain. The salt-sol. and non-protein-N was not altered by freezing at -2.2°. In samples cut prior to the crit. stage, exposure to < -4.4° caused a decline in the total N of grain and flour and an increase in reducing sugar in flour.

A. G. P.

Salt concentration and reversibility of ice formation as related to the hardness of lucerne. S. T. DEXTER (Plant Physiol., 1935, **10**, 403—406).—Less H₂O was frozen at -6° to -90° in lucerne roots which had been hardened than in tender roots. There

appears to be no loss of electrolytes during the hardening process (see also this vol., 263, 266). A. G. P.

Temperature as a predetermining factor in the development of *Avena sativa*. T. M. PLITT (Plant Physiol., 1935, **10**, 269—289).—Oats contain no starch in the embryo when in the resting condition. On germination at 5° starch is deposited in the embryo. During germination at 25° little or no starch appears, but the seedling contains higher proportions of pectin and reducing sugars. Protein is produced more rapidly at the higher temp. Seedlings grown at 25° were tallest, irrespective of the germination temp., and contained least N. Seedlings germinated at 25°, regardless of later conditions, had a higher % of dry matter and carbohydrates, higher ratio of sol. to insol. acid-hydrolysable carbohydrates, and lower % of N than had those germinated at 5°. Oats germinated and grown at 25° with R.H. 40% made less growth, had higher % of dry matter and lower % of carbohydrate than those grown with R.H. 70%. In 6-week plants SiO₂ was deposited in the same manner in erect and recumbent plants, and was localised in cells which did not form a consecutive structure. SiO₂ deposition is unrelated to "lodging."

A. G. P.

Effects of exfloration on plant metabolism. S. AUSTIN (Plant Physiol., 1935, **10**, 225—243).—Cessation of growth associated with fruit development in soya beans is not affected by exfloration. The reproductive phase is controlled by day-length. The behaviour of exflorated plants resembles the response of other plants to K starvation. The length of day affects vegetative growth, probably through its influence on the [K⁺] in plant tissues. Exfloration results in an abnormal accumulation of carbohydrates, but not of N. In control plants the N, Ca, Mg, P, and K contents were not depleted by the development of fruits.

A. G. P.

Limitations of Blackman's law of limiting factors and Harder's concept of relative minimum as applied to photosynthesis. B. N. SINGH and K. N. LAL (Plant Physiol., 1935, **10**, 245—268).—Under low light intensities [CO₂]-assimilation curves are smooth and the stationary phase is either absent or limited to a small range. With high light intensities curves for wheat and linseed are regular, but show a wide range of stationary assimilation. The effects of temp. and light intensity on the photosynthetic process are examined. The theory of relative min. is of limited application. It functions to some extent when [CO₂] and light intensity are low.

P

Formation of chlorophyll and the beginning of photosynthesis. O. L. INMAN (Plant Physiol., 1935, **10**, 401—403).—Evolution of O₂ occurs very soon after chlorophyll is formed in young etiolated leaves in visible amounts, and is not delayed until the leaf is almost fully green. Absorption spectra of extracts of etiolated leaves made between 2 sec. and 2 min. after exposure indicate the formation of chlorophyll long before O₂ evolution occurs.

A. G. P.

Non-indispensability of oxygen for carbon dioxide assimilation by green plants. H. GAFFRON (Naturwiss., 1935, **23**, 528; cf. Kautsky, this

vol., 1177).—When *Chlorella* ferments in the dark in N_2 until completely free from O_2 and is then exposed to light, assimilation of CO_2 at once begins without accompanying evolution of O_2 , such evolution beginning only after some time. If CO_2 replaces N_2 during fermentation, initiation of the assimilation is also retarded. These and other facts indicate that the presence of free or loosely bound O is not essential for the initiation of CO_2 assimilation in green plants. W. McC.

Deficiency experiments in water cultures. II. W. SCHROFF and H. SOUKUP (Landw. Versuchs-Stat., 1935, 122, 263—322; cf. B., 1934, 250).—Comparison is made of various media utilised by different investigators. Results are discussed from the viewpoint of the influence of composition, initial concn., and p_H of the nutrient on the validity of deficiency experiments with different crops. A. G. P.

Nitrogenous and carbonaceous nutrition of *Chlorogonium euchlorum* in the dark. Acetic acid as a product of chlorophyllic assimilation. A. Lvov and H. DUSI (Compt. rend. Soc. Biol., 1935, 119, 1260—1263).— $AcOH$, although favouring the growth of *C. euchlorum* in the dark, is not indispensable: it is probably an intermediary stage in starch synthesis. H. G. R.

Iron absorption and chlorosis in green plants. C. OLSEN (Compt. rend. Lab. Carlsberg, 1935, 21, No. 3, 15—52).—*Lemna polyrrhiza* grown in Knop's solution at p_H 6—7 becomes chlorotic, but remains normal at p_H 4—6 or 7—10. Addition of Fe citrate or humus extract corrects the chlorotic condition. Plants having a high Fe requirement (*Xanthium spinosum*, *Zea mays*) behave similarly, whereas those requiring little Fe show no chlorosis but slightly inhibited growth at p_H 7. Chlorotic maize plants may contain > normal amounts of Fe and always have > normal % of Ca^{++} , PO_4^{+++} , Mg, K, and N as a result of restricted production of org. matter without disturbance of the mineral intake. Fe in chlorotic plants is immobilised by pptn. as phosphate. At p_H 8.0 the PO_4^{+++} of Knop's solution is largely pptd. as $Ca_3(PO_4)_2$, hence the intake of PO_4^{+++} by and the subsequent pptn. of Fe within the plants is decreased. Maize grown in acid media absorbs less PO_4^{+++} and has a more acid tracheal sap which opposes pptn. of Fe. Chlorosis in media of p_H 6—7 is prevented by decreasing the proportion of PO_4^{+++} . Alkaline media may cause chlorosis if the composition is adjusted to give an excess of PO_4^{+++} over Ca^{++} . Fe tartrate is less effective than the citrate owing to the greater ease of decomp. and pptn. as $Fe(OH)_3$. Fe^{II} salts completely prevent chlorosis at p_H 6—7 (cf. B., 1930, 434). A. G. P.

Kinetics of penetration. XI. Entrance of potassium into *Nitella*. A. G. JACQUES and W. J. V. OSTERHOUT (J. Gen. Physiol., 1935, 18, 967—985).—The rate of entrance of K into *N. flexilis* is independent of illumination and of p_H between p_H 6 and 8, over the external concn. range 10^{-2} to $10^{-4}M$, and varies little with external $[K^+]$ between 10^{-2} and $10^{-3}M$, but rather more at lower concns. The K content of the raw sap is > that of ultrafiltered sap. F. A. A.

Chemical restoration in *Nitella*. I. Ammonia and some of its compounds. W. J. V. OSTERHOUT (J. Gen. Physiol., 1935, 18, 987—995; cf. this vol., 1038).—The K effect and the irritability in *Nitella*, removed by immersion in distilled H_2O , can be restored by NH_3 or NH_4Cl solution. The K effect can also be restored by NEt_4Cl . F. A. A.

Appearance of substances functioning like the plant auxin during the development of *DiscoGLOSSUS pictus*. Otth. M. ROSE and H. BERRIER (Compt. rend., 1935, 201, 357—359).—The sperm and egg, in the early stages of segmentation, of *D. pictus* have no auxin-like activity as determined by the behaviour of a coleoptile; at a later stage in the development of the egg activity appears. H. D.

Pure growth effect obtained with heated pregnancy urine. E. HELD and K. PONSE (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 56—59).—By heating to 70° pregnancy urine, previously extracted with Et_2O to remove oestrin, the luteinising principle appears to be destroyed, whilst some oestrogenic principle remains. P. G. M.

Solubility of growth factors from micro-organisms. W. H. SCHOPFER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 18—19).—Vitamin- B_1 has a max. solubility in 70% $EtOH$. Extraction of wheat germ or a conc. extract (obtained by means of 70% $EtOH$) by light petroleum yields a solution containing only lipins and yellow pigment, but $CHCl_3$ liberates a substance which is equally active on vegetative development and zygote formation, and is distinct from vitamin-B, which is almost insol. in $CHCl_3$. P. G. M.

Spectroscopic study of different woods of Fernando Po and the Iberian Peninsula. S. PINA DE RUBIES and L. LEMMEL (Bull. Soc. chim., 1935, [v], 2, 1368—1370).—Spectroscopic estimates of the elements present in 26 woods have been made. Ag, Pb, and Cr are revealed for the first time. Five of the Fernando Po woods fluoresced intensely in ultra-violet light. T. G. P.

Presence in self-blanching celery of unsaturated compounds with physiological action similar to ethylene. R. C. NELSON and R. B. HARVEY (Science, 1935, 82, 133—134).—Golden self-blanching celery in the natural blanching condition produces in the tomato the characteristic curvature of the leaves which results in presence of low concns. of certain substances containing C:C. A celery which is not self-blanching produced no such reaction. C_3H_6 , C_4H_8 , C_5H_{10} , mesityl oxide, vinyl acetate, but not di-, tri-, and tetra-chloroethylene, $COMe_2$, $MeCHO$, Et_2O , and $CHCl_3$, also give the reaction. L. S. T.

Essential oil of black tea. I. Fermented Formosan tea leaf. II. Formosan black tea. R. YAMAMOTO and Y. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 122—129, 130—135).—I. After fermentation, steam-distillation at 100° , extraction of the distillate with Et_2O , and removal of acid constituents, 400 kg. of tea leaves yielded 13 g. of oil consisting of Me salicylate, $CH_2Ph \cdot CH_2 \cdot OH$, citronellol, and their esters, Δ^8 -hexen- γ -ol, Δ^8 -hexen- β -al, Pr^aCHO , Pr^bCHO , Bu^bCHO , geraniol (trace), a

sec.-alcohol, b.p. 62°/4 mm., 187—189°/760 mm., a sec.-alcohol, b.p. 85—90°, and traces of a substance with odour of cinnamon. The acid constituents include salicylic acid and possibly $\text{Pr}^{\text{c}}\text{CO}_2\text{H}$ and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$.

II. Fermented and dried tea leaves were subjected to steam-distillation at 112°. There is no distinct difference between oils of black tea and of fermented tea leaf before drying. An Et_2O extract of the distillate contained Me salicylate, salicylic and palmitic acid, a phenol, possibly $\text{Pr}^{\text{c}}\text{CO}_2\text{H}$, $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, and $\text{Bu}^{\text{c}}\text{CO}_2\text{H}$, and, except the above sec.-alcohol, b.p. 85—90°, all neutral compounds of the fermented tea. Geraniol was isolated. The sec.-alcohol of b.p. 62°/4 mm. is chiefly responsible for the flavour of black tea. Another substance, an ester, sap. val. 17, yielded a primary alcohol, probably an unsaturated terpene, and a trace of an acid, m.p. 128°. E. P.

Isolation and characterisation of a starch polysaccharide from the woody tissue of the apple tree (*Malus malus*). C. NIEMANN, R. H. ROBERTS, and K. P. LINK (J. Biol. Chem., 1935, 110, 727—737).—The polysaccharide, $[\alpha]_{\text{D}}^{25} +185^\circ$ in $\text{HCO}\cdot\text{NH}_2$, $[\alpha]_{\text{D}}^{25} +190^\circ$ in H_2O (triacetate, $[\alpha]_{\text{D}}^{25} +168^\circ$ in CHCl_3), is essentially identical in structure with the β -amylose present in cereal and tuber starches. HCl in MeOH gave a good yield of α -methyl-*d*-glucoside, whilst acid hydrolysis yielded only *d*-glucose with a trace of xylose. J. N. A.

Levosin in grain and meal. H. COLIN and H. BELVAL (Bull. Soc. Chim. biol., 1935, 17, 1040—1044).—The method of extraction of levosin (I) from wheat flour, rye, bran, and stubble is described. Hydrolysis of (I) gives 1 mol. of glucose and 9 mols. of fructose. It is hydrolysed rapidly by common moulds and slowly by yeast extracts, and is probably fermented during the process of bread making. A. L.

Cultivation of *Artemisia*. S. KRISHNA and B. S. VARMA (Current Sci., 1935, 4, 29).—The two periods of max. santonin content of *A. brevifolia* coincide with the appearance of flower buds on the plant. F. N. W.

Existence of two anhydrodigitoxigenins.—See this vol., 1226.

Pigment of egg-plant. II. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1935, 11, 235—237; cf. A., 1933, 651).—Two new constituents of the colouring matter of the epidermis of the egg-plant (*Solanum melongena*, L., var. *esculentum*, Ners.) are described. A, $\text{C}_{27}\text{H}_{31}\text{O}_{17}\text{Cl}_3\text{H}_2\text{O}$, m.p. 197°, gives delphinidin chloride (I) and glucose (II) when hydrolysed by boiling HCl; the carbohydrate may be a disaccharide attached to the 3 position of (I). B (isolated by way of the picrate), $\text{C}_{36}\text{H}_{37}\text{O}_{19}\text{Cl}_3\text{H}_2\text{O}$, gives (I), (II), and *p*-coumaric acid on HCl hydrolysis; the group $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{C}_{12}\text{H}_{21}\text{O}_{11}$ may be attached to the 3 position of (I). P. G. C.

Pigment of "Awobana." III. C. KURODA (Proc. Imp. Acad. Tokyo, 1935, 11, 238—239; cf. A., 1933, 614).—The presence of delphin chloride in the pigment of Awobana (flowers of *Commelina communis*) is shown by analysis and hydrolysis of the substance (m.p. 207°) to delphinidin chloride and glucose, and

by comparison of the absorption spectra and colour reactions. P. G. C.

Pigment of the fruit of *Rosa rugosa*, Thunb. H. WILLSTAEDT (Svensk Kem. Tidskr., 1935, 47, 112—114).—Chromatographic analysis of the pigments of the fruits of *R. rugosa* has yielded rubixanthin, m.p. 160° (cf. A., 1934, 404), in addition to carotene, lycopene, and phytoanthin. W. O. K.

Development of the chlorophyll and carotenoid pigments in barley seedlings. G. MACKINNEY (Plant Physiol., 1935, 10, 365—373).—The chlorophyll : carotene ratio was approx. const. in normal and in chlorotic seedlings. The carotene : xanthophyll ratio approached a val. of 0.60 in normal seedlings, but was consistently lower in chlorosis. An increased supply of K to the seedlings raised the pigment content of plants under certain conditions. A. G. P.

Salt-extractable proteins of wheat-flour. Ultracentrifugal study. L. KREJCI and T. SVEDBERG (J. Amer. Chem. Soc., 1935, 57, 1365—1369).—0.5*N*-KF, -KCl, -KBr, and -KI extract mixtures of proteins of increasing average mol. wt. (in the order quoted) from wheat-flour (I). The crude extracts all contained much non-centrifugible, light-absorbing material (II); pptn. with $(\text{NH}_4)_2\text{SO}_4$ causes an increase in sedimentation const. and a decrease in (II). Successive extraction of (I) with 0.5*N*-KF (3 times) and 0.5*N*-KCl (5 times) and dialysis of the extracts (against distilled H_2O) gives a ppt. consisting largely of gliadin and globulin (III); the material not pptd. is (probably) leucosin and proteose. (III) polymerises in conc. solution and dissociates on dilution. H. B.

Detection of gold in animal tissues. W. J. ROBERTS (Proc. K. Acad. Wetensch. Amsterdam, 1935, 38, 540—544).—A method is described for detection of Au by means of physical development in a solution of gum arabic, AgNO_3 , quinol, and citric acid. H. G. R.

Determination of pyruvic acid.—See this vol., 1223.

Microchemical test for choline and its esters in tissue extracts. F. J. BOOTH (Biochem. J., 1935, 29, 2064—2066).—The Florence reagent (I in aq. KI) may be used to detect 20×10^{-6} g. of choline per 100 g. of tissue. Acetylcholine may be detected after hydrolysis. The H_2O -sol. choline precursor gives a ppt. with (I) only after hydrolysis with aq. HCl. A. L.

Colorimetric determination of serum-bilirubin. Light-extinction curves of azobilirubin. A. KRUPSKI and F. ALMASY (Biochem. Z., 1935, 279, 424—432).—In the spectrophotometric determination of bilirubin as azobilirubin (I) accuracy is increased by the use of light-filters which partly eliminate inequalities of colour in the standard $[\text{KMnO}_4, \text{Co}_2(\text{SO}_4)_3]$ and (I) solutions. The changes in the light extinction curves of (I) produced by alteration of $[\text{H}^+]$ indicate that there are three forms of (I). The colour of the solution employed in the method of Thannhauser *et al.* (A., 1922, ii, 671) is little affected by changes in $[\text{H}^+]$, and hence this method is recommended. W. McC.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1935.

General, Physical, and Inorganic Chemistry.

Absorption spectrum of hydrogen. I. Heat of dissociation of H_2 molecule determined from rotational structure at long-wave limit of absorption continuum at 850 Å. H. BEUTLER (Z. physikal. Chem., 1935, B, 29, 315—327).—Measurement of the absorption of 2-metre layers of $p\text{-}H_2$ and $(\frac{3}{2}o + \frac{1}{2}p)\text{-}H_2$ under pressures up to ~ 0.05 mm. in the vac. spectrograph has shown for H_2 mols. in the rotational levels $K''=0, 1, 2$ $h\nu = D_0 + (1-S-2^2S) - H$, where the last term represents the energy of excitation of the H atom and E''_{rot} is the rotational energy of the absorbing mol., $h\nu$ the light energy required to cause dissociation into $H+H^*$, and D_0 the heat of dissociation. The absorption edge observed by Dieke and Hopfield at 849.43 Å. (A., 1927, 89) is ascribed to H_2 mols. rotating with $K''=3$. The val. 102.72 ± 0.02 kg.-cal. is calc. for D_0 for the ground state of $p\text{-}H_2$ (cf. this vol., 135, 555). R. C.

Triplet band formula for the general intermediate case, and its application to the B^3- , terms of N_2 . A. BUDÓ (Z. Physik, 1935, 96, 219—229). A. B. D. C.

Stark effect in molecular spectra of nitrogen, carbon monoxide, and hydrogen. W. RAVE (Z. Physik, 1935, 96, 276—277).—A correction of a rotation term diagram (cf. this vol., 675). A. B. D. C.

Absorption spectrum of solid oxygen. I. A. PRICHOTKO, M. RUHEMANN, and A. FEDERITENKO (Physikal. Z., Sovietunion, 1935, 7, 410—431).—The absorption spectrum of each of the three modifications of solid O_2 has been studied in the visible, and those of the α - and γ -modifications in the near ultra-violet. Results resemble those for liquid O_2 and compressed gaseous O_2 , except that with α and β structural elements appear in addition to the continuous absorption exhibited by γ and by liquid O_2 . In α there is a characteristic frequency interval of 1400 cm^{-1} . No conclusions could be reached regarding differences in crystal structure nor whether the bands were due to O_2 or O_4 mols. W. R. A.

Effect of a magnetic field on the polarisation of impact radiation. W. H. MCCORKLE (Physical Rev., 1935, [ii], 48, 532—535).—Na D line radiation excited by electrons moving parallel to a magnetic field of < 300 gauss shows about 16% polarisation. In fields 300—0 the polarisation decreases to zero. The variation indicates that the $3^2P_{3/2}$ level is a hyperfine multiplet which undergoes a Paschen-Back effect (cf. Larriek, A., 1934, 1279). N. M. B.

Spark spectrum of chlorine (Cl II). K. MURAKAWA (Z. Physik, 1935, 96, 117—118). A. B. D. C.

Spectra of argon in the extreme ultra-violet. J. C. BOYCE (Physical Rev., 1935, [ii], 48, 396—402).—Term tables of A II, III, IV are revised or extended through new $\lambda\lambda$ measurements. A lines are re-measured, and 23 new lines in A II, 57 in A III, 23 in A IV, and 10 in A V are tabulated. The nebular lines $\lambda 4711.4$ and $\lambda 4740.2$ are due to "forbidden" transitions in A IV. Ionisation potentials are A I 15.69, A II 27.80, A III 40.78, A IV 61 approx., and A V 78 volts approx. N. M. B.

Near ultra-violet spectrum of copper produced by the hot spark *in vacuo*. R. H. ZINSZER (Trans. Kansas Acad. Sci., 1934, 37, 175—185).—Measurements of 536 lines (2175—5428 Å.) are recorded. CH. ABS. (e)

Spectrum of trebly-ionised zinc. T. S. SUBBARAYA (Proc. Indian Acad. Sci., 1935, 2, A, 113—118).—The fundamental multiplets and term vals. of the Zn IV spectrum are deduced and about 50 lines classified. J. W. S.

Molecular spectrum of selenium vapour. II. B. ROSEN and M. DESIRANT (Bull. Acad. roy. Belg., 1935, [v], 21, 723—735; cf. this vol., 799).—The region 3400—8000 Å. of Se is discussed. The ultra-violet spectrum ends sharply at 3400 Å., and these short bands of narrow lines appear to be an independent and not a $^1\Sigma-$ system. A vibrational analysis is examined. There is predissociation at approx. $29,400\text{ cm}^{-1}$. The 5000—8000 Å. system of broad bands is attributed to fluctuations between a quasi-stable and the normal level of the Se_2 mol. Potential energy curves are given, and the calc. dissociation energy of Se_2 is approx. 1.9 volts. An expression is found for the principal $-\text{}^1\Sigma$ system. N. M. B.

Emission spectrum of the flame of bromine burning in hydrogen and mechanism of the reaction. T. KITAGAWA (Proc. Imp. Acad. Tokyo, 1935, 11, 262—264).—Wave-nos. and intensities for the heads of 43 emission bands, degraded towards the red, in the range 6875—5600 Å. are tabulated. A vibrational analysis leads to an expression for the band heads. If ' denotes the excited mol., $HBr' + Br_2 = HBr + Br_2'$ and $HBr' + Br_2 = HBr + 2Br$ may take place simultaneously in the flame, the former showing the mechanism of the emission bands, and the latter with $Br_2' + Br_2 = Br_2 + 2Br$ showing the mechanism of the chain branching in the combustion. N. M. B.

Spectrum of rubidium in mercury arc. I. A. BALINKIN and D. A. WELLS (Physical Rev., 1934, [ii], 45, 124).—At 1.45 amp. and 40 volts, 0.25–2% of Rb suppresses almost completely the Hg lines in the specially-designed Hg-arc lamp, which then operates with full Rb glow. L. S. T.

Rh I-like isoelectronic sequence to the spectrum of Ag III. W. P. GILBERT (Physical Rev., 1935, [ii], 48, 338–342).—Using the spectrum of Ag from the hollow-cathode discharge in He for the range 500–2600 Å. for identification of Ag III lines, 55 terms are established and data and classifications for 257 lines of the spark spectrum of Ag for the range 500–3000 Å. are tabulated. Term vals. are obtained, and the the ionisation potential of Ag III is 35.9 volts. N. M. B.

Spectra of van der Waals molecules. W. FINKELNBURG (Z. Physik, 1935, 96, 699–713).—The properties of van der Waals mols. and of their spectra are discussed. Consideration of the potential curves leads to conclusions regarding the expected spectra. The differences between valency-linked and van der Waals mols. are emphasised. The application of the Franck-Condon principle, and its limitations, are considered. The line resonance fluorescence of van der Waals mols. is considered as the analogue of resonance fluorescence of more stable mols. It is shown that the phenomenon is not connected with the existence of a stable vibration state of the excited mol., but each line absorbed can be re-emitted. Excited van der Waals states in liquids are also considered with special reference to the absorption spectrum of aq. solutions of Hg and the orientation of Hg mols. A. J. M.

Interpretation of the spectrum of the cadmium van der Waals molecule, Cd₂. W. FINKELNBURG (Z. Physik, 1935, 96, 714–719).—The general discussion of the behaviour of van der Waals mols. (cf. preceding abstract) is applied to the absorption spectrum of Cd₂ (A., 1934, 1147). The band at 2125 Å. is shown to be a singlet band and must be ascribed to the 2¹S term. A. J. M.

Isotope displacement in the arc spectrum of tungsten. K. R. MORE (Physical Rev., 1934, [ii], 45, 132–133; cf. A., 1934, 339).—Several of the stronger W I lines in the region 4000–5600 Å. show three components approx. equally spaced and of the same order of intensity, which are hence attributed to W¹⁸², W¹⁸⁴, and W¹⁸⁶. L. S. T.

New energy levels in Au II, Hg III, Tl IV, Pb V, and Bi VI. J. E. MACK and M. FROMER (Physical Rev., 1935, [ii], 48, 357–366).—Corrections of existing data and identifications of all the previously unknown 5d¹⁰, 5d⁹6s, and 5d⁹6p levels and some and 5d⁹7s levels are tabulated. N. M. B.

Spectrum of mercury in the photographic infra-red. K. MURAKAWA (Proc. Phys.-Math. Soc. Japan, 1935, 17, 14–33).—130 lines (6072–11,286 Å.) were measured. CH. ABS. (e)

Effect of heat on the intensity of mercury lines and bands. J. G. WINANS (Physical Rev., 1934, [ii], 45, 125).—The changes in intensity of Hg₂ bands on heating are the same as the well-known effects in

fluorescence. In addition, the continuous spectrum from 2650 to 2536 follows the 3300 Å. band in intensity changes. L. S. T.

Glow discharge with liquid air cooling. H. SCHULER and T. SCHMIDT (Z. Physik, 1935, 96, 485–488).—A glow discharge with both electrodes cooled by liquid air enables hyperfine structure of the Tl 5351 Å. line to be photographed with 10⁻⁶ g. of Tl. A. B. D. C.

Relative intensities in the principal doublet of thallium under arc and fluorescence excitation. L. N. MORSCHER, jun. (Physical Rev., 1935, [ii], 48, 406–407).—In agreement with theory, the components of the Tl resonance doublet (6²P_{1/2}, 3/2—7²S_{1/2}) have approx. the same relative intensities under arc and fluorescence excitations. The average val. of the ratio is 0.92, the violet line being the stronger. N. M. B.

Nature of the "forbidden" lines in the Pb I spectrum. J. BLATON and H. NIEWODNICZANSKI (Physical Rev., 1934, [ii], 45, 64–65).—An interpretation of the lines previously reported (this vol., 138). L. S. T.

Band spectrum of Pb₂ in absorption and emission. E. N. SHAWHAN (Physical Rev., 1935, [ii], 48, 343–346).—A band system was observed when light is absorbed by Pb vapour at about 1400°, and is also found in emission. Data and a vibrational analysis are given for about 90 band heads, of a system degraded towards the red, in the range 4600–5200 Å. N. M. B.

Intensities in 2Π–2Σ transitions in diatomic molecules. L. T. EARLS (Physical Rev., 1935, [ii], 48, 423–424).—Simplified forms of the expressions due to Hill and Van Vleck (cf. A., 1928, 1076) are obtained. Calc. numerical vals. are plotted for all branches in typical cases. N. M. B.

Hyperfine structure in the solar spectrum. E. McMILLAN (Physical Rev., 1934, [ii], 45, 134).—Additional lines showing evidence of hyperfine structure of Mn I, Cu I, and Ba II in the sun have been found. L. S. T.

Dissociation, excitation, and emission in condensed sparks at high pressure. W. FINKELNBURG (Physical Rev., 1934, [ii], 45, 133). L. S. T.

Current-voltage relation for the spray discharge. H. SCHNITZER (Z. Physik, 1935, 96, 551–558).—Current increases with voltage, as does emission of electrons at high field intensities. A. B. D. C.

Measurement of X-ray wave-lengths by large ruled gratings. J. A. BEARDEN (Physical Rev., 1935, [ii], 48, 385–390).—In order to overcome errors of spacing due to using only a few lines of the grating, the latter was placed between the crystals of a double-crystal spectrometer, thus employing a large grating surface to determine the shape of the diffracted line and the position of max. intensity. Measurements were made on the Cu K_α line. Differences between ruled grating and calcite crystal vals. of the lines Cu K_α, β, Cr K_α, β, and Al K_α are found, using as the "true" calcite grating const. d=3.02810 Å. The consts. d, N, e, and h are re-calc. N. M. B.

Retardation loss of cathode rays on encountering atomic nuclei. A. SOMMERFELD and A. W. MAUE (Ann. Physik, 1935, [v], 23, 589—596).—Mathematical. A. J. M.

Scattering coefficients of X-rays at short wave-lengths. S. J. M. ALLEN (Physical Rev., 1934, [ii], 45, 122—123).—Mass absorption coeffs. of homogeneous X-rays have been measured down to λ 0.05 Å., and electronic scattering coeffs. at λ 0.005—0.417 Å. are tabulated for 21 elements. L. S. T.

K-Series of magnesium and sodium. V. KUNZL (Nature, 1935, 136, 437—438).—Using the ionic tube previously described (A., 1933, 881) new lines in the X-ray spectra of Mg and Na have been observed. L. S. T.

K Spectrum of silicon and some of its compounds. I. H. K. SON FLEMBERG (Z. Physik, 1935, 96, 167—172).—K Spectra are given for cryst. Si, SiC, and SiO₂. A. B. D. C.

Direct and fluorescence excitation of the K level in thick targets of gold. K. B. STODDARD (Physical Rev., 1935, [ii], 48, 43—46; cf. this vol., 138).—The ratio of the no. of K α line quanta, produced by direct cathode electron impact, to the no. of quanta produced by fluorescence was measured over a voltage range. The ratio of the probability of K-shell ionisation to continuous quantum excitation was determined. N. M. B.

Relative probabilities of the ionisation of K and L electrons of equal ionisation energy. B. G. EATON (Physical Rev., 1934, [ii], 45, 131).—These probabilities have been determined by measuring, from the X-ray spectra of TlBr and Tl(MoO₄)₂, the relative nos. of quanta emitted from the K and L levels under cathode-ray bombardment. Under such bombardment any K electron is one half as likely to become ionised as any L₂₃. L. S. T.

Wave-length measurements of the Ni L α_1 , α_2 and Ni L β_1 lines of metallic nickel and of nickel salts. J. SHEARER (Phil. Mag., 1935, [vii], 20, 504—513).—Photometric curves and λ data are given for the spectra from Ni, Ni₂O₃, NiO, and NiS. The λ of the max. and of the short- λ edge is approx. the same for each substance. The frequency difference between the Ni L lines equals that between the Ni K α_1 and Ni K α_2 lines. N. M. B.

Ratio between electronic and ionic current on a glow cathode which is subjected to a discharge in mercury vapour. S. GVOSPOVER (Physikal. Z. Sovietunion, 1935, 7, 274—291).—When the conditions at the cathode are such that the field strength is zero, the ratio of the electronic to the ionic current is between 435 and 395. This ratio does not agree with that calc. from the theory of the double space-charge layer. Under certain conditions the current emitted by a W cathode which is surrounded by positive ions is > the saturation current at a similar cathode in a vac. O. J. W.

Ionisation effect of cathode rays in air. W. GERBES (Ann. Physik, 1935, [v], 23, 648—656).—The energy loss ϵ per ion pair ($=V/S$, where V is the initial energy of the electron, and S the no. of ion pairs

produced throughout the whole of its range) has been re-determined. A small correction is necessary in Eisl's val. (A., 1930, 5). ϵ is not independent of electron velocity between 9 and 60 kv., but increases as velocity decreases. A. J. M.

Influence of the medium on the photo-electric effect from metal to dielectric. L. V. GROSCHEV (Physikal. Z. Sovietunion, 1935, 7, 619—630).—The internal photo-electric effect in rock-salt coloured red by colloidal Cu is regarded as an external photo-electric effect from the Cu to the NaCl as dielectric. In the region of complete light absorption the effect increases with decreasing λ . A weak max. at 5900—6000 Å. corresponds with a max. in the absorption curve. The limit for the photo-electric effect of Cu to NaCl is about 6400 Å., as against 2600 Å. for Cu to a vac. J. W. S.

Determination of thermionic work function of metals: application to nickel. G. W. FOX and R. M. BOWIE (Proc. Iowa Acad. Sci., 1933, 40, 154).—The sample is heated by electron bombardment. As it cools, the electron emission from it charges a condenser, which is discharged at intervals through a ballistic galvanometer. Results for Ni agree with photo-electric determinations. CH. ABS. (e)

Theory of thermionic constants for pure metals. D. BLOCHINZEV and S. DRABKINA (Physikal. Z. Sovietunion, 1935, 7, 484—500). W. R. A.

Nuclear photoelectric effect. J. CHADWICK and M. GOLDBABER (Proc. Roy. Soc., 1935, A, 151, 479—493; cf. A., 1934, 1053).—Measurements have been made of the relative effects of the photo-neutrons from D, and Be under the action of Ra and Ra-Th γ -rays, as determined by the relative nos. of slow neutrons obtained in a paraffin scatterer. The reaction $D^2 + h\nu \rightarrow H^1 + n^1$ has been established, both protons and neutrons having been detected. The binding energy of the deuteron is 2.1×10^6 e.v. Using the masses of H and D from disintegration data, the mass of the neutron is 1.0084, definitely > that of the H atom. The probability of disintegration of the deuteron by γ -rays is in agreement with theoretical calculations. The main reaction with Be is $Be^9 + h\nu \rightarrow Be^8 + n^1$, and the energy necessary to remove a neutron from Be is about 1.6×10^6 e.v. No evidence of a nuclear photo-disintegration has been found in any other elements. L. L. B.

Distribution of velocities of photo-electrons in thin metallic films (Al). E. VASSER (Physikal. Z. Sovietunion, 1935, 7, 532—546).—The energy distribution amongst photo-electrons emitted from thin Al films has been investigated as a function of the λ of the light and of the thickness of the Al. The results are discussed with reference to possible deduction of the energy vals. of electrons in the metal and the mechanism of their emission. J. W. S.

Emission of electrons under the influence of chemical action. VI. Reactions of liquid NaK₃ with gaseous ClCN, HgBr₂, (OH)₂, O₃, and with some gases giving small negative emission. A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1935, A, 150, 495—519).—The heterogeneous reactions between liquid NaK₃ and gaseous ClCN,

HgBr₂, (OH)₂, and O₃, at very low pressures, give rise to a negative emission from the metal, comparable in magnitude with that observed with the gaseous halogens (A., 1934, 468). The reactions with MeCl, (CN)₂, Hg(CN)₂, and H₂S give a very small negative emission. The electron energy spectra obtained with HgBr₂, (OH)₂, ClCN, and O₃ are examined with the object of ascertaining their structure by the method based on the relation $E_m = D_0 = \text{const.}$ The theory of the chemical electron emission previously developed (this vol., 557) is supported. L. L. B.

Problems of the new quantum theory of the electron. V. WEISSKOPF (Naturwiss., 1935, 23, 631—637, 647—653, 669—674).—A review.

A. J. M.

Motion of electrons in electric and magnetic fields taking into consideration the action of the space charge. S. J. BRAUDE (Physikal. Z. Sovietunion, 1935, 7, 565—571).—The space-charge density, distribution of potential, and the electron paths are deduced for a plane plate condenser. J. W. S.

Velocity distributions of elastically colliding electrons. P. M. MORSE, W. P. ALLIS, and E. S. LAMAR (Physical Rev., 1935, [ii], 48, 412—419).—Mathematical. The velocity distribution function is determined for the case of electrons in a uniform electric field and for a homogeneous beam of electrons shot into a field-free space. Satisfactory agreement with experiment is found. N. M. B.

Polarisation of electron waves by scattering. H. HELLMANN (Z. Physik, 1935, 96, 247—250).—Theoretical. A. B. D. C.

Total scattering of electrons in helium. A. L. HUGHES and W. HARRIS (Physical Rev., 1935, [ii], 48, 408—411).—Total scattering, measured for the electron energy range 1000—200 volts, agrees with the vals. given by Morse's formula at 1000 and 700 volts; a slight discrepancy at 500 increases down to 200 volts. N. M. B.

Emission of positrons from a thorium-active deposit. A. I. ALICHANOV, A. I. ALICHANIAN, and M. S. KOSODAEV (Nature, 1935, 136, 475—476).—The no. and energy distribution of positrons from Al activated with Th-B+C agree with the Hulme-Jaeger theory of internal conversion of γ -rays on negative levels. L. S. T.

Production of high-energy electron pairs. W. H. FURRY and J. F. CARLSON (Physical Rev., 1934, [ii], 45, 137).—The production of an electron pair by a γ -ray traversing the field of a nucleus has been studied in greater detail. The production of pairs by 3×10^6 volt γ -rays is consistent with experimental results obtained with artificial γ -rays from Be, but for energies $> 2 \times 10^7$ volts the predicted pair production is $>$ that computed by Oppenheimer and Plesset and irreconcilable with experiment. L. S. T.

Production of electron pairs. G. RACAH (Nature, 1935, 136, 393—394).—The cross-section for the production of electron pairs by collisions between electrons and nuclei is discussed, and several approx. formulæ are submitted. L. S. T.

Production of electrons and positrons by a collision of material particles. II. E. LIFSCHITZ (Physikal. Z. Sovietunion, 1935, 7, 385—398; cf. *ibid.*, 1934, 6, 244).—The cross-section for the production of electron pairs by a collision of two particles with a velocity much $<$ that of light is calc. W. R. A.

Statistics of electron interaction. E. L. HILL (Physikal. Z. Sovietunion, 1935, 7, 447—451).—The influence of the Pauli principle on the interaction of electrons is discussed. The theory of Wigner and Seitz (cf. this vol., 153) relating the statistical correlation to repulsive terms only between electrons with parallel spin components should be replaced by different correlations between electrons with parallel or anti-parallel resultant spins. The calculations for two electrons and for a completely degenerate system of many electrons are given. W. R. A.

Radiation from the mutual annihilation of protons and electrons. A. L. HUGHES and G. E. M. JAUNCEY (Physical Rev., 1934, [ii], 45, 217—218). L. S. T.

Light-excitation in He by He atoms of 0 to 6000 volts energy. W. MAURER (Z. Physik, 1935, 96, 489—502).—This excitation process has much in common with excitation by electrons of 0—40 volts energy. A. B. D. C.

Charging and ionising cross-section of helium with respect to He⁺. F. WOLF (Ann. Physik, 1935, [v], 23, 627—647).—Apparatus previously described (this vol., 1048) is used for determining the charging and ionising cross-section of He with respect to He⁺. The charging cross-section decreases in the velocity range 20—1020 volts, with increasing velocity. It is $<$ the effective cross-section. Ionisation of He by He⁺ occurs below 400 volts. The efficiency increases slowly with increasing velocity, but even at 1020 volts ionising cross-section is little $> 0.5 \text{ cm}^2/\text{cm}^3$. A. J. M.

Normal state of the helium molecule ion, He₂⁺. S. WEINBAUM (J. Chem. Physics, 1935, 3, 547—550).—Theoretical. Calc. vals. for D_e and r_e are 2.22 e.v. and 1.097 Å., respectively. H. J. E.

Ionisation of neon and argon by singly-charged magnesium ions. J. C. MOUZON and N. H. SMITH (Physical Rev., 1935, [ii], 48, 420—422).—The efficiency of the Mg ions is about 60% of that of Na ions for both gases. The influence of mean free path is discussed. N. M. B.

Theory of combination coefficients for large ions. W. R. HARPER (Phil. Mag., 1935, [vii], 20, 740).—A correction (cf. A., 1934, 937).

Elastic and inelastic cross-sections of the mercury atom. F. L. ARNOT and G. O. BAINES (Proc. Roy. Soc., 1935, A, 151, 256—274).—Using a new apparatus and method, curves have been obtained showing the variation of the total, elastic, and inelastic cross-sections of the Hg atom for electrons of energy 4—180 volts. The ionisation and excitation functions for the ²³P₁ (4.86 volts), ²¹P₁ (6.67 volts), and ³¹D₂ (8.8 volts) states have also been obtained. L. L. B.

Effective collision cross-sections of the alkali atoms in various gases. S. ROSIN and I. I. RABI (Physical Rev., 1935, [ii], 48, 373—379).—The mean free paths and effective collision cross-sections of neutral atoms of Li, Na, K, Rb, and Cs were measured in H₂, D₂, He, Ne, and Ar by the method of mol. beams. Results show a larger collision cross-section in D₂ than in H₂ for all the alkalis except Li, and this effect is interpreted as due to the smaller spacing of the D₂ rotational levels. N. M. B.

Introduction of quantum periods into Mendeleef's table. A. MAZZUCHELLI (Gazzetta, 1935, 65, 467—473).—The sub-division of Mendeleef's table according to the quantum nos. of the external electrons of the atoms is discussed. O. J. W.

Systematisation of isotopes. K. SITTE (Z. Physik, 1935, 96, 512—519).—Systematisation follows by plotting nuclear charge, Z , against $(m - Z)/Z$, where m is the nuclear mass. A. B. D. C.

Relative abundance of the lithium isotopes. G. P. HARNWELL and W. BLEAKNEY (Physical Rev., 1934, [ii], 45, 117).—Li ions from a filament coated with spodumene gave for the current ratio Li⁷ : Li⁶ an average val. of 8.4. L. S. T.

Isotopes of arsenic, selenium, mercury, and lead. H. J. WATKINS (Phil. Mag., 1935, [vii], 20, 479—481).—Isotopic constitution is discussed on the basis of a theory recently proposed (cf. this vol., 275, 427, 910). N. M. B.

Isotopic constitution of gold from band-spectroscopic examination. S. IMANISHI (Nature, 1935, 136, 476).—The AuH violet band system gives no evidence for the existence of Au¹⁹⁹, in agreement with Dempster's result (this vol., 1048). L. S. T.

Iridium isotopes and their nuclear spins. B. VENKATESACHAR and L. SIBAIYA (Proc. Indian Acad. Sci., 1935, 2, A, 203—207).—The hyperfine structure of Ir lines indicates that it consists of two isotopes with nuclear spins $\frac{1}{2}$ and $\frac{3}{2}$. Consideration of the known isotopes of heavy metals indicates that these have mass nos. 191 and 193, respectively. As the relative abundance is about 1 : 2, the accepted at. wt. of Ir (193.1) is probably too high. J. W. S.

Iridium isotopes and their nuclear spin. B. VENKATESACHAR and L. SIBAIYA (Nature, 1935, 136, 437; see preceding abstract).—The estimated relative abundance of Ir¹⁹¹ and Ir¹⁹³ is 1 : 2, giving an at. wt. < 193. L. S. T.

Efficiency of the tube counter. S. M. SKINNER (Physical Rev., 1935, [ii], 48, 438—447).—A detailed mathematical survey. Expressions are obtained for the efficiency of counting, average recovery time, average voltage impulse delivered to the amplifier, average no. of particles counted per unit time in terms of no. of particles arriving per unit time, the time const. of the counter, and a parameter const. for a given counter. N. M. B.

Collisions of α -particles in hydrogen. E. POLLARD and H. MARGENAU (Physical Rev., 1935, [ii], 48, 402—405; cf. this vol., 910).—The projection of protons by Po α -particles was investigated. The

variation of the yield of projected protons with α -particle velocity agrees with the Rutherford-Darwin law for low velocities, and a smooth rise for higher velocities. No resonance effects were observed. The effect of α -particle straggling on the detectability of resonance effects is examined. N. M. B.

Registration of the ionisation curve of a single α -particle. (A) G. STETTER. (B) H. ALFVEN (Nature, 1935, 136, 394; cf. this vol., 1048).—Polemical. L. S. T.

Radioactivity of solids determined by α -ray counting. (Miss) G. D. FINNEY and R. D. EVANS (Physical Rev., 1935, [ii], 48, 503—511).—A complete theory of α -ray counting for thin and thick radioactive sources is developed, and vals. of numerical consts. are tabulated. New methods for determining the Th content of geological samples are described. Analyses of a series of igneous rocks show Th contents 3.9—16.5 $\times 10^{-6}$ g. Th per g., with an average Th/U ratio of 7. N. M. B.

β -Ray of actinium. D. E. HULL, W. F. LIBBY, and W. M. LATIMER (J. Amer. Chem. Soc., 1935, 57, 1649—1652).— β -Particles from Ac, having a max. energy of about 220,000 e.v., have been detected. E. S. H.

Energy spectrum of the β -rays of radium-E. F. A. SCOTT (Physical Rev., 1935, [ii], 48, 391—395).—Using the magnetic focussing method and Geiger counter, the energy distribution curve was measured. The max. of the spectrum was at 3.87×10^5 e.v., and the end point at $(15.34 \pm 0.28) \times 10^5$ e.v., corresponding with an H_F of 6604 ± 98 . The distribution does not agree with that of Fermi's theory. Available data are examined. N. M. B.

Mass of the neutron. R. M. LANGER (Physical Rev., 1934, [ii], 45, 137).—The mass of the neutron calc. from data for $\text{Li}^7 + \text{H}^2 \rightarrow 2\text{He}^4 + n^1$ (A., 1933, 1100) is $1.0062 \pm < 0.001$, and the binding for H² is of the order of 5×10^5 volts. The val. 1.0062 agrees with Kurie's disintegration experiments (this vol., 7) assuming that the neutron is not captured. Evidence for non-capture disintegrations with neutrons in N₂ is strong. L. S. T.

Mass of the neutron and the stability of heavy hydrogen. R. LADENBURG (Physical Rev., 1934, [ii], 45, 224—225, 495).—Mainly a discussion. L. S. T.

Neutrons. G. E. MONOD-HERZEN (Ann. Physique, 1935, [xi], 4, 137—201).—Using the Wilson cloud-track method and a Po + Be or Rn + Be source, 7500 photographs were taken, giving 85 long and 100 short measurable tracks in H₂ corresponding with fast and slow particles. Statistical interpretation of the measurements indicates that the neutron-proton collision is inelastic, and that the source emits slow neutrons strongly scattered by matter and fast neutrons undergoing little scattering. Examination of the function of neutron mass in nuclei with reference to nuclear binding energy and the no. of isotopes of each element shows that the mass-losses of the nuclei bear a simple relation to the at. no., and that the sub-groups of the at. nuclear sequences coincide

with those arising from the distribution of the isotopes. The neutron mass is taken as 1.009 ± 0.001 .

N. M. B.

Energy of neutrons and the Fermi effect. I. V. KURTSCHATOV, L. MISOVSKI, M. EREMEJEV, and G. SCHTSCHEPKIN (Physikal. Z. Sovietunion, 1935, 7, 257—261).—The radioactivity of Al, Si, P, Fe, Br, Ag, and I excited by neutrons from F and Be has been studied. When the nucleus is formed by capture of a neutron without emission of a heavy particle, radioactivity is produced. Neutrons from F produce artificially radioactive P. O. J. W.

Excitation of γ -rays by slow neutrons. S. KIKUCHI, K. HUSIMI, and H. AOKI (Proc. Imp. Acad. Tokyo, 1935, 11, 253—255).—When bombarded by slow neutrons, γ -rays were emitted by Hg, Au, Cd, Ni, Fe, Cu, and to a smaller extent by Pb and Al. The estimated cross-section of interaction is approx. 5×10^{-24} cm.² for Cu, Fe, and Ni. No Fermi proton effect is shown by Fe and Ni. There is evidence of the reactions $\text{Ni}^{60} + n^1 \rightarrow \text{Ni}^{61} + h\nu$; $\text{Fe}^{56} + n^1 \rightarrow \text{Fe}^{57} + h\nu$. N. M. B.

Cross-section of heavy nuclei for slow neutrons. J. H. VAN VLECK (Physical Rev., 1935, [ii], 48, 367—372).—Mathematical. N. M. B.

Distribution-in-angle of protons projected by neutrons. N. A. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 516—520).—The distribution-in-angle of protons projected from paraffin by neutrons, referred to unit solid angle (0), corresponds with $\cos^3 0$. Using paraffin films 10—25 μ thick the distribution is $\cos 0$ for small 0, since the effective paraffin layer does not then depend on angle. These results correspond with a collision between elastic spheres, in contrast to Bonner and Mott-Smith, and others (cf. A., 1934, 1151). R. S. B.

Scattering of slow neutrons by hydrogen. M. EREMEJEV, I. V. KURTSCHATOV, and G. SCHTSCHEPKIN (Physikal. Z. Sovietunion, 1935, 7, 267—273).—A method for determining the mean free path of slow neutrons in compounds containing H is described. The effective collision radius of slow neutrons with protons is 2×10^{-12} cm. O. J. W.

Emission of protons and neutrons from various targets bombarded by three-million-volt deuterons. E. O. LAWRENCE and M. S. LIVINGSTON (Physical Rev., 1934, [ii], 45, 220; cf. this vol., 141).—Under bombardment by 3×10^6 -volt deuterons the neutron yields from many substances are higher for the lighter elements, but the variation with at. no. is much $<$ is the case with 1.3×10^6 -volt deuterons. Approx. relative yields are Be 100, Li 62, B_2O_3 34, CaF_2 18, NH_4NO_3 10, Al 10, $\text{Ca}(\text{OH})_2$ 8, and Pt 1. With Be the no. of recoil protons corresponds with an emission of approx. 10^7 neutrons per sec., and these high neutron yields with a deuteron current of 3×10^{-8} amp. indicate the possibility of producing neutron radiation of an intensity comparable with that of X-rays. Large proton yields are also obtained from these targets, and their approx. proportionality to the neutron yields suggests a common nuclear reaction, probably disintegration of the deuteron itself. In addition to these protons,

groups of protons of definite range are also obtained from some of the targets. Al emits a group of range 68 cm. approx., which may result from a reaction of deuterons with Al nuclei in which neutrons are added to the nuclei and protons emitted. L. S. T.

Neutron scattering in water and lead. M. DEISENROTH-MISOVSKI, I. V. KURTSCHATOV, G. D. LATISCHEV, and L. MISOVSKI (Physikal. Z. Sovietunion, 1935, 7, 656—669).—The energy distribution of neutrons from Be, B, and F has been investigated by filtration of the neutrons through Pb and H_2O layers of various thicknesses and measurement in a Wilson chamber of the no. of recoil protons emitted by the neutrons from a paraffin plate through various thicknesses of Al. The results indicate that most of the neutrons have an energy of $6\text{--}8 \times 10^6$ e.v., but some attain $10\text{--}12 \times 10^6$ e.v. J. W. S.

Observations in the Wilson chamber and the Fermi effect. I. V. KURTSCHATOV and G. D. LATISCHEV (Physikal. Z. Sovietunion, 1935, 7, 262—266).—The emission of electrons in the disintegration of radioactive Br is much $>$ that of positrons. A considerable proportion of the neutrons emitted by Be and Rn passes through a 10-cm. layer of H_2O . O. J. W.

High-voltage technique for nuclear physics studies. M. A. TUVE, L. R. HAFSTAD, and O. DAHL (Physical Rev., 1935, [ii], 48, 315—337).—A description of the construction and use of electrostatic generators and multiple-section high-voltage tubes of the Coolidge "cascade" type for the production of high-speed protons and deuterons for studies of nuclear transmutations. N. M. B.

Transmutation functions for some cases of deuteron-induced radioactivity. E. O. LAWRENCE, E. McMILLAN, and R. L. THORNTON (Physical Rev., 1935, [ii], 48, 493—499; cf. this vol., 559).—The variation with deuteron energy of the transmutation cross-section was investigated for the radioactivity produced in Na, Al, Si, and Cu bombarded with deuterons of energies $0\text{--}3.6 \times 10^6$ volts. Results agree with Oppenheimer's theory. Results require a proton-neutron binding energy in the deuteron of $2\text{--}2.24 \times 10^6$ volts. N. M. B.

Transmutation function for deuterons. J. R. OPPENHEIMER and M. PHILLIPS (Physical Rev., 1935, [ii], 48, 500—502; cf. preceding abstract).—Mathematical. The effect of the finite size and ready polarisability of the deuteron on the probability of transmutations involving the capture of the neutron is examined. Results are in good agreement with experiment. N. M. B.

Disintegration of lithium by slow neutrons. D. Z. BUDNIZKI, I. V. KURTSCHATOV, and G. D. LATISCHEV (Physikal. Z. Sovietunion, 1935, 7, 474—483).—Collisions between Li and neutrons lead to ${}^3\text{Li}^6 + {}^0n^1 = {}^2\text{He}^4 + {}^1\text{H}^3$, the ${}^2\text{He}^4$ and ${}^1\text{H}^3$ being ejected in opposite directions with ranges of 20 and 65 mm. of air. The collision cross-section for slow neutrons is 2×10^{-22} cm.² W. R. A.

γ -Rays from lithium bombarded with protons. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 63—64).— γ -Rays from LiF bombarded

with protons have approx. the same quantum energy as γ -rays from Ra filtered through 2 cm. of Pb.

L. S. T.

Range of transmuted particles of some light elements obtained by bombardment with rapid protons. H. NEUERT (Physikal. Z., 1935, 36, 629—642).—The ranges of particles obtained by bombarding light elements with 200-kv. protons were determined by the cloud chamber method. For B there was a continuous frequency distribution with a wide max. at 22 mm. and a less well-defined max. at 44 mm. For Be, particles of range 7.5 mm. only were observed. The short-range particles from Li in H_2 possess only two ranges (12 and 8.2 mm.). The mass of He^3 is 3.0172 ± 0.0007 . No transmuted particles could be observed when F was bombarded with 200-kv. protons.

A. J. M.

Disintegration of beryllium by deutons. H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 226—227; cf. A., 1934, 714).

L. S. T.

Disintegration of boron by neutrons. H. J. TAYLOR (Proc. Physical Soc., 1935, 47, 873—876).—A detailed account of results previously reported (cf. this vol., 426). A second mode of disintegration corresponding with $B^{10} + n^1 \rightarrow He^4 + He^4 + H^3$ has been found.

N. M. B.

Carbon radioactivity and other resonance transmutations by protons. L. R. HAFSTAD and M. A. TUVE (Physical Rev., 1935, [ii], 48, 306—315).—From measurements with 200—900 kv. d.c., and currents of deuterons and protons > 10 microamp. excitation function curves are given. The induced radioactivity from the reaction $C + H^1$ is produced by a resonance process with resonance lines at about 400 and 480 kv., but the efficiency of the corresponding process for $C + D^2$ increases approx. exponentially. The γ -rays emitted in the reaction $Li + H^1$ show resonances at 450 and 850 kv.; the γ -rays from $F + H^1$ suggest resonances at 320, 700, and 800 kv.; the γ -rays from $Be + H^1$ do not appear to be produced by a resonance process.

N. M. B.

Disintegration of neon by neutrons. R. JAECKEL (Z. Physik, 1935, 96, 151—162).—Ne always disintegrates by emission of α -particles to O^{17} .

A. B. D. C.

Artificial radioactivity. II. H. FAHLENBRACH (Z. Physik, 1935, 96, 503—511; cf. this vol., 803).—Using α -rays of Th-C' Si gives a transition product, P^{32} , of half-life period approx. 14 days. Mg gives two transition products, Al^{28} , of half-life 2 min., and Mg^{24} , of half-life 6.7 min.

A. B. D. C.

Induced radioactivity of nickel and cobalt. J. ROTBLAT (Nature, 1935, 136, 515).—Bombardment of Ni with neutrons from $Rn + Be$ gives two slight activities, one of a period of a few hr. probably due to $^{58}_{28}Ni + n^1 = ^{59}_{28}Ni$ or $^{62}_{28}Ni + n^1 = ^{63}_{28}Ni$, and another of 20 min. period, probably due to $^{60}_{28}Ni + n^1 = ^{61}_{28}Ni$. Irradiation of Co immersed in H_2O gives, in addition to the known radio- Mn^{56} of approx. 2.5 hr. period, an activity of approx. 20 min., arising from $^{59}_{27}Co + n^1 = ^{60}_{27}Co$, which does not appear in absence of a H medium.

L. S. T.

Artificial radioactivity on irradiating gold with neutrons. I. V. KURTSCHATOV and G. D. LATISCHEV (Physikal. Z. Sovietunion, 1935, 7, 652—655).—Measurements with a Wilson chamber give no evidence of disintegration with emission of heavy particles when Au is irradiated with neutrons from Be. The half-life period of the β -radioactive product is 3 days. No evidence was obtained of a product of half-life period 5 hr. emitting γ -rays (cf. this vol., 426).

J. W. S.

Atomic collision and radiation of meteors. E. ÖPIK (Acta Comm. Univ. Tartu., 1934, A, 26, No. 2, 39 pp.).—Theoretical.

CH. ABS. (e)

Nuclear reactions at stellar temperatures. T. E. STERNE (Trans. Electrochem. Soc., 1935, 68, 275—287).—Surface temp. of stars may be obtained in various ways, and fairly closely concordant vals. are obtained when the methods are applied to the same star.

W. P. R.

Atmospheres of planets. G. PICCARDI (Atti R. Accad. Lincei, 1935, [vi], 21, 576—577).—The presence of CH_4 in the atm. of planets very distant from the sun is more readily explained by the direct formation of the mol. CH , stable at high temp., than by the reduction of CO_2 .

O. J. W.

Theory of the origin of cosmic radiation. R. M. LANGER (Physical Rev., 1934, [ii], 45, 138).—Many cosmic and terrestrial phenomena can be explained on the assumption that nuclear charges can slowly disappear.

L. S. T.

Absorption measurements on the cosmic rays at $11^\circ 30'$ geomagnetic latitude and 2370 metres elevation. S. DE BENEDETTI (Physical Rev., 1934, [ii], 45, 214—215).

L. S. T.

Directional measurements on the cosmic rays near the geomagnetic equator. B. ROSSI (Physical Rev., 1934, [ii], 45, 212—214).

L. S. T.

Penetrating power of cosmic secondary radiation. O. ZEILLER (Z. Physik, 1935, 96, 121—136).—Comparison of Pb and Al absorptions show absorption \propto mass.

A. B. D. C.

Secondary effects of primary cosmic rays. A. SCHWEGLER (Z. Physik, 1935, 96, 62—75).

A. B. D. C.

Progress of the directional survey of cosmic-ray intensities and its application to the analysis of the primary cosmic radiation. T. H. JOHNSON (Physical Rev., 1935, [ii], 48, 287—299).

N. M. B.

Inelastic scattering of quanta with production of pairs. M. S. PLESSET and J. A. WHEELER (Physical Rev., 1935, [ii], 48, 302—306).—Mathematical. The probability of processes in which an incoming quantum produces an electron-positron pair in the field of a nucleus is investigated.

N. M. B.

Nuclear masses. C. F. VON WEIZACKER (Z. Physik, 1935, 96, 431—458).—Theoretical.

A. B. D. C.

Interaction between neutrons and protons. R. M. LANGER (Physical Rev., 1934, [ii], 45, 137—138).—The interaction is probably mainly magnetic.

L. S. T.

Structure of light atomic nuclei. S. FLUGGE (Z. Physik, 1935, 56, 459—472).—Theoretical.

A. B. D. C.

Structure of light atomic nuclei. W. HEISENBERG (Z. Physik, 1935, 96, 473—484).—Mass defects are calc. by an extension of Hartree's method.

A. B. D. C.

Structure of the ionosphere. J. HOLLINGWORTH (Proc. Physical Soc., 1935, 47, 843—851).—Mathematical. A method of finding the approx. intensity of ionisation in the space between the *E* and *F* layers is deduced.

N. M. B.

Dirac's vector model for multiplet spectra. M. MARKOV (Physikal. Z. Sovietunion, 1935, 7, 553—564).—Mathematical.

J. W. S.

Dirac electron in a gravitational field. O. HALPERN and G. HELLER (Physical Rev., 1935, [ii], 48, 434—438).—Mathematical. Special cases are considered. The red shift in a gravitational field is derived without reference to a special at. system, and a treatment of the gyromagnetic effect is given.

N. M. B.

Dirac's spin theory and non-linear field equations. W. WESSEL (Z. Physik, 1935, 96, 520—533).

A. B. D. C.

Three-centre problem. I. G. S. GORDADSE (Z. Physik, 1925, 96, 542—545).

A. B. D. C.

Uncertainty principle and the zero-point energy of the harmonic oscillator. R. A. NEWING (Nature, 1935, 136, 395).—Zero-point vibration energy calc. from the uncertainty principle is $\frac{1}{2}h\nu/2\pi$.

L. S. T.

Elements of the quantum theory. IV. The linear harmonic oscillator. VA. The rigid rotator. S. DUSHMAN (J. Chem. Educ., 1935, 12, 381—389, 436—444; cf. this vol., 1187).

L. S. T.

Atomic energy states for excited helium. W. S. WILSON (Physical Rev., 1935, [ii], 48, 536—537).—Using Slater's method the total at. energies for the excited states $1s^2$, $1s2s$, $1s2p$, $2s^2$, $2s2p$, and $2p^2$ of He have been calc. with the use of Hartree functions previously found (cf. this vol., 804).

N. M. B.

Determination of h by X-rays. P. KIRKPATRICK and P. A. ROSS (Physical Rev., 1934, [ii], 45, 135).

L. S. T.

Polarisability and related properties of molecular hydrogen and the diatomic hydrogen ion. J. O. HIRSCHFELDER (J. Chem. Physics, 1935, 3, 555—556).—Theoretical.

H. J. E.

Four-vector problem and its application to energies and intensities in platinum-like spectra. A. T. GOBLE (Physical Rev., 1935, [ii], 48, 346—356).—Mathematical. The magnetic interaction between the spin and orbital moments of each electron of a two-electron system is examined by a simplified method based on the correspondence principle. Results are checked by reference to an isoelectronic sequence (see Mack, this vol., 1292).

N. M. B.

Gas laws, Wien's displacement law, and the radiation law of the gaseous state. E. WERTHEIMER (Z. Physik, 1935, 96, 137—147).—The gas laws are deduced from Wien's law, and the two are

brought into relation with that for radiation of the gaseous state.

A. B. D. C.

The potential barrier. K. C. KAR (Current Sci., 1935, 4, 93—94).—A discussion.

L. S. T.

Electron theory of metals. I. S. SCHUBIN and S. VONSOVSKI (Physikal. Z. Sovietunion, 1935, 7, 292—328).—Mathematical. A more detailed treatment (cf. A., 1934, 827).

O. J. W.

Thermodynamic foundations of the theory of electrical equilibrium and of permanent currents in metallic conductors. F. ODONE (Atti R. Accad. Lincei, 1935, [vi], 21, 515—521).—Mathematical.

O. J. W.

Fundamental paradox of the quantum theory. R. PEIERLS (Nature, 1935, 136, 395).

L. S. T.

Calculation of the emergence work (Austrittsarbeit) in Sommerfeld's metal model. H. FRÖLICH (Physikal. Z. Sovietunion, 1935, 7, 509—510).—Theoretical.

W. R. A.

Quantum theory of ionisation and neutralisation on metallic surfaces. N. D. MORGULIS (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 684—689).—Theoretical. The probabilities of the ionisation of atoms, and of the neutralisation of gaseous ions, on metallic surfaces were calc.

CH. ABS. (e)

Photochemical reaction of cellulose. III. Determination of the relative spectral distribution of energy in the light from a quartz-mercury vapour lamp. S. OGURI (J. Soc. Chem. Ind. Japan, 1935, 38, 392—393B).—The data reported were obtained with a thermopile and a const. spectrometer slit width. There are max. at about 2500, 3000, 4000, and 5750 Å.

A. G.

Factors affecting ultra-violet solar radiation intensities. W. W. COBLENTZ and R. STAIR (J. Res. Nat. Bur. Stand., 1935, 15, 123—150).—Solar radiation of λ 2900—3500 Å. has been studied under varied conditions of atm. and locality. The spectrum transmitted by fog is diminished in intensity, but approx. unchanged in quality. Snow gives a high degree of reflexion. A rise of 2 km. in altitude corresponds with a 40—50% increase in intensity of the band at 2900—3130 Å. It is inferred that the quantity of O_3 in the stratosphere during the afternoon is < that during the forenoon, and for the same solar altitude decreases with the latitude. Biological effects are discussed.

R. S. B.

N-H bands at λ 3360. G. W. FUNKE (Z. Physik, 1935, 96, 787—798).—An analysis of the N-H bands at λ 3360 and 3370 is given, and their splitting and widening are considered.

A. J. M.

Ultra-violet absorption spectrum of gaseous, liquid, and dissolved ammonia. A. BRIOT and B. VODAR (Compt. rend., 1935, 201, 500—501).—Absorption by liquid NH_3 was continuous and extended to greater λ with rising temp. The absorption bands of gaseous NH_3 were not displaced by changes in temp. and pressure. Absorption by aq. NH_3 was continuous and increased with the concn.

H. J. E.

Molecular spectrum of heavy hydrogen (HD) in the extreme ultra-violet region. Y. FUJIOKA

and T. WADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 210—234).—A no. of lines of the HD mol. in the region 61,000—98,000 cm^{-1} are recorded and classified. J. W. S.

Hydrogen-isotope effect in the OH bands, 3064 and 3121 Å. R. W. SHAW and R. C. GIBBS (Physical Rev., 1934, [ii], 45, 124).—Bands arising from the isotope of H of approx. mass 2 in the OH mol. have been photographed for the cases of the (0,0) and (1,1) vibrational changes, and a rotational analysis is made. The width of the spin doubling for D is $>$ for the ordinary OH mol. L. S. T.

β Bands of boron monoxide. A. ELLIOTT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 736—738).—Measurements of doublet separations are recorded. E. S. H.

Predissociation in the $C^1\Sigma$ state of CO. R. SCHMID and L. GERO (Z. Physik, 1935, 96, 546—550).—Predissociation in this state gives a heat of dissociation for CO of 8.40 volts. A. B. D. C.

5 B Bands of carbon monoxide. R. SCHMID and L. GERO (Z. Physik, 1935, 96, 198—202). A. B. D. C.

Search for TiO isotope bands. H. P. KNAUSS, H. M. STRONG, and H. L. JOHNSTON (Physical Rev., 1934, [ii], 45, 124).—A C arc fed with powdered TiO₂ failed to reveal an isotopic shift, due to Ti⁴⁶, in the (1—0) band at 4955 Å. The existence of Ti⁴⁶ is not excluded. L. S. T.

Spectrum of neodymium oxide in the vapour state. G. PICCARDI (Atti R. Accad. Lincei, 1935, [vi], 21, 584—588).— λ and intensities are recorded for $>$ 200 bands, mostly in the red-green region. There are a few in the violet and none in the ultra-violet region. O. J. W.

Spectrum of samarium oxide in the vapour state. G. PICCARDI (Atti R. Accad. Lincei, 1935, [vi], 21, 589—593; cf. preceding abstract).—Similar data are recorded for Sm oxide. O. J. W.

Absorption spectra of the halides of some elements of the second group: CdCl₂, CdBr₂, CdI₂, ZnCl₂, ZnBr₂, and SrCl₂. C. M. B. RAO and M. KARIM (Current Sci., 1935, 4, 97).— λ of the max. of absorption are recorded. ZnCl₂ does not appear to obey Beer's law. L. S. T.

Absorption spectra of solutions of coloured metallic salts at low temperatures. Y. SHIBATA and K. HARAI (J. Chem. Soc. Japan, 1935, 56, 1—18).—Absorption spectra of CoCl₂, CoBr₂, CoI₂, Co(SCN)₂, NiCl₂, Cu(NO₃)₂, CuBr₂, UO₂(NO₃)₂, FeCl₃, KMnO₄, H₂PtCl₆, and HAuCl₄ in various org. solvents were measured at room temp. and at -60° to -80° . Many bands were observed at low temp. with COMe₂ solutions of CoCl₂, CoBr₂, and UO₂(NO₃)₂. CH. ABS. (e)

Absorption spectrum of tin sulphide. E. N. SHAWHAN (Physical Rev., 1935, [ii], 48, 521—524).—Data are tabulated for bands photographed at moderate dispersion for 3200—4600 Å., and at high dispersion for 4000—4600 Å. An expression is found for the near ultra-violet system, and for a new system in the visible which is limited by predissociation to two ν'' progressions. N. M. B.

Absorption spectrum of diacetylene in the near ultra-violet. S. C. WOO and T. C. CHU (J. Chem. Physics, 1935, 3, 541—543).—The spectrum with a 130 cm. absorption tube at 1 mm. pressure consisted of bands at $\lambda < 2490$ Å. With increasing pressure these were replaced by continuous absorption, additional bands appearing at longer λ (up to λ 2860 Å. at 252 mm. pressure). 80 bands were measured and classified. Resemblances between C₄H₂ and C₂N₂ are discussed. H. J. E.

Absorption spectra and dissociation energies of cyanic acid and some carbimides. S. C. WOO and T. K. LIU (J. Chem. Physics, 1935, 3, 544—546).—The absorption was continuous, the long λ of the continua being: HNCO 2240, MeNCO 2550, EtNCO 2480, PhCNO 2420 Å. For HNCO, 16 diffuse bands between 2570 and 2250 Å. were observed. For PhNCO bands due to the C₆H₅ ring were observed. The optical dissociation energy suffices only for the splitting of the R-N linking. The absence of the characteristic $>$ C:O absorption is discussed. H. J. E.

Ultra-violet absorption spectra of *cis*- and *trans*-dichloroethylenes. H. E. MAHNCKE and W. A. NOYES, jun. (J. Chem. Physics, 1935, 3, 536—540; cf. this vol., 1055).—For both isomerides there is general absorption from approx. 1600 to 2400 Å., the limits depending on the pressure. Bands occur at 1350—1570 Å.; they are shaded to the violet for the *cis*-form (I) and to the red for the *trans*-form (II). For (I) there was continuous absorption at still shorter λ . For (II) there were, in this region, a no. of structureless broad bands, which merged with increasing pressure. Ionisation potentials for (I) were predicted at 9.58, 9.63 e.v. This val. was confirmed by the electron bombardment method. H. J. E.

Ultra-violet absorption spectra of the α -ethylenic nitriles. A. CASTILLE and E. RUPPOL (Bull. Soc. chim. Belg., 1935, 44, 351—375).— λ -log ϵ data are given for the substituted *cis*- and *trans*- α -crotononitriles from C₅ to C₁₂. Absorption is greater in the *trans*-form. J. S. A.

Absorption spectra of free radicals. L. C. ANDERSON (J. Amer. Chem. Soc., 1935, 57, 1673—1676).—The absorption spectrum of CPh₃Br in SO₂ closely resembles that of CPh₃⁺ in H₂SO₄, HClO₄, or Me₂SO₄ (A., 1931, 86); hence CPh₃Br is ionised and (CPh₃)₂ dissociated in SO₂ and CPh₃⁺ is quinonoid. The spectrum of CPh₃ in Et₂O resembles that of solutions of O:C₆H₄:R (R=O, NOH, or NCl); it follows that the non-ionised free radical is quinonoid. In dil. solutions the heights of the quant. absorption curves of CPh₃Br and CPh₃ in SO₂ are the same; the former absorption is unaffected by temp., from which it is concluded that CPh₃Br and (CPh₃)₂ are completely dissociated in dil. solution in SO₂. The spectra of CPh₃ and CPh₃Na (very dil.) in SO₂ are scarcely affected by temp.; that of CPh₃ in Et₂O is very sensitive, probably owing to increasing ionisation at higher temp. R. S. C.

Ultra-violet absorption of aromatic hydrocarbons. III. Constitution of tetrahydrodi-phenyl. M. PESTEMER and L. WILIGUT (Monatsh.,

1935, 66, 119—128; cf. A., 1934, 1287).—The extinction-wave-no. curves for $\text{CHPh}\cdot\text{CH}_2$, $\text{CHPh}\cdot\text{CHMe}$, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}_2$, PhPr , Ph_2 , $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$, and of tetrahydrodiphenyl (I), obtained from Ph_2 by reduction with Na and $\text{C}_5\text{H}_{11}\cdot\text{OH}$, have been determined in C_6H_{14} and MeOH . Comparison shows that the double linking in (I) must be conjugated with the C_6 ring, proving (I) to be identical with 1-phenylcyclohexene.

J. S. A.

Optical absorption and double linking. I. Problems and methods. K. W. HAUSER, R. KUHN, A. SMAKULA, and K. H. KREUCHEN. **II. Polyene aldehydes and polyene carboxylic acids.** K. W. HAUSER, R. KUHN, A. SMAKULA, and M. HOFFER. **III. Furan series.** K. W. HAUSER, R. KUHN, A. SMAKULA, and A. DEUTSCH. **IV. Diphenylpolyenes.** K. W. HAUSER, R. KUHN, and A. SMAKULA (Z. physikal. Chem., 1935, B, 29, 363—370, 371—377, 378—383, 384—389).—I. In determining the absorption spectra of polyene dyes photoelectric photometry, the photographic method, and the spectrophotometer yield concordant results, but the positions of absorption max. obtained with the grating spectroscopy may differ, owing to a contrast effect, by as much as 8 m μ from those found by the other methods.

II. For the aldehydes $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CHO}$ and acids $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CO}_2\text{H}$ (cf. A., 1931, 1273) the absorption coeff. at the absorption max., κ_{max} , and the intensity of absorption, $\{\kappa\cdot d\}$, increase linearly with n . The displacement of the absorption bands towards the visible caused by increase in n falls as n rises.

III. In respect of the position of the absorption bands of longest wave-length of various aldehydes and acids of the furan series the furan ring is practically equiv. to an aliphatic system with two conjugated double linkings. α -Furylheptatrienoic acid, m.p. 199.5—200°, has been prepared from α -furylpentadienal and malonic acid in $\text{C}_5\text{H}_5\text{N}$.

IV. For the diphenylpolyenes, $\text{Ph}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{Ph}$, κ_{max} and the intensity of absorption increase approx. linearly with n (cf. A., 1928, 281). The absorption curves in EtOH are shifted towards shorter wave-lengths compared with those in C_6H_6 by an approx. const. amount, independent of n (cf. A., 1931, 1351).

R. C.

Asymmetric synthesis. II. Addition of chlorine to trinitrostilbene.—See this vol., 1358.

Absorption spectrum and constitution of carvone hydrosulphide. R. PADMANABHAN (Current Sci., 1935, 4, 95—96).—The ultra-violet absorption spectrum favours the structure of Steele (Proc. C.S., 1911, 27, 240).

F. N. W.

Reflexion power of aqueous solutions in the infra-red. F. MATOSI and H. FESSER (Z. Physik, 1935, 96, 12—28).—Reflexion of the 3 and 6 μ fundamental frequencies of H_2O has been measured for solutions of NaCl, NaBr, NaI, LiCl, KCl, CaCl_2 , and LiNO_3 . The positions and intensities of the bands vary with presence of ions, due to their depolymerising effect and their hydration. Decrease of cationic radius increases both depolymerisation and hydration; anions show little hydration, and depolymerisation of the H_2O groups increases with anionic radius. A. B. D. C.

Infra-red absorption spectrum of water containing protium and deuterium. A. L. CASSELMAN (Physical Rev., 1934, [ii], 45, 221—222).—With H_2O containing 56% of D the ordinary H_2O bands at 3 and 6.2 μ are considerably reduced and the 4.8 μ band almost disappears. New bands appear at approx. 4.2 and 6.9 μ . The former is probably due to the combinations $\text{D} \leftrightarrow \text{D}$ and $\text{O}^{16} \leftrightarrow \text{D}$, and the latter to $\text{H}^1 \quad \text{D}$. L. S. T.

Infra-red spectrum of fluorine monoxide. G. HETTER, R. POHLMAN, and H. J. SCHUMACHER (Z. Physik, 1935, 96, 203—209).—The spectrum has been determined between 1 and 27 μ ; intense bands appear near 5.75, 7.8, 10.8, and 12.0 μ , and the angle FOF is 100° (cf. this vol., 428). A. B. D. C.

Infra-red absorption spectrum of solid hydrogen chloride. P. E. SHEARIN (Physical Rev., 1935, [ii], 48, 299—301).—Data for 13 lines of the 3.7 μ band are given. If the centre is taken to be the 2669 cm^{-1} line, the band, in contrast to that of gaseous HCl, has a zero line. N. M. B.

Chemical and physical characteristics of water of crystallisation. I. Hydrates containing up to three molecules of water. II. Hydrates containing more than three molecules of water. L. PASSERINI (Gazzetta, 1935, 65, 502—511, 511—517).—I. The infra-red absorption spectra between 1.30 and 2 μ of the following hydrates are recorded: $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$; citric acid monohydrate; $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$; $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$; $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$; $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$; $\text{NaOAc}\cdot 3\text{H}_2\text{O}$; and $\text{Pb}(\text{OAc})_2\cdot 3\text{H}_2\text{O}$. The two H_2O bands for the various hydrates either coincide with those of H_2O vapour (1.38 and 1.83 μ) or of ice (1.474 and 1.976 μ), or occupy an intermediate position.

II. Similar data are recorded for 16 salt hydrates containing $> 3\text{H}_2\text{O}$. The absorption bands either coincide with those of ice or fall between those of ice and H_2O vapour. O. J. W.

Infra-red band of arsine. W. V. NORRIS and H. J. UNGER (Physical Rev., 1934, [ii], 45, 68).—The weak 1.63 μ band of AsH_3 at 1 atm. has been investigated with the automatic recording spectroscopy.

L. S. T.

Infra-red spectra of acetylene containing H^2 . H. M. RANDALL and E. F. BARKER (Physical Rev., 1934, [ii], 45, 124—125).—The infra-red spectra of acetylene gas generated from D_2O show relatively few mols. of C_2H_2^1 and approx. equal concns. of $\text{C}_2\text{H}_2^1\text{D}$ and C_2D_2 .

L. S. T.

Infra-red absorption spectra of the linear molecules carbonyl sulphide and deuterium cyanide. P. F. BARTUNEK and E. F. BARKER (Physical Rev., 1935, [ii], 48, 516—521).—Data for the vibration-rotation bands of COS are tabulated and the vibrational energy level scheme of the mol. is determined. Data for the rotation lines of the 17.5 μ band of DCN zero branch 570 cm^{-1} and the 14 μ band of HCN zero branch 712 cm^{-1} are tabulated. The moments of inertia are: DCN 22.92×10^{-40} , HCN 18.72×10^{-40} g.- cm^2 , and from these the internuclear distances are: $\text{H}-\text{C}$ 1.06×10^{-8} , $\text{C}-\text{N}$ 1.15×10^{-8} cm.

The zero order quadratic potential energy expression is computed. N. M. B.

Analysis of the infra-red bands of formaldehyde. A. NORDSIECK (Physical Rev., 1934, [ii], 45, 133—134).—The theoretically-expected structure of the infra-red bands of CH_2O has been worked out on the basis of Wang's theory of the asymmetric rotator (*ibid.*, 1929, 58, 730). L. S. T.

Convergence error in depolarisation measurements. R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 133—142).—Errors in depolarisation measurements due to the use of convergent beams are treated mathematically. J. W. S.

Longitudinal light scattering by liquids. S. M. MITRA (Z. Physik, 1935, 96, 34—36).—Plotnikow and Splait's scattering of light parallel to the incident beam could not be observed (cf. A., 1930, 664). A. B. D. C.

Polarisation of scattered radiation. I. Rayleigh scattering. S. M. MITRA (Z. Physik, 1935, 96, 29—34).—The degree of depolarisation of light scattered by C_6H_6 and CS_2 normal to the incident beam is independent of λ . A. B. D. C.

Raman spectrum of heavy water. R. ANANTHAKRISHNAN (Nature, 1935, 136, 551—552).—The principal band of the Raman spectrum of 99.2 wt.-% D_2O consists of three imperfectly resolved components 2646, 2500, and 2366 cm^{-1} , corresponding with 3630, 3435, and 3200 cm^{-1} for ordinary H_2O , and indicating that D_2O is polymerised in a manner similar to H_2O . A new band with a shift of 1231 cm^{-1} occurs with the 4358 and 4046 Å. excitations. A third band of 178 cm^{-1} shift also occurs, due, presumably, not to internal vibrations of the D_2O mol., but to rotation or vibration of the mol. as a whole. L. S. T.

Depolarisation of the light scattered by heavy water. S. BHAGAVANTAM (Current Sci., 1935, 4, 94).—The depolarisation of 99.5% D_2O is 0.04, compared with approx. 0.06 for H_2O , showing that the D_2O mol. is similar to that of H_2O in possessing only feeble optical anisotropy. L. S. T.

Raman spectrum of a ferromagnetic oxide. L. F. BATES and H. E. HOGWOOD (Proc. Physical Soc., 1935, 47, 877—878).—No Raman spectrum was found for Cr_5O_9 . N. M. B.

Raman spectra of iodic acid and the alkaline iodates as solids and solutions. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 119—132).—Cryst. HIO_3 shows 5 intense Raman lines and a no. of weak and sharp lines which are replaced by intense broad bands for solutions. The Raman spectra of 0.15—18*N* solutions show anomalous intensity and frequency changes with concn. Evidence is obtained that dissociation is incomplete at 0.5*N*. It is suggested that the acid is appreciably associated, especially in conc. solution. The spectra of NaIO_3 and KIO_3 show two lines identified with the parallel oscillation of the pyramidal form of mols. of the AX_3 type, whilst LiIO_3 and HIO_3 also show lines corresponding with the two perpendicular oscillations. It is suggested that low frequen-

cies observed with cryst. HIO_3 , LiIO_3 , and KIO_3 are due to oscillational motions or restricted rotations of the mols. in the solid state. Cryst. $\text{KH}(\text{IO}_3)_2$ contains an extra line, indicating the existence of $\text{I}_2\text{O}_6''$ ions. Its solution behaves as a mixture of HIO_3 and KIO_3 . J. W. S.

Raman spectrum of dioxan. M. WOLKENSTEIN and J. K. SYRKIN (J. Chem. Physics, 1935, 3, 594).—Villar's measurements (cf. A., 1931, 145) are amplified and corr. H. J. E.

Comparison of the Raman spectra of $\alpha\alpha\alpha$ - and $\alpha\alpha\beta$ -trichloroethane. G. F. HULL, jun. (J. Chem. Physics, 1935, 3, 534—535).—Vals. are recorded, and their interpretation is discussed. The CCl_3 and CHCl_2 radicals have tetrahedral symmetry. H. J. E.

Raman spectra of isoprene, dipentene, and ocimene. P. S. SRINIVASAN (Proc. Indian Acad. Sci., 1935, 2, A, 105—112).—The Raman frequencies of these compounds are tabulated and discussed with reference to their infra-red absorption frequencies and their structures. J. W. S.

Raman spectrum and symmetry of the benzene molecule. K. W. F. KOHLRAUSCH (Naturwiss., 1935, 23, 624—625).—The identification of the *f* line (1000 cm^{-1}), in the Raman spectrum of mono-, *m*-di-, and 1:3:5-tri-substituted C_6H_6 , with the λ line (992 cm^{-1}) of C_6H_6 , from which it has been argued that C_6H_6 has trigonal symmetry, is incorrect. The conclusion does not agree with the Raman spectra of many C_6H_6 derivatives, nor with the fact that the *p*-form possesses the highest symmetry. The C_6 ring has hexagonal symmetry. The occurrence of the *f* line with C_6H_6 derivatives is due to the activation of a line which in C_6H_6 itself is inactive. The agreement of frequencies of the *f* and λ lines is accidental. The vibrational forms of the C_6 ring are described and the frequencies calc. A. J. M.

Polarisation of Raman radiation of *p*-, *m*-, and *o*-xylene. W. C. NARKIEWICZ (Z. Physik, 1935, 96, 177—190).—Depolarisation and intensity of Raman lines due to the three isomerides have been measured, and from them the symmetry character of the vibrations and the groups to which they belong are deduced. A. B. D. C.

Raman spectrum of isomeric nitrotoluenes. R. M. ANSIDEI (Atti R. Accad. Lincei, 1935, [vi], 21, 581—584).—New measurements of the Raman spectra of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ confirm the existence of the line 1520 cm^{-1} characteristic of the NO_2 group and of the line 990 cm^{-1} characteristic of *m*-disubstituted derivatives (cf. A., 1931, 1353; 1932, 109). O. J. W.

Raman spectra of substances with two benzene nuclei. P. DONZELOT and M. CHAIX (Compt. rend., 1935, 201, 501—503).—Data are recorded for Ph_2 and for mols. of the type XPh_2 ($\text{X}=\text{CH}_2$, O, S, Se, CH-OH, and Hg). H. J. E.

Depolarisation of light scattering in gases and vapours. R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 153—160).—Previous data are criticised. The depolarisation of CH_4 is about

0.3% and is probably due to the highly depolarised vibration Raman lines. The depolarisation increases with increasing mol. wt. in the hydrocarbon series, and, in accord with observations on homologues, the val. for cyclopropane is low (0.52%) and for $\text{CHMe}:\text{CH}_2$ high (2.91). MeCl is more anisotropic than EtCl and much more so than CH_4 . The depolarisation of CCl_4 is about 0.15% and that of A probably 0, whilst H_2S and other hydrides have low vals. (about 0.3%), probably owing to their pseudo-inert gas structures.

J. W. S.

Scattering of light in protein solutions. P. PUTZEYS and J. BROSTEAUX (Trans. Faraday Soc., 1935, **31**, 1314—1325).—In the apparatus described, the relative scattering powers of solutions of ovalbumin, amandin, excelsin, and hæmocyannin are in the ratio of the mol. wt. of the proteins as determined by ultracentrifuge. Ionisation and hydration of the protein play a negligible part in the light-scattering process.

J. G. A. G.

Investigation of mitogenetic radiation with the counter tube. H. BARTH (Naturwiss., 1935, **23**, 688; cf. A., 1932, 544; 1934, 555).—Secondary mitogenetic radiation is detected by means of a counter tube. As primary sources the dissolution of Al in HCl and of mouse carcinoma in Ringer's glucose solution were used. Three methods of investigation are described.

A. J. M.

Fading of zinc phosphors in single crystals. III. V. V. ANTONOV-ROMANOVSKI (Physikal. Z. Sovietunion, 1935, **7**, 366—379; cf. A., 1934, 1290).—The rate of decay of large crystals obeys a bimol. relationship.

O. J. W.

Polarisation of photo-luminescence of dye solutions. A. JABLONSKI (Z. Physik, 1935, **96**, 236—246).—Theoretical. Depolarisation limits are deduced for photo-luminescence arising either from the final absorption level or from another level. Depolarisation varies with the absorption band used in excitation.

A. B. D. C.

Structure of group-resonators. XV. Theory of the fluorescence of organic substances. D. RĂDULESCU and C. DRĂGULESCU. Structure and properties of organic chromophores and group-resonators. XVI. Quantitative law of the frequency of absorption band maxima of group-resonators. D. RĂDULESCU and F. BĂRBULESCU. XVII. Influence of substituents on the absorption bands. D. RĂDULESCU. XVIII. Relation of the frequency of absorption bands in the vapour state. Absorption bands of benzoquinone vapour. XIX. Physical interpretation of the frequency relation between the bands. Relation between the absorption bands and the fluorescence bands of the same substance. XX. Coloured nitro- and polynitro-derivatives of benzene. D. RĂDULESCU and V. ALEXA. XXI. The hydrogen of the benzene nucleus can, under certain conditions of polarity, become ionisable and be replaced by metals. D. RĂDULESCU and S. POPA (Bull. Soc. Chim. Romania, 1935, **17**, 9—37, 39—47, 49—53, 55—61, 63—68, 69—83, 85—86; cf. A., 1931, 1351).—XV. The influence of state, solvents, and substituents on the fluorescence spectra

of anthracene, phenanthrene, pyrene, naphthacene, and perylene has been studied and found to be in accord with the view that the resonator responsible for absorption is identical with that producing fluorescence. The frequencies of the band max. of both spectra are given by $F_z - F_0\rho^{\pm x}$ (i), where x is an integer and $\rho=1.01048$. The frequency of the fluorescent emission is a max. in the vapour state.

XVI. The absorption band max. of a no. of org. compounds calc. with the aid of relation (i) are in close agreement with the most exact experimental vals.

XVII. Absorption bands are replaced by new bands on the introduction of substituents into an org. nucleus, and the new band max. can be calc. from relation (i), where F_0 refers to the parent substance. The variation of x with the type and position of substituents has been studied.

XVIII. Relation (i) applies with great exactitude to the absorption band data of Light for benzoquinone vapour.

XIX. The absorption, fluorescence, and Tesla luminescence spectra of C_6H_6 and C_{10}H_8 consist of identical series of the type (i). Each series is related to a favoured state of excitation of the mol.

XX. $\cdot\text{NO}_2$ can exist in two electromeric forms. That in which N is negative gives coloured compounds. The influence of substituents on the electromeric equilibrium of mono-, di-, and tri-nitro-derivatives is discussed. The absorption band max. is increased in solvents containing strong bases but not displaced, in accordance with the view that the absorption is due to the coloured electromeride of $\cdot\text{NO}_2$.

XXI. $\text{C}_6\text{H}_3(\text{NO}_2)_3$ gives the reddish-brown salt $[\text{C}_6(\text{NO}_2)_3]_2\text{Ba}_3 \cdot 6\text{H}_2\text{O}$ with $\text{Ba}(\text{OH})_2$, showing that the H are ionisable.

R. S.

Luminescence of compounds of organic molecules with metallic salts when irradiated with X-rays. E. WEYDE (Z. wiss. Phot., 1935, **34**, 216—234).—The X-ray luminescence of compounds of heterocyclic bases with metallic chlorides has been investigated with reference to the nature of the inorg. salt and its linking with the base. The intensity of the luminescence of quinoline and other heterocyclic bases is increased by the addition to the base of chlorides of heavy metals which are good absorbers of X-rays. The linking between the salt and the base must not be too strong. Effective chlorides are those of metals which show a tendency towards complex formation (e.g., Hg, Cd, Zn); replacement of Cl by Br or I causes weakening of the luminescence. The metal must be linked with N in the ring. Only those bases of which aq. solutions of the hydrochlorides will themselves show photoluminescence will give X-ray luminescence when combined with metallic chlorides. The purer is the metallic salt the more it is effective. The effect is, therefore, not dependent on the presence of traces of impurities. Only the solid compounds luminesce. At room temp. no phosphorescence is observed, but after irradiation at -80° the substances show phosphorescence on warming to room temp.

A. J. M.

Mechanism of ionic movement in solid electrolytes. W. SCHOTTKY (Z. physikal. Chem., 1935,

B, 29, 335—355).—Theoretical. In the theory of the electrolytic conduction of heteropolar lattices it is not admissible to assume that for each ionic species the no. of ionic voids is equal to the no. of inter-lattice ions of the same species (cf. A., 1934, 11). In close-packed lattices, e.g., the rock-salt type, the concn. of inter-lattice ions is negligible compared with that of voids for each ionic species. The general relation between the concn. of points of disarray and the determining energy magnitudes is derived thermodynamically. It is deduced that in alkali halide and alkaline-earth oxide lattices ionic conduction depends almost entirely on the voids. The method of calculating the concn. of voids is not yet exact.

R. C.

Surface ionisation of potassium iodide on tungsten. M. J. COPLEY and T. E. PHIPPS (J. Chem. Physics, 1935, 3, 594).—The positive ion current obtained with a const. ray of KI mols. striking a W filament has been studied. For a flashed filament the adsorbed salt mol. is first dissociated and the K then ionised.

H. J. E.

Photo- and dark-conductivities of cuprous oxide. D. NASLEDV and L. NEMENOV (Physikal. Z. Sovietunion, 1935, 7, 513—531).—The non-penetration of photo-electrons through the non-illuminated portion of polycryst. Cu_2O at liquid air temp. is attributed to the non-homogeneous nature of the Cu_2O reducing the life of the photo-electrons. The polarisation of Cu_2O at liquid air temp. is similar to that of a dielectric, and the leakage current becomes very low within 5 min. of applying a p.d. The distribution of potential indicates that a large p.d. is created at the Cu_2O -metal interface which diminishes under the influence of light, which, in the limit, renders the potential distribution linear. It is suggested that there is a highly-resistant surface film of unknown structure at the interface.

J. W. S.

Role of photo-conductivity of the stopping layer in the photo-emission at the surfaces of semi-conductors. G. LIANDRAT (Physikal. Z. Sovietunion, 1935, 7, 670—671).—Polemical against Jouse (this vol., 1218).

J. W. S.

Photo-electromotive forces in cuprite crystals. A. JOFFE and A. F. JOFFE (Physikal. Z. Sovietunion, 1935, 7, 343—365).—A study of the potential distribution on the surface of cuprite crystals during illumination indicates that there is a steady flow of electrons from the illuminated area in all directions. This flow is compensated by the conductivity current. An expression for the photo-e.m.f. is derived, which accounts satisfactorily for the variation of the e.m.f. with temp. and light intensity.

O. J. W.

Breakdown of dielectrics under high voltage, with particular reference to thermal instability. S. WHITEHEAD and W. NETHERCOT (Proc. Physical Soc., 1935, 47, 974—997).—Breakdown of a thermal and non-thermal type is discussed. A theory of ionisation coeffs. is developed to explain conductivity phenomena with a.c. and d.c., and ionisation potentials are deduced. Experimental data for cellulose acetate and cellulose Et ether are given.

N. M. B.

Electronic conductance as a result of the non-stoichiometric composition of substances. J. H. DE BOER (Chem. Weekblad, 1935, 32, 106—110).—Wagner's theory (A., 1933, 888) is discussed.

D. R. D.

Electrical conductivity of deformed NaCl crystals and their crystalline structure. Z. GYULAI (Z. Physik, 1935, 96, 210—218).—Pastilles prepared from powdered NaCl at temp. from 20° to 500° and at pressures from 2000 to 23,000 kg. per sq. cm. show ionic loosening potentials similar to those of single crystals. Those prepared at lower temp. show, on further tempering, a sudden increase in conductivity similar to observed sudden recrystallisation.

A. B. D. C.

Electrical conductivity of copper oxide films showing interference colours. F. H. CONSTABLE (Nature, 1935, 136, 517).—The electrical resistance of films of Cu oxide on Cu showing interference colours of the first order varies from 0.002 to 15 ohms per sq. cm. at 25°.

L. S. T.

Electrical conductivity of rust. G. COHN (Z. Elektrochem., 1935, 41, 660—664).—The conductivity of Fe rust is 1—30 mho per cm., which is about 10^6 times as great as that of goethite. The cathodic influence of rust on corrosion is due mainly to the inclusion of graphite and cementite, and to a smaller extent to Fe_3O_4 .

E. S. H.

Electrical properties of mineral aggregates. I. Natural and artificial aggregates of crystallised lead sulphide. R. S. DEAN and J. KOSTER (U.S. Bur. Mines, Rept. Invest. No. 3268, 1935, 21—50).—Massive galena crystals have a normal positive coeff. of resistance, whereas fine-grained steel galena (1) has a negative temp. coeff., the resistance-temp. curve having an exponential form. It behaves somewhat like a leaky condenser, the a.c. resistance being a function of the current passed through the specimen. The d.c. resistance of (1) \propto the square of a superimposed radio-frequency current, but is independent of the frequency. Determinations of the effect of grain size on the voltage-current characteristics at various temp. of synthetic (I) pastilles showed that the graphs are linear for all sizes and temp. The theoretical implications of the results are discussed with reference to the electronic structure.

A. R. P.

Dielectric properties of electrolytically produced layers of aluminium oxide. H. ZAUSCHER (Ann. Physik, 1935, [v], 23, 597—626).—Layers of Al_2O_3 , about 0.1 mm. thick, were produced by anodic oxidation of Al electrodes in $\text{H}_2\text{C}_2\text{O}_4$ solution. With d.c. the layers are vitreous, colourless, and porous; with a.c. yellow. The hygroscopic and dielectric properties of the layers prepared by the two methods are compared. The porosity of the layers decreases as the thickness increases, so that the properties of the layer depend on thickness below 50 μ . The dielectric loss was determined for layers which had been soaked in oil. The loss is $<$ that for dried layers at high alternating potentials.

A. J. M.

Anomalous dispersion of electric waves (3—8 m.) in solutions of organic zwitterions; a mole-

cular resonance phenomenon of sphingomyelin. I. HAUSER, R. KUHN, and F. GIRAL (*Naturwiss.*, 1935, **23**, 639—641).—The dielectric const. (ϵ) has been determined for zwitterions of the formula $^+NMe_3[CH_2]_nCO_2^-$ ($n = 1, 4, 5, 14, 16$) in H_2O and $EtOH$ solution, and for $EtOH$ solutions of sphingomyelin (I), at various concns. (c), temp., and $\lambda\lambda$. For small concns., $\Delta\epsilon$ is a linear function of c . This relationship holds for higher concns. the smaller is the dissolved dipole. The dipole moments are calc. from $\Delta\epsilon/\Delta c$ by the Debye method, if the dissolved mols. behave as a gas. The vals. obtained agree with those calc. from the mol. model. When $n = 4$ and 16, the dipole moments are 18 and 41×10^{-18} , respectively. For (I) it is 30×10^{-18} . The betaine mols. are therefore extended, and the substances are unimol. in solution. In H_2O , the betaines did not show anomalous dispersion, but in $EtOH$ this was found for waves of 3—6 m. For long dipoles the anomalous dispersion depends on the viscosity of the solvent in the case of betaines, but not in the case of (I). This is discussed in the light of the constitutional formula of (I), and it is concluded that the mol. acts as a resonator of very low characteristic frequency. A. J. M.

Absorption of decimetre waves in ionised gases, and the problem of the demonstration of the absorption of longer waves by excited hydrogen atoms. T. HAASE (*Ann. Physik*, 1935, [v], **23**, 657—676).—The absorption of waves of 7—30 cm. in H_2 , N_2 , and CO_2 , during the passage of the glow discharge, has been measured. The no. of electrons in the gas during the passage of the discharge was determined by Langmuir's method, and the measured absorption coeff. agrees with that calc. by Stewart's formula (*Physical Rev.*, 1923, [ii], **22**, 324) from the no. of electrons. The no. of excited atoms caused by the passage of the glow discharge through H_2 was determined from the intensity of the H_α radiation. The no. is so small that it is impossible to show the absorption of 10-cm. waves by excited H atoms. A. J. M.

Tensor nature of the dielectric constant and magnetic permeability in anisotropic media. J. H. VAN VLECK (*Physical Rev.*, 1934, [ii], **45**, 115—116).—Theoretical. L. S. T.

Dipole moments of isotopic molecules. R. P. BELL (*Trans. Faraday Soc.*, 1935, **31**, 1345—1347).—Since, with certain exceptions, the dipole moment, μ , of a mol. is a function of its amplitude of vibration, the μ of isotopic mols. will differ, and such difference should be detectable between compounds of H and D. J. G. A. G.

Dielectric constant and specific conductance of liquid hydrogen sulphide at 194.5° abs. W. G. BICKFORD and J. A. WILKINSON (*Proc. Iowa Acad. Sci.*, 1933, **40**, 89—91; cf. *A.*, 1933, 210).—The sp. conductivity and dielectric const. at 194.5° abs. were 1.17×10^{-9} ohm $^{-1}$ c.c. and 8.3, respectively. CH. ABS. (e)

Dielectric constant of ionised air. S. K. MITRA and S. S. BANERJEE (*Nature*, 1935, **136**, 512—513).—Measurements of the variation of ϵ with wave frequency verify the Eccles-Larmor theory of the decrease of ϵ of ionised air below unity, and show that

the anomalous increase reported by previous investigators is due to the conductivity acquired by the ionised air. L. S. T.

Dielectric constant of water vapour. J. D. STRANATHAN (*Physical Rev.*, 1935, [ii], **48**, 538—544).—Deviations from linearity of the dielectric const.—pressure curves were investigated, and anomalies are corr. or explained. Accurate dielectric data and an expression for these were obtained in the temp. range 21.3—197.9°. Results fall accurately along a Debye line, yielding an electric moment of $(1.831 \pm 0.006) \times 10^{-18}$ c.s.u. for the H_2O mol. N. M. B.

Dielectric constants of gases and vapours. III. M. KUBO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **27**, 295—304; cf. this vol., 916).—By taking into account the mutual action of dipoles, the Debye equation for the mol. polarisation (P) takes the form $P = A + B/T + 3AB^2\rho/8\pi N\beta^3T^2$, where $A = 4\pi N\alpha/3$, $B = 4\pi N\mu^2/9k$, and β is the effective mol. radius. P for H_2 , N_2 , CH_4 , and air is independent of temp. and pressure, in accord with theory, but the small increase of P for CO_2 with increasing pressure must be due to an effect unaccounted for in this equation. P for NH_3 increases linearly with 1/mol. vol., in accord with theory, the val. of the mol. radius calc. from the rate of increase being in accord with vals. calc. from viscosity measurements and from van der Waals' const. b . J. W. S.

Dipole moments of hydrazine and its derivatives. II. H. ULICH, H. PEISKER, and L. F. AUDRIETH (*Ber.*, 1935, **68**, [B], 1677—1682; cf. *A.*, 1933, 339).—Measurements are recorded for $NHMeNH_2$, *o*-, *m*-, and *p*- $C_6H_4MeNHNH_2$, *p*- $C_6H_4BrNHNH_2$, *p*- $NO_2C_6H_4NHNH_2$, and 2:4-(NO_2) $_2C_6H_3NHNH_2$. The results are readily explained qualitatively and quantitatively according to the views of Penney *et al.* (*A.*, 1934, 1158) on the constitution of hydrazines. H. W.

Dielectric investigations of nitromethane and chloropicrin. C. P. SMYTH and W. S. WALLS (*J. Chem. Physics*, 1935, **3**, 557—559).—Measurements at 25° and 50° of dielectric const. for solutions of $MeNO_2$ in C_7H_{16} and of chloropicrin in C_7H_{16} and in C_6H_6 are recorded. The dipole moments are < those for the vapours. Muller's relationship is not satisfied (cf. *A.*, 1933, 1103). Measurements with liquid and solid $MeNO_2$ (−90° to 27.4°) gave no evidence for mol. rotation in the solid state. There was no sudden change in the dielectric const. just above the m.p., showing that there is no increased formation of mol. aggregates in this region. H. J. E.

Dipole moment of ethyl benzoate. E. BERGMANN and A. WEIZMANN (*J. Amer. Chem. Soc.*, 1935, **57**, 1755).—The dipole moment in C_6H_6 solution at 24.6° is 1.91 D. E. S. H.

Dipole moments of some substituted benzaldehydes. J. N. PEARCE and L. BERHENKE (*Proc. Iowa Acad.*, 1933, **40**, 93).—Dielectric consts. of solutions of *p*- C_6H_4MeCHO , *p*-anisaldehyde, and *p*- $OH-C_6H_4CHO$ were determined at 25°. Dipole moments ($\times 10^{-18}$) were 3.26, 3.70, and 4.62, respectively. CH. ABS. (e)

Dielectric investigations on cellulose derivatives in organic liquids. V—VII. S. LEE and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 389B).—The mol. polarisation of ethylcellulose is dependent on the concn. because it associates to a non-polar complex; it is dependent also on the temp. Benzylcellulose and cellulose triacetate are less sol. and have lower dipole moments. A. G.

Orienting action of an electric field on the molecules of anisotropic fluids. V. FREDERIKS and V. TZVETKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 528—534).—The orienting influence of an electric field on films of *p*-azoxyanisole (I), *p*-acetoxybenzylideneazine (II), and dibenzylidenebenzidine (III) has been studied, using a magnetic field to overcome the orienting action of the glass wall. With a field of frequency 10^3 (I) and (II) are oriented perpendicular, and (III) is oriented parallel, to the field. Using a frequency of $3-6 \times 10^5$ the magnetic field may be dispensed with in the case of (II) and (III). The orientation of (III), which is a symmetrical mol., is contrary to Zocher's rule (A., 1928, 226). R. S. B.

Refraction equivalents of the triple carbon linking.—See this vol., 1222.

Rotatory dispersion of organic compounds. XXVIII. Ultra-violet absorption of ketones. T. M. LOWRY and R. E. LISHMUND (J.C.S., 1935, 1313—1319).—Absorption curves which are symmetrical on a scale of $\lambda\lambda$ are given by three alicyclic ketones, two OH-ketones, and two enolic ketones. Curves which are steeper on the side of longer $\lambda\lambda$ are given by simple aliphatic ketones and their Cl-derivatives, as well as by camphor and piperitone. Curves which are symmetrical on a scale of frequencies, or steeper on the side of shorter $\lambda\lambda$, have not been observed. The ketonic absorption band is displaced towards the visible region when H is replaced by Cl, but towards the ultra-violet when replaced by OH. Cooling to the temp. of liquid air displaces λ_{\max} by about 50 Å. towards the extreme ultra-violet, but has no great effect on the intensity of the band. O. J. W.

Evaluation of the structural theory of organic chemistry. I. J. K. SENIOR (J. Chem. Educ., 1935, 12, 409—414).—A lecture. L. S. T.

Mass spectrum analysis of the products of ionisation by electron impact in nitrogen, acetylene, nitric oxide, cyanogen, and carbon monoxide. J. T. TATE, P. T. SMITH, and A. L. VAUGHAN (Physical Rev., 1935, [ii], 48, 525—531).—A special mass spectrograph is described. A direct comparison in a N_2 -A mixture showed that the ionisation potential of N_2 is at least 0.04 volt < that of A, and therefore $> 15.60 \pm 0.05$ volts. The ions formed by electron impacts in C_2H_2 , NO, and C_2N_2 , and their appearance potentials are: $C_2H_2^+$ 11.2 ± 0.1 , C_2H^+ 17.8 ± 0.2 , C_2^+ 23.8 ± 0.3 , CH^+ 22.2 ± 0.5 , C^+ 24.5 ± 1.0 , H^+ 21.7 ± 1.0 and 25.6 ± 1.0 ; NO^+ 9.5 ± 0.1 , N^+ 22.0 ± 0.5 , NO^{++} 44 ± 1.0 ; $C_2N_2^+$ 14.1 ± 0.1 , C_2N^+ 19.8 ± 0.5 , CN^+ 21.3 ± 0.3 , C_2^+ 18.6 ± 0.5 . Negative O^- ions appear in NO. An ion of mass 27 found in C_2H_2 is ascribed to $C^{12}C^{13}H_2$. The calc. $C^{13}:C^{12}$ abundance ratio is 1:100. N. M. B.

Energy formula and potential distribution of diatomic molecules. E. A. HYLLERAAS (J. Chem. Physics, 1935, 3, 595).—Theoretical. H. J. E.

Wave equation for a triatomic molecule. M. ELIASHEVITSCH (Physikal. Z. Sovietunion, 1934, 6, 569—586).—A method of obtaining the vibrational-rotational wave equation is given, and is applied to a non-linear triat. mol. CH. ABS. (e)

M.p. law and lattice binding. R. FORRER (Ann. Physique, 1935, [xi], 4, 202—269).—The m.p. obey the same law, $T = F\sqrt{N}$, as the Curie points, where N is the no. of "contacts" of the at. electrons with those of the neighbouring atoms, and F is a const. having the same val. for each element as in the Curie law. For several elements of low m.p. the no. of contacts is tested by the theory of the electronic lattice, the structure of which determines the rigidity of the solid. Consideration of the no. of electrons in the structure of this lattice leads to the conception of lattice-valency. The relation of a no. of properties of elements to the electronic lattice is discussed. N. M. B.

Exchange of vibration and translation energies between iodine molecules and inert gases. F. ROSSLER (Z. Physik, 1935, 96, 251—267).—Collision efficiency for rotation and vibration energy exchange determined from fluorescence extinction gives cross-sections 25 times the gas kinetic val. and considerably > that given by acoustic dispersion. A. B. D. C.

Current views concerning the liquid state. R. D. SPANGLER (Proc. Iowa Acad. Sci., 1933, 40, 150).—Existing definitions are inadequate. CH. ABS. (e)

Chemical force in the light of quantum mechanics. II. W. JOST (Z. Elektrochem., 1935, 41, 667—674; cf. this vol., 15).—Theoretical. Bimol. and resonance energies are discussed. E. S. H.

EK [energy coefficient] system. A. E. FERSMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 559—566).—With a view of solving geochemical and crystallographical problems, *EK*, the energy contributed to a heteropolar compound by each of the ions brought from infinity, and *u*, the ionisation energy of the compound, have been approx. calc. according to $U = 256.1(aEK_{\text{cat.}} + bEK_{\text{an.}})$, $EK = Kw^2/2R$, where *a* and *b* are the no. of atoms of cation and anion in the compound, and *w* is the valency and *R* the radius of the ion in question. $K=1$ for all anions, and \approx approx. 1 for cations of $R=1.0-1.5$ Å. Tables of *EK* are given for geochemically important ions. Vals. of *U* are additive within 6—12%. R. S. B.

Theory of thermal disarrangement in crystals. W. SCHORTKY (Naturwiss., 1935, 23, 656—657).—The no. of particles in the inter-lattice and lattice holes of a lattice disordered by heat is not necessarily the same. Consideration of the thermal equilibrium leads only to the product of the concns. of particles in the two positions. The individual concns. are dependent on several conditions not previously sufficiently considered. For lattices consisting only of neutral particles, the equilibrium concns. of particles in the holes and within the lattice are dependent only on temp., but may differ widely. In the case of ionic

lattices the new theory suggests possibilities not previously envisaged. A. J. M.

Energy level scheme for electrons in crystals. P. TARTAKOVSKI (Z. Physik, 1935, 96, 191—197).—Energy level schemes are deduced for NaCl, KCl, and diamond. A. B. D. C.

Electronic structure of molecules. X. Aldehydes, ketones, and related molecules. XI. Electroaffinity, molecular orbitals, and dipole moments. XII. Electroaffinity and molecular orbitals, polyatomic applications. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 564—573, 573—585, 586—591; cf. this vol., 1188).—X. Electron configurations are given for the normal states of CH_2O , MeCHO , and COCl_2 , and for the low excited states of CH_2O . The structures, ionisation potentials, and longest λ electronic band spectra of these mols. and other aldehydes, ketones, thioaldehydes, and thioketones, are interpreted in relation to these configurations.

XI, XII. Theoretical.

H. J. E.

Parachor and chemical constitution. III. Structure of carbamide and thiocarbamide. S. K. RAY (J. Indian Chem. Soc., 1935, 12, 404—409).—From measurements of the surface tension and d at 28—30° of aq. solutions of carbamide (I) and thiocarbamide (II), the parachors of (I) and (II) correspond with the carbamide structure and not with Werner's cyclic formulæ. Low vals. of the parachor were obtained for (I) in MeOH and EtOH , owing to mol. association, and in $\text{HCO}\cdot\text{NH}_2$, and for (II) in $\text{C}_5\text{H}_5\text{N}$. J. G. A. G.

Ionisation constants and parachors of some furan compounds. H. GILMAN, W. E. CATLIN, and R. K. DAVIS (Proc. Iowa Acad. Sci., 1933, 40, 115).—2-Furoic acid is distinctly, and 3-furoic acid slightly, stronger than BzOH . Dissociation consts. of halogen-substituted furoic acids indicate that the furan nucleus is non-planar. The parachors of simple furan compounds are normal. CH. ABS. (r)

Parachor of some heteropolar crystals. A. ROMANSKI (J. Phys. Chem. U.S.S.R., 1934, 5, 779—780).—Vals. for Na and K halides are discussed. The accepted val. $\sigma=92$ for KBr is uncertain. CH. ABS. (e)

Multiple Laue spots. C. C. MURDOCK (Physical Rev., 1934, [ii], 45, 117—118).—Double or triple spots were always obtained from a certain specimen of quartz. The triple spots are attributed to the ideally perfect nature of the crystal, and they may provide a method for locating large perfect blocks within a quartz crystal and for surveying their boundaries. L. S. T.

Spectroscopy of ultra-soft X-rays. V. M. SIEGBAHN and T. MAGNUSSEN (Z. Physik, 1935, 96, 1—11).—Data are given for C in the form of graphite, diamond, carbides, and carbonates; the last give exceptionally sharp $K\alpha$ lines. A. B. D. C.

Absorption factor for the powder and rotating-crystal methods of X-ray crystal analysis. A. J. BRADLEY (Proc. Physical Soc., 1935, 47, 879—899).—Mathematical. Data are calc. for obtaining the

absorption factor, accurate to 1%, for any angle of reflexion. N. M. B.

Intensity of X-ray reflexions from crystalline powders. J. C. M. BRENTANO (Proc. Physical Soc., 1935, 47, 932—947).—In the determination of the dispersion of F -vals. in the range of the L -absorption levels, factors determining quant. measurements by the flat powder layer and mixed powders method, effect of the size of crystallites, use of spacing materials, absorption effect of particles of different absorbing power, and reflexions obtained from a flat layer are discussed. N. M. B.

X-Ray interference at the single-crystal anticathode. W. KOSSEL and H. VOGES (Ann. Physik, 1935, [v], 23, 677—704).—X-Ray interference has been produced from the X-ray source itself, viz., a single-crystal anticathode. The observed interferences can be explained as the result of the reflexion of plane waves at lattice planes, and the depth to which the cathode rays have penetrated can be calc. Peculiarities in the reflexions are discussed, particularly variations in intensity ("bright-dark" lines), which can be explained by the new theory of Laue. A. J. M.

Fluorescence X-radiation of single crystals (with a note on electron diffraction). M. VON LAUE (Ann. Physik, 1935, [v], 23, 705—746; cf. this vol., 918).—The theory of the interference of rays emitted from single crystals (see preceding abstract) is developed by combining the Maxwell reciprocal law with the dynamic theory of X-ray interference. A. J. M.

Mosaic zinc crystals. E. P. T. TYNDALL and H. K. SCHILLING (Proc. Iowa Acad. Sci., 1933, 40, 156; cf. Poppy, this vol., 20).—Crystals of a distinct mosaic type were observed. CH. ABS. (e)

Diffraction of X-rays by liquid Na-K alloy in a magnetic field. C. W. HEAPS (Physical Rev., 1935, [ii], 48, 491—493).—Although the alloy shows magnetoresistance, any diffraction change due to a magnetic field is $< 2\%$ in a field of 2700 gauss. An attempt to detect magnetostriction showed no vol. change per unit vol. $> 3 \times 10^{-7}$ in a field of 7800 gauss. N. M. B.

Reflexion of cathode ray from a crystal surface. S. MIYAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 286—294).—The position and breadth of the reflexion spectrum calc. from the wave equation of electrons for a simple potential model in the crystal agree with experiment for ZnS crystals.

Electronic structure of diamond. G. E. KIMBALL (J. Chem. Physics, 1935, 3, 560—564).—Theoretical. The energy levels of the C atom are broadened into bands similar to the energy bands in metals. In a metal there is always an incompletely-filled energy band, whereas in diamond the low-energy bands are all completely filled, and a large amount of energy would be necessary to promote an electron to an unfilled band. H. J. E.

Dynamical theory of the diamond lattice. III. Diamond-graphite transformation. N. S. N. NATH (Proc. Indian Acad. Sci., 1935, 2, A, 143—152;

cf. this vol., 150, 1058).—The transformation of diamond structure into graphite structure is interpreted as a definite relative displacement of the two face-centred lattices, a definite homogeneous dilatation of the whole crystal along the same direction, and a definite homogeneous gliding of the planes obtained by these transformations perpendicular to the same direction. For a certain displacement of the component lattices diamond attains max. energy of its configuration, becomes unstable, and changes to graphite. The calc. temp. of transformation is in good agreement with experiment. J. W. S.

Incomplete atomic arrangement in crystals. E. J. W. VERWEY (J. Chem. Physics, 1935, 3, 592—593).— γ -Fe₂O₃, γ -Al₂O₃, and γ' -Al₂O₃ (obtained by electrolytic oxidation of Al) are averaged structures with regard to the cations. The γ and γ' oxides have the same O lattice, but there is a difference in the degree of incomplete arrangement of the cations. γ - and γ' -Al₂O₃ and Fe₂O₃ are intermediate between the amorphous and the totally arranged state. In γ' -Al₂O₃ only the anions are arranged regularly. On heating to 900°, γ -Al₂O₃ is formed, with a partial arrangement of the cations. Complete arrangement of the cations occurs at > 1000°, α -Al₂O₃ being formed. H. J. E.

Structure of metallic coatings, films, and surfaces. C. H. DESCH (Trans. Faraday Soc., 1935, 31, 1045—1048).—A lecture. E. S. H.

Formation of nuclei in recrystallisation. I. Dependence of incubation period on the deformation and heating conditions. M. KORNFELD (Physikal. Z. Sovietunion, 1935, 7, 432—441).—The dependence of the velocity of formation of nuclei and of the linear velocity of growth of new nuclei on the degree of deformation has been obtained. These data are used to explain the mechanism of the formation of nuclei. W. R. A.

Grain growth in carbonyl iron and the preparation of single crystals of iron. W. TANGERDING (Arch. Eisenhüttenw., 1935—1936, 9, 113—114).—Repeated annealing of carbonyl Fe alternately in oxidising and reducing atm. leads to rapid grain growth, so that it is possible to prepare large Fe single crystals in this way if the metal is free from impurities restraining grain growth. The more rapidly the metal is cooled from above Ac₃ the greater is the veining which occurs in the ferrite and the higher is the coercivity; this behaviour is in agreement with the assumption that the veining constituent is a layer with a distorted α -lattice due to the presence of traces of impurities. A. R. P.

(A) Temperature dependence of the number of crystal nuclei in supercooled liquids. F. K. GORSKI. (B) Velocity of crystallisation in a magnetic field. R. J. BERLAGA and F. K. GORSKI (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 522—526, 527—530).—(A) Without a field the no. of nuclei formed in supercooled piperine as a function of temp. shows max. at 42° and 45°, with a deep min. at 43°. With a field (2000—4300 volts per cm.) the max. and min. are shifted to lower temp., and accentuated.

(B) The linear velocity of crystallisation of H₂O, 4 s

salol, and NHPh₂ was unchanged by fields up to 17,000 gauss. CH. Abs. (c)

Crystallisation of thin metal films. E. N. DA C. ANDRADE (Trans. Faraday Soc., 1935, 31, 1137—1143).—The spherulitic crystallisation of sputtered films of Au and Ag on heating is described. Experiments show that the surface of the metal is mobile at temp. above a crit. val., which depends partly on the thickness of the film. E. S. H.

Function of hydrogen in intermolecular forces. J. D. BERNAL and H. D. MEGAW (Proc. Roy. Soc., 1935, A, 151, 384—420).—An examination of the crystal structure of the metallic hydroxides confirms the hypothesis that the force between OH groups is a function of the charge and size of the cation with which they are linked. With a small, highly-charged ion, this force acquires the character of a secondary linking only less powerful than the H linking of acids. This linking (length 2.7—2.8 Å.) is called the OH linking, and its occurrence is explained in terms of changes in the internal electronic structure of the OII group. The polarised OH group is assumed to have a tetrahedral structure with a negative region which serves to bind the positive H atom of a neighbouring OH. This hypothesis of the OH linking is used to predict the structure of Te(OH)₆. Intramol. H linkings in salicylaldehyde and *o*-nitrophenol are considered. L. L. B.

Powder diagrams of magnetised nickel crystals. S. KAYA and J. SERIYA (Z. Physik, 1935, 96, 53—61).—Discontinuities are shown by the cubic and dodecahedral surfaces according as magnetisation is along the tetragonal or diagonal axis (cf. A., 1934, 1059, 1160). A. B. D. C.

Dispersion of X-rays by nickel. II. Relationship between the intensity of the diffraction lines and the temperature. J. UMANSKI and V. VEXLER (Physikal. Z. Sovietunion, 1935, 7, 336—342).—The intensity of the (311) diffraction line of Ni has been measured in the temp. range 290—740° abs. The intensities observed at 480° and 590° abs. differ only slightly from those calc. by means of Waller's formula. Divergences at higher temp. are discussed. O. J. W.

Lattice dimensions of zinc oxide. C. W. BUNN (Proc. Physical Soc., 1935, 47, 835—842).—High-precision measurements by Cu and Co K α -radiation powder photographs of pure ZnO condensed from the smoke give, at 18°, a_0 3.2426 \pm 0.0001, c_0 5.1948 \pm 0.0003, axial ratio c_0/a_0 1.6020 \pm 0.0001. Comparisons with available data are discussed. N. M. B.

Temperature variation of the lattice constants of manganous oxide. (MLLE.) B. RUHEMANN (Physikal. Z. Sovietunion, 1935, 7, 590—607).—The lattice const. (a) of MnO is 4.4335 Å. at 0°, and its coeff. of expansion is const. at 1.45×10^{-5} down to 175° abs., below which it decreases slowly with fall of temp. At -115.9° abs. it shows an anomaly similar to that of NH₄Br (A., 1930, 936) owing to the appearance of a lattice with const. a' of 4.416 Å. as against 4.4258 Å. for a at this temp. This is in accord with sp. heat data (A., 1928, 936).

The two lattices co-exist between 77° and 116° abs. The lattice with const. a' is not strictly cubic.

J. W. S.

Relation between the alum structures. H. LIPSON (Proc. Roy. Soc., 1935, A, 151, 347—356).—There are ≤ 3 different alum structures, and in order to study the relation between them the parameters of Rb alum (α structure), Cs alum (β), and Na alum (γ) have been determined. The structure of a particular alum is dependent on the radius of the univalent ion. The α structure is typical of medium-sized ions, the β , of larger ions, and the γ , of the small Na atom. The γ structure is not directly related to the other two, but exists merely as an alternative way of fitting together the various groups while maintaining the disposition of linkings around the H_2O mols.

L. L. B.

X-Ray diffraction study of the structure of soda-silica glass. B. E. WARREN and A. D. LORING (J. Amer. Ceram. Soc., 1935, 18, 269—276; cf. B., 1934, 883).—X-Ray diffraction patterns made on seven $\text{Na}_2\text{O}-\text{SiO}_2$ glasses (0–46% Na_2O) showed, for small Na_2O content, a single strong peak at $\sin \theta/\lambda = 0.12$, which diminished in intensity without abrupt change with increasing Na_2O content, a new peak (at $\sin \theta/\lambda = 0.18$) becoming the more pronounced. A picture of the at. arrangement in the glass, yielding theoretical X-ray intensity curves in good agreement with experiment, is described. Each Si atom is tetrahedrally surrounded by four O atoms, part of which are shared between two, and the others linked to one, Si. The doubly-linked O build up a continuous Si-O framework, in the holes of which Na atoms are located at random. There is no evidence for existence of compounds in compositions studied.

A. L. R.

Crystal structure of swedenborgite, $\text{NaBe}_4\text{SbO}_7$. L. PAULING, H. P. KLUG, and A. N. WINCHELL (Amer. Min., 1935, 20, 492—501).—The hexagonal unit, $a\ 5.47$, $c\ 8.92\ \text{\AA}$., contains $2\text{NaBe}_4\text{SbO}_7$; space-group C_{6h}^4 . The crystal contains octahedral SbO_6 groups, and groups of four Be tetrahedra with one corner common to all four, the others being shared with tetrahedra of other groups and with Sb octahedra. The large O and Na ions together form a double hexagonal close-packed aggregate.

L. S. T.

Crystals and melt in stretched rubber. P. A. THIESSEN and W. WITTSTADT (Z. physikal. Chem., 1935, B, 29, 359—362).—In the stretching of rubber, arrangement of the mols. of the melt into a lattice continues for some time after extension has ceased, and for a given extension a definite equilibrium between cryst. material and melt is reached at each temp. over a wide range, the amount of melt increasing with rise in temp. The change is reversible and the equilibrium is affected by pressure.

R. C.

X-Ray investigation of cellotriose and its derivatives. C. TROGUS and K. HESS (Ber., 1935, 68, [B], 1605—1610).—Diagrams are given of cellotriose, its α - (I) and β -hendeca-acetate (II), β -hendecamethylcellotriose, β -octamethylcellobiose, and 2 : 3 : 6-trimethylglucose. With mixtures of (I) and (II) containing $\geq 50\%$ of (I), only the interferences of

(II) are visible in the diagram. The phenomenon, which appears widespread in the carbohydrate and sugar group, is attributed to the widely differing tendencies of the individuals towards crystallisation. Probably the detectable form functions as crystal carrier for the non-recognisable component.

H. W.

X-Ray analysis of textile fibres. III. Structure of the cellulose crystallite as interpreted from X-ray diffraction data. W. A. SISSON (Textile Res., 1935, 5, 119—133; cf. this vol., 18).—A review.

CH. ABS. (p)

Electron diffraction and surface structure. G. I. FINCH, A. G. QUARRELL, and H. WILMAN (Trans. Faraday Soc., 1935, 31, 1051—1080).—A review of the present state of electron-diffraction technique, with special reference to the study of metallic films and surfaces.

E. S. H.

Inner potentials of crystals and electron diffraction. W. E. LASCHKAREV (Trans. Faraday Soc., 1935, 31, 1081—1095).—Theoretical. The effective potential is not a const., but increases with the order of the diffracted reflection, asymptotically approaching the average grating potential. A method for calculating from X-ray data the potential distribution in the grating and the mean grating potential is outlined. The temp. factor is discussed.

E. S. H.

Thickness of the amorphous layer on polished metals. H. G. HOPKINS (Trans. Faraday Soc., 1935, 31, 1095—1101).—Polished Au surfaces were examined by electron-diffraction technique after removing the polished surface progressively by cathodic sputtering. The results show that the thickness of the amorphous layer is about $30\ \text{\AA}$., and that there is a gradual increase in crystal size below the polished surface.

E. S. H.

Structure of polished metal surfaces. C. S. LEES (Trans. Faraday Soc., 1935, 31, 1102—1106).—Electron-diffraction analysis of polished surfaces of Cu and Au, after progressive electrolytic etching, shows that the amorphous surface layer is separated from the polycryst. interior by a layer of oriented crystals. The thicknesses of the layers have been determined. The orientation appears to be due to deformation of the crystals by compression. The actual surface does not consist of crystal faces.

E. S. H.

Molecular layers of fatty substances on metals. J. J. TRILLAT and H. MOTZ (Trans. Faraday Soc., 1935, 31, 1127—1135).—New electronic interferences, foreign to the ordinary diagram of the metals, have been observed in the examination of numerous metallic layers of a thickness of a few μ ; they are independent of the physical treatment of the metal and are particularly intense with aged specimens. Results obtained by the artificial formation of layers of org. mols. on metallic surfaces show that the abnormal diagrams are due to the formation and crystallisation of thin films of fatty substances composed of linear mols. with long chains of C atoms.

E. S. H.

Diffraction experiments with slow electrons at galena, pyrites, and stibnite, the change of

the crystal surface of semi-conductors on electron bombardment, and the effect of temperature on the form of the diffraction curve. R. SUHRMANN and H. HAIDUK (*Z. Physik*, 1935, **96**, 726—740).—The changes in the surfaces of semi-conductors on bombardment with electrons have been examined in the case of PbS, FeS₂, and Sb₂S₃, to elucidate the mechanism of crystal rectification. A method is described by which the intensity of electron beams incident on and reflected from crystal surfaces can be registered photographically after a short exposure, although the beams are very weak (10^{-7} and 10^{-9} amp., respectively). The electron diffraction curves for a Bi layer on FeS₂ and PbS surfaces after bombardment with slow electrons (100 volts; 10^{-5} amp.) are obtained. Electron bombardment results in the removal of the diffraction max., which returns after 1 hr., the time depending on temp. The results can be explained by supposing that the surface crystal lattice is distorted by the incident electrons, in the neighbourhood of the cations. Temp. influences the form of the diffraction max.; the lower is the temp. the steeper is the max. A. J. M.

Inner potential of galena, pyrites, stibnite, and bismuth from diffraction curves with slow electrons. R. SUHRMANN and H. HAIDUK (*Z. Physik*, 1935, **96**, 741—753).—The diffraction max. of PbS, FeS₂, Sb₂S₃, and Bi (cf. preceding abstract) can be explained either by assuming the existence of several diffracting lattice planes, or only one such plane. In both cases the spectra are given by integral order nos., but the vals. of the lattice potentials obtained are different. By the first method the inner potential of PbS is 2.88 volts, and of FeS₂ 7.61 volts. The other substances give negative vals., whilst by the second method all give negative vals. (PbS —3.63, FeS₂ —3.54, Bi —1.72, Sb₂S₃ —1.25 volts). A. J. M.

Diffraction of fast electrons by crystallised rock-salt. S. PINSKER (*Physikal. Z. Sovietunion*, 1935, **7**, 464—467).—Electron diffraction by cryst. NaCl has been studied and interpretations are discussed. W. R. A.

Electron diffraction by vitreous silica powder. N. A. SCHISCHAKOV (*Nature*, 1935, **136**, 514).—The electron diffraction pattern of vitreous SiO₂ powder shows distinct rings indicating the presence of tetragonal cristobalite crystallites constituting the vitreous SiO₂. L. S. T.

Electron diffraction from vacuum-sublimed layers. K. LARK-HOROWITZ, E. M. PURCELL, and H. J. YEARIAN (*Physical Rev.*, 1934, [ii], **45**, 123).—The material is condensed in a high vac. on to a volatile substance, e.g., camphor or C₁₀H₈, at the temp. of liquid air, and the support is allowed to evaporate when the required thickness is attained. Films of Zn thus prepared give an electron diffraction pattern which agrees with the X-ray pattern with only the first two lines differing in intensity distribution. L. S. T.

Distribution of ferromagnetism among the metals. D. R. INGLIS (*Physical Rev.*, 1934, [ii], **45**, 128).—Theoretical. L. S. T.

Magnetic behaviour of superconducting tin spheres. K. MENDELSSOHN and J. D. BABBITT (*Proc. Roy. Soc.*, 1935, **A**, **151**, 316—333).—The magnetic field in the neighbourhood of superconducting Sn spheres has been studied by two methods. When the specimen is cooled in an external field below its threshold val., lines of force are pressed out and the induction decreases, but part of the flux remains in the specimen, and this residual flux is greater for the hollow than for the solid sphere. L. L. B.

Magnetisation cycle of superconducting lead. I. N. RJABININ and L. V. SCHUBNIKOV (*Physikal. Z. Sovietunion*, 1934, **6**, 557—568; cf. *A.*, 1934, 1061).—The magnetisation cycle of polycryst. Pb has been plotted at 4.24° abs. CH. ABS. (e)

Magnetisation curve of single iron crystals. R. JAANUS (*Physikal. Z. Sovietunion*, 1935, **7**, 380—384).—The conclusions of Hill (*A.*, 1934, 1163) are considered to be incorrect. O. J. W.

Abnormal magnetic behaviour of treated cobalt wire. T. F. WALL (*Nature*, 1935, **136**, 397).—Co wire heated in H₂ at 1200° has saturation val. of the intensity of magnetisation only approx. 60% of that for normal Co. L. S. T.

Magnetism and electronic state of metallic solid solutions and elements. U. DEHLINGER (*Z. Elektrochem.*, 1935, **41**, 657—659).—Published vals. for the magnetic saturation moments of Co, Ni, Cu, and their solid solutions deviate only slightly from the theoretical vals. for Co⁺, Ni⁺, and Cu⁺. The greater deviation of Fe is traced to the magnetic difference between α - and γ -Fe. E. S. H.

Layer-like magnetisation in magnetite crystals. N. J. MILLER and D. S. SCHTEINBERG (*J. Exp. Theor. Phys. U.S.S.R.*, 1934, **4**, 717—722).—Magnetisation was in layers perpendicular to the octahedral faces, and having a thickness of 0.03—0.3 mm. In rolled Ni the direction of magnetisation is in that of max. compression. CH. ABS. (e)

Magnetisation curves for magnetite powders. V. H. GOTTSCHALK and F. S. WARTMAN (*U.S. Bur. Mines, Rept. Invest. No. 3268*, 1935, 67—81).—Curves for four varieties of Fe₃O₄ show that at low field strengths the permeability increases with increase in grain size to 40 μ , then remains const. As the field strength is increased the permeability decreases and becomes more uniform, i.e., decrease in grain size has less effect. The coercive force increases linearly with increase in sp. surface and in packing density, and the retentivity increases linearly with increase in sp. surface and parabolically with increase in packing density. A. R. P.

Coercive force of magnetite powders. V. H. GOTTSCHALK (*U.S. Bur. Mines, Rept. Invest. No. 3268*, 1935, 83—90).—The fact that the coercive force of magnetite powders increases with decrease in grain size (cf. preceding abstract) is held to be additional direct proof of the fundamental correctness of the dispersion theory of magnetic hardness previously advanced (*Rept. Invest. No. 3223*). The coercive force of magnetite is decreased by dilution with non-magnetic material. A. R. P.

Magnetic properties of mineral powders and their significance. C. W. DAVIS (U.S. Bur. Mines, Rept. Invest. No. 3268, 1935, 91—100).— Fe_2O_3 obtained by dehydration of lepidocrocite at 370° or by dehydration of artificial γ -hydrated Fe_2O_3 at 250° has a high coercive force and remanence. Fe, Mn, and Mg ferrites produced under conditions which favour the development of a large interfacial area, Fe_3O_4 produced by reduction of Fe_2O_3 , and heat-treated titaniferous magnetite have also similar favourable magnetic properties. The bearing of these results on a.c. magnetic separation of minerals is discussed.

A. R. P.

Elementary theory of galvanomagnetic phenomena in crystals. J. FRENKEL and T. KONTOROVA (Physikal. Z. Sovietunion, 1935, 7, 452—463).—The galvanomagnetic phenomena in bivalent metals with cubic symmetry are discussed by tracing the action of magnetic and electric fields on the separate electrons and positive holes (cf. Blochinzev *et al.*, A., 1933, 893).

W. R. A.

Application of the thermomagnetic analysis to the study of the oxides of iron. G. CHAUDRON (Bull. Soc. chim. Belg., 1935, 44, 339—350).—A lecture on the method of thermomagnetic analysis (cf. this vol., 469). The ferromagnetism of FeS is greatly increased by traces of dissolved S.

R. S.

Magnetic reversal nuclei. V. Propagation of large Barkhausen discontinuities. K. J. SIXTUS (Physical Rev., 1935, [ii], 48, 425—430; cf. A., 1933, 768).—The size and growth are examined of stable regions of antisaturated magnetisation produced by short application of high local fields in a Ni-Fe wire in which a preferred direction of magnetisation is created by application of tension.

N. M. B.

Viscosity bands in magnetic spectra. O. VELETZKAJA (Z. Physik, 1935, 96, 173—176).—Variation of permeability of Fe and permalloys with frequency to λ of 1 cm. is in agreement with Arkadiev's theory of magnetic viscosity (Ann. Physik, 1919, 58, 105).

A. B. D. C.

Electrical conductivity of semiconductors. II. Electrical and optical properties of vanadium pentoxide crystals. A. N. ARSENEIEVA and B. V. KURTSCHATOV (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 576—583; cf. A., 1934, 1291).—Monocryst. V_2O_5 (rhombic; $a:b:c=0.3932:1:0.9590$) was obtained by slow cooling of a melt. Electrical conductivity is due to lower oxides. Vals. in different axial directions are recorded.

CH. ABS. (e)

Some piezoelectric and elastic properties of β -quartz. H. OSTERBERG and J. W. COOKSON (J. Franklin Inst., 1935, 220, 361—371).—The piezoelectric and elastic properties of β -quartz are those which are theoretically characteristic of the hexagonal holohedral class. The simple theory of the yz and zx shear-modes is verified and these modes exist independently in β - but not in α -quartz. 847° is a transition point at which β -quartz changes to another form (γ), not piezoelectric.

W. R. A.

Inversion phenomena in the polarisation of Rochelle salt crystals. I. V. KURTSCHATOV and A. SCHAKIROV (Physikal. Z. Sovietunion, 1935, 7, 631—

638).—For polarising potentials < 160 volts the velocity of depolarisation of the crystals is $>$ the velocity of polarisation, whilst for > 160 volts the reverse is observed. This may be due to mechanical stresses.

J. W. S.

Hall effect in solid gallium. I. FAKIDOV and B. G. LASAREV (Physikal. Z. Sovietunion, 1935, 7, 677—678).—By comparison with Cu the Hall effect const. (R) of Ga has been determined as -6.3×10^{-4} c.g.s. unit. The product $R\sigma$ (σ =sp. conductivity) is 12, the low val. being in accord with the fact that Ga is a superconductor.

J. W. S.

Reflexion of metals (Cu, Zn, Ni, Ag, and "Hochheim" alloys) in the spectral region 300 to 186 m μ . F. HLÚČKA (Z. Physik, 1935, 96, 230—235).

A. B. D. C.

Validity of Drude's optical method of investigating transparent films on metals. L. TRONSTAD (Trans. Faraday Soc., 1935, 31, 1151—1158).—A discussion of theoretical principles, sources of error, and fields of application.

E. S. H.

Optical research on evaporated metal layers. L. S. ORNSTEIN (Trans. Faraday Soc., 1935, 31, 1158—1166).—Technique for determining the optical consts. of thin layers of metal is described, and applications of the method to the investigation of the transition points of metals and to corrosion are indicated.

E. S. H.

Metallic absorption of light. T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 179—194).—Mathematical.

J. W. S.

Optical properties of solids. A. H. WILSON (Proc. Roy. Soc., 1935, A, 151, 274—295).—Mathematical. In deriving the fundamental formula, which is a generalisation of the Kramers-Heisenberg dispersion formula, it is unnecessary to assume that the size of the crystal is small compared with λ . The dispersion formulæ for metals (with special reference to Ag) and insulators are discussed, and the relation between absorption and dispersion is considered. The photo-electric response in an insulator is determined much more by the refractive index than by the absorption coeff.

L. L. B.

Determination of refractive index of vitreous silica and the calibration of silica refraction thermometers between 18° and -200° . J. B. AUSTIN and R. H. H. PIERCE, jun. (Physics, 1935, 6, 43—46).—The variation of n for the He 5877.2 Å. line was determined for vitreous SiO_2 from 18° to -200° , no min. being observed. The results are applied in refraction thermometer calibration.

CH. ABS. (e)

Light absorption in heteropolar crystals. D. BLOCHINZEV (Physikal. Z. Sovietunion, 1935, 7, 639—651).—From the theory developed it is deduced that the widths of the absorption bands of heteropolar crystals should be independent of temp.

J. W. S.

Heat of loosening of metals from recrystallisation data. J. A. M. VAN LIEMPT (Z. Physik, 1935, 94, 534—541).—The heat of loosening of metal lattices has been calc. for Fe, Ni, Au, Ag, Cu, Al, It, Ta, W, Mo, and Pb.

A. B. D. C.

Structure of a deformed crystal and recovery phenomena. M. KORNFELD (Physikal. Z. Sovietunion, 1935, 7, 608—619).—A plastically deformed crystal consists of small particles which are bounded by the slip-planes of the crystal and are partly de-oriented relatively to one another. The lattice is distorted along the edges of the particles. The particles are also elastically distorted. The recovery of distorted Al crystals has been investigated as a function of the time and temp. of heating.

J. W. S.

Transition from brittleness to plasticity with rising temperature of crystals. G. TAMMANN and W. MÜLLER (Z. anorg. Chem., 1935, 224, 194—212).—Many crystals brittle at room temp. become plastic near the m.p. The influence of temp. on the surface figures produced by scratching or pressing crystals of rock-salt, galena, fluor spar, calcite, ice, and quartz has been investigated. Et nitrocinnamate, $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, $p\text{-toluidine}$, $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (I), 2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$, $p\text{-C}_6\text{H}_4\text{Cl}_2$, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$, 1:2:4:6-trinitroanisole (II), azobenzene (III), $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$, $m\text{-nitrotoluidine}$, BzOH, benzoin (IV), and $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (V) show no plasticity up to the m.p. Camphor, camphene, and pinene hydrochloride pressed between glass plates give a thin film with a rounded boundary; borneol, isoborneol, PhCl, PhBr, and $\text{C}_6\text{H}_4(\text{NO}_2)_2$ break into irregular pieces which reunite to partly transparent films; (I), $\text{C}_6\text{H}_4\text{Cl}_2$, (II), (III), trinitrotoluidine, BzOH, (IV), and (V) acid give only fine, opaque powders. The phenomena are discussed.

T. G. P.

Cathode material and the electrical strength of rock-salt. A. VOROBYEV (Z. Physik, 1935, 96, 148—150).—The less is the emission potential of electrons from the cathode material the less is the breakdown potential in approx. homogeneous fields.

A. B. D. C.

Investigation by the optical method of the elastic limit of rock-salt crystals as a function of the rate of increase of the deformative force. V. D. KUZNETZOV and M. M. DEGTIAREV (J. Exp. Theor. Phys. U.S.S.R., 1934, 4, 643—650).—Within certain limits the rate of increase of tension on NaCl does not affect the crit. limit before rupture. Tempering of the crystals at 600—650° must be continued 2—3 days, with slow raising and lowering of the temp., to obtain crystals satisfactory for optical purposes.

CH. ABS. (e)

Plastic deformation of rock salt. III. N. A. BRILLIANTOV and I. V. OBREIMOV (Physikal. Z. Sovietunion, 1934, 6, 587—602).—During deformation of NaCl by compression normal to a cube face, it is postulated that small rotations of the cryst. lattice (about [001] in the (110) glide plane) are the primary effect. This, when extended over large domains, gives the illusion of translation.

CH. ABS. (e)

Increase in deformability and decrease in cleavability [of metals] with rise in temperature. G. TAMMANN and W. MÜLLER (Z. Metallk., 1935, 27, 187—189).—When Zn, Bi, or Sb single crystals are indented with a ball, characteristic twin lamellae appear in well-defined crystallographic direc-

tions around the impression; similarly scratching with a diamond point produces small parallel fissures at an angle to the scratch. As the temp. of the test is raised these phenomena become less marked and eventually disappear at a temp. at which the metal becomes workable; i.e., Zn 130°, Bi 150°, and Sb 300°. Single crystals of Bi can be bent without fracture at > 100°, those of Sb only at > 350°; the brittleness of Bi at 20° is approx. equal to that of Sb at 300°, i.e., the two metals are equally brittle at temp. which are the same fraction of their abs. m.p.

A. R. P.

Corresponding states of deformed lattices. J. A. M. VAN LIEMPT (Chem. Weekblad, 1935, 32, 546—550).—The formula $T(13.5 + \log t) = \text{const.}$ is derived for the recovery of deformed metals. S. C.

Effect of magnetisation on Young's modulus of elasticity of some ferromagnetic substances. K. NAKAMURA (Sci. Rep. Tohoku, 1935, 24, 303—331).—Three methods of measuring Young's modulus and its variation with magnetisation are described. Results for Fe, Co, Ni, and Fe-Ni alloys are discussed (cf. this vol., 816).

W. R. A.

Polymorphism in the series of normal fatty dicarboxylic acids.—See this vol., 1351.

Linear velocity of transformation of white into grey tin. A. KOMAR and B. G. LASAREV (Physikal. Z. Sovietunion, 1935, 7, 468—473).—A method for the electrolytic infection of white Sn by grey is given. The linear velocities of transformation have been investigated from 18° to -80° and are 200 times recorded vals. The dependence of the velocity on supercooling and pressure are discussed.

W. R. A.

Mechanical twinning structure in calc spar. D. B. GOGOBERIDZE and E. G. ANANIASCHVILI (Physikal. Z. Sovietunion, 1935, 7, 547—552).—There is a const. angle between the axes of the two portions of twinned calcite crystals. The lattice is only turned, the form of the X-ray pattern remaining unchanged. The crystal surface is partly distorted along the line of twinning.

J. W. S.

Significance of magnetic measurements for chemical problems. II. W. KLEMM (Angew. Chem., 1935, 48, 617—624; cf. A., 1931, 547).—Chemical applications of magnetic susceptibility measurements are reviewed, with special reference to solid phase equilibria, molecular complexity, and free radicals. The latter have zero orbital moment, i.e., the spin moment of one electron. Neumann's formulation of K peroxide as KO_2 (cf. A., 1934, 242) is not justified.

J. S. A.

Influence of the formation of hydrates on the diamagnetism of chemical compounds. P. S. VARADACHARI (Proc. Indian Acad. Sci., 1935, 2, A, 161—175).—The magnetic susceptibilities (χ) of $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ mixtures containing > and < 86% H_2SO_4 are respectively > and < the vals. calc. from the additivity law. Max. deviations are observed at concns. corresponding with $2\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4\cdot 18\text{H}_2\text{O}$, hydrates which are also indicated by other physical properties. $\text{AcOH--H}_2\text{O}$ mixtures obey the additivity

law, even at the composition of the compound $\text{AcOH} \cdot \text{H}_2\text{O}$. When cryst. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ or its solutions are heated to $> 33^\circ$ no change in χ is observed, suggesting that the binding of the H_2O is very loose compared with that of H_2SO_4 hydrates. Evidence is put forward to indicate that no increase of susceptibility is likely to occur on hydration of KI, as suggested by Cabrera *et al.* (A., 1934, 841).

J. W. S.

Magnetism of copper. S. R. RAO (Nature, 1935, 136, 436).—The diamagnetic susceptibility, χ , of Cu depends on particle-size. χ increases from 0.080 to 0.090×10^{-6} as particle size decreases from 10 to 0.8μ .

L. S. T.

Magnetic properties of Rochelle salt. C. T. LANE (Physical Rev., 1934, [ii], 45, 66).—No variation in magnetic susceptibility in the three principal directions of a single crystal could be detected. χ is -0.54×10^{-6} if χ_{Au} is 0.145×10^{-6} .

L. S. T.

Magnetochemical investigations. XVI. Magnetic investigation of system $\text{CoS}-\text{CoS}_2$. H. HARALDSEN (Z. anorg. Chem., 1935, 224, 85–92).—Susceptibility measurements show that from CoS to $\text{CoS}_{1.3}$ a one-phase system is formed, with χ little dependent on T . Between $\text{CoS}_{1.3}$ and CoS_2 , CoS_2 appears as a second solid phase which becomes ferromagnetic at -183° .

J. S. A.

Magnetic susceptibility of bromine vapour. J. SHUR and R. JAANUS (Physikal. Z. Sovietunion, 1935, 7, 501–506).—An apparatus for the determination of the magnetic susceptibility of active vapours is described. The val. of the susceptibility of Br_2 vapour is -0.46×10^{-6} and is in agreement with the recorded val. for liquid Br_2 .

W. R. A.

Longitudinal thermo-electric effect. II. Nickel in longitudinal magnetic fields. T. H. PR and W. BAND. **III. Aluminium.** M. K. LI and W. BAND. **IV. Further study of aluminium.** W. BAND. **V. Silver.** J. L. CH'EN and W. BAND (Proc. Physical Soc., 1935, 47, 852–858, 859–861, 862–872, 904–909; cf. A., 1934, 950).—II. The e.m.f. produced by asymmetrical temp. distributions in a Ni wire can be represented by a formula similar to that previously found for Cu. The consts. are evaluated, and their variation with magnetic field is investigated.

III. The thermo-electric e.m.f. was investigated. No satisfactory temp. distribution formula could be found.

IV. A formula is found agreeing with the presence of an allotropic form of Al having a transition temp. at 79° , with delayed reverse transition. The crit. temp. is the same for all tensions. A recrystallisation theory is supported.

V. Using improved methods the thermo-electric consts. of Ag are found, and their dependence on tension is shown. The consts. change sharply at a crit. temp. near 200° , connected probably with the elastic limit of the wire.

N. M. B.

Thermo-electric effects of the alkalis. A. SOMMERFELD (Physical Rev., 1934, [ii], 45, 65–66).—Theoretical.

L. S. T.

Change of the resistance of liquid metals in a magnetic field. I. FAKIDOV and I. KIKOIN (Physikal. Z. Sovietunion, 1935, 7, 507–508).—The relative change of resistance for liquid K is dependent on the field H according to $\Delta r/r = aH + b$.

W. R. A.

Standing ultrasonic waves rendered visible in transparent solid substances. II. Optical investigations with a block of glass. E. HIEDEMANN and K. H. HOESCH (Z. Physik, 1935, 96, 268–272; cf. *ibid.*, 95, 383). The line separation of the standing wave lattice varies greatly with the plane of polarisation of the incident light wave.

A. B. D. C.

Precision determinations of elastic constants of isotropic transparent solid substances. E. HIEDEMANN (Z. Physik, 1935, 96, 273–276).—Lattice consts. of the ultrasonic wave lattice determined by the method described (cf. preceding abstract) lead to precise vals. of elastic moduli.

A. B. D. C.

Temperature scales of niobium, thorium, rhodium, and molybdenum at 0.667μ . L. V. WHITNEY (Physical Rev., 1935, [ii], 48, 458–461).—Temp. scales were established by measuring spectral emissivities at $\lambda = 0.667 \mu$, after rigorous heat-treatment. Emissivities and temp. ranges covered are, respectively: Nb, 0.374 , 1300 – 2200° ; Th, 0.380 , 1300 – 1700° ; Rh, 0.242 , 1300 – 2000° ; Mo, 0.382 , 1300 – 2100° abs.

N. M. B.

Theory of solids at high temperatures, with special reference to the variation of C_p with temperature. G. DAMKOHLER (Ann. Physik, 1935, [v], 24, 1–30).—The Grüneisen-Debye theory of solids has been extended by assuming the vibration frequency to be dependent only on temp. The expression obtained for C_p shows that this should decrease again at high temp. An expression is derived for the variation of compressibility with temp. by the use of which the effect of temp. on C_p of NaCl, KCl, KBr, Ag, Cu, and Pb is calc. With the exception of Cu and Pb, C_p decreases at high temp. as expected. The Helmholtz free energy and the Gibbs thermodynamic potential of a linear chain at high temp. are derived.

A. J. M.

Specific heat of superconducting alloys. L. V. SCHUBNIKOV and V. I. TSCHOTKEVITSCH (Physikal. Z. Sovietunion, 1934, 6, 605–607).—The sp. heat curve of a Pb-Bi alloy (65% Pb) was continuous in the range 5 – 12° abs.

CH. ABS. (e)

Specific heat of a superconducting alloy. K. MENDELSSOHN and J. R. MOORE (Proc. Roy. Soc., 1935, A, 151, 334–341).—The sp. heats of the alloy PbTi_2 have been measured in the temp. range 3 – 6° abs. The fact that there is no discontinuity in the sp. heat at the transition point indicates that Rutgers' formula (this vol., 20) is inapplicable in this case.

L. L. B.

Molecular heat capacity equation of sulphur vapour, S_2 . I. N. GODNEV (Physikal. Z. Sovietunion, 1935, 7, 442–446).—The calculation of the mol. heat of S_2 vapour from spectroscopic data is discussed and two equations are derived to fit the theoretical mol. heat curve from 300° to 1300° abs.

W. R. A.

Density of 100% heavy water. L. TRONSTAD, J. NORDHAGEN, and J. BRUN (*Nature*, 1935, **136**, 515).—For pure D_2O , (pycnometric) varies from 1.10711 to 1.10714, the latter being the nearest approach to the correct val. Taylor and Selwood's higher val. (A., 1934, 590) is due probably to a greater % of O^{18} in the samples used. The isotopic ratio of the O in the 100% D_2O products is practically the same as the ordinary ratio. d_{20}^{25} for H_2O with < 1 of D_2O in 2×10^5 is $0.9999815 \pm 1\gamma$. L. S. T.

Specific volume of fused diabase at high temperatures. M. P. VOLAROVITSCH and A. A. LEONTEVA (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **2**, 535—538).—The sp. vol. of diabase has been determined at 1120 — 1360° . At 1160 — 1360° and 1140 — 1160° the coeff. of expansion is respectively 3.15 and 7.08×10^{-4} , a sudden change, due to the beginning of crystallisation, occurring at 1150° . The fluidity at 1250 — 1360° varies linearly with the sp. vol., in agreement with the formula for unassociated liquids; at lower temp. slight curvature indicates some association. R. S. B.

Specific volume of fused salts at high temperatures. M. P. VOLAROVITSCH and A. A. LEONTEVA (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **2**, 539—542).—The coeff. of expansion of fused NaH_2PO_4 , $NaPO_3$, and K_2SiO_3 are, respectively, 5.3×10^{-5} (at 620 — 935°), 4.3×10^{-4} (at 600 — 770°), and 4.6×10^{-5} (at 1000 — 1200°). For NaH_2PO_4 and K_2SiO_3 fluidity varies linearly with sp. vol. except at low temp., where the slight curvature indicates some association. $NaPO_3$ is unassociated. R. S. B.

Vapour pressure of krypton. E. JUSTI (*Physikal. Z.*, 1935, **36**, 571—574).—The v.p. of Kr between 73.33° and 121.16° abs. has been determined. The triple point is $116.11 \pm 0.10^\circ$ abs. and 522.2 mm. The b.p. is $120.86 \pm 0.10^\circ$ abs. The sublimation curve is of the form $\log p = A + B/T + C/T^2 + D/T^3$, A , B , C , and D being const., the vals. of which are given. The form of the sublimation curve excludes the possibility of any allotropic changes in Kr over the temp. range considered. A. J. M.

Comparison of physical properties of hydrogen and deuterium bromides. J. R. BATES, J. O. HALFORD, and L. C. ANDERSON (*J. Chem. Physics*, 1935, **3**, 531—534; cf. this vol., 1064).—The absorption spectra of HBr and DBr have been measured. The frequency difference between their absorption curves is approx. three times as great as can be accounted for by zero-point energy differences. Reasons for this effect are discussed. The v.p. curves are almost identical (b.p. of DBr 206.3° , triple point 185.7°). The heat of vaporisation of DBr is 4258 g.-cal. The effect of the substitution of D for H on Trouton's const. is discussed. H. J. E.

Physical properties of compressed gases. V. Joule-Thomson coefficient for nitrogen. W. E. DEMING and (MRS.) L. S. DEMING (*Physical Rev.*, 1935, [ii], **48**, 448—449; cf. A., 1934, 247).—Previously reported vals. of μ (cf. A., 1931, 553) are corr. const. contours are shown on a p - t diagram. The inversion temp. for zero pressure is approx. 326° . N. M. B.

Joule-Thomson effect in nitrogen. J. R. ROEBUCK and H. OSTERBERG (*Physical Rev.*, 1935, [ii], **48**, 450—457; cf. this vol., 22).—Data for the isenthalpic curves are given and plotted. Vals. of the Joule-Thomson coeff. over the field -150° to 300° and 1 — 200 atm. are calc., plotted, and tabulated as functions of pressure and temp. The inversion curve and C_p data for the pressure and temp. range are given. N. M. B.

New kinetic theory of gases. I. I. RABI (*Rev. Sci. Instr.*, 1935, [ii], **6**, 251—253).—A brief review.

Experimental confirmation of the new theory of the equation of state. W. JACZYNA (*Z. Physik*, 1935, **96**, 119—136; cf. this vol., 1198).

A. B. D. C.

Structure of liquids and the mechanism of viscosity. W. K. LEWIS and L. SQUIRES (*Refiner Nat. Gas Mfr.*, 1934, **13**, 448).—A qual. explanation is given of the effect of mol. wt. and mol. structure on volatility, b.p., liquid d , and on η . CH. ABS. (e)

Viscosity of liquid helium. J. O. WILHELM, A. D. MISENER, and A. R. CLARK (*Proc. Roy. Soc.*, 1935, **A**, **151**, 342—347).—The change in the viscosity of liquid He with temp. has been measured between 4.2° and 2.0° abs. A marked change occurs at 2.19° abs. as the liquid changes from He I to He II. The results suggest that the difference of the two liquid states is intimately concerned with a difference of at. arrangement. L. L. B.

Viscosity data for boron trioxide. G. S. PARKS and M. E. SPAGHT (*Physics*, 1935, **6**, 69—71).—The η of B_2O_3 glass at 267 — 443° varies from 2.1×10^{11} to 2.1×10^5 poises. A val. of 10^{13} — 10^{14} poises is associated with the transition region in glassy materials. CH. ABS. (r)

Viscosity of molten salts. I. V. IPATOV (*J. Phys. Chem. U.S.S.R.*, 1934, **5**, 790—792).—The relation between η and sp. vol. (v) is given for molten NaCl and KNO_3 to $\pm 2\%$ by $\eta = C/(v - \omega)$, where C and ω are for the two salts, respectively, 0.000654 , 0.6080 ; 0.00095 , 0.5036 in the temp. ranges 816 — 997° and 318 — 542° (cf. Dantuma, A., 1928, 1208). CH. ABS. (e)

Diffusion equation with consideration of molecular velocity. B. I. DAVIDOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **2**, 474—478).—Mathematical. W. R. A.

Diffusion of heavy water into ordinary water. M. TEMKIN (*Nature*, 1935, **136**, 552).—Contrary to the results of ORR and Thomson (this vol., 25), the diffusion const. of D_2O is of the expected order of magnitude. L. S. T.

Time variation of gas emission from heated wires in vacuo. G. EURINGER (*Z. Physik*, 1935, **96**, 37—52).—Time variation of H_2 emitted from heated Ni has been determined, and follows diffusion laws; the solubility at 40 mm. and 800° is 0.196 c.c. of H_2 (0° and 760 mm.) per c.c. Ni, and the diffusion coeff. is 1×10^{-7} cm.² per sec. A. B. D. C.

Rate of diffusion of deuterium hydroxide in water. W. J. C. ORR and J. A. V. BUTLER (*J.C.S.*, 1935, 1273—1277).—Measurements have been made of the diffusion coeff. (D) of DOH (about 3%) in

H₂O between 0° and 45°, and from the results an estimate is made of the rate of self-diffusion in H₂O. In neutral solutions the effect of the mobility of the H⁺ ions is probably negligible. This effect should be detectable in *N*-acid solution, but is obscured by a decrease of *D* caused by the electro-striction of H₂O by the ions. O. J. W.

Formation of drops in supersaturated vapour of heavy water. L. TRONSTAD and H. FLOOD (Nature, 1935, 136, 476).—Measurements of the crit. degree of expansion for D₂O–H₂O mixtures with and without an electric field give a val. of 4.5 for the crit. supersaturation of D₂O at 264° abs. To agree with Volmer's theory of nuclei formation, γ for D₂O must be > the val. given by Selwood and Frost (A., 1933, 1233). L. S. T.

Alloys of lithium with mercury and indium. G. GRUBE and W. WOLF (Z. Electrochem., 1935, 41, 675–681).—The compounds Li₆Hg, Li₃Hg (m.p. 375°), Li₂Hg, LiHg (m.p. 590°), LiHg₂, and LiHg₃ are reported. The compound LiIn (m.p. 625°) forms a continuous series of solid solutions with Li.

E. S. H.

β -Transformation in copper alloys. I. OBINATA (Kinzoku, 1934, 4, 289–291, 333–335).—A $\beta \rightarrow$ transformation occurs in the systems Cu–Zn, Cu–Sn, and Cu–Al. There is a eutectic transformation in the β -phase resembling the Al transformation of steel, a metastable intermediate phase being formed. In the Cu–Zn system the β -phase is stable at room temp., but the eutectic transformation may occur below room temp. Ch. Abs. (c)

Arsenic-lead alloys. O. BAUER and W. TONN (Z. Metallk., 1935, 27, 183–187).—The system has been investigated up to 30% As; alloys containing more As cannot be prepared by melting at atm. pressure. At the eutectic (2.6% As and 290°) the Pb retains 0.045–0.05% As in solution; the solubility of As in Pb decreases rapidly with fall in temp. and is < 0.01% at 20°. Since the primary crystals of hypereutectic alloys are almost pure As the solubility of Pb in solid As is practically nil. No segregation occurs in hypoeutectic alloys, but the As tends to rise to the surface in hypereutectic alloys. The *d* of alloys with 0–5% As decreases linearly with increase in As. The Brinell hardness of the cast alloys rises slowly with > 0.1% As up to 9 at the eutectic composition, but that of alloys quenched from 280° reaches 9 at 0.03% As and 12 at 0.06–3.5% As; after ageing for 6 weeks at 20°, the hardness of the quenched alloys falls considerably owing to pptn. of As from solid solution. Addition of As to Pb has no effect on its rate of corrosion in H₂O. A. R. P.

Transformations in irreversible iron-manganese alloys. E. SCHEIL (Arch. Eisenhüttenw., 1935–1936, 9, 115–116).—Recorded irregularities in the dilatometric curves for low-C alloys of Fe with 7–12% are shown to be due to the ϵ - γ transformation. On cooling these alloys, the effects of the γ - α (expansion) and of the γ - ϵ (contraction) changes mask one another to a considerable extent. In the 20% Mn alloy the ϵ - γ transformation occurs at 250° and the α - γ at 560° on heating, and the γ - ϵ at 80° on cooling. A. R. P.

Magnetic susceptibility of some alloys of "γ-brass" structure. C. S. SMITH (Physics, 1935, 6, 47–52).—Changes in diamagnetic susceptibility with composition are recorded for the γ -brass phases of the systems Cu–Zn, Cu–Cd, Ag–Zn, and Ag–Cd. The limits of existence of the γ -phase agree with those determined otherwise. Ch. Abs. (e)

Mutual solubility of heavy water and organic liquids. J. TIMMERMANS and G. POPPE (Compt. rend., 1935, 201, 524–527).—Replacement of H₂O by D₂O in the system H₂O–PhOH increases the crit. solution temp. (*C*) by 12.25°. For MeCN the corresponding increase is 6.5°, whilst for NEt₃ the lower *C* is depressed by 3.8°. The upper *C* for PrCO₂H and H₂O is raised 23.45° by replacing H₂O by D₂O. H. J. E.

Dependence of mist absorption by liquids on the bubble size. II. H. REMY and W. SEEMAN (Kolloid-Z., 1935, 72, 279–291; cf. this vol., 1067).—The regularities formerly described are complicated when the bubble size is altered by varying the diameter of the leading tube. An important factor influencing the amount of absorption is the time of formation of the bubbles. E. S. H.

Solubility equilibria of sodium sulphate at temperatures of 150° to 350°. I. Effect of sodium hydroxide and sodium chloride. W. C. SCHROEDER, A. GABRIEL, and E. P. PARTRIDGE (J. Amer. Chem. Soc., 1935, 57, 1539–1546).—Solubility data for Na₂SO₄ and NaCl in H₂O are recorded and the solid phases in equilibrium with aq. Na₂SO₄ indicated. Addition of NaOH decreases the solubility of Na₂SO₄ at 150–250°, but increases it at 300–350°; addition of NaCl decreases the solubility of Na₂SO₄ at 150–300°, but causes a slight increase at 350°. In mixtures of NaOH and NaCl, each constituent exerts its effect on the solubility of Na₂SO₄ independently of the presence of the other. E. S. H.

Solubility of alkali chlorides in liquid ammonia and their influence on each other's solubility. G. PATSCHEKE and C. TANNE (Z. physikal. Chem., 1935, 174, 135–155; cf. A., 1933, 456).—The solubility of KCl in liquid NH₃ is small and falls with rise of temp.; the eutectic point is –77.2°. No solid compounds are formed. The solubility is considerably increased by the presence of NH₄Cl or NaCl. Data for the system NaCl–NH₄Cl–NH₃ at –10°, 0°, and 10° are recorded; moderate amounts of NH₄Cl increase the solubility of NaCl. The solubility of NH₄Cl has been determined at –53° to 37°. NaCl crystallises from solutions in NH₃ containing KCl or NH₄Cl in octahedra truncated by cube faces. R. C.

Solubility of strong, highly soluble electrolytes in methyl alcohol- and hydrogen peroxide-water mixtures at 25°. G. ÅKERLOF and H. E. TURCK (J. Amer. Chem. Soc., 1935, 57, 1746–1750).—Data for NaCl, KCl, NaNO₃, KNO₃, KBr, KI, K₂SO₄, NH₄Cl, and Pb(NO₃)₂ in MeOH–H₂O and for NaCl, KCl, NaNO₃, KNO₃, K₂SO₄, KClO₄, and NaF in H₂O₂–H₂O are recorded. The influence of changes in the dielectric const. is discussed. E. S. H.

Determination of the solubility of acetophenone and chloroacetophenone in several solvents.

V. A. KIREEV, S. I. KAPLAN, and K. I. VASNEVA (J. Phys. Chem. U.S.S.R., 1934, 5, 739—741).—Data are recorded for the solubility of CPhMe in C_6H_6 (I) and EtOH at -15° to 20° , and for $CH_2Cl-CPh$ in C_6H_6 (II), EtOH, CPhMe (III), and CCl_4 at -23° to 53.5° . The systems (I), (II), and (III) show eutectics at -15° , -1.6° , and 5.9° (57, 76, and 70% of solute), respectively. CH. ABS. (e)

Solubility and surface tension. V. K. SEMEN-TSCHENKO (Uspekhi Khim., 1934, 3, 710—751).—Using the Boltzmann principle and the idea of generalised moments, solubility and surface tension are explained on a common basis. Data for the systems $Pr^bOH-NaCl-H_2O$, $iso-C_5H_{11}OH-(CH_2OH)_2-H_2O$, and $PrOH-NaBr-H_2O$ are discussed.

CH. ABS. (e)

Arbitrarily induced crystallisation of melts. C. WEYGAND (Z. anorg. Chem., 1935, 224, 265—272; cf. Meyer *et al.*, this vol., 811).—The influence of temp., pressure (rubbing, scratching, etc.), and nuclei on the nature of substances crystallising from melts is discussed in the light of the available data.

T. G. P.

Solubility of hydrogen in molten aluminium. L. L. BIRCUMSHAW (Trans. Faraday Soc., 1935, 31, 1439—1443).—The vols. at n.t.p. of H_2 dissolved by 100 g. of Al at 700° , 800° , 900° , and 1000° are respectively 0.23, 0.89, 1.87, and 3.86 c.c. The calc. heat of dissolution, assuming the H to be dissolved as atoms, is 43.4 kg.-cal. per mol.

F. L. U.

Hydrogen in palladium. J. FRANCK (Physical Rev., 1934, [ii], 45, 290).

L. S. T.

Permeability of palladium to hydrogen. V. Influence of temperature. Experiments with commercial and pure palladium. Permeability at low temperatures. V. LOMBARD and C. EICHNER (Bull. Soc. chim., 1935, [v], 2, 1555—1577; cf. A., 1934, 250, 497, 1302).—The vol. (c.c.) of H_2 which diffuses per hr. through 1 sq. cm. of Pd 1 mm. thick can be expressed by $V-AT^{\frac{1}{2}}e^{-B/T}$ at $250-650^\circ$. For a commercial sample of Pd A and B were found to be 27.75 and 2165 as compared with 9.55 and 1279 for pure Pd. The diffusibility is reduced to 1/2000 on cooling from 225° to 125° , and a delay in recovery occurs on reheating. Variable results were obtained at $180-190^\circ$.

J. W. S.

Adsorption of hydrogen. T. D. PHILLIPS (Physical Rev., 1934, [ii], 45, 215).—The rate of adsorption of H_2 by charcoal at liquid air temp. depends on the time which elapses between the outgassing and the commencement of adsorption. The results support the view that physical adsorption consists of the formation of concentric rows of adsorbed mols. (cf. A., 1931, 1005).

L. S. T.

Sorption of hydrogen in tungsten. W. FRANKENBURGER and R. HODLER (Naturwiss., 1935, 23, 609).—The sorption of H_2 by W powder at -80° to -10° and 60° to 180° has been regarded as an example of "activated adsorption," but since the phenomenon is dependent on the time which elapses between the outgassing and the adsorption, on the thermal treatment of the W, and on the type of apparatus used, other factors must be considered. The phenomenon

of "activated adsorption" completely disappears when the W is carefully purified, but reappears when traces of org. vapours (tap-grease etc.) and O_2 are admitted. Neither the org. compounds nor the O_2 alone restore the effect. The phenomena mistaken for "activated adsorption" are due to self-purification of the metal, traces of oxide oxidising the adsorbed org. mols.

A. J. M.

Adsorption of hydrogen by iron synthetic ammonia catalysts. P. H. EMMETT and R. W. HARKNESS (J. Amer. Chem. Soc., 1935, 57, 1631—1635).—Determinations of the rates and amounts of adsorption as a function of pressure (25—760 mm.) and temp. (-195° to 450°) indicate the existence of two types of activated adsorption, (a) above -90° , (b) above 100° , in addition to the usual physical adsorption. Both types appear to be due in part at least to adsorption on the surface rather than to activated diffusion into cracks or to dissolution within the lattice.

E. S. H.

Diffusibility of deuterium in metals. T. FRANZINI (Atti R. Accad. Lincei, 1935, [vi], 21, 577—580).—Further evidence is provided to show that H occluded by Pd is removed by the application of an electric field (cf. A., 1934, 949). There is no analogous effect with D.

O. J. W.

Sorption of gases by titania gel. I. Relation between the condition of preparation and the sorptive power of the gel. I. HIGUTI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 853—861).—The concn. of the Ti salt solution and the nature, concn., and rate of addition of the precipitant used in preparing TiO_2 gel by coagulation do not greatly affect the adsorptive power of the gel for SO_2 at 0° and 1 atm., but $SO_4^{''}$ is better than Cl' . The presence of a little Fe_2O_3 increases the activity. No difference is shown by gels made by dehydration of α - and β -titanic acids.

J. W. S.

Effect of temperature on selective adsorption by silica gel from binary mixtures. M. R. A. RAO (J. Indian Chem. Soc., 1935, 12, 371—378; cf. A., 1930, 1109; 1931, 1006).—The selectivity of the adsorption by SiO_2 gel from each of the binary mixtures (i) $C_6H_6-C_2H_6$, (ii) $EtOH-C_6H_6$, and (iii) $C_5H_5N-H_2O$ over the entire ranges of concn. decreases by sp. amounts as the temp. is raised from 30° to 98° , but the point of zero selectivity is unchanged in the S-shaped curve of system (iii). Systems (i) and (ii) give U-shaped selectivity curves, and an equation is deduced consistent with the results.

J. G. A. G.

Adsorption of sodium hydroxide and sodium carbonate by aluminium hydroxide. I. I. ISKOLIDSKI and B. V. GROMOV (Legk. Metal., 1934, 3, No. 9, 29—39).—The size of the Al_2O_3 particles pptd. by adding CO_2 to Na_3AlO_3 solutions (80 g. of Al_2O_3 per litre) is greatest when pptd. at 25° or 50° ; with 300 g. of Al_2O_3 per litre the max. size occurs at 75° . The $[Na_2O]$ in the ppt. increases with $[Al]$, temp., time of contact of ppt. with solution, and with the presence of $CO_3^{''}$ and HCO_3' in the solution.

CH. ABS. (e)

Sorption of water vapour on cellulosic materials. E. FILBY and O. MAASS (Canad. J. Res.,

1935, **13**, B, 1—10).—Sorption and desorption measurements have been carried out in an all-glass apparatus free from stopcocks and Hg. Data are given for standard cellulose, white spruce, bleached surgical cotton, Kodak rag cellulose, and bleached sulphite pulp. R. S.

Phenomena of hygroscopicity. P. DEMOUGIN (*Chim. et Ind.*, 1935, **34**, 517—525).—A review.

H. J. E.

Behaviour of water held in fine-pored media. B. H. WILSDON, D. R. G. BONNELL, and (Miss) M. E. NOTTAGE (*Trans. Faraday Soc.*, 1935, **31**, 1304—1312).—The force of retention of H_2O by kaolin, ball clay, puzzuolana, sand, and carborundum has been determined at 20° by four methods. In all cases, the vals. calc. from the osmotic data are very much $>$ the vals. from the hydrostatic experiments. This and other anomalies may be due to mol. orientation effects in thin liquid films occurring in fine-pored systems. J. G. A. G.

Sorption in an ideal soil. W. O. SMITH (*Physical Rev.*, 1934, [ii], **45**, 767).—The sorption of vapour is discussed. During dehydration, saturation can exist at a v.p. $<$ that which prevails when the soil is hydrated. Hydration from complete dryness to saturation, and the reverse process with dehydration, are followed, and the intersections of the two curves determined. Hysteresis occurs during the absorption cycle. Surface adsorption is important only when the grains approach colloidal size. L. S. T.

Fine structure of wood. II. Vapour-pressure lowering of different liquids on their adsorption by wood and lignin. H. SAECHTLING and H. ZOCHER (*Kolloid-Z.*, 1935, **72**, 336—345; cf. this vol., 165).—The v.-p. isotherms of C_6H_6 , Et_2O , and $COMe_2$ are of one type, and those of $MeOH$ and H_2O are of another type, independently of the adsorbent. Lignin adsorbs preferentially Et_2O and $COMe_2$; wood adsorbs preferentially $MeOH$ and H_2O . E. S. H.

Inner adsorption in salt crystals. D. BALAREV (*Z. anal. Chem.*, 1935, **102**, 241—262; cf. this vol., 819).—The influence of all relevant factors on the purity of analytical ppts. is discussed in the light of the author's theory of inner adsorption. The greater unsaturation obtaining at the edges of crystallites is held to counterbalance the increased solubility of small particles, so that this attains a min. for particles of a certain size (unit crystallites). The law of const. proportions can be true only in the limit for pptd. cryst. substances. J. S. A.

Activated adsorption. J. B. ZELDOVITSCH (*J. Phys. Chem. U.S.S.R.*, 1934, **5**, 924—925).—A discussion. CH. ABS. (e).

Thermodynamic foundations of the adsorption of gaseous mixtures. I. R. KRITSHEVSKI (*J. Phys. Chem. U.S.S.R.*, 1934, **5**, 742—749).—Theoretical. It is shown that when one gas is only slightly adsorbed, the adsorption of the second may be increased. The behaviour of $O_2 + CO_2$ towards SiO_2 gel is discussed. CH. ABS. (e)

Cathode-ray oscillography of gas adsorption phenomena. I. Method for measuring high-

velocity approach to certain physical and chemical equilibria. II. Duration of an adsorbed state of oxygen on tungsten. M. C. JOHNSON and F. A. VIELS (*Proc. Roy. Soc.*, 1935, **A**, 151, 296—307, 308—316).—I. By connecting the plates of a cathode-ray oscillograph across a high resistance carrying a thermionic current from a filament, before, during, and after exposure of the latter to an adsorbable gas, photographic traces are obtained recording the progress of any gas reactions which modify the electron emission from a solid surface. A new time control is described, and an analysis is made of the transient thermal and pressure instabilities which occur when gas is admitted to a high vac., or the temp. of a solid is suddenly raised.

II. The above method has been used to determine the average time interval (τ) between deposition and re-evaporation of O_2 on W at high temp. A linear relation is maintained between $\log \tau$ and $1/T$, from which the val. $147,000 \pm 3000$ g.-cal. per g.-atom is calc. for the heat of evaporation. The val. of τ increases from 0.36 sec. at 2548° abs. to 3.49 sec. at 2362° abs. The val. 8×10^{-14} sec. is calc. for the τ_0 of Frenkel's theory, which supports the suggestion that τ_0 is closely associated with the period of vibration of an atom in the metal lattice. L. L. B.

Adsorption theory of electrokinetic potential. A. MARCH (*Trans. Faraday Soc.*, 1935, **31**, 1468—1478).—Reasons are given for regarding the total p.d. (ϵ) between a colloidal particle and the dispersion medium as composed of a part ζ (electrokinetic) and another part ($\epsilon - \zeta$) which are independent and have different origins. The general behaviour of ζ is adequately accounted for on the basis of the unequal adsorption of ions, and its order of magnitude can be correctly calc. from experimental data. F. L. U.

Surface chemistry. N. K. ADAM (*Nature*, 1935, **136**, 499—500). L. S. T.

Surface energy experiment. J. R. CALDWELL (*J. Chem. Educ.*, 1935, **12**, 444—445).—The spontaneous emulsification of castor oil in H_2O and the spontaneous dispersion of rosin in H_2O are described. L. S. T.

Surface tension and solvation. H. G. TRIE-SCHMANN (*Z. physikal. Chem.*, 1935, **B**, **29**, 328—334).—The surface tension, γ , of binary mixtures of alcohols with org. liquids indicates that solutes with little or no tendency to solvation give non-linear γ -concn. curves. The degree of curvature may serve as a measure of solvation. Inorg. salts are surface-inactive in aq. solution owing to the heavy ionic hydration. Introduction of a double linking into a solute in a polar solvent depresses the surface activity. In polar solvents solute mols. which have a strongly polarisable residue as well as a polar group, or which are dipole-free but easily polarised, are surface-inactive. R. C.

Surface tensions of ternary solutions. I. Surface tensions of aqueous solutions of (a) sodium and potassium chlorides, (b) sodium chloride and hydrochloric acid. II. Surface tensions of (a) ethyl alcohol-water-salt mix-

tures, (b) acetic acid-water-salt mixtures. J. W. BELTON (Trans. Faraday Soc., 1935, 31, 1413—1419, 1420—1425).—I. The variation of surface tension (σ) with concn. has been determined for aq. solutions of NaCl, KCl, HCl, NaCl-KCl, and NaCl-HCl. The changes in σ produced by the mixtures are approx. additive. The surface adsorption of H_2O is calc. by Gibbs' equation.

II. In presence of aq. EtOH (2 mol.-%) σ diminishes, linearly at first, with increase of [salt], whilst it increases in presence of AcOH (0.35 mol.-%). The results are discussed in relation to Gibbs' equation.

F. L. U.

Titration of some substances affecting the surface tension of water. E. ANGELESCU and N. MAZILU (Bull. Soc. Chim. Romania, 1935, 17, 151—176; cf. A., 1930, 692).—The point of inflexion in the surface tension-titration curve of cresols with NaOH and $Ba(OH)_2$ approximates to the equivalence point only in dil. solutions. No point of inflexion is obtained with NH_3 . The titration of toluidines with strong acids gives accurate vals., but weak acids show no inflexion owing to hydrolysis. Assuming that the change in surface tension is due only to adsorbed mols., dissociation consts. have been calc. These are abnormally low because of strong adsorption in the dil. solutions.

R. S.

Superficial salting-out by electrolytes. I. Superficial salting-out and dielectric constant. V. K. SEMENTSCHENKO and E. A. DAVIDOVSKAJA. II. **Dependence on temperature.** V. K. SEMENTSCHENKO and A. F. GRATSHEVA (Kolloid-Z., 1935, 73, 24—30, 30—35).—I. The surface tensions, γ , of solutions of isoamyl alcohol in (a) H_2O and (b) $(CH_2OH)_2$, in presence and in absence of NaBr, have been determined. In both solvents at a certain concn. of isoamyl alcohol γ is independent of [NaBr]. The variation of this crit. concn. with the dielectric const. of the solvent is discussed.

II. Measurements of γ for BuOH solutions in H_2O containing NaBr show that the [BuOH] at which γ becomes independent of [NaBr] increases with rise of temp. In the system H_2O -NaBr-BuOH at 0°, 20°, and 40°, the surface activity, G , is related to [NaBr], C_e , by the expression $G = G_0 + \alpha \sqrt{C_e^3}$, where G_0 is the surface activity in absence of electrolyte and α const.

E. S. H.

Mutual interaction of liquid films. J. DON and J. HARRISON (Kolloid-Z., 1935, 72, 257—261).—Oleic acid in contact with acid $KMnO_4$ gives a film, which is characteristically altered by the presence of many org. compounds. The changes produced by the addition of human blood sera have been examined photomicrographically. Sera which show the Wassermann reaction cause a marked change in the film, but the effect is not sp. for syphilitic sera.

E. S. H.

Laminar systems. II. Kinetics of the formation of uni- and multi-molecular layers of cupric sulphide at the surface of copper sulphate solutions. S. G. MOKRUSCHIN and N. M. DEM-JANOVA (Kolloid-Z., 1935, 72, 261—267; cf. this vol., 161).—The influence of concn. of reagents and duration of reaction has been studied, and an equation for the rate of growth of the film developed. CuS films of

thickness 60—80 Å. are impermeable to H_2S . The thickness of the unimol. layer is calc. as 3.23 Å.

E. S. H.

Theory of flotation. P. SIEDLER (Z. physikal. Chem., 1935, 174, 73—76).—Polemical against Ostwald (this vol., 1201).

R. C.

Electro-osmosis at certain porcelain diaphragms. J. VELÍŠEK and A. VASIČEK (Chem. Listy, 1935, 29, 250—253).—Measurements of the conductivities of 0.0000216—0.2N-KCl on both sides of a porcelain diaphragm indicate the validity of Ohm's equation, $V = Il/\lambda q$ (V = p.d., I = intensity of current, λ = actual conductivity within diaphragm), showing that the resistance of the diaphragm remains const. over the range of concns. studied.

R. T.

Electro-endosmosis. VII. Measurements with non-aqueous liquids and high voltages. H. P. DAKIN, F. FAIRBROTHER, and A. E. STUBBS (J.C.S., 1935, 1229—1233).—The electro-endosmosis of a no. of alcohols and ethers through a diaphragm of sintered Jena glass powder has been measured with applied voltages (E) up to nearly 6000 volts per cm. At low voltages the relation between E and velocity of flow of the liquid is linear, or nearly so, but departs to an increasing degree at high E . A continuous photographic method of recording the rate of electro-endosmosis is described, which permits observations to be made of high speeds over a short time and of any change of speed during a run. The electro-endosmotic flow attains a const. speed within a very small fraction of a sec. after E is applied.

O. J. W.

Osmotic pressures of a mixed vapour. [EARL OF] BERKELEY (Phil. Mag., 1935, [vii], 20, 481—504).—Mainly mathematical. Since satisfactory membranes are not available for the investigation of mixed vapours, the pressure of the pure vapour in osmotic equilibrium with the mixed vapour cannot be determined experimentally. Methods for calculating this quantity are considered.

N. M. B.

Compressions and specific volumes of aqueous solutions of resorcinol and methyl alcohol at 25° and the behaviour of water in these solutions. R. E. GIBSON (J. Amer. Chem. Soc., 1935, 57, 1551—1557).—The apparent compression of resorcinol (I) varies linearly with $\sqrt{\text{concn.}}$. The apparent vols. of (I) and the apparent compressions and vols. of MeOH in aq. solution bear a less simple relation to concn. The effect of concn. on the partial vols. of the components indicates that MeOH and (I) promote the association of H_2O . The sp. compressions (up to 1000 bars) of all MeOH- H_2O mixtures from 0 to 15% are the same as for H_2O . The compressions of pure MeOH determined at various pressures up to 1000 bars do not agree with published vals.

E. S. H.

Viscosity of dilute solutions of non-electrolytes. B. PRASAD (J. Indian Chem. Soc., 1935, 12, 499—503).—The viscosities of dil. aq. solutions of sucrose, fructose, and glucose have been determined. The results can be represented by $\eta/\eta_0 = 1 + \alpha C$, where α is independent of temp., but changes with the solute.

R. S.

Properties of higher polymerides in solution.
II. Viscosity of solutions of aliphatic hydrocarbons. K. H. MEYER and A. VAN DER WYK (Helv. Chim. Acta, 1935, 18, 1067—1079).—Measurements of η in CCl_4 solution are recorded for 7 saturated hydrocarbons between $\text{C}_{17}\text{H}_{36}$ and $\text{C}_{34}\text{H}_{70}$. For solutions containing 0.886% of solute $\eta_{\text{sp.}} \times 10^5 = 195.6n - 1421$, where n = no. of C atoms in the chain. Data for *iso*- and *cyclo*-paraffins and other long mols. are recorded. The val. of η is determined by the constitution as well as by the length of the mol.

H. J. E.

Effect of pressure on the refractive index of aqueous solutions of ethyl alcohol. F. E. POINDESTER and J. S. ROSEN (Physical Rev., 1934, [ii], 45, 760).—From 1 atm. to 1800 kg. per sq. cm. $n = a + bp + cp^2 + dp^3$, the coeffs. of which are tabulated for the Hg arc lines 4060, 4360, 5460, and 5790 Å.

L. S. T.

Dielectric behaviour of dilute binary solutions. F. E. HOECKER (Physical Rev., 1934, [ii], 45, 741).—Dil. solutions of EtOH in CCl_4 , C_6H_6 , and CS_2 exhibit the usual anomalous behaviour of polar liquids in non-polar solvents at low concns. By considering the dissolved solute as a vapour occupying the entire vol. of the solution, the effect is shown to be probably fictitious.

L. S. T.

Frictional dispersion of polar solutions with short electric waves. W. MÜLLER (Ann. Physik, 1935, [v], 24, 99—112).—The dielectric const. (ϵ) of a 10 vol.-% solution of PhNO_2 in paraffin and in Shell oil (I) have been determined for λ 60 cm. and at 2—40°. For the solution in (I) ϵ varies considerably with temp., since the frequency for this solution falls within the range of frictional dispersion. The relaxation time and transport coeff. (α) have been determined.

A. J. M.

B.-p. elevation in solutions of potassium iodide in ethyl alcohol. J. N. PEARCE and M. L. McDOWELL (Proc. Iowa Acad. Sci., 1933, 40, 93—94).—The b.-p. elevation-molality curve follows closely that of a normal undissociated solute. The activities and free energy relations are calc.

CH. ABS. (e)

Vapour pressure of phosphoric acid solutions. I. A. KABALUKOV and K. I. ZAGVOSDKIN (Z. anorg. Chem., 1935, 224, 315—321; cf. this vol., 694).

T. G. P.

Viscosity of electrolytes in aqueous solution and the lyotropic numbers. J. H. C. MERCKEL (Kolloid-Z., 1935, 73, 67—75).—Viscosity determinations for aq. solutions of a large no. of salts of alkali and alkaline-earth metals show that for a given cationic or anionic series there is a linear relation between η and the lyotropic no. of the ion. The results are discussed in relation to the determination of degrees of hydration.

E. S. H.

Determination of dielectric constants of aqueous solutions of strong electrolytes by means of a high-frequency bridge. E. FISCHER (Physikal. Z., 1935, 36, 585—593).—A high-frequency bridge for use with solutions of electrolytes over the frequency range 10^6 — 10^7 is described. Solutions of NaCl, Na_2SO_4 , $\text{Ca}(\text{NO}_3)_2$, MgSO_4 , CaSO_4 , CdSO_4 ,

and $\text{Ba}_2\text{Fe}(\text{CN})_6$ were used, and give results agreeing in general with the Debye-Falkenhagen theory, although deviations occur at the higher concns. ($>0.002N$), the dielectric const. being $<$ that required by theory. With smaller frequencies ($\lambda=300$ m.) there are no deviations.

A. J. M.

Faraday effect of strong electrolytes in aqueous solutions. II. A. OKAZAKI (Mem. Ryojun Coll. Eng. Inouye Comm. Vol., 1934, 209—212; cf. A., 1934, 723).—Vals. of Scharf's "corr." sp. rotation are recorded for aq. HCl, LiCl, NaCl, and KCl.

CH. ABS. (e)

Observation of the Brownian movement with the unaided eye. E. KAPPLER (Physikal. Z., 1935, 36, 643—646; cf. this vol., 699).—The effect observed with the unaided eye is attributable to a variation of brightness and colour of the surface elements of the prep. and is not due to Brownian movement. The conditions under which the phenomenon is observed indicate that it is an interference effect.

A. J. M.

Preparation of mercury sols by reduction. E. SAUER and D. STEINER (Kolloid-Z., 1935, 73, 42—44).—Hg sols may be prepared from aq. HgCl_2 by reducing with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in presence of NaOH and gum arabic. Under similar conditions $\text{Hg}(\text{NO}_3)_2$, $\text{Hg}(\text{ClO}_4)_2$, and $\text{Hg}(\text{CN})_2$ do not give stable sols of Hg. The conditions for formation of a stable sol are (1) slight dissociation of Hg^{++} and (2) ability to form colloidal Hg_2O as an intermediate.

E. S. H.

Determination of particle size of silicic acid in a silicic acid glycerosol. F. ERBE (Kolloid-Z., 1935, 73, 1—14).—The properties of $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ sols in aq. glycerol have been investigated. The mean particle diameter has been determined by ultramicroscopy (<160 m μ), ultrafiltration (>30 m μ), centrifuging (<42 m μ), diffusion in porous glass discs (>57 m μ), and diffusion in agar gels (45 m μ).

E. S. H.

(A) Electrical charges of disperse systems forming the seats of physico-chemical reactions.
 (B) Mechanism of division of small liquid systems. II. Instability of two-phase systems. N. RASHEVSKY (Physics, 1935, 6, 33—34, 35—37).—(A) A discussion of the factors which affect an ionic reaction occurring within a liquid drop.

(B) Theoretical. A discussion of the conditions of stability of two concentric spherical drops, when an ionic reaction occurs only in the external phase.

CH. ABS. (e)

Diffuse dispersion of light in white, non-metallicsols. G. P. LUTSCHINSKI (Kolloid-Z., 1935, 73, 39—42).—The distribution of intensity in the incident and scattered light has been studied with sols of AgCl and colophony. A modification of Lambert's formula is proposed.

E. S. H.

Viscosity and plasticity of disperse systems.
 VI. Influence of temperature and electrolytes on the plastic properties of kaolin. M. VOLAROVITSCH and D. M. TOLSTOI. VII. Investigation of plastic flow. D. M. TOLSTOI (Kolloid-Z., 1935, 73, 92—96, 96—101; cf. this vol., 932).—VI. Between 10° and 57° the flow resistance θ of kaolin- H_2O mix-

tures is independent of temp.; η does not decrease with rising temp. so markedly as in the case of H_2O . Increase of $[\text{NaOH}]$ (0.0096—0.96%) diminishes the plastic const.; increase of $[\text{NaCl}]$ (1—7%) increases η and decreases θ slightly.

VII. Apparatus and technique for the determination of flow-resistance are described. E. S. H.

Highly-polymerised compounds. CXVII. Classification of colloids. H. STAUDINGER. **CXVIII. Viscosity of organic spheroidal and linear colloids.** H. STAUDINGER and E. HUSEMANN (Ber., 1935, 68, [B], 1682—1691, 1691—1697).—CXVII. Colloids are subdivided into those with spherical particles solutions of which obey Einstein's law and can only have low viscosity and conform to the Hagen-Poiseuille law, and those with extended particles (linear colloids) solutions of which exhibit deviations from the above laws. Characteristic of the latter is their ability to form gel solutions. It is further deemed advisable to classify colloids according to their chemical as well as their physical properties, and thus to distinguish between inorg. colloids, mainly elements, or their heteropolar compounds, and org. colloids the variety of which is due to the homopolar C-C and C-H linking. Org. colloids are further subdivided into micellar colloids with spherical particles including suspensoids and emulsoids of org. substances in suitable media (a micelle is defined as a no. of small mols. held together by van der Waals forces) and micellar colloids with rod-like particles such as solutions of soap in H_2O and many org. media. The most important group of org. colloids is that of the mol. colloids which includes the complex natural products. These are arranged into mol. colloids with spherical particles, illustrated by a series of albumins, but not hitherto obtained synthetically, and mol. colloids with thread-like mols. The homopolar subdivision of the latter class is subdivided into hemicolloids of mol. wt. about 10,000 and chain length 50—250 Å. which give sol solutions, are powdery or sticky when solid, yield films of little tenacity, and dissolve without swelling, mesocolloids of chain length about 250—2500 Å., and eucolloids with chain length > 2500 Å. which are characterised by forming gel solutions. The heteropolar mol. colloids are similarly subdivided, but in consequence of the action of the thread ions the colloidal phenomena are far more complex than with the homopolar division. Mol. colloids with thread mols. are also classified according to their limited or unlimited swelling ability.

CXVIII. Re-calculation of η_{sp}/c for suspensions of latex and S sols gives the theoretical val. 0.025 if the concn. is not too great; this val. is also shown by solutions of glucose, galactose, maltose, lactose, sucrose, erythritol, and mannitol in H_2O at 20°, of glucose penta-acetate in COMe_2 , and *m*-cresol, of $(\text{CH}_2)_6\text{N}_4$ in CHCl_3 , and of CPh_3Cl in CCl_4 . Polystyrene latex is obtained by heating an emulsion of styrene in Na oleate solution at 30—100° for 2—6 days. From it, polystyrene can be pptd. by acids, EtOH, or COMe_2 , and after reprecipitation from C_6H_6 by EtOH or COMe_2 forms a fibrous mass similar to a eupolystyrene prepared from pure styrene at low

temp. Since the mol. wts. of the two products are closely similar, emulsion-polymerisation affords a ready method of rapidly obtaining eucolloids. The η_{sp}/c val. of the synthetic latex is about 0.025, is independent of the particle size of the latex droplets and of the mol. wt. of the polystyrenes from which the droplets are derived, and is const. over a relatively large range of concn. As spherocolloid, the latex obeys Einstein's law. On the other hand, the sp. viscosity of similarly conc. solutions of polystyrenes in C_6H_6 varies greatly with the length of the dissolved thread mols. Similar results are obtained with an emulsion-polymerisate of vinyl acetate and butyrate. Latex emulsions do not show deviations from the Hagen-Poiseuille law, and an evaporated latex can be emulsified in H_2O without swelling. Solutions of linear colloids do not obey this law, and show macromol. viscosity phenomena. Linear colloids usually dissolve with marked swelling. H. W.

Dielectric investigations of benzene solutions of ethyl- and benzyl-cellulose. I. SAKURADA and S. LEE (Kolloid-Z., 1935, 72, 320—325).—Dielectric const. and d have been determined at different temp. and concn. The mol. polarisation of ethylcellulose varies greatly with concn., and the val. of the dipole moment varies with temp. E. S. H.

Structure of cellulose nitrate solutions. S. A. GLIKMAN (J. Phys. Chem. U.S.S.R., 1934, 5, 885—893).—Solutions of cellulose nitrate (I), acetate, or benzoate, which have macro- or microscopic aggregates, do not obey Poiseuille's law. Ca^{++} adsorbed on (I) increases η , but Na^+ does not. With increasing [(I)] the ζ -potential decreases; it is lowered by Ca salts or acids and raised by alkalis. The η of various fractions obtained by partial pptn. are not always in the same order as the particle size. CH. ABS. (e)

Stability of silver iodide sols. G. N. GORODVOSKI and J. R. PROTASS (Z. physikal. Chem., 1935, 174, 122—134).—The stability in presence of excess of I^- or Ag^+ has been examined by measuring the light scattering power of the sol. The isoelectric point is at 4.2—5.5, depending on the concn. of the sol. At η 2.5—3.25 and p_i 2.75—3.0 the stability is a max. The points of max. stability correspond with saturation of the inner coating of the double layer with Ag^+ and I^- , respectively; further increase in the concn. of excess electrolyte probably consolidates the diffuse coating and thus lowers the ζ -potential. Foreign cations which do not obey the Paneth-Fajans rule have an influence on the stability very similar to that of Ag^+ and I^- ; this suggests that the influence is a pure adsorption effect. These conclusions have been tested by ζ -potential measurements. Th^{+++} is able to charge AgI positively. R. C.

Coagulation of organosols of cellulose nitrate by electrolytes. I. S. PAKOV (Kolloid-Z., 1935, 73, 82—84).—High concns. of FeCl_3 and ZnCl_2 are required to coagulate sols of cellulose nitrate in COMe_2 . The process is complicated by the action of the hydrolysis products of the electrolytes. E. S. H.

Upper stability limit of drops in collision. S. V. GORBATSCHEV and V. M. NIKIFOROVA (Kolloid-

Z., 1935, 73, 14—20).—Studies of collisions between H_2O droplets in air show that when the velocity of collision is between 0.1 and 1.5 m. per sec. the droplets neither coalesce nor disintegrate. The dependence of the crit. velocity for disintegration on the angle of collision and the influence of surface-active substances have been determined. The crit. velocity increases as the size of the droplets decreases. E. S. H.

Lower stability limit of drops in collision. S. V. GORBATSCHEV and E. R. MUSTEL (Kolloid-Z., 1935, 73, 20—24; cf. preceding abstract).—The lower limiting velocity at which droplets of H_2O in air coalesce on collision has not been determined accurately, but is about 6.4 cm. per sec. for droplets of about 1 mm. diameter. This val. is not altered by the presence of surface-active substances. E. S. H.

Action of water and alkali on the coagulation of albumin. J. L. DONNELLY (Kolloid-Z., 1935, 73, 76—82).—Attention is directed to the different behaviour of diluted albumin on coagulation. It is recommended that tests be carried out with the original substance. E. S. H.

Cryolysis, diffusion, and particle size.—See this vol., 1276.

Chemical and physical characteristics of water contained in colloidal substances. I. Some organic colloids. II. Some inorganic colloids. L. PASSERINI (Gazzetta, 1935, 65, 518—528, 529—533).—I. The infra-red absorption spectra between 0.8 and 2 μ of org. gels and sols (gelatin, agar-agar, sol. starch, egg-albumin, dextrin, and gum arabic) have been examined. In the gels the H_2O bands are appreciably displaced (up to $5 \times 10^{-2} \mu$) towards longer λ compared with those of pure H_2O . This displacement is the larger the higher is the concn. of the gel. A parallelism between the amount of displacement and certain physical properties of the gel, e.g., rigidity, is indicated. With sols the displacement of the H_2O bands ($1-2 \times 10^{-2} \mu$) is appreciable only with the more viscous preps., e.g., natural albumin and 60% gum arabic.

II. Infra-red absorption spectra of gels of opal, $Si(OH)_4$, $Sn(OH)_4$, $Al(OH)_3$, $Ti(OH)_4$, $ZnHAsO_4$, $MnHAsO_4$, $FePO_4$, and $NiHPO_4$ have been measured. Except in the case of opal and of an aged $Si(OH)_4$ gel, the spectra are similar to that of pure H_2O . The state of the H_2O in the various substances is discussed. O. J. W.

Structure of rigid gels, such as that of silicic acid. W. O. SMITH (Physical Rev., 1934, [ii], 45, 748).—Theoretical. L. S. T.

Properties of gels. N. A. YAJNIK, D. N. GOYLE, J. D. VERMA, and C. L. RAMPAL (Kolloid-Z., 1935, 73, 57—67).—Velocity of gelation, surface tension, elasticity, d , velocity of sound, resistance to cutting, loss of liquid on heating, diffusion of solutions, transparency, light absorption, and surface reflexion of light have been studied for gels of Sn phosphate, SiO_2 , agar, Th phosphate, Mn arsenate, and cellulose acetate. E. S. H.

Influence of ultrasonic waves on the colloid solubility of metal hydroxides. I. N. SATA and

S. WATANABE (Kolloid-Z., 1935, 73, 50—57).—The peptisation of $Fe(OH)_3$ (prepared from $FeCl_3$ and aq. NH_3) is increased under the influence of ultrasonic waves; peptisation occurs in the almost complete absence of electrolytes. The solid-phase rule appears to hold good and the sols thus formed are more sensitive to coagulation by electrolytes than those prepared by other methods. E. S. H.

Iodine-amylum reaction. G. VAN ITERSOM, jun., and J. COUMOU (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 700—705).—The temp. of gelation of starch solutions is raised by adding aq. I and lowered by aq. KI. A suspension of starch in 10% aq. KI, saturated with I, cannot be brought to gelation even at the b.p. E. S. H.

Chemical reactions between colloids. II. Mercury and sulphur. E. SAUER and D. STEINER (Kolloid-Z., 1935, 73, 45—47; cf. this vol., 1074).—When sols of Hg and S are mixed and excess of S is removed by extraction with conc. aq. Na_2SO_3 , the residue consists of HgS . E. S. H.

Sedimentation thixotropy of stabilised suspensions. N. JERMOLENKO (Kolloid-Z., 1935, 72, 312—320).—The stability of suspensions of CuO in dil. aq. NH_3 , and of Ni_2O_3 and Fe_2O_3 in dil. aq. HCl has been investigated. The stability is at a max. when a medium amount of solid phase is present; the max. is const. after repeated shaking. The conditions existing at the surface of the particles are reviewed in the light of recent theories. E. S. H.

Extension of theory of complex coacervation to ionic disperse systems. H. R. KRUYT and H. G. B. DE JONG (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 714—721).—An intermediate stage in the separation of solid from certain supersaturated aq. electrolyte solutions is described; it is analogous to the complex coacervation observed when two oppositely-charged hydrophilic sols are mixed. E. S. H.

Lyophilic colloids. VIII (2). Interaction of agar fractions. S. M. LIEPATOV and A. A. MOROSOV (Kolloid-Z., 1935, 72, 325—335; cf. this vol., 932).—Fractionation of agar by progressive washing shows that the more insol., highly associated fractions are stabilised by the more sol. fractions. The sol. fractions also influence the swelling and peptisation of the more insol. fractions, and reduce the viscosity. E. S. H.

Inductive precipitation and dissolution processes in which ferric and chromic salts participate. Z. KARAOGLANOV and B. SAGORTSCHEV (Kolloid-Z., 1935, 72, 291—301).—When aq. solutions containing $Fe(NO_3)_3$, $Cr(NO_3)_3$, and NH_4OAc are boiled, colloid systems are formed; their properties vary with the ratio $Fe:Cr$. The pptd. product contains $Fe(OH)_3$, $Cr(OH)_3$, and OAc' . E. S. H.

Humic acids. I, II. W. SCHEEL, W. SCHULZE, and H. SPANDAU (Kolloid-Z., 1935, 72, 301—312; 73, 84—90).—I. The equiv. wt. of humic acid, prepared from different sources by different methods, has been determined by conductometric and potentiometric methods. The results for the different preps. are all about 150. In spite of the agreement in equiv. wt., it is believed that there is a variation in mol. wt.

II. Na humate is decomposed by excess of aq. NaOH, especially in hot solution, with the formation of one or more H_2O -sol. products having acidic properties. E. S. H.

Periodic phenomena in colloidal systems. P. F. MICHALEV (J. Phys. Chem. U.S.S.R., 1934, 5, 820—823).—Periodic layers are formed by the diffusion of sols of $Fe(OH)_3$, gum mastic, As_2S_3 , and Au into $EtOH$, $(CH_2OH)_2$, Et_2O , Bu^oOH , allyl alcohol, and $COMe_2$. CH. ABS. (e)

Morphology of chemical reactions in gels. VIII. Effect of acids and alkalis on Liesegang rings and the "radial rosette," and some observations in the absence of gels. F. M. SCHEMJAKIN (J. Phys. Chem. U.S.S.R., 1934, 5, 755—762).—Liesegang ring formation in gelatin has been studied with $K_2Cr_2O_7$, $NaCl+0.0005M-H_2SO_4$, $KCNS$, and $KCNS+0.00005M-H_2SO_4$ as the inner and $AgNO_3$ as the outer electrolyte. Diffusion rosettes are obtained, without gelatin, from $UO_2(NO_3)_2$, or $CuSO_4$, and $NaOBz$ (I). $AgNO_3$ and (I), $KCNS$, or HCl give periodic structures. $UO_2(OAc)_2$ with (I) or Na salicylate gives rings only in absence of gelatin. Addition of H_2SO_4 or KOH changes considerably the shape of the ring formation in all cases. CH. ABS. (e)

Precipitation of *l*-, *dl*-, and *m*-cystine by phospho-12-tungstic acid.—See this vol., 1356.

Phosphatide auto-complex coacervates as ionic systems and their relation to the protoplasmic membrane. H. G. B. DE JONG and J. BONNER (Proc. R. Akad. Wetensch. Amsterdam, 1935, 38, 797—806).—The characteristics of auto-complex coacervates of phosphatides are described. Interaction of the phosphatide ions in the coacervate is determined by (a) electrostatic attraction due to oppositely-charged, ionised groups, (b) repulsion due to hydration, and (c) attraction due to "lipophilic" groups. The phosphatide ions in the surface of the coacervate are oriented with their polar groups inwards and their hydrocarbon chains outwards. It seems probable that, when two such oriented films meet, a highly stable double film is produced. The special properties of the protoplasmic membrane may depend on the existence of such a double film. E. S. H.

Electric streaming potential in turbulent flow. H. REICHARDT (Z. physikal. Chem., 1935, 174, 15—21).—It is deduced theoretically that flow in the electric double layer remains viscous, and Helmholtz' streaming potential equation therefore remains valid, even when flow within the tube is turbulent. Experiment shows that the ratio of streaming potential to pressure head is const., independent of the type of flow. R. C.

Relation between particle size and cataphoretic mobility. I. KEMP (Trans. Faraday Soc., 1935, 31, 1347—1357).—The mobilities, U , of SiO_2 and gamboge particles in 10^{-2} — $10^{-4}N$ -Na K acetate buffers at const. ionic strengths vary little with changes of p_H , showing that p_H has little effect on the surface charge density of the particles. In 10^{-2} — $10^{-5}N$ -KCl, U decreases with decrease of radius of particle and

the slope of the curve relating U to radius (0.1 — 1.0μ) increases as $[KCl]$ decreases. The results agree with the predictions of Henry's formula (A., 1931, 1232) within the limits of experimental error ($\pm 5\%$). J. G. A. G.

Microscopical observation of the electrophoresis of dyes, bacteria, blood corpuscles, etc. with Cellophane as semi-conductor. H. H. WAELSCH (Kolloid-Z., 1935, 73, 36—39).—The migration of the individual particles in liquid drops, hanging from the semi-conductor, has been observed. E. S. H.

Equilibrium between *n*-propyl alcohol, propyl ether, and water at 190° .—See this vol., 1349.

First ionisation constant of carbonic acid, 0° to 38° , from conductance measurements. T. SHEDLOVSKY and D. A. MACINNES (J. Amer. Chem. Soc., 1935, 57, 1705—1710).—Determinations of the conductance of aq. H_2CO_3 and $KHCO_3$ yield the ionisation const. 4.31×10^{-7} at 25° and 4.82×10^{-7} at 38° . The calc. heat of ionisation at 25° is 2075 g.-cal. E. S. H.

Thermodynamic ionisation constants of carbonic acid at 38° from electromotive force measurements. D. A. MACINNES and D. BELCHER (J. Amer. Chem. Soc., 1935, 57, 1683—1685).—The vals. 4.91×10^{-7} and 6.25×10^{-11} have been obtained for the first and second dissociation consts., respectively. E. S. H.

Activity coefficients of HCO_3' ions. Y. KAUKO and J. CARLBERG (Z. Elektrochem., 1935, 41, 721—724).—Measurements of p_H lead to a val. which is in good agreement with published work. E. S. H.

Ionisation constant of acetic acid in methyl alcohol-water mixtures from 0° to 40° . H. S. HARNED and N. D. EMBREE (J. Amer. Chem. Soc., 1935, 57, 1669—1670).—E.m.f. of the cells $H_2|AcOH(m_1), NaOAc(m_2), NaCl(m_3)|AgCl|Ag$ in 10% and 20% aq. MeOH have been determined at 10° intervals from 0° to 40° . From these and electrode potential data the ionisation const. of AcOH has been calc. Log. K is approx. \propto the reciprocal of the dielectric const. E. S. H.

Electron-sharing ability of organic radicals. IX. Dissociation constants of amines and acids in ethyl alcohol. L. D. GOODHUE and R. M. HIXON (J. Amer. Chem. Soc., 1935, 57, 1688—1691; cf. A., 1934, 868).— K is determined for AcOH, $n-C_6H_4Me \cdot CO_2H$, $BzOH$, $p-C_6H_4Br \cdot CO_2H$, $m-C_6H_4Cl \cdot CO_2H$, NH_2Bu , $o-C_6H_4Cl \cdot CH_2 \cdot NH_2$, $p-C_6H_4Me \cdot NH_2$, NH_2Ph , and $m-C_6H_4Cl \cdot NH_2$ in EtOH, using a H_2 electrode. The $Hg-HgI_2$ half-cell is a suitable reference electrode for MeOH or EtOH solutions. R. S. C.

Apparent dissociation constants of canavanine and canaline. T. TOMIYAMA (J. Biol. Chem., 1935, 111, 45—49; cf. A., 1933, 1059).—The titration curves of canavanine (I) and canaline (II) are determined with the glass electrode and the p_H , and free energy change of ionisation are calc. The basic group of (I) lies between those of the guanidine group of arginine and the glyoxaline group of histidine.

The basic character of (II) apart from the α -NH₂ is very weak. H. D.

Polyvanadates existing in alkaline solution. H. BRINTZINGER and J. WALLACH (Z. anorg. Chem., 1935, 224, 103—106).—Determination of ionic wts. from the rate of electrodialysis in alkaline Na₃VO₄ solutions of varying p_H indicates the existence of the following ions. From p_H 14.0 to 12.2, V₂O₇⁴⁻ or [VO₃(H₂O)₆]³⁻; p_H 11.0 to 10.0, [V₂O₇(H₂O)₆]⁴⁻ or V₃O₁₀⁵⁻; p_H 8.8 to 7.0, V₄O₁₃⁶⁻. J. S. A.

Molybdate and tungstate ions in solutions of varying hydrogen-ion concentration. H. BRINTZINGER and C. RATANARAT (Z. anorg. Chem., 1935, 224, 97—102).—Ionic wt. determinations by the method of electrodialysis in solutions of Na₂MoO₄ of varying p_H show the uniform presence of MoO₄²⁻ at p_H 8.0 to 7.0, and of [Mo₆O₂₀]⁴⁻ or [Mo₆O₂₁]⁶⁻ at p_H 5.0 to 1.5. Between p_H 7 and 5 two or more species coexist. Potentiometric titration confirms the ionic wt. measurements and indicates the existence of trimolybdate between p_H 5.2 and 6.3. Aq. Na₂WO₄ similarly contains the ion WO₄²⁻ at p_H 7.5—8.0, and [W₆O₂₀]⁴⁻ or [W₆O₂₁]⁶⁻ at p_H 6.0—7.0. At p_H 4.5 a dodecatungstate [W₁₂O₃₈] or [W₁₂O₃₉] is present. J. S. A.

Interpretation of the dissociation pressures of the palladium-hydrogen system. M. H. HEY (J.C.S., 1935, 1254—1258).—An equation is derived from simple kinetic considerations which gives a satisfactory account of the dissociation pressures of the Pd-H system, on the assumption that there is only one phase present throughout. The limiting composition of the system is PdH, which possibly has a NaCl type structure. O. J. W.

Lower sulphides of palladium. Equilibrium diagram of system Pd-PdS. F. WEIBKE and J. LAAR [with K. MEISEL] (Z. anorg. Chem., 1935, 224, 49—61).—Thermal analysis, coupled with micrographic and X-ray examination, shows that the only lower sulphide stable at room temp. is Pd₄S. A solid β -phase stable at high temp. undergoes peritectic decomp. at 554° into Pd₄S + PdS (m.p. of PdS, 970°). With < 69.5 at.-% Pd, two liquid phases occur. S is insol. in solid Pd. J. S. A.

Equilibrium of Fe₃O₄, Fe₂O₃, and oxygen. J. W. GREIG, E. POSNJAK, H. E. MERWIN, and R. B. SOSMAN (Amer. J. Sci., 1935, [v], 30, 239—316; cf. A., 1931, 310).—Hematite (I) containing < 1% of Fe₃O₄ in solid solution coexists in stable equilibrium with solid solutions of magnetite (II) containing approx. 30%, 24.5%, and 13% of Fe₂O₃ at 1452° ± 5, 1388° + 3, and 1200°, respectively, in presence of O₂ at 1 atm., 159 mm., and approx. 2 mm., respectively. In a sealed SiO₂ tube, (I) coexists with (II) containing 8.5% and 16.8% of Fe₂O₃ at approx. 1085° and 1300°, respectively. The m.p. of Fe₃O₄, 1591° ± 5 under low p_{O_2} , is depressed by increasing p_{O_2} and O₂ is absorbed. A eutectic between (I) and (II) (solid solution) is inferred. The relation between temp. and composition of (II) in equilibrium with O₂ at 1 atm. and 159 mm. has been determined at 1400—1565°. The pressure-temp. relations are illustrated by a diagram, and certain optical and crystallographic data are recorded. J. G. A. G.

Systems BeSO₄-H₂O and BeSO₄-H₂SO₄-H₂O. L. SCHREINER and A. SIEVERTS (Z. anorg. Chem., 1935, 224, 167—172).—Ice and BeSO₄·4H₂O coexist at the eutectic (27% BeSO₄, -18°). Isotherms at 0°, 25°, 50°, and 75° for BeSO₄-H₂SO₄-H₂O suggest that BeSO₄·4H₂O and possibly anhyd. BeSO₄ are stable solid phases. T. G. P.

Application of the thaw-melt method to binary inorganic systems. A. BENRATH, P. HARTUNG, and M. WILDEN (J. pr. Chem., 1935, [ii], 143, 298—304).—The nitrate hexahydrates of Co, Ni, Mg, and Mn form mixed crystals in all proportions with one another, and that of Zn forms unstable 1:1 compounds with the others. The nitrate tetrahydrates of Zn and Co form mixed crystals. Co(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O give a eutectic. The tetra- and hexa-hydrates of the same nitrate give peri-eutectics, and the m.p. of the tetrahydrate is only slightly depressed by small additions of the hexahydrate. This is best explained by assuming that the melt of the hexahydrate contains both hydrates and H₂O in equilibrium. This assumption agrees with a max. m.p. in mixtures of Ni(NO₃)₂·6H₂O and Zn(NO₃)₂·4H₂O, which presumably give an equilibrium of the hexa- and tetra-hydrates of each salt in the melt. Systems containing AgNO₃ or NH₄NO₃ form eutectics and afford evidence of 1:1 compounds. The perchlorate hexahydrates of Ni, m.p. 209°, Co, m.p. 191°, Mg, m.p. 193°, Mn, m.p. 153°, and Zn, m.p. 163° (cf. lit.), form mixed crystals in all proportions. The system Mg(ClO₄)₂·6H₂O-Ni(NO₃)₂·6H₂O is characterised by a eutectic. R. S. C.

Systems alkaline-earth chloride-alkaline-earth oxide and the decomposition of alkaline-earth chlorides by steam. B. NEUMANN, C. KROGER, and H. JUTTNER (Z. Elektrochem., 1935, 41, 725—736).—Equilibrium data are recorded for the systems SrCl₂-SrO, BaCl₂-BaO (800—1300°), and CaCl₂-CaO (600—1300°). The existence of 4SrCl₂·SrO, SrCl₂·2SrO, BaCl₂·2BaO, BaCl₂·3BaO, and 4CaCl₂·CaO has been established. Steam begins to decompose SrCl₂ at 950°, BaCl₂ at 910°, and CaCl₂ at 780°. The reactions have been studied over a range of temp. and are discussed in relation to the equilibrium diagrams. E. S. H.

Effect of pressure on phase equilibria of sodium tungstate and related thermodynamic properties. R. W. GORANSON and F. C. KRACEK (J. Chem. Physics, 1935, 3, 546; cf. this vol., 447).—A correction. H. J. E.

Cryoscopic investigation of anomalies in the behaviour of ethylene chloride. H. HUETTIG, jun., and C. P. SMYTH (J. Amer. Chem. Soc., 1935, 57, 1523—1526).—F.-p. data give no evidence of compound formation in the system C₂H₄Cl₂-C₆H₆, but indicate the existence of an unstable compound C₂H₄Cl₂·3Et₂O. E. S. H.

Heterogeneous equilibria in two-component systems with thymol as one component. K. HRYNAKOWSKI and M. SZMYT [with S. KUROWSKI, R. PERTKIEWICZ, J. MARCZUK, M. NIKLEWICZ, and (MLES.) H. PRZEDPELSKA, W. JURKOWSKA, and E. NIZIOLEKIEWICZ] (Arch. Pharm., 1935, 273, 418—

427).—M.p. have been determined for mixtures of thymol (I) with $\text{CO}(\text{NH}_2)_2$ (43°; 95.5%), NHPhAc (16.5°; 65%), PhOH (6.7°; 37.5%), $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (46.2°; 96.2%), and salol (15.6°; 37.5%), the figures in parentheses being the m.p. and % of (I) for the eutectic mixtures. (I) and antipyrine probably form a 1:1 compound. (I) with 30–70% of camphor has m.p. < –15° and is probably associated in the mixtures. R. S. C.

Molecular compounds in the systems acid-salt, anhydride-salt, acid-ester (acetic, butyric, phenylacetic acids). M. BAKUNIN and E. VITALE (*Gazzetta*, 1935, 65, 593–616).—Thermal diagrams have been obtained for the following binary systems: $\text{AcOH}\cdot\text{MOAc}$ ($\text{M}=\text{K}, \text{Na}$); $\text{Pr}^n\text{CO}_2\text{H}\cdot\text{Pr}^n\text{CO}_2\text{Na}$; $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{M}$ ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Ba}$, various radicals); $(\text{CH}_2\text{Ph}\cdot\text{CO})_2\text{O}\cdot\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{M}$ ($\text{M}=\text{Na}, \text{Li}$). Several mol. compounds are recorded. The influence in the Perkin synthesis of compound formation and of the nature of the metal or radical which replaces the carboxylic H is discussed. O. J. W.

System water-potassium chloride-cupric chloride. A. CHRETIEN and R. WEIL (*Bull. Soc. chim.*, 1935, [v], 2, 1577–1591).—The system has been studied between –65° and 121.5°. $\text{KCl}\cdot\text{CuCl}_2$ is stable between 119.9° and 59°, but at 75° and below it has not a congruent solubility. The compound $\text{CuCl}_2\cdot\text{KCl}\cdot 2\text{H}_2\text{O}$ occurs at 50° and below, but without congruent solubility. $\text{CuCl}_2\cdot 2\text{KCl}\cdot 2\text{H}_2\text{O}$ occurs between 92° and –63.2° without congruent solubility. The ternary eutectic corresponding with $\text{CuCl}_2\cdot\text{KCl}\cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, and ice is reached at –65° and contains 39.9% CuCl_2 and 0.20% KCl . J. W. S.

System $\text{NH}_4\text{Cl}\cdot\text{NH}_4\text{NO}_3\cdot\text{H}_2\text{O}$ at 0.4°, 25°, and 50°. C. F. PRUTTON, J. C. BROSEER, and S. H. MARON (*J. Amer. Chem. Soc.*, 1935, 57, 1656–1657).—No evidence of the formation of complex salts, solid solutions, or hydrates has been obtained. E. S. H.

System potassium fluoborate-potassium periodate-water at 35°. R. C. RAY and H. C. MITRA (*Trans. Faraday Soc.*, 1935, 31, 1312–1314).—The solubility data show that no double salt is formed. It is suggested that IO_4^- is too large to replace BF_4^- in the lattice of KBF_4 . J. G. A. G.

System alkali oxide- $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{CO}_2$. IV. CO_2 pressure of the silica-rich portion of the system $\text{Li}_2\text{O}\cdot\text{SiO}_2\cdot\text{CO}_2$ and the action of alumina on lithium carbonate. C. KROGER and E. FINGAS (*Z. anorg. Chem.*, 1935, 224, 289–304; cf. this vol., 935).—Pressure-temp. diagrams for the systems $\text{Li}_2\text{O}\cdot\text{SiO}_2\cdot\text{CO}_2$ and $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{CO}_2$ have been derived from a study of the reactions between Li_2CO_3 and (a) $\text{Li}_2\text{O}\cdot\text{SiO}_2$ mixtures and (b) Al_2O_3 . From the temp. dependence of the equilibria, heats of reaction and heats of formation of the silicates and aluminates are calc. T. G. P.

Ternary system stannous oxide-sulphur trioxide-water. H. G. DENHAM and W. E. KING (*J.C.S.*, 1935, 1251–1253).—The existence of the following solid phases has been established: $\text{SnSO}_4\cdot 2\text{SnO}\cdot 4\text{H}_2\text{O}$ at 25°; $\text{SnSO}_4\cdot 2\text{SnO}\cdot 2\text{H}_2\text{O}$ at 50°;

and SnSO_4 (cf. A., 1926, 587) at both temp. The solubility data at 25° and 50° afford no evidence of a hydrated normal sulphate. O. J. W.

Solid-liquid equilibria in ternary systems in which congruently melting binary compounds are formed. II. K. HRYNAKOWSKI and M. SZMYT (*Z. physikal. Chem.*, 1935, 174, 60–72; cf. this vol., 825).—The equilibrium diagrams for the systems salicylic acid- $\text{CO}(\text{NH}_2)_2\cdot\text{NHPhAc}$ and $\text{CO}(\text{NH}_2)_2\cdot\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}\cdot\text{NH}_2\text{Ac}$ have been obtained. R. C.

Equilibrium between cobalt aquopentammine sulphate and its sulphuric acid solution at 45°. O. T. LIU and S. M. WANG (*Contr. Inst. Chem. Nat. Acad. Peiping*, 1934, 1, 49–101; *Bull. Nat. Acad. Peiping*, 1934, 5, No. 5, 15–67).—From analytical data for the solid residue and mother-liquor the composition of the solid phases in equilibrium with various $[\text{H}_2\text{SO}_4]$ is deduced. CH. ABS. (c)

Equilibrium: $\text{NaCl(s)} + \text{NaHSO}_4\text{(s)} \rightleftharpoons \text{Na}_2\text{SO}_4\text{(s)} + \text{HCl(g)}$. F. ISHIKAWA, K. MASUDA, and T. TAKAI (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 833–843).—From measurements of the equilibrium pressure of this reaction the following data are deduced for 1 atm. pressure: $\Delta H_{25^\circ}^\circ = -10.45$ kg.-cal. The temp. coeffs. are also derived. For the reactions $\text{S} + \text{Na} + 0.5\text{H}_2 + 2\text{O}_2 = \text{NaHSO}_4\text{(s)}$, $2\text{NaHSO}_4\text{(s)} = \text{Na}_2\text{S}_2\text{O}_7\text{(s)} + \text{H}_2\text{O(g, 1 atm.)}$, and $2\text{S} + 2\text{Na} + 3\frac{1}{2}\text{O}_2 = \text{Na}_2\text{S}_2\text{O}_7\text{(s)}$ $\Delta F_{25^\circ}^\circ = -235,508$, 8950, and –407,560 g.-cal., respectively. The pressure at 100° decreases with increasing $[\text{Na}_2\text{SO}_4]$, but when the latter is > six times the $[\text{NaCl}]$ the pressure becomes independent of its concn. The velocity of reaction between NaHSO_4 and NaCl and between Na_2SO_4 and HCl follows the law $p = a + b \log t$ (p = pressure, t = time, and a and b are consts.). J. W. S.

Oxidation equilibrium of magnesium chloride. K. SANO (*Sci. Rep. Tohoku*, 1935, 24, 240–249).—The equilibrium const. of $\text{MgCl}_2 + 0.5\text{O}_2 = \text{MgO} + \text{Cl}_2$, determined by passing O_2 over MgCl_2 at 592°, 632°, 652°, and 670°, is given by $\log K_p = -1413/T + 1.93$, whence $\Delta F_{25^\circ}^\circ = 4770$ g.-cal., $\Delta H_{25^\circ}^\circ = 8560$ g.-cal., $\Delta S_{25^\circ}^\circ = 12.71$ g.-cal. per degree. The following vals. for $\text{Mg} + \text{Cl}_2 = \text{MgCl}_2$ are also calc.: $\Delta F_{25^\circ}^\circ = -140,890$, $\Delta H_{25^\circ}^\circ = -151,500$, $\Delta S_{25^\circ}^\circ = -35.60$. J. W. S.

Designation of Nernst's heat theorem as a third law of thermodynamics. H. SCHMOLKE (*Z. Elektrochem.*, 1935, 41, 654–657).—A discussion. E. S. H.

Development of thermochemistry. F. D. ROSSINI (*J. Washington Acad. Sci.*, 1935, 25, 399–403).—Historical. C. W. G.

Ionic activities of hydrochloric acid. Z. SZABO (*Z. physikal. Chem.*, 1935, 174, 22–32).—A method of determining diffusion potentials by measurements with concn. cells with transport is described. For $\text{HCl}|\text{HCl}$ at 25° the diffusion potential is given by the empirical equation $\epsilon = -36.79 \log m$ mv. (m = molality) up to $m = 0.2$. This disagrees with the vals. calc. by Henderson's equation. It is deduced that up to $m = 0.2$ both ionic activity coeffs. are equal to each other and to the mean ionic activity coeff.,

but the vals. differ from those calc. by Lewis and Randall ("Thermodynamics," p. 382). R. C.

Heat of dilution of nitric acid. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1935, 174, 104—114).—The heat of dilution at 20° has been measured from $\text{HNO}_3 \cdot 4.5\text{H}_2\text{O}$ to $\text{HNO}_3 \cdot 3800\text{H}_2\text{O}$. It is so small as to be negligible in practice, and for bomb calorimetry the heat of formation of HNO_3 can be taken as const. = 14.8_8 g.-cal. per millimol. R. C.

Heat of formation of zinc sulphide. Comments on the sodium peroxide method of Mixer. H. ZEUMER and W. A. ROTH (Z. anorg. Chem., 1935, 224, 257—264).—Errors in Mixer's method (A., 1917, ii, 123) are discussed. Previous vals. for heats of formation of metallic oxides obtained by this method are uncertain. $\text{Zn} + \text{S}_{\text{rhomb.}} = \text{ZnS}_{\text{reg.}} + 41.5 \pm 1.5$ kg.-cal. per mol. at 20°. T. G. P.

Heats of formation and dissolution of potassium dithionate. H. ZEUMER and W. A. ROTH (Z. anorg. Chem., 1935, 224, 253—256; cf. this vol., 1078).—Since $\text{K}_2\text{S}_2\text{O}_6 = \text{K}_2\text{SO}_4 + \text{SO}_2 - 5.03 \pm 0.13$ kg.-cal. per mol., the heat of formation of $\text{K}_2\text{S}_2\text{O}_6$ from the elements is 418.9 kg.-cal. per mol. at 20°. The heat of dissolution of $\text{K}_2\text{S}_2\text{O}_6$ is $-13.1(5)$ kg.-cal. per mol. T. G. P.

Heat of formation and specific heat of aluminium nitride. S. SATOH (Bull. Inst. Phys. Chem. Res. Tokyo, 1935, 14, 862—871).—The mean sp. heat of AlN is $0.1803 + 2.750 \times 10^{-4}t - 1.937 \times 10^{-7}t^2$. From this equation and equilibrium data for the system $\text{Al}_2\text{O}_3\text{--C--N}_2\text{--CO--AlN}$ at high temp. the heat of formation of AlN is 74,700 g.-cal. per mol. J. W. S.

Analysis of admissible error in calculating heat of isothermal evaporation of salt solutions relative to pure water. K. P. MISCHTSCHENKO and I. Z. PRONINA (J. Appl. Chem. Russ., 1935, 8, 769—778).—Mathematical. R. T.

Heats of transition of triglycerides. M. M. R. RAO and S. K. K. JATKAR (J. Indian Chem. Soc., 1935, 12, 574—581).—The heats of dissolution of the two forms of tristearin, tripalmitin, and trilaurin have been measured in various org. solvents using a double calorimeter. The difference in the heats of dissolution of the two forms is const. (about 15 g.-cal. per g.) and equal to the difference in the latent heats (heat of transition). The latent heats of fusion of the two forms of tristearin have been measured. O. J. W.

Thermal data. IV. Heats of combustion of adenine, hypoxanthine, guanine, xanthine, uric acid, allantoin, and alloxan. V. Heat capacities, entropies, and free energies of adenine, hypoxanthine, guanine, xanthine, uric acid, allantoin, and alloxan. R. D. STIEHLER and H. M. HUFFMAN (J. Amer. Chem. Soc., 1935, 57, 1734—1740, 1741—1743; cf. this vol., 304).—IV. The heats of combustion determined are: adenine 663.74 ± 0.21 , hypoxanthine 580.20 ± 0.14 , guanine 596.89 , xanthine 516.02 ± 0.36 , uric acid 458.84 ± 0.20 , allantoin 409.55 ± 0.16 , alloxan 273.58 ± 0.16 kg.-cal.

V. Heat capacities of the above substances have been determined over the range 90—298.1° abs., and the entropies and free energies calc. E. S. H.

Electrical conductivity of some strong electrolytes in dilute solution and its variation over the temperature range 18—85°. C. J. B. CLEWS (Proc. Physical Soc., 1935, 47, 818—823).—Work previously described (cf. this vol., 37) is extended to 0.0005*N* solutions of KNO_3 , K_2SO_4 , and Na_2SO_4 . Results support the Debye-Hückel theory of univalent electrolytes. Agreement is less satisfactory for Na_2SO_4 and K_2SO_4 . N. M. B.

Conductivity of strong acids in mixtures of light and heavy water. A. FINK, P. GROSS, and H. STEINER (Monatsh., 1935, 66, 111—118).—The conductivity of HCl and HClO_4 (about 0.01*N*) in H_2O containing 0—97% of D_2O has been measured at 18°, and calc. therefrom. Λ_∞ falls from 377 in H_2O to 250 in 100% D_2O . Reasons for the non-linear variation of Λ with $[\text{D}_2\text{O}]$ are discussed. J. S. A.

Mobility of the hydrogen-ion constituent in aqueous mixtures of hydrogen chloride and calcium chloride at 25°. L. G. LONGWORTH (J. Amer. Chem. Soc., 1935, 57, 1698—1700).—The mobility of H^+ in aq. HCl- CaCl_2 mixtures, of which the total concn. is 0.1*N*, has been calc. from transport and conductance data. The decrease in mobility when HCl is replaced by CaCl_2 is compared with the val. calc. from the interionic attraction theory. E. S. H.

Anomalous forms of ionic movements. D. KREIGHGAUER and F. MÖNCH (Z. Physik, 1935, 96, 107—116).—Current is carried through ZnSO_4 solutions for a time by the Zn ions alone. This is a labile state and passes over to that in which both move; the smaller is the current, the greater the concn., or the higher the temp., the longer is the life of the labile state. A. B. D. C.

Normal potential of the silver-silver iodide electrode from 5° to 40°. B. B. OWEN (J. Amer. Chem. Soc., 1935, 57, 1526—1528).—The normal potential has been obtained without extrapolation by comparing the AgI and AgCl electrodes in NaBO_3 solutions containing the corresponding halide. Results obtained with electrolytic and with fused AgI are practically identical. Determinations of the dissociation const. of HBO_2 agree with previously reported vals. obtained by extrapolation. E. S. H.

Molal electrode potential of the silver-silver chloride electrode in methyl alcohol-water mixtures. H. S. HARNED and H. C. THOMAS (J. Amer. Chem. Soc., 1935, 57, 1666—1668).—E.m.f. of the cells $\text{H}_2|\text{HCl}(m)$ in 10% and 20% aq. MeOH| $\text{AgCl}|\text{Ag}$ have been determined at 5° intervals from 0° to 40°. The v.p. and d of MeOH- H_2O mixtures have been measured over the same range. The mol. electrode potential in 10% aq. MeOH is given by $0.21818 - 555.63 \times 10^{-6}(t-20) - 4.128 \times 10^{-6}(t-20)^2$ and in 20% aq. MeOH by $0.21151 - 529.10 \times 10^{-6} \times (t-20) - 4.706 \times 10^{-6}(t-20)^2$. E. S. H.

Standard electrode potential of lithium in methyl alcohol. A. MACFARLANE and (SIR) H. HARTLEY (Phil. Mag., 1935, [vii], 20, 611—616).—The val. -3.095 volts has been obtained from measurements with amalgam electrodes in the cell

0.35% Li amalgam|LiCl in MeOH|AgClAg. The standard electrode potentials of Li, Na, Tl, H, Ag, I, Br, and Cl in MeOH, EtOH, and H₂O, and the observed and calc. partial molal free energies of transfer of a no. of electrolytes between infinitely dil. solutions in these solvents are given and the limitations of Born's equation for the calculation of free energies of transfer are discussed. N. M. B.

Dependence of the electrochemical properties of an element on the state of aggregation. I. Potential of gallium and gallium amalgam in gallium salt solutions. O. STELLING (Z. Elektrochem., 1935, 41, 712—721).—The behaviour of Ga amalgam electrodes in dil. aq. HCl and NaOH has been studied. Similar experiments with Ga in HCl gave nobler potentials than with the amalgam, but in no case were reversible conditions realised. Passivation readily occurs, particularly with liquid Ga. When a Ga electrode in aq. GaCl₃ is warmed, the potential suddenly becomes somewhat less noble at 29.5°, but at 30° there is a rapid change of about 0.3 volt in the opposite direction; on cooling no essential change occurs at the f.p., but the reverse change of potential takes place suddenly with the solidification of the Ga at about 25°. A max. difference of about 0.4 volt between the potentials of solid and supercooled liquid Ga at the same temp. has been observed. E. S. H.

Theoretical evaluation of electrode potentials. S. MAKISHIMA (Z. Elektrochem., 1935, 41, 697—712).—Theoretical. The thermodynamics of the following cyclic process are discussed: the metal is vaporised, the vapour ionised, the ions are dissolved in a solvent, and the solvated ions brought back to the metal through the electrode process. Formulae are derived for calculating the normal potential of the metal in terms of the energy changes involved in the different stages of these processes. The nature of electrode potential and its relation to the Volta effect and the emission of photo- and thermo-electrons are discussed. E. S. H.

Influence of hydrogen-ion concentration on the potential of African manganese dioxide. N. C. CAHOON (Trans. Electrochem. Soc., 1935, 68, 323—331).—The potential $E_{H^+=0}$ of African MnO₂ in ZnCl₂-NH₄Cl solutions is given by $E_{H^+=0}=1.070-0.0608p_H$ over the range p_H 1—12. Previous failure to obtain a linear relation is due to the presence of HCl in the electrolyte. S. J. G.

Physico-chemical characteristics of the eutectic point. P. Z. FISCHER (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 191—195).—The electrode potentials and rates of dissolution in 4.8*N*- and 6.6*N*-HCl of Cd-Pb, Cd-Bi, Cd-Zn, and Sn-Zn alloys have been determined. Slowly cooled eutectics are always more electropositive than the corresponding mixtures which have been rapidly cooled. Their rates of dissolution in HCl are greater, and the tendency to become passive when used as anode is less. CH. ABS. (c)

Capacity of polarised mercury electrode. P. P. PORFIROV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 542—548).—The polarisation capacity (c) of a Hg electrode has been measured using a.c. and d.c.

simultaneously. c increases with the density of the a.c., the effect of which depends on the p.d. and not on the frequency. The increase in c and decrease in effective resistance give rise to a decrease in H overvoltage. The intermediary resistance (r) has also been measured. It is inferred that r is not the sole cause of H overvoltage, and that the formation of a H envelope, to which r is due, begins at very small cathode polarisation. r decreases with increasing density of the d.c. The max. val. of r corresponds with the beginning of the ascent of the c.d. on the curve c.d.-p.d. R. S. B.

Significance of depolarisation potentials deduced from the current-voltage curves in electrolysis with a dropping mercury electrode. J. HEYROVSKÝ and D. ILKOVIČ (Chem. Listy, 1935, 29, 234—238).—Published data (this vol., 936) are discussed. R. T.

Potential oscillations of iron in nitric acid. II. M. KARSCHULIN (Z. Elektrochem., 1935, 41, 664—667; cf. this vol., 706).—The reddish-brown film, which forms periodically over the surface of Fe in HNO₃ under certain conditions, has been shown by spectrographic observations to consist of Fe[NO](NO₃)₂. E. S. H.

Dissolution of metallic monocrystals. L. E. SABININA and L. A. POLONSKAJA (J. Phys. Chem. U.S.S.R., 1934, 5, 946—953).—During the initial stages of dissolution of a Zn monocrystal in 0.1*N*-H₂SO₄ the potential increases rapidly by about 5%. In *N*-H₂SO₄ it passes through a high max., and then falls rapidly. CH. ABS. (c)

Surfaces of contact between solutions. V. ČUPR (Chem. Listy, 1935, 29, 253—257).—After a short period the sum of the diffusion potentials between the four layers *N*-HCl|0.01*N*-KCl|0.0*N*-HCl+0.005*N*-KCl|*N*-HCl is equal to zero, and remains so for several hr., after which it gradually approaches -1.46 mv., in accordance with the val. calc. from Planck's equation. A theoretical interpretation of the phenomena is given. R. T.

Variation of diffusion potential with concentration. I. Z. SZABÓ (Z. physikal. Chem., 1935, 174, 33—40).—Diffusion potentials at the junctions HCl|HCl and HCl|KCl up to 0.5*M* are, for a fixed concn. on one side, a linear function of the logarithm of the concn. on the other. At the junction between solutions of different concn. of the same electrolyte the potential is independent of the structure of the transition layer and const.; the superposition principle is strictly valid. To obtain steady and reproducible potentials between solutions of different electrolytes the transition layer must have cylindrical symmetry. R. C.

Salt effect of certain indicators in slightly buffered solutions. J. A. DUDYCHA and B. H. PETERSON (Proc. Iowa Acad. Sci., 1933, 40, 97).—The colorimetric and quinhydrone electrode vals. of p_H have been compared for a series of salt solutions. The salts used increase the p_H according to the electrode indications, but reduce it according to the colorimetric observations; the effect is more

pronounced at lower concns. The colorimetric is unchanged at concns. from 1*M* to saturation.

CH. ABS. (e)

Acid-base equilibrium and the Henderson formula. D. VAN SLYKE (Bull. Soc. Chim. biol., 1935, 17, 1184—1186).—Inaccuracy in the p_H determination is the chief source of error in the calculation of the CO_2 pressure by the Henderson formula.

A. L.

Fuel cell working at moderately high temperatures. I. General treatise and preliminary experiments. S. TAMARU and K. OCHIALI. II. **Main difficulties and their elimination.** S. TAMARU and M. KAMADA (J. Chem. Soc. Japan, 1935, 56, 92—102, 103—113).—I. The e.m.f. of the cell at 560—640° is 0.8—0.9 volt, corresponding with $2CuO + C = Cu_2O + CO$. The electrodes are Cu covered with an oxide film, and C, the electrolyte being a mixture of K_2CO_3 , Na_2CO_3 , and KF, NaF, or NaCl.

II. Polarisation at 550—600° can be eliminated by addition of salts of Mn and B as O carriers.

CH. ABS. (e)

Thallous-thallic oxidation-reduction potential. J. R. PARTINGTON and H. I. STONEHILL (Trans. Faraday Soc., 1935, 31, 1357—1371).—Liquid contact potentials etc. are eliminated by extrapolating to $[Tl] = 0$ vals. of the e.m.f. of the cells (i) $Pt|Tl_2SO_4 + Tl_2(SO_4)_3 + H_2SO_4(c)|H_2SO_4(c)|H_2, Pt$, (ii) $Pt|Tl_2SO_4 + Tl_2(SO_4)_3 + H_2SO_4(c) + Hg_2SO_4(sat.)|Hg|Hg_2SO_4(sat.) + H_2SO_4(c)|H_2, Pt$ obtained when c is const., $[Tl]$ is varied, and $[Tl]/[Tl^{III}] = 1.0022$. The extrapolation vals., E' , from (i) and (ii) coincide for each val. of c in the range 1.0—0.0125*M*. By extrapolating a function of E' to $c = 0$, the standard Tl potential, E_0 , at 25° referred to the standard H electrode ($a_H = 1$) is -1.1992 volt, but vals. of a_H , for aq. H_2SO_4 are somewhat untrustworthy. Vals. of a_H calc. from the e.m.f. of the cell $Hg|Hg_2SO_4, H_2SO_4|H_2, Pt$, and data involving liquid junction potentials lead to E_0 1.2207, which is preferred.

J. G. A. G.

Redox potential of glutathione.—See this vol., 1265.

Redox potential of porphyrexide and porphyrindine.—See this vol., 1252.

Electrical activation of passive iron wires in nitric acid. R. S. LILLIE (J. Gen. Physiol., 1935, 19, 109—126).—The electrical behaviour under various conditions is described, and resemblances are found with the electrical stimulation of living tissues.

F. A. A.

Passivity. XXVII. Anodic behaviour of iron in sodium chloride and hydrochloric acid solutions. W. J. MÜLLER and W. MACHU (Z. Elektrochem., 1935, 41, 641—653; cf. this vol., 1079).—Film passivity is observed at all concns., but the current-time curves differ from those for Fe in H_2SO_4 and sulphates. The end-val. is higher throughout, indicating that the film produced in Cl⁻ solutions is more porous than that in SO_4^{2-} solutions. Periodic changes in potential have been observed under certain conditions in NaCl solutions. Observations in the polarisation microscope show the duration of the

primarily-formed salt film to be very short. The influence of concn. and p_H on the passivation time has been investigated. Chemical passivity, involving the entry of Fe^{III} into solution, occurs only at very high c.d. (> 0.5 amp. per sq. cm.), and is never complete; the production of Fe^{III} reaches a max. val. of 55% in saturated aq. NaCl at 0° with a c.d. of 8 amp. per sq. cm. Rise of temp. favours the production of Fe^{III} .

E. S. H.

Passivity of gold. W. J. MÜLLER and E. LOW (Trans. Faraday Soc., 1935, 31, 1291—1299).—Trustworthy vals. for the time of passivation, t , are obtained only with "protected" electrodes which prevent convection etc. Optical methods show that a strongly anisotropic metal surface is laid bare immediately the current, i , is passed through a Au anode in 5*N*-HCl. Such a surface darkens progressively on exposure to air, and t is thereby diminished. The phenomena are due to an oxide film and not to a superficial change in the structure of the Au. When i falls sharply to the val. characteristic of passivity, the diffuse layer of crystals deposited on the Au is transformed into a continuous strongly reflecting layer. The electrode then exhibits alternating periods of passivity and activity, showing that during passivity the oxide film is slowly destroyed. In *N*- and 0.05*N*-HCl, a passivated electrode becomes reactivated only on interrupting the current. Two kinds of oxide layers are inferred: (i) the air-formed layer scarcely sol. in dil. acid, and (ii) the layer produced by chemical passivation and sol. in dil. acid. These results and those of others (cf. A., 1932, 1209; 1933, 1242; this vol., 38) are in accord with the theory of passivation by layers.

J. G. A. G.

Cathode passivity of silver in silver nitrate solution. A. G. SAMARTZEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 478—485).—Experiments on electrolytic crystallisation of Ag from $AgNO_3$ solutions showed that metallic deposition on active portions of the cathode was possible only at definite c.d. The passivation of the Ag surface is due to oxide or adsorption layers.

W. R. A.

Structure of the dielectric in aluminium-electrolyte condensers. A. SIMON and O. JAUCH (Z. Elektrochem., 1935, 41, 739—759).—The oxide film covering the Al surface is porous; the pores penetrate to the bare metal and occupy about 10^{-5} — 10^{-6} of the total surface area. The layer also contains O_2 ; the dependence of the residual current on p.d. and temp. is traced to variations in the velocity of diffusion of O_2 through the pores. The "forming" velocity is independent of the concn. of electrolyte and the temp. Addition of colloids to the electrolyte has a deleterious effect on "forming." The capacity of the condenser varies with the concn. of electrolyte, but the thickness of the oxide layer remains const. A theory of the valve action of this layer is advanced, according to which it offers resistance to anions but not to electrons.

E. S. H.

Primary molecular interaction in chemical kinetics. P. V. ZIMAKOV (J. Phys. Chem. U.S.S.R., 1934, 5, 824—831).—A theoretical review.

CH. ABS. (e)

Spark ignition of low inflammable gas mixtures. III. Influence of presence of nitrogen on the spark ignition of hydrogen-oxygen mixtures. K. YUMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 275—285).—In mixtures with low and const. $[H_2]$, the spark energy required for ignition initially decreases with increasing $[N_2]$ up to 5% N_2 , but at higher $[N_2]$ increases with increasing $[N_2]$. With const. low $[O_2]$ the addition of N_2 decreases the sparking energy required for ignition. Differences exist between the mechanisms of ignition by an ordinary spark and by a capacity spark. J. W. S.

Oxidation and ignition at hot surfaces. PRETTRE (Mem. Poudres, 1934—1935, 26, 239—267).—The homogeneous reaction of a $2H_2 + O_2$ mixture in contact with a hot glass wall covered with KCl is about 0.02 as fast as when it is in contact with a vitreous wall. The chief characteristics of the reaction (high apparent order, accelerating effect of inert gases, and inhibition by the wall) are, however, not appreciably different. The reaction is therefore a chain reaction, as it also is on glass, SiO_2 , and porcelain. KCl cannot be regarded as being more effective than vitreous materials. All of the surfaces promote the formation of active centres, which initiate chains, these not being initiated in the gaseous phase, and KCl forms far fewer chains than the vitreous surfaces. There is therefore a considerable retardation of the reaction and a consequent reduction of the ignition temp. KCl plays a part in the initial stages of the reaction alone. W. J. W.

Ignition temperatures of diethyl ether and ethylene in air and oxygen. G. W. JONES, W. P. YANT, W. E. MILLER, and R. E. KENNEDY (U.S. Bur. Mines Rept. Invest., 1935, No. 3284, 6 pp.).—By the drop method, the min. temp. of inflammation, t , of Et_2O in air is $304\text{--}380^\circ$, depending on the conditions. With O_2 , t is 182° . Et_2O containing 3.5% of $EtOH$ gives slightly higher vals. of t . With 3—38 vol.-% C_2H_4 -air mixtures, t has a min. val., 490° , with 28% of C_2H_4 . Vals. of t by the concentric-tube method (i) are slightly > by the SiO_2 -bulb method (A., 1933, 1249) at low $[C_2H_4]$. The min. val. of t for 3—62.4% C_2H_4 - O_2 mixtures by method (i) is 485° with 34.5% of C_2H_4 . J. G. A. G.

Thermal decomposition of *n*-pentane.—See this vol., 1348.

Rates of reaction of sodium atoms with hydrogen and deuterium chlorides. C. E. H. BAWN and A. G. EVANS (Trans. Faraday Soc., 1935, 31, 1392—1400).—The reactions have been studied by the diffusion flame method and found to proceed at approx. equal rates, although the zero point energies of HCl and DCl differ by 1200 kg.-cal. The activation energies of the reactions differ by 300 kg.-cal., which approx.=the difference in zero point energies of the mols. in the initial and transition states. F. L. U.

Mechanism of reactions between alkali [metal] atoms and halogen hydrides. A. G. EVANS and M. G. EVANS (Trans. Faraday Soc., 1935, 31, 1400—1410; cf. preceding abstract).—The mechanism of reactions of Na and K vapours with HCl, HBr, and

HI is discussed and the calc. and experimental results are compared. F. L. U.

Kinetics of the oxidation of gaseous glyoxal. E. W. R. STEACIE, W. H. HATCHER, and J. E. HORWOOD (J. Chem. Physics, 1935, 3, 551—555).—Oxidation at 220° yielded CO_2 , CO , H_2O , and glyoxylic acid, the proportions changing with the temp. The oxidation is a chain reaction, to which the general mechanism of Steacie *et al.* for the oxidation of gaseous aldehydes is applicable (cf. this vol., 308). The rate was approx. $\propto [C_2H_2O_2]^2$ and was independent of $[O_2]$, provided the latter was in excess of a 1:1 mol. ratio. H. J. E.

Valency chemistry of the phosphorus sulphides. W. D. TREADWELL and C. BEELI (Helv. Chim. Acta, 1935, 18, 1161—1171).—The production of P_4S_5 by Boulouch's method (A., 1904, ii, 253) was confirmed. It is unimol. in CS_2 solution. The heats of formation of P_4S_3 from the elements and of P_4S_7 from P_4S_3 and S were 29.4 and 36.3 kg.-cal., respectively. The reaction of I with P_4S_3 in CS_2 solution is $7P_4S_3 + 24I_2 = 16PI_3 + 3P_4S_7$. That of Br is similar. The potentiometric titration of P, P_4S_3 , and P_4S_7 with 0.1N-KBr-KBrO₃ is described. Vals. for d of P-S melts are recorded. Analyses of the products of acid and alkaline hydrolysis of P_4S_3 , P_4S_7 , and P_4S_{10} are given. The electronic structures are discussed. H. J. E.

Rate of alkaline chlorination of ketones.—See this vol., 1353.

Influence of substituents on energy of activation. D. H. PEACOCK (J.C.S., 1935, 1326).—Polemical (cf. A., 1934, 35). J. G. A. G.

Reaction between potassium permanganate and oxalic acid. O. M. LIDWELL and R. P. BELL (J.C.S., 1935, 1303—1305).—If insufficient or only a small excess of $H_2C_2O_4$ is added to $KMnO_4$ - $MnSO_4$ - H_2SO_4 mixtures, the reaction is not unimol., but there is an initial rapid reaction which gives way abruptly to a slower change, the velocity of which is probably determined by the complex $[Mn(C_2O_4)_3]^{3-}$. The results negative Launer's reaction mechanism (A., 1932, 1002) and indicate that the velocity is independent of $[C_2O_4']$. J. G. A. G.

Kinetics of hypobromite decomposition. C. F. PRUTTON and S. H. MARON (J. Amer. Chem. Soc., 1935, 57, 1652—1655).—In buffered solutions within the range p_H 6.4—7.8, at 25° , the complete rate equation is given by $d[HOBr]/dt = k_3[HOBr]^2[OH]$, where k_3 is 4.4×10^8 when the time is in min. and concns. in g.-mol. per litre. E. S. H.

Influence of temperature on velocity of ionic reactions in aqueous solutions of non-electrolytes. A. VON KISS and I. BOSSANYI (Z. anorg. Chem., 1935, 224, 33—39).—The temp. coeff. of the $CH_3Br \cdot CO_2$ and $S_2O_3^{2-}$ reactions in aq. MeOH, EtOH, PrOH, $COMe_2$, $CO(NH_2)_2$, and sucrose between 15° and 55° decreases with rise in temp., and is lowered by the non-electrolyte \propto [non-electrolyte] except for $CO(NH_2)_2$ and sucrose. The energy of activation calc. from both k and Bronsted's h is lowered $\approx 7\%$ by the presence of non-electrolytes. J. S. A.

Mechanism of reactions in which the reactants diffuse through a membrane. A. VON KISS and A. URMANCZY (Z. anorg. Chem., 1935, 224, 40—48).—The velocity of dialysis of HCl, HNO₃, H₂SO₄, AcOH, and NaOH, in H₂O and neutral salt solutions, $\propto \sqrt{R}$ (R =rate of stirring) for highly permeable membranes, and the rate of neutralisation then $\propto \sqrt[3]{R}$. The rates of dialysis and neutralisation in salt solutions are sp. functions of the compounds concerned. J. S. A.

Exchange reaction between acetone and deuterium oxide. Kinetics and equilibrium. J. O. HALFORD, L. C. ANDERSON, J. R. BATES, and R. D. SWISHER (J. Amer. Chem. Soc., 1935, 57, 1663—1665).—The introduction of the first D is a pseudo-unimol. reaction, which has a high-temp. coeff., approx. zero heat of reaction, and limiting equilibrium const. 2.1. Considerable amounts of acetones of higher D content are formed. E. S. H.

Stability against interchange of the iodine atoms in diphenyliodonium iodide. F. JULIUSBURGER, B. TOPLEY, and J. WEISS (J.C.S., 1935, 1295—1296).—Using radioactive NaI prepared by neutron bombardment, the facility of interchange, in solution, of iodide ions with the two different I atoms in Ph₂I⁺·I[−] has been examined by means of a Geiger counter. In EtOH and in aq. EtOH interchange occurs with the negative I only. In a solution of Ph₂I⁺·I[−] (with the I[−] active) in PhI no detectable exchange takes place even under conditions so extreme that considerable decomp. into 2PhI occurs. If both the decomp. and exchange reactions involve an activated complex it is probable that the activation energy for decomp. is < for exchange. O. J. W.

Stimulus to precipitate formation. N. P. SMIRNOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 548—555).—The stimulus to ppt. formation (ϕ) is defined by $\phi = A^p B^q / L$, where A and B are the concns. and p and q the charges of ions, and L is the solubility product. When $\phi = 1$, $L = A^p B^q$ (at the beginning and end of pptn.); when $\phi > 1$, the ppt. forms, and when $\phi < 1$ it dissolves. It is contended that ϕ is a dynamic quantity which measures the stimulus. R. S. B.

Velocity of reaction in systems consisting of two liquid phases. G. I. TSCHUFAROV and N. N. AGAFONOV (J. Phys. Chem. U.S.S.R., 1934, 5, 926—935).—The reaction of I and Na₂S₂O₃ was studied at 25° in the stirred systems CCl₄-H₂O, CHCl₃-H₂O, and CS₂-H₂O, the I being dissolved in the first component and the Na₂S₂O₃ in H₂O. The reaction was pseudo-unimol. Surface-active substances (e.g., stearic acid or CH₂Ph·CO₂H) do not affect the reaction proceeding on the phase boundary. NaI accelerates the reaction by changing the distribution coeff. CH. ABS. (e)

Kinetics of decomposition of solid solutions of silicon in aluminium. M. I. ZACHAROVA (Z. Physik, 1935, 96, 754—760).—The effect of temp. and duration of tempering on the decomp. of solid solutions of Si in Al has been investigated. The rate of decomp. is accelerated by plastic deformation. The isothermal decomp. of undeformed alloys at 218° and 280° shows three stages: (1) a latent period,

in which the lattice constns. remain unchanged. This period is the longer the lower is the temp. (2) A period of spontaneous decomp. (3) A period of growth and coagulation of crystallites. The Brinell hardness reaches a max. at the beginning of the third period. A. J. M.

Oxidisability of nickel. G. VALENSI (Compt. rend., 1935, 201, 523—524).—Measurements of the rate of oxidation of Ni at 715—1045° confirm Pilling and Bedworth's results (B., 1923, 359). For pure Ni oxidation starts at 550°. This temp. is lowered by the presence of H₂O, or of impurities in the Ni. The product, from X-ray analysis, consists of NiO. Some O, is dissolved and can be pumped off in vac. H. J. E.

Induced reaction. R. HORIUCHI (Bull. Chem. Soc. Japan, 1935, 10, 314—318).—Examples are discussed. It is suggested that inducer and acceptor must be chemically similar. R. S.

Chemical induction. A. SKRABAL (Monatsh., 1935, 66, 129—168).—A mathematical investigation of the kinetics of systems with successive and simultaneous reactions. The relation of the latter type to induced reactions and to induced catalysis is discussed. J. S. A.

Effect of neutral salts on the rate of hydrolysis of ethyl acetate in presence of strong acids, and the theory of Brønsted. N. V. SAPOSHNIKOVA and Z. A. PETSCHERKINA (J. Phys. Chem. U.S.S.R., 1934, 5, 116—125).—The effects of NaCl, KCl, MgCl₂, and NaCl+KCl in 0.1N-HCl, and of Na₂SO₄, MgSO₄, K₂SO₄, KCl+K₂SO₄, and NaCl+Na₂SO₄ in 0.1—0.5M-H₂SO₄ were studied. The rise in reaction velocity continues for each addition of chloride. With sulphates in acid solution the velocity decreases with each addition of sulphate to approx. 1M, further additions being almost without effect. CH. ABS. (e)

Effect of strong electrolytes on the rate of inversion of sucrose at 25°. J. N. PEARCE and M. THOMAS (Proc. Iowa Acad. Sci., 1933, 40, 93).—For each salt the inversion coeff. \propto the molality, the order of decreasing effect on the coeff. being BaCl₂, NaCl, KCl. The velocity is decreased by K₂SO₄ owing to formation of HSO₄[−]. The results are discussed from the viewpoint of dipole orientation and ionic charge. CH. ABS. (e)

Auto-esterification of lactic acid. P. DUQUÉNOIS (J. Pharm. Chim., 1935, [viii], 22, 251—254).—The amount of self-esterification in *N*-lactic acid has been determined. Sb₂O₃ has little effect on the [free acid] or on the [ester]. R. S.

Rôle of ozone as oxidation catalyst. IX. Ozonisation of anisaldehyde, vanillin, and piperonal. E. BRINER and A. GELBERT (Helv. Chim. Acta, 1935, 18, 1239—1242; cf. A., 1932, 1212).—Treatment of these aldehydes, and of methyl- and ethyl-vanillin, in CCl₄ solution with 2—4% ozonised O₂ gave a yield of acid > that attributable to the action of O₃ alone. The O₃ induces the reaction of part of the O₂. No peroxidation products were detected. H. J. E.

Oxidation of sugars by air in presence of ceric hydroxide sol and cerous hydroxide gels. J. C.

GHOSH and P. C. RAKSHIT (J. Indian Chem. Soc., 1935, 12, 357—370).—Rates of oxidation of glucose (I) and fructose (II) were determined at 27—48° in solutions with p_H vals. between 6.6 and 8.8. The rate of oxidation of (II) in presence of $Ce(OH)_4$ sol is accelerated by rise of p_H and by illumination, the quantum efficiency of the light reaction being 0.3—1.1. The data are consistent with (II) being strongly adsorbed by and reacting at the surface of the colloid particles. (I) gives similar results. With $Ce(OH)_3$ gel, a brown ppt. of ceric hydroperoxide (III) is formed, showing that H_2O_2 is produced. It is inferred that the sugars are dehydrogenated on the gel particles preliminary to the combination of the H_2 with O_2 to form H_2O_2 . A steady rate of O_2 absorption is eventually attained which is the difference between the rates of H_2O_2 formation and decomp. of (III). Glycine retards the oxidation and (III) is not formed. J. G. A. G.

Inhibition in the benzoin reaction. B. F. FERREIRA and T. S. WHEELER (Current Sci., 1935, 4, 94—95).—Contamination with benzoquinone (1 part in 10^7), I (1 part in 5×10^5), or S (1 part in 2×10^4) causes a measurable fall in the rate of reaction between solid KCN and PhCHO. Traces of H_2O tend to increase the rate. F. N. W.

Effect of calcium fluoride on the thermal synthesis of calcium ferrites. S. NAGAI and T. YOSHIURA (J. Soc. Chem. Ind. Japan, 1935, 38, 374—376B).— CaO, Fe_2O_3 and $2CaO, Fe_2O_3$ are formed by heating a mixture $2CaO + Fe_2O_3$ at 1000—1100° and 1200°, respectively. Addition of 1% of CaF_2 lowers the temp. of formation by 50—100° (e.g., reaction is completed after 1 hr. at 1100°). J. A. S.

Effect of heating a nickel catalyst on its ability to accelerate the transformation of para-hydrogen, and dependence of pyrophoric property of nickel on the temperature of heating. G. TAMMANN (Z. anorg. Chem., 1935, 224, 25—26).—The loss of pyrophoric properties and a decrease in the catalytic activity of reduced Ni towards the ortho-para- H_2 conversion set in roughly simultaneously on heating at 355—390°. J. S. A.

Catalytic interconversion of ortho-para-hydrogen over iron, platinum, and nickel catalysts. P. H. EMMETT and R. W. HARKNESS (J. Amer. Chem. Soc., 1935, 57, 1624—1631).—The ortho-para conversion over Fe catalysts has been studied as a function of temp., pressure, time of contact, and the presence of various poisons; kinetic expressions have been obtained. The poisoning effect of activated adsorption of H_2 on the para-ortho conversion at -190° over Pt and Ni is strong evidence that the activated adsorption is in part at least a surface phenomenon. E. S. H.

Adsorption of light and heavy hydrogen in connexion with hydrogenation of ethylene. II. R. KLAR (Z. physikal. Chem., 1935, 174, 1—14; cf. A., 1934, 593).—The rate of hydrogenation with D_2 , K_D , on an Fe catalyst was up to $\sim 100^\circ <$, but at 100 — $175^\circ >$, the rate of hydrogenation with H_2 , K_H . K_D was a max. at $\sim 150^\circ$, K_H at $\sim 125^\circ$, and K_H/K_D at 53° . The heat of activation for reaction with H_2

is 10.0 kg.-cal., and that for D_2 8.0 kg.-cal. up to 50° and 12.5 kg.-cal. above. It is suggested that in the reaction with D_2 at higher temp. hydrogenation is preceded by an exchange reaction between activated adsorbed D_2 and the H atoms of activated adsorbed C_2H_4 ; the rate of the process as a whole is decided by the rate of activation of C_2H_4 . From measurements of the rate of adsorption of H_2 and D_2 on Ni (cf. this vol., 27) it is calc. that at 0— 30° the energy of activation of H_2 is 1.49 and that of D_2 2.37 kg.-cal.; at 80— 120° the difference between the two rises to 1800 g.-cal. R. C.

Simple demonstration of catalysis. H. KAMMIN (J. Chem. Educ., 1935, 12, 362).—The decomp. of H_2O_2 by MnO_2 is used. L. S. T.

Effect of porous silica gel catalyst carrier on the velocity of oxidation of sulphur dioxide gas. I. G. I. TSCHUFAROV, N. N. AGAFONOV, E. P. TATIEVSKAJA, and K. I. KULPINA (J. Phys. Chem. U.S.S.R., 1934, 5, 936—945).—Vals. are recorded for the SO_3 yield as a function of gel porosity for 16 platinised gels (porosities 118 to 19) at 360— 500° . At porosities > 50 the difference in yield is small. Below 50 it falls rapidly, particularly at low temp. Decreased yields also occur with porosities > 100 . CH. ABS. (e)

Sulphuric acid catalysis. VI. Vanadic acid contact masses.—See B., 1935, 898.

Platinised copper gauze for oxidation of ammonia.—See B., 1935, 946.

Use of van der Waals adsorption isotherms in determining the surface area of iron synthetic ammonia catalysts. S. BRUNAUER and P. H. EMMETT (J. Amer. Chem. Soc., 1935, 57, 1754—1755).—Van der Waals adsorption isotherms for N_2 at -195.8° and -183°, O_2 , CO, and A at -183°, CO_2 at -78.5°, and $n-C_4H_{10}$ at 0° have been determined. By extrapolation the vol. of gas needed to form a unimol. layer on the catalyst, and hence the area of the catalyst surface, has been calc. Results obtained for the different gases are in good agreement. E. S. H.

Catalytic oxidation of ammonia-methane mixtures to hydrocyanic acid. L. ANDRUSOV (Angew. Chem., 1935, 48, 593—595).—The catalytic oxidation of equimol. $CH_4 + NH_3$ mixtures to HCN, and of NH_3 to N_2O , in presence of Pt is discussed in terms of the author's nitroxyl theory of NH_3 oxidation. Pt is a sp. catalyst, Ni being ineffective. J. S. A.

[Catalytic] preparation of carbon tetrachloride.—See B., 1935, 938.

[Catalytic] hydrolysis of chlorobenzene in the vapour phase.—See B., 1935, 938.

Cascade electrolytic process for separating the hydrogen isotopes. H. C. UREY and M. H. WAHL (Physical Rev., 1935, [ii], 45, 566).—An outline of the method is given. L. S. T.

Fractionation of the isotopes of oxygen in a commercial electrolyser. E. R. SMITH and M. WOJCIECHOWSKI (J. Res. Nat. Bur. Standards, 1935, 15, 187—188; cf. this vol., 175).—Commercial electrolytic "equilibrium" H_2O after treatment with

NH_3 and purification gave d 11 p.p.m. $>$ for normal pure H_2O , instead of 31 p.p.m. as previously reported, due to enrichment in O^{18} . The electrolytic separation factors for the H and O isotopes are, respectively, 3.5 (lit. 2.4) and 1.05. R. S. B.

Concentration of the heavier isotopes of oxygen in commercial electrolytic cells. W. H. HALL and H. L. JOHNSTON (J. Amer. Chem. Soc., 1935, 57, 1515—1517).—Samples of electrolyte from cells which had been in use for 7 years showed an increase of 4 p.p.m. in d of H_2O as a measure of the enrichment of O^{17} and O^{18} . E. S. H.

Electrolytic preparation of hydrogen peroxide. H. SIDERSKY (J. South African Chem. Inst., 1935, 18, 44—61).—The electrolytic prep. of $\text{K}_2\text{S}_2\text{O}_8$ gave low current yields and on distilling the aq. solution conc. distillates of H_2O_2 could not be obtained without extensive loss of active O. With $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ as anolyte, 50% H_2SO_4 as catholyte, and porous pot for separation, 83% current yield of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was obtained, 82% of the active O coming over as H_2O_2 on distillation. A Pb cathode was not detrimental, but traces of Cr, Mn, and Fe must be avoided if economic yields are desired. By fractional condensation it is possible to concentrate dil. H_2O_2 solutions up to 30%. S. J. G.

Large-scale laboratory experiments for making calcium. Z. V. VASILIEV, V. P. MASCHOVETZ, B. V. POPOV, and A. J. TAITZ (Legk. Metal., 1934, 3, No. 10, 28—34).—Fused CaCl_2 and NH_4Cl were electrolysed in a graphite cell with an Fe cathode. With external heating, 430 g. of Ca were obtained at a consumption of 32 kw.-hr. per kg. CH. ABS. (e)

Electrosynthesis of silver, tin, and zinc amalgams and their chemical structure. K. DUCZKO (Wiadom. Farm., 1934, 61, 633—636, 667—671, 683—686, 698—700).—The amalgams were prepared by a modification of Kerp's method (A., 1898, ii, 516), or by mixing electrolytically dispersed Ag with Hg. The Ag amalgams contain the compound AgHg , those of tin contain Sn_7Hg , and Zn amalgams are physical mixtures. CH. ABS. (e)

Electrolytic deposition of metals from their pyrophosphate solutions. S. KOYANAGI (Bull. Chem. Soc. Japan, 1935, 10, 355—356).—Conditions are given for the deposition of Ni, Co, Cu, Zn, and Cd. R. S.

Simultaneous discharge of nickel and hydrogen ion from the solutions of simple nickel salts. O. ESSIN and E. ALFIMOVA (Trans. Electrochem. Soc., 1935, 68, 255—262).—Current efficiencies calc. from the equation for the simultaneous discharge of two ions (cf. this vol., 450) are in agreement with experimental data over a range of $[\text{Ni}^{++}]$, $[\text{H}^+]$, cathode c.d., and electrolyte temp. R. S.

Cathodic film in the electrolytic reduction of aqueous chromic acid solutions. E. MÜLLER (Trans. Faraday Soc., 1935, 31, 1194—1203).—When pure aq. HCrO_4 is electrolysed with a smooth Pt cathode, continuous reduction does not occur; a film of reduction product is formed at the cathode surface and is impermeable to HCrO_4 . The film is permeable to H^+ and to HSO_4' , and on addition

of H_2SO_4 breaks down, so that continuous reduction proceeds. The conditions of stability of the film have been studied by determining the c.d.-p.d. curves in electrolytes containing different amounts of H_2SO_4 . Within certain limits of c.d. and concn. the formation of the film occurs periodically with time and is accompanied by regular pulsations of p.d. The mechanism is discussed. E. S. H.

Mechanism of chromium deposition from the chromic acid bath.—See B., 1935, 857.

Electrolysis of salts of weak bases. M. LEMARCHANDS and J. DEBIESSE (Bull. Soc. chim., 1935, [v], 2, 1697—1698).—Dil. solutions of Cu, Pb, Ni, and Zn salts on electrolysis using a high c.d. yield deposits consisting of a mixture of the metal and its hydroxide. Since this effect is increased by increased dilution, by increased c.d., or by addition of NaOAc , it is attributed to cataphoresis of the hydroxide produced by hydrolysis of the salts. Limiting concns. at which the effect is observable with various c.d. and with various metals are recorded. J. W. S.

Alternating-current corrosion.—See B., 1935, 855.

Electrodeposition of iron-nickel alloys.—See B., 1935, 905.

Conditions governing the formation of highly-insulating anodic layers on aluminium.—See B., 1935, 955.

Electrolytic preparation of thin layers of U_3O_8 . M. FRANCIS (Compt. rend., 1935, 201, 473—474; cf. this vol., 589).—If the U salt is insufficiently pure the first material deposited contains Pa, Ra, Po, and other radioactive elements. The radioactivity of such a deposit will be $>$ that for pure U_3O_8 . H. J. E.

Arrangements of micro-crystals in lead deposited by electrolysis. H. HIRATA, Y. TANAKA, and H. KOMATSUBARA (Bull. Chem. Soc. Japan, 1935, 10, 391—396; cf. this vol., 920).—Needle-shaped and foliated deposits of Pb have been examined by X-rays. The angles between the directions of max. growth of the micro-crystals coincide with the angles between their (211) axes. R. S.

Electrodeposition of lead from perchloric acid solution.—See B., 1935, 906.

Electrolysis of organic substances in non-aqueous media. I.—See this vol., 1349.

Electrolytic reduction of succinimide.—See this vol., 1378.

Photolysis of dry ozone at $\lambda\lambda$ 208, 254, 280, and 313 m μ . II. Reaction kinetics. L. J. HEIDT (J. Amer. Chem. Soc., 1935, 57, 1710—1716; cf. A., 1934, 1079).—Quantum yields, referred to O_3 mols. decomposed per quantum absorbed, are approx. equiv. at 208 and 313 m μ . The temp. coeff., 1.15 ± 0.02 at 0—60°, is apparently independent of the mol. fraction of O_3 in O_2 , and of the temp. interval, even when the dark rate is 20% of the total decomp. The temp. coeff. of the dark rate at 20—60° is 3 ± 0.1 for small mol. fractions of O_3 in O_2 . The mechanism is discussed. E. S. H.

Photo-dissociation of single crystals of nitrates in polarised light. L. K. NARAYANSWAMY (Trans. Faraday Soc., 1935, **31**, 1411—1412).—Crystals of metal nitrates undergo dissociation in light of $\lambda < 250$ m μ , giving nitrite which is confined to a thin surface layer. KNO_3 is much more sensitive to light vibrating in the plane of the NO_3' ions than to light vibrating normally to this plane. Similar behaviour is shown by single crystals of NaNO_3 and NH_4NO_3 . F. L. U.

Influence of time, light, and temperature on the keeping of hypochlorite solutions. R. P. JACQUEMAIN and J. H. DOLL (Bull. Soc. chim., 1935, [v], **2**, 1669—1678).—Addition of KI to a mixture of NaOCl , NaClO_2 , and NaClO_3 in dil. AcOH , followed by titration with $\text{Na}_2\text{S}_2\text{O}_3$, permits determination of $[\text{NaOCl}] + [\text{NaClO}_2]$, whilst the same reaction in conc. HCl gives $[\text{NaOCl}] + [\text{NaClO}_2] + [\text{NaClO}_3]$. Titration of the mixture with KI in presence of NaHCO_3 until I is just formed, owing to reaction of the IO_3' produced with I' , determines the $[\text{NaOCl}]$. This system of analysis is applied to the study of the decomp. of NaOCl solution. This reaction is principally controlled by light, rise of temp. having little effect, and the initial product is NaClO_2 . The decomp. of the latter to NaClO_3 and NaCl is scarcely influenced by light, but is greatly accelerated by rise of temp. Dil. solutions are more readily decomposed than conc. solutions. J. W. S.

Inorganic photosyntheses. G. CALCAGNI (Gazzetta, 1935, **65**, 558—566).—By the action of sunlight on S, Se, P, As, Sb, B, and Si suspended in H_2O , the following have been obtained: H_2SO_4 , H_2SeO_3 , H_3PO_4 , H_3PO_3 , H_3AsO_3 , H_3SbO_3 , H_3BO_3 , and $\text{SiH}(\text{OH})_3$. O. J. W.

Photochemical investigations. I. Effect of ammonia pressure on the quantum yield for the decomposition of ammonia. E. O. WING (J. Amer. Chem. Soc., 1935, **57**, 1559—1562).—The quantum yield for λ 2100 Å. depends on the NH_3 pressure, rising from about 0.10 at 1—10 mm. to about 0.30 at 65—120 mm., and then falling to 0.18 at 1 atm. E. S. H.

Photodissociation of nitrous oxide. P. K. SEN-GUPTA (Nature, 1935, **136**, 513—514).—A crit. discussion (cf. A., 1934, 1153). L. S. T.

Action of light in the dissolution of amorphous selenium in carbon disulphide. J. SHIDEI, S. HASHIZUME, and S. KITAHARA (Bull. Chem. Soc. Japan, 1935, **10**, 374—378).—The velocity of dissolution of amorphous Se is accelerated, whilst that of monoclinic Se is unaffected. R. S.

Influence of atmospheric oxygen on the photographic process of bleaching out. M. BLAU (Phot. Korr., 1935, **71**, Beil. 3, 21—28; cf. A., 1935, 177).—The Herschel effect is less in vac. than in air, especially in plates desensitised with pinakryptol-yellow; desensitised plates show an increase of sensitivity in vac. Detailed experiments show that in all cases O_2 plays an important part; the theory of bleaching processes is discussed. J. L.

Topographical relations in image reversals. LÜPPO-CRAMER (Phot. Korr., 1935, **71**, 89—92).—Desensitised AgBr emulsions show a quicker second

reversal by light of high intensity; this is attributed to penetration of the light to depths in the AgBr grain where dye has not reached. AgI emulsions show no solarisation if a halogen acceptor is present; the solarisation of pure AgI emulsions, which is also dependent on the intensity of the light, is ascribed to a "regression" (rehalogenation) process. Various data bearing on the latter theory are discussed.

J. L.

Theory of desensitisation and the Herschel effect. K. WEBER (Phot. Korr., 1935, **71**, 107—111).—The desensitising power of a dye is the greater the more positive is the reduction-oxidation potential (ϵ_h), the vals. for neutral-red, phenosafranine, Nile-blue, and methylene-blue being -0.320 , -0.230 , -0.080 , and -0.005 , respectively; thionine ($\epsilon_h + 0.045$) falls into line for physical development, but not for chemical development, wherein a catalytic acceleration of the development appears to be produced. Since the potential for $\text{Ag}|\text{AgNO}_3$ is $+0.77$ volt, for $\text{Ag}|\text{AgBr}$ $+0.44$ volt, and for nascent Ag about 0.0, desensitisation cannot be due to oxidation of Ag, except to a small extent, as the formation of leucobase would at once hinder such a reaction. Various other factors (cf. Mudrovcic, B., 1929, 227) lead to the conclusion that desensitisation is due to oxidation of the optical or chemical sensitisers present, leucobase formed being rapidly re-oxidisable to dye by atm. O_2 . The Herschel effect must also be due to an oxidation process, since it is not obtainable in a vac., and the relation of desensitising action to ϵ_h also holds for this effect. The Ag latent image is in a state of excitation on exposure to red light and has then a more negative ϵ_h than normal Ag, and thus becomes oxidisable. J. L.

Photographic development effect. P. O. HOFMANN (Physikal. Z., 1935, **36**, 650).—If two exposures are made on a plate (1) with long exposure (t) and small intensity (I), and (2) with short t and great I , so that the blackening produced on normal development would be the same, the exposure made under the first conditions always appears first on development. A. J. M.

Relation between density of blackening and X-ray intensity for characteristic copper radiation and Agfa-Laue film. F. D. MILES (Trans. Faraday Soc., 1935, **31**, 1452—1460).—The relation between photographic density (D) and the intensity of $\text{Cu } \alpha$ radiation, determined by two methods, is nearly linear. The error involved in assuming linearity up to $D=1.0$ is $\pm 4\%$ of the highest D measured. There is no evidence of threshold effect. F. L. U.

Formation of the Röntgen image with regard to scattered irradiation. G. SPIEGLER (Z. wiss. Phot., 1935, **34**, 197—204, 205—215).—By placing Pb plates at varying angles and distances from the film, in a scattering cell filled with H_2O , the contrast of the shadow in relation to the object distance is measured. The results are given with and without a scattered light screen. A method of evaluating density differences of images is outlined. J. L.

Sensitivity of certain reactions to light. C. WINTHER (Z. physikal. Chem., 1935, **174**, 41—48).—

Contrary to the findings of Bhattacharya and Dhar (A., 1929, 37) the oxidation of citric, tartaric, lactic, and oxalic acids by H_2CrO_4 and of KI by $\text{K}_2\text{S}_2\text{O}_8$ is not sensitive to light. R. C.

Photochlorination of pentane. T. D. STEWART and B. WEIDENBAUM (J. Amer. Chem. Soc., 1935, 57, 1702—1704).—The reaction in the liquid phase, using λ 3650 Å., has a quantum efficiency of 192 ± 14 at 25°. The reaction rate $\propto [\text{Cl}_2]$ at const. light intensity. E. S. H.

Effect of slow electrons on metal surfaces. J. B. PHILLIPSON (Proc. Iowa Acad. Sci., 1933, 40, 150—151).—Differences in reactivity were observed after bombardment. CH. ABS. (e)

Effect of cathode rays on metal surfaces. E. WILCOX (Proc. Iowa Acad. Sci., 1933, 40, 150).—Metal surfaces which have been bombarded with cathode rays have a different chemical reactivity towards vapours from those not so bombarded. H. J. E.

Effect of low-voltage cathode rays on photographic film. A. R. BROWN (Proc. Iowa Acad. Sci., 1933, 40, 151).—Differences were observed in the effect of electrons at different voltages. CH. ABS. (e)

Heavy hydrogen (deuterium) and its compounds. E. DARMOIS (Bull. Soc. chim., 1935, [v], 2, 1513—1544).—A lecture.

Preparation of hydrogen peroxide [from potassium persulphate].—See B., 1935, 849.

Li_3FeF_6 . A. H. NIELSEN (Z. anorg. Chem., 1935, 224, 84).—The compound Li_3FeF_6 is obtained as an insol., white isotropic powder (n 1.42) by the action of aq. Li_2CO_3 on a solution of FeCl_3 in HF . J. S. A.

Percarbonates. R. R. KAMTIKAR and S. HUSAIN (J. Osmania Univ. Coll., 1934, 2, 39—40).—The so-called compounds $\text{Na}_2\text{C}_2\text{O}_6$ and $\text{Na}_2\text{CO}_4 \cdot 1.5\text{H}_2\text{O}$ obtained by action of CO_2 on Na_2O_2 or NaO_2H (Wolffenstein *et al.*, A., 1908, ii, 180) are mixtures of Na_2CO_3 and NaHCO_3 with a small amount of active O, probably due to Na_2O_2 and NaO_2H ; whilst the $\text{Na}_2\text{C}_2\text{O}_6 \cdot \text{H}_2\text{O}_2$ is $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}_2 \cdot x\text{EtOH}$. The formula of Tanatar's compound $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot 0.5\text{H}_2\text{O}$ (A., 1899, ii, 482) is confirmed. J. W. S.

Dissolution of silver in potassium cyanide solutions. A. SIMON and H. DECKERT (Z. Elektrochem., 1935, 41, 737—738).—Evidence is adduced in support of the view that H_2O_2 is formed as an intermediate product when Ag dissolves in aq. KCN. Small amounts of H_2O_2 ($> 0.3\%$) increase the rate of dissolution, but greater amounts retard it. E. S. H.

Compounds of basic oxides and metalloids [non-metals]. M. LEMARCHANDS and (Mlle.) D. SAUNIER (Bull. Soc. chim., 1935, [v], 2, 1709—1716).—A detailed account of work already noted (A., 1934, 613; this vol., 592). J. W. S.

Action of charcoal on aqueous solutions of silver nitrate. T. R. BOLAM and W. A. PHILLIPS (Trans. Faraday Soc., 1935, 31, 1443—1452).— AgNO_3 is rapidly adsorbed, and then slowly reduced

to Ag, by carefully purified sugar C. The Ag thus formed does not remain on the surface of the C. Experiments are described to show the influence of concn., acidity, duration of contact, ageing, and preliminary treatment of the C. F. L. U.

Behaviour of metal ammoniates in water containing deuterium oxide. H. ERLÉNMEYER and H. LOBECK (Helv. Chim. Acta, 1935, 18, 1213—1215; cf. A., 1934, 1321).—Bankowski's results (this vol., 458) are criticised on the grounds that interchange with undissolved complex salt is incomplete, and that fractionation may have occurred during distillation. Complete exchange occurs for the NH_3 and H_2O groups of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$. H. J. E.

Yellow cuprous oxide. M. STRAUMANIS and A. CIRULIS (Z. anorg. Chem., 1935, 224, 107—112).—The identical lattice dimensions of red and yellow Cu_2O prepared by various methods indicate their identity. Yellow Cu_2O passes into red on growth of the crystallites, *e.g.*, on ignition, as is shown by the increase in sharpness and no. of the diffracted Röntgen lines with the redness of the material. J. S. A.

Double salt of copper chloride and lithium chloride. J. M. LOPATKIN (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 13—21).—Solubility data for the system $\text{CuCl}_2\text{—LiCl—H}_2\text{O}$ are recorded. The compound $\text{CuCl}_2 \cdot 4\text{LiCl} \cdot 10\text{H}_2\text{O}$ was isolated. It is very hygroscopic, and decomposes with H_2O to form $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$. CH. ABS. (e)

Action of carbon monoxide on ammoniacal solutions of cupric salts. I. Carbon monoxide and aminocupric compounds in absence of metallic copper. II. Carbon monoxide and aminocupric compounds in presence of metallic copper. H. MÖLLER (Z. anorg. Chem., 1935, 224, 113—129, 130—152).—I. CO is absorbed by aq. NH_3 solutions of tetramminocupric hydroxide, carbonate, acetate, chloride, sulphate, and nitrate to give CO_2 and Cu^+ salts. Absorption is most rapid in the hydroxide solution, and slowest in solutions of the mineral acid derivatives. Slow initially, it accelerates autocatalytically or on addition of a small amount of aminocuprous salt, in presence of which the solutions might be applied to gas analysis or to the technical prep. of Cu^+ salts. Mechanisms are discussed.

II. Absorption of CO by solutions of tetramminocupric hydroxide, carbonate, chloride, and sulphate is strongly accelerated by addition of Cu, which acts partly catalytically and partly by dissolving to form aminocuprous salts. The initial velocities of absorption vary with the acid radical in the opposite direction to those recorded in the absence of Cu (above). The rate of dissolution of Cu in the above tetramminocupric salts in absence of CO depends on [Cu]. Mechanisms are suggested to explain these processes, and the pptn. of Cu by amino-cupric or -cuprous salts saturated with CO. Tetramminocupric salts + Cu are suggested for use in gas analysis and for the technical prep. of Cu^+ salts. T. G. P.

Action of carbon monoxide on cupric salts. H. MÖLLER and K. LESCHEWSKI (Z. anorg. Chem.,

1935, 224, 153—172; cf. preceding abstract).—CO is absorbed (a) rapidly by aq. $\text{CuCl}_2 + \text{Cu}$, especially in presence of conc. HCl, and (b) slowly by aq. $\text{NH}_3 + \text{Cu}$. $\text{CO} + \text{O}_2$ are absorbed (a) rapidly by aq. $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2 + \text{Cu}$ and (b) more rapidly by aq. $\text{NH}_3 + \text{Cu}$ than is pure CO. Mechanisms are discussed.

T. G. P.

Boric acid and alkali borates. VIII. (Addendum.) System $\text{B}_2\text{O}_3\text{--H}_2\text{O}$. H. MENZEL (Z. anorg. Chem., 1935, 224, 23—24; cf. A., 1934, 1174).—Tensimetric measurements show that no higher hydrate than H_3BO_3 exists at 0° .

J. S. A.

Boric acid and alkali borates. IX. System $\text{Na}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$. H. MENZEL [with H. SCHULZ, L. SIEG, and M. VOIGT] (Z. anorg. Chem., 1935, 224, 1—22; cf. A., 1934, 1174).— $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (I) undergoes dehydration in two ways. (a) (I) previously incubated at 50° passes reversibly into cryst. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ (II) ("stable dehydration"). (b) Fresh (I) passes irreversibly at very low v.p. of H_2O into an amorphous material with about $2\text{H}_2\text{O}$ ("unstable dehydration"), which may be rehydrated to (II). (II) dehydrates reversibly over drying agents or in boiling xylene to an amorphous $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$, which passes into amorphous $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$ at 190° . Anhyd. $\text{Na}_2\text{B}_4\text{O}_7$ is formed by dehydration at $>400^\circ$, and crystallises rapidly at 600° . Supercooled melted $\text{Na}_2\text{B}_4\text{O}_7$ glass crystallises in three crystallographically distinct forms: form B, m.p. 738° , stable at high temp., on inoculation, and on spontaneous crystallisation either forms A, m.p. 710° , or C, m.p. 663° . $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ does not occur in the dehydration of higher hydrates. For analytical purposes, (I) should be hydrated over saturated aq. $\text{NaCl} + \text{sucrose}$.

J. S. A.

Hydrothermal synthesis of kaolinite, dickite, beidellite, and nontronite. R. H. EWELL and H. INSLEY (J. Res. Nat. Bur. Stand., 1935, 15, 173—186).—On keeping copptd. hydrogels of Al_2O_3 and SiO_2 (ratio 1:2) for 21 days the product remains amorphous, in disagreement with Schwarz and Brenner (A., 1923, ii, 569). No crystallisation occurs at 95° , but at 310° and 97 atm. kaolinite (I), $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, is formed. At $345\text{--}365^\circ$ and 157—202 atm. dickite (II), $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, results. (I) may also be formed from the mixed gels, and bohmite from copptd. gels of $\text{Al}_2\text{O}_3 : \text{SiO}_2 > 1:2$. Beidellite (III), $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (n variable), is formed from mixtures of Al_2O_3 and SiO_2 at $350\text{--}390^\circ$ and 167—260 atm., and from copptd. $\text{Al}_2\text{O}_3 : 2\text{SiO}_2$ gels at 390° and 260 atm. Measurements in which the oxides react after diffusion show that (III) is formed by transport of dissolved SiO_2 to solid Al_2O_3 , and that NaOH must be present. Nontronite, $\text{Fe}_2\text{O}_3 \cdot 3 \cdot 43\text{SiO}_2 \cdot 1 \cdot 04\text{H}_2\text{O}$ (pure = $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$), has been synthesised from copptd. $\text{Fe}_2\text{O}_3 : 2\text{SiO}_2$ gels at 350° under pressure. In all cases optical and X-ray characteristics of the synthetic agree with those of the natural materials. The stability ranges of (I), (II), and (III) probably occur in the order given with rise of temp., in agreement with geological evidence.

R. S. B.

Thermal investigation of aluminium hydroxide-aluminium oxide by emanation method.

R. JAGITSCH (Z. physikal. Chem., 1935, 174, 49—59).—The nature of specimens of $\text{Al}(\text{OH})_3$ prepared in various ways and the changes on heating at $20\text{--}1300^\circ$ have been studied. With rise of the temp. of pptn. the rate of transformation of the $\text{Al}(\text{OH})_3$ formed initially (cf. A., 1926, 34) increases rapidly. On heating, the surface reaches a max. in the region of existence of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}$ ($200\text{--}300^\circ$). Above 300° $\gamma\text{-Al}_2\text{O}_3$ is formed and corresponding with increasing grain size the emanating power gradually declines. At $1100\text{--}1200^\circ$ there is a rapid change in structure, due to transformation of $\gamma\text{-}$ into $\alpha\text{-Al}_2\text{O}_3$. The emanating power of $\text{Al}(\text{OH})_3$ falls when the latter is kept over drying agents.

R. C.

Separation of europium from other rare earths. H. N. MCCOY (J. Amer. Chem. Soc., 1935, 57, 1756).—The mixture of rare-earth chlorides, containing dil. AcOH , is passed through a column of amalgamated Zn. EuCl_3 is reduced to EuCl_2 , which is collected in aq. MgSO_4 in a CO, atm., giving a ppt. of EuSO_4 .

E. S. H.

Substances analogous to graphite. IV. R. CIUSA and F. BELLINO (Gazzetta, 1935, 65, 461—464; cf. A., 1932, 1109).—Various "graphites" are obtained by heating tetraiodofuran (new prep. described) to temp. of $300\text{--}910^\circ$. The product of heating at 500° has the approx. composition $(\text{C}_4\text{O})_n$. After heating at 910° the substances still contain 2.60% O.

O. J. W.

Intermediate states of oxidation of stannous chloride. T. R. BALL, W. WULFKUEHLER, and R. E. WINGARD (J. Amer. Chem. Soc., 1935, 57, 1729—1730).—Magneto-optical analysis of the partial oxidation of SnCl_2 in HCl with $\text{K}_2\text{Cr}_2\text{O}_7$ indicates the existence of $> 0.01\%$ of SnCl_3 .

E. S. H.

Double compound of stannic chloride and acetic acid. C. N. MURTI and S. HUSAIN (J. Osmania Univ. Coll., 1933, 1, 87—93).—Attempts to prepare $\text{SnCl}_4 \cdot 2\text{AcOH}$ by the method of Fichter *et al.* (A., 1928, 603) were unsuccessful. Evaporation of anhyd. or hydrated SnCl_4 with glacial AcOH in a vac. over CaCl_2 yields a syrup of $\text{SnCl}_4 \cdot 4\text{AcOH}$, which shows no change in composition after 3 months. Use of NaOH as drying agent decomposes the compound, which could not be obtained solid. Distribution coeff. measurements between H_2O and xylene confirm the existence of $\text{SnCl}_4 \cdot 4\text{AcOH}$ in solution. The f.-p. depression of H_2O by a mixture of SnCl_4 and AcOH is $>$ the sum of the effects of the components. It is suggested that this may be due to decomp. of the SnCl_4 into SnCl_2 and Cl_2 .

J. W. S.

Hydrolysis of phosphorus trichloride. B. BLASER (Ber., 1935, 68, [B], 1670—1674).—Hydrolysis of PCl_3 , best by passing the vapour in a stream of dry N_2 through a well-stirred phosphate buffer solution with initial p_H 6.3, gives a 75% yield of a compound, probably an isomeride of $\text{P}(\text{OH})_3$, which is very stable in approx. neutral solution but passes fairly rapidly into $\text{P}(\text{OH})_3$ in an acid medium. It differs from $\text{P}(\text{OH})_3$ in its great stability towards I in acid and H carbonate in alkaline solution.

H. W.

Thermal degradation of sulphur in blue ultramarine. K. LESCHEWSKI and E. PODSCHUS

(Ber., 1935, 68, [B], 1872—1876; cf. A., 1934, 1318).—Ultramarine-blue (I) is essentially characterised by a peculiar cryst. structure in which S, alkali, and O are arranged in proportions variable within certain limits. The elastic receptivity for the 3 structural elements is dependent on the "cavity lattice" structure of (I) and the possibility of schematic representation is excluded. (I) is unaffected in N_2 at 800° , gradually loses lustre and colour at $>800^\circ$, and becomes colourless at 950° . The changes are accompanied by increasing loss of S, which is almost complete at $>1000^\circ$, whereas alkali and Al silicate remain almost unchanged. The lattice of (I) passes at $>950^\circ$ into that of nepheline (II), which persists at 1200° . The decolorisation of (I) in flowing H_2 at 400° is ascribed to the penetration of at. H into the cavities in which it becomes loosely attached to the firmly bound S. At higher temp. the colour becomes dark blue and then bluish-green without appreciable change in S content or lattice. At 850 – 875° S is almost completely evolved as H_2S ; colour disappears and the lattice of (I) is replaced by that of (II). In flowing O_2 dry (I) retains its lattice and approx. its composition at 600° . At 600 – 750° about half the S is oxidised to sulphite and sulphate, which are retained in the lattice, whilst the remainder is evolved as SO_2 or SO_3 . Products obtained at $>700^\circ$ do not evolve H_2S when treated with acid. At $>750^\circ$ they pass into alkali aluminosilicates with deposited sulphate-S with a lattice differing slightly from that of (I). Above 1100° S is more and more completely lost and almost S-free alkali aluminosilicates remain, the lattice of which has nothing in common with (I) or (II). H. W.

Reactions in liquid sulphur dioxide. J. CORNIG and V. A. LAMB (Proc. Iowa Acad. Sci., 1933, 40, 97—98).—The solvent usually participates in reactions in liquid SO_2 . At atm. pressure it does not react appreciably with Cl_2 except in presence of a catalyst. The reaction $SOCl_2 + Na_2SO_3 = 2NaCl + 2SO_2$ does not take place in liquid SO_2 . ICl and $KCNS$ in SO_2 form $I(CNS)_3 \cdot 2SO_2$ and I . CH. ABS. (e)

Reaction between sulphurous and nitrous acids in a dilute system.—See B., 1935, 848.

Properties of the alkaline persulphates. H. BOTTU (J. Pharm. Chim., 1935, [viii], 22, 247—251).—The stability of $K_2S_2O_8$ in H_2O , dil. H_2SO_4 , aq. K alum, Na_2CO_3 , and $Na_2CO_3 + NaCl$ has been studied. Decomp. is a min. in the alkaline solutions. R. S.

Yellow coloration of hydrochloric acid containing selenium. II. Behaviour of hydrochloric acid containing selenium on cooling and on diluting with water. F. ULLRICH and H. DITZ (Z. anorg. Chem., 1935, 224, 213—224; cf. this vol., 181).—Titration with $SnCl_2$ has also been studied.

T. G. P.

Fractionation of isotopic isomerides by distillation. D. F. STEDMAN (Canad. J. Res., 1935, 13, B, 114—121).—Fractionation of CCl_4 with a special column gave a head fraction containing Cl of at. wt. 0.042 < normal val. For CH_2Cl_2 the isotopic separation by fractionation was very small. Fractionation of H_2O gave a head fraction in which 26.5%

of the original O^{18} content was shown by mass spectrum analysis to have been removed. By fractionation of liquid O_2 the $[O^{18}]$ was raised from 0.2 to 0.25%. The b.p. of MeD is approx. 0.5° < that of CH_4 . Separation of MeD from natural CH_4 is possible. Published vals. for the v.p. of D_2O at $<40^\circ$ may be slightly high.

H. J. E.

Reaction between chlorine monoxide and ammonia. R. SCHWARZ and H. STRIEBICH (Z. anorg. Chem., 1935, 224, 29—32).— Cl_2O reacts with NH_3 at low temp. ($<-101^\circ$) to give NH_4Cl , H_2O , and N_2 . Since ammonolysis of the O does not occur, Cl is to be regarded as the more electropositive element in Cl_2O .

J. S. A.

Bromine oxide Br_2O . W. BRENSCHKE and H. J. SCHUMACHER (Z. physikal. Chem., 1935, B, 29, 356—358).—By reaction between HgO and a CCl_4 solution of Br the Br may be partly converted into Br_2O . The solution is stable in the dark at -20° , but in light or at room temp. decomposes: $Br_2O \rightarrow Br_2 + 0.5O_2$; $Br_2O + CCl_4 \rightarrow COCl_2 + Br_2 + Cl_2$. R. C.

Preparation of dibromoamine and its reactions with Grignard reagents. G. H. COLEMAN, C. B. YAGER, and H. SOROOS (Proc. Iowa Acad. Sci., 1933, 40, 112; cf. A., 1934, 615).— $NHBr_2$ was prepared by passing dry NH_3 into Br in cold Et_2O . The solution is stable at -72° and decomposes rapidly at 0° . $NHBr_2$ reacts with $MgRX$ to give NH_2R , NHR_2 , NH_3 , and N_2 , the % yields from $MgBuCl$ being: NH_2Bu 7.8, $NHBu_2$ 2.2, NH_3 79.0, and N_2 5.9%, and for $CH_2Ph \cdot MgCl$: $NH_2 \cdot CH_2Ph$ 29.6, $NH(CH_2Ph)_2$ 5.5, NH_3 42.8, and N_2 4.7%.

CH. ABS. (e)

Lower oxides and sulphates of iodine. R. K. BAHL and J. R. PARTINGTON (J.C.S., 1935, 1258—1263).—Contrary to published work, interaction of conc. HNO_3 (d 1.50) and I produces I_2O_5 . The intermediate product in the prep. of I_2O_4 from HIO_3 and hot conc. H_2SO_4 is an approx. equimol. mixture of $I_2O_4 \cdot H_2SO_4$ and $I_2O_3 \cdot H_2SO_4$ (cf. J.C.S., 1909, 95, 656), but if the mixture is heated until I is evolved, or if I is added, the product is chiefly $I_2O_3 \cdot H_2SO_4$. $I_2O_3 \cdot SO_3 \cdot 0.5H_2O$ was not obtained. I_2O_4 decomposes at $>85^\circ$ and at 110 – 130° the reaction is $5I_2O_4 = 4I_2O_5 + I_2$. I_4O_9 is produced in a gas phase reaction by passing ozonised O_2 over warm I. I_4O_9 is a hygroscopic solid which decomposes at $>75^\circ$; at 85 – 120° the reaction is $4I_4O_9 = 6I_2O_5 + 2I_2 + 3O_2$.

J. G. A. G.

Oxidation of oxalic acid by iodic acid and interference with the assumption of a stationary state by the reaction intermediate. E. ABEL and L. BLUMENKRANZ (Monatsh., 1935, 66, 181—192).—The stationary concn. of I' in the oxidation of $H_2C_2O_4$ to CO_2 by HIO_3 has been artificially altered by addition of $AgI + AgIO_3$. The liberation of I is not entirely suppressed. Addition of I by partition from a C_6H_6 solution favours the oxidation of $H_2C_2O_4$.

J. S. A.

Amorphous and crystalline oxide hydrates and oxides. XXIII. Formation of ozone during the oxidation of ferric hydroxides and ferric oxides. Existence of peroxide compounds of

iron. A. KRAUSE [with E. KEMNITZ, F. WYSZYNSKI, and J. SAWICKI] (Ber., 1935, 68, [B], 1734—1743).—O₃ is evolved from boiling solutions of K₂S₂O₈ and dil. H₂SO₄. With increasing [H₂SO₄], O₃ is produced in increasing amount which is at a max. with an optimal concn. of acid. At higher concns. (> 3*N*) the formation of O₃ declines and H₂O₂ is formed in ever-increasing quantity. The formation of H₂O₂ is related to the hydrolysis of Caro's acid which under certain conditions is formed in this system. O₃ is produced in addition to O₂ as a result of the reducing action of H₂O₂ on the remaining K₂S₂O₈. Addition of Fe^{III} hydroxides and Fe₂(SO₄)₃ induces formation of O₃ at [H₂SO₄] at which it is not produced in their absence. Under certain conditions FeSO₄ is more effective than Fe₂(SO₄)₃. On the other hand, Fe compounds can accelerate the decomp. of O₃. Fe(OH)₃ and γ-FeO₂H exhibit individuality in their ability to promote the production of O₃. It is therefore probable that an unstable intermediate Fe^{III} peroxide exists analogous in structure to Caro's acid. For the production of such a compound the rate of dissolution of the Fe^{III} compound must keep pace with the rate of oxidation in order that the favourable moment for its formation may not be passed. This explains why Fe^{III} oxides can cause evolution of O₃ only when they are suitably sol. The sparingly sol. goethite, α-Fe₂O₃·H₂O, behaves similarly. Too sparing solubility reacts unfavourably on the yield of O₃, whereas too rapid dissolution causes decomp. of O₃. The final result in the system K₂S₂O₈—H₂SO₄ is due to several single processes which influence the production of O₃ and H₂O₂ favourably and unfavourably. H. W.

Behaviour of ferric chlorosulphate. F. SCAFILE (Gazzetta, 1935, 65, 588—593).—Fe^{III} chlorosulphate is not a complex salt, but a double salt of probable formula Fe₂(SO₄)₃·FeCl₃·18H₂O. By pptn. with EtOH of a solution containing this salt and Na₂SO₄ the compound 3Na₂SO₄·Fe₂(SO₄)₃·2FeSO₄(OH)·7H₂O is obtained. O. J. W.

Oxalato-compounds. H. BRINTZINGER and W. ECKARDT (Z. anorg. Chem., 1935, 224, 93—96).—The complex oxalates of bivalent Fe, Co, Ni, Mn, Cu, Cd, and Zn, empirically formulated R₂[M(C₂O₄)₂] (I), are shown by measurements of electroanalysis to have the doubled ionic formula [M₂(C₂O₄)₄]⁴⁻. The ions [M(C₂O₄)₃] of trivalent Fe, Co, Mn, Cr, and the bivalent compounds (I) with M = TiO, VO, UO₂, have the simple formula. Complex oxalates of Th and Zr have ionic wts. corresponding with [Th₂(C₂O₄)₈]⁸⁻ and [Zr₄(C₂O₄)₁₆]¹⁶⁻, respectively. J. S. A.

Complex pyrroly- and indylo-salts. O. SCHMITZ-DUMONT and S. PATERAS (Z. anorg. Chem., 1935, 224, 62—72).—Excess of the K salt of pyrrole (I), prepared from (I) and KNH₂, reacts with [Fe(NH₃)₆]Cl₂ in liquid NH₃ to give *dipotassium tetrapyrroly-iron*, [Fe(C₄H₃N)₄]K₂. Attempts to obtain the simple Fe salt Fe(C₄H₃N)₂ led to ammonolysis, forming Fe(NH₂)₂ and ultimately Fe nitride. [Ni(NH₃)₆]Cl₂ similarly gives with indole the compound [Ni(C₈H₆N)₄]K₂. The salts are readily sol. in liquid NH₃, and sensitive to air and moisture. CoCl₂ in

liquid NH₃ gives the deep violet-blue, partly ammonolysed, unstable *potassium di-indyloamino-cobalt*, [(C₈H₆N)₅CoNH₂]K. With [Cr(NH₃)₅Cl]Cl₂, C₈H₆NK forms the salt [(C₈H₆N)₃Cr·NH₂(NH₃)₂]K. [Co(NH₃)₆]Cl₃ similarly gives the μ-diamino-binuclear complex salt [(C₈H₆N)₃(NH₃)Co(NH₂)₂Co(C₈H₆N)₃(NH₃)]K₂. By the action of KNH₂ on CrCl₃ in liquid NH₃, the insol. *amide* [(NH₃)₃Cr(NH)₃] is obtained.

Purification and analysis of purpureo-cobaltic chloride. F. J. GARRICK (Z. anorg. Chem., 1935, 224, 27—28).—Crude [Co(NH₃)₅Cl]Cl₂ (I) is converted into [Co(NH₃)₅H₂O](C₂O₄)₃, which is separated from insol. [Co(NH₃)₆](C₂O₄)₃ by dissolution in cold dil. aq. NH₃. (I) is finally purified by one pptn. with HCl from cold aq. solution. For analysis, the acidified solution of (I) is treated at 0° with a slight excess of 0.1*N*-AgNO₃. The AgCl is separated from the bulk of liquid by decantation, thereby avoiding reaction with complex-bound Cl. J. S. A.

Affinity. LXV. Tensimetric analysis of system CoS—CoS₂. O. HULSMANN and W. BILTZ [with K. MEISEL] (Z. anorg. Chem., 1935, 224, 73—83).—The highest sulphide of Co is CoS₂, which is partly miscible with both S and CoS. The reported Co₂S₃, from the action of H₂S on complex Co salts, is a mixture of CoS and CoS₂. Linneite, Co₃S₄, is not formed during tensimetric degradation of CoS₂. J. S. A.

Constitution, optical activity, and photochemical behaviour of platinum complexes. I. I. LIFSCHITZ and W. FROENTJES (Z. anorg. Chem., 1935, 224, 173—193).—An attempt is made to assess the hypothesis that α- and β-bisdiethyl sulphide platinum dihalides are structural isomerides (A., 1934, 397). α-, β-, and a dimeric form of (MeEtS)₂PtCl₂, m.p. 63°, 127°, and 133°, respectively, were isolated. Optical resolution of the β-form yielded indefinite results. *r*-S-Ethyl-α-thiolactic acid, b.p. 134—135°/23 mm., yielded *d*- and *l*-forms, [α]_D¹⁸ +107° in EtOH, ±127.8° in C₆H₆. Each acid gave two forms of Pt(CHMe·SEt·CO)₂ [=PtX₂], converted into *dichlorides* by HCl: α-PtX₂, m.p. 208—209°; β-PtX₂, m.p. 188—189°; α-Cl₂Pt(XH)₂, m.p. 149—150°; β-Cl₂Pt(XH)₂, m.p. 163—164°; α-*d*- (or *l*-)PtX₂, m.p. 205—206° (decomp.), [α]_D¹⁸ +80° (EtOH), +93.8° (COMe₂), +76.6° (H₂O); β-*d*- (or *l*-)PtX₂, m.p. 180—182°, [α]_D¹⁸ 85.3° (COMe₂); α-*d*- (or *l*-)Cl₂Pt(XH)₂, m.p. 140—142°, [α]_D¹⁸ +9.7° (EtOH); β-*d*- (or *l*-)Cl₂Pt(XH)₂, m.p. 170—171°, [α]_D¹⁸ +15.5°. α-forms of Cl₂Pt(XH)₂ react rapidly, β- only slowly, with AgNO₃. All α-forms give β- on irradiation with ultra-violet light. A solution of *d*-α-form yields on crystallisation *d*-α- and *l*-β-; *l*-α- yields *l*-α- and *d*-β-. The results are difficult to reconcile with the Werner formulation (A., 1914, i, 13). T. G. P.

Analytical applications of the Raman effect. L. PIAUX (Chim. et Ind., 1935, 34, 507—516).—A comprehensive review of applications of the method in the study of liquid mixtures. H. J. E.

Mass-spectrograph determination of the relative abundance of heavy hydrogen in a sample. O. LUHR and L. HARRIS (Physical Rev., 1934, [ii],

45, 843).—The ion of mass 4 ($\text{H}^1\text{H}^1\text{H}^{2+}$) is used in the mass spectrograph to determine the concn. of D when the relative % is small. A four-fold enrichment of D by diffusion of H_2 through Pd is thus indicated (cf. A., 1934, 156). L. S. T.

Antimony electrode for measuring p_{H} . G. A. BRAVO (*L'Ind. Chimica*, 1935, 17, 521—523).—The vals. of a and b in $E=a+bp_{\text{H}}$ for this electrode are, respectively, -0.008 and 0.0525 at 15° , -0.007 and 0.0545 at 20° , and -0.005 and 0.059 at 25° . Measurements in presence of NaCl , KCl , KNO_3 , Na_2SO_4 , and NaBr give irregular results, especially at low p_{H} vals., $[\text{H}^+]$ being not raised, as would be expected, but lowered. This is explained by the formation of additive compounds, by mol. hydration, and by the presence of OH-acids in the buffer solutions. The Sb electrode may be used in presence of substances which prevent the use of the H_2 or quinhydrone electrode and does not alter the composition of the solution being tested. T. H. P.

Mixed indicators. H. A. J. PIETERS (*Chem. Weekblad*, 1935, 32, 539—541).—The following mixed indicators are recommended: bromocresol-green and Me-red (1:1, colour change red to green, p_{H} 5.6) for NH_3 titrations; neutral-red and bromothymol-blue (I) (3:4, red to green, p_{H} 7.0) for strong acids and bases; cresol-red and (I) (5:1, yellow to violet, p_{H} 7.9) for picric acid. Me-orange is the best indicator for $\text{CO}_3^{''}$ titrations. S. C.

p_{H} determination with two-colour indicators by a dilution method. J. McCRAE (*J. South African Chem. Inst.*, 1935, 18, 62—66).—9.7 c.c. of $\text{H}_2\text{O}+0.25$ c.c. of indicator solution are put in each of two test-tubes, 0.75 in. diameter, placed one behind the other; 2 drops of dil. alkali are added to one and 2 drops of dil. acid to the other. The total colour is compared with that of 9.5 c.c. of the solution under test in a third tube, either the acid or the alkali solution being diluted 0.1 c.c. at a time until an approx. match is obtained. A final exact match is made after diluting the coloured test solution to $20D/(D+1)$ c.c. with fresh test solution so as to equalise total indicator concn. of comparison tubes with that of test solution [D =dilution= $v/(v+10)$, v being vol. added to comparison tube]. The unknown $p_{\text{H}}=p_{\text{K}}\pm\log D'$, where D' =dilution for exact match, and p_{H} the p_{H} val. at middle point of colour change of the indicator. The p_{K} of the indicator chosen must lie within ± 0.8 of the p_{H} of the solution under test. S. J. G.

Determination of water. E. VON MIGRAY (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 348).—The procedure is (1) distillation of the material with xylene or PhMe, (2) dehydration of the distillate with a weighed amount of anhyd. CuSO_4 , and (3) determination of H_2O from the increase of wt. of the CuSO_4 . E. S. H.

Comparison of several electrometric and nephelometric methods for the determination of small amounts of chloride. N. H. FURMAN and G. W. Low, jun. (*J. Amer. Chem. Soc.*, 1935, 57, 1588—1591).—Comparison of three electrometric and two nephelometric methods shows that the electrometric methods are quicker and more accurate.

A new photronic nephelometer is described. The chief difficulty in nephelometry is the reproducibility of the suspensions. E. S. H.

Use of the concentration cell in quantitative analysis. I. Determination of small amounts of chloride in salts. N. H. FURMAN and G. W. Low, jun. (*J. Amer. Chem. Soc.*, 1935, 57, 1585—1588).—The procedure consists in measuring the e.m.f. between two Ag-AgCl electrodes, one of which is immersed in a solution containing the unknown amount of Cl' , and the other in a similar solution to which is added a known amount of Cl' . An advantage over the nephelometric method is that foreign salts do not cause difficulties; 0.00035 g. of Cl' per litre can be determined accurately. E. S. H.

Titration of iodides in presence or absence of chlorides and bromides with starch iodide as indicator. E. CHIRNOAGA (*Z. anal. Chem.*, 1935, 102, 339—342).—Addition of I from extraneous sources in Kolthoff's method (A., 1917, ii, 420) is avoided by adding 1—2 drops of aq. $\text{Fe}_2(\text{SO}_4)_3$ as oxidant. In presence of Cl' , but not of Br' , NaOAc may be added in place of $(\text{NH}_4)_2\text{CO}_3$. J. S. A.

Simplified Penfield method for determination of fluorine in phosphorites and apatites. S. N. ROSANOV (*Z. anal. Chem.*, 1935, 102, 328—336; cf. B., 1930, 55).—Simplifications in the author's variation of the Penfield-Treadwell method are described. J. S. A.

Colorimetric determination of dissolved oxygen [in water].—See B., 1935, 928.

Determination of oxygen with alkaline solutions of trihydroxybenzenes and of sodium hyposulphite in varying concentrations.—See B., 1935, 947.

Separation and determination of [elementary] sulphur and selenium. E. CHERASKOVA and L. VEISSBRUTH (*Z. anal. Chem.*, 1935, 102, 353).—Material containing free S and Se is boiled for 2 hr. with 10% aq. Na_2SO_3 , whereby $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SSeO_3 are formed. The solution is warmed with CH_2O , when Se is deposited. S is determined in the solution as $\text{Na}_2\text{S}_2\text{O}_3$. J. S. A.

Successive potentiometric determination of sulphide, thiocyanate, and chloride ions. A. I. BURSUK and A. M. ZANIKO (*Ber. Ukrain. wiss. Forsch.-Inst. phys. Chem.*, 1934, 4, 83—88).—To the aq. solution of the alkali salts are added 10 g. $\text{Ba}(\text{NO}_3)_2$ and 10 ml. of conc. aq. NH_3 , the solution being diluted to 100 ml. The solution is titrated potentiometrically with AgNO_3 with a Ag electrode, the first break in the curve giving the $\text{S}^{''}$ content. The solution is then acidified with HNO_3 . The next break gives the CNS' and the last the Cl' . CH. ABS. (c)

Analysis of mixtures of sulphites, sulphates, meta-arsenites, and arsenates. V. S. MALINOVSKI and E. P. LOPATINA (*J. Appl. Chem. Russ.*, 1935, 8, 944—947).— $\text{SO}_3^{''}+\text{SO}_4^{''}$ are determined by oxidation with $\text{Br}-\text{H}_2\text{O}$, followed by pptn. as BaSO_4 , $\text{AsO}_2'+\text{AsO}_4^{''}$ by oxidation with $\text{Br}-\text{H}_2\text{O}$, followed by reduction to AsO_2' , and I titration,

$\text{SO}_3'' + \text{AsO}_2'$ by I titration, and AsO_2' by adding aq. CH_2O , NaOAc , and AcOH , and titrating with 0.1N-I. R. T.

Determination of sulphate in water.—See B., 1935, 880.

Potentiometric titration of hyposulphite. T. MUROOKA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 844—852).— $\text{Na}_2\text{S}_2\text{O}_4$ can be titrated potentiometrically with AgCl or AgNO_3 in NH_3 solution, with HgI_2 , 2KI in NaOH solution, with $\text{Hg}(\text{CN})_2$, 2KCN in AcOH solution with or without addition of acetate, or with CuSO_4 in NH_3 solution. J. W. S.

Rapid gravimetric determination of selenates. R. RIPAN-TILICI (Z. anal. Chem., 1935, 102, 343—344).— PbSeO_4 is pptd. by adding a slight excess only of aq. $\text{Pb}(\text{NO}_3)_2$, and 30 vol.-% of EtOH is added. The ppt. is collected after 4 hr., and dried at room temp. J. S. A.

Colour reaction of ammonia with hypobromite and thymol. P. A. HANSEN (Z. anal. Chem., 1935, 102, 279).—Priority is claimed over Lapin and Hein (A., 1934, 1189). J. S. A.

Volumetric determination of nitrites by means of ceric sulphate solution. H. BENNETT and H. F. HARWOOD (Analyst, 1935, 60, 677—680).—The NO_2' is added to excess of $\text{Ce}(\text{SO}_4)_2$, which is titrated back with $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ using erioglaucine as internal indicator. Small amounts of K may be determined by pptn. as cobaltinitrite, which is similarly titrated. E. C. S.

Stable colorimetric scale for rapid determination of nitrates in water. R. GROS (J. Pharm. Chim., 1935, [viii], 22, 244—246).—The NO_3' is converted into $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{ONH}_4$, which is determined colorimetrically. Standard comparison solutions containing $\text{K}_2\text{Cr}_2\text{O}_7$ and NiSO_4 are described. R. S.

Electroscopic detection of yellow phosphorus in presence of tetraphosphorus trisulphide. W. D. TREADWELL and C. BEELI (Helv. Chim. Acta, 1935, 18, 1052—1060).—An apparatus for the measurement of ionisation in an air stream is described. The P is vaporised in a stream of N_2 and mixed with air in the ionisation chamber. P mixed with P_4S_3 may be detected by this method. H. J. E.

Analysis of phosphorus sulphides. C. BEELI (Helv. Chim. Acta, 1935, 18, 1172—1180).—Mixtures of P_4S_3 and P_4S_7 , and of P_4S_7 and P_4S_{10} , may be separated by fractional crystallisation from CS_2 . A melt of the composition P_2S_3 was separated by this method into P_4S_5 and P_4S_7 . White P could be separated from a liquid mixture with S by fractional sublimation in a vac. Complete separation of P_4S_3 and P, of P_4S_3 and S, and of P_4S_7 and P_4S_{10} , by vac. sublimation was not possible. Pure P_4S_3 could be sublimed from a mixture of it with P_4S_7 . S could be similarly separated from P_4S_{10} . The rates of sublimation were compared with the solubilities in CS_2 . The ease of reaction with H_2O increases in the order P_4S_3 , P_4S_{10} , and P_4S_7 . This serves to differentiate the sulphides. H. J. E.

Separation and determination of metal and phosphate ions in presence of one another. II. S. ISHIMARU (J. Chem. Soc. Japan, 1935, 56, 62—75; cf. this vol., 56).—After removal of metals of the third group by 8-hydroxyquinoline, the PO_4''' remaining in the solution may be determined by the molybdate method. CH. Abs. (e)

Potentiometric determination of phosphate. J. A. ATANASIU and A. J. VELCULESCU (Z. anal. Chem. 1935, 102, 344—350).— PO_4''' is titrated potentiometrically at 60—70° with $\text{UO}_2(\text{OAc})_2$ in presence of 0.5—1% of $p\text{-C}_6\text{H}_4(\text{OH})_2$, using Pt-Ni, but not Pt- Hg_2Cl_2 , electrodes. The solution should have p_H 5.5—6. With mono-, di-, or tri-basic orthophosphates, the end-point occurs when $\text{UO}_2'' : \text{PO}_4''' = 1 : 1$. J. S. A.

Removal of phosphoric acid in qualitative micro-analysis. (MLLE.) S. GINSBURG and H. PRINGSHEIM (Bull. Soc. chim., 1935, [v], 2, 1694—1697).— H_3PO_4 can be removed from solutions buffered with NH_4OAc by aged $\text{Fe}(\text{OH})_3$ sol, preferably with two successive additions and filtrations. NiSO_4 , FeCl_3 , MnSO_4 , $\text{Al}_2(\text{SO}_4)_3$, and ZnSO_4 do not affect the extraction, but in presence of $\text{Cr}_2(\text{SO}_4)_3$ a greater quantity of $\text{Fe}(\text{OH})_3$ is required. J. W. S.

Test for phosphate and arsenate. L. W. MARRISON (Chem. and Ind., 1935, 872).—A drop of solution + a drop of 0.02N aq. Na_2S , on filter-paper, is allowed to mix with a drop of dil. $(\text{NH}_4)_2\text{MoO}_4$, acidified with H_2SO_4 . In presence of 0.0005 mg. of PO_4''' or AsO_4''' a blue colour develops. SCN' , $\text{Fe}(\text{CN})_6'''$, and $\text{Fe}(\text{CN})_6''''$ should be absent. J. S. A.

Micro-alkalimetric studies. I. J. MIKA (Publ. Dept. Min. Met. Palatin-Joseph Univ., 1934, 6, 227—237).—Micro-titrations of borax with 0.01N-HCl can be made with an accuracy of 0.1%. CH. Abs. (e)

Volumetric determination of silicic acid. S. KITAJIMA (Bull. Chem. Soc. Japan, 1935, 10, 341—345).—The conditions for the complete pptn. of SiO_2 by $(\text{NH}_4)_2\text{MoO}_4$ have been studied. The SiO_2 in the ppt. can be determined gravimetrically, by titration with NaOH , or by reduction and back-titration with KMnO_4 . R. S.

Determination of very small amounts of carbon monoxide in air.—See B., 1935, 880.

Photocolorimetric determination of carbon dioxide in air.—See B., 1935, 976.

Determination of fumigants. I. Residual hydrocyanic acid in stored products.—See B., 1935, 928.

Zinc cobaltinitrite for the detection of potassium. J. ADAMS, M. HALL, and W. F. BAILEY (Ind. Eng. Chem. [Anal.], 1935, 7, 310—311).—Zn cobaltinitrite may be used in place of the Na salt when the solution has subsequently to be tested for Na. A yellow ppt. forms after 15 min. when 0.4—0.6 mg. of K⁺ per c.c. is present. E. S. H.

[Determination of potassium, iron, and magnesium in water.]—See B., 1935, 880.

Determination of potassium.—See B., 1935, 966.

Determination of alkalis in feldspars. Modified hydrofluoric acid method. E. W. KOENIG (Ind. Eng. Chem. [Anal.], 1935, 7, 314—315).—Modified procedure for removal of Al, Fe, Mg, Ca, F, and SiO₂ is recommended. E. S. H.

Determination of calcium as oxide. A. IEVINŠ (Latvij. Univ. Raksti, 1935, 2, 465—472).—If either the carbonate or oxalate is ignited over the blast or Bunsen burner the resulting oxide will contain SO₄. A protector should be used or the ignition conducted in an electric furnace. E. H. S.

Calcium, strontium, barium, and magnesium oxalates. J. HASLAM (Analyst, 1935, 60, 668—672).—The behaviour of the oxalates, separately and together, when pptd. and washed by Dick's method (A., 1929, 901), has been investigated. For Ca, titration of C₂O₄ in the ppt. gives more trustworthy results than weighing, particularly when sintered glass crucibles are used, but EtOH must be completely removed by heating at 100°. Sr is pptd. as SrC₂O₄·H₂O, but pptn. is incomplete, the ppt. is unstable at 100°, and its titration is unsatisfactory owing to interference of SrSO₄. Ba is pptd. as BaC₂O₄·0.5H₂O, which is fairly stable at 100°. Titration is unsatisfactory in presence of H₂SO₄ (cf. Sr), but may be carried out in presence of HClO₄. Mg is pptd. as MgC₂O₄·2H₂O, which is sol. in aq. NH₃, but is likely to be co-pptd. with Ca, so that a double pptn. of Ca should be carried out in presence of Mg. Sr and Ba interfere with the determination of Ca. E. C. S.

Argentometric determination of barium oxide and sulphide in barium aluminate.—See B., 1935, 947.

Gravimetric determination of lead as lead salicylaldoxime and its solubility measurement by using Th-B as radioactive indicator. M. ISHIBASHI and H. KISHI (Bull. Chem. Soc. Japan, 1935, 10, 362—368; cf. this vol., 577, 720).—Pptn. of Pb is quant. from solutions of $p_K \leq 6.5$ (neutral or NH₃). R. S.

Electrolytic determination of lead as dioxide and its conversion into lead monoxide by ignition. A. J. LINDSEY (Analyst, 1935, 60, 598—599).—Determination of Pb in electrodeposited PbO₂ by ignition to PbO in an electric furnace at 700° is impracticable owing to slow volatilisation of PbO at this temp. E. C. S.

Spectral analytical determination of lead in commercial tin.—See B., 1935, 954.

Electrolytic determination of tin and lead in ores.—See B., 1935, 955.

Electrometric determination of thallium. W. R. A. HOLLENS and J. F. SPENCER (Analyst, 1935, 60, 672—676).—Tl^I is oxidised to Tl^{III} with Cl₂, which is completely removed. The I liberated by Tl^{III} from KI is then titrated with Na₂S₂O₃ or Na₃AsO₃, using Foulk and Bawden's bimetallic electrode (A., 1926, 927). Good end-points are obtained with as little as 0.002N-Tl. In the case of Na₂S₂O₃, the [AcOH] may be varied within wide

limits. Zn and Fe^{II} do not interfere, but Cu behaves similarly to Tl and must be determined separately. E. C. S.

Macro- and micro-gravimetric determination of copper. G. SPACU and C. G. MACAROVICI (Z. anal. Chem., 1935, 102, 350—352).—To a cold dil. aq. solution containing Cu, NH₄CNS is added and then a 2% solution of benzidine in EtOH. [Cu(C₆H₄·NH₂)₂(CNS)₂] is pptd. The ppt. is washed with H₂O and ignited to CuO. Tolidine may also be used. J. S. A.

Determination and separation of metals with "thionalide." II. R. BERG and W. ROEBLING (Angew. Chem., 1935, 48, 597—601; cf. this vol., 591, 950).—Cu, Ag, Hg, and Bi may be quantitatively pptd., and separated from Pb, Cd, and Tl, by addition of 1—2% aq.-EtOH or -AcOH solutions of "thionalide" (thioglycollic naphthalide) (I) to their dil. HNO₃ solution. The ppts. may be dried at 100°, or ignited, or may be determined volumetrically with I, or by Bucherer's filtration method. Fe and other oxidising agents must be absent. [Cl] must be < 0.1N. Excess of (I) may be removed as insol. (C₁₀H₇·NH·CO·CH₂·S)₂ by treatment of the solution with I. J. S. A.

Application of X-ray spectroscopic method to the analysis of the rarer elements. III. Determination of praseodymium in rare-earth mixtures. S. SHINODA. **IV. Determination of gadolinium in rare-earth mixtures.** K. KIMURA and Y. TSUNODA (J. Chem. Soc. Japan, 1935, 56, 76—80, 81—91).—III. The intensities of the L_{β2} line of Pr and the L_{β3} line of Nd are equal when the oxides are mixed in the wt. ratio Nd₂O₃/Pr₆O₁₁ = 6.4. **IV.** The intensities of the L_{α1} lines of Gd and Nd are equal when Nd₂O₃/Gd₂O₃ = 4.45. CH. ABS. (e)

Volumetric determination of aluminium. W. DAUBNER (Angew. Chem., 1935, 48, 589).—The Al solution (neutral or slightly acid with AcOH; 1 mg. Al in 10 c.c.) is added in the cold to a solution containing NH₄Cl 5, AcOH 5, and As₂O₅ 0.45%. The mixture is heated to the b.p. AlAsO₄ is pptd., washed with EtOH, dissolved in HCl, and the H₃AsO₄ determined volumetrically. With > 0.53% of As₂O₅ in the pptg. solution high vals. are obtained, due to incomplete conversion of Al₂(HASO₄)₃ into AlAsO₄. With < 0.38% of As₂O₅, Al₄(AsO₄)₃(OH)₃ is pptd., and the result is low. Silicates do not interfere. Fe must first be separated from the Al. H. J. E.

Volumetric determination of aluminium in solutions. M. K. BACHMUTOVA (Legk. Metal., 1934, 3, No. 9, 37—41).—Al was determined in HCl solution by titrating one portion with NaOH (phenolphthalein) to determine the total acidity. To a second portion a slight excess of K₂C₂O₄ is added to bind the Al, and the free acid is titrated with NaOH [K₄Fe(CN)₆ indicator]. CH. ABS. (e)

Quantitative separation of aluminium from manganese, nickel, cobalt, and zinc. T. KÔZU (J. Chem. Soc. Japan, 1935, 56, 22—30).—Al is pptd. alone at room temp. by (CH₂)₆N₄ (1 mol., slightly acidic with H₂SO₄) from a mixture containing Al, Mn, Ni, and Co. CH. ABS. (e)

Modified persulphate-arsenite method for determination of manganese.—See B., 1935, 854.

Victoria-blue BX as internal indicator in ceriometry. J. M. CALDWELL and M. E. WEEKS (Trans. Kansas Acad. Sci., 1934, 37, 117—118).—The colour change is from sky-blue to light pink. It is irreversible, but overstepped end-points can be redetermined by adding a Fe^{II} solution and further indicator. The indicator is unsuitable for Fe determinations with the SnCl_2 method of reduction, but works well with reduction by means of Cd, Al, or Zn. To the reduced Fe solution 5 c.c. of H_3PO_4 (d 1.70), 20 c.c. of 10N- H_2SO_4 , and 5 drops of 0.2% dye solution in EtOH are added, and the solution is titrated with $\text{Ce}(\text{SO}_4)_2$. CH. ABS. (e)

Determination of iron in iron ores and silicates.—See B., 1935, 853.

Errors in quantitative spectrographic analysis in the iron-silicon system.—See B., 1935, 854.

Application of citric acid to determination of nickel in presence of salts of iron and of phosphoric acid. V. P. GOLENDEEV (Rep. U.S.S.R. Fat and Margarine Inst., 1935, No. 2, 22—26).—10 c.c. of 10% aq. Na citrate are added to 20 c.c. of solution, the mixture is heated at 100° for 15—20 min., cooled, 10 c.c. of 10% aq. NH_3 are added, and H_2O to 250 c.c. 10 c.c. of 0.04N-KCN are added to 20 c.c. of this solution, and excess of KCN is titrated with 0.02N- AgNO_3 . R. T.

Potentiometric titration of organic precipitates. II. Indirect volumetric determination of nickel. S. ISHIMARU (J. Chem. Soc. Japan, 1935, 56, 19—21).—The end-point in the titration of excess of $\text{K}_2\text{Cr}_2\text{O}_7$ with FeSO_4 is determined potentiometrically (cf. *ibid.*, 1933, 54, 367). This is more convenient for larger amounts of Ni. CH. ABS. (e)

Titration of chromium. II. Oxidation of trivalent chromium to hexavalent chromium. D. BRAED (Ann. Chim. Analyt., 1935, [iii], 17, 257—262).— Cr^{III} is oxidised to CrO_4^{II} by heating with $\leq 50\%$ $\text{HClO}_4 + \text{H}_2\text{SO}_4$. The solution is diluted, and boiled to remove Cl. CrO_4^{II} is then determined volumetrically or, with < 0.3 mg., colorimetrically with diphenylcarbazide. $\text{K}_2\text{S}_2\text{O}_8$ in presence of AsNO_3 may also be used as oxidant in absence of Cl. J. S. A.

Colorimetric determination of molybdenum in special steels.—See B., 1935, 952.

Colorimetric determination of titanium in cast iron and steel.—See B., 1935, 952.

Reactions of titanium and manganese with hydrogen peroxide in basic solution. L. E. PORTER and G. N. CADE, jun. (J. Amer. Chem. Soc., 1935, 57, 1604—1605).—The impossibility of separating Ti from Mn by the use of H_2O_2 and NaOH is due to the adsorption of peroxidised Ti by the pptd. MnO_2 . The amount of Ti in the ppt. is reduced by increasing $[\text{H}_2\text{O}_2]$. E. S. H.

Determination of small quantities of zirconium in rocks by the phosphate method. V. A. OSCHMAN and T. K. ZERTSCHANINOVA (Redk. Met., 1934, 3, No. 6, 36—37).—Zr should be pptd. in 1%

H_2SO_4 ; more conc. solutions cause considerable loss. Ti must first be eliminated. In testing qualitatively for Zr with 2 : 1- $\text{NO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, sulphates, if present, must be removed with BaCl_2 .

CH. ABS. (e)

Hexammine cobaltic compounds in the gravimetric determination of vanadium. W. G. PARKS and H. J. PREBLUDA (J. Amer. Chem. Soc., 1935, 57, 1676—1678).—When $\text{Co}(\text{NH}_3)_6^{\text{III}}$ is added to neutral, basic, and acid solutions, respectively, of VO_3^{I} , the compounds pptd. are $\text{Co}(\text{NH}_3)_6(\text{VO}_3)_3$, $[\text{Co}(\text{NH}_3)_6]_4(\text{V}_2\text{O}_7)_3$, and $[\text{Co}(\text{NH}_3)_6]_4(\text{V}_6\text{O}_{17})_3$. The ppt. formed in acid solution can be used for the quant. separation of V from P, $\text{AsO}_4^{\text{III}}$, Fe^{III} , Cu^{II} , and Ca^{II} , but not from WO_4^{II} , MoO_4^{II} , or Pb^{II} . E. S. H.

Photometric titration. Application of the copper-cuprous oxide cell, and determination of vanadium in steel.—See B., 1935, 854.

Analysis of bismuth by means of selenious acid. O. FUNAKOSHI (Bull. Chem. Soc. Japan, 1935, 10, 359—362).—The influence of $[\text{SeO}_2]$, $[\text{HNO}_3]$, and various cations on the pptn. of Bi has been studied. Bi is most accurately determined if weighed as Bi_2O_3 . R. S.

Detection and determination of gold by means of carbon monoxide. R. N. COSTEANU (Z. anal. Chem., 1935, 102, 336—338).—A few mg. of material are dissolved in $\text{HCl} + \text{HNO}_3$, and the solution is applied to filter-paper. The purple colour produced by the action of CO at room temp. during 20—30 min. is matched against that of paper treated with Au solutions of known concn. J. S. A.

Toluene-mercury thermo-regulator for room control. H. BARRELL and J. C. EVANS (J. Sci. Instr., 1935, 12, 281—284).—The bulb has a very large sp. surface. Room temp. may be kept const. to 0.1° . C. W. G.

Apparatus for raising or lowering the temperature of a laboratory furnace in a predetermined manner. F. ADCOCK (J. Sci. Instr., 1935, 12, 285—288).—A moving potential divider provides a steadily increasing or decreasing e.m.f., opposing that due to a thermocouple in the furnace. The resulting current, by means of a relay, controls the heating current. C. W. G.

Temperature bath for scientific measuring instruments. L. UBBELOHDE and C. WALTHER (Oel u. Kohle, 1935, 11, 610).—The instrument (*e.g.*, a viscosimeter) is supported in a vapour bath which can be used with liquids of different b.p. The condensing surface is H_2O -cooled, and forms part of an inverted cone at the top of the boiling tube. H. J. E.

Heat capacities and entropies of organic compounds. I. Thermodynamic temperature scale in terms of the copper-constantan thermocouple from 12° to 273° abs. J. G. ASTON, E. WILLIHNGANZ, and G. H. MESSERLY (J. Amer. Chem. Soc., 1935, 57, 1642—1646).—The Cu-constantan couples have been compared with a He thermometer. The temp. scale derived is in satisfactory agreement with the Leiden scale, using H_2 and O_2 v.-p. thermometers. E. S. H.

Electrical method of determining specific heats. E. C. McCracken (Proc. Iowa Acad. Sci., 1933, 40, 157).—Sp. heats were measured by comparing the rate of heating of H_2O by direct passage of current with that when the H_2O contains small particles of the material. The method is specially applicable when the method of mixtures cannot be used. CH. ABS. (e)

Nickel-plated Parr bombs for peroxide fusion. C. L. TSENG, M. HSU, and M. HU (Sci. Quart. Nat. Univ. Peking, 1935, 5, 382).—Ni bombs for peroxide fusions for As determinations etc. can be replaced by Ni-plated steel bombs provided these are polished before and after plating. They should be replated after being used 2 or 3 times. H. G. M.

Use of oil diffusion pumps for evacuating X-ray tubes. J. A. BEARDEN (Rev. Sci. Instr., 1935, [ii], 6, 276—277).—The oil is heated by an immersed nichrome wire coil. C. W. G.

Colorimeter tube for p_H determinations. K. BUCH (Finska Kem. Medd., 1934, 43, 112—114).—The tube is provided with two very short side arms which are ground and fitted with plane glass, the solution being viewed perpendicular to the longitudinal axis of the tube. CH. ABS. (e)

Electrode arrangement for spark spectrography. P. S. WILLIAMS and G. H. SCOTT (Rev. Sci. Instr., 1935, [ii], 6, 277—278).—The electrode lines are eliminated by the optical configuration of the apparatus. C. W. G.

Illuminator for printing Laue photographs. C. H. DWIGHT and H. KERSTEN (Rev. Sci. Instr., 1935, [ii], 6, 287).—By means of a non-rectilinear sector in a rotating disc the negative is so illuminated that the centre of the positive is not over-exposed. C. W. G.

Reproducible process for accurate photomicrography of dispersions, with special reference to the examination of bituminous emulsions for road construction. I. HVIDBERG (Kolloid-Z., 1935, 72, 274—279).—A description of technique. E. S. H.

Integrating α -ray photometer for X-ray crystal analysis. G. J. MUELLER (Physical Rev., 1934, [ii], 45, 762). L. S. T.

X-Ray camera for low temperatures. (MLLE.) B. RUHEMANN (Physikal. Z. Sovietunion, 1935, 7, 572—582).—In the vac. X-ray camera described, the substance under test, but not the film, is in a vac. One form can be used for any temp. between room temp. and that of liquid H_2 with a constancy of $\pm 0.1^\circ$ during exposure for several hr. J. W. S.

Determination of refractive index of liquids.—See B., 1935, 833.

Method for determining the orientation of a crystal under a microscope. R. G. WOOD and S. H. AYLIFFE (J. Sci. Instr., 1935, 12, 299).—The microscope, with its axis horizontal, is placed between the collimator and telescope of a photogoniometer. A stage goniometer is mounted on the microscope. C. W. G.

Purification of electrode carbons for spectral analysis. T. ZÜRRER and W. D. TREADWELL (Helv. Chim. Acta, 1935, 18, 1181—1189).—C electrodes are readily purified by passing a flame arc (12 amp.) for 2—3 min. in an atm. of A or N_2 . Addition of 5% of Cl_2 to the inert gas assists the purification, and is essential for the removal of B, Cu, and Mg. Addition of HCl hinders the purification. H. J. E.

Preparation of light pencils and ovens from Nernst oxides. C. TINGWALDT (Physikal. Z., 1935, 36, 627—629).—Four methods of prep. are described. A. J. M.

Microcolorimeter. T. W. PRATT and A. L. TATUM (Science, 1935, 82, 305—306). L. S. T.

Preparation of the sample in X-ray emission spectroscopy. E. A. W. MÜLLER (Z. wiss. Phot., 1935, 34, 181—196).—A review discussing the avoidance of impurities in the anode in X-ray emission spectroscopy, and describing the procedure adopted for compact solids, powders, gases, and substances of high v.p. and low m.p., by the primary and secondary methods. A. J. M.

Hydrogen discharge tube for absorption spectroscopy. W. H. WATSON and D. G. HURST (Canad. J. Res., 1935, 13, A, 19—21).—A compact H_2O -cooled tube with the capillary and electrodes arranged axially is described. H. J. E.

Standards of electromotive force. G. W. VINAL, D. N. CRAIG, and L. H. BRICKWEDDE (Trans. Electrochem. Soc., 1935, 68, 263—274).—Saturated and unsaturated forms of Cd standard cells are briefly described, and statistical data on the constancy of commercial unsaturated cells are given. Methods employed at the Bureau of Standards for the construction of saturated (both neutral and acid types) cells are described. Traces of Pb, Ca, and Cr can be eliminated from Cd by two distillations under reduced pressure. The "conductivity" H_2O employed has a conductivity of $< 1 \times 10^{-6}$ ohm. The choice of glass for the cell is important, but in acid cells soft glass can be used. W. P. R.

Line-operated vacuum-tube voltmeter. R. L. GARMAN and M. E. DROZ (Ind. Eng. Chem. [Anal.], 1935, 7, 341—342).—The apparatus is capable of operating on a.c. and d.c. lines and is designed to minimise the effects of line-voltage variations. E. S. H.

Conducting films in high vacua. C. L. HENSHAW (Rev. Sci. Instr., 1935, [ii], 6, 287—288).—Connexion between the metal film and wire seal is made by means of a drop of Aquadag. C. W. G.

Non-metallic conducting films. S. BLOOMENTHAL (Physical Rev., 1934, [ii], 45, 122).—Immutable conducting films, which adhere to any clean solid, have been prepared from synthetic resin solutions containing finely-powdered C in suspension. With a const. thickness, the resistivity depends chiefly on the proportion of binder and the type of C used. L. S. T.

Direct current in measurement of electrolytic conductance. J. N. BRÖNSTED and R. F. NIELSEN (Trans. Faraday Soc., 1935, 31, 1478—1481).—A high degree of accuracy is attainable by the use of

d.c. instead of a.c. in measuring electrolytic conductance, using H electrodes. The procedure is described in detail. The chief advantage of the method, which is recommended, is simplicity.

F. L. U.

Electronic bridge balance indicator for conductance measurements. R. L. GARMAN and G. F. KINNEY (Ind. Eng. Chem. [Anal.], 1935, 7, 319—320).—The apparatus permits resistances to be determined with a precision of $\pm 0.01\%$.

E. S. H.

Wilson cloud chambers with an increased time of sensitivity. J. A. BEARDEN (Rev. Sci. Instr., 1935, [ii], 6, 256—259).—By using H_2O for the floor of the expanding space and a slow rate of expansion, the time of sensitivity is increased to 2 sec.

C. W. G.

Counter tubes with alkali [metal] cathodes. W. CHRISTOPH (Ann. Physik, 1935, [v], 23, 747—760).—The construction of a Geiger-Müller counter for the visible spectrum, employing alkali-metal cathodes (Na and K), is described. The behaviour of the counter could not, however, be stabilised.

A. J. M.

Geiger-Müller counter suitable for the measurement of diffracted Mo K X-rays. D. P. LE GALLEY (Rev. Sci. Instr., 1935, [ii], 6, 279—283).—The impulses are amplified and recorded mechanically by a thyratron circuit, at rates up to 600 per min.

C. W. G.

Investigation of an alternating-current [bridge] method of determining critical potentials [in a vapour]. R. W. HICKMAN (Physical Rev., 1934, [ii], 45, 287).

L. S. T.

Electron microscope. C. J. CALBICK and C. J. DAVISSON (Physical Rev., 1934, [ii], 45, 764).—The images obtained reveal the crystal structure of the emitting surface together with activation and deactivation effects.

L. S. T.

Improvement in precision potentiometers. D. C. GALL (J. Sci. Instr., 1935, 12, 284—285).—The residual potential is overcome, so that very small potentials, either positive or negative, can be measured.

C. W. G.

Apparatus for electron diffraction at high voltages. G. P. THOMSON (Trans. Faraday Soc., 1935, 31, 1049—1051).—The apparatus uses the principle of two-stage acceleration and works over the range 45,000—85,000 volts.

E. S. H.

High-intensity discharge tube. D. S. STEVENS (Rev. Sci. Instr., 1935, [ii], 6, 260).—A tube previously described (this vol., 466) is improved.

V G

Silver-silver bromide electrode suitable for measurements in very dilute solutions. A. S. KESTON (J. Amer. Chem. Soc., 1935, 57, 1671—1673).—Reproducible $Ag|AgBr$ electrodes are prepared by heating an intimate mixture of Ag_2O and $AgBrO_3$ at 650° . E.m.f. of the cell $H_2|HBr(m)|AgBr|Ag$ have been determined over a range of concns. The mol. electrode potential of the $Ag|AgBr$ electrode is 0.0711 volt.

E. S. H.

Germanium-germanium dioxide electrode. M. L. NICHOLS and S. R. COOPER (Ind. Eng. Chem.

[Anal.], 1935, 7, 350—352).—The p.d. against the calomel electrode varies with p_H , but the $Ge|GeO_2$ electrode is unsatisfactory for p_H determinations.

E. S. H.

Potentiometric titrations with the germanium-germanium dioxide electrode. M. L. NICHOLS and S. R. COOPER (Ind. Eng. Chem. [Anal.], 1935, 7, 353—355).—The $Ge|GeO_2$ electrode is satisfactory for the potentiometric titration of many org. and inorg. acids, and $NaOH$; it is not satisfactory for weak bases and salts, except NH_3Ph and Na_2CO_3 . It may be used in solutions of HNO_3 , $HClO_4$, maleic and fumaric acids, where the H_2 electrode is unsatisfactory.

E. S. H.

Apparatus for determining magnetic constants of mineral powders. V. H. GOTTSCHALK and C. W. DAVIS (U.S. Bur. Mines, Rept. Invest., 1935, No. 3268, 51—65).—A modified isthmus permeameter having a spark-suppressed primary and a multiplier in the secondary circuit to regulate the effect of capsules of the mineral powder functioning as a twin isthmus is described, and normal induction and hysteresis curves obtained by means of the instrument with various magnetite and pyrrhotite samples are given and discussed.

A. R. P.

Magnetometer for crystal ferromagnetism and its application to iron-cobalt alloy crystals. L. W. MCKEEHAN and J. W. SHIH (Physical Rev., 1934, [ii], 45, 742; cf. A., 1934, 1061).

L. S. T.

Apparatus for the study of liquid-vapour equilibrium compositions. R. M. WILEY and E. H. HARDER (Ind. Eng. Chem. [Anal.], 1935, 7, 349—350).—With $EtOH-H_2O$ mixtures the apparatus gives results in good agreement with published vals.

E. S. H.

Apparatus for decomposition of [mineral] specimens without admitting air. A. M. VASILIEV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 133—135).—An apparatus for determining FeO after dissolution of the specimen in a CO_2 atm. is described.

CH. ABS. (e)

Determination of combustible gases in the air of the uppermost strata of the earth by means of a new apparatus. A. GRAF (Oel u. Kohle, 1935, 11, 644—648).—A portable micro-calorimeter, comprising a bridge, galvanometer, and small metal gas holder, is used. Combustible gases burn at a Pt filament and current measurements are made.

C. C.

Apparatus for potentiometric determination of atmospheric carbon dioxide.—See B., 1935, 926.

Glass electrode for p_H measurements. K. SCHWABE (Z. Elektrochem., 1935, 41, 681—694).—A review of published work on apparatus, technique, and applications.

E. S. H.

Absorption apparatus for micro-determination of volatile substances. III.—See this vol., 1436.

Detector for determination of low concentrations of hydrogen sulphide.—See B., 1935, 947.

Magneto-optic method of chemical analysis. F. G. SLACK and J. A. PEOPLES, jun. (Physical Rev., 1934, [ii], 45, 126; cf. A., 1934, 1321). L. S. T.

Device to compensate for magnetic field fluctuation in a mass spectrograph. A. O. NIER (Rev. Sci. Instr., 1935, [ii], 6, 254—255).—By means of a vac.-tube rectifier the electric field is caused to vary as the magnetic field changes, so that the deflexion of an ion is unaltered. C. W. G.

Höppler viscosimeter versus Vogel-Ossag viscosimeter. J. J. LEENDERTSE (Chem. Weekblad, 1935, 32, 553—555). C. G. VERVER (*Ibid.*, 1935, 32, 555—556).—A reply to Cannegieter (this vol., 1098). The Höppler instrument is adversely criticised as being too empirical for a standard instrument. S. C.

Viscosity measurements by R. O. Herzog and collaborators. L. URBELOHDE (Cellulosechem., 1935, 16, 64).—Polemical. A. G.

Precision viscosimeter. O. FITZSIMONS (Ind. Eng. Chem. [Anal.], 1935, 7, 345—347).—The Ubbelohde capillary viscosimeter is modified by using dual capillaries and mounting in a vapour bath. E. S. H.

Constant-flow orifice meters of low capacity. R. T. PAGE (Ind. Eng. Chem. [Anal.], 1935, 7, 355—358).—The construction and calibration of the orifice are described. E. S. H.

Determination of specific gravity of gases. Improvements in the effusion method. L. C. KEMP, jun., J. F. COLLINS, jun., and W. E. KUHN (Ind. Eng. Chem. [Anal.], 1935, 7, 338—341).—Sources of error in the usual determination have been traced. With the technique described an accuracy of about 2.5% is obtained when d is <1.30 . Stainless steel is recommended as a substitute for Pt in making the orifice plate. E. S. H.

Reflux regulator for laboratory stills. J. H. BRUUN (Ind. Eng. Chem. [Anal.], 1935, 7, 359—360). E. S. H.

Oxygen liquefier. G. WINCHESTER and D. M. HILL (Rev. Sci. Instr., 1935, [ii], 6, 288).—O₂ under pressure enters a Cu vessel through $\frac{1}{16}$ -in. holes and condenses in a surface cooled by liquid air. 1 litre of the latter produces about 750 c.c. of liquid O₂. C. W. G.

Speed of divergent-nozzle pumps. M. J. COPLEY, O. C. SIMPSON, H. M. TENNEY, and T. E. PHIPPS (Rev. Sci. Instr., 1935, [ii], 6, 265—267).—Long divergent nozzles give greater speed factors than straight or short divergent ones. C. W. G.

Device for determining the surface tension of small amounts of liquid. S. NATELSON and A. H. PEARL (J. Amer. Chem. Soc., 1935, 57, 1520—1523).— γ of 0.1 c.c. of a liquid is determined by the rise in a very fine capillary tube (0.2—0.3 mm. diam.), sealed to a wider capillary. R. S. C.

Method of attaching a fluorite window to glass apparatus. F. PALMER, jun. (Physical Rev., 1934, [ii], 45, 556—557). L. S. T.

Capillaroscopy. A new capillarscope. E. L. LEDERER (Kolloid-Z., 1935, 72, 267—273).—Apparatus

for determining the rate of spreading of liquids in capillary structures is described, and results are given for many org. liquids, aq. solutions, and natural oils. The results can be expressed in the form $s^2 = k'\sigma t/\eta$, where s is the distance penetrated in time t , σ the surface tension, and η the viscosity. E. S. H.

Ultracentrifuge. E. G. PICKELS (Physical Rev., 1934, [ii], 45, 748—749).—Further improvements are described (cf. A., 1934, 625). L. S. T.

Automatic recording mass spectrograph. P. T. SMITH, W. W. LOZIER, and W. BLEAKNEY (Physical Rev., 1934, [ii], 45, 761—762). L. S. T.

Micro-pyknometer method for density determinations. G. R. CLEMO and A. MCQUILLEN (J.C.S., 1935, 1220).—Dimensions of and method of using a micropyknometer and vals. obtained with C₆H₆ are given. The mean deviation from the mean of 29 weighings is 0.005 mg. P. G. C.

Method for studying the performance of continuous filters. G. NETZEL (Chem.-Ztg., 1935, 59, 701—704).—The performance of rotary filters of the "Imperial" type, fitted with cord devices for stripping the cake, can be accurately investigated by means of a model laboratory apparatus (described in detail), in which a small filter-plate (10×15 cm.), fitted with a cord-frame for removing the cake and connected to a manometer and filter-pump, is employed and the operations of dipping, washing, clearing, etc. are performed by hand and accurately timed. E. L.

Characteristics of mercury-vapour pumps. L. E. PINNEY (Proc. Iowa Acad. Sci., 1933, 40, 157).—Curves showing the relation between the fore pressure and the flow of Hg vapour required to produce a definite vac. are recorded. CH. ABS. (c)

Technique of ultrafiltration with a Cellophane membrane. L. BRULL (Compt. rend. Soc. Biol., 1935, 120, 98—99).—An apparatus is described. R. N. C.

Fractional ultrafiltration. H. C. ALLISBAUGH and R. R. HYDE (Amer. J. Hyg., 1935, 21, 64—93).—The prep. of collodion ultrafilter membranes is described. The particle size of *Staph. aureus* (I) was found to be practically the same by ultrafiltration and by direct measurement. That of filterable viruses falls between those of (I) and colloidal Au. Association with a protein carrier may cause their retention by relatively large pores. CH. ABS. (c)

Use and regeneration of drierite [CaSO₄]. W. A. HAMMOND (J. Chem. Educ., 1935, 12, 445—446).—Directions are given. L. S. T.

Methods of weighing by swings. H. L. LOCHE (J. Chem. Educ., 1935, 12, 414).—One set of 5 swings may introduce an error of approx. 0.1 mg. owing to poor reproducibility of the rest point; the average of 3 sets of 3 swings gives results practically as trustworthy as the average of 3 sets of 5 swings, whilst the average of 2 or 3 sets of deflexion data obtained by Pregl's method agrees well within 0.1 mg. with the average of 3 sets of 5 swings and is more rapidly and simply obtained. L. S. T.

Demonstration of rotating-vibrating diatomic molecules. T. H. HAZLEHURST, jun. (J. Chem.

Educ., 1935, 12, 353—355).—A device for illustrating the motions of atoms in a rotating-vibrating diat. mol. is described. L. S. T.

Simple mercury seal. T. RICHES and W. B. MANN (J. Sci. Instr., 1935, 12, 298).—A Hg-operated ball-valve is made by pressing a steel ball against a shoulder in Pyrex tubing while the latter is soft. C. W. G.

Instrument for measuring evaporation from surfaces. J. S. OWENS (J. Sci. Instr., 1935, 12, 291—293).—The evaporating pan is supplied with H₂O from a graduated tube. C. W. G.

Use of the McLeod gauge with non-permanent gases. M. FRANCIS (Trans. Faraday Soc., 1935, 31, 1325—1331).—Deviations from the gas laws are insufficient to account for the supposed failure of the McLeod gauge to measure pressures of non-permanent gases, but good agreement between the readings taken at different points in the capillary does not prove that sorption errors are absent. The differences between measurements made with SO₂ and air were small at pressures > 0.004 mm. Vols. for the quantity of gas transferred calc. from observed pressure changes and known vols. are not trustworthy owing to movements of sorbed gas when the pressure is changed. J. G. A. G.

Humidity slide rule. E. G. BILHAM (J. Sci. Instr., 1935, 12, 318—322).—V.p., dew point, R.H., and H₂O content can be found from readings of wet and dry bulb thermometers. C. W. G.

Gas-specific gravity balance. J. S. HALES and W. C. MOSS (J. Sci. Instr., 1935, 12, 309—313).—The upthrusts of different gases on a glass bulb are balanced by the adjustment of riders. C. W. G.

Modified Soxhlet extractor. E. W. BLANK (Cereal Chem., 1935, 12, 543—544).—The difficulty of the preferential passage of the ether through the filter-paper is obviated by using a glass tube open at both ends and of such a diameter as to fit closely in the thimble. When the material is to be weighed before and after extraction, a cut-off test-tube, with holes blown in the round end and containing a layer of cotton at the bottom, is used as a thimble. E. A. F.

Chemistry in the Bucheum. J. R. PARTINGTON (Chem. and Ind., 1935, 884—886).

When and by whom was alcohol first prepared from ethylene? B. HERSTEIN (Chem. and Ind., 1935, 881—884).

Discovery of tellurium. M. E. WEEKS (J. Chem. Educ., 1935, 12, 403—409).—Historical. L. S. T.

Geochemistry.

Hydrogen in the upper atmosphere. J. KAPLAN (Nature, 1935, 136, 549—550).—The effect of H₂ on N afterglow is discussed in relation to the occurrence of H₂ in the upper atm. L. S. T.

Variability of nitrogen compounds (NO₂, NO₃, and NH₃) in Baltic sea-water. H. PILWAT (Angew. Chem., 1935, 48, 590—591).—The NO₂' content of the H₂O decreases on keeping. Data for the variation of [NH₃] and [NO₃'] on storage, and for seasonal variations in concns., are recorded. H. J. E.

Indian Hot Springs, Graham County, Arizona. M. M. KNECHTEL (J. Washington Acad. Sci., 1935, 25, 409—413).—Analyses are given. C. W. G.

Presence of lithium in waters from the Turin hills. M. JARACH (Annali Chim. Appl., 1935, 25, 385—388).—Certain of the waters of the hilly zone to the west of Turin show by spectroscopic tests > 0.5 mg. of Li per litre. T. H. P.

Iron in the sea and in marine plankton. L. H. N. COOPER (Proc. Roy. Soc., 1935, B, 118, 419—438).—Fe in true solution in sea-H₂O is < 2 mg. per cu.m., [Fe⁺⁺⁺] > 10⁻¹² mg. per cu.m., the solubility being controlled by that of a sparingly sol. basic salt. The Fe requirement of diatoms is > that of plankton, the Fe content of which is about 0.5 mg. per cu.m. 2 : 2' : 2''-Tripyridyl is the most sensitive reagent for detection of Fe in sea-H₂O, 1 mg. per cu.m. being determined with certainty. H. G. R.

Springs of Fairmount Park. F. N. MOERK, D. C. A. BUTTS, F. C. LAWLER, and P. A. MATTIS (Amer. J. Pharm., 1935, 107, 358—372).—21 springs

have been analysed chemically, microscopically, and biologically by standard methods. E. J. B.

Waters, magmatic and meteoric. W. LINDGREN (Econ. Geol., 1935, 30, 463—477).—The quantity and distribution of meteoric waters are discussed, and the view that in permeable sedimentary rocks meteoric waters may reach a depth of 8000 and possible > 10,000 ft. is advanced. In igneous and metamorphic rocks, cementation generally prevents active penetration by surface waters to > 3000 ft. The present distribution and composition may be entirely different from that prevailing at an earlier date and may have changed several times. Magmatic waters are discussed as a principal agent in the formation of mineral deposits. Hot springs are generally a mixture of meteoric waters and magmatic emanations. The "telemagmatic" Pb-Zn deposits of the Mississippi Valley and of Europe have been formed probably by mixtures of magmatic and meteoric waters at comparatively low temp. The deep waters in the Witwatersrand are also discussed. L. S. T.

Testing a theory of the earth's interior. R. A. DALY (J. Washington Acad. Sci., 1935, 25, 389—399).—The author's views of an elastico-viscous interior are discussed. C. W. G.

Geochemical zone-like character of the distribution of metals in the Far East. M. N. IVANTSCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 572—580).—The distribution of metals in the Far East falls into various zones, the polymetal regions of the Küsten Province and Upper Seja, the As zone of Ussuri and Lower Amur, the Mo zone of Bureja, and

the Selemdsha Au zone. The distribution is discussed in terms of ionic radius and valency.

R. S. B.

Dielectric constant and specific resistance of rocks. B. DOSTOVALOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 87—90).—The dielectric const., ϵ , and sp. resistance of about 50 samples of rocks have been determined. No connexion could be traced between ϵ and composition, but texture affects ϵ .

A. J. M.

Identification of types of chalcocite by use of the carbon arc. M. M. STEPHENS (Econ. Geol., 1935, 30, 604—629; cf. Amer. Min., 1931, 16, 532).—Argentite (I), stromeyerite (VII), polybasite (II), stephanite (III), pyrargyrite, proustite, pearceite, andorite (IV), petzite (V), hessite (VI), coloradoite, etc. react characteristically when exposed to rays from a C arc conc. by suitable lenses. The rate of reaction varies with the orientation of the mineral and the aperture of the lens. (I)—(IV) yield a sublimate of S. Thermal rays speed up the actinic action, and (IV)—(VII) and chalcocite (VIII) react almost entirely to heat. The heat-etch pattern with (VIII) is produced by etch lines and fractures which develop along internal structures. The pattern is characteristic for certain types of (VIII) and much of the history of the specimens has been inferred from it. When replaced by (VIII) under certain conditions bornite transmits its etch pattern to (VIII). Covellite > a certain % in solid solution in (VIII) inhibits an etch reaction. Hypogene and supergene (VIII) can be distinguished by their reactions to acid and heat, and strains and distorting pressure are reflected in the etch lines.

L. S. T.

Geology of Castle-an-Dinas wolfram mine, Cornwall. E. H. DAVISON (Econ. Geol., 1935, 30, 689—694).—The sequence of events which culminated in the formation of the lode described appears to have been a folding and cleaving of the Devonian slates, intrusion of the granite followed by the action of the granite volatiles, resulting in the deposition of cassiterite in the slate and the formation of greisen, kaolin, and tourmalinised slate, opening of the lode fissure and filling by magmatic solutions giving rise to a pegmatite which, near the surface of the granite, became a quartz wolfram lode.

L. S. T.

Martic overthrust and the age of the Glenarm series in S.E. Pennsylvania. J. H. MACKIN (J. Geol., 1935, 43, 356—380).—Evidence for the view that the Glenarm series of metamorphic rocks of the Pennsylvania Piedmont region is Paleozoic rather than pre-Cambrian in age is presented.

L. S. T.

Colloidal primary copper ores at Cornwall mines, S.E. Missouri. G. W. RUST (J. Geol., 1935, 43, 398—426).—The primary ore consists of the sulphides of Cu, Fe, and Zn with chalcopyrite as the most abundant mineral. Other primary minerals occurring in smaller but important amounts are quartz, pyrite, sphalerite, marcasite, bornite (I), calcite, and dolomite, and there are rare occurrences of primary enargite (II), famatinite (?) (III), chalcocite (IV), covellite (V), galena, and fluorite. Secondary minerals, with little or no enrichment, occur in considerable amounts. (I)—(V) indicate a hydrothermal

ancestry for the mineralising solutions, and lack of alteration of the wall indicates a moderate temp. Several unusual types of structure and texture suggest ore deposition from colloidal solutions, for which a deep-seated, magmatic source is postulated. The orders of introduction and flocculation of the minerals are discussed.

L. S. T.

Sudburite, a metamorphic rock near Sudbury, Ontario. R. THOMSON (J. Geol., 1935, 43, 427—435).—Sudburite, essentially plagioclase + pyroxene, with hornfels texture, occurs in proximity to the Sudbury Ni intrusive. It is probably due to recrystallisation of greenstone and other rocks older than the Ni intrusive, which was the cause of its formation.

L. S. T.

"Offset dikes" of the nickel intrusive, Sudbury, Ontario. R. THOMSON (Amer. J. Sci., 1935, [v], 30, 356—367).—Analyses are given.

C. W. G.

Silicification of shale in the Mogul mine. G. M. SCHWARTZ (J. Geol., 1935, 43, 524—529).—The exposed shale of the Mogul mine in the Black Hills of S. Dakota shows marked silicification. Petrographic examination reveals much chalcedony, opal, and residual, fine-grained kaolinitic material. Analyses show a large gain in SiO₂, and considerable losses of K₂O and Al₂O₃, partly by replacement.

L. S. T.

Thin-section mechanical analysis of indurated sediments. W. C. KRUMBEIN (J. Geol., 1935, 43, 482—496).—A new method in which the data obtained from thin sections are utilised is described, and checked by analyses on St. Peter sandstone and a glacial sand. It has been applied to a pre-Cambrian quartzite in which secondary growth has completely cemented the grains.

L. S. T.

Granite-porphyrries of Great Bear Lake, Northwest Territories, Canada. C. RILEY (J. Geol., 1935, 43, 497—523).—A granite-porphyry mass, one of a no. of porphyries with complex relationships occurring in the pre-Cambrian of Great Bear Lake, is defined. The various phases of the formation, its contact phenomena, apophyses, form and origin, and post-intrusives of a pneumatolytic character are described.

L. S. T.

Age of allanite from Amherst County, Virginia, U.S.A. J. P. MARBLE (Amer. J. Sci., 1935, [v], 30, 349—352).—The Pb ratio indicates an age of 8×10^8 years.

C. W. G.

Revision of data of the enstatite-hypersthene series. R. WALLS (Min. Mag., 1935, 24, 165—172).—Four new analyses are given of hypersthene from Aberdeenshire, together with partial optical data. The results are plotted, together with selected data from the literature, showing an increase in γ and $2V$ with the Fe content.

L. J. S.

Anomalies in the determination of water in epidote. A. F. SMETHURST (Min. Mag., 1935, 24, 173—179).—In analyses of epidote from the Malvern Hills, H₂O expelled at 1000° in a current of air amounted to only 0.06—0.35%. With prolonged blasting rather more was expelled, and two fusions with Na₂WO₄ gave 0.76—1.32%. Epidote from other localities gave 1.25—1.68%. The amount required by the

formula $\text{HCa}_2\text{Al}_3\text{Si}_3\text{O}_{13}$ is 2.0%. The analyses show F only 0.03–0.08%. Similar difficulties have been met with in expelling the H_2O from a few other refractory silicates.

L. J. S.

Late Palaeozoic quartz-dolerites and tholeiites of Scotland. F. WALKER (Min. Mag., 1935, 24, 131–159).—These rocks, occurring in dikes and sills, are very similar both chemically and mineralogically to those of the Whin Sill (A., 1928, 1211). New analyses show SiO_2 47.39–49.36%, and in the residual glass of a tholeiite 66.80%. In the quartz-dolerites the silica-rich residuum is represented by micropegmatite. The origin of the rocks from an olivine-basalt magma is considered.

L. J. S.

Zeolites. VIII. Theory of vapour pressure of the zeolites, and of diffusion of water or gases in a zeolite crystal. M. H. HEY (Min. Mag., 1935, 24, 99–130; cf. A., 1934, 862).—With many assumptions, complex formulæ are deduced as a first approximation. Some new v.-p. data are given for edingtonite and mesolite.

L. J. S.

Constitution of zeolites. L. PASSERINI (Gazzetta, 1935, 65, 534–542).—Infra-red absorption spectra between 1.30 and 2.00 μ of the following zeolites have been measured: analcite, natrolite, heulandite, stilbite, chabasite, and skolezite. The H_2O bands of the first five zeolites are the same as those of pure H_2O , but with skolezite they are displaced towards higher λ .

O. J. W.

Occurrence of mendozite and tamarugite in Missouri. W. D. KELLER (Amer. Min., 1935, 20, 537–539).—Efflorescences occurring on the Joachim dolomite near Eureka, Missouri, and on the basal Cherokee conglomerate at Fulton, Callaway Co., Missouri, are composed largely of mendozite with some tamarugite. Oxidising pyrite appears to be the source of the SO_4^{2-} .

L. S. T.

Spectrographic analysis of tourmalines with correlation of colour and composition. T. W. WARNER, jun. (Amer. Min., 1935, 20, 531–536).—Spectra of different specimens of tourmaline from Brazil and San Diego show that Li, Na, Mg, Ca, Al, B, Ga, Mn, and Si are always present, and V, K, Cu, Fe, Pb, Sn, Ti, and Be present in some samples but not in all. Ag, Ge, Re, As, Hf, Rh, Sb, Ru, Bi, Hg, Sc, Au, In, Ta, Ir, Te, Cb, La, Th, Cd, Mo, U, Ce, Ni, W, Co, P, Yt, Pd, Zn, and Pt were absent (< 0.0005%). The first 7 elements remain practically const. in amount in all the samples tested, but any variation does not coincide with differences in colour. Sn is slightly more pronounced in pink than in green specimens, and Cu is more common in green than in pink. The Fe content \propto the depth of colour in the green and inversely \propto the depth in the pink and red specimens, being either absent, or present only as minute traces, in the red. The natural colour of tourmaline is probably pink or red and is changed to green by Fe, which is probably the most important factor in gem coloration.

L. S. T.

Evolution of the White Mountain magma series. R. W. CHAPMAN and C. R. WILLIAMS (Amer. Min., 1935, 20, 502–530).—The chief characteristics of the volcanic and plutonic rocks of the

series are described and chemical analyses of these and the dyke rocks and the minerals of the series are recorded. Theories of origin of rock types are discussed, and a theory which combines fractional crystallisation, pure melting, and assimilation for the evolution of the White Mountain magma series is advanced.

L. S. T.

Lindgrenite, a new mineral. C. PALACHE (Amer. Min., 1935, 20, 484–491).—Lindgrenite, monoclinic, holohedral, occurs as green, transparent crystals, cleavage perfect, $a : b : c = 0.5941 : 1 : 0.5124$, $\beta 92^\circ 12'$, in veinlets in limonitic quartz from Chuquicamata, Chile. The mineral is biaxial, negative, with $n_a 1.930 \pm 0.003$, $n_\beta 2.002 \pm 0.003$, $n_\gamma 2.020 \pm 0.003$, $d 4.26$, and hardness 4.5; sol. in HCl and HNO_3 . The analysis [F. A. GONYER] CuO 40.62, MoO_3 50.97, H_2O 3.30, Fe_2O_3 1.43, insol. 3.34, total 99.66%, gives the formula $2\text{CuMoO}_4 \cdot \text{Cu}(\text{OH})_2$. X-Ray measurements [BERMAN] give $a 8.45$, $b 14.03$, $c 7.04 \text{ \AA}$, $\beta 92.5^\circ$ for the unit cell $\text{Cu}_{12}(\text{MoO}_4)_8\text{H}_8\text{O}_8$.

L. S. T.

Structural relationship of nontronites and montmorillonite. J. W. GRUNER (Amer. Min., 1935, 20, 475–483).—X-Ray powder diagrams of nontronite (I), morencite, pinguite, faratsihite, chloropal, and stilpnochloran establish the structural identity of these so-called species. The structure is practically identical with that of montmorillonite (bentonite) (II). (I), (II), and beidellite form an isomorphous, completely-miscible series. As in (II), the H_2O content of nontronites may vary, and since they are layer structures and not zeolitic, it controls the distance between the layers, which may vary between 9.2 \AA . at 575° and 15.8 \AA . when the sample is moist. a and b average 5.23 and 9.06 \AA ., respectively. When dehydrated at 575° , (I) is similar in structure to pyrophyllite. The best formula for the series is $\text{OH}_8(\text{Al}, \text{Fe}^{\text{III}})_{8+n/3}[\text{Si}_{16-n}(\text{Al}, \text{Fe}^{\text{III}})_n]\text{O}_{40} \cdot m\text{H}_2\text{O}$, with n between 0 and 4. For (I), n is seldom < 2, and for (II), n is usually < 1. For air-dried material, m lies between 8 and 22. Hisingerite appears to be amorphous, but 4 or 5 indistinct bands in the X-ray spectrum agree with intense lines of (I).

L. S. T.

Position of montmorillonite among the phyllosilicates. J. DE LAPPARENT (Compt. rend., 1935, 201, 527–529).—A discussion of the formula of montmorillonite.

H. J. E.

Origin of barite in the Appalachian Valley. G. W. CRICKMAY (Econ. Geol., 1935, 30, 563–564).—A criticism (cf. *ibid.*, 1931, 26, 776).

L. S. T.

Staining minerals for easier identification in quantitative mineragraphic problems. A. M. GAUDIN (Econ. Geol., 1935, 30, 552–562).—The various methods available for changing the appearance of minerals to facilitate identification are reviewed and practical applications are described.

L. S. T.

Relations of hydrothermal alteration of porphyries to ore deposition in the Alma district, Colorado. Q. D. SINGEWALD (Econ. Geol., 1935, 30, 518–539).—The five different intrusive porphyries of early Tertiary age found among the wall rocks of many mesothermal veins in this district each appear to have undergone (i) an early, widespread, hydro-

thermal alteration, and (ii) a later, local alteration as an early stage of ore deposition. Details of these two types of alteration are given. L. S. T.

Nature and occurrence of carbonates in veins.

G. H. CHARLEWOOD (Econ. Geol., 1935, 30, 502—517).—Carbonatisation is more typical of regions of Au-bearing veins of the hypothermal and mesothermal types than of any others. This is especially the case in Ontario. Analysis are recorded and show a wide range of composition for vein carbonates (I). The composition of the wall rocks has little, if any, effect on that of (I) in the veins, the composition of which is controlled by the composition, temp., and pressure of the vein-forming solutions at the time of filling. Zoning of the (I) composition occurs in some veins. In the four representative deposits investigated the FeCO_3 , and to a smaller extent the CaCO_3 , in ankerite (II), siderite, and dolomite (III) increases with depth, whilst MgCO_3 decreases correspondingly. The development of carbonatised rocks along the vein zones and in regions of Au-bearing quartz veins is characteristic of a large part of the Canadian shield. (II) is almost invariably pre-ore, whilst carbonates of post-ore age are more commonly (III) or calcite.

L. S. T.

Origin of the gypsum deposits near Sandusky, Ohio. V. JONES (Econ. Geol., 1935, 30, 493—501).—The general geology, the relations to gypsum areas of New York and Ontario, and the mineral relationships, dolomite (I)—anhydrite (II), (II)—gypsum (III), and (I)—(III), are described. The deposits probably represent surface hydration products formed from the deeper-lying anhydrite beds.

L. S. T.

Rock alteration at the Amulet mine, Noranda district, Quebec. M. E. WILSON (Econ. Geol., 1935, 30, 478—492).—The ore deposits of the mine belong to the aggregates of sulphide ore masses of the Noranda type and occur chiefly in Abitibi lavas distributed in two groups, the older consisting of rhyolite and rhyolite breccia and the younger of andesite. They lie mainly in the rhyolite breccia and consist chiefly of pyrite (I), pyrrhotite, sphalerite (V), chalcocopyrite (II), granular quartz, the minerals of the dalmatianite rock, and a small proportion of arsenopyrite (III), tetrahedrite (IV), and calcite. (I) and (III) carry Au and were deposited first, and (II), (IV), and galena carry Au, and with (V) were deposited last. The dalmatianite, a cordierite-bearing alteration rock, is the most unique feature of the mine. It has been formed by hydrothermal alteration effected by the emanations from which the ore was deposited. Analyses are recorded.

L. S. T.

Mineralogical constituents of clays, especially fuller's earth. H. LONGCHAMON (Compt. rend., 1935, 201, 483—485).—In the clays examined sepiolite could not be detected. The main constituent in those of the fuller's earth type has a composition similar to that of palygorskite or pilolite, and may be regarded as an isomorphous mixture of sepiolite ($2\text{MgO} \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$) and paramontmorillonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 6\text{H}_2\text{O}$). It is suggested that these palygorskite clays have been derived by the alteration

of pyroxenes and amphiboles, whilst kaolinic clays have been derived from feldspars and micas. L. J. S.

An essential constituent of fuller's earth. J. DE LAPPARENT (Compt. rend., 1935, 201, 481—483).—Two analyses of fuller's earth from Attapulgis, Georgia, U.S.A. (and Mormoiron, Vaucluse, France), gave: SiO_2 53.7 (53.6), Al_2O_3 9.0 (10.6), Fe_2O_3 3.6 (6.5), FeO 0.2 (0.3), MgO 9.6 (4.6), CaO 1.2 (2.1), Na_2O 0.9 (0.8), K_2O 0.5 (0.5), $\text{H}_2\text{O} + 11.6$ (9.4), $\text{H}_2\text{O} - 9.7$ (11.6). They are expressed as a mixture of $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 4.5\text{SiO}_2 \cdot 6\text{H}_2\text{O}$, and suggest palygorskite, but the new name attapulgit is proposed. This is regarded as a constituent of fuller's earth distinct from kaolin, halloysite, and montmorillonite. L. J. S.

Bentonite. J. N. WILSON (Sands, Clays, and Min., 1934, 2, 45—47).—A review of properties.

CH. ABS (e)

Pyrite nodules in coal measures, with special reference to the Yen Tai and Pen Hsi Hu coal-fields, South Manchuria. T. OGURA and H. MATSUMOTO (Mem. Ryojun Coll. Eng., Inouye Comm. Vol., 1934, 243—255).—Analyses of pyrite, found in lenses in the Permian Seams, are given, and the mode of production is discussed.

CH. ABS. (e)

Carboniferous rocks. J. E. METCALFE (Sands, Clays, and Min., 1934, 2, 27—31).—Carboniferous rocks of the British Isles are described.

CH. ABS. (e)

Emeralds, their occurrences and genesis. P. P. PIATNITZKI (Trans. Geol. Hyd. Geod. Trust Ukraine, 1934, 5—48).—The deposits north-east of Sverdlovsk are described.

CH. ABS. (e)

Lacustrine and bog-ores of the Kouch Lake and Sego Lake regions of the Karelian A.S.S.R. E. KOPTSCHENOVA (Trans. Sci. Inst. Geol. Min. U.S.S.R., 1934, 3, 3—26).—Analyses are recorded.

CH. ABS. (e)

Dispersion of mullite. M. SAWATARI (Mem. Ryojun Coll. Eng., Inouye Comm. Vol., 1934, 41—47).—Mullite with $n > 1.67$ is most easily distinguished from sillimanite by measurement of the dispersion. Vals. are recorded for two samples of artificial mullite (0.80, 1.86% TiO_2).

CH. ABS. (e)

Physical studies of the manganous hydroxides, pyrochroite and backstromite. D. P. GRIGORIEV (Mem. Soc. Russe Min., 1934, 63, 67—80).—Pyrochroite from Langban, Sweden, contained hausmannite. The lower the temp. of prep. of cryst. $\text{Mn}(\text{OH})_2$ the more developed was the {1100} form. Part of the pyrochroite-backstromite phase diagram was obtained.

CH. ABS. (e)

Pegmatites at Collins Hill, Connecticut. W. F. JENKS (Amer. J. Sci., 1935, [v], 30, 177—197).—Three phases are distinguished. (1) Magmatic, with quartz, microcline, muscovite, and black tourmaline. (2) Transitional, mainly cleavelandite, with spodumene, lepidolite, coloured tourmaline, columbite, etc. (3) Hydrothermal, with a potash-bearing albite, tourmaline, cookeite, sulphides, phosphates of Li and Mn, apatite, etc. Analyses and optical data are given for some of these minerals.

Weathering of volcanic rocks. I, II. Basalts. M. HARADA (J. Agric. Chem. Soc. Japan, 1935, 11, 456—472).—Changes in the composition and nature of various types of basalts due to weathering were determined. F. O. H.

Relationship of mud to electrical coring. H. C. H. THOMAS (J. Inst. Petroleum Tech., 1935, 21, 774—784).—The effects of mud on the resistivity and porosity of permeable rocks are discussed and the consequent effects of mud on electrical profiles are outlined. C. C.

Water in inorganic compounds. II. Water content of Odo acid clay at various temperatures in an air current at constant water vapour pressure. M. NAKAMOTO (Bull. Chem. Soc. Japan, 1935, 10, 369—374; cf. B., 1933, 268).—Hydration and dehydration data are given for temp. $\pm 800^\circ$. The monohydrate decomposes above 300° . R. S.

Genesis of agates. P. P. PILIPENKO (Bull. Soc. nat. Moscou, Sect. Geol., 1934, 12, 279—299).—The formation cannot be accounted for solely by Licsegang's assumption of slow diffusion of SiO_2 gel. The banded structure and pigmentation are better explained by an intermittent deposition of chalcedony from H_2O solutions. CH. ABS. (e)

Thermal analysis of chrysotile asbestos. F. V. SUIROMATNIKOV (Bull. Soc. nat. Moscou, Sect. Geol., 1934, 12, 137—149).—Many chrysotile samples showed, when heated, an endothermic reaction (70 — 100°) due to loss of adsorbed H_2O , an exothermic reaction (max. 400°) due to escape and combustion of C compounds, and oxidation of FeO, an endothermic reaction (max. 725°), due to separation of constitutional H_2O , and an exothermic reaction (600 — 800°) due to olivine formation. There was no evidence of a brucite stage near 400° . The probable formula was $(\text{OH})_2\text{Mg}_{12}\text{Si}_8\text{O}_{22}\cdot 7\text{H}_2\text{O} + a\text{q}$. CH. ABS. (e)

Dependence of chemical composition of sedimentary iron ores on the conditions of their formation. A. D. ARCHANGELSKI and E. V. KOPT-SCHENOVA (Bull. Soc. nat. Moscou, Sect. Geol., 1934, 12, 262—278).—Ores formed in an oxidising medium have a much higher average content of P, As, and Cr than siderites or oxidised siderites formed in a reducing medium. V is always present in ores of the former type and absent in the latter. CH. ABS. (e)

Igneous rocks from the iron-producing district of Bilbao (Vizcaya), Spain. H. SERVICE (Bull. Inst. Min. Met., 1935, No. 372, 17 pp.).—The primary ore, chalybite, is a metasomatic replacement of limestone by Fe-bearing, carbonated, hydrothermal solutions. Later oxidation of this gave hematite and limonite. The associated igneous rocks are also carbonated. Descriptions are given of carbonated gabbro, olivine-dolerite, spilite, and trachyte. L. J. S.

Origin of iron ores in Singhbhum, India. J. A. DUNN (Econ. Geol., 1935, 30, 643—654).—The associated banded quartzites are not sedimentary, but are due to secondary silicification of material now represented by ferruginous, chloritic or C shales or phyllites, many of which originated as tuffs. This silicification was

probably in part contemporaneous with deposition of the beds, and resulted from thermal activity accompanying the formation of the volcanic series. The Fe was derived partly from oxidation of tuffs and flows *in situ*, and partly represents a wash from the latter. Later solutions rearranged the Fe content to give the massive Fe ores. L. S. T.

Fictitious occurrences of iron silicide (ferrosilicon). L. J. SPENCER (Min. Mag., 1935, 24, 160—164).—Bright, steel-grey pellets and nodules of FeSi, very resistant to acids (except HF) and to weathering, are sometimes present in commercial CaC_2 . These have been found at various times in strange situations, and have been described as new minerals or thought to be meteorites. Finds in the concentrates of gold dredgers in British Guiana and in the diamond fields of South Africa are readily explained by the use there of acetylene flares. Crystals of FeSi are tetrahedral-cubic. L. J. S.

Geological significance of magnetic properties of [iron] minerals. C. W. DAVIS (Econ. Geol., 1935, 30, 655—662).—Lodestones are of variable composition and the manner and degree of their magnetisation are accidental. Their actual magnetic properties show little relation to their present state of magnetisation. If coercive forces and remanences are large enough, many natural and artificial magnetites will simulate lodestones after magnetisation. Fe oxides formed by regulated dehydration of $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (lepidocrocite) are strongly ferromagnetic and have high coercive force and remanence, whilst $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (goethite) forms ordinary Fe_2O_3 on dehydration. The diagnostic possibilities of magnetites for ore genesis are discussed. L. S. T.

Porphyryns in coal. A. TREIBS (Annalen, 1935, 520, 144—150).—Porphyryns were detected in the $\text{C}_5\text{H}_5\text{N}$ extracts of 22 out of 30 samples of coal in quantities varying from 0.5 to 2000×10^{-6} g. per 30 g. of coal. Aetioporphyryns are most common, acid porphyryns only being detected in a few cases. Deoxyphyllerythro- and meso-aetioporphyryn are found only in one type (cannel and boghead coal). Deuteroaetioporphyryn is common and was identified spectroscopically. The porphyrin content of other mineral materials is tabulated. J. W. B.

Resins in bituminous coals. H. WINTER (Angew. Chem., 1935, 48, 610—614).—A review is given, with photomicrographs, of their composition, properties, and probable method of formation. S. M.

Fossil resins in brown coals. H. STEINBRECHER (Angew. Chem., 1935, 48, 608—610).—Two classes are distinguished. (a) "Bituminous" resins which are intimately mixed with up to about 78% of a wax and are distributed throughout the coal so that they are extractable only by means of suitable solvents, e.g., C_6H_6 —EtOH, after swelling in $\text{C}_5\text{H}_5\text{N}$. After removal of the wax they are sol. in C_6H_6 , COMe_2 , Et_2O , etc. They are dark reddish-brown and transparent in thin layers. (b) "Retinite" resins which occur less frequently in hard, brittle, wax-free pieces of varying size (origin, *d*, m.p., and C, H, and O contents of 9 samples are tabulated). They are only partly sol. in common org. solvents and have a

yellow to bright reddish-brown colour. Both types probably had their origin in the same class of tree (Conifers) as amber because (i) their acid and saps, and elementary analyses (tabulated) are on the whole comparable, and in both cases (ii) free rosin acids have been detected, (iii) distillation yields small quantities of succinic acid. The (b) type exuded from the tree before submersion, and underwent oxidation and polymerisation, whereas the (a) type remained enclosed in the plant cells. The effect of these resins on the coal and some of their uses are discussed.

S. M.

Silurian petroleum in Central Asia. S. N. SIMAKOV, N. A. SCHVEMBERGER, and O. S. VIALOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 567—

568).—Petroleum-bearing shales at the mouth of the Kschut (112 km. east of Samarkand) are described, with evidence that they belong to the Silurian period.

R. S. B.

Silurian petroleum in Central Asia. N. A. SCHVEMBERGER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 569—571).—The petroleum-bearing shales of Kschut contain 2% of org. compounds, and cover a layer of bituminous combustible shale. The origin of the petroleum is discussed.

R. S. B.

Basaltic soils in Fukuoka Prefecture. R. KAWASHIMA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 108—109).—The soils are mainly sub-allitic in nature. Analyses are given.

P. G. M.

Organic Chemistry.

Classification of catalytic reactions in organic chemistry. II. Method of finding a complete system of doublet reactions and the calculations for the atoms H, C, N, O, S, Cl and the linkings from 0 to 4. A. A. BALANDIN (J. Phys. Chem. U.S.S.R., 1934, 5, 679—706).—By means of a matrix formulation a possible 810,000 compounds are classified in such a way that reactions can be generalised by means of classification symbols. The method is applied particularly to hydrogenation.

CH. ABS. (r)

Reaction of paraffins with olefines. V. N. IPATIEV and A. V. GROSSE (J. Amer. Chem. Soc., 1935, 57, 1616—1621).—In the presence of suitable catalysts paraffins and olefines react thus: $\text{>CH} + \text{>C:C<} \rightarrow \text{>C-CH<}$. C_3H_6 and higher olefines are polymerised by BF_3 step by step at room temp., but C_2H_4 reacts only if finely-divided metals, e.g., Ni, are present. Paraffins are unaffected by BF_3 at 50° . Paraffins with a *tert.*-C are alkylated at 10—30°/5—20 atm. in presence of BF_3 , finely-divided Ni, and H_2O (or anhyd. HF). CHMe_3 with C_2H_4 gives mixtures of hydrocarbons, C_5 to C_8 , mostly C_6H_{14} and C_8H_{18} , and with isobutylene 32% of C_8H_{18} and 15% of $\text{C}_{12}\text{H}_{26}$. isopentane and C_2H_4 give mostly C_7H_{16} and C_8H_{18} . $\beta\beta$ -Trimethylpentane and C_2H_4 give a mixture of paraffins and high-boiling olefines. BF_3 reacts by formation of complexes with the olefine. R. S. C.

Thermal decomposition of *n*-pentane. J. J. MORGAN and J. C. MUNDAY (Ind. Eng. Chem., 1935, 27, 1082—1086).—The gaseous products from the pyrolysis of C_5H_{12} with and without steam (in a SiO_2 reactor without catalysts) were examined. At 600° the rate of decomp. is not changed by moderate dilution with steam (although at partial pressures < 50 mm., the rate falls); this indicates a reaction of the first order. The proportions of CH_4 , C_3H_6 , C_2H_4 , and Δ^2 -butene are not affected by decreases in partial pressure (< 1 atm.), but increasing the dilution decreases the C_2H_6 and increases the C_2H_4 and H_2 . This change is also well marked at higher temp. This may be explained by applying the free radical hypothesis of Rice to the reaction $\text{C}_5\text{H}_{12} \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_6$ (or

$\text{C}_2\text{H}_4 + \text{H}_2$). C_2H_2 and Δ^2 -butadiene were detected in the products of the pyrolysis at 700 — 800° , the formation of the former being favoured by dilution with steam. Slight evidence of the formation of aldehydes was obtained, but no significant formation of CO or CO_2 occurs up to 800° from any reaction between steam and hydrocarbon.

C. C.

Preparation of certain alkenes, alkadienes, and alkinies. S. P. MULLIKEN, R. L. WAKEMAN, and H. T. GERRY (J. Amer. Chem. Soc., 1935, 57, 1605—1607).—Unsaturated hydrocarbons are prepared by the Grignard reaction. The following appear to be new. *8-Methyl- Δ^8 -heptene*, b.p. 113.8 — 114.1° , and *-octene*, b.p. 137.3 — 137.9° ; $\delta\epsilon$ -, b.p. 135 — 136.1° , and *$\delta\zeta$ -dimethyl- Δ^8 -heptene*, b.p. 129.5 — 130.1° ; *$\delta\epsilon\epsilon$ -trimethyl- Δ^8 -hexene*, b.p. 128.7 — 129.5° ; *8-methyl- Δ^8 -heptadiene*, b.p. 110.5 — 110.9° ; *$\delta\epsilon$ -dimethyl- Δ^8 -octadiene*, b.p. 152.9 — 153.8° ; *Δ^8 -octadiene*, b.p. 133.5 — 134° ; *$\beta\beta$ -dimethyl- Δ^8 -hexadiene*, b.p. 107.4 — 108° . Physical data for these and 24 other hydrocarbons are reported.

R. S. C.

Recovery of Δ^2 -butene from air by silica gel. I. A. VOLSHINSKI, V. A. GLOBOV, and Z. A. CHRENOVA (Sintet. Kautschuk, 1934, No. 1, 1—12).—The SiO_2 gel was activated by heating in an electric furnace for 3.5—4 hr. at 270 — 280° . The average absorption was 4 wt.-% of $(\text{CHMe})_2$ at 20° (max. 5%), with a speed of air passage of 0.0025 — 0.1295 m. per sec. The gas was recovered (75—94 wt.-%), and the gel regenerated, by heating to 200 — 225° , the regenerated gel being somewhat less adsorptive.

CH. ABS. (e)

Gadusene.—See this vol., 1264.

Preparation of alkyl bromides by the phosphorus tribromide method. II. Preparation of hexyl, cyclohexyl, and *tert.*-amyl bromides. C. L. TSENG, M. Hsu, and M. Hu (Sci. Quart. Nat. Univ. Peking, 1935, 5, 371—374).— PBr_3 is slowly added to the cold alcohol and the mixture gently refluxed. The product is separated, washed with conc. H_2SO_4 , and distilled under ordinary pressure. On keeping, hexyl and *tert.*-amyl bromide lose HBr and become unsaturated. *cyclohexyl* bromide is comparatively stable.

H. G. H.

Preparation of *n*-butyl bromide. C. L. TSENG, T. S. HO, and P. T. CHIA (Sci. Quart. Nat. Univ. Peking, 1935, 5, 375—381).—Of four methods for the prep. of BuⁿBr the most satisfactory was that involving the use of HBr-H₂SO₄-BuⁿOH (Kamm and Marvel, "Org. Syntheses," coll. vol., 1932, I, 26, 33).

H. G. M.

Action of inorganic bases on (A) isobutyl bromide, (B) *tert*-amyl halides. (A) H. E. FRENCH and W. H. WADE. (B) H. E. FRENCH and A. E. SCHAEFER (J. Amer. Chem. Soc., 1935, 57, 1574—1576, 1576—1578).—(A) BuⁱBr does not rearrange before reaction with aq. KOH, NaOH, or AgOH. Reaction is faster in more dil. solution, but H₂O does not react. Increase in temp. or concn. of alkali increases the proportion of olefine formed. In all circumstances alcohol formation predominates over that of olefine.

(B) Similar results are recorded for *tert*-amyl chloride and bromide with various alkalis. The chloride gives slightly more olefine than does the bromide.

R. S. C.

Action of zinc dust and alcohol on the hydrochlorides of gutta-percha and balata. T. HARDIE and J. A. MAIR (J.C.S., 1935, 1239—1241).—Prolonged action of gutta-percha hydrochloride in boiling C₂H₅Cl₂ with Zn-EtOH gives α -monocyclogutta-percha, (C₅H₈)_x, m.p. 85—90° after softening at 70°, and some of the β -isomeride, m.p. 84—86° after softening at 65—68°. The unsaturation of both isomerides is half that of gutta-percha, which indicates that cyclisation has occurred (cf. A., 1926, 840). Similarly prepared, α - and β -monocyclobalata have m.p. 100—105° and about 100° (after softening at 85—90°), respectively. The cyclised products have a mol. wt. (Rast) of 2000—4000 depending on the concn. Neither α -isomeride distills even at 360°/2—3 mm., but polycyclo-compounds are formed (cf. A., 1926, 841) which have an unsaturation of about 25% of the original hydrocarbon. Reduction (Pd-H₂) is not accomplished at atm. pressure and room temp., but the isomerides yield hydrochlorides and hydrobromides which have cyclic structures as indicated by their *d*.

J. L. D.

Electrolysis of organic substances in non-aqueous media. I. G. GIACOMELLO (Gazzetta, 1935, 65, 546—554).—Electrolysis of solutions of NaOMe in anhyd. MeOH gives, at the cathode, H₂, CH₄, CO, CO₂, and, at the anode, CH₂O and HCO₂H. Me₂SO₄ gives at the cathode H₂, CH₄, CO, and O₂. NaOAc gives at the cathode H₂, CH₄, CO₂, O₂, and CO, and at the anode, C₂H₆, CO₂, CH₄, H₂, O₂, CO, and unsaturated hydrocarbons; the solution contains CH₂O, CHO·CO₂H, and HCO₂H. Proportions of products vary with conditions. The results are discussed on the hypothesis that MeOH ionises thus: OH' + Me' \rightleftharpoons MeOH \rightleftharpoons MeO' + H'. E. W. W.

Manganous ethoxide. Preparation and hydrolysis. B. KANDELAKY, I. SETASCHWILI, and I. TAWBERIDGE (Kolloid-Z., 1935, 73, 47—49).—The prep. of Mn(OEt)₂ from MnCl₂ and NaOEt is described. Sols of Mn(OH)₂ are formed by hydrolysis of Mn(OEt)₂ and can be stabilised by addition of protective colloids.

E. S. H.

Equilibrium between *n*-propyl alcohol, propyl ether, and water at 190°. N. G. GAJENDRAGAD and S. K. K. JATKAR (J. Indian Chem. Soc., 1935, 12, 486—493).—84% of PrⁿOH is converted into Pr₂O at 190°. Pr₂O is more stable at 230° than PrOH, whence it is inferred that Pr₂O is not an intermediate in the formation of C₃H₆.

R. S.

Crystalline and gelatinous salts of phosphoglyceric acids. C. NEUBERG and W. SCHUCHARDT (Biochem. Z., 1935, 280, 293—296; cf. A., 1934, 1202; this vol., 471).— γ - β -Phosphoglyceric acid (I) has less tendency to yield gelatinous salts (Fe^{II}, Co^{II}, Cd, Mn^{II}, UO₂) than has the *d*(-)-acid, and of the *dl*- α -acid (II) only the UO₂ salt has been obtained as a jelly (the Cd salt is amorphous). The prep. of cryst. Ba and benzidine salts of (I) and (II) and of the gelatinous salts is described.

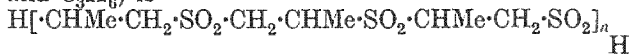
W. McC.

Platinous complexes [with alkyl sulphides].—See this vol., 1335.

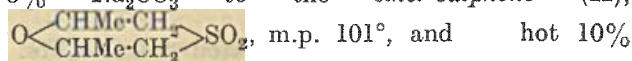
Vulcanisation reactions. K. H. MEYER and W. HOHENEMSER (Helv. Chim. Acta, 1935, 18, 1061—1066).—Evidence in favour of the view that cold vulcanisation of caoutchouc proceeds according to 2·CMe·CH· + S₂Cl₂ \rightarrow S·(CH·CMeCl)₂ + S is afforded by extraction of about 50% of the S from the product by Na₂S, but not by CS₂ or COMe₂, and by its reaction with MeI to yield a sulphonium iodide the I content of which corresponds with the presence of about 1% of sulphide-S; under the conditions employed, SH does not react with MeI. Hot vulcanisation in the absence of accelerators gives products with 3% and 4% of sulphide-S. Experiments with cyclohexene and S at 140—150° establish the formation of cyclohexyl mercaptan (I), b.p. 38—39°/12 mm. [cyclohexyl 2:4-dinitrophenyl sulphide (II), m.p. 147°], and dicyclohexyl sulphide, b.p. 130—132°/11 mm., m.p. -8° (methiodide, m.p. (110-5°)). The requisite H is probably derived from (I), which is thus partly converted into (II). S+boiling styrene give exclusively 2:4-diphenylthiophen, m.p. 119—120°, whereas CPh₃:CHPh and S scarcely react at 180°.

H. W.

Reaction between sulphur dioxide and olefines. II. Propylene. M. HUNT and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1691—1696; cf. A., 1934, 1095).—Polypropylene sulphone (I) (from SO₂ and C₃H₆) is



The C-S skeleton is proved by degradation by hot 5% Na₂CO₃ to the ether-sulphone (II),



aq. NaOH to MeCHO-resin (1 mol.) and Me·SO₂·CH₂·CHMe·SO₂Na + H₂O (III) (1 mol.), the structure of both these sulphones being proved by synthesis. Cold *N*-alkali gives a product, m.p. 320°, shown to be SO₂ < $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{array}$ > SO₂ (IV) (cf. this

vol., 604). The terminal OH is proved by the solubility of (I) in alkali and its reaction with PCl₅ (with or without preliminary H₂O₂-oxidation) to give a sulphonyl chloride; the N content of the derived anilide, m.p. 240—255° (decomp.), shows that *n*=19—

20. Linkage of the two *sec*.-C as a sulphinic ester is not excluded, but is improbable. (III) with aq. HgCl_2 at 90° gives the substance, $\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{HgCl}$, m.p. $>200^\circ$, with $\text{Br}\cdot\text{CCl}_4$ *Me* β -bromo- β -sulphino-*n*-propyl sulphone, m.p. 76° , and with H_2O_2 *Me* β -sulphonon-*n*-propyl sulphone (V) (*Na* salt; *sulphonyl chloride*, m.p. 100° ; *sulphonanilide*, m.p. 105°). *Na* β -bromopropyl- α -sulphonate (from $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{Br}$ and Na_2SO_3 in aq. EtOH) and *NaSMe* give *Na* β -methylthiolpropyl- α -sulphonate, oxidised by KMnO_4 to *Me* α -sulphonopropyl sulphone (*chloride*, m.p. 65°). β -Methylthiolisopropyl alcohol (from Pr^βBr and *NaSMe*), b.p. $67^\circ/20$ mm., with SOCl_2 gives the *chloride*, b.p. $67^\circ/37$ mm., which with aq. Na_2SO_3 affords *Na* α -methylthiolpropyl- β -sulphonate, oxidised by KMnO_4 to (V). (IV) and hot 10% NaOH give a product, converted by H_2O_2 into (V). Na_2S and $(\text{CH}_2\text{Cl}\cdot\text{CHMe})_2\text{O}$ in hot EtOH give 2 : 6-dimethyl-*p*-thioxan, b.p. 172° , oxidised, best by CrO_3 in AcOH , to (II). R. S. C.

Mechanism of three-carbon tautomerism. D. J. G. IVES and H. N. RYDON (*Nature*, 1935, 136, 476—477).—Equilibration measurements of vinylacetic (I), crotonic, and butyric acids in presence of 1.05 mols. of NaOH in dil. D_2O at 100° show that substantial interchange occurs in the case of (I). The results indicate a parallelism between isotopic interchange and isomerisation, and that purely intramol. mechanisms for three-C tautomerism are unacceptable. L. S. T.

Electroreduction of unsaturated acids.—See this vol., 1205.

Catalytic chlorination of acetic acid. L. D. LJUBARSKI (*Ber. Ukrain. wiss. Forsch.-Inst. phys. Chem.*, 1934, 3, 85—91; cf. Brückner, A., 1927, 959).— $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ (I) is prepared by passing dry Cl_2 (5 c.c. per sec. increasing to 10—12 c.c. per sec.) into AcOH containing 1% of I, 2% of red P, and 4% of PCl_5 , and heated on the water-bath. The product is cooled and (I) filtered off; the filtrate may be further chlorinated. CH. ABS. (r)

Compound of stannic chloride and acetic acid.—See this vol., 1333.

Fractional distillation in a vacuum as a method of purifying fats. I. Application to alkyl oleates. L. KEFFLER (*Bull. Soc. chim. Belg.*, 1935, 44, 425—434).—Single fractionation is insufficient to purify alkyl oleates, as is shown by heats of combustion; after repeated fractionation, the following vals. are found: Me, 9562; Et, 9632; Pr^a oleate, 9699 g.-cal. per g. E. W. W.

Polymerisation of unsaturated fatty acids. J. K. CHOWDHURY, A. C. CHAKRABORTY, and A. MAJUMDER (*J. Indian Chem. Soc.*, 1935, 12, 441—454).—Oleic acid is polymerised at 100° by SnCl_4 in CO_2 with evolution of HCl and CO_2 . The properties of the product depend on the amount of SnCl_4 used. The I and acid vals. diminish whilst d and η increase as polymerisation progresses. The highest average mol. wt. (determined cryoscopically) was 1610; Staudinger's method for the determination of the mol. wt. is inapplicable. Stearic acid was formed during the polymerisation. The properties (mol. wt.,

d , n , η , I and acid vals.) of the product when ZnCl_2 , AlCl_3 , SbCl_3 , and BiCl_3 are used as catalysts are also tabulated. Polymerisation is diminished considerably when Me or glyceryl oleate is employed. Linoleic acid is polymerised differently by means of SnCl_4 ; the acid val. remains nearly const., whilst the I val. falls rapidly. When ricinoleic acid is polymerised by this method, the Ac val. falls, whilst the acid and I vals. remain const. (except when >20 vol.-% of SnCl_4 is used). Decarboxylation of these products gives viscous hydrocarbons similar to lubricating oils obtained from petroleum. The modes of polymerisation are discussed. H. G. M.

(A) **Synthesis of esters of oleic and elaidic acids.** (B) **Relative velocities of hydrogenation of esters of oleic and elaidic acids.** A. K. PLISOV and V. P. GOLENDEEV (*Rep. U.S.S.R. Fat and Margarine Inst.*, 1935, No. 2, 3—11, 12—21).—(A) The following esters are described: Pr^a , b.p. $216\text{—}220^\circ/14$ mm., Pr^β , b.p. $215\text{—}217^\circ/14\text{—}15$ mm., Bu^a , b.p. $223\text{—}227^\circ/14\text{—}15$ mm., Bu^β , b.p. $220\text{—}224^\circ/12\text{—}13$ mm., and *allyl oleate*, b.p. $218\text{—}221^\circ/12\text{—}13$ mm., Bu^a , b.p. $224\text{—}227^\circ/14$ mm., Bu^β , b.p. $222\text{—}226^\circ/12\text{—}13$ mm., and *allyl elaidate*, b.p. $215\text{—}220^\circ/13\text{—}15$ mm. Isomerisation of oleic to elaidic acid takes place in presence of oxides of N, but not of H_2SO_4 .

(B) The velocity of hydrogenation (Pd-black) of the above esters of oleic acid is slightly $>$ that of those of elaidic acid, whence it is concluded that oleic acid has the *cis*-configuration. R. T.

Behaviour of iodostarin in light. E. BAUR (*Helv. Chim. Acta*, 1935, 18, 1149—1156).—Irradiation of iodostarin in CHCl_3 causes dissociation into tariric acid and I, $\text{Me}\cdot[\text{CH}_2]_{10}\cdot\text{Cl}\cdot\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$ $\text{Me}\cdot[\text{CH}_2]_{10}\cdot\text{C}:\text{C}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H} + \text{I}_2$; the change is reversible and follows the law of mass action at room temp., whereas at higher temp. deviations from this behaviour are observed. In so far as the equilibrium in light obeys the law of mass action, it is independent of the strength of the light. The rates of formation and decomp. directly \propto strength of the light. Decomp. is caused by the rays absorbed by I, and photolysis must therefore be regarded as sensitised by I. H. W.

Oiticica fat [oil] and its fundamental difference from Chinese wood oil. C. P. A. KAPPELMEIER (*Fettchem. Umschau*, 1935, 42, 145—152).—The characteristic acid of oiticica oil, which corresponds with the "couepic acid" of van Loon and Steger (A., 1932, 498; 1931, 1034), now termed α -couepic acid (I), is converted by exposure to light in the presence of traces of I into the comparatively stable β -couepic acid (II), m.p. $101\text{—}102^\circ$, presumably a geometrical isomeride (stable cryst. *K*, m.p. $>200^\circ$, and NH_4 , m.p. 127° , salts; unstable *Me* ester, m.p. 41° ; *semicarbazone*, m.p. $134\text{—}137^\circ$), hydrogenated to a ketostearic acid (*hexahydrocouepic acid*, $\text{C}_{18}\text{H}_{34}\text{O}_3$, m.p. $96\text{—}97^\circ$ (*semicarbazone*, m.p. $135\text{—}5^\circ$), which appears identical with the hexahydrolicanic acid of Brown and Farmer (this vol., 607). Hence (I) and (II) are probably identical with licanic and isolicanic acids, respectively; probably also, the cryst. acid, of m.p. 94° (Wilborn and Löwa, B., 1930, 25), was (II). Acids of the elaeostearic series may be present in oiticica oil as well as (I) and (II). E. L.

Auto-esterification of lactic acid.—See this vol., 1328.

Polymembered heterocyclic compounds.
VIII. Polymembered mono- and poly-lactone rings. M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1935, 18, 1087—1125; cf. A., 1934, 1201).—The behaviour of $\text{OH} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ (I) in boiling C_6H_6 shows that autocatalysis caused by H from (I) depends on the presence of H_2O , and that when the $[\text{H}_2\text{O}]$ has reached a min. (I) is relatively stable at 80° . Addition of PhSO_2H causes immediate and complete formation of lactone. Extension of the observations to higher OH-acids shows that under the chosen conditions the final result of attempted lactonisation is not appreciably affected by hydrolytic, esterifying, or resinifying counter-reactions with rings containing > 8 members. The % composition of the reaction products therefore gives a complete picture of the course of the change in the prep. of the lactones. Conclusions as to the order of reaction cannot be based on volumetric determinations of the rate of change in those cases in which the reactions may be accompanied by simultaneous polymerisation and ring formation. Also deduction of the degree of polymerisation from the volumetrically determined reaction coeff. of the first order is inadmissible. Every apparently unimol. change must be controlled by gravimetric analysis of the products. The influence of the consecutive reactions caused by simultaneous polymerisation and ring formation on the volumetrically-determined rates of reaction is determined and discussed for rings of different size, and the influence of polymerisation on the mean velocity coeff. is elucidated. The cyclisation const. is more precisely defined; it may be directly \propto the frequency of intramol. collisions. The physical consts. of mono- and poly-lactone rings are discussed in relationship with the spatial structure of the rings. Similarity in structure causes a close analogy between the properties of mono- and tri-lactones. The theory of min. ring formation is extended, more closely defined, and brought into harmony with observed data by involving energy relationships. The following compounds appear new: ϵ -hydroxyhexo-mono-, b.p. $98-100^\circ/9$ mm., and -tri-, b.p. $190-205^\circ/0.3$ mm., -lactone; ζ -hydroxyhepto-mono-, b.p. $97-117^\circ/0.45$ mm., -di-, m.p. $40-41^\circ$, and -tri-, b.p. $202-205^\circ/0.3$ mm., -lactone; η -hydroxyocto-mono- and -di-, b.p. $150-152^\circ/0.3$ mm., m.p. $92.5-93.5^\circ$, -lactone; θ -hydroxynono-mono-, b.p. $71-78^\circ/0.5$ mm., -di-, b.p. $155-158^\circ/0.03$ mm., m.p. $56-57^\circ$, and -tri-, m.p. 20° , -lactone; ι -hydroxydeco-mono-, b.p. $67-75^\circ/0.3$ mm., m.p. $4-5^\circ$, -di-, b.p. $190-192^\circ/0.3$ mm., m.p. $96-97^\circ$, and -tri-, m.p. $28-29^\circ$, -lactone; κ -hydroxyundeco-mono-, b.p. $58-60^\circ/0.04$ mm., m.p. $< 0^\circ$, -di-, m.p. $71.5-72^\circ$, and -tri-lactone; λ -hydroxydodeco-mono-, b.p. $88-90^\circ/0.25$ mm., m.p. 0° , -di-, m.p. $100-101^\circ$, and -tri-lactone; μ -hydroxytrideco-mono-, b.p. $139-142^\circ/10$ mm., m.p. $20-21^\circ$, and -di-, m.p. $80-81^\circ$, -lactone; ν -hydroxytetradeco-mono-, b.p. $106-109^\circ/0.2$ mm., and -di-, m.p. $106-107^\circ$, -lactone; χ -hydroxypentadeco-mono-, b.p. $105-107^\circ/0.01$ mm., m.p. $34-35^\circ$, -di-, m.p. $103-107^\circ$, and -tri-, m.p. $70-72^\circ$, -lactone; ψ -hydroxyheptadeco-mono-, b.p. $135-138^\circ/0.2$ mm., m.p. $40-41^\circ$, and -di-, m.p. $96-97^\circ$, -lactone; φ -

hydroxyoctadeco-mono-, b.p. $136-138^\circ/0.15$ mm., m.p. $36-37^\circ$, -di-, m.p. $113-114^\circ$, and (?) -tri-, m.p. $80-90^\circ$, -lactone; ψ -hydroxytricoso-mono-, b.p. $174-176^\circ/0.2$ mm., m.p. $35-36^\circ$, and -di-, m.p. $104-105^\circ$, -lactone; ν -pentadeco-mono-, b.p. $108-109^\circ/12$ mm., and -di-, m.p. $117.5-118^\circ$, -lactone. Diethylene glycol, Na, and $\text{CH}_2\text{Br} \cdot [\text{CH}_2]_6 \cdot \text{CO}_2\text{Me}$ (II) yield after hydrolysis of the product, the acid $\text{C}_{15}\text{H}_{30}\text{O}_5$, m.p. $52-53^\circ$, whence the mono-, b.p. $120-125^\circ/0.11$ mm., and di-, m.p. $54.5-55^\circ$, -lactone. Similarly, trimethylene glycol and (II) give the acid $\text{C}_{14}\text{H}_{28}\text{O}_4$, m.p. $50-50.5^\circ$ (*Et* ester, b.p. $164-167^\circ/0.1$ mm., m.p. $22-23^\circ$), whence the mono-, b.p. $88-90^\circ/0.01$ mm., m.p. $14-15^\circ$, and di-, m.p. $59-60^\circ$, -lactone. H. W.

Oxidation of oxalic acid by iodic acid.—See this vol., 1334.

Calcium, strontium, barium, and magnesium oxalates.—See this vol., 1338.

Oxalato-compounds.—See this vol., 1335.

Oxidation of ethyl hydrogen dimethylmalonate with potassium persulphate. F. FICHTER and J. HEER (Helv. Chim. Acta, 1935, 18, 1276—1280).—Partial hydrolysis of $\text{CMe}_2(\text{CO}_2\text{Et})_2$ with KOH in EtOH at room temp. gives *Et H dimethylmalonate* (I), b.p. $101-102^\circ/0.5$ mm., which is oxidised by $\text{K}_2\text{S}_2\text{O}_8$ in neutral solution at 100° to CO_2 , Et_2 tetramethylsuccinate (II) (yield 23.9%), and by-products among which $\text{Pr}^i\text{CO}_2\text{Et}$ (III) and $\text{CHMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ are identified. Small amounts of (II) or $(\text{CMe}_2 \cdot \text{CO}_2\text{H})_2$ are obtained by oxidising $\text{CH}_2\text{Pr}^i \cdot \text{COEt}$ or $\text{CH}_2\text{Pr}^i \cdot \text{CO}_2\text{H}$, respectively, with $\text{K}_2\text{S}_2\text{O}_8$ in addition to C_3H_8 , propylene, and CO. (III) is not regarded as an intermediate in the production of (I) from (II). H. W.

Polymorphism in the series of normal fatty dicarboxylic acids. F. D. LA TOUR (Compt. rend., 1935, 201, 479—481; cf. A., 1932, 1192).—The α -form of pimelic acid is obtained when the molten acid is allowed to cool slowly in the absence of air. It is monoclinic and has a 22.20, b 9.59, c 45.4 Å., β $137^\circ 14'$, with 32 mols. in the unit cell, whilst that of the β - (stable) form has 4 mols. The transition temp. $\beta \rightarrow \alpha$ is $74-75^\circ$. The reverse change does not occur on cooling to room temp., but takes place when the α -form is ground at this temp. The α -form of azelaic acid can be obtained by a similar method, and is identical with the form obtained by Caspari (A., 1930, 139) by allowing a warm solution to cool slowly. H. G. M.

Plant growth substances. XV. Synthesis of auxin-glutaric acid and of some isomerides. F. KOGL and H. ERXLEBEN [with, in part, R. MICHAELIS and H. S. VISSER]. **XVI. Constitutional specificity of hetero-auxin.** F. KOGL and D. G. F. R. KOSTERMANS (Z. physiol. Chem., 1935, 235, 181—200, 201—216; cf. A., 1934, 1332, 1419; this vol., 418).—XV. (+)- α -Methylvaleric acid passed in CO_2 over MnO at $400-420^\circ$ gives (+)- $\gamma\eta$ -dimethylnonan- ϵ -one, which with Na and $\text{Et}_2\text{C}_2\text{O}_4$ yields 2:5-disec-butylcyclopentane-1:3:4-trione (I) (di-oxime, m.p. 109°). (I) with $\text{H}_2 + \text{Pt}$ gives 2:5-disec-butylcyclopentane-1:3:4-triol, m.p. $110-114^\circ$. $[\alpha]_D^{20} -7.8^\circ$ in EtOH, which is oxidised first with $\text{Pb}(\text{OAc})_4$ and then with alkaline N-KMnO_4 to

β -hydroxy- $\alpha\alpha'$ -disec.-butylglutaric acid, m.p. 97—100°, $[\alpha]_D$ —6.5° in EtOH. This acid is converted into a mixture of isomeric $\alpha\alpha$ -disec.-butylglutaric acids (II), $[\alpha]_D$ —6.9° in EtOH, on boiling with HI and red P. One of the fractions obtained during crystallisation of the brucine salts of (II) when further resolved by means of the cinchonidine salt, $[\alpha]^{20}$ —98.7°, has m.p. 129°, $[\alpha]^{20}$ —11.3° in EtOH, and is identical with the acid $C_{13}H_{24}O_4$ obtained from auxin-*a* and -*b* by oxidation with alkaline $KMnO_4$. Bu⁺I boiled with $Et_2\alpha\alpha'$ -dicarbethoxyglutarate and NaOEt gives $Et_2\alpha\alpha'$ -dicarbethoxy- $\alpha\alpha'$ -dibutylglutarate, b.p. 214—220°/11 mm., which yields $\alpha\alpha$ -dicarboxy- $\alpha\alpha'$ -dibutylglutaric acid, m.p. 178° (decomp.) [anhydride (III)], b.p. 187—189°/11 mm., obtained by boiling the acid with Ac_2O for 5 hr., on alkaline hydrolysis. (III) boiled with H_2O gives $\alpha\alpha$ -dibutylglutaric acid, m.p. 93—94° [meso-acid, m.p. 95—96° (brucine salt, $[\alpha]^{20}$ —12.73° in EtOH), *r*-acid, m.p. 53—56°]. The *r*-acid is partly resolved (*l*-acid, $[\alpha]^{20}$ —5.49° in EtOH; *d*-acid, $[\alpha]^{20}$ +2.77° in EtOH) by means of the brucine salts (brucine salt of *l*-acid has $[\alpha]_D$ —30.66° in EtOH). Octyl iodide with $CH_2Ac\cdot CO_2Et$ and NaOEt gives *Et* octylacetoacetate, b.p. 159°/15 mm., which with $CH_2I\cdot CH_2\cdot CO_2Et$ and NaOEt yields $Et_2\alpha$ -acetyl- α -octylglutarate (IV), b.p. 166°/0.54 mm. Alkaline hydrolysis of (IV) gives *r*-octylglutaric acid, m.p. 48° [*l*-acid, m.p. 48°, $[\alpha]^{20}$ —9° in EtOH (strychnine salt, $[\alpha]^{20}$ —28°)].

XVI. The effect of alterations in the mol. of 3-indolylacetic acid (V) on its physiological activity was examined. As regards their activity the acid and its esters form the series (V) > Me > Et > Pr^a > Pr^b. The *picrates* of the Me, Et, Pr^a, and Pr^b esters have, respectively, m.p. 125°, 84°, 105°, 100—101°. 2:3-Dihydroindolyl-3-acetic acid (*picrate*, m.p. 168°) and its *Me* ester (*picrate*, m.p. 178°) are inactive. 1-Methylindolyl-3-acetic acid (VI) has one thousandth of the activity of (V), but its Et ester is inactive. 2-Methylindolyl-3-acetic acid is 4 times as active as (V), its *Me* ester being inactive. 2-Ethylindolyl-3-acetic acid, m.p. 100—101°, obtained from the phenylhydrazone of homolævulic acid by the action of H_2SO_4 , is inactive, but 3-methylindolyl-3-acetic acid, m.p. 151° (from Et formylpropionate and $p\text{-}C_6H_4Me\cdot NH\cdot NH_2$), has 50 times, and its *Me* ester (*picrate*, m.p. 122—123°) 40 times, the activity of (VI). 2:5-Dimethylindolyl-3-acetic acid, m.p. 172—173° [from lævulic acid and $p\text{-}C_6H_4Me\cdot NH\cdot NH_2$ (*p*-tolylhydrazone, m.p. 97°)], is inactive. Indolyl-3- α -propionic acid (*picrate*, m.p. 146—147°) has one fifth of the activity of (V). *l*- and *r*- β -Indolyl-lactic acids are inactive, but 3-indolylpyruvic acid (m.p. of compound with AcOH 210°) is about 7 times as active as (VI).

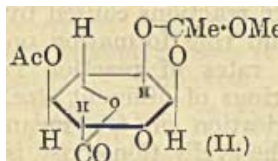
W. McC.

Constitution of aleuritic acid. H. RAUDNITZ, H. SCHINDLER, and F. PETRU (Ber., 1935, 68, [B], 1675—1676).—Aleuritic acid (I), m.p. 102°, obtained by alkaline hydrolysis of technical unbleached shellac, is oxidised by $Pb(OAc)_4$ in AcOH to η -aldehydo-octoic acid. Although the expected ζ -hydroxyheptaldehyde could not be isolated, it is thereby established that (I) is $OH\cdot[CH_2]_6\cdot[CH\cdot OH]_2\cdot[CH_2]_2\cdot CO_2H$.

H. W.

isoCitric [α -hydroxypropane- $\alpha\beta\gamma$ -tricarboxylic] acid from blackberries. W. F. BRUCE (J. Amer. Chem. Soc., 1935, 57, 1725—1729).—*Me*₃ isocitrolactone (I) (prep. from blackberries), m.p. 106—107°, b.p. 204—206°/26 mm., $[\alpha]^{25}_{500}$ —65° in dioxan, with alkali rapidly becomes dextrorotatory and gives solutions of the β -*Me* ester *Na*₃ salt, $CO_2Na\cdot CH(OH)\cdot CH(CO_2Me)\cdot CH_2\cdot CO_2Na$, and more slowly loses the second Me to give the *Na*₃ salt. With hot *N*-HCl it affords isocitrolactone, m.p. 153—154°, $[\alpha]^{20}_{500}$ —62° in H_2O [*Et*₂ ester (II), b.p. 167—169.5°/2.5 mm., $[\alpha]^{20}_{500}$ —54.2°], which with NaOH becomes less levorotatory to give the *Na*₃ salt. (I) yields the *amide*, decomp. 204°, $[\alpha]^{20}_{500}$ —5° in H_2O , and *hydrazide*, m.p. 208—209° (decomp.). (I) was const. in various preps., and the variation observed by Nelson (A., 1930, 1163) was probably due to varying decomp. of his *Et*₃ ester to (II). R. S. C.

Derivatives of glycuronic acid. V. Synthesis of glycuronides. W. F. GOEBEL and F. H. BABERS (J. Biol. Chem., 1935, 110, 707—717).—By condensation with dry MeOH- Ag_2CO_3 at 0°, 1-chlorodiacetyl-glycuron (I) (A., 1933, 808) affords diacetyl-glycuron methylglycoside (II), m.p. 110—111°, $[\alpha]^{25}_D$ +112.5° in $CHCl_3$, and Me 1-chlorotriacetyl-glycuronate (III) gives the methylglycoside (IV), m.p. 118°, $[\alpha]^{25}_D$ +54.0° in $CHCl_3$. Both (II) and (IV) possess an orthoacetate



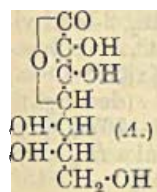
structure [as (II)], since 1 Ac is unaffected by titration with a dil. base, and both are hydrolysed (unimol. $k=0.054$ and 0.025 min.^{-1} , respectively) with loss of the glycosidic group by $0.005N\text{-HCl}$ in aq. 95% dioxan.

Such hydrolysis of (II) affords an equimol. mixture of cryst., $[\alpha] +115^\circ$ in 95% dioxan, and oily, $[\alpha] +143^\circ$ in 95% dioxan, hydroxydiacetyl-glycuron; (IV) similarly gives cryst., m.p. 126°, $[\alpha] +146.8^\circ$ in 95% dioxan, and oily, $[\alpha] +76^\circ$ in 95% dioxan, Me hydroxytriacetyl-glycuronate. Condensation of (I) and (III) with $p\text{-}NO_2\cdot C_6H_4\cdot CH_2\cdot OH\text{-}Ag_2CO_3$ in $CHCl_3$ affords, respectively, the *p*-nitrobenzylglycoside, m.p. 133—134°, $[\alpha]^{25}_D$ +39.9° in $CHCl_3$, of diacetyl-glycuron, and the *p*-nitrobenzylglycoside, m.p. 175—176°, $[\alpha]^{25}_D$ —57.8° in $CHCl_3$, of Me triacetyl-glycuronate, which, unlike (II) and (IV), are true glycosides. J. W. B.

Derivatives of *d*-galacturonic acid. II. Synthesis of methyl α -1-bromo-*d*-galacturonate triacetate and its conversion into β -methyl-*d*-galacturonide. S. MORELL, L. BAUR, and K. P. LINK (J. Biol. Chem., 1935, 110, 719—725).—Me *d*-galacturonate 1:2:3:4-tetra-acetate (this vol., 608) is converted by $HBr\text{-}Ac_2O$ at 0°, and then at room temp., into Me α -1-bromo-*d*-galacturonate 2:3:4-triacetate, m.p. 129.5—130.5°, $[\alpha]^{25}_D$ +248° in $CHCl_3$, converted by $MeOH\text{-}Ag_2CO_3$ into the corresponding β -1-methyl-galacturonide, m.p. 118—120°, $[\alpha]^{25}_D$ +15.3° in $CHCl_3$ (normal glycoside structure), hydrolysed by $0.242N\text{-Ba(OH)}_2$ in aq. $COMe_2$ (N_2 stream) to β -1-methyl-*d*-galacturonic acid + H_2O , sinters (oily with rapid heating) 125—135°, m.p. 163—165° (from 95% EtOH), 159—161° (from $COMe_2$), $[\alpha]^{25}_D$ —39.6° in H_2O [Ehrlich *et al.*, A., 1933, 258, give m.p. 134° (decomp.)], and anhyd., m.p. 163—165° (decomp.), $[\alpha]^{25}_D$ —43.0° in

H₂O. Good yields are obtained in all the above stages. J. W. B.

Synthesis of *l*-ribo- γ -ketoheptonolactone (*l*-alloascorbic acid). M. STEIGER (Helv. Chim. Acta, 1935, 18, 1252—1254).—Crude *l*-psicose



is converted into *l*-allosazone, from which *l*-allosone (I) is obtained by means of PhCHO. Treatment of (I) with HCN and subsequent hydrolysis with HCl affords *l*-ribo- γ -ketoheptonolactone (*l*-alloascorbic acid) (A), m.p. about 176—177° (decomp.), $[\alpha]_D^{21} +29.3^\circ$ in 0.01N-HCl. H. W.

Argentometric determination of formaldehyde. J. A. FIALKOV and S. D. SCHARGORODSKI (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 209—221).—CH₂O reduces AgNO₃ in a solution which is approx. 0.05N in NH₃. The Ag pptd. is dissolved in HNO₃ and determined (Volhard). CH. ABS. (e)

Aldol condensations. III. Formation of the chain of carotenoids by condensation of β -methyl- Δ^5 -butenal. F. G. FISCHER and K. HULTZSCH (Ber., 1935, 68, [B], 1726—1734; cf. A., 1931, 335).—The action of weak alkalis in H₂O on CMe₂:CH·CHO leads mainly to dehydrocitrinal [β κ -dimethyl- $\Delta^{5,7}$ -octatrienal] (I), which could not thus be obtained pure, whereas NaNH₂ in Et₂O causes synthesis along diene lines with production of 2:2:4-trimethyl- $\Delta^{4,10}$ -cyclohexadiene-aldehyde (II), b.p. 85—86°/9 mm. (semicarbazone, m.p. 213°). Under certain conditions (not described) linear condensation of CMe₂:CH·CHO proceeds smoothly; about 50% of the condensed material can be distilled directly in a high vac., of which about half consists of homogeneous (I), m.p. 40.5—41° [semicarbazone, m.p. 224—225° (decomp.); phenylhydrazone, m.p. 141—142°; p-nitrophenylhydrazone, m.p. 193—194°; oxime, m.p. 123°], and one fifth of β κ -trimethyl- $\Delta^{5,7,9}$ -dodecapentaenal (farnesinal) (III), m.p. 120—121° (semicarbazone, decomp. 236°; oxime, m.p. 192°); in addition, small amounts of red, non-volatile, more complex aldehydes are produced. Linear condensation predominates, but (II) and a monocyclic aldehyde C₁₅H₂₀O of unknown structure are produced in small amount. The structure of (I) is established by catalytic hydrogenation to tetrahydrocitrinal, and by its oxidation by Ag₂O to dehydrogeranic acid. (I) is converted by Al(OPrⁱ)₃ in PrⁱOH into γ γ -dimethyl- $\Delta^{8,9}$ -octatrienol (dehydrogeraniol), m.p. 46—47°, which is very readily autoxidised. (III) cannot be oxidised by Ag₂O to the acid, the attempt to prepare which through the oxime failed on account of the stability of the cryst. nitrile. Hydrogenation of (III) leads to hexahydrofarnesal. Treatment of (III) with Al(OPrⁱ)₃ in PrⁱOH affords γ γ λ -trimethyl- $\Delta^{8,9,10}$ -dodecapentaenol (farnesinol), m.p. 136—137°.

Kinetics of oxidation of gaseous glyoxal.—See this vol., 1327.

Glyoxal. III. Syntheses with glyoxal semi-acetal; nitrolactaldehyde. H. O. L. FISCHER, E. BAER, and H. NIDICKER (Helv. Chim. Acta, 1935, 18, 1079—1087).—Glyoxal semiacetal condenses with NO₂Me in presence of K₂CO₃ to nitrolactaldehyde Et₂

acetal (I), NO₂·CH₂·CH(OH)·CH(OEt)₂, b.p. 136—138°/10 mm., m.p. 30°, which does not reduce boiling Fehling's solution and gives a transitory brownish-red colour with FeCl₃. It is hydrolysed by 0.1N-H₂SO₄ at 80—85° to (presumably dimeric) nitrolactaldehyde (II), decomp. about 160° when slowly heated or m.p. 181° (decomp.) when placed in a bath preheated to 175°. (II) reduces cold NH₃-Ag₂O and Fehling's solution if the concn. of alkali is low. It is gradually dissolved by warm H₂O to a unimol. solution. The aldehydic nature of (II) is established by the isolation of the 2:4-dinitrophenylhydrazone, m.p. 167—168°, 2:4-dinitrophenylsazone, m.p. 294—297° when rapidly heated, and the (anhydro)dimedon compound, C₁₉H₂₅O₆N, incipient decomp. 180° when slowly heated, m.p. about 190° when rapidly heated. (II) cannot be titrated (Willstätter-Schudel), but can be determined by Ripper's method. Catalytic hydrogenation (Pd-BaSO₄) of (I) in presence of H₂C₂O₄ affords hydroxylaminolactaldehyde Et₂ acetal oxalate, m.p. 113.5°, whereas reduction by activated Al in Et₂O gives aminolactaldehyde Et₂ acetal, b.p. 111—112°/10 mm., m.p. 41°, hydrolysed by fuming HCl to aminolactaldehyde hydrochloride, decomp. 143—145°. H. W.

Specific effect of zinc on the dismutation of methylglyoxal. C. NEUBERG and M. KOBEL (Biochem. Z., 1935, 280, 297—306).—At p_H about 6.0 and 37° and 100° ZnO and ZnCO₃ convert AcCHO in 60 and 76% yield, respectively, into lactic acid (I), together with small amounts of reducing substances. The yield of (I) is higher (and that of reducing substances lower) with lower [AcCHO]. With CaCO₃ at p_H about 7.0 the yield of (I) is only 13—22% of that obtained with ZnCO₃. At p_H 6.4 and 100° the NaHSO₃ compound (II) of Ca dihydroxyacetone phosphate yields, by the action of CaCO₃, an amount of (I) corresponding with the AcCHO equiv. of (II), but by the action of ZnCO₃ it yields only 10.7% of the calc. amount of (I). W. McC.

Rate of alkaline chlorination of ketones. P. D. BARTLETT and J. R. VINCENT (J. Amer. Chem. Soc., 1935, 57, 1596—1600).—The rates of chlorination of CPhMe, COMe₂, and COMeBu^t are measured in aq. NaOH up to M concn. and are bimol. if the p_H is >11. They pass through a min. at a low [NaOH], but in >0.3M-NaOH $k \propto [OH']$. Chlorination thus involves reaction of the enol and enolate ion with HOCl and OCl'. k decreases in the order of ketones given above and is more dependent on structure than is the rate of enolisation in acid solution. R. S. C.

Action of sodium or silver on ketals of symmetrical dichloro- or dibromo-acetone. N. D. PRIANISCHNIKOV and V. A. LEONTOVITSCH (Ber., 1935, 68, [B], 1866—1869).—Treatment of CO(CH₂Cl)₂ with MeOH and HCl affords α γ -dichloro- β β -dimethoxypropane (I), m.p. 81.5°, less advantageously obtained by use of CH(OAlk)₃. α γ -Dichloro- β β -diethoxypropane (II), m.p. 28°, and α γ -dibromo- β β -dimethoxypropane (III), m.p. 62.5°, are prepared analogously. (I) does not react with KI in warm MeOH. Treatment of (I), (II), or (III) with Na in xylene gives dark brown resins and a little oil which does not yield

$\text{CH}_2\text{CH}\cdot\text{CHO}$ when warmed with H_2SO_4 ; with mol. Ag reaction is extremely slow, and here also there is no evidence of production of cyclopropanone ketals. (I), (II), and (III) are unusually stable to acid.

Preparation of crystalline dihydroxyacetone.—See this vol., 1282.

Molecular structure of carbohydrates. W. N. HAWORTH (Chem. and Ind., 1935, 859–868).—A lecture.
H. W.

Degradation of *l*-arabinal to *l*-erythrose. G. E. FELTON and W. FREUDENBERG (J. Amer. Chem. Soc., 1935, 57, 1637–1640).—This degradation is effected by O_3 . Arabinose and $\text{HBr}\cdot\text{AcOH}$ give β -acetobromoarabinose (bromoarabinose penta-acetate), m.p. 132°, $[\alpha]_D^{25} -134.8^\circ$ in CHCl_3 . Hydrogenation (Pd-black) of arabinal, m.p. 81–82°, $[\alpha]_D^{25} -199.5^\circ$, in EtOH gives dihydroarabinal, b.p. 83–85°/1 mm., $[\alpha] +48.2^\circ$ in H_2O . Ozonisation of arabinal diacetate in AcOH gives a mixture (I) of *l*-erythrose (II), $[\alpha]_D +11.5^\circ \rightarrow +30.5^\circ$ in H_2O (isolated as 2:3-isopropylidenemethylerythroside, b.p. 45–50°/2 mm., $[\alpha] +58^\circ$ in CHCl_3 , hydrolysed by 0.1N- H_2SO_4), and 4-formylaldehydeerythrose (III), isolated as Me, acetal, $[\alpha]_D^{25} +53.4^\circ$ in H_2O . (I) and 0.75% $\text{HCl}\cdot\text{MeOH}$ give (III) and a methyl-2-deoxyribose, m.p. 81–82°, $[\alpha] +218.5^\circ$ in H_2O . (I) is not fermented by yeast.
R. S. C.

Determination of pentosans by reduction with furfuraldehyde. G. OSCHMIAN (Brodil. Prom., 1934, 11, No. 5, 26–28).—The sample is twice distilled with HCl (d 1.06), the second distillation serving to destroy any hydroxymethylfurfuraldehyde formed. Furfuraldehyde in the distillate is reduced with Fehling's solution, and the Cu titrated with KMnO_4 .
CH. ABS. (e)

Oxidation of reducing sugars by oxygen. O. SPENGLER and A. PFANNENSTIEL (Z. Wirts. Zuckerind., 1935, 85, 546–552).—Oxidation of glucose, fructose, and mannose in alkaline solution by O_2 instead of air as used by Nef (B., 1908, 31; 1917, 1022) is accompanied by complete loss of reducing power without darkening, and in all cases the main product is arabonic acid (yield 70%), formed by fission of the terminal C atom as HCO_2H and oxidation of the adjacent group to $\cdot\text{CO}_2\text{H}$. A high yield of erythronic acid was obtained similarly from arabinose.

J. H. L.

Emil Fischer's assignment of configuration to *d*-glucose. Penta-acetates of *d*-arabitol and *d*-xylitol. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1935, 57, 1753).—The configuration of glucose is best demonstrated by the activity, $[\alpha]_D^{25} +37.2^\circ$ in CHCl_3 , of *d*-arabitol penta-acetate, m.p. 74–75° (corr.), and inactivity of *d*-xylitol penta-acetate, m.p. 61.5–62.5° (corr.).

R. S. C.

Carbohydrates. V. Specificity of sugar hydroxyl groups. T. LIESER and R. SCHWEIZER. VI. Xanthate reaction of glucose. T. LIESER and E. LECHZYCK (Annalen, 1935, 519, 271–278, 279–291).—V. α -Methylglucoside in $\text{C}_5\text{H}_5\text{N}$, even with small quantities of BzCl at low temp., gives the

2:6-*Bz*₂ derivative, m.p. 144°, $[\alpha]_D^{25} +80.37^\circ$ in CHCl_3 . Glucosemethylmercaptal forms the 6-*Bz*, m.p. 114°, glucosebenzylmercaptal the 6-*Bz*, $[\alpha]_D -63.10^\circ$ in COMe_2 , thioethylglucoside the 6(?) -*Bz*, m.p. 144–145°, $[\alpha]_D +67.27^\circ$ in CHCl_3 , galactose-ethylmercaptal the 6-*Bz*, m.p. 139°, $[\alpha]_D^{25} +14.22^\circ$ in COMe_2 , 2-methylglucose-ethylmercaptal the 6-*Bz*, m.p. 134°, arabinose-ethylmercaptal the 5(?) -*Bz*, m.p. 119°, $[\alpha]_D^{25} +49.48^\circ$ in CHCl_3 [phenylhydrazone, m.p. 168° (decomp.)], β -phenylglucoside the 6-*Bz*, m.p. 166–167°, $[\alpha]_D^{25} -31.68^\circ$ in COMe_2 , xylosebenzylmercaptal a *Bz*₂, m.p. 114°, and xylose a *Bz*₄, m.p. 178°, $[\alpha]_D^{25} -47.45^\circ$, derivative.

VI. α -Methylglucoside with $\text{Ba}(\text{OH})_2$ and CS_2 , followed by CO_2 and AgNO_3 , yields an Ag salt, with which MeI gives Me α -methylglucosidyl xanthate (I), $[\alpha]_D^{25} +122.7^\circ$ in EtOAc. This forms *Bz* (II), m.p. 125–126°, $[\alpha]_D^{25} +61.24^\circ$ in CHCl_3 , *Bz*₃, m.p. 105–109°, and *Ac*₃, m.p. 75–76°, derivatives. Treated in H_2O with Ag_2CO_3 , (I) liberates α -methylglucoside. With AgNO_3 in H_2O , (II) yields benzoyl- α -methylglucosidyl methylmonothiocarbonate, m.p. 104–105°, $[\alpha]_D^{25} +77.66^\circ$ in CHCl_3 , and α -methylglucoside 6-benzoate (III), m.p. 174–175°, also obtained when (II) is treated in MeOH with Ag_2CO_3 , and the resulting benzoyl- α -methylglucosidyl Me, orthocarbonate, m.p. 164–165°, is hydrolysed by MeOH-HCl. With $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$, (III) yields α -methylglucoside 2:6-dibenzoate, and it is therefore regarded as α -methylglucoside 6-benzoate. Me β -methylglucosidyl xanthate, m.p. 158–159°, $[\alpha]_D^{25} -5.01^\circ$ in EtOH, forms *Bz*, m.p. 177–179°, and *Ac*₃, m.p. 112–113°, derivatives, which with Ag_2CO_3 in MeOH yield, respectively, benzoyl-, m.p. 187–188°, and triacetyl-, m.p. 108–109°, β -methylglucosidyl Me carbonate. β -Phenylglucoside, $\text{Ba}(\text{OH})_2$, and CS_2 , followed by CO_2 and I, form the compound, $\text{C}_{26}\text{H}_{30}\text{O}_{12}\text{S}_4$, $[\alpha]_D^{25} +150.8^\circ$ in EtOH, which with Ag_2CO_3 in MeOH forms β -phenylglucosidyl Me carbonate, m.p. 152°, $[\alpha]_D^{25} -64.97^\circ$ in COMe_2 (*Ac*₃, m.p. 112–113°, $[\alpha]_D -22.17^\circ$ in CHCl_3 , and *Bz*, m.p. 164–170°, derivatives). Treatment of Ba β -phenylglucosidyl xanthate with AgNO_3 gives β -phenylglucosidyl Me xanthate, m.p. 173–184°, $[\alpha]_D^{25} -55.21^\circ$ in EtOH. E. W. W.

Fructose anhydrides. XVI. Identity of inulin from different plants. Problem of the terminal groups of inulin. H. H. SCHLUBACH and H. SCHMIDT (Annalen, 1935, 520, 43–52).—Inulin from Jerusalem artichoke, when dried for 2 hr. at 60° in high vac., has $[\alpha]_D^{25} -40.1^\circ$, and inulin from dahlia has a similar val. Inulin from chicory has a lower $[\alpha]$; when the Ac derivative is fractionally pptd., and hydrolysed, only a small proportion of the product has $[\alpha]_D^{25} -40.0^\circ$, the main product having $[\alpha]_D^{25} -38.1^\circ$. Chicory inulin has also a shorter half-decomp. period (cf. infra). After mild hydrolysis, inulin from the above sources gives only 0.1–0.4% of aldohexose (method of Auerbach and Bodländer), and the reduction val. (Bertrand) is sometimes 0.1–0.3%, but often zero. This conflicts with the view that inulin consists of a chain of fructose units. Possible structures in which the “terminal” groups are bound are discussed.
E. W. W.

Half-decomposition period in acid hydrolysis as a constant for characterising sugar anhydrides

and glucosides. A new fructose [analysis] table. H. KNOOP (Annalen, 1935, 520, 34—43).—The method of Schlubach and Knoop (A., 1933, 938) is modified; 1/100*n* g.-mols. of substance (*n*=no. of O-bridges) are treated with 100 c.c. of *N*-H₂SO₄ at 20°, 60°, or 100°, and the time (in min.) for 50% hydrolysis, as measured by reducing power, is compared with the following empirical vals.: inulin (Jerusalem artichoke) 389, (dahlia) 384, (chicory) 372; irisin (*Iris pseudacorus*) 225; graminin (rye) 214; sucrose 291 (all at 20°); trehalose 86 (at 100°); and other vals. previously determined. An empirical table for the determination of 10—100 mg. of fructose by the Bertrand method is given. The reducing power of fructose which has been kept for 6 hr. at 12 mm. and 20° is 100%; at 40°, 99.4%; at 60°, 97.8%; at 80°, 97.0%; at 100°, 87.1%, of the original val. E. W. W.

Rearrangement of sugar acetates by aluminium chloride. Neolactose and *d*-altrose. N. K. RICHTMYER and C. S. HUDSON (J. Amer. Chem. Soc., 1935, 57, 1716—1721).—The discrepancy between the α recorded for altrose (A., 1926, 941; 1934, 759) is due to formation of the sugar anhydride by hot acid. α -Acetochloroneolactose (modified prep. in 45% yield from lactose octa-acetate by AlCl₃-PCl₅ in CHCl₃) with Ag₂CO₃ in aq. COMe₂ gives neolactose β -hepta-acetate (I), m.p. (+COMe₂) 53—54° and (anhyd.) 135—136°, [α] +10° in CHCl₃ \rightarrow +21° in 3—4 days, and " α hepta-acetate (II), m.p. 85—95°, [α] +23.3° in CHCl₃ \rightarrow +21°. (I) in Ac₂O-C₅H₅N at -10° gives neolactose β -octa-acetate, m.p. 148—149°, [α] -6.3° in CHCl₃, also obtained with 47.7% of α -octa-acetate from (II). (II) is thus a mixture of about equal parts of (I) and the true α -hepta-acetate. (I) or (II) with Ba(OMe)₂ in dry, cold MeOH yields neolactose, m.p. 190° (decomp.) (lit. a syrup), [α]_D²⁰ +34.6° in H₂O \rightarrow +35.5° in 20 min., which with hot *N*-HCl affords *d*-galactose (removed by fermentation) and a syrup (III), [α] -91° in H₂O (cf. *loc. cit.*). (III) and CH₂Ph-SH in conc. HCl give benzylthiol-*d*-altrose, m.p. 121—122°, [α] +39.4° in C₅H₅N [the 1-form, from *l*-altrose (IV), had m.p. 121—122°, and [α] -39.2° in C₅H₅N], which with CaCO₃ and HgCl₂ in H₂O at 50° affords *d*-altrose (V), m.p. 103—105°, [α] +32.6° in H₂O (no mutarotation). Both (V) and (IV) in hot conc. HCl give an equilibrium mixture (VI), [α] 98°, with 57% of a non-reducing anhydride, for which [α] -220° is calc. (III) is thus (VI). R. S. C.

Cardiac glucosides. XIII. Empirical formula of scillaridin A and its derivatives. A. STOLL, A. HOFMANN, and J. PEYER (Helv. Chim. Acta, 1935, 18, 1247—1251).—Determinations of the equiv. of isoscillardic acid A by titration with NaOH in presence of phenolphthalein in conjunction with similar determinations with several bile acids establish the formula C₂₄H₃₀O₃ (not C₂₅H₃₂O₃) for scillaridin A. The formulae of its derivatives require corresponding alteration. H. W.

Digitalis glucosides. A. STOLL (Chem.-Ztg., 1935, 59, 773—776).—A review.

Digitalis glucosides. V. Constitution of digoxigenin. S. SMITH (J.C.S., 1935, 1305—1309).—Digoxigenin with CrO₃ in 80% AcOH at room temp.

gives a diketone, digoxigenone, m.p. 265° (decomp.) [monoxime, m.p. 235° (decomp.); monosemicarbazone, m.p. 268° (decomp.)]. Similarly, isodigoxigenin affords a diketone, m.p. 335° [monoxime, m.p. 305° (decomp.); monosemicarbazone, m.p. 295° (decomp.)], as does dihydrodigoxigenin to give a diketone, m.p. 243° (monoxime, m.p. 250°; monosemicarbazone, m.p. 260°), and anhydrodigoxigenin, a diketone, m.p. 260° (di-oxime, m.p. 270° (decomp.); semicarbazone (mono+di-), decomp. at about 260°] (also obtained from digoxigenone with warm conc. HCl). isoDigoxigeninic acid (A., 1931, 74) with CH₂N₂ in Et₂O gives the *Me* ester, m.p. 145° (+*MeOH*, m.p. 156°), oxidised (Kiliani's reagent) to *Me* isodigoxigenonate, m.p. 248°, as a result of the oxidation of two CH-OH groups. iso-Digoxigenin with boiling EtOH-10% NaOH, followed by treatment with NaOBr, gives isodigoxigenic acid, m.p. 235° (decomp.) (pyridine salt, m.p. 260°; *Me* ester, m.p. 208°), oxidised to isodigoxigenonic acid, m.p. 260° (*Me* ester, m.p. 253°). Digoxigenone with warm 10% MeOH-KOH gives isodigoxigenone. The reaction is accomplished by participation of the *tert*-OH (cf. A., 1931, 74) (moreover, isodigoxigenin gives a Ac₂ derivative and forms no anhydro-compound). The *tert*-OH is assigned position 14 in the digitoxigenin skeleton, this being the nearest position available to the lactone group, which is probably at C17 by analogy with the close similarity in properties and inter-relationships in this series with those of the digitoxigenin series (cf. A., 1934, 1355; this vol., 497). One CH-OH is probably in position 3. J. L. D.

Molecular sizes of methylated oligosaccharides. Significance of molecular weights by Hess and collaborators. F. KLAGES (Annalen, 1935, 520, 71—87).—The chain theory of cellulose structure is supported. Low vals. of mol. wts. (*M*) determined cryoscopically are due to non-applicability of Raoult's law. The dialysis coeff. (*D*) of MeOH, EtOH, glycerol, glucose, sucrose, lactose, raffinose, two tetramethylglucoses, β -pentamethylglucose (I), β -octamethylcellobiose (II), β -hendecamethylcellobiose (III), and hendecamethylraffinose (IV) are determined by a modification of Brintzinger's apparatus (A., 1931, 416), using a Cellophane membrane. The constancy of *DM*¹ (cf. *loc. cit.*) does not hold for higher vals. of *M*, for which *DM* is more nearly const.; in the same class, substances of equal *M* have, however, equal *D*. Thus *D* of (IV) and (V) are approx. equal, indicating that (IV) has *M* 658. Velocity of partial hydrolysis of (I), (II), and (III) is measured; α agrees with the calc. vals. From (III), 2:3:6-trimethyl- β -methylglucoside and heptamethylcellobiose, m.p. 81—83°, b.p. 190—195°/0.3 mm., are obtained. The mol. wt. of (III) as determined cryoscopically by the method of Karagunis (A., 1931, 169) shows apparent dissociation, but (IV) gives similar results, the apparent mol. wt. decreasing in each case with increasing dilution. Possible reasons for this are discussed. E. W. W.

Polysaccharides. XXII. Constitution and molecular structure of α -amylodextrin. W. N. HAWORTH, E. L. HIRST, and A. C. WAINE (J.C.S., 1935, 1299—1303).—Amylose (this vol., 1226) with barley amylase in H₂O at 55° affords α -amylodextrin

(I), which is sol. when fresh in cold H_2O , and gives a characteristic reddish-violet colour with I. (I) with Ac_2O in $AcOH$ containing Cl_2 and SO_2 at 50° affords an acetate, mol. wt. 12,000 (about 40 glucose units), whereas with $Ac_2O-C_5H_5N$ at room temp., two Ac derivatives are formed; one (II), sol. in $COMe_2$, is similar to the above, but has mol. wt. 22,000 (about 80 glucose units), and the other, insol. in $COMe_2$, resembles an amylopectin. The acetate of mol. wt. 12,000 with Me_2SO_4 in $COMe_2-30\%$ $NaOH$ gives a OMe -derivative, mol. wt. 8000, determined viscosimetrically (about 40 glucose units), which indicates the absence of mol. disaggregation as a result of methylation, but gravimetric assay of the end group shows 7.1% of tetramethylglucose, equiv. to a chain-length of 16—17 glucose units (mol. wt. 3500) (*loc. cit.*). The OMe -derivative with saturated HCl at 0° affords a product which is converted by 1% $MeOH-HCl$ into a mixture of tetramethylmethylglucoside (corresponding with a chain-length of 16—17 glucose units; mol. wt. about 3500) and trimethylmethylglucoside. The P content of (I) is very high, but there is no correlation between it and the tendency towards aggregation. The P appears to be combined chemically. (II) with Me_2SO_4 in $COMe_2-30\%$ $NaOH$ gives a OMe -derivative, the formation of which is accompanied by irregular variations in OMe content of the product (the phenomenon is probably connected with progressive disaggregation during methylation) finally to yield one of mol. wt. 6500, indistinguishable from the OMe -derivative described above.

J. L. D.

Starch polysaccharide from woody tissue of the apple tree.—See this vol., 1290.

X-Ray investigation of cellotriose and derivatives.—See this vol., 1308.

Preparation of trimethylcellulose. K. HESS, G. ABEL, W. SCHÖN, and W. KOMAREWSKY (*Cellulosechem.*, 1935, **16**, 69—77).— Me_2SO_4 decomposes more slowly in 45% $NaOH$ than in more dil. solution. Rate of methylation of ramie increases with increasing rate of stirring and increasing $[NaOH]$. More conc. $NaOH$ gives a better yield and less disintegration, and 35% is recommended. 41—43% OMe can be attained at 0° . Disintegration is diminished by low temp., and by the use of spun and unchemicked fibre. When the conditions of prep. and the % OMe are the same, spun fibre yields more viscous solutions than loose fibre. Too prolonged methylation results in diminished OMe content. Details are given of three methods of methylation.

A. G.

Fractionation of trimethylcellulose. G. ABEL and K. HESS (*Cellulosechem.*, 1935, **16**, 78—79).—By appropriate methods trimethylcellulose (44.5% OMe) can be separated into fractions insol. and sol. in C_6H_6 , respectively; both have the same OMe content. Trimethylcellulose can be dissolved in H_2O if first dissolved in $CHCl_3$ and reprecipitated with light petroleum.

A. G.

Fusion of methylcellulose. II. Characterisation of methylcellulose. K. HESS, C. TROGUS, and G. ABEL (*Cellulosechem.*, 1935, **16**, 79—84).—Numerical data and photographs are given of X-ray diagrams of various preps. of trimethylcellulose after

heating above the m.p. for various times. The diagrams pass through the sequence methylcellulose $I \rightarrow III' \rightarrow III \rightarrow X$ at different rates, and photographs taken after a fixed time of heating can be used to differentiate the specimens.

A. G.

Preparation of dibromoamine and its reactions with Grignard reagents.—See this vol., 1334.

Determination of hexamethylenetetramine. R. GROS (*J. Pharm. Chim.*, 1935, [viii], **22**, 241—244).—The $(CH_2)_6N_4$ is decomposed by dil. H_2SO_4 and the CH_2O formed is titrated by a special Nessler reagent in the presence of $BaSO_4$, using the vac. pipette (A., 1934, 384). The NH_3 is separately determined.

R. S.

Phosphocholine from ox liver.—See this vol., 1265.

Nature of the reaction which takes place between certain amino-acids and formaldehyde. T. TOMIYAMA (*J. Biol. Chem.*, 1935, **111**, 51—59).—The variation of p_H of NH_2 -acid solutions on addition of CH_2O is determined and the equilibrium constants of the reactions are calc. It is deduced that 1 mol. of NH_2 -acid combines with 1 mol. of CH_2O between p_H 10 and 8. It is suggested that the reaction occurs by a co-ordinate linking with N as donor and the C of CH_2O as acceptor.

H. D.

Aminolysis of leucine. E. BAUR and G. SCHINDLER (*Helv. Chim. Acta*, 1935, **18**, 1147—1149).—The isolation of fermentation amyl alcohol by the action of bone-C on leucine in absence of air shows that hydrolysis occurs, $CH_3Pr^{\beta}CH(NH_2)CO_2H + 2H_2O = CH_3Pr^{\beta}CH_2OH + NH_4^+ + HCO_3^-$. *iso*-Valeraldehyde appears also to be formed.

H. W.

Reactions of δ -aminovaleric acid and its derivatives. L. E. SCHNIEPP and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1935, **57**, 1557—1558).— δ -Benzamidovaleric acid (modified prep. from cyclopentanoneoxime) and Br-red P give α -bromo- δ -benzamidovaleric acid and $\beta\beta$ -dibromo- N -benzoyl- α -piperidone, m.p. 115—116° (also obtained from N -benzoyl- α -piperidone). δ -Carbomethoxyaminovaleric acid, m.p. 71—72°, and Br give $\beta\beta$ -dibromo- α -piperidone. δ -Ureidovaleric acid, m.p. 176°, and Br give a substance, m.p. 195—215° (decomp.).

R. S. C.

Proteolytic enzymes. VI. Specificity of papain.—See this vol., 1416.

Precipitation of *l*-, *dl*-, and *m*-cystine by phospho-12-tungstic acid. G. TOENNIES and M. ELLIOTT (*J. Biol. Chem.*, 1935, **111**, 61—74).—The curves of cystine (I) against phosphotungstic acid (II) concns. under the conditions for the pptn. of (I) are plotted for the three isomerides. The (I) : (II) ratio in the ppt. varies with the relative concns. of the reactants from 1.10 to 1.75. Titration curves of (I) indicate a total of 6 completely dissociated acid groups. Max. pptn. of *m*-, *dl*-, and *l*-cystine was obtained at concns. of (II) of 0.02*M*, 0.04*M*, and 0.01*M*, respectively.

H. D.

Synthesis of asterubin. D. ACKERMANN and E. MÜLLER (*Z. physiol. Chem.*, 1935, **235**, 233—234; cf. this vol., 1004).—Improved yield (42.6%) is obtained by oxidation of tetramethyldiguanylcystamine (this

vol., 1265) with H_2O_2 in presence of $\text{Fe}^{\text{II}} \text{NH}_4$ sulphate. W. McC.

Preparation of ethyl α -cyanobutyrate from butyric acid and its conversion into veronal. T. NISHIKAWA (Mem. Ryojun Coll. Eng. Inouye Commem. Vol., 1934, 389—393).—A 72% yield of Et α -cyanobutyrate (I) is obtained by refluxing 50 g. of $\text{CHBrEt}\cdot\text{CO}_2\text{Et}$ (II) with 50 c.c. of 50% aq. EtOH and 24 g. of KCN for 80 min., adding 10 g. KCN and refluxing for a further 80 min., heating in an open dish to 105° , treating the residue with 30 c.c. of EtOH and 40 c.c. of conc. H_2SO_4 , and refluxing for 4 hr. A smaller yield of (I) is obtained from $\text{CHBrEt}\cdot\text{CO}_2\text{H}$. $\text{CN}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$ is also prepared from (II). The esterification of (II) and the hydrolysis of (I) are unimol. (I) condenses (NaOEt) with $\text{CO}(\text{NH}_2)_2$ to yield 4-imino-5-ethyluracil. (I), with EtI and $\text{CO}(\text{NH}_2)_2$, affords 4-imino-5:5-diethyluracil (III), which yields veronal with dil. HCl. The prep. of $\text{CN}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ and its condensation with $\text{CO}(\text{NH}_2)_2$ to yield (III) are described. CH. ABS. (r)

Action of magnesium phenyl bromide on α -bromobutyrdimethylamide. P. T. SOU (Bull. fac. sci. univ. franco-chin. Peiping, 1934, No. 1, 1—40).—The products of the reaction are described and a mechanism is advanced to explain their formation. CH. ABS. (r)

Synthesis of carbamide from carbon dioxide and ammonia. I. M. TOKUOKA (J. Agric. Chem. Soc. Japan, 1934, 10, 1333—1344).—A detailed study of the conditions necessary for the production of NH_4 carbamate (I) from CO_2 and NH_3 . Vals. for the remarkably high dissociation pressure of (I) between 72° and 120° are given. CH. ABS. (r)

Relative anaesthetic effects of [alkylated] carbamides.—See this vol., 1155.

Physiological action of asterubin and of other sulphur-containing derivatives of guanidine.—See this vol., 1265.

Action of diazomethane on imides. II. L. IRRERA (Gazzetta, 1935, 65, 464—466).—Glutarimide and CH_2N_2 yield glutarmethylimide (A., 1933, 512); from diphenimide, *diphenmethylimide*, m.p. 168° , is obtained, with substances of m.p. 183° and 150° . E. W. W.

Ultra-violet absorption spectra of the α -ethylnitriles.—See this vol., 1299.

Geometrical isomerides of undecenitrile. R. VAN CAILLIE (Bull. Soc. chim. Belg., 1935, 44, 438—440).— α -Bromoundecitrile (A., 1933, 1281) is converted by $\text{C}_5\text{H}_5\text{N}$ into a mixture of *cis*-, b.p. 119.7 — $119.9^\circ/10$ mm., and *trans*- Δ^a -undecenitrile, b.p. 127.9 — $128.1^\circ/10$ mm. (separated by way of the amides, m.p. 76 — 77° and 114 — 115° , respectively). Vals. of d^{20} , n^{20} , and R^{20} for the nitriles are given. E. W. W.

Geometrical isomerides of heptenitrile. C. DE HOFFMANN (Bull. Soc. chim. Belg., 1935, 44, 435—437).—From $\text{Me}\cdot[\text{CH}_2]_5\cdot\text{Br}$, by way of $\text{Me}\cdot[\text{CH}_2]_5\cdot\text{CN}$ and $\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CHBr}\cdot\text{CN}$ (treated with $\text{C}_5\text{H}_7\text{N}$), a mixture of *cis*-, b.p. 60.2 — $60.4^\circ/12.5$ mm., and *trans*- Δ^a -heptenitrile, b.p. $67.8^\circ/15$ mm. (cf. A., 1932, 1119), is prepared, and separated by fractionation,

and through the amides, new m.p. 61 — 61.4° and 122.8° , respectively. Vals. of d , n , and R for the nitriles at 15° and 30° are given. E. W. W.

Organic compounds of selenium. I. W. E. BRADT (J. Chem. Educ., 1935, 12, 363—366).—The known classes are listed and a few of the simpler types discussed. L. S. T.

Monomagnesium acetylene. F. K. CHÉOU (Contr. Inst. Chem., Natl. Acad. Peiping, 1934, 1, 127—149).— $(\text{CMgBr})_2$ is prepared by passing C_2H_2 into MgEtBr ; subsequent passage of C_2H_2 (under pressure) produces $\text{CH}\cdot\text{C}\cdot\text{MgBr}$, which yields propiolic acid with CO_2 . With alkyl halides it affords substituted acetylenes, $\text{CH}\cdot\text{CBu}$ (61% from BuBr) and $\text{CH}\cdot\text{C}\cdot\text{CH}_2\text{Ph}$ (70% from $\text{CH}_2\text{Ph}\cdot\text{Br}$) being so obtained. EtBr affords only $(\text{CET})_2$ (20% yield).

CH. ABS. (r)

Metallic uranium in organic synthesis. I. J. B. LAL AND S. DUTT (J. Indian Chem. Soc., 1935, 12, 389—394).—U powder may be used in the Friedel-Crafts (Ph_2 , CHPh_2 , CPh_3Cl , CPh_2Cl_2 , COPhMe , COPh_2), Ullmann (Ph_2 , $(\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, adipic acid, Ph_2O , $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$), Zincke [CH_2Ph_2 (40% yield), $\text{CH}_2\text{Ph}\cdot\text{CHPh}_2$, and *o*- and *p*- $\text{C}_6\text{H}_4(\text{CH}_2\text{Ph})_2$ (all from C_6H_6 and CH_2PhCl), *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, *p*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, and (?) *dibenzylanisole*, b.p. 376 — 382°], and Reformatsky reactions ($\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$), but the yields are poor. The prep. of the substances in parentheses by this method is described. J. W. B.

Hydrogenation of the simplest homologues of cyclopentane with fission of the ring and transformation into hydrocarbons of the paraffin series. N. D. ZELINSKI, B. A. KASANSKI, and A. F. PLATE (Ber., 1935, 68, [B], 1869—1872).—Ring fission cannot be ascribed mainly to strain, since it occurs only in the presence of H_2 and under conditions under which in its absence the ring is unchanged by the temp. and catalyst employed. Methylcyclopentane at Pt-C (20%) at 305 — 310° gives mainly β -methylpentane. Ethyl- and propylcyclopentane yield mainly *iso*-hydrocarbons, but a more profound decomp. is evidenced in the case of the latter. H. W.

Reaction of naphthenic hydrocarbons with olefines. V. N. IPATIEV, V. I. KOMAREWSKY, and A. V. GROSSE (J. Amer. Chem. Soc., 1935, 57, 1722—1724).—With AlCl_3 at 50 — $75^\circ/1$ — 15 atm. cyclohexane (I) and C_2H_4 give 1:3-dimethyl- (II), (? 1:2:3:4- and 1:2:3:5-)tetramethylcyclohexane (III), and some C_6Et_6 (IV). (II) probably arises by isomerisation of ethylcyclohexane, (III) by that of the 1:3-Et₂-hydrocarbon, and (IV) by dehydrogenation of hexaethylcyclohexane, as some C_2H_6 is also formed. The structure of (II) is proved by dehydrogenation to *m*-xylene [Br_4 -derivative, m.p. 243° ; oxidised to *m*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$]. Methyl- and methylisopropylcyclohexane also give only cycloparaffins. (I) does not react with C_2H_4 in presence of BF_3 , but at 20 — $30^\circ/5$ — 15 atm. methylcyclohexane and -pentane give much substituted cycloparaffin, some paraffin, and some polymerisation product from the C_2H_4 . R. S. C.

Isomerisation phenomena in the cracking of cyclohexane derivatives by aluminium chloride. M. B. TUROVA-POLLAK (Ber., 1935, 68, [B], 1781—1785).—Treatment of methylcyclohexane with AlCl_3 at 120—130° followed by examination of the product by catalytic dehydrogenation and then by the NH_4Ph point method establishes the production of hexa- (I) and penta-methylenes (II) and paraffins (III) in the ratio 78.57 : 20.40 : 1.03. Similar treatment of dimethylcyclohexane gives fractions in which (I) : (II) : (III) = 68.89—84.62 : 19.40—11.47 : 11.71—4.00. Isomerisation during the cracking of ethylcyclohexane leads mainly to 1:3-dimethylcyclohexane. H. W.

Properties of α - and β -carotene.—See this vol., 1434.

Raman spectrum and symmetry of the benzene molecule.—See this vol., 1301.

Organic reactions with boron fluoride. X. Condensation of propylene with aromatic hydrocarbons. S. J. SLANINA, F. J. SOWA, and J. A. NIEUWLAND. **XI. Condensation of propylene with *m*- and *p*-hydroxybenzoic acids.** W. J. CROXALL, F. J. SOWA, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 1547—1549, 1549—1551; cf. this vol., 744).—X. Et_2O and EtOAc do not catalyse condensation of C_3H_6 and C_6H_6 by BF_3 , but $\text{CCl}_3\cdot\text{CO}_2\text{H} > \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} > \text{AcOH}$ do so. H_2SO_4 is most effective (? because it is the strongest acid), the ratio of Pr^{β} to Pr^{α} derivatives depending on the H_2SO_4 : BF_3 ratio. Temp. (0—80°) is without effect. The catalyst deactivates rapidly, very little $\text{C}_6\text{H}_5\text{Pr}^{\beta}$ being formed from C_6H_6 , although $\text{C}_6\text{H}_5\text{Pr}^{\beta}$ readily gives the Pr^{β} and Pr^{α} derivatives. $\text{PhOH}\cdot\text{BF}_3$ gives all derivatives up to $\text{C}_6\text{H}_2\text{Pr}^{\beta}_4$. C_6H_6 and $\text{C}_6\text{H}_4\text{Pr}^{\beta}_2$ do not react in presence of $\text{BF}_3\text{--H}_2\text{SO}_4$. 98% of *p*-, 2% of *o*-, and no *m*- $\text{C}_6\text{H}_4\text{Pr}^{\beta}_2$ are formed. C_4H_8 condenses readily, but not C_4H_6 . PhMe reacts (to give *p*-cymene) rather more readily with $\text{H}_2\text{SO}_4\text{--BF}_3$ than does C_6H_6 . C_{10}H_8 gives (?) 2- $\text{C}_{10}\text{H}_7\text{Pr}^{\beta}$. The following and other physical data are recorded. PhPr^{β} , b.p. 151°/740 mm.; *p*- $\text{C}_6\text{H}_4\text{Pr}^{\beta}_2$, b.p. 204.5°/736 mm.; 1:2:4- $\text{C}_6\text{H}_3\text{Pr}^{\beta}_3$, b.p. 237°/736 mm.; 1:2:4:5- $\text{C}_6\text{H}_2\text{Pr}^{\beta}_4$, m.p. 119°.

XI. *p*-OH· C_6H_4 · CO_2H (I), C_3H_6 , and BF_3 in CCl_4 give *p*- OPr^{β} · C_6H_4 · CO_2H (II) and its Pr^{β} ester and 4-isopropoxy-3-isopropylbenzoic acid. *m*-OH· C_6H_4 · CO_2H (III) affords *m*- OPr^{β} · C_6H_4 · CO_2H (IV) and its Pr^{β} ester, *Pr* $^{\beta}$ 3-isopropoxy-4-isopropylbenzoate, b.p. 155—156°/10 mm., and a little *m*-OH· C_6H_4 · $\text{CO}_2\text{Pr}^{\beta}$. Reaction of (I) is thus primarily etherification, but in that of (III) esterification occurs simultaneously. (II) and BF_3 give mainly 4-hydroxy-3-isopropylbenzoic acid and its Pr^{β} ester gives first (II), but both (IV) and its Pr^{β} ester give mainly 3-hydroxy-4-isopropylbenzoic acid. R. S. C.

Absorption spectra of free radicals.—See this vol., 1299.

Constitution of tetrahydrodiphenyl.—See this vol., 1299.

Di-*p*-alkylphenyldiphenylene-ethanes. Effect of the *p*-alkyl group on the dissociation of the ethane. L. E. SCHNIEFF and C. S. MARVEL (J.

Amer. Chem. Soc., 1935, 57, 1635—1636; cf. this vol., 1115).—Introduction of *p*-alkyl groups into the Ph of *s*-diphenyldiphenylene-ethane greatly increases the ease of oxidation, and the ethanes could not be obtained pure. Fluorenone and Grignard reagents from *p*-tolyl-, *p*-ethyl-, *n*-propyl-, and cyclohexyl-phenyl bromide give oily carbinols, whence are obtained 9-chloro-9-*p*-alkylphenylfluorenes, in which the alkyl is Me, m.p. 96—97°, Et, m.p. 56—57°, Pr and cyclohexyl, oils. These with hot MeOH or EtOH afford 9-methoxy-9-*p*-*n*-propyl-, m.p. 82—83°, and -cyclohexyl-, m.p. 119—120°, and 9-ethoxy-9-*p*-ethyl-phenylfluorene, m.p. 103°, and 9-ethoxy-9-*p*-tolylfluorene, m.p. 123°. The chlorides with Cu-bronze in C_6H_6 (the Pr derivative only by the Me ether with Na-Hg and $\text{Br}\cdot[\text{CH}_2]_4\cdot\text{Br}$) give the hexa-arylethane, obtained only as coloured solutions, which with air give 9-*p*-tolyl-, m.p. 200—201°, 9-*p*-ethylphenyl-, m.p. 186—187°, and 9-*p*-*n*-propylphenyl-fluorenyl 9-peroxide, m.p. 127—128°.

R. S. C.

Asymmetric synthesis. II. Addition of chlorine to trinitrostilbene. T. L. DAVIS and R. HEGGIE (J. Amer. Chem. Soc., 1935, 57, 1622—1624; cf. this vol., 480).—Trinitrostilbene (I) in PhNO_2 does not absorb light of λ 5890—5896 Å., and in circularly polarised light of this λ does not give an active product with Br. In circularly polarised light of λ 3600—4500 Å. it reacts with Cl_2 more rapidly than with Br, giving an active dichloride (II) (max. α 0.034° after 45 min.), racemised on keeping or faster on further irradiation (particularly with green light). The absorption spectra of (I), (II), and the dibromide are measured.

R. S. C.

Octadeuteronaphthalene. G. R. CLEMO and A. McQUILLEN (J.C.S., 1935, 1325).—EtOH separates the mixture of picrates obtained in the prep. of hexadeuterobenzene (cf. this vol., 967) into a *picrate*, m.p. 205° (hydrocarbon, $\text{C}_{18}\text{D}_{12}$, m.p. 135°), and a mixture, from which octadeuteronaphthalene, m.p. 77.5°, and liquid hydrocarbons are isolated. J. L. D.

Phenanthrene synthesis. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1935, 57, 1508—1509).—3 : 4-Dihydronaphthalene-1 : 2-dicarboxylic anhydride (I) adds dimethylmaleic anhydride (II) at the 1:2-ethylenic linking to give the *adduct*, m.p. 75.5—76.5°, hydrogenated (Adams) to the *H*₂-*adduct*, m.p. 117—118°, which by fusion with KOH at 320—400° and subsequent distillation affords 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylphenanthrene (70%), b.p. 194—197°/19 mm., dehydrogenated by Se in good yield to 2 : 3-dimethylphenanthrene, m.p. 78—78.5°. Butadiene gives similarly phenanthrene. Et γ -1-naphthylbutyrate and $\text{Et}_2\text{C}_2\text{O}_4$ lead to 3 : 4-dihydrophenanthrene-1 : 2-dicarboxylic anhydride, m.p. 263.5—264.5° [*adduct* with (II), m.p. 196—196.5°], dehydrogenated by S to phenanthrene-1 : 2-dicarboxylic anhydride, m.p. 311—312°. Naphthalene-1 : 2-dicarboxylic anhydride is obtained in 76% yield from (I) by dehydrogenation with S. R. S. C.

Triphenylene as companion of chrysene in coal tar. H. KAFFER (Ber., 1935, 68, [B], 1812—1813).—Extraction of the chrysene fraction with solvent benzene at 15—20° yields 1 : 2 : 3 : 4-dibenzonaphthalene, m.p. 196.5°. H. W.

1':9-Methylene-1:2:5:6-dibenzanthracene. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1935, 57, 1681—1683).—1':9-Methylene-1:2:5:6-dibenzanthracene (I) resembles 1:2:5:6-dibenzanthracene closely in absorption spectrum and is less carcinogenic (if at all) to mice than cholanthrene and methylcholanthrene. 1-Iodoacenaphthene (prep. described), m.p. 86—87°, b.p. 189—193°/8.5 mm., gives a good yield of unreactive Grignard reagent. The 1-Li-derivative with α -C₁₀H₇-COCl (II) gives (21% yield) 1- α -naphthoylacenaphthene, m.p. 107—108° or 102—104°, converted (32% yield) at 400—415° (15 min.) into (I), m.p. 266—267° (corr.) [*dipicrate*, m.p. 201—201.5° (corr.)], also obtained in very poor yield with 76% of 3- α -naphthoylacenaphthene, m.p. 159—160° (corr.), from acenaphthene, (II), and AlCl₃ in C₂H₂Cl₄. R. S. C.

Polycyclic aromatic hydrocarbons. XIII. Condensed fluorene derivatives. J. W. COOK, A. DANI, C. L. HEWETT, J. IBALL, W. V. MAYNEORD, and (Miss) E. ROE (J.C.S., 1935, 1319—1325).—2-C₁₀H₇-CH₂-MgBr with 2-methylcyclohexanone in Et₂O at room temp. affords α -di-2-naphthylethane (cf. A., 1922, i, 740) and a hydrocarbon, b.p. 178—185°/6 mm., which reacts with Br, and is cyclised (AlCl₃-CS₂) to methylhexahydro-3:4-benzfluorene (?), b.p. 200—205°/7 mm. (*picrate*, m.p. 114—118°). The K derivative of Et cyclohexanone-2-carboxylate with 2-C₁₀H₇-CH₂Br in boiling C₆H₆ gives Et 2- β -naphthylmethylcyclohexanone-2-carboxylate, m.p. 69—71°, converted by boiling aq. H₂SO₄, followed by Se at 300—320°, into 3:4-benzfluorene, m.p. 124—125° (*picrate*, m.p. 130—131°), which is oxidised (Na₂Cr₂O₇-AcOH) to 3:4-benzfluorenone (cf. A., 1916, i, 731) [*semicarbazone*, m.p. 235° (decomp.)]. Et 2-benzyl- and Et 2- β -phenylethylcyclohexanone-2-carboxylate are not cyclised by boiling aq. H₂SO₄ (A., 1933, 820; this vol., 968). Phenanthrene with 40% CH₂O in conc. HCl containing dry HCl at 90° gives 9-chloromethylphenanthrene, m.p. 101—101.5° (*picrate*, m.p. 99.5—100.5°), oxidised to 9-phenanthroic acid, the chloride (A., 1930, 1438) of which is converted (Pt-H₂-EtOH) through 3-phenanthraldehyde (this vol., 622) into a carbinol which affords 3-bromomethylphenanthrene (I) (A., 1933, 951). The K derivative of Et cyclohexanone-2-carboxylate with (I) in boiling PhMe gives Et 2-(3'-phenanthrylmethyl)cyclohexanone-2-carboxylate, m.p. 98—98.5°, which with boiling 65% H₂SO₄, followed by Pt-black at 320°, affords 1':2'-naphtha-2:3-fluorene (II), m.p. 226—226.5° (confirmed by crystallographic measurements), oxidised (Na₂Cr₂O₇-boiling AcOH) to 1':2'-naphtha-2:3-fluorenone, m.p. 214.5—215°, which with conc. H₂SO₄ gives a magenta colour in contrast to the intense purple colour given by the oxidation product of Diels' hydrocarbon. The ultra-violet absorption spectrum of (II) when compared with those of 2':1'-naphtha-1:2-fluorene (III) (this vol., 74) and of Diels' hydrocarbon, C₂₅H₂₄, from cholesterol indicate that (III) is the parent hydrocarbon of the sterol and bile acid dehydrogenation products. (II) is different from the hydrocarbon "C₂₁H₁₆" (cf. A., 1933, 278; 1934, 398) [believed (this vol., 286) to have 22 C], which may be a Me derivative of (III). 2-C₁₀H₇-CH₂Br with

CNaMe(CO₂Et)₂ in boiling C₆H₆ gives an ester, hydrolysed to methyl-2-naphthylmethylmalonic acid, m.p. 166—168°, which is decarboxylated at 170° to give β -2-naphthyl- α -methylpropionic acid, m.p. 90°, converted by anhyd. SnCl₄ at 120° into 2-methyl-6:7-benzhydrindone, m.p. 51—52°. The last named with CH₂Ph-CH₂-MgCl in dry Et₂O at room temp. affords a carbinol, dehydrated (KHSO₄) to 3- β -phenylethyl-2-methyl-4:5-benzindene, a viscous oil (*dipicrate*, m.p. 132°), which is cyclised (AlCl₃-CS₂ at 0°) to methyl-tetrahydro-1:2:5:6-dibenzfluorene, a viscous oil (*picrate*, m.p. 155°), further dehydrogenated (Se at 310—320°) to 1:2:5:6-dibenzfluorene, m.p. 171—172°. J. L. D.

Molecular rearrangement of N-thiolanilides. I. M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 1517—1519).—o-NO₂-C₆H₄-SCl (I) and o-C₆H₄Me-NH₂ in Et₂O give N-o'-nitrophenylthiol-o-toluidide, o-C₆H₄Me-NH-S-C₆H₄-NO₂ (o-), m.p. 119.5—120°, which is hydrolysed by dil. HCl, o-C₆H₄Me-NH₂-HCl (II), or long heating in AcOH to (II) and (o-NO₂-C₆H₄-S)₂, but, when heated alone at 150—160°, gives a poor, or in o-C₆H₄Me-NH₂ at 180—190° a 70%, yield of 2-nitro-4'-amino-3'-methylidiphenyl sulphide, m.p. 103° (*hydrochloride*, m.p. 235°). o-, m.p. 95°, and p-Nitrophenylthiolanilide, m.p. 75°, and o-nitrophenylthiol-p-toluidide, m.p. 135° (similarly prepared), give similarly 2-nitro-4'-amino- (III), m.p. 70—76° (*hydrochloride*, m.p. 225°), 4-nitro-4'-amino- (IV), m.p. 140—141° (*hydrochloride*, m.p. 200°), and 2-nitro-2'-amino-5'-methylidiphenyl sulphide, m.p. 88—90° (*hydrochloride*, m.p. 190°), thus confirming the hypothesis (this vol., 1118) that thiolanilides are intermediate products in the reaction of amines, S, and PbO. 2-Nitro-4'-hydroxydiphenyl sulphide, m.p. 130°, is prepared from p-NO₂-C₆H₄-SCl and PhOH in Et₂O and by diazotisation of (IV); the 4-NO₂-4'-OH-compound is similarly prepared from (I) and from (III). R. S. C.

[Action of thionyl chloride on certain anilides, carbamides, and urethanes.] H. STEPHEN and O. G. BACKEBERG (Ber., 1935, 68, [B], 1891).—A comment on the publication of Warren *et al.* (this vol., 855). H. W.

Nitration of s-diarylcarbamides. E. HARRISON (J.S.C.I., 1935, 54, 282—284r).—Bis-o- and -m-tolylcarbamide and bis-o- and -m-chlorophenylcarbamide are nitrated in AcOH suspension to mixtures of o- and p-substitution products from which the 4:4'-(NO₂)₂-derivatives are separated by crystallisation. Hydrolysis of the mixture by boiling moist C₅H₅N or AcOH yields the corresponding bases. Bis-6-nitro-m-tolyl-, m.p. 276°, bis-2-chloro-4-nitrophenyl-, m.p. 255°, bis-3-chloro-6-nitrophenyl-, m.p. 230°, and bis-3-chloro-4-nitrophenyl-carbamide, m.p. 275°, are also obtained by passing COCl₂ into the PhMe solution of the corresponding base in NPhMe₂. Bis-4:6-dinitro-o-tolyl-, m.p. 265°, bis-2-chloro-4:6-dinitrophenyl-, m.p. 240°, and bis-3-chloro-4:6-dinitrophenyl-carbamide, m.p. 245—250°, are obtained by the action of fuming HNO₃ on the corresponding un-nitrated compounds. Bis-p-chlorophenylcarbamide nitrated in AcOH suspension gives bis-4-chloro-2-nitrophenylcarbamide, m.p. 228°, also

obtained from 4-chloro-2-nitroaniline and COCl_2 . Nitration with fuming HNO_3 gives 4-chloro-2:6-dinitrophenylcarbamide, m.p. 255–260° (decomp.). Bis-*m*-xylylcarbamide nitrated in AcOH gives bis-5-nitro-*m*-xylylcarbamide, m.p. 290° (decomp.), also obtained from 5-nitro-*m*-xyldine and COCl_2 . Bis-*p*-xylylcarbamide nitrated in AcOH solution gives bis-4-nitro-2:5-dimethylphenylcarbamide, m.p. 280°, and by further action of HNO_3 bis-4:6-dinitro-2:5-dimethylphenylcarbamide, m.p. 262°. Nitration of bis-*o*-tolyl-*N*-ethylcarbamide gives 75% of bis-5-nitro-*o*-tolyl-*N*-ethylcarbamide, m.p. 120°.

Effect of substituents on the formation of thio-carbanilides by various methods. L. C. RAIFORD and G. M. McNULTY (Proc. Iowa Acad. Sci., 1933, 40, 114; cf. A., 1934, 520).—Br when *o*- to an NH_2 of a primary amine hinders the reaction > a Cl similarly placed. *o*- NO_2 inhibits the reaction. Alkyl or Ph as an *o*- or *p*-nuclear substituent has little effect. CH. ABS. (e)

Naphthalenesulphonic acids. I. Hydrolysis of naphthsultamdisulphonic acid. A. VOLODARSKI and I. KOLOSOVA (Anilinokras. Prom., 1935, 5, 260–265).—Naphthsultamdisulphonic acid is quantitatively hydrolysed by boiling with excess of 60% H_2SO_4 . Using 27% H_2SO_4 , the chief product is 1:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$, further hydrolysed to $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$. R. T.

Constitution of thiohydrazides. H. WUYTS and (Mlle.) A. LACOURT (Bull. Soc. chim. Belg., 1935, 44, 395–410; cf. A., 1933, 498, 821).—The following are prepared by the usual methods: β -thio-*o*- (I) and -*p*-tolu- α -*o*-tolyl- (II), m.p. 110° and 93°, and -*p*-tolu- α -*p*-tolyl- (III), m.p. 98°, -hydrazides; β -thioacet- α -phenyl- α -methyl- (IV), m.p. 59°, and - α -phenyl- α -benzyl- (V), m.p. 143.5°, -hydrazides; and β -thio-m-tolylacet- α -phenyl- α -methylhydrazide (VI), m.p. 91°. Dithiophenylacetic acid and $\text{NHMe}\cdot\text{NHPh}$ yield β -thiophenylacet- α -phenyl- β -methylhydrazide (VII), m.p. 99°. The *S*-Me derivatives of (I)–(III), prepared by action of Me_2SO_4 or of MeI and Na , have m.p. 107°, 62°, and 63°, respectively; of (IV), b.p. 115–125°/2 mm.; of (V), m.p. 78°, and of (VI), m.p. 59°. β -Thiocyclohexylcarboxy- (VIII) and β -thiophenylacet- α -phenyl- α -methylhydrazide (IX) form *S*-Me derivatives, b.p. 150°/1 mm., and m.p. 76°, respectively. That in these compounds Me is attached to the S is shown by their insolubility in alkali. The following are obtained by action of BzCl etc. on the hydrazides in $\text{C}_6\text{H}_5\text{N}$. α -Benz- β -thiobenz- α -phenyl-, m.p. 160°, β -1-thionaphth- α -phenyl-, m.p. 181°, β -*o*-thiotolu- α -*o*-tolyl-, m.p. 182°, and β -phenylacet- α -phenyl-, m.p. 171°; α -*p*-nitrobenz- β -thiophenylacet- α -phenyl-, m.p. 182°, β -*S*-methylthiobenz- α -phenyl- (X), m.p. 188°, and β -*S*-methyl-1-thionaphth- α -phenyl- (XI), m.p. 151°; α -benz- β -*S*-methyl-*p*-thiotolu- α -*p*-tolyl- (XII), m.p. 143.5°, and β -thiophenylacet- α -phenyl- β -methyl-, m.p. 122°, -hydrazide. Action of Ac_2O on the corresponding hydrazide gives β -thiobenz- α -acet- α -phenylhydrazide, m.p. 161°. 10% aq. NaOH converts (IV) into the *Na* derivative, m.p. 148° (decomp.). HgO in EtOH converts (I) into the *Hg* derivative, m.p. 154°. MgEtBr in Et_2O or Pr_2O liberates MeSH from

S-methylated thiohydrazides, giving bases. Thus the *S*-Me derivative of (IX) gives MeSH and a base ($\text{CH}_3\text{Ph}\cdot\text{COEt}$ phenylmethylhydrazone ?), m.p. 138° (hydrochloride, m.p. 235°); those of (I) and (III), MeSH and bases; (VII), however, liberates H_2S , and yields a base, m.p. 182° (hydrochloride, m.p. 240°; *Ac* derivative), which may be α -phenyl- β -(β' -phenyl-ethyl)- β -methylhydrazine. MeOH-HCl converts the *S*-Me derivative of (VIII) into $\text{NPhMe}\cdot\text{NH}_2$, MeSH , β -cyclohexylcarboxy- α -phenyl- α -methylhydrazide, m.p. 138°, and Me cyclohexanecarboxylate. $\text{HI-Ac}_2\text{O}$ does not demethylate (IV), (VI), (VIII), or (IX) at 325°; (VII) is partly demethylated. The *S*-Me derivatives of (I)–(VI), and of (VIII) and (IX), and the substances (X)–(XII) lose 1 Me at 180–190°. E. W. W.

Azo-dyes. A. ROLLETT, N. KUNZELMANN, and M. BALOG (Monatsh., 1935, 66, 193–196).—The qualitative effect of *p*-substituents on the colour of 2-benzeneazo-dyes from naphthionic, Laurent's, and *H*-acid, and α -naphthol-4- and -5-sulphonic acid is noted.

R. S. C.
Sulphide analogues of azo-dyes having bactericidal properties. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 607–609).— p - $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ and p - $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SPh}$ give 2-hydroxy-5-phenylthiol-4'-ethoxyazobenzene (I). $\text{S}(\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}\cdot p)_2$ and 2:6-diaminopyridine (II) give pp' -bis-(2:6-diaminopyridine-3-azo)diphenyl sulphide (III). p - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}\cdot p$ and (II) give 2:6-diamino-3:5-di- pp' -aminothiobenzeneazopyridine (IV). Tested by the "cup" method (I) and (III) are quite inactive and (IV) is only slightly active against *Staph. aureus*. R. S. C.

Preparation and properties of *m*- and *p*-amino-azo-derivatives of β -naphthol and of β -hydroxynaphthoic arylamides. F. M. ROWE and R. L. M. ALLEN (J. Soc. Dyers and Col., 1935, 51, 314–318).—The following aminoazobenzeneazo- β -naphthols and - β -hydroxynaphthoic anilides (respective m.p. in parentheses) are obtained by reducing the corresponding NO_2 -derivatives with Na_2S or NaHS in aq. suspension. 3- NH_2 - (179°; —) [6-*Me* (173–174°; 246.5°); 6-*OMe*- (187.5°; 215°)]; 4- NH_2 - (159°; 265°) [6-*Me* (170°; 255°); 6-*OMe* (217–218°; 262°) (β -hydroxynaphthoic *p*-aniside, 248°)]. They are of no interest as dyes for cellulose acetate or as diazo-components for azoics. β -Hydroxynaphthoicamidobenzeneazo- β -hydroxynaphthoic anilide, m.p. 291°, is also described. S. C.

Phenol-2:4-sulphonates. J. ŠIRUČEK (Chem. Listy, 1935, 29, 243–245).—The following salts are described [$\text{R} = \text{OH}\cdot\text{C}_6\text{H}_3(\text{SO}_3)_2$]: $\text{Li}_2\text{R}\cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{R}\cdot \text{H}_2\text{O}$, $\text{K}_2\text{R}\cdot \text{H}_2\text{O}$, $\text{BeR}_2\cdot 4\text{H}_2\text{O}$, $\text{MgR}_2\cdot 8\text{H}_2\text{O}$, $\text{ZnR}_2\cdot 7\text{H}_2\text{O}$, $\text{CdR}_2\cdot 3\text{H}_2\text{O}$, $\text{CaR}_2\cdot 2\text{H}_2\text{O}$, $\text{SrR}_2\cdot 3\frac{1}{2}\text{H}_2\text{O}$, $\text{BaR}_2\cdot 4\text{H}_2\text{O}$, $\text{CuR}_2\cdot 6\text{H}_2\text{O}$, $\text{MnR}_2\cdot 4\text{H}_2\text{O}$, $\text{NiR}_2\cdot 7\text{H}_2\text{O}$, $\text{CoR}_2\cdot 7\text{H}_2\text{O}$, and $\text{Al}_2\text{R}_3\cdot 12\text{H}_2\text{O}$. R. T.

Ring fission of *o*-nitrophenols by sulphuric acid. II. O. NEUNHOEFFER (Ber., 1935, 68, [B], 1774–1781; cf. this vol., 484).—A trustworthy method for the prep. of saturated and unsaturated dicarboxylic acids can be based on the fission of *o*-nitrophenols by 100% H_2SO_4 if the temp. is carefully regulated and the initial material is as pure as possible.

p-Chloro-*o*-nitrophenol is added gradually to 100% H_2SO_4 at 110° , and the temp. is raised to 125° ; the product is poured on ice, whereupon a small amount of the *pyrrolone* derivative, $\text{CH}_3\text{CO}-\text{NH}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CO}_2\text{H}$, m.p. 250° (decomp.) (*Me* ester, m.p. 133°), separates. Extraction of the filtrate with Et_2O (free from EtOH) yields β -chloromuconolactone (I),

$\text{CH}_3\text{CO}-\text{O}-\text{CH}=\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 123° (*Me* ester, m.p. 40°). Reduction of (I) by $\text{Na}-\text{Hg}$ in strongly alkaline solution gives Δ^2 -hydromuconic acid, m.p. 195° , better obtained by use of $\text{Zn}-\text{Cu}$ in dil. H_2SO_4 , whilst moderated reduction ($\text{Na}-\text{Hg}-\text{Na}_2\text{CO}_3$) yields muconic acid with much by-product. In one instance β -hydroxymuconic acid, m.p. 198° (decomp.), was isolated.

Addition of NaNO_2 to a solution of 5-amino-hydrindene (II), KNO_3 , and H_2SO_4 in H_2O and heating of the product to $40-60^\circ$ leads to 6-nitro-5-hydroxyhydrindene (III), m.p. 66° [*Me* ether, m.p. 77° , oxidised by KMnO_4 to 5-nitro-4-methoxy-*o*-phthalic acid (*Me* ester, m.p. 118°)]. 5-Hydroxyhydrindene, prepared by diazotising (II), is converted by HNO_3 into a mixture of (III) and 4-nitro-5-hydroxyhydrindene, m.p. 74° (*Me* ether, m.p. 94°). (III) and 100% H_2SO_4 at 65° yield the acid $\text{C}_9\text{H}_{11}\text{O}_4\text{N}$, m.p. 169° , transformed by boiling $\text{MeOH}-\text{HCl}$ into $\text{NH}_4\cdot\text{OMe}$ and the *Me*₂ ester, b.p. $165^\circ/15$ mm., of a doubly unsaturated cyclopentanediacetic acid, m.p. 220° (decomp.), which is hydrogenated (PtO_2 in EtOH) to cyclopentanediacetic acid (*cis*-form, m.p. 171°). H. W.

Preparation of acyl and benzenesulphonyl derivatives of *o*-aminophenol. L. H. AMUNDSEN and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1536-1537).—*o*- $\text{PhSO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\text{Ph}$ (*K* salt, m.p. about 220°) and the appropriate acid chloride in dioxan give *o*-(*NN*-dibenzenesulphon-), m.p. $164-164.5^\circ$, *N*-benzenesulphon-*N*-acet., m.p. $115-116^\circ$, *N*-benz-, m.p. $125.5-126^\circ$, and *N*-benzyl-amidophenyl benzenesulphonate, m.p. $144.5-145.5^\circ$. *o*- $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ and BzCl in hot PhNO_2 give *o*-*NN*-dibenzamidophenyl benzoate, m.p. $170.5-171.5^\circ$. *o*-Amino-*p*-anisoylphenol, m.p. $171.5-172^\circ$ (*O*- PhSO_2 -derivative, m.p. $113.5-114.5^\circ$), and *o*-benzenesulphonamidophenyl benzoate, m.p. $143.5-144.5^\circ$, are prepared. *o*- β -Phenylpropionamidophenyl isovalerate has m.p. $113.5-114.5^\circ$ (lit. $92-93^\circ$). R. S. C.

Carboaryloxy-radical in the migration of acyl from nitrogen to oxygen in *o*-aminophenol derivatives. L. C. RAIFORD and G. O. INMAN (Proc. Iowa Acad. Sci., 1933, 40, 109).—In general, only one acetylbenzoyl derivative of *o*-aminophenols can be prepared, regardless of the order in which the acyl groups are introduced. In this product the *Bz* is always attached to N. CH. ABS. (e)

Diphenyl series. I. Synthesis of unsymmetrical derivatives of diphenyl. II. Synthesis of 9-hydroxyphenanthrene. N. CHATTERJEE (J. Indian Chem. Soc., 1935, 12, 410-417, 418-420).—I. Addition of the appropriate diazonium salt as cold aq. solution to the cresol at 95° and steam-distillation of the product affords a mixture of the diphenyl ether and the diphenyl derivative. Orient-

ation of the latter is established by methylation followed by oxidation to the carboxylic acid and decarboxylation to 2- or 4-methoxydiphenyl. The following are new: 4-hydroxy-2-, b.p. $180^\circ/15$ mm. (*Me* ether, b.p. $164^\circ/12$ mm.; *Ac* derivative, b.p. $168^\circ/12$ mm.), and -3-methyl-, m.p. 114° (*Me* ether, m.p. 76° ; *Ac* derivative, m.p. 83°), -3:2', b.p. $160^\circ/10$ mm. (*Me* ether, b.p. $125^\circ/10$ mm.; *Ac* derivative, b.p. $130^\circ/10$ mm.), -3:3', b.p. $175^\circ/9$ mm. (*Me* ether, b.p. $150^\circ/10$ mm.; *Ac* derivative, b.p. $158^\circ/10$ mm.), -3:4', m.p. 136° (*Me* ether, m.p. 80° ; *Ac* derivative, m.p. 74°), -2:2', b.p. $185^\circ/15$ mm. (*Me* ether, b.p. $170^\circ/15$ mm.; *Ac* derivative, b.p. $175^\circ/12$ mm.), -2:3', b.p. $195^\circ/15$ mm. (*Me* ether, b.p. $185^\circ/15$ mm.; *Ac* derivative, b.p. $186^\circ/15$ mm.), and -2:4'-dimethyl-, b.p. $225^\circ/15$ mm. (*Me* ether, b.p. $205^\circ/13$ mm.; *Ac* derivative, b.p. $210^\circ/15$ mm.); 2-hydroxy-2':5-, b.p. $195^\circ/14$ mm. (*Me* ether, b.p. $185^\circ/13$ mm.; *Ac* derivative, b.p. $186^\circ/10$ mm.), -5:3', b.p. $210^\circ/14$ mm. (*Me* ether, b.p. $200^\circ/13$ mm.; *Ac* derivative, b.p. $204^\circ/15$ mm.), and -5:4'-dimethyl-, b.p. $225^\circ/15$ mm. (*Me* ether, b.p. $205^\circ/42$ mm.; *Ac* derivative, b.p. $215^\circ/15$ mm.), -diphenyl; 2:3', b.p. $170^\circ/17$ mm., 3:4', b.p. $175^\circ/17$ mm., and 2:4', b.p. $180^\circ/17$ mm., -dimethyldiphenyl ether. By oxidation of the *OMe*-derivatives are obtained 4-methoxydiphenyl-3-, m.p. 172° , and -2-carboxylic acid, m.p. 135° ; 4-methoxydiphenyl-3:2', m.p. 210° , -3:3', m.p. 232° , -3:4', m.p. 275° , -2:2', m.p. 210° , -2:3', m.p. 240° , and -2:4', m.p. 280° , -dicarboxylic acid; 2-methoxydiphenyl-5:2', -5:3', and -5:4'-dicarboxylic acid, all not melting below 300° .

II. Reduction of the anhydride of diphenic acid with 5% $\text{Na}-\text{Hg}-\text{EtOH}$ affords (together with the *Me* H ester) the lactone of 2-hydroxymethyldiphenyl-2'-carboxylic acid, converted by heating with KCN into 2-cyanomethyldiphenyl-2-carboxylic acid, m.p. 240° , hydrolysed by boiling 30% KOH to 2'-carboxydiphenyl-2-acetic acid, m.p. 295° . Distillation of the *Ca* salt of this affords 9-hydroxyphenanthrene.

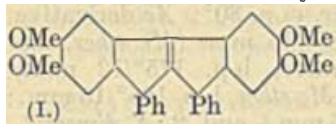
J. W. B.

Preparation of *o*-, *m*-, and *p*-hydroxyphenoxy-alkylamines. J. DRUEY (Bull. Soc. chim., 1935, [v], 2, 1737-1741).—*o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ heated with $(\text{CH}_2\text{Br})_2$ and KOH in EtOH gives 1-benzyloxy-2- β -bromoethoxybenzene (I), m.p. $45-46^\circ$, and bis-2-benzyloxyphenyl ethylene ether, m.p. $88-89^\circ$. (I) with 3 mols. of NHMe_2 in C_6H_6 (sealed tube) gives 1-benzyloxy-2- β -dimethylaminoethoxybenzene, b.p. $153-156^\circ/0.4$ mm. (hydrochloride, m.p. $142-144^\circ$), which when heated with 6*N*- HCl in EtOH yields 2- β -dimethylaminoethoxyphenol hydrochloride, m.p. $215.5-216.5^\circ$. The following are prepared from the appropriate phenols and bases: 1-benzyloxy-2- β -diethylaminoethoxybenzene, b.p. $170-172^\circ/0.65$ mm. (hydrochloride, cryst.), 2- β -diethylaminoethoxyphenol hydrochloride, m.p. $162-163^\circ$, 1-benzyloxy-2- β -methylaminoethoxybenzene, b.p. $152-155^\circ/0.5-0.6$ mm. (hydrochloride, m.p. $102-103^\circ$), 1-benzyloxy-3- β -bromoethoxybenzene, b.p. $180-185^\circ/0.4$ mm., 1-benzyloxy-3- β -dimethylaminoethoxybenzene, b.p. $166-169^\circ/0.4$ mm. (hydrochloride, m.p. $125-130^\circ$), 3- β -dimethylaminoethoxyphenol hydrochloride, 1-benzyloxy-4- β -bromoethoxybenzene, m.p. $84-85^\circ$, bis-4-benzyloxyphenyl ethylene ether, m.p. $172-172.5^\circ$, 1-benzyloxy-4- β -dimethylaminoeth-

oxybenzene hydrochloride, m.p. 171—172°, 4- β -dimethyl-aminoethoxyphenol hydrochloride, m.p. 174—176°.

F. R. G.

Condensing power of pyrocatechol derivatives. P. DREYFUSS (Gazzetta, 1935, 65, 498—501).—A discussion of work previously published (Diss., Bonn, 1933). Guaiacol combines with PhCHO to form, according to the proportions of the reactants, 2:3:6:7-tetramethoxy-9:10-diphenyldihydroanthracene or 3:4:3':4'-tetramethoxytriphenylmethane; with CH_2O , the last combines to a 6:6'-dihydroxy-methyl derivative. With PhCHO, α :3:4:3':4'-tetramethoxydiphenylethylene yields tetramethoxydiphenylindenoindene (I). Other examples of p -condensation to OH or OMe groups in pyrocatechol derivatives are quoted.



E. W. W.

Mechanism of chemical reactions. VI. Significance of molecular compounds in catalytic hydrogenations. II. K. KINDLER and W. PESCHKE (Annalen, 1935, 519, 291—296).— β -Methoxy- β :3:4-dimethoxy- and -methylenedioxy-phenyl-nitroethane are reduced catalytically (Pd in AcOH) to the corresponding -ethylamines. When, however, conc. H_2SO_4 is also present, β -OMe is removed during the reduction, β :3:4-dimethoxy- and -methylenedioxy-phenylethylamine being formed. Since H_2SO_4 has practically no action on the starting material in absence of Pd and H_2 , it is assumed that it forms a mol. compound (at the N) in which the β -C becomes unsaturated and attracts H, after which MeOH is eliminated. Action of Pd- H_2 on 3:4-dimethoxyoximinacetophenone yields, in absence of H_2SO_4 , first ω -amino-3:4-dimethoxyacetophenone, then β -hydroxy-3:4-dimethoxyphenylethylamine; in presence of H_2SO_4 the product is β :3:4-dimethoxyphenylethylamine.

E. W. W.

Unsaturated ethers of pyrogallol. C. H. HURD and C. I. PARRISH (J. Amer. Chem. Soc., 1935, 57, 1731—1734).—Pyrogallol (I), $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Br}$, and K_2CO_3 in COMe_2 give, according to the proportion of (I), pyrogallol triallyl, m.p. 3.5—4°, diallyl {two isomerides [Me ethers (II)]}, and allyl ether, m.p. 68—70° [mixture of 3- (Pb salt) and 2-ethers (4:1)]; mixed Me_2 ether, m.p. 160—164°. Both isomerides (II) rearrange at 190°, but one also decomposes. The prep. of α -bromo- Δ^2 -hexene, b.p. 44—46°/14 mm. (from $\text{CH}_2\text{:CH}\cdot\text{CHPr}^a\cdot\text{OH}$), and Δ^2 -heptene, b.p. 71—73°/17 mm., are modified. These with (I) and $\text{NaOEt}\cdot\text{EtOH}$ afford pyrogallol tri- and di-hexenyl [two isomerides (III)], heptenyl (Et_2 ether), and diheptenyl ether. Most of the products must be distilled in a mol. still, but even at this vac. (III) rearrange to dihexenylpyrogallols (IV). (IV) had a PhOH coeff. 20 and 250 against *Staph. aureus* and 110 and 325 against *Strept. haemolyticus*, respectively, but < 11 against *B. typhosus*. Heptenylpyrogallol, m.p. 52—53°, has a coeff. of 120 against *Staph. aureus*, but the other products have low coeffs.

R. S. C.

Heterogeneous equilibria in two-component systems with thymol as one component.—See this vol., 1322.

Production of substituted phenols.—See B., 1935, 841.

Preparation of salts of pyrocatechol borate.—See B., 1935, 841.

Phenolic derivatives of diaryl sulphides.—See B., 1935, 841.

Preparation of p -sec.-alkylaminophenols.—See B., 1935, 894.

Preparation of ethers of hydroxy-aldehydes by the oxidation of α -ethers of glycerol by lead tetra-acetate. (MME.) S. SABETAY (Bull. Soc. chim., 1935, [v], 2, 1744—1746).—The Na derivative of glycerol with CH_2PhCl yields chiefly $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which with $\text{Pb}(\text{OAc})_4$ in C_6H_6 gives $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHO}$ (cf. A., 1932, 384).

F. R. G.

Use of ψ -nitrosites of propenylphenyl ethers for the synthesis of α -aryl- β -hydroxylamino- and - β -amino-propyl alcohols. Migration of acyl groups. II. *iso*Eugenol derivatives. V. BRUCKNER and A. KRAMLI (J. pr. Chem., 1935, [ii], 143, 287—297; cf. this vol., 971, 972).—The dimeride (I), m.p. 128° (decomp.), of acetylisoegenol ψ -nitrosite is merely isomerised by MeOH, but behaves as expected on electrolytic reduction, and the NH_2 - and $\text{NH}\cdot\text{OH}$ -derivatives have the expected properties. (I) and Ac_2O with a little H_2SO_4 give β -nitro- α - p -acetoxy- m -methoxyphenylpropyl acetate (II), m.p. 120°, which with 10% KOH-aq. MeOH at room temp. gives β -nitroisoegenol, m.p. 100°, also obtained directly from (I). Electrolytic reduction of (II) gives according to the conditions β -N-acetylhydroxylamino-, m.p. 178° (decomp.), or β -acetamido- α - p -acetoxy- m -methoxyphenylpropyl alcohol (III), m.p. 165°, which with HCl-MeOH and HCl-COMe₂ at room temp. give β -hydroxylamino- (IV) and β -amino- α - p -acetoxy- m -methoxyphenylpropyl alcohol hydrochloride, m.p. 165—166° (decomp.) and $+2\text{H}_2\text{O}$, m.p. 192°, respectively; the reverse ($\text{O} \rightarrow \text{N}$) migration occurs with saturated aq. Na_2CO_3 at room temp., but this change is not instantaneous, since (IV) with Na_2CO_3 and the aldehyde affords nitrones with CH_2O , m.p. 161—162°, PhCHO, m.p. 144°, and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 204°. (III) and 2N-HCl at room temp. give slowly β -amino- α - p -hydroxy- m -methoxyphenylpropyl alcohol hydrochloride, m.p. 176°. (I) and hot MeOH give by monomerisation and isomerisation p -acetoxy- m -methoxyphenyl α -nitroethyl ketoxime, m.p. 134—136° (decomp.), converted by alkali into the glyoxime peroxide, m.p. 179°, also obtained from (I) and 1.5% HCl-MeOH at 50°.

R. S. C.

Amino-alcohols having a secondary alcoholic function. J. MATTI and E. BARMAN (Bull. Soc. chim., 1935, [v], 2, 1742—1744).— $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHO}$ with MgPhBr yields diethyl- γ -hydroxy- γ -phenyl- $\beta\beta$ -dimethylpropylamine, b.p. 123.5°/0.4 mm. [hydrochloride, m.p. 196° (benzoate, m.p. 180°)]. $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHO}$ with MgPhBr , MgEtI , and MgBu^aBr yields, respectively, dimethyl- γ -hydroxy- γ -phenyl- $\beta\beta$ -dimethylpropylamine, b.p. 115°/0.4 mm. [hydrochloride, m.p. 181° (benzoate, m.p. 208°)], dimethyl- γ -hydroxy- $\beta\beta$ -dimethylamylamine, b.p. 83°/17 mm. (benzoate hydrochloride, m.p. 163.5°; m -amino-

benzoate hydrochloride, m.p. 184.5°; *p*-aminobenzoate hydrochloride, m.p. 194°; *p*-nitrobenzoate hydrochloride, m.p. 185°; cinnamate hydrochloride, m.p. 177°, dimethyl- γ -hydroxy- $\beta\beta$ -dimethylheptylamine, b.p. 119.5°/27 mm. [benzoate hydrochloride, m.p. 115° (hygroscopic); *p*-nitrobenzoate hydrochloride, m.p. 174°; *p*-aminobenzoate hydrochloride, m.p. 182°]. Vals. of n_D and d are given for the free bases. The esters possess anæsthetic properties. F. R. G.

Production of diamino-alcohols of the aromatic series.—See B., 1935, 840.

Metacholesterol and its separation from cholesterol. V. I. LIFSCHUTZ (Biochem. Z., 1935, 280, 65—71).—The separation of metacholesterol (I) (A., 1922, i, 541) from cholesterol (II) is described, advantage being taken of the fact that (I) but not (II) remains in colloidal aq. solution in presence of protein, fat, etc. P. W. C.

7-Dehydrocholesterol. A. WINDAUS, H. LETTRE, and F. SCHENCK (Annalen, 1935, 520, 98—106).—7:8-Dehydrocholesterol (I) differs from 22:23-dihydroergosterol (II) in having a side-chain of 8 instead of 9 C; like (II), it becomes strongly antirachitic when irradiated. 7-Ketocholesteryl acetate (improved prep.) is reduced by $Al(OPr^i)_3$ in Pr^iOH to 7-hydroxycholesterol (bis-3:5-dinitrobenzoate, m.p. 196—197°, $[\alpha]_D^{20} + 77.4^\circ$ in $CHCl_3$), of which the dibenzoate, m.p. 171.5—172°, $[\alpha]_D^{20} + 94.1^\circ$ in $CHCl_3$, is converted by heating at 200° in vac. into 7:8-dehydrocholesteryl benzoate, m.p. 139—140° (to a cloudy liquid, clearing at 183°), $[\alpha]_D^{20} - 53.2^\circ$ in $CHCl_3$. The last is hydrolysed (KOH-EtOH) to 7:8-dehydrocholesterol (I) m.p. 142—143.5°, $[\alpha]_D^{20} - 113.6^\circ$ in $CHCl_3$ (3:5-dinitrobenzoate, m.p. 207°, $[\alpha]_D^{20} - 45.7^\circ$ in $CHCl_3$; digitonin compound), which has the same spectrum as ergosterol, and approaches it in antirachitic power; after irradiation it contains 8000 antirachitic units per mg. E. W. W.

Local anæsthetic action of dialkylaminoethoxyethyl *p*-aminobenzoates. L. A. RUBERG and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1581—1583).—*sec*-Amines and $(CH_2)_2O$ at < 60° in MeOH give mixtures of alcohols, $NR_2 \cdot [CH_2]_n \cdot OH$ (I) and $NR_2 \cdot [CH_2 \cdot CH_2 \cdot O]_n \cdot H$ (II). (I) and $(CH_2)_2O$ give also (II). Thus are obtained β -(β' -dimethyl-, b.p. 78—79°/3.5 mm. (hydrochloride, m.p. 104—105.5°), -ethyl-, -*n*-propyl-, b.p. 102—103°/2.5 mm., and -*n*-butyl-aminoethoxy)-ethyl alcohol, b.p. 117—121°/1 mm., converted by *p*-NO₂-C₆H₄-COCl in hot C₆H₆ into the *p*-nitrobenzoates, m.p. 97—99° (not obtained pure), 106—108°, and 99—101°, respectively, which are hydrogenated to yield the corresponding *p*-aminobenzoate hydrochlorides, m.p. 150—152°, 150—152°, 128.5—130°, and 134—136°, respectively. The toxicity and local anæsthetic action of the NH₂-esters increase with increasing mol. wt. of the *N*-substituent. R. S. C.

Xylic acids obtained in the oxidation of 5-bromo- and 5-nitro-*p*-cumene. C. H. FISHER and C. T. WALLING (J. Amer. Chem. Soc., 1935, 57, 1700—1702).—The acid, m.p. 173—174° (lit. 172—173°), from 5-bromo-*p*-cumene and HNO₃, previously considered to be 5-bromo-2:4-xylic acid

(I), is shown to be a const.-melting mixture of (I) and 4-bromo-2:5-xylic acid (II). 5-Nitro-*p*-cumene and HNO₃ give 5-nitro-2:4-xylic acid (III), m.p. 197.5—198.5°. 4-Bromo-2:5-xylnitrile (from the amide), m.p. 103—104°, gives (II), m.p. 171.5—172.5° (amide, m.p. 209—210°). Acet-*p*-xylylide and fuming HNO₃ give mainly the 3:5-dinitro-derivative, but conc. HNO₃-H₂SO₄ gives 5-nitro- (IV), m.p. 168—169°, and 3-nitro-acet-*p*-xylylide. Hydrolysis of (IV) gives the amine, m.p. 144—145°, which yields 4-nitro-2:5-xylnitrile, m.p. 160—161°, and 4-nitro-2:5-xylic acid, m.p. 165.5—166.5°. 2:4-Dimethylacetophenone gives the 5-NO₂-ketone, converted by NaOBr into (III). R. S. C.

***cis*-Cinnamic acids.** J. MEYER (Z. physikal. Chem., 1935, 174, 77—78).—The view that the three forms are not chemical isomerides, but merely polymorphic modifications, is defended (cf. this vol., 916). R. C.

Resolution of an allenic compound. E. P. KOHLER, J. T. WALKER, and M. TISHLER (J. Amer. Chem. Soc., 1935, 57, 1743—1745).—The structure of $\alpha\gamma$ -diphenyl- γ -naphthyllallenecarboxylic acid (I) is proved by conversion into and prep. from the ester, oxidation of the ester by KMnO₄ to C₆H₅-CO₂H and C₆H₅-C₁₀H₇, and hydrogenation (Pd-CaCO₃) to *Et* $\alpha\gamma$ -diphenyl- γ -naphthylbutyrate, m.p. 124—125° (corresponding acid, m.p. 147°). The chloride of (I), m.p. 122° (stable in air), gives the *Me* ester (also prep. from the Ag salt), m.p. 110°, and with OH-CH₂-CO₂H and C₅H₅N in dry Et₂O, carboxymethyl $\alpha\gamma$ -diphenyl- γ -naphthyllallene- α -carboxylate, m.p. 195°, resolved by brucine to the *l*-acid, m.p. 145—146°, $[\alpha]_D^{20} + 29.5^\circ$ in EtOAc (brucine salt, m.p. 145°). R. S. C.

Constituent of *Bacomyces roseus*.—See this vol., 1432.

Catalytic hydrogenation of benzoylmandelonitrile and of amygdalin. H. RUPE and K. ENGEL (Helv. Chim. Acta, 1935, 18, 1190—1203).—Catalytic hydrogenation of OH-CHPh-CN in presence of Ni proceeds rapidly at first, but stops suddenly owing to poisoning of the catalyst by liberated HCN. Similar treatment of OBz-CHPh-CN affords β -phenylethylamine (I), di- β -phenylethylamine (II), b.p. 190°/10 mm. (hydrochloride, m.p. 259—260°), and benz- β -hydroxy- β -phenylethylamine, m.p. 149°, thus: OBz-CHPh-CN + 3H₂ = CH₂Ph-CH₂-NH₂ + BzOH. Hydrogenation of amygdalin proceeds readily when a large excess of Ni is used and ceases after absorption of 2H₂. (I) and (II) are formed with a brown amorphous material from which, after acetylation, β -acetamido- α -phenylethylgentiobioside hepta-acetate (III), m.p. 178°, $[\alpha]_D^{20} - 51.47^\circ$ in C₆H₆, is isolated; the residues from (III) on hydrolysis yield lævulic acid and largely racemised β -hydroxy- β -phenylethylamine (IV). The yields of the base are small, showing that the sugar residue is largely eliminated in the initial stages, thus leading to much (I) and (II). In hepta-acetylamygdalin the sugar residue is more firmly attached, and hydrogenation gives, after hydrolysis, β -amino- α -phenylethylgentiobioside (V), decomp. 231—233°, $[\alpha]_D^{20} - 103.22^\circ$ in H₂O [whence (III)], and an amorphous material which affords

BzOH when hydrolysed with HCl. Hydrolysis of (V) gives partly racemised (IV). Repetition of the work of Read *et al.* (A., 1931, 218) leads to the vals. $[\alpha]_D^{25} -44.30^\circ$ and $[\alpha]_D^{25} +53.58^\circ$ in H_2O for homo-genous (IV) and its tartrate, respectively. H. W.

α -Aldehydotropic ester. H. GAULT and M. COGAN (Compt. rend., 1935, 201, 477—479).— $CHO \cdot CHPh \cdot CO_2Et$, CH_2O , and K_2CO_3 at room temp. yield *Et* α -aldehydotropate, m.p. 92—93° (*Ac* derivative, m.p. 76°, b.p. 212—213°/15 mm.), which gives the usual reactions for an aldehyde and regenerates the original reactants when heated above 100°. It is saponified to a mixture of $CH_2Ph \cdot CO_2H$, tropic acid, and a little atropic acid, the relative proportions of which depend on the temp. and the alkali concn. H. G. M.

Stereochemistry of diphenyls. XL. Effect of temperature and solvent on the rate of racemisation of 2-nitro-6-carboxy-2'-alkoxydiphenyls. C. C. LI and R. ADAMS. XLI. Effect of 4'-substitution on the rate of racemisation of 2-nitro-6-carboxy-2'-methoxydiphenyl. W. E. HANFORD and R. ADAMS (J. Amer. Chem. Soc., 1935, 57, 1565—1569, 1592—1595; cf. this vol., 742).—XL. The rates of racemisation of 2-nitro-2'-methoxy- (I), -ethoxy- (II), and -propoxy-diphenyl-6-carboxylic acid (III) in C_5H_5N , $COMe_2$, $AcOH$, $MeOH$, $EtOAc$, and dioxan are determined at about 25° and in $EtOH$, at 0—35°, and of the brucine salts in $CHCl_3$, and Na salts in H_2O and $EtOH$. In all cases these rates are in the approx. ratio 1:5:7; a rise in temp. increases the rate. There is no connexion between the rate of racemisation and the nature of the solvent. The van 't Hoff-Arrhenius equation applies. The heat of activation is about 20,000 g.-cal. for all the acids. *o*-Nitro-ethoxy-, b.p. 146—148°/15 mm., -propoxy-, b.p. 155—156.5°/15 mm., -butoxy-, b.p. 171—172°/19 mm., and -amyloxy-benzene, b.p. 177—178°/15.5 mm., give by Fe and H_2O *o*-ethoxy-, b.p. 224—229°, *o*-propoxy-, b.p. 120—130°/14—15 mm. (*Bz* derivative, m.p. 49—51°), -butoxy-, b.p. 135—139°/15.5 mm. (*p*- $C_6H_4Me \cdot SO_2$ derivative, m.p. 85—88°, insol. in alkali), and -amyloxy-aniline, b.p. 152.5—153.5°/16 mm. (*p*- $C_6H_4Me \cdot SO_2$ derivative, m.p. 88—90°, insol. in alkali), converted (diazo-reaction) into *o*-iodo-ethoxy-, b.p. 121—131°/17—18 mm., *o*-iodo-propoxy-, b.p. 138—139°/15 mm., -butoxy-, b.p. 152—154°/18 mm., and -amyloxy-benzene, b.p. 126—129°/1—1.5 mm., which, when condensed with *Me* 2-bromo-3-nitrobenzoate and *Cu* at 210—260° and subsequently hydrolysed, afford (II), m.p. 153—155° [*l*-form, racemised at m.p. 153—155°, $[\alpha]_D^{25} -145.6^\circ$ in $EtOH$ (*brucine* salt, m.p. 167—176° (decomp.), $[\alpha]_D^{25} -220.2^\circ$ in $CHCl_3$)], (III), m.p. 133—135° [*l*-form, double m.p. 95—97° and 132.5—133.5°, $[\alpha]_D^{25} -110.6^\circ$ in $EtOH$ (*brucine* salt, m.p. 157—162° (decomp.), $[\alpha]_D^{25} -182.9^\circ$ in $CHCl_3$)], 2-nitro-2'-butoxy-, m.p. 117—119°, and -amyloxy-diphenyl-6-carboxylic acid, m.p. 89—92°. (I), m.p. 196—197°, gives the *d*-form, m.p. (with racemisation) 195—197°, $[\alpha]_D^{25} +26.9^\circ$ in $EtOH$ (*brucine* salt, $+H_2O$, m.p. 219—220°, $[\alpha]_D^{25} +97.9^\circ$ in $CHCl_3$). The salts of the second forms could not be isolated.

XLI. The half-life periods at 25° of 4'-derivatives

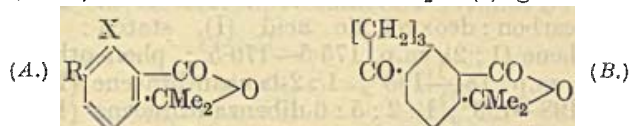
of (I) in $COMe_2$ are NO_2 115, Br 25, Cl 12, Me 2.6, and OMe 3.6 min. The rates of racemisation of the acids in $EtOH$, the cinchonine salts in $CHCl_3$, and the Na salts in H_2O and $EtOH$ are determined. The stability in the 4'-series (except for the NO_2 -derivative) is less than in the 5'-series, and in the 3'-, 4'-, and 5'-series increases with the negativity of the substituent. The following are described. 2-Bromo-*o*-nitroanisole (from the 2- NH_2 -compound), m.p. 104°. 2-Iodo-5-methylanisole (from the 2- NO_2 -compound), b.p. 109.5—110°/3 mm. 5-Nitro-, m.p. 156—157° (lit. 153—154°), and 5-amino-2-acetamidoanisole, m.p. 119—120° (lit. 72°). 5-Bromo-2-amino-, m.p. 61—62°, and -2-iodo-anisole, m.p. 37°, b.p. 161—162°/8 mm. *o*-Chloro-2-iodoanisole, b.p. 135°/10 mm., m.p. about 20°. 2-Nitro-2':4'-dimethoxy-, m.p. 213—214° (cinchonine salt of *l*-form, m.p. 198—205°), 2:4'-dinitro-2'-methoxy-, m.p. 203.5—206° (cinchonine salt of *d*-form, m.p. 188—189°), 2-nitro-4'-chloro-2'-methoxy-, m.p. 160—160.5° (cinchonine salt of *l*-form, m.p. 192—193.5°), 2-nitro-4'-bromo-2'-methoxy-, m.p. 160—161° [cinchonine salt of *l*-form, m.p. 193—195° (decomp.)], and 2-nitro-2'-methoxy-4'-methyl-diphenyl-6-carboxylic acid, m.p. 171—172° (cinchonine salt of *l*-form, m.p. 201—204°). R. S. C.

Bromination of 3-ketobisnorcholanic acid and 3-ketobisnorallocholanolic acid; Δ^4 -3-ketobisnorcholonic acid and Δ^1 -3-ketobisnorallocholenic acid. A. BUTENANDT and L. MAMOLI (Ber., 1935, 68, [B], 1854—1859).—3-Hydroxybisnorcholonic acid is transformed by the successive action of Br and CrO_3 in $AcOH$ into Δ^4 -3-ketobisnorcholonic acid (I), m.p. 268° (decomp.), $[\alpha]_D^{25} +60^\circ$ in $CHCl_3$, reduced (Pd-black in Et_2O) to 3-ketobisnorallocholanolic acid (II), m.p. 244°, and 3-ketobisnorcholanic acid (III), m.p. 184°, $[\alpha]_D^{25} +4.55^\circ$ in $CHCl_3$. (III) is readily brominated to 4-bromo-3-ketobisnorcholanic acid, m.p. 221°, which loses HBr in boiling C_5H_5N with formation of (I). (II) is similarly converted into 2-bromo-3-ketobisnorallocholanolic acid, m.p. 230° (decomp.), from which HBr is eliminated with difficulty ($KOAc \cdot AcOH$ at 175—185°) giving Δ^1 -3-hydroxybisnorallocholenic acid, m.p. 235° (decomp.). The changes are therefore similar to those observed with pregnandione and allopregnandione (this vol., 1370). H. W.

Germicidal properties and mercuration of alkylresorcinolcarboxylic acids. S. C. OVERBAUGH and R. B. SANDIN (J. Amer. Chem. Soc., 1935, 57, 1658—1659).—5-Ethyl-, m.p. 166—170°, -propyl-, m.p. 177—182°, -butyl-, m.p. 115—116°, and -hexyl- β -resorcylic acid have Rideal-Walker coeff. < 0.7 , < 0.7 , 0.9, and 1.6, respectively, and afford 3-hydroxy-mercuri-5-ethyl-, anhydro-3-hydroxymercuri-5-propyl-, yellow, -n-butyl-, and -hexyl- β -resorcylic acid, yellow, all sol. in dil. aq. NaOH, but decomposed thereby with pptn. of Hg. R. S. C.

Constitution of the aromatic rearrangement products of picrotoxin. K. TETTWEILER and I. DRISHAUS (Annalen, 1935, 520, 163—184; cf. Mercer *ibid.*, this vol., 1236).—Oxidation ($KMnO_4$ - l - N -NaOH) of the lactone-dicarboxylic acid (I) [*A*; $R=CO_2H$, $X=[CH_2]_3 \cdot CO_2H$], m.p. 188°, obtained by oxidation of picrotic acid (II) (Angelico, A., 1910, i, 404) gives a keto-dicarboxylic acid (*A*; $R=CO_2H$,

X=CO-CO₂H), m.p. 194° (decomp.), converted by KOH at 250° into isophthalic acid, H₂C₂O₄, and COMe₂, and further oxidised by KMnO₄-dil. H₂SO₄ to α -dimethylphthalide-3:4-dicarboxylic acid (III) (A; R=X=CO₂H), m.p. 284°, identical with that obtained by oxidation of the hydrolysis product of picrotoxin ketone (IV) (A; R=Me, X=CH₂Ac; Angelico, A., 1913, i, 69), decarboxylated by "naturkupper-C" in boiling quinoline to α -dimethylphthalide, and giving hemimellitic acid by fusion with KOH. Oxidation of the tricarboxylic acid C₁₂H₁₂O₆ (2- γ -carboxy-*n*-butylisophthalic acid; Angelico *et al.*, A., 1924, i, 183) with KMnO₄-NaOH gives 2:6-dicarboxyphenylglyoxylic acid (Graebe *et al.*, A., 1893, i, 593). When distilled with Ac₂O (I) gives the



ketone (B), m.p. 154° (semicarbazone, sinters 270°, decomp. 315°), and the dicarboxylic acid C₁₂H₁₄O₄ (2- γ -carboxy-*n*-butyl-*m*-toluic acid; A., 1924, i, 183) by distillation with Ac₂O, or of its Ca salt, affords 5-keto-1-methyl-5:6:7:8-tetrahydronaphthalene, identical with a synthetic specimen (Harvey *et al.*, A., 1930, 593), showing that the side-chain is a *n*-butyric acid. The oximino-derivative of (IV) is converted by a Beckmann change (SOCl₂) into the nitrile, m.p. 208°, hydrolysed to the lactone-monocarboxylic acid (A; R=Me, X=CO₂H), m.p. 149°, oxidised to (III), and converted by 50% KOH at 260° into 3-methylphthalic acid. Angelico's α -chloroketone, m.p. 114—115° (A; R=Me, X=CH₂·CO·CH₂Cl), obtained either by the action of NaOCl-NaOH on (IV) or of HCl-AcOH at 100° on picrotinetol (A; R=Me, X=CH₂·CO·CH₂·OH) (Hormann *et al.*, A., 1921, i, 347), is converted by hot MeOH-KOH into α :3:4-tetramethylphthalide, similarly obtained (*loc. cit.*) from (IV). The structure A (R=Me, X=[CH₂]₃·CO₂H) is thus established for (I), whence the above structures of its derivatives are deduced. J. W. B.

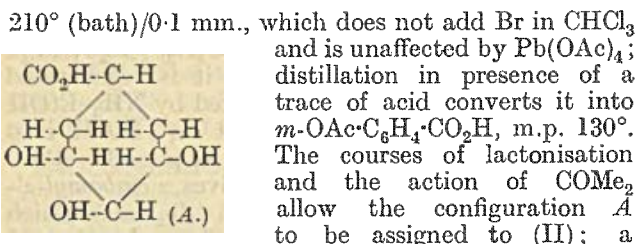
Condensation of benzoylformanilide with cyano-activated methylene compounds. J. V. SCUDI and H. G. LINDWALL (J. Amer. Chem. Soc., 1935, 57, 1646—1648).—COBz·NHPh (I), CH₂(CN)₂, and a little NHEt₃ in EtOH at 0° give α -cyano- β -phenylcarbamylcinnamionitrile (II), NHPh·CO·C(Ph)·C(CN)₂, m.p. 206—207°, which with HCl gives α -carbamyl- β -phenylcarbamylcinnamamide (III), m.p. 216°, and with Na₂S₂O₄ in aq. EtOH gives α -cyano- β -phenylcarbamyl- β -phenylpropionitrile (IV), m.p. 215° (decomp.), reconverted into (II) by long boiling in EtOH. (II) is reduced by aq. Na₂S₂O₄ at 50° to α -carbamyl- β -phenylcarbamyl- β -phenylpropionamide, m.p. 164—165°, which is hydrolysed by 10% NaOH to CO₂H·CHPh·CH₂·CO₂H (V), also obtained similarly from (IV). (I), CN·CH₂·CO·NH₂, and a little NHEt₃ in cold aq. EtOH give 3-hydroxy-5-imino-4-carbamyl-3-phenyl-2-pyrrolidone (VI), m.p. 209—210° (decomp.), hydrolysed by HCl to α -carbamyl- α' -phenylmaleinanil, m.p. 207°, which with P₂O₅ gives the α -cyano-anil (VII), m.p. 118—119°, is reduced by Na₂S₂O₄ in cold aq. EtOH to α -carbamyl-

α' -phenylsuccinanil (VIII), m.p. 193—194°, and with NHEt₃ forms a compound, C₂₁H₂₃O₃N₃·H₂O, m.p. 163—164° (decomp.), from which it is regenerated by hot conc. HCl. (VII) is converted by NH₃-EtOH into (VI) and by Na₂S₂O₄ in hot aq. EtOH into α -cyano- α' -phenylsuccinanil (IX), m.p. 135—136°. (IX) or (VIII) with 10% NaOH gives α -carbamyl- α' -phenylsuccinic acid, m.p. 156—157° (Ag₂ salt), which yields phenylsuccinanil with hot HCl or when heated above the m.p. (I) (1 mol.), CN·CH₂·CO·NH₂ (1 mol.), and (a) NHEt₃, (b) piperidine, or (c) NaOH (1 mol.) in EtOH at 0° give compounds, (a) C₂₁H₂₃O₃N₃ (X), m.p. 156—158° (decomp.), (b) C₂₂H₂₃O₃N₃, decomp. 124—126°, and (c) C₁₇H₁₅O₃N₂Na decomp. 225—226° (corresponding Ag salt), respectively, which with cold dry HCl-EtOH or hot EtOH, H₂O, COMe₂, or 10% NaOH give (VII). (X) is also obtained from (VII) by NHEt₃ in EtOH at 0°.

R. S. C.

Quinic acid and its derivatives. VI. Degradation of shikimic acid to aconitic acid. VII. Configuration of shikimic acid. H. O. L. FISCHER and G. DANGSCHAT (Helv. Chem. Acta, 1935, 18, 1204—1206, 1206—1213; cf. A., 1935, 1222).—VI. In very dil. solution shikimic acid (I) (or its Me ester) is converted by successive oxidations with HIO₄ and perpropionic acid into *trans*-aconitic acid, m.p. 184—191°, hydrogenated (Pd) to tri-carballylic acid. If the process is interrupted when the action of HIO₄ is complete the dialdehyde of aconitic acid is obtained, isolated as the di-2:4-dinitrophenylhydrazone, m.p. 169°, of the Me ester.

VII. (I) is hydrogenated (Pd-BaSO₄-EtOH) to dihydroshikimic [3:4:5-trihydroxyhexahydrobenzoic] acid (II), m.p. 180° (decomp.), [α]_D²⁵ -13.6° in H₂O, which consumes 2 mols. of HIO₄ in H₂O and 3 mols. of Pb(OAc)₄ in AcOH; it is transformed by Ac₂O-ZnCl₂ into triacetyldihydroshikimic anhydride, m.p. 171—173°, whence triacetyldihydroshikimic acid, b.p. 200°/0.3 mm., m.p. 78—80° (corresponding cryst. chloride and anilide, m.p. 145—147°). When heated at 190—220°/0.2 mm., (II) passes into dihydroshikimolactone (III), m.p. 146—147° after softening, [α]_D²⁵ -145.2° in H₂O, which is indifferent to Pb(OAc)₄, thus showing that OH at 4 is involved in lactone formation and that 4-OH and CO₂H have *cis*-relationship. (II) and boiling Ac₂O or (III) and Ac₂O-C₅H₅N afford diacetyldihydroshikimolactone, m.p. 145—146°, [α]_D²⁵ -138.3° in CHCl₃. (I) or its Me ester is converted by HCl-COMe₂ into isopropylideneshikimic acid, m.p. 184° (decomp.), and Me isopropylideneshikimate, b.p. (bath) 150°/0.3 mm., respectively. The latter is transformed by *p*-C₆H₄Me·SO₂Cl in C₅H₅N into Me *p*-toluenesulphonyl-isopropylideneshikimate, m.p. 66—68°, whence Me *p*-toluenesulphonylshikimate, m.p. 137—138°, which consumes 1 mol. of Pb(OAc)₄ in AcOH. Similarly, Me benzoylisopropylideneshikimate, b.p. 180° (bath)/0.1 mm. (acid, m.p. 121°), affords Me benzoylshikimate, m.p. 136°. isoPropylideneshikimamide, m.p. 150°, is hydrogenated to the non-cryst. H₂-derivative, whence monoacetylisopropylidenedihydroshikimamide, m.p. 125°, and monobenzoylisopropylidenedihydroshikimonitrile, m.p. 168—169°. (I) and Ac₂O-C₅H₅N at room temp. yield triacetylshikimic acid, b.p. 200—



β-Arylglutaconic acids. II. Condensations with phenolic ethers. G. R. GOGTE (Proc. Indian Acad. Sci., 1935, 2, A, 185—198; cf. A., 1934, 1352).—Acetonedicarboxylic acid and *p*-C₆H₄Me·OEt condense (H₂SO₄) to a mixture of β-6-ethoxy-*m*-tolylglutaconic acid (I), m.p. 153° (decomp.) (hydroxy-anhydride, m.p. 112°; semi-anilide, m.p. 136°; hydroxyanil, m.p. 163°), the monolactone of ββ'-6:6'-diethoxy-*m*-tolylglutaric acid (II), m.p. 205° (Et ester, m.p. 124°), and 2:2'-diethoxy-5:5'-dimethylchalkone-α-acetic acid (III), m.p. 232° [semicarbazone, m.p. 264° (decomp.); Et ester, m.p. 133°, and its semicarbazone, m.p. 171° (decomp.)]. (II) and (III) are also obtained from (I) and *p*-C₆H₄Me·OEt. (III) with 80% H₂SO₄ forms 7-ethoxy-3-keto-4-methylindoneacetic acid, m.p. 216° (decomp.) [semicarbazone, m.p. 247° (decomp.), Et ester, m.p. 169°, and its semicarbazone, m.p. 208° (decomp.)], and with H₂SO₄ at 60° forms a neutral substance, m.p. 165° [semicarbazone, m.p. 245° (decomp.)]. (II) and H₂SO₄ give 6-methylcoumarin-4-acetic acid and the dilactone of ββ'-6:6'-diethoxy-*m*-tolylglutaric acid, m.p. 184°, hydrolysed to the acid, m.p. 219° (decomp.) [Et₂ ester, m.p. 82°; Me₂ ester, m.p. 105°; anhydride, m.p. 189°; acid-anilide, m.p. 193° (decomp.); anil, m.p. 216°]. Hydrolysis of this glutaric acid followed by methylation gives ββ'-6:6'-dimethoxy-*m*-tolylglutaric acid (IV), m.p. 192° (decomp.).

p-C₆H₄Me·OMe and acetonedicarboxylic acid yield β-6-methoxy-*m*-tolylglutaconic acid and 2:2'-dimethoxy-5:5'-dimethylchalkone-α-acetic acid, m.p. 252° [semicarbazone, m.p. 277° (decomp.); Et ester, m.p. 122°, and its semicarbazone, m.p. 219° (decomp.)], but no (IV) is formed. The chalkone acid and H₂SO₄ lead to the corresponding indone-acetic acid and a neutral substance, m.p. 214° [semicarbazone, m.p. 263° (decomp.); benzylidene derivative, m.p. 174°]. The reactions indicate that there is restricted rotation around the linking joining the β-C to the phenolic ether in (I) and in the chalkone-acetic acids.

F. R. S.

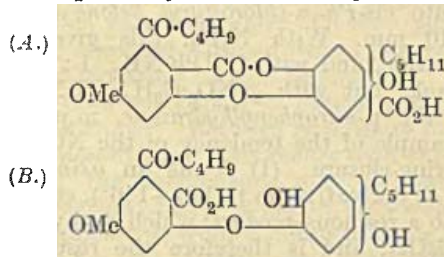
Condensation of ethyl chloroformylcholate with amines and phenols. A. VERDINO and E. SCHADENDORFF (Monatsh., 1935, 66, 169—175).—The following are prepared from Et chloroformylcholate and the requisite base or phenol under the conditions stated in parentheses. They are difficult to purify. Et cholate-3-urethane (NH₃-Et₂O), m.p. 155°, and -*p*-phenyl- (Et₂O), amorphous, sinters from about 80°, -*o*-tolyl- (Et₂O, slowly), -*o*- (hot COMe₂; NHPh₂ catalyst), -*m*- (hot COMe₂; NHPh₂), m.p. 118°

after sintering from 100°, and -*p*-nitrophenyl- (hot COMe₂), amorphous, sinters from 94°, -*o*-carboxyphenyl- (cold COMe₂, slowly), m.p. 220° after sintering from 217°, α-naphthyl, +EtOH or EtOAc, m.p. 141° after sintering from 136°, and -anilino-urethane (Et₂O), m.p. 192° after sintering from 156°. Et cholate 3-phenyl- (Et₂O, Na), m.p. 120°, and 3-β-naphthyl-carbonate (C₆H₆, C₅H₅N), m.p. 163°. Resorcinol, m.p. 203° after sintering at 189°, and quinol di-(Et cholate-3-carbonate) (both in C₆H₆, C₅H₅N), m.p. 217° after sintering at 213°. R. S. C.

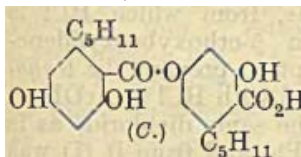
Choleic acids of certain carcinogenic hydrocarbons. L. F. FIESER and M. S. NEWMAN (J. Amer. Chem. Soc., 1935, 57, 1602—1604).—The following compounds are formed in EtOH in the ratio, hydrocarbon:deoxycholic acid (I), stated: acenaphthene (1:2), m.p. 175.5—176.5°; phenanthrene (1:3), m.p. 184—185°; 1:2-benzanthracene (1:3), m.p. 198—199°; 1:2:5:6-dibenzanthracene (1:4), form A (from EtOH), m.p. 223—224°, and B (from dioxan; more readily formed), m.p. 221.5—222.5°; methylcholanthrene (II) (1:4), m.p. 193.5—194.5°; hexahydromethylcholanthrene (1:4), m.p. 191.5—192.5°; dioxan, m.p. 173.5—174.5°; hexadecane, m.p. 192—193°; and dodecane, m.p. 186—187°. Absorption spectra indicate complete or nearly complete dissociation in EtOH or Et₂O. The compound from (II) is about as carcinogenic to mice as (II) itself, but is much less toxic than free (I). Compounds could not be obtained from anthracene, naphthacene, chrysene, pyrene, fluoranthene, triphenylene, perylene, 1:2-benzpyrene (m.p. 178.8—179.3°), 4'-methyl-1:2-benzpyrene (m.p. 219.5—220°), or 1':2'-dihydro-4'-methyl-1:2-benzpyrene (m.p. 162—163°), but this may be connected with relative solubilities and degrees of dissociation rather than with inability to combine, as, even when compounds are obtained, other solvents (except dioxan in one case) proved useless. The no. of mols. of (I) combined increases with the mol. wt. of the hydrocarbon. M.p. are corr. and (for the new compounds) preceded by sintering. R. S. C.

Lichen substances. LVI. Constitution of lobaric acid. I. Y. ASAHINA and S. NONOMURA. LVII. New depside (anziaic) acid and the components of certain *Anzia* types. LVIII. Components of *Thamnolia vermicularis*, Schaer, var. *Faurica*, Schaer. Y. ASAHINA and M. HIRAIWA (Ber., 1935, 68, [B], 1698—1704, 1705—1708, 1708—1710; cf. this vol. 749, 1238).—VI. Exhaustive extraction with warm Et₂O of the thalli of *Stereocaulon paschale*, Ach., *S. exutum*, Nyl., or *S. sorediiferum*, Hue, affords atranorin and lobaric acid (I), m.p. 192°, [α]_D²⁰ ± 0°, identical with the stereocaulic acid of Zopf. (I) is C₂₅H₂₆O₈ and yields a Me ester, m.p. 122°, Me ester Me ether (II), m.p. 102°, Ac derivative, m.p. 186°, and a monoxime, m.p. 193°. Mild hydrolysis with alkali transforms (I) into lobariolcarboxylic acid, C₂₅H₃₀O₉, m.p. 193° [Me₂ ether Me₂ ester, m.p. 104°, also obtained by treating (II) with KOH-MeOH and the product with CH₂N₂]. (I) with boiling Ba(OH)₂ gives lobariol (III) (usnetol), C₂₄H₃₀O₇, m.p. 168° (Me ester, m.p. 140°; Me ester Me₂ ether, b.p. about 130°/1 mm.; monoxime, m.p. 173°; anhydrosemi-

carbazone, $C_{25}H_{31}O_6N_2$, m.p. 128° , which does not undergo Wolff's reduction; *anhydrazonone*, $C_{24}H_{30}O_5N_2$, m.p. $158-159^\circ$. (I) is converted by molten KOH into Bu^oCO_2H and $m-C_6H_4(OH)_2$. Reduction of (III) with HI (d 1.7) and red P leads to *norlobarilolide*, $C_{23}H_{28}O_6$, m.p. 210° (*tribromide*, m.p. 211°), a phthalide-like lactone formed with loss of Me; this, when treated with CH_2N_2 and then oxidised with $Na_2Cr_2O_7$, gives a yellow product, $C_{25}H_{30}O_7$, m.p. $138-139^\circ$. Treatment of (III) with hot conc. KOH followed by reduction with Na and boiling abs. EtOH gives after methylation a non-cryst. product (?), $C_{25}H_{36}O_4$, oxidised by CrO_3 to 6-methoxy-1-n-amy-*p*-benzoquinone. For (I) and (III) the structures A and B, respectively, are tentatively advanced.



LVII. Extraction of the air-dried thall of *Anzia gracilis*, Y. Asahina, with purified Et_2O at $15-20^\circ$ yields atranorin and *anziaic acid* (V), $C_{24}H_{30}O_7 \cdot 0.5H_2O$, m.p. 124° (decomp.) (*Me* ester, m.p. 102°). Since (V) is hydrolysed to olivetolcarboxylic acid and Me



olivetolcarboxylate (*Me*₂ ether, m.p. $52-53^\circ$) and converted by CH_2N_2 into Me perlatolate *Me*₂ ether, it has the structure C. Extraction of *A. japonica*, Mull.

Arg, with Et_2O gives atranorin and divaricatic acid, whereas (I) is obtained from *A. hypoleucoides*, Müll. Arg.

LVIII. Extraction of *Thamnia vermicularis*, var. *taurica* (Japan), with hot $COMe_2$ gives squamatic acid, m.p. about 220° (decomp.) (best identified as the *Me*₂ ester *Me*₂ ether, m.p. 132°), and thamnic acid (*anil*, m.p. 207°).

H. W.

Basic properties of hydrazones. IX. R. CIUSA and G. OTTOLINO (Gazzetta, 1935, 65, 542-545).—*pp'*-Bis-(α -methyl- β -benzylidenehydrazino)triphenylmethane (I) exists in two modifications, one, m.p. 136° (cf. A., 1932, 1132), obtained by crystallisation from PhMe, and the other, m.p. 163° (cf. A., 1934, 408), by adding light petroleum to the PhMe solution. When the condensation product of PhCHO and its phenylmethylhydrazone is boiled with 10% H_2SO_4 , the sulphate of m.p. 205° (cf. A., 1934, 408) filtered off, and the liquid treated with aq. NH_3 , the triphenylcarbinol corresponding with (I) is pptd. This is converted by dil. H_2SO_4 into *pp'*-bis- α -methylhydrazinotriphenylmethyl *H* sulphate, $NH_2 \cdot NMe \cdot C_6H_4 \cdot CPh \cdot C_6H_4 \cdot NMe \cdot (NH_2) \cdot HSO_4 \cdot 2H_2O$, and by HCl into the compound of m.p. 170° (A., 1932, 51). The H_2SO_4 solution of the hydrolysis product gives an immediate green reaction with aldehydes (32 examples), except pyrrole-aldehyde and aldehydic sugars, but not with ketones (12 examples); this new

reagent for aldehydes is more sensitive than Schiff's reagent.

E. W. W.

Condensation of vanillin substitution products with methylene derivatives. L. C. RAYFORD and D. E. FOX (Proc. Iowa Acad. Sci., 1933, 40, 111; cf. this vol., 214).—In condensing vanillin substitution products with $MeNO_2$, NH_4OAc in glacial AcOH is a suitable condensing agent. On replacing $MeNO_2$ by 2:4- $C_6H_3Me(NO_2)_2$, piperidine was most suitable.

CH. ABS. (e)

Ozonisation of anisaldehyde, vanillin, and piperonal.—See this vol., 1328.

Alicyclic compounds. I. Synthesis of β -ketoamines. F. PIRRONE (Atti R. Accad. Lincei, 1935, [vi], 21, 521-524).—Interaction of PhCHO, NH_3 , and cyclohexanone in the cold yields: (1) 2- ω -benzylidenaminobenzylcyclohexanone (I), m.p. $181-183^\circ$, which forms a semicarbazone, m.p. $199-200^\circ$, an oxime, m.p. $182-184^\circ$, and a hydroxylaminoxime, m.p. $199-200^\circ$, and on treatment with HCl gives 2:6-dibenzylidenecyclohexanone: (2) 2- ω -(ω -aminobenzyl)aminobenzylcyclohexanone, m.p. $188-189^\circ$, and (3) the 6-benzylidene derivative of (I), m.p. $170-171^\circ$.

T. H. P.

Kinetics of the Friedel-Crafts ketone and hydrocarbon synthesis.—See this vol., 1207.

Influence of nuclear substituents on side-chain reactions. II. Acid-catalysed prototropy of nuclear-substituted acetophenones. III. Base-controlled phototropy of substituted acetophenones.—See this vol., 1209.

Reaction of $\omega\omega$ -dihalogenoacetophenones with alkali. C. H. FISHER and C. T. WALLING (J. Amer. Chem. Soc., 1935, 57, 1562-1564).— $\omega\omega$ -Dihalogenoacetophenones dissolve unchanged in aq. alkalis if substituted by Me in the 2- and 6-positions, but the 2-*Me* compounds give the mandelic acids. *m*- NO_2 -groups enhance the acidity, and 3:5-dinitro-2:4:6-trimethylphenyl $CHBr_2$ ketone (I) may be titrated with alkali. $\omega\omega$ -Di-chloro- and -bromo-acetylmesitylene (II) dissolve in 10% KOH at room temp., the former much the more rapidly, and are pptd. unchanged. 2:4- $C_6H_3Me_2 \cdot CO \cdot CHBr_2$ (from 2:4- $C_6H_3Me_2 \cdot CO \cdot Me$ or its ω -Cl-derivative) and 2:4:5- $C_6H_2Me_3 \cdot CO \cdot CHBr_2$ [from 2:4:5- $C_6H_2Me_3 \cdot CO \cdot CH_2Cl$ (obtained from ϕ -cumene with a substance, m.p. $55-56^\circ$)] with 10% KOH give 2:4-dimethyl- and 2:4:5-trimethyl-mandelic acid, respectively. The latter acid yields 2:4:5- $C_6H_2Me_3 \cdot CO_2H$, m.p. $149-150^\circ$ (lit. $148-149^\circ$). (II) and $HNO_3-H_2SO_4$ give (I), m.p. $168-169.5^\circ$, also obtained by NaOH from $\omega\omega$ -tribromo-3:5-dinitroacetylmesitylene, into which it is converted by NaOBr.

R. S. C.

Biochemical hydrogenations. II. Hydrogenation of unsaturated ketones by fermenting yeast. F. G. FISCHER and O. WIEDEMANN (Annalen, 1935, 520, 52-70; cf. this vol., 123).—Unsaturated ketones in which the C:C and C:O linkings are co-ordinated are reduced when dissolved or emulsified in H_2O and dropped on to actively fermenting yeast. Thus $CHPh:CH \cdot COMe$ yields $CH_2Ph \cdot CH_2 \cdot CHMe \cdot OH$,

CHPh:CH·CHMe·OH, and CH₂Ph·CH₂·COMe. From C₄H₉O·CH:CH·COMe, the products are 2- γ -hydroxybutylfuran, b.p. 96—98°/13 mm., and furethyl Me ketone. CMe₂:CH·COMe gives very small quantities of CHMeBu^B·OH. 1-Methyl- Δ^1 -cyclohexen-3-one yields 1-methylcyclohexan-3-ol and -3-one, with probably the Δ^1 -cyclohexen-3-ol. Pulegone and carvone apparently give the saturated ketones; yields in each case are poor. CHMe:CH·CH:CH·COMe yields, comparatively readily, Δ^8 -hepten- ϵ -ol, b.p. 62—64°, and - ϵ -one (A., 1928, 740) (semicarbazone, m.p. 108°). CHPh:CH·CH:CH·COMe gives Δ^2 - α -phenylhexen- ϵ -ol and - ϵ -one (semicarbazone, m.p. 132°). Δ^8 -Hexen-8-ol and Δ^2 -buten-8-ol (3:5-dinitrobenzoate, m.p. 50°) are unchanged. Δ^2 -Hexen- ϵ -one yields the - ϵ -ol. Unsaturated ketones are hydrogenated by yeast more slowly than unsaturated aldehydes or primary alcohols. The action of yeast in converting an unsaturated ketone into an unsaturated alcohol is the first example of this type of reduction. The mechanism of the reactions is discussed.

E. W. W.

Reactions catalysed by aluminium chloride.

XII. Migration of halogen in carbon chains and rings. C. D. NENITZESCU and I. G. GAVAT (Annalen, 1935, 519, 260—271).—AlCl₃ promotes the migration of Cl in chloro-ketones or -acids to a more remote position in the chain or ring, but not to a terminal Me. Thus cyclohexene, AcCl, and AlCl₃ in CS₂, followed by C₆H₆, give, not 2-, but 4-acetyl-1-phenylcyclohexane, b.p. 161—164°/11 mm. (semicarbazone, m.p. 190—191°). This is oxidised (NaOBr) to 1-phenylcyclohexane-4-carboxylic acid, m.p. 204° (of which the Me ester, m.p. 28°, b.p. 172—173°/15 mm., is reduced to 1-phenylcyclohexyl-4-carbinol, m.p. 49°, b.p. 177—178°/15 mm.), and is dehydrogenated (Pt at 300°) to 4-ethyldiphenyl. Similarly, cyclopentene, AcCl, and AlCl₃, followed by C₆H₆, give, not 2-, but 3-acetyl-1-phenylcyclopentane, b.p. 163—165°/16 mm. (semicarbazone, m.p. 170—171°), oxidised (NaOBr) to 1-phenylcyclopentane-3-carboxylic acid, b.p. 196—198°/5 mm. (chloride, b.p. 159—162°/15 mm.; amide, m.p. 149°; anilide, m.p. 107°), which is synthesised from $\alpha\delta$ -dibromo- β -phenylbutane and Et malonate. Using C₂H₄, under the same conditions, CH₂Ph·CH₂·COMe is formed by way of CH₂Cl·CH₂·COMe. With CHMe:CH₂, the product is β -phenylpropyl Me ketone, b.p. 113—115°/13 mm. (semicarbazone, m.p. 137°), also obtained from CH₂:CH·CH₂·COMe, C₆H₆, and AlCl₃. Similarly CHMe:CHMe gives β -phenylisobutyl Me ketone, b.p. 239—240° (semicarbazone, m.p. 176°); in neither of these cases is there migration of Cl. From CHEt:CH₂, however, the product is not β -, but γ -phenyl-n-butyl Me ketone, b.p. 122—125°/9 mm. (semicarbazone, m.p. 147°), also obtained from propylideneacetone. Butylideneacetone, C₆H₆, and AlCl₃ yield not β -, but δ -phenylamyl Me ketone, b.p. 136—140°/13 mm. (p-nitrophenylhydrazone, m.p. 117°), which is oxidised to δ -phenylhexoic acid, b.p. 173—175°/11 mm. (chloride, b.p. 134—136°/13 mm.), and is synthesised by condensing γ -phenylbutyl bromide with the Na₂ derivative of CH₂(CO₂Et)₂ to form Et γ -phenylbutylmalonate, b.p. 143—145°/0.5 mm., converting this into δ -phenylhexoic acid, and

passing this with excess of AcOH over ThO₂ at 400°. Δ^1 -cyclohexene-1-carboxylic acid with C₆H₆ and AlCl₃ yields 1-phenylcyclohexane-4-carboxylic acid. Migration of Cl is considered to explain the failure of AlCl₃ to convert 1-phenylacetyl- Δ^1 -cyclohexane into a tricyclic compound.

E. W. W.

Chlorinated benzylideneacetophenones and hydrindones. K. VON AUWERS and R. HÜGEL (J. pr. Chem., 1935, [ii], 143, 157—173).—Compounds prepared in an attempt to compare the Beckmann rearrangement of oximes of *cis*- and *trans*-forms of α - and β -chlorobenzylideneacetophenone are described. CHPh:CH·COPh is treated in CHCl₃ with Cl₂, and the resulting dichloride converted by KOAc in EtOH into *cis*-Ph α -chlorostyryl ketone (I), b.p. 204—205°/10 mm. With N₂H₄, this gives 3:5-diphenylpyrazole, and with NHPh·NH₂, 1:3:5-triphenylpyrazole, but with *p*-NO₂·C₆H₄·NH·NH₂ the product is the *p*-nitrophenylhydrazone, m.p. 177—179°, an example of the tendency of the NO₂-group to hinder ring-closure. (I) forms an oxime, m.p. 156—157° (Bz derivative, m.p. 145—146°), converted by PCl₅ into a resinous product, which on hydrolysis furnishes BzOH, and is therefore the result of a Beckmann transformation into the substance CHPh:CCl·NHBz. The oxime is converted by KOH-EtOH into 3:5-diphenylisooxazole, readily prepared by treating (I) with NH₂OH and NaOH in excess. The action of NaOEt on (I) gives rise to α -chloro- β -ethoxy- α -benzoyl- β -phenylethane, from which HCl is lost (KOH-EtOH) to form β -ethoxybenzylideneacetophenone. In an attempt to prepare the *trans*-isomeride of (I), it was treated with HCl in AcOH at 100°, but the product was the same dichloride as is obtained from CHPh:CH·COPh, and from it (I) was regenerated. Another attempt was made, combining α -chloro*trans*-cinnamoyl chloride with C₆H₆ (AlCl₃), but the product was 2-chloro-3-phenyl-1-hydrindone (II), m.p. 94—96°, b.p. 198—202°/9 mm., which is free from chlorobenzylideneacetophenone, since no trace of 3:5-diphenylisooxazole was obtained by treating it with NH₂OH-NaOH. (II) forms an oxime, m.p. 80—90° (impure), containing Cl, but with N₂H₄ the product is 3-phenylindonehydrazone, m.p. 140—141°; similarly, 3-phenylindone-*p*-nitrophenylhydrazone, m.p. 266—267°, is obtained. β -Chloro*trans*-cinnamoyl chloride and C₆H₆ (AlCl₃) yield 3:3-diphenyl-1-hydrindone, new m.p. 132° (*p*-nitrophenylhydrazone, new m.p. 248—250°). It was hoped that Me groups would hinder condensation to the hydrindone. 2:4-Dimethylbenzylideneacetophenone was converted into the dichloride, and thence into *cis*-Ph α -chloro-2:4-dimethylstyryl ketone (III), b.p. 226—228°/12 mm., oxidised to methylterephthalic acid and BzOH. (III) forms an oxime, m.p. 183—186°, which is not hydrolysed when heated with conc. HCl for 24 hr., but with 67% H₂SO₄ yields a Cl-free and N-free substance, m.p. 70—71°; with PCl₅ the oxime gives an oil which on hydrolysis furnishes NH₃ and *m*-xylylic acid, and thus contains the amide CHPh:CCl·NH·CO·C₆H₃Me₂. Combination of α -chloro*trans*-cinnamoyl chloride with *m*-xylene (AlCl₃) yields 2-chloro-3-phenyl-5:7-dimethyl-1-hydrindone, m.p. 127—129° (oxime, m.p. 172°), which gives rise

to 3-phenyl-5:7-dimethylindone-p-nitrophenylhydrazone, m.p. $> 280^\circ$, and is oxidised (KMnO_4 in COMe_2) to 6-benzoyl-2:4-dimethylbenzoic acid, m.p. 125° (p-nitrophenylhydrazone, m.p. $125\text{--}126^\circ$). The $\alpha\text{-Cl}$ thus neutralises the hindrance to ring-closure offered by the Me groups.

E. W. W.

Chemical morphology in homologous series. C. WEYGAND and L. MENSDOFF [with F. STROBELT] (Ber., 1935, 68, [B], 1825—1838).—Between immediate neighbours in the different homologous series (normal chains, terminal Pr^2 , etc.) up to octyl-chalkone, morphologically comparable pairs of polymorphic forms invariably exist. With a single exception ($\text{Bu}^n\text{-n-C}_5\text{H}_{11}$) seeding relationship exists between neighbours with respect to certain of such comparable pairs of forms. Further, such relationships are observed between isomerides, but a certain degree of variation cannot be exceeded; for normal series it does not appear to extend beyond the next but one member. Between immediate neighbours it may be non-existent, but recurs with the succeeding member; the phenomenon may be connected with the alternation of m.p. in homologous series.

n-Nonylbenzene, from *n*-nonyl bromide, PhBr , and Na, has b.p. $98\text{--}100^\circ/1$ mm. The following substituted acetophenones are obtained by gradual addition of AcCl and benzenoid hydrocarbons to AlCl_3 covered with CS_2 or light petroleum: *p*-n-butyl-, b.p. $140\text{--}141^\circ/14$ mm. (semicarbazone, m.p. 185°); *p*-isobutyl-, b.p. $135^\circ/16$ mm.; *p*-n-amyl-, b.p. $159\text{--}5^\circ/17$ mm.; *p*-isoamyl-, b.p. $153^\circ/16$ mm.; *p*-tert.-amyl-, b.p. $144\text{--}146^\circ/13$ mm.; *p*-n-hexyl-, b.p. $171\text{--}172^\circ/18$ mm.; *p*-n-heptyl-, b.p. $176\text{--}179^\circ/13$ mm.; *p*-n-octyl-, b.p. $184\text{--}188^\circ/13$ mm., m.p. 18° ; *p*-n-nonyl-, b.p. $165^\circ/3$ mm. The ketones are condensed with PhCHO at 0° in presence of NaOMe or KOH , thus giving the following Ph styryl ketones; the m.p. of the various forms of each member are given in order of stability at room temp.: chalkone, m.p. $59^\circ, 57^\circ, 48^\circ, 49^\circ, 28^\circ, 18^\circ$; *p*'-methyl-chalkone (*p*-tolyl styryl ketone), m.p. $75^\circ, 57^\circ, 56^\circ, 55^\circ, 46^\circ, 48^\circ, 45^\circ$; *p*'-ethyl-, m.p. $63^\circ, 47^\circ$; *p*'-n-propyl-, m.p. $47^\circ, 33^\circ$; *p*'-isopropyl-, m.p. $65^\circ, 45^\circ, 18^\circ$; *p*'-n-butyl-, m.p. $35^\circ, 33^\circ, 28^\circ$; *p*'-isobutyl-, m.p. $71^\circ, 69^\circ$; *p*'-tert.-butyl-, m.p. $98^\circ, 62^\circ$; *p*'-n-amyl-, m.p. $51^\circ, 33^\circ$; *p*'-isoamyl-, m.p. $50^\circ, 46^\circ, 45^\circ, 44\text{--}5^\circ, 36^\circ$; *p*'-tert.-amyl-, m.p. 121° ; *p*'-n-hexyl-, m.p. $52^\circ, 46^\circ, 44^\circ$; *p*'-n-heptyl-, m.p. $43^\circ, 35^\circ, 33^\circ$; *p*'-n-octyl-, m.p. $38^\circ, 40^\circ, 35^\circ$; *p*'-n-nonyl-, m.p. 43° . The seeding relationships of the various types are recorded.

H. W.

Addition to conjugated systems in the anthracene series. II. Behaviour of certain anthranols. P. L. JULIAN and W. COLE (J. Amer. Chem. Soc., 1935, 57, 1607—1611).—1:6-Addition of Grignard reagents to 10-methyleneanthrone (I) (A., 1934, 1356) is confirmed. The structure and anticipated great lability (1:5-OH migration) of 10-benzylidene-9-phenyl-9:10-dihydroanthranol (II) (not fluorescent) are proved. Hydrogenation (Pd) of benzylideneanthrone (III) in EtOH and treatment of the resulting solution with O_2 gives the peroxide (IV), which is obtained by acting with O_2 on the solution obtained from (I) and MgPhBr . If, however, peroxide formation is prevented in these reactions, the

product is 10-benzylanthrone, m.p. $143\text{--}144^\circ$ (lit. $133\text{--}134^\circ$) [a substance, m.p. $221\text{--}222^\circ$, is also obtained from (I)], the structure of which is proved by conversion by MgPhBr into 9-phenyl-10-benzylanthrone. The production of $\text{CH}_2\text{Ph}\cdot\text{OH}$ by pyrolysis of (IV) is confirmed by its isolation as 3:5-dinitrobenzoate, m.p. 114° . (I) and MgMeI or MgEtI give 10-ethyl-, m.p. 164° , and -propyl-anthranol peroxide, m.p. 122° , respectively, giving EtOH or PrOH on pyrolysis. (II) and $\text{Br}\cdot\text{CHCl}_3$ give 9-bromo-10-phenylantracene by way of 10-bromo-9-phenyl-10- α -bromobenzyl-9:10-dihydroanthranol, which appears to be stable at low temp., but loses HBr and PhCHO at room temp. (II) with CrO_3 gives 9-phenyl-oxanthrone, and with hot AcOH or Ac_2O fluorescent 9-phenyl-10- α -acetoxybenzylantracene, m.p. 160° . With dry HCl or SOCl_2 (II) gives fluorescent 9-phenyl-10- α -chlorobenzylantracene, m.p. 189° , and with dry HBr the 10- α -bromobenzyl compound (V), m.p. 188° , also obtained from 9-phenyl-10-benzylantracene and Br in warm CS_2 . (II) is isomerised by a little H_2SO_4 in warm COMe_2 to fluorescent 9-phenyl-10- α -hydroxybenzylantracene (VI), + αEtOH or COMe_2 and anhyd., m.p. 187° , which with CrO_3 , Ac_2O , HCl, HBr, or Br gives the same products as does (II); the reaction with Br is probably preceded by isomerisation to (II), a small amount of which probably exists in equilibrium with (VI) in solution. (V) and Ag in C_6H_6 give $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-9-phenylantraceny-10-ethane, m.p. $252\text{--}253^\circ$.

R. S. C.

Carvacrol. IV. Acylmethylisopropylphenols. H. JOHN and P. BEETZ (J. pr. Chem., 1935, [ii], 143, 342—346).—Synthetic carvacrol gives (Friedel-Crafts; PhNO_2) 2-hydroxy-5-propionyl-, m.p. 76° , -n-butyl-, m.p. 66° , -iso-valeryl-, m.p. 86° , and -benzoyl-1-methyl-4-isopropylbenzene, m.p. 126° , in poor yields.

R. S. C.

Inhibition in the benzoin reaction.—See this vol., 1329.

Autoxidation phenomena in the indene series. P. PFEIFFER and H. L. DE WAAL (Annalen, 1935, 520, 185—200).— $\beta\beta$ -Diphenylpropionyl chloride is converted by AlCl_3 into 3-phenyl- α -hydrindone (I) (cf. Kohler, A., 1904, 595) [2-benzylidene, m.p. 158° , 2-anisylidene, m.p. 174° , and 2-(3':4'-dimethoxybenzylidene), m.p. 174° , derivatives], the 2-oximino-derivative, decomp. $201\text{--}202^\circ$, of which with $\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$ -NaOAc affords the dioxime, decomp. $196\text{--}196\text{--}5^\circ$, of (III) [below: also from $\text{NH}_2\cdot\text{OH}$ and (III)]. (I) condenses with PhNO in aq. EtOH-NaOH to give 2-anilo-3-phenyl- α -hydrindone (II), m.p. $149\text{--}150^\circ$, hydrolysed (cold conc. H_2SO_4) to 1:2-diketo-3-phenylhydrindene (III), m.p. $137\text{--}138^\circ$ [semicarbazone, m.p. 252° (decomp.); quinoxaline, m.p. 173°]. Oxidation of (II) with boiling 30% H_2O_2 affords a compound, m.p. 160° , which is either $\text{C}_6\text{H}_4\text{CHPh}\cdot\text{C}\cdot\text{NPh}$ or $\text{C}_6\text{H}_4\text{CHPh}\cdot\text{CO}\cdot\text{NPh}$, hydrolysed by boiling 20% KOH

to an α -phenylhomophthalanilic acid, m.p. 192° , converted by warm AcOH-dil. H_2SO_4 into α -phenylhomophthalic acid, m.p. $157\text{--}158^\circ$. Similarly (I) condenses (N_2) with $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ to give its 2-p-dimethylaminoanilo-derivative, m.p. $148\text{--}150^\circ$, oxidised in air

to 4-hydroxy-1:3-diketo-4-phenyl-2-p-dimethylamino-phenyl-1:2:3:4-tetrahydroisoquinoline, m.p. 214.5°, converted by hot 20% KOH into 1-keto-3-phenyl-2-p-dimethylaminophenyl-1:3-dihydroisoindole (IV), m.p. 270° (decomp.) [*H* sulphate, m.p. 223—224° (decomp.)], which is hydrolysed to α -phenylphthalide (V) by 48% H₂SO₄, and is identical with a specimen synthesised from (V) and *as*-dimethyl-*p*-phenylenediamine (VI). An attempt to synthesise the 3-OH-derivative of (IV) by condensation of (VI) with *o*-benzoylbenzoic acid gave benzophenone-*p*-dimethylaminocanil-2-carboxy-*p*-dimethylaminocanilide, m.p. 245°. Similarly the 2-*p*-methoxyanilo-derivative, m.p. 118°, of (I) is autoxidised to 4-hydroxy-1:3-diketo-4-phenyl-2-*p*-anisyl-1:2:3:4-tetrahydroisoquinoline, m.p. 168°, whence 1-keto-3-phenyl-2-*p*-anisyl-1:3-dihydroisoindole, m.p. 201° (also synthesised), is obtained. Many of the above are halochromic. J. W. B.

Magnetochemical investigations of organic substances. III. Deeply coloured dimeric keten of W. Langenbeck. E. MÜLLER (Ber., 1935, 68, [B], 1883—1885; cf. this vol., 1116).—The magnetochemical behaviour of Langenbeck's 3:3:4:4-tetraphenylcyclobutane-1:2-dione (A., 1928, 762) affords no evidence of the presence of the diradical $\cdots\text{CPh}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CPh}_2\cdots$. The uncertainty as to the influence of a 4-membered ring is removed by examination of Et. cyclobutane-1:1-dicarboxylate.

H. W.

Perylene and its derivatives. XLIV. A. PON-GRATZ and G. MARKGRAF (Monatsh., 1935, 66, 176—180; cf. A., 1934, 1359).—3:9-Di-*p*-toluoylperylene, m.p. 317.5—318.5°, is obtained from perylene (I) and *p*-C₆H₄Me·COCl (II) or perylene-3:9-dicarboxyl chloride and PhMe in CS₂ with AlCl₃, thus proving *p*-condensation in the latter reaction. (I), (II), and AlCl₃ without a solvent give, however, 3:4-di-*p*-toluoylperylene (III), m.p. 351—352°. (I), *p*-C₆H₄Cl·COCl, and AlCl₃ without a solvent give similarly 3:4-di-*p*-chlorobenzoylperylene (IV), m.p. 346—347°. Clemmensen reduction of (III) and (IV) gives 1:2-di-*p*-tolyl- (V; R=C₆H₄Me), m.p. 326.5—327.5°, and -chlorophenyl-azeperylene, m.p. 317—318°. M.p. are corr.

R. S. C.

Isomeric allopregnan-3-ol-20-one. A. BUTENANDT and L. MAMOLI (Ber., 1935, 68, [B], 1847—1850).—Hydrolysis of allopregnanolone acetate (I) with KOH-EtOH affords allopregnanolone (II) and isoallopregnanolone (III), m.p. 148°, [α]_D²⁰ +6.05° in EtOH (acetate, m.p. 101°). Both substances immediately yield sparingly sol. additive products with digitonin. (III) is largely isomerised to (II) by EtOH-KOH. (II) is oxidised by CrO₃ to allopregnanone (IV), also formed with isoallopregnanone, m.p. 134—135°, [α]_D -14.56° in EtOH, when (III) is oxidised. (I) and (II) therefore differ only in the steric arrangement around C17. The ability of (I) and (IV) to give sparingly sol. products with digitonin shows that the presence of OH at C3 is not essential for this reaction.

H. W.

Δ^1 -alloPregnen-3:20-dione. Specificity of the corpus luteum action. A. BUTENANDT and L. MAMOLI (Ber., 1935, 68, [B], 1850—1854).—allo-Pregnanone is smoothly transformed by Br in AcOH into the Br₁-derivative (I), m.p. 199° (decomp.), converted by KOBz in BzOH at 205° into 2-hydroxypregnan-3:20-dione benzoate, m.p. 235°. (I) loses HBr with difficulty, but is transformed by KOAc in AcOH at 175—185° into a singly unsaturated α - β -diketone, m.p. 140°, [α]_D¹⁸ +68.6°, not identical with progesterone, and regarded as Δ^1 -allopregnen-3:20-dione; it is physiologically inactive. H. W.

Transformation of dehydroandrosterone into Δ^4 -androsten-17-ol-3-one (testosterone); method of preparing testosterone from cholesterol. A. BUTENANDT and G. HANISCH (Ber., 1935, 68, [B], 1859—1862).—The physiological activity of androstendione, m.p. 169°, [α]_D¹⁸ +185°, towards rodents exceeds that of any other member of the androsterone group. Reduction of dehydroandrosterone with Na and PrOH gives an androstendiol, C₁₉H₃₀O₂, m.p. 177—178°, [α]_D¹⁸ -55.5°, which has little physiological activity. It is converted by boiling Ac₂O into the diacetate, m.p. 158.5°, [α]_D¹⁸ -56.5°, partly hydrolysed to androstendiol 17-monoacetate (I), m.p. 146°. Bromination of (I) followed by oxidation with cold CrO₃ and debromination of the product with Zn dust and NaI affords Δ^4 -androsten-17-ol-3-one acetate, m.p. 138°, [α]_D +87.5°, hydrolysed to Δ^4 -androsten-17-ol-3-one, m.p. 151°, [α]_D +104° (oxime, m.p. 215°), which is highly active physiologically and probably identical with testosterone. H. W.

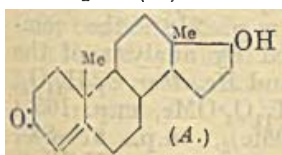
Androsterone. R. E. MARKER (J. Amer. Chem. Soc., 1935, 57, 1755—1756).—Androsterone (I) is conveniently synthesised by one of the following series of reactions. Cholesteryl chloride (prep. by PCl₅ or SOCl₂) gives cholesterol when hydrolysed, but, when hydrogenated (PtO₂) in Et₂O, gives rapidly α -cholestyl chloride (II). β -Cholestanol with PCl₅ gives β -cholestyl chloride (III), but with SOCl₂ gives (II). Similarly epicholestanol (IV) gives (II) with PCl₅, but (III) with SOCl₂. Hydrolysis of (II) gives (IV). Walden inversion thus occurs at unidentified points. Oxidation of (II) gives α -chloroandrosterone, whence (I) is obtained by KOAc.

R. S. C.

Systematic degradation of 3-hydroxyallocholanolic acid to androsterone. O. DALMER, F. VON WERDER, H. HONIGMANN, and K. HEYNS (Ber., 1935, 68, [B], 1814—1825).—Me 3-hydroxyallocholanate is transformed by MgPhBr in Et₂O-C₆H₆ into diphenyl-3-hydroxynorallocholylicarbinol, m.p. 150°, [α]_D²⁰ +20° in EtOH, acetylated and then oxidised by CrO₃ in AcOH to 3-acetoxynorallocholanolic acid (I), m.p. 235°, [α]_D²⁰ +26° in CHCl₃ [Me ester (II), m.p. 189—190°, [α]_D²⁰ +26° in CHCl₃]. (I) is hydrolysed to 3-hydroxynorallocholanolic acid, m.p. 205—207°, [α]_D +21° in EtOH, converted by CH₂N₂ into the Me ester, m.p. 169—170°, [α]_D²⁰ +21° in CHCl₃. Treatment of (II) with MgPhBr followed by hydrolysis leads to diphenylbisorallocholylicarbinol, a yellow resin, which is acetylated and then oxidised to 3-acetoxybisorallocholanolic acid, m.p. 225—227°, [α]_D +2° in CHCl₃ [Me ester (III), m.p. 128—129°, [α]_D²⁰ +10° in CHCl₃]; 3-hydroxybisorallocholanolic acid,

m.p. 220°, $[\alpha]_D^{25} +17^\circ$ in EtOH, and its *Me* ester, m.p. 162—163°, $[\alpha]_D^{25} +12^\circ$ in CHCl_3 , are described. (III) is transformed successively into *diphenyl-3-hydroxytrinallocholylcarbinol* and *3-acetoxyætiolallocholan acid* [*Me* ester (IV), m.p. 201—202°, $[\alpha]_D^{25} +56^\circ$ in CHCl_3]. (IV) and MgPhBr followed by hydrolysis yield *diphenyl-3-hydroxyætiolallocholylcarbinol*, dehydrated at 150—200°/1 mm., acetylated, and then ozonised in CHCl_3 to *3-epiacetoxyætiolallocholan-17-one* [semicarbazone, m.p. 272—273° (decomp.)], whence androsterone (V). The possibility of converting a native bile acid into (V) is thereby established. In the hope of shortening the course of operations the possibility of obtaining acids with abbreviated side-chains by suitable oxidation of hydrogenated and epimerised sterols is examined. Thus, sitostanone is hydrogenated (PtO , in AcOH —48% HBr) to *episitostanol*, m.p. 203°, $[\alpha]_D^{25} +26^\circ$ in CHCl_3 , the *acetate*, m.p. 88°, $[\alpha]_D^{25} +28^\circ$ in CHCl_3 , of which is oxidised by CrO_3 in AcOH to (I). Similarly, *stigmastanol* (VI) is oxidised to *stigmastanone hydrate*, $\text{C}_{29}\text{H}_{50}\text{O}_2\cdot\text{H}_2\text{O}$, m.p. 81—82°, $[\alpha]_D^{25} +23^\circ$ in CHCl_3 (*oxime*, m.p. 219°, $[\alpha]_D^{25} +30^\circ$ in CHCl_3), transformed by BzCl in $\text{C}_5\text{H}_5\text{N}$ into *stigmastanone*, m.p. 157°, $[\alpha]_D^{25} +42^\circ$ in CHCl_3 . Catalytic reduction of (VI) gives *epistigmastanol*, m.p. 200°, $[\alpha]_D^{25} +25^\circ$ in CHCl_3 , the *acetate*, m.p. 85°, $[\alpha]_D^{25} +27^\circ$ in CHCl_3 , of which likewise affords (I). *epiCholestanyl acetate* yields *3-hydroxyallocholan acid* (*Me* ester, m.p. 164—165°, and its *acetate*, m.p. 147—148°, $[\alpha]_D^{25} +21^\circ$ in CHCl_3) in 11% yield. The $\text{C}_{10}\text{H}_{21}$ side-chain of sitostanol can be partly resolved into $\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{C}_6\text{H}_{13}$.

Sexual hormones. VII. Synthetic preparation of the testicular hormone, testosterone (androsten-17-ol-3-one). L. RYZICKA and A. WETTSTEIN (Helv. Chim. Acta, 1935, 18, 1264—1275).—*trans*-Dehydroandrosterone is reduced by Na and Pr^iOH or catalytically in presence of Ni to *trans-Δ⁵-androsten-3:17-diol* (I), m.p. 182—183° (corr.); *trans-Δ⁵-androsten-3:17-diol 3-monoacetate* (II), m.p. 147—148° (corr.), is obtained catalytically from *trans-Δ⁵-3-acetoxyandrosten-17-one*. Mild treatment of (I) with Ac_2O affords the corresponding *diacetate*, m.p. 165—166°, which decolorises Br in AcOH and gives a yellow colour with $\text{C}(\text{NO}_2)_4$; it is transformed by cautious treatment with KOH in MeOH at 15° into *trans-Δ⁵-androsten-3:17-diol 17-monoacetate* (III), m.p. 146.5—148.5°, which depresses the m.p. of (II). Addition of Br followed by oxidation



with CrO_3 and debromination of the product with Zn and AcOH or NaI in EtOH leads to *Δ⁴-17-acetoxyandrosten-3-one*, m.p. 139—141°, hydrolysed to *Δ⁴-androsten-17-ol-3-one* (A), m.p. 154.5—155.5°, $[\alpha]_D^{25} +109^\circ$ in abs. EtOH (*oxime*, m.p. 222—223°, chemically and biologically identical with testosterone. A. W.

Effect of the ketodiviny chain on the colour of metallic salts of hydroxyvinyl ketones. I. Salts of disalicylideneacetone. (Unsaturated chromophores. II.) A. MANGINI (Gazzetta, 1935, 65, 474—486).—Disalicylideneacetone forms three

series of salts (A), stable red; (B), stable yellow; and (C), salts pptd. in an unstable red form, passing into a yellow form. In each case the mol. combines with two equivs. of the metal. The following are described. (A): *Mg* (+4 H_2O), *Ca* (+6 H_2O), *Sr* (+7 H_2O), *Ba* (+5 H_2O), *Cd* (+2 H_2O), *Pb* (+2 H_2O), *cuprammonium*, *Ag* (greyish-black), *Tl* (blackish-red), and *NH₄*; (B): *Cu* (+ H_2O), *Zn* (+2 H_2O), *Hg*⁺ (+ H_2O), *Fe*⁺⁺ (+6 H_2O), *Al* (+6 H_2O), *Be*, and *Cr*; (C): *Mn* (+ H_2O), *Fe*⁺⁺ (+3 H_2O), *Ni* (+3 H_2O), *Co* (+2 H_2O), and *Hg*⁺ (+6 H_2O) salts. The structure of these salts is discussed: it is suggested that (B) are simple co-ordinated compounds, and that in (A) the mol. has become ionised into a dipole.

E. W. W.

4:4'-Dibenzylidiphenylmethane. E. CONNERADE (Bull. Soc. chim. Belg., 1935, 44, 411—424).— CH_2Ph_2 with CH_2O in AcOH in presence of H_2SO_4 gives a 2 to 3% yield of 4:4'-*dibenzylidiphenylmethane* (I), m.p. 91.5°, with resinous products. 4:4'-*Dichloromethyldiphenylmethane* (II) with AlCl_3 in C_6H_6 yields CH_2Ph_2 and resinous products, without (I). MgPhBr has no action on (II), which is converted by LiPh into an amorphous *polymeride*, with much Ph_2 ; the mechanism of the last reaction is discussed. 4:4'-*Di(chloromethyl)benzophenone* with AlCl_3 in C_6H_6 gives a quant. yield of 4:4'-*dibenzylbenzophenone*, m.p. 85—87° (*oxime*, m.p. 130—131°), which is reduced by Na—Hg to 4:4'-*dibenzyl-diphenylcarbinol*, and oxidised (CrO_3) to 4:4'-*dibenzoyldibenzophenone* (III), m.p. 227.5° (*trioxime*). Benzophenone-4:4'-dicarboxyl chloride with AlCl_3 in C_6H_6 yields (III), with 4-*benzoylbenzophenone-4'-carboxylic acid*, m.p. 268°. (III) is reduced by Na—Hg in EtOH to 4:4'-*di-ω-hydroxybenzylidiphenylcarbinol* (IV), m.p. 176.5°, with a substance (V), m.p. 105—110°. (IV) is converted by HCl in C_6H_6 into 4:4'-*di-ω-chlorobenzylidiphenylmethyl chloride* (VI), m.p. 73°, and (V) into an amorphous compound (VII). (IV) and (V) are regarded as stereoisomeric, as are (VI) and (VII).

E. W. W.

Condensation of resorcinol with α-chloroisobutyl cyanide and isobutyldehyde cyanohydrin. M. YAMASHITA (Sci. Rep. Tohoku, 1935, 24, 205—207).—Resorcinol with $\text{CHPr}^i\text{Cl}\cdot\text{CN}$ gives (Hoesch) 5-*hydroxy-1-isopropylbenzofuran-2-one*, m.p. 174—176°, and with $\text{OH}\cdot\text{CHPr}^i\text{CN}$ 2:4-*dihydroxyphenyl α-hydroxyisobutyl ketone*, m.p. 124—126°, but neither product could be converted into oreoselone.

R. S. C.

Steric hindrance as a factor in the hydrolytic stability of aromatic ketimines. J. B. CULBERTSON, R. ALBRIGHT, D. BAKER, and P. SWETZER (Proc. Iowa Acad. Sci., 1933, 40, 113).—2-Methyldiphenylketimine hydrochloride is hydrolysed much more slowly than the 3- and 4-Me isomerides; this may be due to steric hindrance. The very slow hydrolysis of 2:4:6-trihydroxydiphenylketimine hydrochloride is ascribed to the occurrence of tautomerism with the enamine forms; the much slower hydrolysis of 4:6-dihydroxy-2-methyldiphenylketimine hydrochloride may be a steric effect. CH. ABS. (r)

Formoins. II. P. KARRER and C. MUSANTE (Helv. Chim. Acta, 1935, 18, 1140—1143; cf. this

vol., 623).—Introduction of *p*-Cl or *p*-Br into benzoylformoin greatly increases the tendency towards enolisation. *p*-C₆H₄Cl·COMe is oxidised by SeO₂ in boiling EtOH to *p*-chlorophenylglyoxal, m.p. 122°, converted by KCN in 50% EtOH at room temp. into *pp'*-dichlorobenzoylformoin [*β*-hydroxy- α,δ -triketo- α,δ -di-*p*-chlorophenyl-*n*-butane], m.p. 190°. Similarly, *p*-bromophenylglyoxal monohydrate, m.p. 125°, is transformed into *pp'*-dibromobenzoylformoin, m.p. 196°. H. W.

Condensation of glutar- and adip-dinitriles with resorcinol and phloroglucinol. M. YAMASHITA (Sci. Rep. Tohoku, 1935, 24, 192—196).—CN·[CH₂]₃·CN with resorcinol (I) gives by the Hoesch reaction only γ -2 : 4-dihydroxybenzoylbutyric acid, m.p. 175—178°, but with phloroglucinol (II) gives γ -2 : 4 : 6-trihydroxybenzoylbutyric acid, m.p. 286—286.5°, and α,ϵ -di-2 : 4 : 6-trihydroxyphenylpenta- α,ϵ -dione, m.p. 247—249°. CN·[CH₂]₄·CN with (I) yields α,ϵ -di-2 : 4-dihydroxyphenylhexa- α,ϵ -dione, m.p. 285—288°, and δ -2 : 4-dihydroxybenzoylvaleronitrile, m.p. 157—159°, whilst with (II) only α,ϵ -di-2 : 4 : 6-trihydroxyphenylhexa- α,ϵ -dione, decomp. 265°, could be obtained.

R. S. C.

Condensation of dienes with alkylated quinones. L. F. FIESER and A. M. SELIGMAN (Ber., 1935, 68, [B], 1747—1751).—Contrary to Chuang *et al.* (this vol., 863), hydroaromatic compounds with "angular" Me groups can be obtained from butadiene and alkylated quinones; the Me hamper but do not inhibit the reaction. Treatment of *p*-xyloquinone (I) with butadiene in EtOH containing a little AcOH for 62 hr. at 100—105° affords 12 : 14-dimethyl-1 : 4 : 5 : 8 : 11 : 12 : 13 : 14-octahydroanthraquinone, m.p. 171°, in 2% yield (cf. Adler, this vol., 983) and butadiene-*p*-xyloquinone, b.p. 124—125°/9.5 mm. (semicarbazone, m.p. 200—201°), in 75% yield. Similarly, (I) and CH₂:CMe:CMe:CH₂ afford 2 : 3-dimethylbutadiene-*p*-xyloquinone, b.p. 135—136°/9 mm. (monosemicarbazone, m.p. 205—207°), and di-2 : 3-dimethylbutadiene-*p*-xyloquinone, m.p. 208—209°, in similar yield. C₆H₆ may replace EtOH as solvent, but the use of higher temp. appears to encourage side reactions. The use of pure materials appears essential, and the stability of the products at a given temp. depends somewhat on the solvent employed. Piperylene and 2 : 6-dimethyl-1 : 4-naphthaquinone in EtOH-AcOH at 100—105° give piperylene-2 : 6-dimethyl-1 : 4-naphthaquinone as a viscous oil; piperylenethymoquinone, b.p. 126—128°/2.5 mm., is obtained similarly.

[With J. L. HARTWELL.] The elimination of a loosely-united substituent during the condensation is illustrated by the production of 2 : 3-dimethylantraquinone when 2-hydroxy-1 : 4-naphthaquinone is heated with CH₂:CMe:CMe:CH₂ and air is drawn through the alkaline solution of the product; it is also produced by protracted action from 2-methoxy-1 : 4-naphthaquinone, whereas isonaphthazarin is recovered unchanged.

H. W.

Diene synthesis of anthraquinones. L. F. FIESER and (MRS.) M. FIESER (J. Amer. Chem. Soc., 1935, 57, 1679—1681).— β -Aroylacrylic acids condense with butadiene or (CMe:CH₂)₂ to aroyl- Δ^4 -tetrahydrobenzoic acids, the esters of which are smoothly dehydrogenated and, after hydrolysis, readily yield

anthraquinones. Dehydrogenation or ring-closure of the H₄-acids is not feasible. The β -aroylacrylic acids are prepared in 70—75% yield from the C₆H₆ derivative (0.2 mol.), maleic anhydride (0.21 mol.), and AlCl₃ (0.45 mol.) in C₂H₂Cl₄ at room temp. and by "diene"-addition in dry EtOH at 100—105° give usually > 95% yields of 2-*p*-toluoyl- Δ^4 -tetrahydrobenzoic acid (I), m.p. 151.5°, 2-benzoyl-, m.p. 143° (and a little of an isomeride, m.p. 189°), 2-*p*-toluoyl-, m.p. 167.5°, 2-2' : 4'-, m.p. 150.5° (and a little of an isomeride, m.p. 165.5°), and 2-2' : 5'-dimethylbenzoyl-, m.p. 151°, and *p*-anisoyl-, m.p. 149°, -4 : 5-dimethyl- Δ^4 -tetrahydrobenzoic acid. The Me esters thereof, all oils, with S at 240—245° (30 min.) give *Me* 2-benzoyl-, m.p. 123.5°, 2-*p*-toluoyl-, m.p. 121°, 2-2' : 4'-, m.p. 103.5°, and 2-2' : 5'-dimethylbenzoyl-, m.p. 110°, and 2-*p*-anisoyl-benzoate (II), an oil, whence the corresponding acids, m.p. 197.5°, 194.5°, 204.5°, 230°, and 195.5°, respectively, are obtained. These acids, except (II), with conc. H₂SO₄ at 100° give 2 : 3-dimethyl-, 2 : 3 : 6-trimethyl-, and 2 : 3 : 6 : 8-, m.p. 196°, and 2 : 3 : 5 : 8-tetramethyl-anthraquinone, m.p. 178°. Reduction (Zn dust-NaOH) of (II) gives 2-*p*-methoxybenzyl-4 : 5-dimethylbenzoic acid, m.p. 142°, dehydrated to 6-methoxy-2 : 3-dimethylanthr-10-one, m.p. 151.5°, which yields 6-methoxy-2 : 3-dimethylantraquinone, m.p. 212°. (I) could not be successfully dehydrogenated as acid or ester and gave only a small yield of 2-methylantraquinone.

R. S. C.

Derivatives of phenanthraquinone. A. J. JAKUBOVITSCH and E. VOROBJOVA (J. pr. Chem., 1935, [ii], 143, 281—286).—The prep. of phenanthraquinone is modified. The 2- and 4-NH₂-quinones give (Sandmeyer) 2-, m.p. 243—244°, and 4-chlorophenanthraquinone, m.p. 162—163°, reduced by SO₂ to the corresponding unstable quinols, m.p. 147—149° and 171—172°, respectively. 2-Nitrophenanthraquinone and hot NHPh·NH₂ in C₅H₁₁·OH yield the quinol, which with CH₂N₂ gives 2-nitro-9 : 10-dimethoxyphenanthrene, m.p. 126—127°, reduced by 4% Na-Hg and EtOH (not by SnCl₂) to the unstable 2-NH₂-compound, m.p. 257—258° (decomp.).

R. S. C.

Santal, pterocarpin, and homopterocarpin, the colourless companions of santalin. II. H. RAUDNITZ and G. PERLMANN (Ber., 1935, 68, [B], 1862—1866; cf. A., 1934, 900).—Sandal wood is extracted with Et₂O and the dried extract is treated with EtOAc; after removal of santalin, the filtrate slowly deposits a mixture of crystals, which is separated into its components by CCl₄ or EtOH. Thus are isolated: santal, C₁₃H₁₀O₅, m.p. 218°, the composition of which is supported by analysis of the diacetate, C₁₇H₁₄O₇, m.p. 152°, and *Me*₂ ether, C₁₅H₁₄O₅, m.p. 141°; pterocarpin, C₁₆H₁₁O₄·OMe, m.p. 165°, homopterocarpin, C₁₅H₁₀O₂(OMe)₂, m.p. 87—88°, which is possibly not homogeneous.

H. W.

The original acids in American pine resin. K. KRAFT (Annalen, 1935, 520, 133—143).—Sapic acid (I) (Voeke, A., 1934, 193) is separated by fractional crystallisation from COMe₂ into mixture-A, m.p. 141—144°, [α]_D -60° to -80°, and -B, m.p. 140—142°, [α]_D -126.2°, and *d*-pimaric acid (II). When boiled with AcOH only 80% of A isomerises to abietic acid [from (II)]. In the H₂-PtO₂-EtOH reduction of A

the mother-liquor, after separation of the H_2 -derivative, m.p. 195—198° (*loc. cit.*), affords dihydro-*d*-pimaric acid, separated through the NH_4 and Na salts. Ozonolysis of the Me esters gives an acid product from which is isolated the Me ester of the keto-dibasic acid, $C_{15}H_{22}O_5$, similarly obtained from abietic acid (Ruzicka *et al.*, A., 1933, 279). From the cryst. NH_4 salt of *B* (1% aq. NH_3 < 60°, exclusion of O_2 and light) both *l*- (III) and *d*-pimaric acid are isolated by fractional crystallisation of the Na salts. (I) contains (II) and (III) and, probably, a rearrangement product (IV) of (III). The absorption spectrum of *A* (flat max. at 250 $m\mu$) is probably due to (III) (sharp max. at 272.5 $m\mu$) and (IV). J. W. B.

Cerin and friedelin. I. Their mol. wts. and empirical formulæ. N. L. DRAKE and R. P. JACOBSEN (J. Amer. Chem. Soc., 1935, 57, 1570—1574).—Cork yields to $EtOAc$ cerin (I), $C_{30}H_{50}O_2$, m.p. 247—251° (decomp.), $[\alpha]_{D}^{25} +44.5^\circ$, and friedelin (II), $C_{30}H_{50}O$, m.p. 255—261°, $[\alpha]_{D}^{25} -29.4^\circ$ (enol acetate, benzoate, m.p. 255—262°, $[\alpha]_{D}^{25} +66.2^\circ$, phenylacetate, m.p. 244—251°, $[\alpha]_{D}^{25} +57.1^\circ$, β -phenylpropionate, m.p. 229—233°, $[\alpha]_{D}^{25} +52.8^\circ$, and *p*-iodobenzoate, m.p. 271—274°, $[\alpha]_{D}^{25} +61.2^\circ$), and a trace of a sterol, $C_{27}H_{50}O_2$. (II) is a ketone, (I) a OH-ketone. Both are reduced (Clemmensen) to a hydrocarbon, $C_{30}H_{52}$, m.p. 245—249°. (II) is probably [*n* and $C(NO_2)_4$ -colour] tetracyclic with one unreactive ethylenic linking. R. S. C.

Lignin and related compounds. XII. Methanol-lignin. F. BRAUNS and H. HIBBERT. XII. Structure and properties of glycol-lignin. K. R. GRAY, E. G. KING, F. BRAUNS, and H. HIBBERT. XIV. Action of lead tetra-acetate and of mercuric acetate on glycol-lignin. K. R. GRAY, F. BRAUNS, and H. HIBBERT. XV. Phenol-lignin. F. BRAUNS and H. HIBBERT (Canad. J. Res., 1935, 13, B, 28—34, 35—47, 48—54, 55—60; cf. this vol., 623).—XII. Methanol-lignin (I) (prep. from spruce wood meal, MeOH, and 2% of HCl at 90—100°) (OMe 21.5%) is sol. in NaOH, from which it is pptd. by CO_2 or acids, gives with $Ac_2O-C_5H_5N$ an *Ac* derivative (OMe : OAc = 6 : 4 mols.), insol. in NaOH, and with CH_2N_2 in dioxan a *Me* derivative (II) (OMe 24.1%), insol. in NaOH; (II) gives an *Ac* derivative (OMe : OAc = 7 : 3 mols.), which with Me_2SO_4-NaOH in aq. $COMe_2$ at 40° affords a *product* (III) (OMe 32.3, OAc 0%). If (I) is homogeneous, native lignin (IV) is $C_{42}H_{32}O_6(OH)_5(OMe)_5$. (I) is the Me_6 , (II) the Me_7 , and (III) the Me_{10} ether.

XIII. (IV) contains three primary OH. Glycol-lignin (V), prepared by extraction with glycol and HCl, is probably $C_{42}H_{32}O_6(OH)_4(OMe)_5 \cdot O \cdot [CH_2]_2 \cdot OH$. Glycol compounds give apparent OMe vals. in the Zeisel determination; the necessary correction is determined. (V) is shown to contain $O \cdot [CH_2]_2 \cdot OH$ by the fact that extraction with $OH \cdot [CH_2]_2 \cdot OMe$ gives a *product* with higher OMe content (20%). (V) is a mixture of $CHCl_3$ -insol. (75%; OMe, 17, C 62.6%) and $CHCl_3$ -sol. (25%; OMe 17, C 63.15%) portions, both of which give the same *Ac*₅ (VI), *Bz*₅, (*p*- C_6H_4BrCO)₅, (*p*- $NO_2-C_6H_4CO$)₅, (*p*- $C_6H_4MeSO_2$)₅, and $(CPh_3)_4$ (*Ac* derivative) derivatives, and with CH_2N_2 the

(OMe)₆-compound (VII). (VII) gives a $(CPh_3)_3$ (*Ac* derivative), *Ac*₄, *Bz*₄, and (*p*- $C_6H_4MeSO_2$)₄ derivative and with Me_2SO_4 a (OMe)₁₀-derivative (VIII) (OMe 31.4%), also obtained similarly from (VI). (V) with $HBr-Ac_2O-AcOH$ at 120° gives a *product* (OMe : OAc = 4 : 6 mols.), but with $HI-PhOH$ a *PhOH* condensation product. The mother-liquors from the prep. of (V) contain a lignin-carbohydrate compound.

XIV. (VIII) and $Hg(OAc)_2$ in MeOH-dioxan-AcOH (10 : 1 : 1.5) at 100° give a *product*, $C_{42}H_{32}O_6(OMe)_9 \cdot (HgOAc)_5 \cdot O \cdot [CH_2]_2 \cdot OMe$, sol. in dioxan, indicating the absence of ethylenic linkings and the presence of 5 C_6H_6 or (possibly fewer) heterocyclic rings; previous work is inconclusive in this respect. $Pb(OAc)_4$ in dioxan gives a *product* containing Pb, which after removal of Pb by cold $Ac_2O-C_5H_5N$ has *Ac* 8.35 and OMe (corr.) 25.9%, but reaction was possibly incomplete.

XV. Condensation of (IV) with *PhOH* during extraction is confirmed by union of (V) and its derivatives with 3*PhOH* in presence of HCl without loss of H_2O , etc. (V), *PhOH*, and dry HCl (5%) at 100° give a *product*, $C_{42}H_{32}O_6(OH)_4(OMe)_x \cdot O \cdot [CH_2]_2 \cdot OH, 3PhOH$ (*A*; *x*=5), giving *Bz*₈ and *Ac*₈ derivatives and with CH_2N_2 the compound (IX), $C_{42}H_{32}O_6(OH)_3(OMe)_6 \cdot O \cdot [CH_2]_2 \cdot OMe, 3PhOMe$. (VII) gives the compound (*A*; *x*=6) (*Bz*₇ derivative); (VIII) gives according to the conditions the compound, $C_{42}H_{32}O_6(OMe)_9 \cdot O \cdot [CH_2]_2 \cdot OMe, 3PhOH$, or, by loss of 2Me, the compound, $C_{42}H_{32}O_6(OH)_2(OMe)_7 \cdot O \cdot [CH_2]_2 \cdot OMe, 3PhOH$, affording with CH_2N_2 the (OMe)₁₁-compound, which loses another Me to give the compound, $C_{42}H_{32}O_6(OMe)_6(OBz)_3 \cdot O \cdot [CH_2]_2 \cdot OMe, 3PhOMe$. (IX) and Me_2SO_4 give the *Me*₁₃ ether, $C_{42}H_{32}O_6(OMe)_9 \cdot O \cdot [CH_2]_2 \cdot OMe, 3PhOMe$. Quercetin does not condense with *PhOH*, indicating that flavone groupings are not responsible for the reaction.

R. S. C.

Lignin and related compounds. XVI. Phenol-lignin from spruce wood, from Freudenberg spruce lignin, and Willstatter spruce lignin. I. K. BUCKLAND, F. BRAUNS, and H. HIBBERT. XVII. Methylation of Willstatter and Freudenberg lignins. F. BRAUNS and H. HIBBERT. XVIII. Ligninsulphonic acid—its isolation and structure. E. G. KING, F. BRAUNS, and H. HIBBERT. XIX. Alkali-lignin. H. B. MARSHALL, F. BRAUNS, and H. HIBBERT (Canad. J. Res., 1935, 13, B, 61—77, 78—87, 88—102, 103—113).—XVI. Crude phenol-lignin (OMe 6.4%) which contains one fewer OMe group than the original lignin (cf. B., 1926, 146; A., 1931, 941) is separated by dioxan-Et₂O into lignins $C_{42}H_{32}O_6(OMe)_4(OH)_5(OPh)_3PhOH$ (I) (OMe 10.3%) and $C_{42}H_{32}O_6(OMe)_5(OH)_4(OPh)_3PhOH$ (II) (OMe 5.3%). (I) with $Ac_2O-C_5H_5N$ at room temp. gives an *Ac*₃ derivative (OMe 7.9%) and with CH_2N_2 a (OMe)₅-derivative (OMe 21.6%), probably $C_{42}H_{32}O_6(OMe)_6(OH)_3(OPh)_3PhOH$, which is further acetylated to a *Ac*₃ derivative (OMe 19.1%). The latter or the octa-acetate with $Me_2SO_4-30\% NaOH$ at 40—42° is completely methylated to an (OMe)₈-derivative (OMe 28.2%), probably $C_{42}H_{32}O_6(OMe)_9(OPh)_3PhOMe$. The analytical data from these compounds and the application of the

Brauns-Hibbert hypothesis (A., 1934, 74) indicate that in phenol-lignin, four phenolic residues are associated with the lignin mol., one in the form of an ether (and accounts for the loss of one OMe) and three so as to give free OH-groups. (II) affords a similar series of products [Ac_8 (OMe 4.4%), (OMe)₅- (OMe 22.8%) which with Ac_2O gives a Ac_6 derivative (OMe 21.5%), and (OMe)₈- (OMe 27.3%) -derivatives]. Calculations based on the analytical figures indicate that 1 mol. of lignin has reacted probably with 15 mols. of PhOH, which are firmly bound to the lignin and are not merely adsorbed. Willstätter lignin (III) (cf. A., 1928, 743) and Freudenberg lignin (IV) (cf. A., 1929, 1046) similarly afford phenol-lignins (OMe 12.3 and 11.5%, respectively) which resemble (I), but which have not lost 1 OMe in their formation. The former affords an Ac_8 (OMe 9.6%), a (OMe)₅- (OMe 23.9%) [Ac_3 derivative (OMe 21.6%)], and an (OMe)₈- (OMe 30.0%) -derivative. The latter affords corresponding derivatives with 9.2, 23.5, 21.6, and 29.1% OMe, respectively, somewhat lower than in the above series because they contain the methylene oxide group (see below). The CH_2N_2 and fully methylated products above have a higher OMe content (corresponding with one additional OH capable of methylation) than the analogous derivatives of (I).

XVII. (III) and (IV) (see above) are methylated (CH_2N_2) to compounds (OMe 21.3 and 20.4%, respectively) which with PhOH containing dry HCl at 80° afford sol. phenol-lignins which have one more OMe group than the phenol derivatives of (III) and (IV). Complete methylation of the above four phenol-lignins gives two pairs of compounds (OMe 30.4, 30.0; 28.2, 29.1%, respectively) having the same OMe content, those from (IV) having a lower OMe content probably because of the persistence of a methylene oxide group (cf. A., 1927, 342; 1928, 1227; 1931, 1278). The acetylated and completely methylated phenol-lignins prepared from (III) and (IV), premethylated with CH_2N_2 , are similar to those described previously (see above). (III) and (IV), premethylated with CH_2N_2 , when heated with anhyd. MeOH containing dry HCl under pressure afford methanol-lignins (OMe 24.4 and 22.6%, respectively), different from those obtained by interaction of (III) and (IV) with MeOH. Me_2SO_4 -NaOH at room temp. with (III) and (IV) affords fully methylated lignins, the latter being unchanged by heating with MeOH-HCl under pressure.

XVIII. Ligninsulphonic acid (V) [isolation by a modification of Freudenberg's method (A., 1933, 276) described] with CH_2N_2 in MeOH gives a product (OMe 18.4%) insol. in hot and cold NaOH [with Me_2SO_4 a fully methylated product (OMe 27.7%) is obtained], as does reaction with Ac_2O - C_5H_5N , which probably indicates that a structural change involving $-SO_3H$ accompanies methylation, whereas with MeOH-dry HCl at 80° under pressure it affords a compound, sol. in H_2O and MeOH, which contains one OMe more than the original acid. The neutral *Na* salt of (V) (prepared by pptn. from a solution containing NaOAc with EtOH, by dialysis of a solution containing excess of $NaHCO_3$, and electrometrically) in H_2O at 0° with CH_2N_2 affords a OMe-derivative (OMe 19.4%) [the Ag salt of which with MeI and CH_3PhCl in MeOH

at 80° affords a *Me* (OMe 22.0%) and *benzyl* ester (OMe 18.1%), respectively, in poor yield] sol. in MeOH and H_2O , and with Me_2SO_4 -30% NaOH in $COMe_2$ at 25° gives a fully methylated derivative (OMe 27.7%; cf. A., 1933, 276). Theoretical considerations and analytical figures suggest that formation of (V) is preceded by removal of 1 mol. of H_2O , and support the empirical formula for lignin proposed by Brauns and Hibbert (A., 1934, 74).

XIX. Alkali-lignin, prepared by Mehta's method (A., 1926, 209), is separated into fractions (A) and (B) (OMe 14.9 and 14.0%, respectively), which are insol. and sol. in dioxan- Et_2O , respectively. (A), $C_{61}H_{46}O_{10}(OMe)_6(OH)_7$, with CH_2N_2 in dioxan gives a *product* (OMe 22.2%), insol. in NaOH, which with Ac_2O gives an *Ac* derivative (OMe 19.5%) converted after de-acetylation into a fully methylated *substance* (OMe 31.5%) (fully acetylated analogue has OMe 12.0%). The OMe content of (A) after treatment with MeOH-dry HCl is raised to 20.4% (which indicates the presence of a reactive OH); treatment with CH_2N_2 gives a compound with OMe 28.6%. (A) reacts with PhOH-dry HCl to give a condensation product (OMe 12.9%) of 1 mol. of (A) with 2 mols. of PhOH [Ac_9 (OMe 10.3%), (OMe)₆- (with CH_2N_2) (OMe 25.7%), which with Ac_2O - C_5H_5N gives a Ac_3 derivative (OMe 23.9%), and (OMe)₉- (OMe 30.4%) -derivatives with Me_2SO_4 -KOH, or by simultaneous methylation and de-acetylation of the Ac_9 derivative]. 1 Mol. of (A) condenses with *o*- or *p*- $C_6H_4Br \cdot OH$ (1 mol.) to give products of const. composition (OMe 13.4 and 13.6%, respectively) (cf. Part XVI). (B), $C_{99}H_{69}O_{17}(OMe)_9(OH)_{11}$, affords (Ac_2O - C_5H_5N) an Ac_{11} derivative (OMe 11.7%), an (OMe)₈-derivative (OMe 24.8%) with CH_2N_2 , which with Ac_2O gives an Ac_3 derivative (OMe 22.3%), and the latter with Me_2SO_4 -NaOH gives an (OMe)₁₁-derivative (OMe 28.7%). (B) with PhOH-dry HCl gives two products in which 1 mol. of (B) reacts with 3 mols. and 5 mols. of PhOH, respectively; in each case, one PhOH group is linked through its O atom.

J. L. D.

Jute-lignin. VII. Behaviour of organic compounds towards ClO_2 and its significance for the constitution of lignin. P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 470-475).—The action of ClO_2 on numerous aromatic and aliphatic substances has been examined. Phenols are readily oxidised, especially when >1 OH is present. Phenols become more resistant to oxidation when acetylated or methylated, or when Br, Cl, or NO_2 is present as substituent. Aliphatic OH is attacked by ClO_2 , but not when methylated or acetylated. The CH_2O_2 and CO_2H attached directly to the ring are unattacked by ClO_2 , but side-chains are oxidised to carboxylic acids. That lignin is slowly attacked by ClO_2 is no proof of the existence of a phenolic OH. Pectin in jute is unattacked by ClO_2 and is therefore considered to be aliphatic (cf. A., 1926, 441). From a comparison of the above results with those obtained with various lignins, it is concluded that chloro-, bromo-, and nitro-lignin contain Cl, Br, and NO_2 at least partly in the benzene ring, and that jute-lignin is less highly polymerised than wood-lignins (cf. A., 1933, 1050). The chlorolignin obtained from ClO_2 and lignin is

almost identical with that obtained in the usual way with Cl_2 . H. G. M.

Constitution of abrin. T. HOSHINO (Annalen, 1935, 520, 31—34).—A detailed account of work already noted (this vol., 1131). E. W. W.

Columbin.—See this vol., 1432.

Chemical composition of sundew. II. W. R. WITANOWSKI (Wiadom. Farm., 1935, 62, 1—3; cf. this vol., 420).—Droserone (from *Drosera rotundifolia*, L.) is almost identical with plumbagin. In both the OMe and OH are attached to the benzene, not the quinone, ring. The red colouring matter of *D. rotundifolia* is a pelargonidin pentoside.

CH. ABS. (r)

Constituents of *Cuscuta reflexa*, Roxb.—See this vol., 1432.

Constituents of hsi-hsin.—See this vol., 1433.

Essential oil of *Aristolochia indica*, Linn.—See this vol., 1433.

Catalytic action of active carbon on terpenes and related compounds. S. KIMURA (Bull. Chem. Soc. Japan, 1935, 10, 330—340).—*l*-Menthone and piperitone when heated with active C at 220° give *m*-cresol (I) and thymol, which with C gives (I) and 2:5-dimethylcoumarone. *d*- and *l*- α -Terpineol give dipentene (II). *l*-Menthol and *d*-borneol yield Δ^3 -*p*-menthene and camphene, respectively. Geraniol and linalool give (II), myrcene, and α -camphorene. Citral yields *p*-cymene, whilst citronellal yields isopulegol and diisopulegol ether. Safrole and isosafrole yield dihydrosafrole, 1:3:4- $\text{C}_6\text{H}_3\text{Pr}(\text{OH})_2$, and *p*-cresol. Similarly methyl-eugenol and -isoeugenol yield 1:3:4- $\text{C}_6\text{H}_3\text{Pr}(\text{OMe})_2$ and 4:1:3- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{OMe}$. F. R. G.

Slow combustion of liquid pinane. D. SHOCHET (Bull. Soc. chim. Belg., 1935, 44, 387—394).—When *d*-pinane (99 g.) is oxidised by air at 110° , O_2 (12 litres in 3 weeks) is rapidly absorbed after a short induction period, the residual gas contains O_2 0.6, CO_2 33.3—35.6, CO 8.8—10.1, H_2 23.8—26, and CH_4 0.95%, and the liquid products contain 4-acetyl-1:1-dimethyl-2-ethylcyclobutane (less probably 1:1-dimethyl-2- γ -keto-*n*-butylcyclobutane) (I), b.p. 80—82°/16 mm., $[\alpha]_{\text{D}}^{25} + 74.74^\circ$ (semicarbazone, m.p. 196.1°; gives CHI_3 with NaOI), a small amount of a ketone (semicarbazone, m.p. 228°), a mixture, b.p. 92—102°/10 mm. (about $\text{C}_{10}\text{H}_{18}\text{O}$), of neutral substances (including an alcohol), acids, and more highly oxygenated neutral substances. (I) is shown to differ from tetrahydrocarvone, prep. from carvone by H_2 -Pd-black in Et_2O . R. S. C.

Transformation of camphene into isobornyl esters. G. BRUS and J. VEBRA (Bull. Inst. Pin, 1935, 109—120, 187—192).—Camphene (I) and AcOH or HCO_2H with or without catalysts give optimum yields of about 92 and 98%, respectively, of isobornyl esters and some unchanged (I). The esters decompose into (I) and some diterpene in presence of the catalyst. The existence of an equilibrium is thus proved; it is believed to be ionic in nature, since the speed with which it is attained increases with the *k* of the acid. The following complexes (*X*—isobornyl

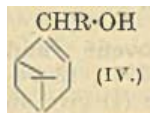
acetate) are isolated; they are probably intermediates in and catalysts for the formation and decomp. of the esters. $\text{X}\cdot\text{H}_3\text{PO}_4$, m.p. 64—66°; $\text{X}\cdot\text{SbCl}_3$, m.p. 72—73°; $\text{X}\cdot\text{ZnCl}_2$; $2\text{X}\cdot\text{H}_4\text{P}_2\text{O}_7$. Similar complexes are formed by bornyl acetate, but not by the formates. R. S. C.

Alkaloid salts of camphorsulphonic acid. D. Fusco (Boll. Chim. farm., 1935, 76, 585—587).—The hydrochlorides of optochin (*M*) and of quinine (*N*) react with the Ca salt of camphorsulphonic acid (*HX*) to form the camphorsulphonates, $\text{M}\cdot 2\text{HX}$ and $\text{N}\cdot\text{HX}\cdot 9\text{H}_2\text{O}$. The latter is sufficiently sol. to be employed therapeutically in aq. solution. E. W. W.

Caryophyllene series. IV. Clovene and clovenic acid. R. D. BLAIR (J.C.S., 1935, 1297—1298).— MgMeI and clovenic anhydride (I) give an acid product, $\text{C}_{16}\text{H}_{23}\text{O}_3$, m.p. 195° , reduced (Na) to an acid substance, m.p. 137—138°. (I) and MgPhBr yield a neutral product (II), $\text{C}_{27}\text{H}_{32}\text{O}_2$, m.p. 212° , and an acid product, $\text{C}_{21}\text{H}_{28}\text{O}_3$, m.p. 269° ; (II) is oxidised ($\text{CrO}_3\text{--AcOH}$) to a neutral substance, $\text{C}_{27}\text{H}_{28}\text{O}_3$, m.p. 244° , and an unsaturated acid, $\text{C}_{23}\text{H}_{17}\text{O}_3$, m.p. 185—186°. Clovenic acid and anhydride give the same $(\text{NH}_4)_2$ salt, m.p. 168—170° (decomp.). The structure of clovenic acid is discussed. F. R. S.

Synthese in the myrtenol series. W. S. ZACHAREWICZ (Bull. Inst. Pin, 1935, 143—167).—*dl*-, *d*-, and *l*-Pinene with SeO_2 at $60\text{--}70^\circ$ give myrtenal (I) 14.3, myrtenol (II) 32.8, and hydrocarbons (III) 25.8%. The following are described. *d*-, b.p. 106—107°/11 mm., $[\alpha]_{\text{D}} + 44.11^\circ$ (*H phthalate*, m.p. 114—115°, $[\alpha]_{\text{D}} + 21.25^\circ$ in EtOH; benzoate, b.p. 102.5—104°/9 mm., $[\alpha]_{\text{D}} + 45.32^\circ$), *l*-, b.p. 111—112°/11 mm., $[\alpha]_{\text{D}} - 42.73^\circ$ (acetate, b.p. 134.5—135.5°/38 mm.), and *dl*-myrtenol, b.p. 106.5—107°/13 mm. (*H phthalate*, m.p. 120—120.5°). 1-Myrtenyl chloride (prep. by PCl_5 in ligroin), b.p. 112°/45 mm., $[\alpha]_{\text{D}} - 29.2^\circ$. *d*-, b.p. 99—100°/15 mm., $[\alpha]_{\text{D}} + 14.75^\circ$ [obtained with $[\alpha]_{\text{D}} + 17.02^\circ$ from (II) and CrO_3], *l*-, b.p. 115.5—117°/31 mm., $[\alpha]_{\text{D}} - 16.72^\circ$, and *dl*-myrtenal, b.p. 94—95°/11 mm. (*d*-, two forms, m.p. 225° and 217°, respectively, and *dl*-semicarbazone, m.p. 200.5°; *d*-, m.p. 70.5—71.5°, $[\alpha]_{\text{D}} + 16.25^\circ$ in EtOH, and *dl*-oxime, m.p. 101°). *d*-Myrtenonitrile, b.p. 106°/12 mm., $[\alpha]_{\text{D}} + 54.89^\circ$. *d*-Myrtenic acid (from the nitrile or aldehyde), m.p. 53—54°, $[\alpha]_{\text{D}} + 51.13^\circ$ in EtOH. (I) and KMnO_4 give an active pinic acid, m.p. 80—81°, and the *dl*-form, m.p. 101—102.5°. The Cannizzaro reaction proceeds anomalously. (I), COMe_2 , and aq. $\text{Ba}(\text{OH})_2$ give *d*-myrtenylideneacetone, b.p. 158—159°/20 mm., $[\alpha]_{\text{D}} - 28.42^\circ$ (oxime, an oil; semicarbazone, m.p. 209—209.5°, $[\alpha]_{\text{D}} - 23^\circ$ in EtOH), hydrogenated (PtO_2) in AcOH with absorption of 6H to a mixture, b.p. about 142.5—143.5°/15 mm., $[\alpha]_{\text{D}} + 26.18^\circ$. By aerial oxidation of *d*-pinene in presence of Co abietate are prepared *d*-verbenol, b.p. 99—100°/11 mm., $[\alpha]_{\text{D}} + 103.35^\circ$, and *d*-verbenone, b.p. 104—105°/15 mm., +237.4° [semicarbazone, m.p. 206—207° (decomp.), $[\alpha]_{\text{D}} + 77.6^\circ$ in EtOH; hydroxylamino-oxime, m.p. 163° (decomp.); oxidised by KMnO_4 to pinonic acid, m.p. 130—131°]. The *H phthalates* of (II) with Na in xylene give *l*-, b.p. 126.5—127.5°/22 mm., $[\alpha]_{\text{D}} - 26.06^\circ$ (*H phthalate*, m.p. 108.5—109°,

$[\alpha]_D -15^\circ$ in EtOH; *acetate*, b.p. 127.5—128.5°/18 mm., $[\alpha]_D -21.51^\circ$, and *dl-trans-myrtanol*, b.p. 122—123°/19 mm. (*H phthalate*, m.p. 114.5—116°), oxidised by CrO_3 to *dl-trans-myrtanal*, b.p. 100—112°/14 mm. (*semicarbazone*, m.p. 169—170°). Hydrogenation (PtO_2) of (I) or (II) in AcOH gives *d-*, b.p. 122°/20 mm., $[\alpha]_D +20.67^\circ$, *l-*, b.p. 127.5—128.5°/26 mm., $[\alpha]_D -24.48^\circ$ (*H phthalate*, m.p. 124.5—125.5°, $[\alpha]_D +3.75^\circ$, -4.6° in EtOH; *d-acetate*, b.p. 132.5—133.5°/26 mm.), and *dl-cis-(iso)myrtanol*, b.p. 125—126°/21 mm. (*H phthalate*, m.p. 126.5—127.5°; *chloride*, unstable, b.p. about 87—97°/22 mm.), oxidised to *dl-cis-(iso)myrtanal* (*semicarbazone*, m.p. 194—195°). *l-Myrtanal* gives by the Grignard reaction "*l-methyl-*" (IV; $\text{R}=\text{Me}$), b.p. 108—109°/13 mm., $[\alpha]_D -40.14^\circ$, "*l-ethyl-*" b.p. 117.5—119°/18 mm., $[\alpha]_D -31.72^\circ$, and "*l-phenyl-myrtanyl*



alcohol," b.p. 180—182°/13 mm., $[\alpha]_D -10.03^\circ$ (*H phthalate*, an oil). Hydrogenation (PtO_2) of (IV; $\text{R}=\text{Me}$) in AcOH gives an *alcohol*, b.p. 114—115°/12 mm., $[\alpha]_D -22.19^\circ$ (*acetate*, b.p. 122.5—123.5°/15 mm., $[\alpha]_D -22.56^\circ$), whereas Na in xylene gives an *alcohol*, b.p. 121—122°/16 mm., $[\alpha]_D -19.28^\circ$ (*acetate*, b.p. 126—127°/18 mm., $[\alpha]_D -16.75^\circ$). (IV; $\text{R}=\text{Et}$) gives similarly *alcohols*, b.p. 119—120°/12 mm. and 130—131°/14 mm., $[\alpha]_D -27.44^\circ$ and -23.87° , respectively (*acetate* of the second, b.p. 136—137°/19 mm., $[\alpha]_D -27.72^\circ$), and with CrO_3 gives a *substance*, b.p. 130—133°/12 mm. [*semicarbazone*, m.p. 192—193° (decomp.); *oxime*, an oil]. (III) consists mostly of *nopinene* (V) (*l-* from *d-* and *d-* from *l-pinene*) and small amounts of a diethylenic (conjugated) *hydrocarbon* (VI) (of opposite α to that of the pinene used). Hydrogenation of the first fractions of (III) gives a mixture of *pinane* [from the (V)] and *pinene* [from the (VI)]. Oxidation gives *nopinic acid*, a neutral *substance*, m.p. 126—126.5°, $\text{H}_2\text{C}_2\text{O}_4$, and an *acid*, possibly $\delta\epsilon$ -*diketo- β -carboxy- $\gamma\gamma$ -dimethylheptioic acid*, m.p. 226—227°. (VII) is thus probably $\Delta^{1,5}$ -*pinadiene*. Physical data and Raman spectra are given, the latter being much used for identification.

R. S. C.

Constitution of cedrene. W. F. SHORT (Chem. and Ind., 1935, 874).—The annexed

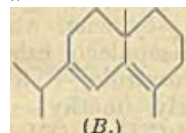
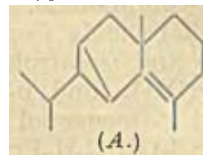


suggested structure reconciles that proposed by Ruzicka and van Melsen (A., 1929, 932) with the formation of *camphoronic acid* on oxidation (this vol., 983).

E. C. S.

Elucidation of the constitution of sesquiterpenes by powerful oxidative degradation. II. α -*Gurjunene* and *gurjun-azulene*. W. TREIBS (Ber., 1935, 68, [B], 1751—1756).—The proportion of α -gurjunene (I) in an oil of balsam, $\alpha_D -75^\circ$, could be increased to about 90% by fractional distillation in a vac., whilst β -gurjunene (II) could be isolated from a second oil, $\alpha_D +12^\circ$, by destruction of (I) by oxidation. A partial separation of (I) and (II) can be achieved by fractional extraction with EtOH, in which (II) is more freely sol. Catalytic hydrogenation (Pd-sponge) of (I) and (II) affords α - (III), $\alpha_D -18^\circ$, and β -, $\alpha_D -42^\circ$, -gurjunane, the physical consts. of which show the sesquiterpenes to

belong to different ring systems. Contrary to Deussen *et al.* (A., 1915, i, 273), the regenerated product from α -gurjugene hydrochloride differs from (I) in α_D according to the temp. at which the hydrochloride is produced; since on hydrogenation it yields essentially (III), the operations are not accompanied by ring fission and formation of a new double linking, but by transposition of an existing linking. A hydrochloride could not be isolated from (II) and HCl; isomerisation occurs with production of iso- β -gurjunene, $\alpha_D -36^\circ$, hydrogenated to a *tetrahydride*, $\alpha_D -15^\circ$, thus establishing the conversion of a tricyclic sesquiterpene with a double linking into a bicyclic system with two double linkings. A similar isomerisation is observed in the action of hot $\text{AcOH-H}_2\text{SO}_4$ on (I), whereby iso- α -gurjunene (IV), $\alpha_D -135^\circ$ (*tetrahydride*, $\alpha_D -10^\circ$), which does not add HCl, is produced. (I) is oxidised by hot aq. KMnO_4 to $\text{H}_2\text{C}_2\text{O}_4$ and AcOH , whereas CH_2O or COMe_2 is not produced. More powerful oxidation by KMnO_4 in COMe_2 affords $\text{H}_2\text{C}_2\text{O}_4$ and much $(\text{CH}_2\text{-CO}_2\text{H})_2$, but not $\text{CMe}_2(\text{CO}_2\text{H})_2$, thus establishing the absence of CMe_2 . Still more drastic action of KMnO_4 succeeded by prolonged treatment of the product with hot, dil. HNO_3 gives a liquid tricarboxylic acid $\text{C}_9\text{H}_{14}\text{O}_6$, which yields a Me_3 ester, b.p. 165—167°/20 mm., $\alpha_D \pm 0^\circ$; 0.1N-KOH hydrolyses two ester groups of the latter, whereas N-KOH is required for hydrolysis of the third group. The formulæ A and B are therefore suggested for (I) and (IV), respectively:



H. W.

Essential oil of black tea.—See this vol., 1289.

Decarboxylation of furantetracarboxylic acid. H. GILMAN, H. OATFIELD, and W. H. KIRKPATRICK (Proc. Iowa Acad. Sci., 1933, 40, 112).—Et furantetracarboxylate is prepared by the self-condensation of Et oxalacetate and may be progressively decarboxylated. Of the products, *uran-3:4-dicarboxylic acid* is of interest for purposes of abs. orientation; the method is the best available for the prep. of 3-furoic acid.

CH. ABS. (r)

Optical absorption and double linking.—See this vol., 1300.

Substances analogous to graphite.—See this vol., 1333.

Synthesis of 6-hydroxy-7-methoxycoumarin-5-acrylollactone. M. YAMASHITA (Sci. Rep. Tohoku, 1935, 24, 202—204).—Pyrogallol and $\text{CH}_2\text{Cl-CN}$ yield (Hoesch) ω -chlorogallacetophenone, which with malic acid and conc. H_2SO_4 gives a poor yield of 7:8-dihydroxy-6-chloroacetyl coumarin, m.p. 228—229°, converted by warm aq. NaHCO_3 into 6-hydroxy-7-methoxycoumarin-5-acrylollactone, m.p. 229—230.5°.

R. S. C.

Pyrylium derivatives by condensation of saturated ketones. T. L. DAVIS and (Miss) C. B. ARMSTRONG (J. Amer. Chem. Soc., 1935, 57, 1583—1585).— $p\text{-OMe-C}_6\text{H}_4\text{-COMe}$ and H_2SO_4 yield *s*-tri-anisylbenzene (11%; cf. A., 1913, i, 172) and

2 : 4 : 6-trianisylpyrylium *H* sulphate [corresponding picrate, m.p. 283—284°, and platinichloride, m.p. 261.5—263.5° (decomp.)]. COPhMe yields similarly a 2 : 4 : 6-triphenylpyrylium salt. Anisylidene-*p*-methoxyacetophenone gives by Diltney's method 2 : 4 : 6-trianisyl-3-methylpyrylium picrate, m.p. 190.4—195° [platinichloride, m.p. 239—240° (decomp.)], thus confirming the loss of Me in the above reactions. R. S. C.

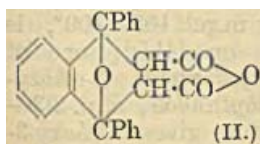
Reactions of *o*-hydroxybenzylidenediace-
tophenones. IV. Unsymmetrical 1 : 5-diketones. D. W. HILL. V. Functional group reactions of salicylidenediace-
tophenone. A. S. GOMM and D. W. HILL (J.C.S., 1115—1118, 1118—1120).—IV. α -Dibenzoyl- α -phenyl- β -*o*-hydroxyphenylpropane, m.p. 198° [from Ph styryl ketone (I) and deoxybenzoin (II)], is incompletely converted by AcOH into a mixture of 4-(α -phenylphenacyl)flavene (III), m.p. 135—136°, and 4-(α -phenylphenacylidene)flavene, m.p. 162—163°, and by HCl-AcOH-FeCl₃ into flavylum ferrichloride (IV). (III) with HCl and FeCl₃ affords 4-(α -phenylphenacyl)flavylum ferrichloride, m.p. 196°. 2-(β -Benzoyl- α -*o*-hydroxyphenylethyl)cyclohexanone (V), m.p. 157—158° [from (I) and cyclohexanone], with AcOH gives 11-hydroxy-9-phenacyl-1 : 2 : 3 : 4 : 10 : 11-hexahydroxanthene (VI), m.p. 123°, and with HCl-AcOH followed by FeCl₃ affords 1 : 2 : 3 : 4-tetrahydroxanthylum ferrichloride, m.p. 127°, also prepared from (VI). 2-(β -Benzoyl- α -*o*-hydroxyphenylethyl)cyclopentanone, m.p. 195° [from (I), cyclopentanone, and NH₄Et₂], is converted into (IV) by HCl-AcOH-FeCl₃. A by-product formed in the reaction between (I) and (II) is shown to be identical with a condensation product of (II) with COPhMe.

V. Salicylidenediace-
tophenone (VII) has been treated with various reagents to decide whether the *o*-hydroxybenzylideneacetophenones which are insol. in alkali and give no colour with FeCl₃ have the diketone or chromanol structure. (VII) with Ac₂O gives an Ac derivative, and with CH₂N₂ *o*-methoxybenzylidenediace-
tophenone. The products from (VII) and MgPhBr depend on the conditions; in C₆H₆, 2 : 2 : 4-triphenylchroman (VIII), m.p. 216—217°, is obtained, but in Et₂O the product is probably α α -triphenyl- γ -(*o*-hydroxyphenyl)-*n*-propyl alcohol (IX), m.p. 185°. 4-Phenacylflavene and MgPhBr give 4-(β -hydroxy- β -diphenylethyl)flavene, m.p. 194°. Formation of (VIII) and (IX) is accounted for by elimination of one of the COPh·CH₂ groups of (VII). 4-Phenacylidene-flavene and MgPhBr do not interact. It is suggested that the diketone and chromanol forms are tautomeric. P. G. C.

Constitution of the anthocyanins. L. F. LEVY (J. S. African Chem. Inst., 1935, 18, 27—35).—A review.

Action of maleic anhydride on diphenylisobenzofuran. E. DE B. BARNETT (J.C.S., 1935, 1326).

—Maleic anhydride and 1 : 2-diphenylisobenzofuran (I) C₂H₄Cl₂ give an *adj*ect (II), m.p. 279° (decomp.), which decomposes easily in solution. Benzquinone and (I) similarly form a product, m.p. 203° (decomp.). F. R. S.



Chemical morphology in the benzene, thiophen, and furan series. C. WEYGAND and F. STROBELT (Ber., 1935, 68, [B], 1839—1847).—The seeding relationships and morphology of a series of compounds obtained by replacing the Ph of Ph styryl ketone by thiophen or furan residues are described in detail. The following are described: 2-thienylideneacetophenone, $\text{CH}=\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{S} \end{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{Bz}$, forms, m.p. 59°, 58°, from thiophen-2-aldehyde (I) and COPhMe; benzylidene-2-acetothienone,

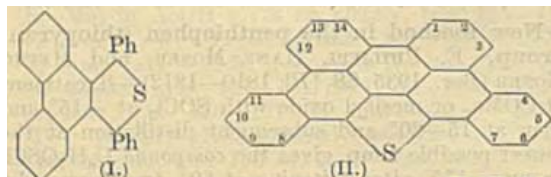
$\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{S} \cdot \text{CH} \end{smallmatrix}$, forms, m.p. 82°, 74°; 2-thienylidene-2-acetothienone, varieties, m.p. 99°, 91°, 85°, 83°, 79°, 75°, 66°, 43°, from (I) and 2-acetylthiophen; 2-furfurylideneacetophenone, forms, m.p. 46°, 36°, 29°; 2-benzylideneacetofurone, forms, m.p. 88°, 45°, 41°; 2-furfurylidene-2-acetofurone, forms, m.p. 89°, 61°, 57°; 2-furfurylidene-2-acetothienone, forms, m.p. 71°, 54°, 53°; 2-thienylidene-2-acetofurone, forms, m.p. 80°, 72°, 48°. H. W.

New method in the penthiophen (thiopyran) group. E. PHILIPPI, HANS MOSER, and HEIMO MOSER (Ber., 1935, 68, [B], 1810—1812).—Treatment of COMe₂ or mesityl oxide with SOCl₂ at -15° and then at 15—20° and subsequent distillation at the lowest possible temp. gives the compound C₆H₇OSCl, decomp. 125° after softening at 80°, transformed by dil. alkali into 5-keto-3-methylpenthiophen (I), $\text{CH} \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{S}$, m.p. 182° (decomp.) (phenylhydrazones, m.p. 141°). (I) is very stable towards acids; when warmed with alkali and then acidified it affords H₂S and resinous material. H. W.

Comparison of heterocyclic systems with benzene. IV. Thionaphthenquinones. L. F. FIESER and R. G. KENNELLY (J. Amer. Chem. Soc., 1935, 57, 1611—1616; cf. A., 1932, 170).—Thionaphthenquinones are synthesised and found to have a reduction potential about 75 mv. > the corresponding naphthaquinones, indicating that the thiophen ring is less aromatic than the C₆H₆ ring; other considerations indicate a still greater difference, and the S may be responsible for the relatively small difference in reduction potential. 4-Nitrothionaphthen-1-carboxylic acid, m.p. 239—241° (modified prep. from *o*-C₆H₄Cl·CHO by way of 3-chloro-6-nitrobenzaldehyde, m.p. 72—77°), with Cu in quinoline at 180—190° gives CO₂ and 4-nitrothionaphthen, m.p. 149—150°, reduced by SnCl₂ to the 4-NH₂-compound, which yields 51% of pure 4-hydroxythionaphthen, m.p. 103—104°. This with NaNO₂ and ZnCl₂ in EtOH gives the Zn salt of its 3-NO-derivative, which on reduction by SO₂ and subsequent sulphonation gives 3-amino-4-hydroxythionaphthen-6-sulphonic acid, cryst. This is oxidised by 33% HNO₃ at 30° to 3 : 4-thionaphthenquinone-6-sulphonic acid (K salt, +H₂O), which with H₂SO₄-MeOH gives 4-methoxy-3 : 6-thionaphthenquinone (I), m.p. 205—206°. Thiophen and (CH₂·CO)₂O with AlCl₃ in PhNO₂ yield γ -keto- γ -1-thienyl-*n*-butyric acid, m.p. 119—120°, reduced (Clemmensen, cold, not hot) to γ -1-thienyl-*n*-butyric acid, m.p. 13.5—15°, b.p. 130—134°/1.5 mm., the acid chloride (prep. by SOCl₂), b.p. 104—110°/2 mm., of which with SnCl₄ in CS₂,

gives 3-keto-3:4:5:6-tetrahydrothionaphthen, b.p. 102—110°/2 mm., m.p. 35.5—37°; this is dehydrogenated by S (badly by Se) to give a 46% yield of 3-hydroxythionaphthen (II), m.p. 80—81° (lit., 72°). With $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ this phenol yields 4-thionaphthoacetic acid, m.p. 152—153°. 6-Amino-3-hydroxythionaphthen hydrochloride, cryst., prepared from (II) by way of the $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2$ -compound, with $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ gives 3:6-thionaphthenquinone, m.p. 130—131° [monosemicarbazone, probably a mixture, m.p. 235° (decomp.)], which with $\text{H}_2\text{SO}_4\text{-Ac}_2\text{O}$ at 40° yields 3:4:6-triacetoxylthionaphthen, m.p. 151—153°, converted by hydrolysis, FeCl_3 -oxidation, and methylation into (I). R. S. C.

Thiophen series. XXIX. Flavophen. W. STEINKOPF (Annalen, 1935, 519, 297—300).—When tetraphenylthiophen is heated with AlCl_3 at 115—120°, 2:5-diphenyl-3:4-phenanthrenothiophen (I), m.p. 260°, and flavophen (II), m.p. 391—392° (2:5:7:8:10:13-hexanitro-derivative), are formed.



Reactions of diphenylethyleneimines and attempts to prepare aminoethenes. G. H. COLEMAN and G. P. WAUGH (Proc. Iowa Acad. Sci., 1933, 40, 115).—Diphenylethyleneimine (I) is unaffected by O_3 ; BzCl in $\text{C}_5\text{H}_5\text{N}$ yields the Bz derivative, but in dil. NaOH $\alpha\beta$ -diphenyl- β -chloroethylamine is formed, which yields benzoyldiphenylethyleneimine with NaOEt . (I) rearranges to benzylidenbenzylamine on heating to 225°. CH. ABS. (r)

Electrolytic reduction of succinimide. B. SAKURAI (Bull. Chem. Soc. Japan, 1935, 10, 311—313).—Electrolytic reduction at 38—40° of the imide in 50% H_2SO_4 using a Zn-Hg cathode with c.d. 100 amp. per sq. dm. gives 28% of pyrrolidine.

F. R. G.

Synthesis of pyrrole alcohols. Q. MINGOIA (Gazzetta, 1935, 65, 459—461).—The main product of the action of CH_2O on Mg-pyrrole is the di-ether described by the author (A., 1932, 1261); the 1-pyrrolylcarbinol obtained by Taggart and Richter (A., 1934, 901) is regarded as a secondary product formed at low temp. E. W. W.

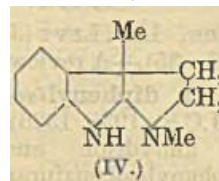
Reactivity of the carbonyl group in γ -pyrones and in γ -pyridones. D. N. BEDEKAR, R. P. KAUSHAL, and S. S. DESHPANDE (J. Indian Chem. Soc., 1935, 12, 465—469).— γ -Pyrones and γ -pyridones manifest carbonyl-reactivity when a sufficiently reactive phenylhydrazine is used. Thus, Et chelidonate, when heated with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ (I) in EtOH, yields its *p*-nitrophenylhydrazone, m.p. 216°, which with AcOH-HCl regenerates the pyrone. Et 3:5-dibromochelidonate *p*-nitrophenylhydrazone, similarly prepared, has m.p. 120°. $\text{CO}[\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}]_2$ when boiled for a short time with (I) in EtOH affords Et 1-*p*-nitroanilino-4-pyridone-2:6-dicarboxylate, m.p.

146°, and some of its *p*-nitrophenylhydrazone, m.p. 210°. This last is the chief product when heating is continued for 1 hr. (I) when refluxed with diacetylacetone and EtOH during 10 min. yields 1-*p*-nitroanilino-2:6-dimethyl-4-pyridone, m.p. 136° (*p*-nitrophenylhydrazone, m.p. 215°). No reaction occurs with (I) and dimethyl-, diethyl-, or dipropyl-pyrone, but with pyrone and hot AcOH 1-*p*-nitroanilino-4-pyridone-*p*-nitrophenylhydrazone, m.p. 242°, is obtained. Similarly (I) when heated with chelidonic acid in dil. AcOH yields 1-*p*-nitroanilino-4-pyridone-2:6-dicarboxylic acid *p*-nitrophenylhydrazone, m.p. 210°, and (I) with Et comanate in EtOH yields Et 1-*p*-nitroanilino-4-pyridone-2-carboxylate *p*-nitrophenylhydrazone, m.p. 220°. H. G. M.

Production of 3:6-diamino-2-alkylpyridines.—See B., 1935, 894.

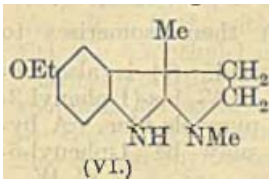
Preparation of substituted indoles by catalytic decomposition of phenylhydrazones. A. E. ARBUSOV, J. A. SAIZEV, and A. J. RASUMOV (Ber., 1935, 68, [B], 1792—1794).—Catalytic decomp. of $\text{C}(\text{EtPr})\cdot\text{N}\cdot\text{NHPh}$ in presence of CuCl at 200—250° yields 2:3-diethyl- or 3-methyl-2-*n*-propyl-indole, b.p. 167°/15 mm. (picrate, m.p. 144°). $\text{CMeBu}^n\cdot\text{N}\cdot\text{NHPh}$ similarly affords NH_3 , NH_2Ph , and 2-methyl-3-*n*-propylindole, b.p. 159—161°/11 mm. (picrate, m.p. 134°), whilst 2-phenyl-3-methylindole, m.p. 112.5° (picrate, m.p. 138.5—139°), is derived from *Ph Et ketone phenylhydrazone*, m.p. 47°. H. W.

Synthesis in the indole group. XIII. Synthetical experiments with eserine. IV. Synthesis of *dl*-eserethole. T. HOSHINO and T. KOBAYASHI. XIV. Synthesis of bufotenin. 3- β -Hydroxyethylindolenine. T. HOSHINO and K. SHIMODAIRA (Annalen, 1935, 520, 11—19, 19—30).—XIII. When *l*-eserethole methiodide is heated with AgCl in EtOH and the product distilled in vac., physostigmol Et ether is obtained. By action of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ on tryptamine, or of $\text{NHPh}\cdot\text{NH}_2$ and ZnCl_2 in EtOH on γ -*p*-toluenesulphonamidobutaldehyde Et₂ acetal (I) (obtained from the amine), *p*-toluenesulphonyltryptamine [3-(β -*p*-toluenesulphonamidoethyl)indole] (II), m.p. 113—114° (*Bz*₂ derivative, m.p. 176—177°), is obtained. Action of MeI-NaOH on (II) or of $\text{NHPh}\cdot\text{NH}_2$ on γ -*p*-toluenesulphonmethylamidobutaldehyde Et₂ acetal (III) [from (I) and MeI] yields 3-(β -*p*-toluenesulphonmethylamidoethyl)indole, m.p. 116—117°. The last is converted by NH_4Ph , $\text{NH}_2\text{Ph}\cdot\text{HCl}$, and EtOH into *N*-methyltryptamine [3- β -indolylethylamine], m.p. 89—90° (picrate, m.p. 190—191°; *Bz* derivative, m.p. 144—145°), which

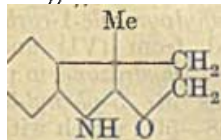


with MgEtI , followed by MeI, yields isodeoxynereseroline (IV), m.p. 111—112°. Using 5-ethoxytryptamine and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, or $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, and (I), 5-ethoxy-3-(β -*p*-toluenesulphonamidoethyl)indole, m.p. 108—109°, is obtained. Action of MeI on this, or of $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ on (III), yields 5-ethoxy-3-(β -*p*-toluenesulphonmethylamidoethyl)indole, m.p. 93—94°, which when treated as before gives 5-ethoxy-3- β -methylaminoethylindole (V), m.p. 99—100°, b.p. 179—184°/2—3 mm. (picrate, m.p. 209—210°; *Bz*₂

derivative, m.p. 119—120°; *flavinate*, m.p. 217—219°). With MgEtI followed by MeI , this furnishes *isonoreserethole* (VI), m.p. 71—72° (*Bz* derivative; *H* oxalate, m.p. 152—153°), of which the *hydrochloride* is converted by MeI into *di-eserethole* (cf. this vol., 227, 499, 765).



XIV. The following experiments were with the object of preparing (V) (above) from 5-ethoxy-3- β -hydroxyethylindole. The *Et* ester, b.p. 195—196° (*picrate*, m.p. 120°), of 2-methyl-3-indolylacetic acid is converted (Na in EtOH) into 2-methyl-3- β -hydroxyethylindole, m.p. 55—56° (*picrate*, m.p. 134—5°; *Ac*₂ derivative, m.p. 96—97°). This with PBr_3 forms 2-methyl-3- β -bromoethylindole, which with NHMe , in MeOH at 100° yields 2-methyl-3- β -dimethylaminoethylindole, m.p. 97—98° (*picrate*, m.p. 174—175°; *methiodide*, m.p. 238—239°), with NH_2Me yields the 3- β -methylaminoindole, m.p. 82—83° (*picrate*, m.p. 193—194°), and with aq. NH_3 and MeOH at 100° forms β -2-methylindolyethylamine (A., 1933, 164). From *Et* 3-indolylacetate, tryptophol is prepared, new m.p. 58—59° (cf. A., 1931, 97), and converted (PBr_3) into β -3-indolyethyl bromide, m.p. 98—99°, and thence, by use of NHMe_2 , NH_2Me , or NH_3 , into *NN*-dimethyltryptamine, m.p. 49—50°, b.p. 165—168°/3.5 mm. (*picrate*, m.p. 170—171°; *methiodide*, m.p. 210—211°), *N*-methyltryptamine (see above), or tryptamine. 5-Ethoxy-3-indolylacetic acid, m.p. 91—92°, is prepared from the nitrile, and its *Et* ester, m.p. 89—90°, is reduced to α -ethoxy-3- β -hydroxyethylindole, m.p. 75°. The 3- β -bromoethyl compound when treated with NHMe_2 in MeOH yields 5-ethoxy-*NN*-dimethyltryptamine (*bufotenin Et ether*) (VII), b.p. 230—232°/5 mm. (*dipicrate*, m.p. 124—125°, which when cryst. from C_6H_6 gives the *picrate*, m.p. 144—145°), with a substance, m.p. 145° (decomp.), regarded as *dimethylbis*- β -5-ethoxy-3-indolyethylammonium bromide (*picrate*, m.p. 120°). (V) and α -ethoxytryptamine are similarly prepared. AlCl_3 in C_6H_6 converts (VII) into *bufotenin* (cf. A., 1934, 1232) (*mono*- and *di*-*picrates*, each m.p. 177—178°; mixed m.p. 164°). Tryptophol treated with MgEtI , followed by MeI , gives 3-methyl-3- β -hydroxyethylindolenine, m.p. 42—43°, b.p. 110—112°/2 mm. (*Ac* derivative, m.p. 74—75°, without basic properties; *Bz*, m.p. 151—152°, and *NO*-, m.p. 63—64°, derivatives), which is considered to exist in the furan form :



E. W. W.

Synthesis of sulphur derivatives of indole. H. WUYTS and (MLLE.) A. LACOURT (Bull. Acad. roy. Belg., 1935, [v], 21, 736—743).—When heated with 10% MeOH-HCl β -phenylthioacetyl- and β -*m*-tolylthioacetyl- α -phenyl- α -S-dimethylhydrazine (this vol., 1119) are converted with loss of NH_3 into 2-methylthiol-3-phenyl-, m.p. 96°, and 2-methylthiol-3-*m*-tolyl- (*picrate*, m.p. 84°) -1-methylindole, respectively. β -Phenylthioacetyl- α -phenyl- α -methylphenylhydrazine is similarly converted into 2-thion-3-phenyl-1-

methyl-2:3-dihydroindole, b.p. 200°/1 mm., m.p. 57° (*picrate*, m.p. 141°), but $\text{CH}_2\text{Ph-C(SH)-N-NHPh}$ gives mainly hydrolysis products and a small amount of a yellow oil which is probably the indole.

J. W. B.

Synthesis of amino-acids. III. Tryptophan. W. J. BOYD and W. ROBSON (Biochem. J., 1935, 29, 2256—2258).—By using piperidine for condensation of indole-3-aldehyde with hydantoin, and $(\text{NH}_4)_2\text{S}$ as a reducing and hydrolytic agent, a 60—70% yield of tryptophan can be obtained, and pptn. with HgSO_4 is avoided. The method is applicable to the prep. of small quantities of the NH_2 -acid.

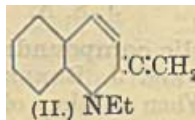
J. N. A.

Action of acetylsalicyl chloride on magnesyndoles. II. C. TOFFOLI (Gazzetta, 1935, 65, 487—497; cf. A., 1934, 1110).—Acetylsalicyl chloride and Mg indolyl bromide in Et_2O yield *o*-hydroxyphenyl-3-indolyl ketone, m.p. 171° (*hydrochloride*, m.p. 170°; *Ac*₂, m.p. 60°, and *Bz*₂, m.p. 152°, derivatives; *phenylhydrazone*, m.p. 166°), with some 3-acetylindole, and small amounts of *o*-hydroxyphenyl 2-indolyl ketone, m.p. 142°, of *o*-hydroxyphenyl 1-acetyl-2-indolyl ketone, m.p. 148° (to a red liquid, perhaps with isomerisation to the 3-Ac compound), and of a *phenylenetri-indolyl-methane*, m.p. 145—150° (*picrate*, m.p. 150—155°). From Mg 3-methylindolyl bromide, *o*-hydroxyphenyl 3-methyl-1-indolyl ketone, m.p. 151° (*Bz* derivative, m.p. 89°), and 1-acetyl-3-methylindole are obtained, or, at higher temp., *o*-hydroxyphenyl 3-methyl-2-indolyl ketone, m.p. 124°, with a substance, m.p. about 200°.

E. W. W.

Manufacture of aminoalkylated pyridines and quinolines.—See B., 1935, 940.

Condensation of quinaldine ethiodide and formaldehyde. K. LAUER and M. HORIO (J. pr. Chem., 1935, [ii], 143, 305—324).—The purity of pinacyanol (I), m.p. between 286° and 296° according to rate of heating (cf. lit.), is determined spectrophotometrically. The effect on the yield of pure dye of varying the conditions, proportions of reactants and the solvent, and of adding various substances is investigated. Max. yields (40% of pure dye) are obtained with 2 mols. of quinaldine ethiodide, 2 of NaOH (or KOH), and 1 of CH_2O in H_2O without any addition. Excess of CH_2O leads to formation of 2-ethylquinoline, probably formed by way of (II). 2- β -Hydroxyethylquinoline does not yield (I). Koenig's mechanism for the formation of (I) is thus probably correct, (II) acting as H acceptor. The sensitisation of plates is unaffected by <50% of impurity in (I).



R. S. C.

[β -Hydroxyphenylethylamines and their transformations. III. Synthesis of benzylisoquinolines under physiological conditions.] E. SPATH and F. KUFFNER (Ber., 1935, 68, [B], 1744—1746).—A reply to Hahn *et al.* (this vol., 357).

H. W.

Synthesis of 8-hydroxy-5-benzylquinoline. Antiseptic activity of its sulphate. L. MCMASTER and W. M. BRUNER (J. Amer. Chem. Soc., 1935, 57, 1697—1698).—2-Nitro-4-benzylphenol and

Fe-HCl give 2-amino-4-benzylphenol [3-amino-4-hydroxydiphenylmethane], m.p. 133° [hydrochloride, m.p. about 200° (decomp.)], converted (Skraup) into 8-hydroxy-5-benzylquinoline (86% yield), m.p. 111° (hydrochloride, m.p. 244°), the sulphate, m.p. 216—217°, of which is at least as toxic to *B. coli* as, and less irritant than, the free base. R. S. C.

Sulphonation of acridone. K. MATSUMURA (J. Amer. Chem. Soc., 1935, 57, 1533—1536).—Acridone is obtained in poor yield by heating *o*-NHPh·C₆H₄·CO₂H with H₂SO₄ at 80° for 30 min., but further heating gives much acridone-2- (I), +H₂O, m.p. 318° (decomp.) (*Ba* salt, +4H₂O, m.p. >360°), and a little 4-sulphonic acid (II), +H₂O, m.p. 268° (*Ba* salt, +3H₂O, m.p. >360°), converted into the corresponding hydroxyacridones by KOH-fusion. Attempts to prepare 9-aminoacridone-2-sulphonic acid failed, the 9-NH₂-group having exceptional mobility owing to the negative substituent in position 2. 2-Methoxyacridone has m.p. 274—276° (lit. 263—265°). (I) and Na-Hg in H₂O at 80° give acridine-2-sulphonic acid, +H₂O, m.p. >360° [*Ba* salt, +6H₂O, m.p. >360°; *amide*, m.p. 258° [hydrochloride, m.p. 278° (decomp.)]; *chloride*, m.p. >357°]. 9-Chloroacridine-2-sulphonyl chloride, m.p. 165—167°, with aq. NH₃ and Cu(OAc)₂ at 135° gives the chlorosulphonamide, decomp. 353—360°, and 9-aminoacridine-2-sulphonamide, m.p. 298° (decomp.) [hydrochloride, m.p. 318 (decomp.)], with EtOH the *Et* ester, m.p. 254—255° (decomp.), and with KOH-EtOH at room temp. *Et* acridone-2-sulphonate, decomp. 255°. (I) leads also to diacridyl 2:2'-disulphide, m.p. 245—246° [dihydrochloride, m.p. 255° (decomp.)], and 2-thiolacridine, m.p. 120—130° (*Bz* derivative, m.p. 178—179°).

R. S. C.

New synthesis of glyoxaline derivatives. R. WEIDENHAGEN and R. HERRMANN (Angew. Chem., 1935, 48, 596—597).— α -Hydroxyketones are rapidly oxidised by NH₃-Cu⁺⁺ solutions to α -diketones (I). In presence of aldehydes (I) condense with the NH₃ and aldehyde to the corresponding glyoxalines (II), which are pptd. as insol. Cu⁺ complexes. (II) are liberated from these by treatment with H₂S. Condensation of (II) with NH₃ without aldehyde leads to formation of 2:4-disubstituted glyoxalines, and of 1:4-disubstituted 3-hydroxypyrazines as by-products. The condensation may be applied to dihydroxyacetone and reducing sugars. J. S. A.

Degradation of nitrogenous cyclic compounds by animal charcoal. F. LIEBEN and J. BENEK (Biochem. Z., 1935, 280, 88—91).—When solutions of glyoxaline, uracil, and guanine are heated for a long time with animal charcoal, only slight degradation occurs, but with histidine (I), uric acid, and allantoin the effect is considerable, both NH₃ and new NH₂ groups arising. With (I), more NH₃ is formed than corresponds with the decrease in the Van Slyke val.

P. W. C.

Action of hydrogen peroxide on 1-phenyl-3-methyl-5-pyrazolone. G. PERRONCITO (Gazzetta, 1935, 65, 554—558).—This substance is converted by H₂O₂ in AcOH at the b.p. into 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone (I), probably by the

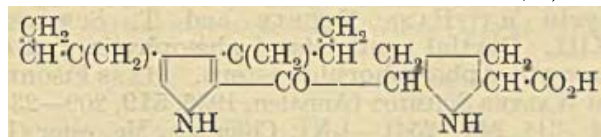
formation of phenylnitrosoamine and the condensation of this to the phenylhydrazone NHPh·N:C<math display="block">\begin{matrix} \text{CMe:N} \\ \text{CO-NPh} \end{matrix} which then isomerises to the hydroxybenzeneazo-compound. (I) is also obtained by action of H₂O₂ on 4:4'-bis-(1-phenyl-3-methyl-5-pyrazolone), and on pyrazole-blue. A by-product of m.p. 248—250° may be 1-phenyl-5-pyrazolone-3-carboxylic acid. E. W. W.

Manufacture of 5-pyrazolone derivatives.—See B., 1935, 974.

Alkylation and acylation of pyrazoles. K. VON AUWERS and T. BREYHAN (J. pr. Chem., 1935, [ii], 143, 259—280; cf. A., 1934, 305).—No regularities exist for the alkylation of pyrazoles by CH₂N₂, MeBr, or MeI-Na. Acylation of pyrazoles and their salts proceeds similarly. 3-Chloro-5-methylpyrazole with CH₂N₂ in Et₂O gives mainly the 1:3- (I) and a little 1:5-Me₂ (II) derivative, but almost entirely (I) with MeBr at 100°. 3-Phenylpyrazole (III) with MeBr at 100° gives mostly the 3- and a little 5-phenyl-1-methyl derivative, but the Na salt with MeI affords only the latter; with ClCO₂Me it gives *Me* 3-phenylpyrazole-1-carboxylate (IV), m.p. 76°. γ -Keto- γ -phenylpropaldehydecarbomethoxyhydrazone, m.p. 152° (prep. from COPh·CH·CH·ONa and NH₂·NH·CO₂Me at room temp.), with POCl₃ in CHCl₃ gives *Me* 5-phenylpyrazole-1-carboxylate, m.p. 63—64°, which is partly isomerised to (IV) and partly decarboxylated by boiling in vac. for 1 hr. (no change in 15 min.). (III) with Cl₂ or S₂Cl₂ in AcOH etc. gives 4-chloro-5-phenylpyrazole (V), m.p. 102°, b.p. 193°/11 mm., which with MeI-NaOMe in absence of H₂O or Me₂SO₄-NaOH gives about equal amounts of 4-chloro-3- (VI), b.p. 163—165°/9 mm. [hydrobromide, m.p. 83°; hydrochloride, m.p. 79°; also obtained from (I) and S₂Cl₂ in AcOH], and 5-phenylpyrazole, b.p. 153—156°/12 mm. [hydrochloride, m.p. 54°; perchlorate, an oil; also obtained from (II)], but MeBr yields mostly the former, whereas CH₂N₂ does not react. Chlorination of the appropriate esters affords *Me* 4-chloro-3-, m.p. 89—90° [also obtained from (V) and ClCO₂Me], and 5-phenylpyrazole-1-carboxylate, m.p. 113—115°. 5-Phenyl-3-methylpyrazole with MeBr at 100° or MeI-Na gives mostly the 1:5-dimethyl-3-phenyl with a little 1:3-dimethyl-5-phenyl derivative, and with ClCO₂Me yields *Me* 3-phenyl-5-methylpyrazole-1-carboxylate, m.p. 74—75° (unchanged by MeBr), which with S₂Cl₂ affords *Me* 4-chloro-3-phenyl-5-methylpyrazole-1-carboxylate, m.p. 107°, also obtained from (VI) and ClCO₂Me. Benzoylacetonecarbomethoxyhydrazone, m.p. 121—122°, with cold POCl₃ gives *Me* 5-phenyl-3-methylpyrazole-1-carboxylate, m.p. 58—59°, which with S₂Cl₂ forms the 4-Cl-derivative, m.p. 97°. *Me* pyrazole-3-carboxylate, m.p. 139—140° (prep. by MeOH-H₂SO₄), with MeBr or CH₂N₂ gives mainly *Me* 1-methylpyrazole-5- (VII), b.p. 70—76°/9 mm., and a trace of 3-carboxylate, b.p. 120—126°/9 mm. (VII) and CH₂N₂ give much *Me* 1:3-dimethylpyrazole-5-carboxylate, b.p. 90—92°/9 mm., and a little *Me* 1:5-dimethylpyrazole-3-carboxylate, b.p. 140—144°/9 mm. The *Et* ester corresponding to (VII) does not react with MeBr at 100°, but with CH₂N₂ gives

much 1 : 3-Me₂ (VIII) and a little 1 : 5-Me₂ derivative (IX), whilst (IX) is the sole product with MeI; the Na salt in C₆H₆ with MeI gives mainly (VIII), with EtI the 5-methyl-1-ethyl compound, with AcCl the 1-acetyl-5-methyl derivative, m.p. 68.5—69.5° (corresponding Me ester, m.p. 67—68°), and with ClCO₂Me in Et₂O the 1-carbomethoxy-5-methyl compound. Me 3-phenylpyrazole-5-carboxylate does not react with MeBr at 130—140°, with MeI at 100° or MeI-Na in C₆H₆ gives Me 3-phenyl-1-methylpyrazole-5-carboxylate, m.p. 62° [previously (A., 1927, 1088) considered to be the Et ester], and with ClCO₂Me alone or in Et₂O a CO₂Me-derivative, m.p. 93°. Et 3-phenylpyrazole-5-carboxylate is unchanged by EtBr; the Na salt with EtI at 100° gives the 1-Et ester, but does not react with AcCl in C₆H₆. 3-Phenylpyrazole-5-carboxylic acid (X) with ClCO₂Me gives a CO₂Me-derivative, m.p. 126—126.5°, which is hydrolysed but not chlorinated by S₂Cl₂ in AcOH. (X) and S₂Cl₂ in AcOH gives the 4-Cl-derivative, m.p. 258—261°, unchanged by boiling ClCO₂Me, but decomposed thereby at 130°. R. S. C.

Compounds with condensed pyrrole nuclei, having behaviour analogous to that of urobilin. II. G. ILLARI (Gazzetta, 1935, 65, 453—459).—Action of K₂Cr₂O₇-H₂SO₄ on the substances (I) and (II) obtained by action of SO₂ on pyrrole (this vol., 364) gives succinic acid and Me vinyl ketone, indicating the presence of pyrrolidine rings and of unsaturated side-chains respectively. Conductometric titration of (I) with aq. NH₃ shows that it is a weak acid, consistent with the annexed formula. (II) may



be regarded as a bimol. anhydro-derivative of (I).

E. W. W.

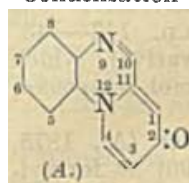
Pyrimidines. II. R. ROBINSON and (Miss) M. L. TOMLINSON (J.C.S., 1935, 1283—1284).—6-Ethyl-2-thiouracil, m.p. 228°, obtained from Et propionylacetate, CS(NH₂)₂, and Na, is converted by HNO₃ into ethyluracil and by HNO₃-H₂SO₄ into 5-nitro-6-ethyluracil, m.p. 230° (decomp.). This compound and POCl₃ yield 2 : 4-dichloro-5-nitro-6-ethylpyrimidine, m.p. 31°, which with aq. NH₃ forms 2-chloro-5-nitro-4-amino-, m.p. 140—141°, reduced (SnCl₂-HCl) to the 4 : 5-diamino-compound, m.p. 203°; this condenses with benzil to 7-chloro-2 : 3-diphenyl-5-ethylpyrimidazine, m.p. 179—181°, which shows bluish-green fluorescence in aq. EtOH solution, and with palladised SrCO₃, 4 : 5-diamino-6-ethylpyrimidine, m.p. 159—160°, is obtained. The analogy between these substances and those derived from vitamin-B, is discussed. F. R. S.

Synthesis of C-substituted pyridylpyrrole derivatives. II. E. OCHIAI, K. TSUDA, and S. IKUMA (Ber., 1935, 68, [B], 1710—1716; cf. this vol., 1253).—Catalytic reduction (Pd-C) of a mixture of CH₃Ac·CO₂Et and Et oximinoacetoacetate in AcOH, EtOAc, and 5% KOH affords Et₂ 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, m.p. 136°, in 83%, 47%,

and 67% yield, respectively. The less reactive CMeAc·N·OH similarly gives Et 2 : 3 : 5-trimethylpyrrole-4-carboxylate, m.p. 105°, in 41% yield (in AcOH). The method is simpler, more easily regulated, and gives better yields of purer products than reduction with Zn. Et nicotinate and EtOAc in presence of NaOEt afford Et nicotoylacacetate, b.p. 144—146°/4 mm. (whence 1-phenyl-3 : 3'-pyridylpyrazolone, m.p. 188—189°), converted by NaNO₂ in AcOH into Et oximinonicotoylacacetate (I), m.p. 152°. Reduction of (I) and CH₃Ac·CO₂Et with Zn dust in AcOH or catalytically (Pd-C) in AcOH leads to Et₂ 4-3'-pyridyl-2-methylpyrrole-3 : 5-dicarboxylate (II), m.p. 139—140° (picrate, m.p. 211°). (I) and CH₃Ac₂ are hydrogenated to Et 4-3'-pyridyl-3-acetyl-2-methylpyrrole-5-carboxylate, m.p. 131° (picrate, m.p. 204—206°; semicarbazone, decomp. 245°; perchlorate, m.p. 135—136°), hydrolysed to 4-3'-pyridyl-3-acetyl-2-methylpyrrole-5-carboxylic acid, decomp. 239°, decarboxylated at about 250° to 4-3'-pyridyl-3-acetyl-2-methylpyrrole, m.p. 142—144° (perchlorate, m.p. 198°; picrate, decomp. 229—230°). Partial hydrolysis of (II) followed by decarboxylation affords Et 4-3'-pyridyl-2-methylpyrrole-3-carboxylate, m.p. 126—127° (picrate, m.p. 192—193°; perchlorate, m.p. 167°), whence 4-3'-pyridyl-2-methylpyrrole, m.p. 166—167° (picrate, decomp. 194°; perchlorate, decomp. 202°).

H. W.

Application of carbohydrates to the synthesis of heterocyclic compounds. Glucazidone, hydroxyglucazidone, and their chemical behaviour. K. MAURER, B. SCHIEDT, and H. SCHROETER (Ber., 1935, 68, [B], 1716—1726; cf. this vol., 224).—The ability to condense with o-C₆H₄(NH₂)₂ to tetrahydroxybutylquinazoline appears to be restricted to glucose, fructose, and mannose. Galactose or pentoses afford benziminazole derivatives. Substitution in the C₆ nucleus also affects the course of condensation. Tolylenediamine and C₆H₃(NH₂)₂·CO₂H yield benziminazoles; the difficulty can be partly overcome by using partly oxidised sugar derivatives. Condensation of the substituted quinazolines to



glucazidones (cf. A) can be effected with 60—100% acid; addition of condensing agents does not affect the yield. The structure assigned to glucazidone (I) (loc. cit.) is confirmed by its oxidation by KMnO₄ in COMe₂ to quinazoline-2-carboxylic acid, m.p. 210° (decomp.) (Me ester, m.p. 113°), decarboxylated to quinazoline (platinichloride) and by the formation of a NO₂-derivative C₂H₇O₃N₃, m.p. 215°. The compound obtained by the action of MgPhBr on (I) is now regarded as 10-phenyl-9 : 10-dihydroglucazidone, since it is converted by very cautious treatment with NaNO₂ in AcOH into a NO-derivative, m.p. 138° (decomp.), loses 2H when heated or boiled with tetrahydronaphthalene giving 10-phenylglucazidone, m.p. 125° (platinichloride; Br-, m.p. 170°, and NO₂-, m.p. 235°, -derivatives), and is oxidised by KMnO₄ in COMe₂ to 3-phenylquinoxaline-2-carboxylic acid, m.p. 153° (decomp.) (Na salt), which is decarboxylated to 3-phenylquinoxaline. Similarly 10-benzyl-9 : 10-dihydroglucazidone is readily dehydrogenated to 10-benzylglucazidone, m.p. 94°,

and 10-methyl-9:10-dihydroglucuzidone affords 10-methylglucuzidone, m.p. 98° (platinichloride; aurichloride). 3-Hydroxyglucuzidone (II), m.p. 159° (K and Hg salts; hydrochloride, m.p. 203° after softening), obtained as by product in the prep. of (I), affords an *Ac*, m.p. 103°, and *Bz*, m.p. 128°, derivative and is converted by CH_2N_2 in $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$ into 3-methoxyglucuzidone, m.p. 139°, transformed by MgPhBr into 3-methoxy-10-phenyl-9:10-dihydroglucuzidone, m.p. 178° [picrate, m.p. 167° (decomp.); hydrochloride, m.p. 139° (decomp.); *NO*-derivative, m.p. 153° (decomp.) which is decomposed in warm AcOH into 3-methoxy-10-phenylglucuzidone, m.p. 98°]. (II) and MgPhBr gave a compound, m.p. 147° [non-cryst. picrate; hydrochloride, m.p. 158° (decomp.); diacetate $\text{C}_{22}\text{H}_{18}\text{O}_4\text{N}_2$, m.p. 150°]. Methoxyglucuzidone methiodide, m.p. 241° (decomp.), is oxidised by alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ to 10-keto-3-methoxy-9-methylglucuzidone, m.p. 131°. Treatment of 3-hydroxy-2-tetrahydroxybutylquinazoline with conc. H_2SO_4 at 100° affords 10-hydroxyglucuzidone, m.p. 264°, which cannot be acylated and does not react with Grignard reagents. H. W.

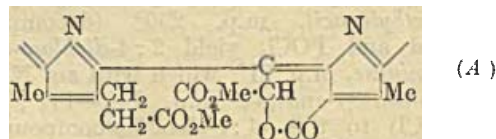
γ -Triazines. XXIV. Melamine. A. OSTROGOVICH (Gazzetta, 1935, 65, 566—588).—Melamine, new m.p. 347° (354°, corr.), forms a picrate, m.p. 316—317° (decomp.); with HCO_2H , a triformate (I), also obtained from the monoformate; a triacetate, also obtained from the monoacetate; an aurichloride, m.p. 265—266°, and bisaurichloride, (+ $4\text{H}_2\text{O}$), m.p. 290—291° (decomp.), (+ $2\text{H}_2\text{O}$), m.p. 281—282°; a mono-oxalate, and a dioxalate, the last existing in two cryst. forms. With $\text{HCO}\cdot\text{NH}_2$, melamine gives an 80% yield of a formyl derivative (II), also obtained, in small yield, when HCO_2Et is used; with HCO_2H , (II) yields (I). With Ac_2O , a Ac_2 derivative, m.p. 305—306° (decomp.), is formed [picrate, m.p. 209—210° (decomp.); aurichloride; Ag_2 derivative], also obtained from melamine and thioacetic acid; with Ac_2O and AcOH , or on prolonged heating with Ac_2O , the Ac_3 derivative, m.p. 298—300°, is formed. $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$ does not give a *Bz* derivative, but Bz_2O yields the Bz_3 derivative, m.p. 142—143° (picrate, m.p. 228—229°; Ag_2 derivative), which crystallises with $2\text{Pr}^n\text{OH}$, and forms a mol. compound, m.p. 182—183°, with PhOH .

The substances regarded by Mulder (A., 1875, 445) and by Gerlich (A., 1876, ii, 196) as formyl- and tribenzoyl-melamine, respectively, have not these structures. The tetracyclic structure for melamine proposed by Barnett (A., 1930, 1193) is criticised, the structure $\text{N} \begin{smallmatrix} \text{C}(\text{NH}_2)\cdot\text{NH} \\ \text{C}(\text{NH})\cdot\text{NH} \end{smallmatrix} \text{C}\cdot\text{NH}$ being preferred. E. W. W.

Synthesis of lactoflavin (vitamin- B_2). R. KUHN, K. REINEMUND, F. WEYGAND, and R. STROBELE (Ber., 1925, 68, [B], 1765—1774).—Condensation of 4-amino-5-*d*-1'-ribitylamino-*o*-xylene (I) with alloxan in AcOH containing $\text{B}(\text{OH})_3$ at 15—20° gives 6:7-dimethyl-9-*d*-riboflavin (II) (90—95% yield), chemically and physiologically identical with lactoflavin from milk. The synthesis of (I) is effected by three methods of which the last is most satisfactory. Ca *d*-gluconate is transformed through *d*-arabinose,

acetobromo-*d*-arabinose, *d*-arabinal diacetate, and *d*-arabinal into *d*(-)-ribose, m.p. 87°, $[\alpha]_D^{25} - 23.7^\circ$ (equilibrium val.) in H_2O . *d*-Riboseoxime, m.p. 141°, $[\alpha]_D^{25} + 54^\circ$ to $+ 6.3^\circ$ (equilibrium in H_2O), is reduced by Na-Hg to *d*-ribamine, which is condensed with 4:5-dinitro-*o*-xylene in 80% EtOH at 130° to 4-nitro-5-*d*-1'-ribitylamino-*o*-xylene, m.p. 127°, reduced (PtO_2 in 80% EtOH) and directly condensed with alloxan to (II). 3-Methyl-lactoflavin, m.p. 272° (decomp.), analogously obtained from methylalloxan, is physiologically inactive. 4:5-Dinitro-*o*-xylene is transformed by NH_3 into 4-nitro-5-amino-*o*-xylene, which with COCl_2 in $\text{C}_6\text{H}_6\text{--PhMe}$ affords 4-nitro-5-carbimido-*o*-xylene, m.p. 87.5°, converted by hot EtOH into 4-nitro-5-carbomethoxylamido-*o*-xylene, m.p. 58°. This is hydrogenated to the corresponding NH_2 -urethane, which is condensed with *d*-ribose (Pd-H_2) to 4-carbomethoxylamido-5-*d*-1'-ribitylamino-*o*-xylene, m.p. 169°, whence (II). 4-Nitro-5-amino-*o*-xylene (III) is condensed with *d*-ribose in hot EtOH to the mixture of isomerides, $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{N}\cdot\text{CH}\cdot[\text{CH}(\text{OH})]_3\cdot\text{CH}_2\cdot\text{OH}$, which is catalytically reduced. The condensation of *o*-nitroanilines with pentoses or hexoses is an equilibrium change. The yield of product is therefore increased by use of an excess of base, which is readily removed from the product by chromatographic treatment with Al_2O_3 . (III) and *l*-arabinose give the substance $\text{C}_{13}\text{H}_{18}\text{O}_6\text{N}_2$, m.p. 166°. H. W.

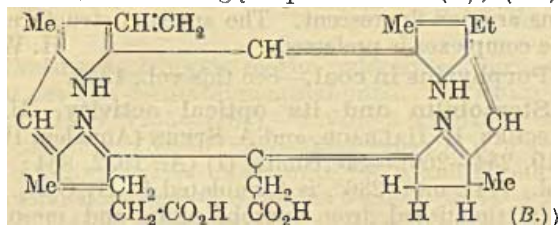
Chlorophyll. LXI. *iso*Chlorin e_4 and phyllochlorin. HANS FISCHER and H. KELLERMANN. LXII. Some derivatives of hydroxyphæoporphyrin a_5 . HANS FISCHER and T. SCHERER. LXIII. Partial synthesis of phæophytin and of some other phæoporphorbide esters. HANS FISCHER and WALTER SCHMIDT (Annalen, 1935, 519, 209—234, 234—244, 244—254).—LXI. Chlorin e_6 Me_2 ester (I), m.p. 212° (*Na* salt; *Cu* salt, m.p. 198°), obtained from chlorin e_5 and cold MeOH-HCl , was formerly thought to contain $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in position 6. Reduction of (I) by HI-AcOH gives, however, a porphyrin which is insol. in alkali, contains 2 OMe, and is identified with chloroporphyrin e_7 lactone ester (II), m.p. 284° [partial structure (4)], oxidation at position 10



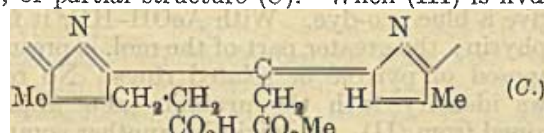
having been effected by I set free. Reduction of (I) under N_2 yields chloroporphyrin e_6 Me_2 ester, which with CH_2N_2 gives phæoporphyrin a_5 , and is oxidised in Et_2O by I-AcOH (or by $\text{C}_5\text{H}_5\text{N-NaOH}$ and air) to (II). Chlorin e_6 similarly treated with I-AcOH yields chloroporphyrin e_5 , by oxidation, loss of CO_2 , and ring-closure. The same product is obtained by action of $\text{C}_5\text{H}_5\text{N-NaOH}$ in presence of air, but in absence of air chloroporphyrin e_4 is formed. The last is unchanged by I-AcOH in Et_2O . $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$ converts (I), or its *Na* salt, into chlorin e_6 Me_2 ester-benzoic anhydride, $\text{C}_{43}\text{H}_{44}\text{O}_7\text{N}_4$, m.p. 205°, $[\alpha] - 125^\circ$, unstable, regenerating (I) when treated with AcOH or $\text{C}_5\text{H}_5\text{N}$; with HI , it yields (II). With $(\text{CH}_2\cdot\text{OH})_2$, the anhydride forms

chlorin e_6 Me, monoglycol ester, $C_{38}H_{44}O_7N_4$, m.p. 172° (Cu salt, m.p. 185°), converted by HI in COMe, into a chloroporphyrin, m.p. 249° , decomp. 253° , spectroscopically identical with chloroporphyrin e_6 Me₃ ester, and by C_5H_5N -NaOH into pyrophæophorbide a Me ester, which is isomerised by HI to phylloerythrin ester.

Decarboxylation of (I) at 212 – 220° , or of its Cu salt at 210° , gives, with much phylloporphyrin, the alkali-insol. isochlorin e_4 Me₂ ester (III), $C_{35}H_{49}O_4N_4$, m.p. 170° (Cu salt, m.p. 162°), of which the spectrum is displaced towards the blue. With MeOH-KOH in C_5H_5N at 150° , (III) yields phylloporphyrin, without rhodoporphyrin, which accompanies the former when chlorin e_4 Me₂ ester is similarly treated. isoChlorin e_4 , $[\alpha] -515^\circ$, is accordingly represented as (B); (III) is



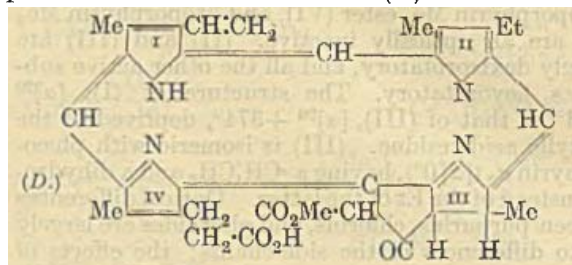
remarkably stable towards AcOH-I, and only after $\frac{1}{2}$ hr. yields porphyrins; the main product is dihydroisochlorin e_4 , H_2 having been added at the $\cdot CH:CH_2$ [the presence of which in (III) is shown by reaction with $CHN_2 \cdot CO_2Et$]. Hydrogenation to the leuco-compound, and re-oxidation, gives a porphyrin, m.p. 230° , spectroscopically identical with phylloporphyrin, with which, however, there is depression of m.p. The new product is therefore probably an isochloroporphyrin e_4 ester, of partial structure (C). When (III) is hydro-



lysed (MeOH-KOH) and heated with C_5H_5N , and the product esterified (CH_2N_2), phyllochlorin Me ester (IV), m.p. 189° , $[\alpha] -425^\circ$ (Cu salt, m.p. 140°), is obtained. That this retains $\cdot CH:CH_2$ is shown by its reaction with $CHN_2 \cdot CO_2Et$. With MeOH-KOH at 140° , (IV) yields mainly phylloporphyrin, which is also obtained when (IV) is hydrogenated, through the H_2 -compound, to the leuco-compound, and this re-oxidised. (IV) thus has the structure (B), in which *tert*- $CH_2 \cdot CO_2H$ has been replaced by Me, and is probably identical with Conant's pyrrochlorin (A., 1931, 368). Free phyllochlorin is obtained readily from free chlorin e_6 , which is heated above its m.p.; the esterified product is identical with (IV). Gentle oxidation (2–3 sec.) of methylphæophorbide a yields a mixture containing phyllochlorin ester, but no isochlorin e_4 . The phyllochlorin now described is not identical with that prepared from phylloporphyrin and NaOEt (A., 1929,

From formula (B) above, it will be seen that a new formulation for chlorophyll has been adopted, in which two additional H atoms are attached in the β -positions in the pyrrole ring III. This is because rhodochlorin (Conant's chlorin f), prepared from phæopurpurin 7, has $[\alpha] -453^\circ$, which optical activity

can be explained only by a reduced ring. Phæophorbide then has the structure (D):



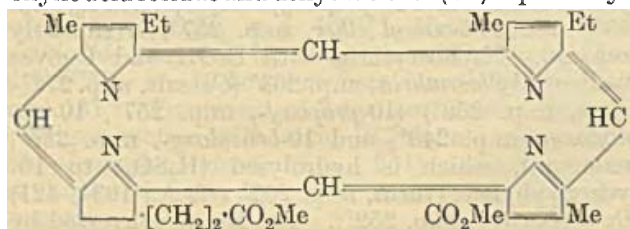
LXII. Phæoporphyrin a_5 Me ester, obtained by hydrogenation of methylphæophorbide, is converted by Pr^aOH and I into 10-propoxyphæoporphyrin a_5 , m.p. 245° ; the 10-isoamyl ether, m.p. 257° , is similarly prepared. Phylloerythrin with EtOH and I gives 10-ethoxyphylloerythrin, m.p. 263° (Cu salt, m.p. 272° ; oxime, m.p. 258°) (10-propoxy-, m.p. 257° , 10-isoamyl-, m.p. 248° , and 10-benzyl-, m.p. 256° , analogues), which is hydrolysed (H_2SO_4) to 10-hydroxyphylloerythrin, m.p. 262° (cf. A., 1934, 421) (Bz derivative, m.p. 252°). The last is converted by HI-AcOH, followed by a stream of air, into chloroporphyrin e_5 , presumably with intermediate formation of hydroxymethylrhodoporphyrin lactone. 10-Ethoxyphylloerythrin with MeOH-KOH readily gives rhodoporphyrin- γ -carboxylic acid.

LXIII. Phæophorbide a in C_5H_5N combines with higher alcohols under the influence of $COCl_2$, to form waxy esters. Thus geraniol yields phæophorbide a geranyl ester, m.p. 138° ; this when treated with MeOH and fractionally adsorbed gives a substance, m.p. 214° , and can be hydrolysed by a chlorophyll-free prep. of chlorophyllase. With phytol, phæophorbide a phytol ester, m.p. 129° , is formed, identical with natural phæophytin, which is hydrolysed by chlorophyllase, and is converted into chlorin e_6 Me ester (showing that the phytol group is truly attached to the propionic acid residue). Phæophorbide a cetyl ester, m.p. 141° , is similarly prepared and hydrolysed. Phæophorbide a (1-menthyl ester, m.p. 186° (sinters at 160°), $[\alpha]^{20} -210^\circ$, and (d)-bornyl ester, m.p. 229° (sinters at 188°), $[\alpha]^{20} -217^\circ$, and mesoporphyrin di-(1-menthyl ester, m.p. 166° , $[\alpha]^{20} -83.2^\circ$, and dicetyl ester, m.p. 126° , are not hydrolysed by chlorophyllase.

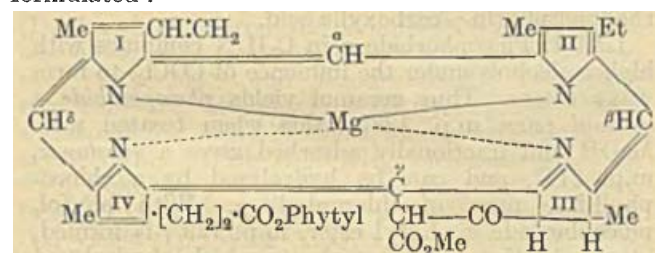
E. W. W.

Chlorophyll. LXIV. Fine structure of chlorophyll. HANS FISCHER and A. STERN (Annalen, 1935, 520, 88–97; cf. this vol., 1135).—Vals. of $[\alpha]^{20}$, in COMe₂, C_5H_5N , or C_6H_6 , are given for 10-acetoxymethylphæophorbide a , chlorin e_6 Me₂ ester-benzoic anhydride, dihydroethylphæophorbide a , isochlorin e_4 Me ester, rhodochlorin (chlorin f) (I), dihydrochlorin e_6 Me₃ ester, dihydromethylphæophorbide a , Zn salts of methylphæophorbide a and pyrophæophorbide a , pyrophæophorbide b , dihydromethylphæophorbide b Me ester, phæophorbide $a+b$, rhodin g_7 Me₃ ester and its Cu salt, dihydrorhodin g_7 Me₃ ester, rhodin g_5 Me₂ ester and its Cu salt, the Cu salt of rhodin g_5 Me₂ ester nitrile, rhodin g_3 Me ester, dihydropurpurin 7 (two sources) (II), purpurin 7 Me₃ ester (III), and pseudochlorin p_6 Me₃ ester (IV). Hæmin, hæmatoporphyrin, coproporphyrin Me ester, uro-

porphyrin, glaucobilin, pseudoverdoporphyrin Me₂ ester (V), phylloerythrin, dihydrophæophorbide α, verdoporphyrin Me₂ ester (VI), and uroporphyrin Me₃ ester are all optically inactive. (II) and (III) are strongly dextrorotatory, and all the other active substances lævorotatory. The structure of (I), $[\alpha]^{20}_{\text{D}} -453^\circ$, is that of (III), $[\alpha]^{20}_{\text{D}} +374^\circ$, deprived of the glyoxylic acid residue. (III) is isomeric with phæoporphyrin a₇ ($[\alpha] 0^\circ$), having a $\cdot\text{CH}:\text{CH}_2$ and a dihydro-ring instead of the Et of the latter. Optical differences between purpurins, chlorins, and phorbides are largely due to differences in the side-chains; the effects of these are discussed. The conversion of (III) into (V) (which contains $\cdot\text{CH}:\text{CH}_2$) consists in loss of the glyoxylic acid residue and dehydration. (VI) is probably:



(II) can give rise to rhodoporphyrin. The γ -C in (I) cannot be asymmetric; the former structure is therefore modified, and chlorophyll-a (VII) now formulated:



Optical inactivation of chlorophyll and its derivatives is discussed. It is suggested that (IV) may be the optical antipode of chlorin *p*₆ and that chlorophyll-b has the structure of (VII) in which Me in pyrrole ring II is replaced by CHO. E. W. W.

Properties of porphyrin-metal complexes and their dependence on the valency and susceptibility of their metallic atoms. F. HAURWITZ [with E. CLAR, Z. HERMANN, H. KITTEL, and F. K. MUNZBERG] (Ber., 1935, 68, [B], 1795—1806).—The mol. vols. of porphyrin-metal complexes (I) depend little on the nature of the metal and are only 4–7% > that of porphyrin (II). Since also the Debye-Scherrer diagrams of (I) and (II) are closely similar, the lattice of (II) undergoes no essential change on introduction of the metal. The latter appears to occupy the "empty" space of the porphyrin ring and always the same central position in the mol., thus explaining its slight influence on the solubility of the complex. The complex nature of the metallic union follows from the resistance of the compounds towards acids, their peculiar absorption spectra and electrochemical behaviour. Complexes with univalent metals are very labile. Those with bivalent metals (*Ag*, *Co*, *Sn*, *Tl*, *Pb*) are pink and characterised by two intense green bands; they are stable towards H₂O and dil. acids, sometimes towards

conc. acid. Those with trivalent metals are reddish-brown in solution and sharply distinguished in absorption spectra from those with bivalent metals. A negative residue is attached to the third valency. The absorption spectra of (II) and (I) differ only at the visible end and show no important differences in the ultra-violet. The at. groups of (I) and not the metallic ions are chromophores in (II). With increasing paramagnetic susceptibility of the metallic atom the max. of the absorption spectra are displaced towards the ultra-violet. The complexes with diamagnetic metal ions show orange-yellow fluorescence, whereas those with paramagnetic ions are non-fluorescent. The annexed structure for the complexes is preferred. H. W.

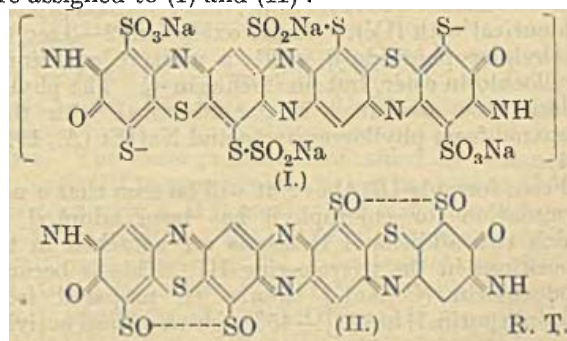
Porphyrins in coal.—See this vol., 1347.

Stercobilin and its optical activity. HANS FISCHER, H. HALBACH, and A. STERN (Annalen, 1935, 519, 254—260).—Stercobilin (I) (A., 1932, 864; this vol., 774), m.p. 236°, is formulated C₃₃H₄₆O₆N₄. It is distinguished from mesobilirubin and mesobilirubinogen (II) (optically inactive) by having $[\alpha]^{20}_{\text{D}} -863^\circ$ and $[\alpha]^{20}_{\text{D}} -824^\circ$, in AcOH; its hydrochloride has $[\alpha]^{20}_{\text{D}} -1586^\circ$ to -1874° , $[\alpha]^{20}_{\text{D}} -850^\circ$ to -1091° , in AcOH. When (I) is hydrogenated, reduced by Na-Hg, re-oxidised, or its hydrochloride treated with Zn(OAc)₂ or with (NH₄)₂CO₃ and UO₂(NO₃)₂, the optical activity is lost. (I) is oxidised by CrO₃-H₂SO₄ to (CH₂·CO₂H)₂, and is reduced by HI-AcOH to basic and acidic pyrrole compounds; it does not couple with PhN₂Cl, but its leuco-compound does so, to give a blue azo-dye. With AcOH-HBr it forms a porphyrin; the greater part of the mol. is presumably composed of pyrrole or related rings. No reaction shows identity with the urobilin (new m.p. 190°) obtained from (II). Prodigiosin, another comparable substance, is optically inactive. E. W. W.

Complex pyrrolo- and indylo-salts.—See this vol., 1335.

Blue-fluorescing substance from corpus luteum.—See this vol., 1265.

Structure of sulphur-black. II. I. CHEMELNITZKAJA and V. VERCHOVSKAJA (Anilinokras. Prom., 1935, 5, 67—75).—Nigrosulphine (I), [C₂₄H₄O₁₂N₆S₁₀Na₄·5H₂O]_n, cannot be diazotised or acetylated, and yields sulphur-black (II), C₂₄H₆O₆N₆S₆, on hydrolysis with acids. The following structures are assigned to (I) and (II):



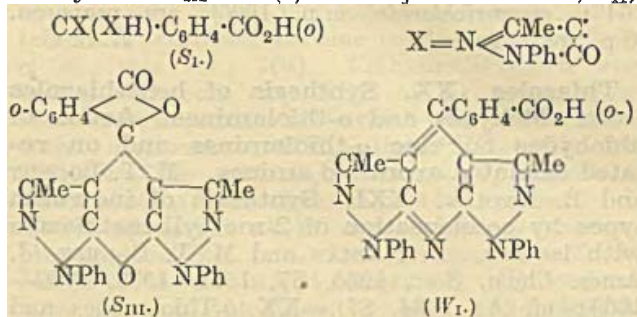
Action of benzoyl chloride and of hydrogen sulphide on cyclic methyleneamines. J. GRAY-MORE (J.C.S., 1935, 865—866).—These bases form amorphous additive compounds with BzCl, decomp. in H_2O to give amine, amide, and CH_2O , thus: $2(NR_2CH_2)_3 + 3BzCl + 6H_2O \rightarrow 3NHRBz + 3NH_3RCl + 6CH_2O$. Thus trimethyl- (I) and triethyl-trimethyleneamine form additive compounds, decomp. to $NHMeBz$ and $NHEtBz$, with the amines; *tris-β-phenylethyltrimethyleneamine*, b.p. 255°, obtained from $CH_2Ph \cdot CH_2 \cdot NH_2$ and CH_2O , forms an additive compound, decomp. similarly. With H_2S in aq. solution at 0°, (I) gives the substance C_3H_7NS (A., 1932, 627); at higher temp., NH_2Me and methylthioformaldin (II) (hydrochloride, m.p. 170°) are obtained. In Et_2O , the product is a hydrosulphide, decomposed by H_2O to give (II). E. W. W.

Alkaline hydrolysis of the azlactones derived from certain o-nitrobenzaldehydes. H. BURTON (J.C.S., 1935, 1265—1267).—2-Nitro-5-benzoyloxybenzaldehyde, m.p. 75—76° (phenylhydrazone, m.p. 180°; 2:4-dinitrophenylhydrazone, m.p. 199°), and hippuric acid condense ($Ac_2O-NaOAc$) to 5-keto-2-phenyl-4-(2'-nitro-5'-benzoyloxybenzylidene)-4:5-dihydro-oxazole (I), m.p. 157°, hydrolysed to 2-nitro-α-benzamido-5-benzoyloxybenzylidene-4:5-dihydro-oxazole (I), m.p. 219—220° (decomp.). 6-Nitro-m-cresol, CH_2PhCl , and NaOH give 2-nitro-5-benzoyloxytoluene, m.p. 73—74°, which is formed, along with BzOH and $H_2C_2O_4$, by boiling (I) with NaOH for 0.5 hr. 5-Keto-2-phenyl-4-(2'-nitro-5'-methoxybenzylidene)-4:5-dihydro-oxazole, m.p. 218—219°, is hydrolysed on short treatment with NaOH, to 2-nitro-α-benzamido-5-methoxybenzylidene-4:5-dihydro-oxazole, m.p. 222—223° (decomp.), and on prolonged boiling to 2-nitro-5-methoxytoluene. 5-Keto-2-phenyl-4-(2'-nitro-5'-acetoxybenzylidene)-4:5-dihydro-oxazole, m.p. 165—166°, is hydrolysed to 6-nitro-m-cresol, and 5-keto-2-phenyl-4-o-nitrobenzylidene-4:5-dihydro-oxazole, m.p. 167—168°, is hydrolysed on short boiling to o-nitro-α-benzamidocinnamic acid, m.p. 181—182°, and on prolonged treatment to o- $C_6H_4Me \cdot NO_2$. 5-Keto-2-phenyl-4-m- and -p-nitrobenzylidene-4:5-dihydro-oxazoles are not hydrolysed to the nitrotoluene (cf. Douglas and Gulland, A., 1932, 69); the p-azlactone yields p-nitro-α-benzamidocinnamic acid, m.p. 243° (decomp.). The o- NO_2 is the controlling factor in the hydrolysis.

F. R. S.

Action of ammonia on the fluoran from 1-phenyl-3-methyl-5-pyrazolone. G. ROHDE [with H. MÜLLER, M. BAUER, H. SCHENKENBERGER, W. SIMON, J. EDERER, W. NICOLAUS, H. LUFTSCHITZ, and M. KOLB] (J. pr. Chem., 1935, [ii], 143, 325—341).—The fluoran, S_{III} , from 1-phenyl-3-methyl-5-pyrazolone (I) (prep. from S_I and $Ac_2O-H_2SO_4$), with 10% NH_3-EtOH (2.5 mols.) at 110° gives the red acid, R_I , o- $CO_2H \cdot C_6H_4 \cdot CX \cdot C \begin{smallmatrix} \text{CMe}=\text{N} \\ \text{C(NH}_2\text{)} \cdot \text{NPh} \end{smallmatrix}$ forms, +EtOH, m.p. about 172—173°, and anhyd., m.p. 190—224° and about 209°, and a little of a colourless, fluorescent, dimorphic acid, W_I , $C_{28}H_{21}O_2N_5$, m.p. 277—278°, and an orange acid, m.p. 268°, probably o- $CO_2H \cdot C_6H_4 \cdot CX \cdot C \begin{smallmatrix} \text{C(XH)} \cdot \text{NPh} \\ \text{CMe}=\text{N} \end{smallmatrix}$ [also obtained as by-product if the temp. is too high in the prep. of

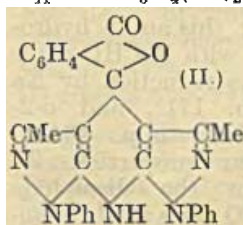
S_I from o- $C_6H_4(CO)_2O$ and (I), and nearly quantitatively from S_{III} and (I) at 175°]. The lactone, S_{II} ,



$C_6H_4 \begin{smallmatrix} \text{CX} \\ \text{CO} \end{smallmatrix} O$ (1 mol.) and (I) (1 mol.) at 125° give R_I and the acid, R_g , o- $CO_2H \cdot C_6H_4 \cdot CX \cdot NH \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CMe} \\ \text{NPh} \cdot \text{N} \end{smallmatrix}$,

m.p. 242° (decomp.). If R_I is heated with $PhNO_2$ and then treated with EtOH it gives S_{II} (25%) and probably (I). R_I in hot $PhNO_2$ (without EtOH treatment) gives R_g , which, when further heated in $PhNO_2$ or, better, in Ac_2O with a few drops of H_2SO_4 , gives S_{II} and probably (I). and $MeOH-H_2SO_4$ give the ester, o- $CO_2Me \cdot C_6H_4 \cdot CO \cdot XH$, and probably (I). R_I , when melted, decomposes into R_g , a trace of W_I , and varying amounts of the imide,

$C_6H_4 \begin{smallmatrix} \text{CX} \\ \text{CX} \end{smallmatrix} NH$, m.p. 278° [also obtained (a) from S_{II} or o- $C_6H_4(CO)_2NH$ and (I) and (b) from S_I and



stable to Na_2CO_3 and dil. aq. NaOH. R_I with SO_2Cl_2 followed by MeOH gives its red Me ester, m.p. 203° (gives W_I with hot alkali), an orange substance, m.p. 240°, and the Me ester of W_I , but with H_2SO_4-MeOH there are formed mainly a colourless substance, R_{III} , $C_{28}H_{21}O_2N_5$, m.p. 314° (Ac derivative, m.p. 218—219°, regenerates with hot KOH-EtOH), and a little of the Me ester of S_I . R. S. C.

Crystalline vitamin- B_1 . IX. Action of concentrated hydrochloric acid. E. R. BUCHMAN and R. R. WILLIAMS (J. Amer. Chem. Soc., 1935, 57, 1751—1752; cf. this vol., 1035).—Vitamin- B_1 (I) and conc. HCl at 150° give 60% of a "chloro-oxvitamin," $[C_{12}H_{16}ON_3SCl]Cl_2 + MeOH$, decomp. 150°, which resembles (I) so closely in reactions (and fairly closely in absorption spectrum) that rearrangement is improbable. (I) thus contains an aliphatic OH. In the prep. of Smakula's product (this vol., 261), $C_{12}H_{15}O_2N_3S$, this OH probably remains intact, but the aminopyrimidine grouping is hydrolysed.

R. S. C.

2-Methyl- and -ethyl-4-p-fluorophenylthiazoles and their derivatives. J. P. WETHERILL and R. M. HANN (J. Amer. Chem. Soc., 1935, 57, 1752—1753).—2-Methyl-, m.p. 81° (hydrochloride, m.p. 131°; picrate,

m.p. 161°; *mercurichloride*, m.p. 160°), and 2-ethyl-4-p-fluorophenylthiazole, m.p. 15—16° (*picrate*, m.p. 154°; *mercurichloride*, m.p. 160°), are prepared. M.p. are corr. R. S. C.

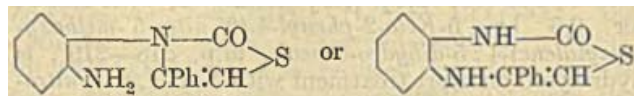
Thiazoles. XX. Synthesis of benzthiazoles from aldehydes and *o*-thiolamines. Action of aldehydes on zinc *o*-thiolamines and on related thiolated aromatic amines. M. T. BOGERT and B. NAIMAN. **XXI.** Synthesis of indirubin types by condensation of 2-methylbenzthiazole with isatins. B. NAIMAN and M. T. BOGERT (J. Amer. Chem. Soc., 1935, **57**, 1529—1533, 1660—1663; cf. A., 1934, 87).—XX. *o*-Thiolamines and aldehydes condense to give successively an aldol-condensation product, anil, benzthiazoline, and benzthiazole. Existence of the first product is made probable by dissolution of the reactants, that of the second and last by isolation. Neither the thiazoline nor products formed by its oxidation could be isolated when $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ and PhCHO react. $(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S})_2\text{Zn}$ and PhCHO give *Zn o-benzylideneaminothiophenol*, m.p. 230—232°, converted by short heating in AcOH or more slowly in EtOH , Et_2O , or COMe_2 into 2-phenylbenzthiazole (I). *Zn salicylidene-*, decomp. 250°, *piperonylidene-*, decomp. 245—250°, and 2-furfurylidene-aminothiophenol, decomp. 232—240°, are similarly prepared and give the benzthiazoles in hot AcOH . $(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S})_2$ and PhCHO , when heated alone or in xylene, give (I), but in hot EtOH *o-benzylideneaminophenyl disulphide*, m.p. 140°, is obtained; this anil is hydrolysed by hot AcOH or aq. EtOH , with PhCHO alone or in xylene gives (I), and resists reduction by Na or Na-Hg . *o-Salicylidene-*, m.p. 171°, and *o-2-furfurylidene-aminophenyl disulphide*, m.p. 134·5°, similarly prepared, have similar properties. *Zn 4-chloro-2-aminothiophenol* (from the disulphide and *Zn* dust in AcOH) with PhCHO gives *Zn 4-chloro-2-benzylideneaminothiophenol*, m.p. 207—208° (corr.), which, when further heated alone, in AcOH , EtOH , or ligroin gives 5-chloro-2-phenylbenzthiazole, m.p. 138·5—139° (lit. 127°).

XXI. Indirubin-type dyes are prepared from 2-methylbenzthiazole (II) (modified prep.) (6-*Br*-derivative, decomp. 190—220°, prep. in AcOH at 100°). (II) and isatin with or without ZnCl_2 at 150° give 3-(2'-benzthiazolylmethylene)oxindole (III), m.p. 262—263° (SO_3H -derivative, dyes wool yellow, fast to light but not to washing), which with 40% KOH at 100° gives $(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S})_2$ and other products, and is reduced by *Zn* dust and AcOH to 2-hydroxy-3-(2'-benzthiazolyl)methylindole, m.p. 171°. (III) is also obtained from (II) and isatin α -chloride at 110°, but in hot C_6H_6 with 2 drops of piperidine 2-(2'-benzthiazolyl)methylene- ψ -indoxyl, m.p. 223·5—224°, is obtained, which gives a similarly unstable leucobase. Similarly are prepared 3-(2'-benzthiazolyl)methylene-5-bromo-, m.p. 315—317°, -5:7-dibromo-, m.p. 300—304°, and -5-nitro-oxindole, m.p. 316—320°, 3-(2'-benzthiazolyl)methyl-5-bromo-2-indolol, m.p. 210°, and 3-(6'-bromo-2'-benzthiazolyl)methyleneoxindole, m.p. 320—324°. $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ and pyrrole-2-carboxyl chloride give 2-(2'-pyrryl)benzthiazole, m.p. 130—133°. M.p. are corr. R. S. C.

Retene [derivatives]. IV. Synthesis of 6-thiolretene and of related and derived compounds. T. HASSELSTROM and M. T. BOGERT (J. Amer. Chem. Soc., 1935, **57**, 1579—1581; cf. A., 1934, 646).—Retene-6-sulphonyl chloride is reduced by *Zn* and H_2SO_4 to 6-thiolretene (I), an oil (*Bz* derivative, m.p. 115·5—116·5°), oxidised by FeCl_3 or air to the disulphide, m.p. 226·5—227·5°. Reduction by *Zn* and H_2O gives, however, the disulphoxide, m.p. 142·5—143·5°. (I) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ give 6-rectylthiolacetic acid, m.p. 138·5—139·5°, converted by ClSO_3H into 8-isopropyl-7''-methyl-naphtho-3'':2'-5':6-thioindoxyl (II), solid, and the disulphonic acid of the corresponding indigo. (II) condenses with isatin and aldehydes to give dyes which could not be purified. M.p. are corr. R. S. C.

Production of compounds containing an ethylenic linking or a polymethine chain [quinolines and benzthiazoles].—See B., 1935, 894.

Condensation of ω -bromoacetophenone with *s*-phenyl-*o*-aminophenylthiocarbamide. K. B. PATHAK (J. Indian Chem. Soc., 1935, **12**, 463—465).—The structure advanced by Ghosh (A., 1931, 854) for the compound, m.p. 223° (decomp.) [Ghosh gives m.p. 230° (decomp.)], obtained from $\text{COPh}\cdot\text{CH}_2\text{Br}$ and $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ in 95% AcOH is invalid. The compound is shown to be the hydrobromide of a base, m.p. 164°, for which the structure



is proposed. The mechanism of the reaction is discussed. H. G. M.

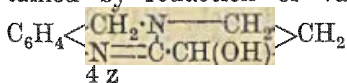
Gramine from Swedish strains of barley. H. VON EULER and H. ERDTMAN (Annalen, 1935, **520**, 1—10).—Gramine (cf. A., 1933, 877; 1934, 1419; this vol., 1040), m.p. 132·5—133·5° (*picrate*, m.p. 142—144°; methiodide, m.p. 175—176°), now obtained in larger quantity from the mutant *Primus* I, is identical in properties with donaxine (this vol., 634); from its behaviour, before and after decomp., towards Ehrlich's reagent, it is now regarded as 2-dimethylamino-3-methylindole. For comparison, 2-(dimethylaminomethyl)indole, b.p. 180—183°/20 mm. (*picrate*, m.p. 184—185°; hydrochloride, m.p. 189—190°), is prepared (NaOMe at 300° in H_2) from dimethylaminoacet-*o*-toluidide, m.p. 62—64° (hydrochloride, m.p. 212—213°). The last is obtained by action of NHMe_2 in C_6H_6 on chloroacet-*o*-toluidide; with NH_2Me this yields methylaminoacet-*o*-toluidide, b.p. 198—201°/15 mm. (hydrochloride, m.p. 235—237°; *Bz*₂ derivative, m.p. 130—131°), which does not condense to an indole. β -Chloropropion-*o*-toluidide, m.p. 84—85°, obtained from the acyl chloride, reacts with NHMe_2 to form β -dimethylaminopropion-*o*-toluidide (hydrochloride, m.p. 148—150°); distillation in vac. of the crude reaction product yields acryl-*o*-toluidide, m.p. 110°. With NH_2Me , -methyliminodipropion-*o*-toluidide, m.p. 145°, and β -methylaminopropion-*o*-toluidide (hydrochloride, m.p. 143—145°) are formed. β -Iodopropion-*o*-toluidide, m.p. 112—113°, reacts similarly. E. W. W.

Effect of electrolysis on nicotine. G. S. ILJIN (Sborn. Rabot Chim. Tabak. Bull., 1935, No. 125, 67—74).—After electrolysis of neutralised nicotine, the picrate has a m.p. different from that of the nicotine picrate. E. P.

Tobacco bases. III. l-Nornicotine. E. SPATH and E. ZAJIC (Ber., 1935, 68, [B], 1667—1670; cf. this vol., 1136).—The residues from a Kentucky tobacco are rendered strongly alkaline and extracted with Et₂O. The residue from the extract is distilled under diminished pressure and the distillate, dissolved in Et₂O, is fractionally extracted with HCl-NaCl. The acid solutions are basified and distilled with steam in vac., whereby nicotine is removed. The non-volatile base is purified by means of picric acid followed by HClO₄, thus leading to l-nornicotine, [α]_D²⁵ -88.8° [dipicrate, m.p. 191—192° (vac.); diperchlorate], converted by HCO₂H and CH₂O into l-nicotine. H. W.

Senecio alkaloids. II. Platyphylline. A. OREKHOV and R. KONOVALOVA [with W. TIEDEBEL] (Ber., 1935, 68, [B], 1186—1190; cf. this vol., 764).—Fresh analyses of platyphylline perchlorate, m.p. 222—223°, indicate the formula C₁₈H₂₅O₅N (not C₁₇H₂₅O₅N) for platyphylline (I); this harmonises with the now established formula C₈H₁₅O₂N for platynecine (II), which has been obtained cryst., m.p. 148—148.5°, [α]_D -56.8° in CHCl₃ (picrate, m.p. 184—185°; hygroscopic hydrochloride; perchlorate; aurichloride, m.p. 199—200°; methiodide, m.p. 202—203°, stable towards cold 50% NaOH). (II) does not contain NMe, so that N is probably dicyclic. Zerevitinov's method shows 2 OH, but only a Bz₁ derivative, m.p. 119—120°, [α]_D -87.9° in EtOH, containing 1 active H, could be isolated. (II) is transformed by conc. H₂SO₄ at 100° into anhydroplatynecine (III), C₈H₁₃ON, b.p. 194—195°/750° mm., [α]_D -25.19° [picrate, m.p. 265—270° (decomp.); picrolonate, m.p. 226—227° (decomp.); methiodide, m.p. 211—213°], which is not catalytically hydrogenated, does not contain active H, and does not react with NH₂OH or NH₂·CO·NH·NH₂. Electrochemical reduction (Tafel) of (II) gives (III), also obtained by the successive action of SOCl₂ and KOH-EtOH on (II). Hydrolysis of (I) with conc. H₂SO₄ affords (III). H. W.

Constitution of vasicine. H. R. JUNEJA, K. S. NARANG, and J. N. RAY (J.C.S., 1935, 1277—1279).—o-Nitrobenzylsuccinamic acid, m.p. 116°, is reduced (FeSO₄) to the NH₂-acid, m.p. 145°, which with NaOAc gives a compound CH₂< $\begin{matrix} \text{N}=\text{C}\cdot\text{CH}_2 \\ \text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CO} \end{matrix}\text{CH}_2$, m.p. 192°, reduced electrolytically to a base having a picrolonate, m.p. 203—210° (decomp.). Succino-o-nitrobenzylimide, m.p. 130°, obtained from o-NO₂·C₆H₄·CH₂Cl, and K succinimide, is reduced to a base (II), C₆H₄< $\begin{matrix} \text{CH}_2\cdot\text{N}\cdot\text{CO} \\ \text{N}=\text{C}\cdot\text{CH}_2 \end{matrix}\text{CH}_2$, m.p. 186°. Reduction of (II) electrolytically gives a picrolonate, m.p. 207—213° (decomp.), identical with that obtained by reduction of vasicine, which must be



F R. S.

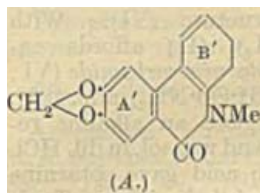
Vasicine. M. L. BERI, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1935, 12, 395—399; cf. this vol., 765).—The following unsuccessful attempts to synthesise vasicine are described (cf. Spath et al., this vol., 764). CH₃EtBr·CO·NHPh when heated with conc. aq. KOH at 50° gives 3-ethyl-indolenone, m.p. 264—265°, which would not condense with urethane. o-NH₂·C₆H₄·CO·NH₂ (I) with CH₃EtBr·COBr with C₅H₅N in C₆H₆ affords its α-bromobutyl derivative, m.p. 144°, converted by NaOH-aq. EtOH at 50° into 4-hydroxy-2-α-bromopropylquinazoline, m.p. 218° (reduced by Zn-3% NaOH to the 2-n-propyl compound). (I) condenses with itaconic anhydride to give o-(β-carboxy-Δ^β-butenoylamido)benzamide, m.p. 174—176° (decomp.), cyclised (NaOH) to the quinazolone

$$\text{C}_6\text{H}_4\left\langle \begin{matrix} \text{N} \\ \text{CO}\cdot\text{N} \end{matrix} \right\rangle \text{C}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2, \quad 197—198^\circ,$$

which could not be decarboxylated. J. W. B.

Alkaloids of Ammodendron Conollyi, Bge. I. A. OREKHOV and N. PROSKURNINA [with G. LAZUREVSKI] (Ber., 1935, 68, [B], 1807—1809).—The leaves of A. Conollyi when extracted with C₂H₅Cl₂ yield pachycarpine (d-sparteine) and ammodendrine (I), C₁₂H₂₀ON₂ (also + 1H₂O), m.p. 73—74°, [α]_D ± 0° (non-cryst. hydrochloride, hydrobromide, and sulphate; hydriodide, m.p. 218—220°; perchlorate, m.p. 199—200°). Treatment of (I) with MeI yields N-methylammodendrine, C₁₃H₂₂ON₂, m.p. 65—66° (hydriodide, m.p. 183—185°), the methiodide, m.p. 163—165°, of which is stable towards alkali. (I) is therefore a monacidic, sec. base; the second N and O are non-reactive, pointing to the presence of N·CO. (I) gives a non-cryst. Bz derivative. H. W.

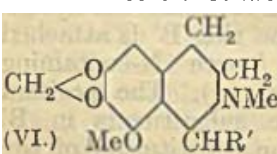
Lycoris alkaloids. IX. 6:7-Methylenedioxy-N-methylphenanthridone as product of the degradation of lycorine. H. KONDO and S. UYEO (Ber., 1935, 68, [B], 1756—1760).—The skeleton of lycorine (I) is a 6:7-methylenedioxyhydrophenanthridine in which CH₂O₂ is attached to the C₆ nucleus A', whilst the hydrobenzene ring B' is attached to a fourth N-containing ring (cf. A). The position of the substituents in B' and the constitution of the fourth ring are not elucidated. Phenanthridine is isolated



from the products of the distillation of (I) with Zn dust. The change is not accompanied by isomerisation, since (I) is transformed by the successive action of MeI and Ag₂O into lycorineanhydromethine, C₁₇H₁₅O₂N, m.p. 98.5° [picrate, m.p. 141—142° (decomp.)], which is oxidised by KMnO₄ to an acid (II), C₁₇H₁₁O₆N (+ H₂O), m.p. 252° (decomp.) (Me ester, m.p. 208°), and an acid (III), C₁₆H₁₁O₅N, m.p. 288° (decomp.) (Me ester, m.p. 195°), which does not react with NH₂OH or -NO₂·C₆H₄·NH·NH₂ or absorb H, but gives Gaebel's reaction. (II) is oxidised to (III) by H₂O₂ in alkaline solution and hence is an α-CO-acid. Decarboxylation of (III) yields 6:7-methylenedioxy-10-methylphenanthridone (IV) (A), m.p. 238°, which is prepared thus: 6-bromopiperonal and o-C₆H₄Br·NH₂ give the corresponding Schiff's

base, transformed by Cu powder in CO_2 at 180—200° into 6:7-methylenedioxyphenanthridine, m.p. 181°; the *methiodide*, decomp. 255° after darkening at 246°, of the latter is oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution to (IV). H. W.

Cotarnine series. II. Reactivity of the aldehyde group in cotarnine and benzoylcotarnines. III. Isomeric biscotarninoacetones. B. B. DEY and (Miss) P. L. KANTAM (J. Indian Chem. Soc., 1935, 12, 421—429, 430—435; cf. this vol., 366).—II. Cotarnineoxime (I) [formed in the cold from cotarnine (II), $\text{NH}_2\text{OH}\cdot\text{HCl}$, NaOAc , and H_2O] with PhNCO in C_6H_6 yields the phenylcarbamate of cotarnomethylphenylcarbamidoxime, and with PhNCS yields cotarnomethylphenylthiocarbamidoxime (cf. *loc. cit.*). (I) with $N\text{-NaOH}$ and BzCl affords the *benzoylated oxime of benzoylcotarnine* (III), m.p. 158°, and with Ac_2O affords the *acetylated oxime of acetylcotarnine*, m.p. 113°. Both are insol. in alkali. (I) is reduced by Na-EtOH (hot) to hydrocotarnine. Benzoylcotarnine (IV) (improved prep.) (*azine*, m.p. 220°; *o*-, m.p. 150, *m*-, m.p. 113°, and *p*-toluidil, m.p. 111°; *p*-phenetidil, m.p. 135°) is oxidised to benzoylcotarninic acid, and yields an oxime (*Ac* derivative, m.p. 152°) the *Bz* derivative of which is identical with (III). (II) and $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ afford *o*-nitrobenzoylcotarnine, m.p. 138° (*oxime*, m.p. 193—194°; *anil*, m.p. 164°). These results favour the structure $\text{CHO}\cdot\text{R}\cdot[\text{CH}_2]_2\cdot\text{NMeBz}$ for (IV) ($\text{R}=\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}\cdot\text{OMe}$). Cotarnine *anil*, *o*-, m.p. 119°, and *p*-toluidil (V), m.p. 114—115°, unlike the corresponding derivatives of (IV), are unstable and decomposed by alkali. This is attributed to the presence of a *sec. imino-H* in (II). Attempts to benzoylate (V) failed, the product being benzo-*p*-toluidide. (II) and *p*-aminoacetophenone in EtOH when heated at 40° (15 min.) yield *anhydrocotarnino-p-aminoacetophenone* (VI; $\text{R}'=\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$), m.p. 190—191° (*Ac*₁ derivative, m.p. 105°, sol. in dil. acids), which contains a free diazotisable NH_2 . These results favour the structure (VI). With $\text{CO}(\text{NH}_2)_2$ (II) affords *anhydrocotarninocarbamide* (VI; $\text{R}'=\text{NH}\cdot\text{CO}\cdot\text{NH}_2$), m.p. 182°, which gave an alkaline reaction and was sol. in dil. HCl .

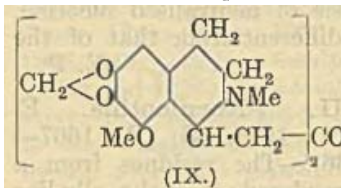


A hot aq. solution with picric acid gave cotarnine picrate. Similarly (II) with phthalimidine affords *anhydrocotarninophthalimidine* (VI; $\text{R}'=$

$\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}$), m.p. 143—144°, decomposed by boiling H_2O ; with $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ affords *anhydrocotarninoresorcinol Me. ether*, m.p. 221—222°; and with 2-nitroresorcinol affords *anhydrocotarnino-2-nitroresorcinol*, m.p. 201° (sparingly sol. *hydrochloride*). Attempts to condense (II) with *o*-, *m*-, and *p*-cresol and α - and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ were unsuccessful.

III. The compound, m.p. 83°, obtained by Liebermann *et al.* (A., 1904, i, 263) by condensing (II) with COMe , in presence of Na_2CO_3 is biscotarnylideneacetone (VII) [*methiodide* (VIII), m.p. 168° (lit., m.p. 144°)]. When the condensation is carried out with EtOH as solvent, the product is an isomeride, *biscotarninoacetone* (IX), m.p. 150—151° [*methiodide*

+ $2\text{H}_2\text{O}$ (X), m.p. 210°], sol. in dil. acids and not acted on by Ac_2O , BzCl , or PhNCO . It is also formed when (VII) is treated with warm EtOH , and is reduced by Na-Hg to *biscotarninoisopropyl alcohol*, m.p. 108° (decomp.). (X) when boiled with an excess of 20% alkali



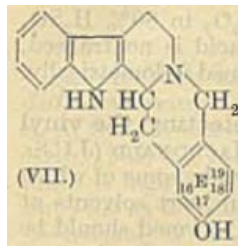
yields *N-methylbiscotarnylideneacetone* [*hydrochloride*, m.p. 182° (decomp.)]; *platinichloride*, which with MeI is converted into (VIII). (VIII) and NaOH when steam distilled yield NMe_3 and *biscotarnonideneacetone* as an oil which slowly solidified and was N -free. (VII) with Ac_2O does not give the expected *Ac* derivative, but is converted into (IX). Two isomeric compounds could not be obtained from (II) and COPhMe , the *isoquinoline* derivative being the only recognisable product. H. G. M.

Papaverine phenylethylbarbiturate ("pavemal"). A. MOSSINI and G. RECORDATI (Boll. Chim. farm., 1935, 74, 638—639).—*Papaverine phenylethylbarbiturate*, m.p. 145—146°, is prepared from the acid and the base in EtOH , and its existence confirmed by a m.-p. graph. E. W. W.

Synthesis of tetrahydroharman derivatives under physiological conditions. II. G. HAHN, L. BÄRWALD, O. SCHALES, and H. WERNER. III. **Synthesis of the yohimbine skeleton.** G. HAHN and H. WERNER (Annalen, 1935, 520, 107—123; 123—133).—II. Under such conditions tryptamine condenses more readily, and to give better yields, with α -keto-acids (I) than it does with the corresponding aldehydes. The yield depends on p_H , the optimum val. (in parentheses) of which varies with different (I), decreases with rise of temp. $>25^\circ$, and with increase in the no. of OMe in the phenylpyruvic acid, and is increased by light. Thus tryptamine *hydrochloride* (II) with homopiperonal in H_2O (p_H 6.2) at 23° affords (8 days: 15% yield) 3-(3:4-methylenedioxybenzyl)-3:4:5:6-tetrahydronorharman isolated as its *hydrochloride*, decomp. 273°. Similarly (II) and 3:4:5- $\text{C}_6\text{H}_3(\text{OMe})_3\cdot\text{CH}_2\cdot\text{CHO}$ gives (16, 0, and 20% yields, respectively, at p_H 6.2, 5.2, and 3.8) 3-(3:4:5-trimethoxybenzyl)-, m.p. 85° (III), and with PhCHO (p_H 5.2), 3-phenyl-, m.p. 158—160° [*hydrochloride*, m.p. 253° (decomp.)], -3:4:5:6-tetrahydronorharman. Methylglyoxal becomes oxidised to AcCO_2H and with (II) gives (IV) (below); furfuraldehyde gives a substance, m.p. 122°. By condensation of (II) with the appropriate (I) are obtained 3-methyl- (IV), decomp. 220° (p_H 6.2) [*Me* ester, m.p. 138° (*hydrochloride*, decomp. 268°)], 3-benzyl-, decomp. 253° (p_H 6.2), 3-(3:4-methylenedioxybenzyl)-, decomp. 250° (p_H 6.2), 3-(4-hydroxy-3-methoxybenzyl)-, decomp. 239—240° (p_H 6.2) (from 4-hydroxy-2-methoxyphenylpyruvic acid, decomp. 161°), 3-(3:4-dimethoxybenzyl)-, decomp. 230—232° (p_H 4.2), and 3-(3:4:5-trimethoxybenzyl)-, decomp. 191° (p_H 5.3), -3:4:5:6-tetrahydronorharman-3-carboxylic acid. By heating with MeOH-HCl these are decarboxylated to give the *hydrochlorides* of 3-benzyl- (this vol., 224), 3-(3:4-methylenedioxybenzyl)-, decomp. 268°, 3-(4-hydroxy-3-methoxybenzyl)-, decomp. 252—254°, and 3-(3:4-

dimethoxybenzyl)-, decomp. 230°, -3:4:5:6-tetrahydronorharman, and the free base (III).

III. Condensation of *p*- and *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ with (II) (p_H 4.2) at 25° (sunlight) affords, respectively, 3-*p*-, decomp. 240—241°, and 3-*m*-hydroxybenzyl-3:4:5:6-tetrahydronorharman-3-carboxylic acid, decomp. 225—227°, decarboxylated to the hydrochloride, decomp. 246—247°, of 3-*p*- (V) and the hydrochloride, decomp. 245—246°, of 3-*m*-hydroxybenzyl-3:4:5:6-tetrahydronorharman (VI). With warm 40% CH_2O at p_H 4.4, (VI) readily condenses to give 3-(3-hydroxy-6-hydroxymethylbenzyl)-3:4:5:6-tetrahydronorharman hydrochloride, decomp. 283—285°, which undergoes ring-closure on basification to give a hexadehydro-yohimbol (VII), decomp. 267—269°. Since (V) does not condense

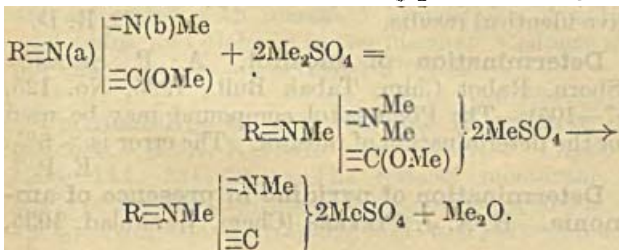


with CH_2O under the same conditions the OH in yohimbine (already shown to be in ring E) is most probably at C_{17} .

J. W. B.

Cactus alkaloids. XVI. Synthesis of anhalonine and of lophophorine. E. SPATH and F. KESZTLER (Ber., 1935, 68, [B], 1663—1667).—Synthetic *dl*-anhalonine (A., 1924, i, 69) is resolved by *l*-tartaric acid in MeOH into *l*-anhalonine (I), m.p. 85—86°, $[\alpha]_D^{25} -56.3^\circ$ in CHCl_3 , identical with the natural base; treatment of the mother-liquors with *d*-tartaric acid affords *d*-anhalonine, m.p. 84.5—85.5°, $[\alpha]_D^{25} +56.7^\circ$ in CHCl_3 . (I) is converted by CH_2O and HCO_2H into *N*-methyl-*l*-anhalonine $[\alpha]_D^{25} -47.0^\circ$ in CHCl_3 (picrate, m.p. 162—163°), identical with natural lophophorine. H. W.

Strychnine and brucine. XXXIV. Action of methyl sulphate on methoxymethylhydroneobrucidine and similar bases in boiling benzene solution. O. ACHMATOWICZ and R. ROBINSON (J.C.S., 1935, 1291—1294).—Methylation (Me_2SO_4) of neobrucidine gives neobrucidine dimethiodide (+0.5 H_2O), m.p. 298° (decomp.), identical with so-called methoxymethylhydroneobrucidine dimethiodide-*B* (cf. A., 1927, 889). Dihydrobrucidine methosulphate, m.p. 287—288° (decomp.), gives the methiodide, m.p. 298° (decomp.), identical with methoxymethyltetrahydrobrucidine methiodide-*B*, and the methosulphate also yields the dimethiodide (+0.5 H_2O), m.p. 286—288° (decomp.). Methoxybenzylhydroneobrucidine and Me_2SO_4 followed by NaI form *N*(a)-methyl-*N*(b)-benzylneobrucidinium di-iodide, m.p. 246—248° (decomp.), which gives the dichloride (+7 H_2O), m.p. 90—92°. The OMe-bases (A., 1927, 888, 889) when heated with Me_2SO_4 give Me_2O , the measurement of the vol. corresponding in amount with the yield of dimetho-salts, the action taking place in 3 stages:



The bearing of this theory on hitherto inexplicable facts is discussed. F. R. S.

Strychnos alkaloids. LXXXVII. Hydrogenation of the isomeric brucinolones. H. LEUCHS and A. DORNOV (Ber., 1935, 68, [B], 1785—1791).—Catalytic hydrogenation of brucinolone *b* (I) (PtO_2 -50% AcOH) gives dihydrobrucinolone *b*, m.p. 285°, $[\alpha]_D^{20} -9^\circ$ in AcOH; dihydroisobrucinolone (II), m.p. 260°, $[\alpha]_D^{20} -26^\circ$ in AcOH, is obtained similarly. Another dihydrobrucinolone, m.p. 290° (decomp.), $[\alpha]_D^{20} +2^\circ$ to $+3^\circ$ in AcOH, which cannot be further hydrogenated catalytically, is obtained from brucinonic acid and Na-Hg, whilst under like conditions (II) is produced in small yield from dihydrobrucinonic acid. The following are obtained by reduction (Adams) of the requisite Ac derivatives: acetyldihydrobrucinolone *b*, m.p. 253°, $[\alpha]_D^{20} -34.5^\circ$ in AcOH; acetyldihydrokryptobrucinolone, m.p. (indef.) 235—238°, $[\alpha]_D^{20} -113^\circ$ to -108° in AcOH; acetyldihydroisobrucinolone, m.p. 185°, $[\alpha]_D^{20} -58.0^\circ$ in AcOH. Brucinolone *b* hydrate hydrochloride, $\text{C}_{21}\text{H}_{24}\text{O}_6\text{N}_2\cdot\text{HCl}\cdot 0.5\text{H}_2\text{O}$, $[\alpha]_D^{20} +16.5^\circ$ in H_2O , is obtained by the successive action of 9*N*- H_2SO_4 and BaCl_2 on (I). The corresponding perchlorate, $\text{C}_{21}\text{H}_{24}\text{O}_6\text{N}_2\cdot\text{HClO}_4$, m.p. about 230° (decomp.), $[\alpha]_D^{20} +15.6^\circ$ in H_2O (perchlorate of Me ester, m.p. 157—158°, $[\alpha]_D^{20} +21.2^\circ$ in H_2O), rapidly absorbs 2 H in H_2O without completion of the action which, if interrupted at this stage, gives small amounts of a perchlorate, $\text{C}_{21}\text{H}_{26}\text{O}_6\text{N}_2\cdot\text{HClO}_4$ or $\text{C}_{21}\text{H}_{24}\text{O}_4\text{N}_2\cdot\text{HClO}_4$, m.p. about 220° (decomp.), $[\alpha]_D^{20} +6.2^\circ$ in H_2O , whereas if hydrogenation passes to completion in H_2SO_4 a OMe-free salt, $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2\cdot\text{HClO}_4$, m.p. 285° (decomp.), $[\alpha]_D^{20} -39^\circ$ in H_2O , which does not give the red brucine colour or the Otto reaction results. isobrucinolone hydrate perchlorate, m.p. 195—200°, $[\alpha]_D^{20} +4^\circ$ in H_2O , similarly yields (I). Brucinolone hydrate II, as perchlorate, absorbs 2 H with production of a compound, $\text{C}_{21}\text{H}_{24}\text{O}_5\text{N}_2\cdot\text{H}_2\text{O}$, m.p. 250°, $[\alpha]_D^{20} -11.9^\circ$ in AcOH. H. W.

Tylophorine and tylophorinine from Tylophora.—See this vol., 1433.

Alkaloids of mu-fang-chi.—See this vol., 1433.

Arsenated phenoxyethanols [isopropanols]. M. R. STEVINSON and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 1600—1601).— $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ and $\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{OH}$ in 6*N*-NaOH give *p*-3-hydroxy-*n*-propoxyphenylarsinic acid (I), m.p. 132° (*H Na* salt), which with HNO_3 (*d* 1.9; 1 mol.) at 0° gives the nitrate, m.p. 158—159°, or (2 mols.) α -2-nitro-4-arsinophenoxyisopropyl nitrate, m.p. 183° (decomp.), hydrolysed by 3*N*- H_2SO_4 to the alcohol (II), m.p. 175°. (II) is hydrogenated (Raney Ni; 2 atm.) in dil. NaOH to α -2-amino-4-arsinophenoxypropan-1-ol, + H_2O , m.p. 87°, and anhyd., m.p. 137° [*Na H* and *K H* salts; anhydride, m.p. 200° (decomp.); *N*-Ac derivative, m.p. 153°]. (II) is reduced (SO_2) to *p*- β -hydroxy-*n*-propoxyphenylarsinoxide, m.p. >250°. By reduction with H_3PO_2 are prepared 1:1'-arseno-3:3'-diamino-, m.p. 156—158° (decomp.), and -dinitro-4:4'-di- β -hydroxy-*n*-propoxybenzene, m.p. 200—205° (decomp.) [*dinitrate*, m.p. 158—160° (decomp.)]. R. S. C.

Esters of thio-acids. I. Esters of thio-acids of arsenic and antimony. R. KLEMENT and R. REUBER (Ber., 1935, 68, [B], 1761—1765).—Thioarsenious esters are obtained from AsCl_3 and NaSR in warm EtOH , whilst the corresponding Sb compounds are unstable towards EtOH and are obtained directly from their components. When treated with S they afford thioarsenates and thioantimonates, respectively. The As compounds are only slowly attacked by boiling H_2O , whereas the Sb compounds are readily hydrolysed to Sb_4O_6 and the mercaptan, which is largely oxidised immediately to the corresponding disulphide. With Na_2S reaction occurs thus: $\text{Sb}(\text{SR})_3 + 3\text{Na}_2\text{S} = \text{Na}_3\text{SbS}_3 + 3\text{NaSR}$. The chemotherapeutic action of the compounds has been investigated. The following thioarsenites are described: Ph_3 , m.p. 95° ; tribenzyl, a liquid which cannot be distilled in a high vac. without decomp.; $(p\text{-C}_6\text{H}_4\text{Me})_3$, m.p. 76° (whence tri-*p*-tolyl thioarsenate, m.p. 74°); tri-*p*-methylbenzyl, an oil (*p*-methylbenzyl mercaptan, b.p. $93^\circ/12$ mm.). The following thioantimonites have been obtained: Ph_3 , m.p. $70\text{--}71^\circ$; tribenzyl, an oil; $(\text{C}_6\text{H}_4\text{Me})_3$, m.p. 95° (decomp.) [tri-*p*-tolyl thioantimonate, m.p. $91\text{--}93^\circ$]. H. W.

Configuration of heterocyclic compounds. III. Optical resolution of 10-ethylphenoxarsine-2-carboxylic acid. (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1935, 1268—1269).—dl-10-Ethylphenoxarsine-2-carboxylic acid, m.p. $162\text{--}163^\circ$, prepared from 10-chlorophenoxarsine-2-carboxylic acid and MgEtI , is resolved through strychnine d-, m.p. $247\text{--}248^\circ$ (decomp.), $[\alpha]_{\text{D}}^{20} + 57.4^\circ$ in CHCl_3 , and l-10-ethylphenoxarsine-2-carboxylate, m.p. $188\text{--}189^\circ$, $[\alpha]_{\text{D}}^{20} - 63.2^\circ$ in CHCl_3 , into *d*- and *l*-acids, m.p. $128\text{--}129^\circ$, $[\alpha]_{\text{D}}^{20} \pm 139.0^\circ$ in EtOH . The optical stability of the ions is of the same order as that of the Me acid (A., 1934, 1118). F. R. S.

Mercuration of *p*-cymene. J. E. NEWSTROM and K. A. KOBE (J. Amer. Chem. Soc., 1935, 57, 1640—1642).—*p*-Cymene and $\text{Hg}(\text{OAc})_2$ in EtOH-AcOH , when well stirred at $< 135^\circ$, give *p*-cymene-di-(mercuric chloride) (13%), amorphous, decomp. at $<$ the m.p., -2- (I) (38%) and -3-mercuric chloride (II) (26%), m.p. $177.5\text{--}178^\circ$. 3-Di-*p*-cymyl mercury has m.p. $102\text{--}102.2^\circ$. The mixed m.-p. diagram of (I) and (II) shows a min.-melting mixture [50—60% of (I)] with m.p. 127° . (I) and (II) distil at 760 mm., but cannot be separated thus. R. S. C.

Chemical groups of proteins which possess affinity for polysaccharides. IV. Role of tyrosine. S. J. VON PRZYŁECKI and H. RAFALOWSKA. **V. Silk fibroin and peptone.** H. RAFALOWSKA, J. KRASNODEBSKI, and E. MYSTKOWSKI (Biochem. Z., 1935, 280, 92—96, 96—98).—IV. Free tyrosine unites with P-free polysaccharides, mol. compounds existing over a considerable range of p_{H} (7.5—3).

V. Fibroin adsorbs amylose and dextrin. The greater is the surface and degree of purity, the greater is the amount of polysaccharides adsorbed. Elution occurs much more readily than with the polysaccharide-tyrosine symplex. Considerable affinity exists also between amylose and silk peptone (Fischer's tetrapeptide), the ppt. at p_{H} 7 containing 10% of peptide. P. W. C.

Vitamin-E. III.—See this vol., 1287.

Protein determination from acid-combining power.—See this vol., 1261.

Influence of hydrogen peroxide on the precipitability of proteins.—See this vol., 1266.

Titrimetric determination of organic substances by oxidation with chromic acid. H. C. S. SNETHLAGE (Z. anal. Chem., 1935, 102, 321—328; cf. this vol., 1140).—The substance is oxidised with a known vol. of standard aq. $\text{K}_2\text{Cr}_2\text{O}_7$ in 80% H_2SO_4 solution at 100° . The excess of acid is neutralised, and the excess of $\text{K}_2\text{Cr}_2\text{O}_7$ determined iodometrically. J. S. A.

Formaldehyde method of detecting the vinyl group. G. R. CLEMO and J. M. MACDONALD (J.C.S., 1935, 1294—1295).—Many compounds, some of which do not contain the vinyl group, in inert solvents at 0° give CH_2O with O_3 . The CH_2O formed should be determined (as the dimedon compound), because compounds containing the vinyl side-chain give about 10 times as much CH_2O as those without it. J. L. D.

Volumetric determination of some carbonyl compounds. I. Review of literature. S. HAHNEL (Svensk Kem. Tidskr., 1935, 47, 235—248). E. P.

Determination of creatine and creatinine. F. EGGS and G. VANOLI (Klin. Woch., 1935, 14, 204—205).—Benedict's method for determination of creatine gives inaccurate results, part of the creatinine formed being destroyed by the high temp. By evaporating to dryness after addition of two vols. of 0.1*N*-HCl at $> 60^\circ$ an accuracy within 4—5% can be obtained for pure solutions and urine.

NUTR. ABS. (m)

Colorimetric determination of polypeptides by triketohydrindene hydrate (ninhydrin). M. POLONOVSKI (Compt. rend. Soc. Biol., 1935, 120, 28—29).—Ninhydrin reacts only with polypeptides containing a glycol unit with its NH_2 free. R. N. C.

Colour reaction of some phenylamines. RAYMOND-HAMET (Bull. Sci. pharmacol., 1934, 41, 481—489; Chem. Zentr., 1935, i, 1095).—Reactions are given for dihydroxyphenylethylmethylamine, adrenaline, noradrenaline, dihydroxynor- β -ethyladrenaline, dihydroxynor- and *o*- and *p*-methoxynor-ephedrine, ethylaminethanol-pyrocatechol, ammo-, methyl-amino-, and ethylamino-acetopyrocatechol, *o*-, *m*-, and *p*-methoxy-, dihydroxy-, dimethoxy-, 3:4:5-, 2:4:5-, and 2:3:4-trimethoxy-, and 3:4:5-trimethoxy-phenylethylamine. J. S. A.

Iodometric determination of phenol. H. A. J. PIETERS (Chem. Weekblad, 1935, 32, 508—509).—The d'Ans (A., 1934, 268) and Koppeschaar methods give identical results. D. R. D.

Determination of inositol. A. P. SMIRNOV (Sborn. Rabot Chim. Tabak Bull., 1935, No. 125, 87—105).—The Pb-inositol compound may be used for the determination of inositol. The error is $> 6\%$. E. P.

Determination of pyridine in presence of ammonia. H. A. J. PIETERS (Chem. Weekblad, 1935,

32, 509).—Houghton's method (B., 1909, 1195) gives high results unless the last traces of NH_3 are removed by distillation with excess of an alkaline hypobromite solution.
D. R. D.

Hydrochloric acid as reagent for proteins and their derivatives. H. KÜHL (Pharm. Zentr., 1935, 76, 625—629).—The violet colour formed by the

action of HCl on some proteins and their decomp. products is sp. only for those containing $\cdot\text{CHO}$ or $\cdot\text{CO}$ groups. Aldehydic or ketonic carbohydrates or the simple aldehydes and ketones produce red to brown colours. Furfuraldehyde is the simplest compound which gives the violet colour, and it is also formed by pyrrole when an aldehyde containing a Me group is present.
E. H. S.

Biochemistry.

Respiratory exchange of oxygen and carbon dioxide during re-breathing from a rubber bag. S. A. GLADSTONE and S. DACK (Proc. Soc. Exp. Biol. Med., 1935, 32, 1315—1319).— CO_2 discharge into the lungs is high during the first period of re-breathing, but falls as alveolar CO_2 increases. O_2 absorption is $>$ normal in the first stage, and falls later. The R.Q. is > 1 in the first period, but falls rapidly in later periods. Addition of O_2 to the bag scarcely affects O_2 absorption; CO_2 discharge and the R.Q. are slightly depressed. Addition of CO_2 causes marked depressions in O_2 absorption, CO_2 discharge, and the R.Q.
R. N. C.

Respiratory quotients less than 0.7 in certain poikilotherms. L. DONTCHEFF and C. KAYSER (Compt. rend., 1935, 201, 474—476).—Poikilotherms react differently to hypertension of CO_2 , some (e.g., tortoise) responding by a hyperventilation, as with most homeotherms, whilst others (e.g., frog) do not change their respiratory rate, and consequently experience an increase in alkaline reserve. Vals. of R.Q. < 0.7 obtained with fasting frogs are erroneous.
F. O. H.

Changes in human cerebral blood-flow consequent on alterations in blood-gases. F. A. GIBBS, E. L. GIBBS, and W. G. LENNOX (Amer. J. Physiol., 1935, 111, 557—563).—Cerebral blood-flow in man increases and decreases \propto CO_2 tension and inversely \propto O_2 tension in the arterial blood. The changes due to CO_2 are $>$ those due to O_2 .
R. N. C.

Comparison of various concentrations of sodium oxalate solution with heparin for the determination of packed cell volume. O. S. WALTERS and J. W. MAY (J. Lab. Clin. Med., 1935, 20, 385—390).—Vals. obtained in the centrifugal method by the use of 1.5% $\text{Na}_2\text{C}_2\text{O}_4$ solution were identical with those obtained with heparin.
CH. ABS. (p)

Factors influencing the sedimentation rate of erythrocytes. T. H. CHERRY (J. Lab. Clin. Med., 1934, 20, 257—271).—Changes in sedimentation rates are caused by disturbances in the balance between cellular and fluid elements in the blood. High rates are associated with increased proportions of fibrin, euglobulin, and globulin in the plasma. Changes are not characteristic of particular diseases.
CH. ABS. (p)

Permeability of the red-cell membrane to glucose. K. A. KLINGHOFFER (Amer. J. Physiol., 1935, 111, 231—242).—The red-cell membrane is freely permeable to glucose (I) in solutions of concn. $< 2.3\%$. Addition of < 2 parts of (I) to 5 parts of blood

results in an increase in corpuscular vol. comparable with that produced by H_2O or urea solution and approx. equal in % to the serum vol. Addition of > 2 parts of (I) results in an increase in cell vol. $<$ with the same vol. of H_2O ; the change in permeability is not due to dilution of the serum or serum electrolytes, but is partly due to the increased (I) concn. There is no evidence that the permeability of the cell to bases is affected by increase of the concn. of serum non-electrolytes.
R. N. C.

Effect of cortico-adrenal extract on leucocytes in blood of normal adult rabbits. C. A. FOX and R. W. WHITEHEAD (Proc. Soc. Exp. Biol. Med., 1935, 32, 756—757).—The leucocyte counts are unaffected by prolonged treatment.
R. N. C.

Erythrocytes, hæmoglobin, and leucocyte count in cancerous affections of the bird. R. SALGUES (Compt. rend., 1935, 201, 430—432).—Cancerous growths in various situations cause a decrease in the no. of erythrocytes, % of hæmoglobin, and the leucocyte count, although the last two are sometimes increased.
J. L. D.

Hæmatological studies on cattle. I. Hæmoglobin, erythrocytes, and leucocytes in different breeds of cattle. M. MANRESA and N. C. REYES (Philippine Agric., 1934, 23, 588—603).—The hardness of cattle was \propto the hæmoglobin content of the blood.
CH. ABS. (p)

Regeneration of hæmoglobin. H. L. KEIL and V. E. NELSON (Proc. Iowa Acad. Sci., 1933, 40, 103—107; cf. this vol., 380).—Feeding Fe (as FeCl_3) in amounts > 10 mg. daily did not stimulate hæmoglobin (I) regeneration in anæmic rats. Of a no. of elements examined, only Cu produced positive effects. Intraperitoneal injection of FeCl_3 or Fe^{III} citrate into rats with nutritional anæmia increased (I), as also did $\text{Fe}(\text{OH})_3$ in rats receiving milk and Cu .
CH. ABS. (p)

Amount of hæmoglobin in the blood. E. R. HOLIDAY, P. M. T. KERRIDGE, and F. C. SMITH (Lancet, 1935, 229, 661—665).—A crit. survey of the hæmoglobinometers in present use, and their standardisation.
L. S. T.

Can hæmatoprosthetin be regarded as a mixture of oxyhæmin and oxyhæmin anhydride? A. HERZOG (Biochem. Z., 1935, 280, 137—147).—Tables summarise the % C and Fe of a no. of preps. of hæmatin and oxyhæmin (I). The higher or lower vals. of the $\text{C} : \text{Fe}$ ratio for these preps. depend on the method of prep., and the low C vals. cannot always be explained by assuming the entry of O or H_2O into the

mol. Hæmatoprosthetin is not a mixture of (I) and its anhydride. P. W. C.

Number of carbon atoms in the prosthetic group of blood-pigment. A. HERZOG (Biochem. Z., 1935, 280, 148—155).—The author's view, based on the results of analysis, that the low vals. for C obtained with hæmatoprosthetin are due not to entry of O or H₂O into the mol., but to loss of C, is further supported by new determinations of the Fe content of Teichmann's hæmin, oxyhæmin, hæmatoprosthetin, and chlorohæmatoprosthetin, and by the results of a guaiacol colour reaction which detects the C eliminated. P. W. C.

Action of sodium hydroxide on Teichmann's hæmin, hæmatoprosthetin, and hæmoglobin. A. HERZOG (Biochem. Z., 1935, 280, 156—160).—In alkaline solution the absorption spectra of Teichmann's hæmin, hæmatoprosthetin, and methæmoglobin differ according to the time of action and [NaOH]. A degradation of hæmoglobin under these conditions could not be detected. P. W. C.

Properties of reptilian blood. IV. The alligator (*Alligator mississippiensis*, Daudin). D. B. DILL and H. T. EDWARDS (J. Cell. Comp. Physiol., 1935, 6, 243—254).—The alkaline reserve of reptilian blood is not affected by exposure to high or low temp. Blood-lactate is apparently const. at 5° or 38° body-temp. Oxygenated red corpuscles of the alligator and crocodile have a buffer val. per unit of hæmoglobin (I) > that of human or lizard blood. The Bohr effects in human and lizard (I) are < in crocodile and alligator (I); the effect of O₂ on the base-binding capacity of (I) varies similarly. R. N. C.

Cholesterol of maternal and foetal blood at the conclusion of pregnancy. D. ROSENBLUM (Proc. Soc. Exp. Biol. Med., 1935, 32, 908—910).—Cholesterol in maternal is > in foetal blood. R. N. C.

Determination of blood-cholesterol. J. E. ANDES (J. Lab. Clin. Med., 1935, 20, 410—415).—The sample (0.25 c.c.) of whole blood or plasma is mixed with anhyd. CaSO₄. After 30 min. at room temp. the mass is extracted with CHCl₃ and the colour developed by the Liebermann-Burchard method. CH. ABS. (p)

Colorimetric determination of blood-cholesterol. R. S. FIDLER (J. Lab. Clin. Med., 1934, 20, 307—311).—The Liebermann-Burchard procedure is modified. An artificial standard is prepared from naphthol-green B. CH. ABS. (p)

Portal and hepatic blood-sugar after glucose administration. G. GIRAGOSSINTZ and J. M. D. OLMSTED (Proc. Soc. Exp. Biol. Med., 1935, 32, 668—670).—Injection of moderate amounts of glucose (I) into the duodenum of the decerebrate cat or amytalised dog sometimes, but not always, increases portal blood-(I) to vals. > hepatic (I). After 1 hr., while absorption is still taking place, hepatic (I) is always > portal (I), whilst portal lactic acid (II) is > hepatic (II), although the difference does not account for the whole of the difference between hepatic and portal (I). R. N. C.

Distribution of glucose in blood. J. M. D. OLMSTED (Amer. J. Physiol., 1935, 111, 551—553).—

The corpuscles of rabbit, rat, guinea-pig, cat, dog, and human blood contain no glucose (I), either in normal conditions or high and low blood-sugar, after adrenaline and insulin, respectively. C₂O₄'' renders the corpuscles permeable to (I), human corpuscles being particularly sensitive. R. N. C.

Determination of glucose in 0.1 ml. of blood by a modified Folin-Malmros method. H. S. H. WARDLAW (Med. J. Austral., 1934, 2, 571—573).—Details of the technique are given. CH. ABS. (p)

Hagedorn-Jensen method for [determining] blood-sugar. G. D. MACCO (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 561—563).—The Zn(OH)₂-protein ppt. is centrifuged instead of filtered. CH. ABS. (p)

Application of Yamada's colorimetric cryogenin method to the micro-determination of fructose and the determination of true glucose. H. OKAMURA (Japan J. Med. Sci., II, Biochem., 1935, 3, 9—14).—Deproteinisation of blood is effected with CdCl₂ and true total sugar determined in the same filtrate as fructose. The true glucose val. is obtained by difference. NUTR. ABS. (m)

Factors affecting blood glycolysis *in vitro* and *in vivo*. F. Y. HSU (J. Physiol., 1935, 84, 173—185).—The view that the glycolytic rate of the blood of pigs and sheep is < that of dogs and cats is confirmed. Individual differences in the glycolytic rate of dog's defibrinated blood are due to variations in the leucocyte content. Glycolysis is also observed in the blood in blood-vessels, which can also produce lactic acid at the expense of blood-sugar; this phenomenon may explain the same property in lung tissue. R. N. C.

Glycolysis in the blood of the goat. J. T. CUTTER (Proc. Soc. Exp. Biol. Med., 1935, 32, 921—926).—The rate of glycolysis in goat-blood is > in dog-blood. Inorg. PO₄''' rises slowly without any initial decrease; it is only slightly retarded by addition of glucose, and unaffected by NaF, even though this suppresses glycolysis. R. N. C.

Effect of arginase activators on the free arginine of blood. M. REISS, F. FLEISCHMANN, and L. SCHWARZ (Z. physiol. Chem., 1935, 236, 73—78; cf. this vol., 1014).—The free arginine content of rabbits' blood is decreased following intravenous administration of glutathione (I), cysteine (II), FeCl₂, and ascorbic acid (III) (and subcutaneous administration of toxic doses of FeCl₃ and MnSO₄), the max. effect appearing after about 1 hr. FeCl₂ given with or immediately after (I), (II), and (III) causes no appreciable increase in the reduction. In pregnant rabbits and in those inoculated with carcinoma the reduction produced by the activators before the physiological or pathological reduction sets in is > that in normal rabbits. W. McC.

Glutathione. II. Relation between reduced and oxidised glutathione and the oxygen content and capacity of blood. F. W. OBERST and E. B. WOODS. III. Disappearance of glutathione added to various solutions and biological fluids. F. W. OBERST (J. Biol. Chem., 1935, 111, 1—7, 9—16).—II. There is no direct relation between the

degree of O_2 saturation of blood and the % of un-reduced glutathione (I), which was never found $> 30\%$. The higher total (I) vals. are associated with higher cell vols. and O_2 capacities.

III. (I) is destroyed in aq. solutions of urinary albumin and globulin, ovalbumin, caseinogen, gelatin, heparin, serum, aq. humour, vitreous humour, and Bactopeptone. (I) added to whole blood is destroyed, and hæmolysis lowers the normal whole-blood val. A suspension of laked or unlaked erythrocytes in isotonic saline loses (I) as slowly as in whole blood. It is concluded that the small losses in whole blood are due to the diffusion of (I) from the cells and its subsequent destruction by the serum-proteins.

H. D.

Determination of blood-urea. G. L. PESKETT (Brit. J. Exp. Path., 1934, 15, 306—308).—The vol. of the digestion mixture in Cole's method is limited to 2 ml., the amount of EtOH is reduced to < 1 third, and the sensitivity of the titration end-point is increased sufficiently to permit the use of 0.006*N*-acid and -alkali. Slightly warming the mixture before distillation flocculates proteins, and the clear supernatant liquid is practically colourless.

CH. ABS. (p)

Micro-determination of urea in blood. A. W. WITTELMANS (Nederland. Tijdschr. Geneesk., 1935, 79, 311).—The procedure combines the urease method (Conway's units) with the indophenol-blue NH_3 reaction, a simple photo-electric apparatus being used for colorimeter. 0.1 ml. of blood suffices for duplicate determinations; the accuracy is about ± 2.5 mg. per 100 ml.

NUTR. ABS. (m)

Effect of administered glucose on the amino-nitrogen content of the blood. J. M. LUCK, B. L. DAVIS, jun., and W. VAN WINKLE, jun. (Proc. Soc. Exp. Biol. Med., 1935, 32, 1039—1041).—Ingestion of glucose (I) in human subjects is followed by a fall of blood- NH_2-N , considered to be due to increased adrenaline secretion evoked by the increased insulin secretion after ingestion of (I).

R. N. C.

Micro-determination of biological carbon, especially of residual carbon in blood. (A) W. STEPP. (B) V. RUPPERT (Z. physiol. Chem., 1935, 235, 273—275, 276).—(A) Ruppert's conception (this vol., 674) of residual C is less useful than the usually accepted one and he overlooks the author's work (Ergebn. Physiol., 1921, 19, 290—325).

(B) The author's views are maintained.

W. McC.

Friend's method for the determination of chlorides [in blood]. J. E. HEARN (J. Lab. Clin. Med., 1934, 20, 302—303).—A solution of $AgNO_3$ of which 1 c.c. is equiv. to 1 mg. of NaCl is substituted for the 0.02*N* solution used originally (A., 1922, ii, 389).

CH. ABS. (p)

Blood-calcium in southern Chinese. W. W. CADBURY and T. T. YAN (Chinese Med. J., 1935, 49, 700—702).—Blood-Ca approximates to that of the white race.

H. G. R.

Determination of serum-iron. F. C. BING and R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1935, 32, 1013—1014).—Serum is ashed with conc. H_2SO_4 and

30% H_2O_2 , diluted, $KMnO_4$ added until pink, the solution covered with EtOAc, and NH_4CNS added. The EtOAc layer is compared colorimetrically with a standard. The benzidine method can be used for hæmoglobin, but allowance must be made for the serum-proteins, which affect the colour. The non-hæmoglobin Fe is inorg.

R. N. C.

Phosphorus of blood. III. Phosphorus partition in whole blood and in serum, and the serum-calcium and plasma-phosphatase during healing of late rickets. G. STEARNS and E. WARWEG (Amer. J. Dis. Children, 1935, 49, 70—90; cf. this vol., 374).—The org. acid-sol. or ester fraction of the P of red corpuscles is lowered in untreated active late rickets. On administration of vitamin-D vals. increase in advance of the inorg. P of serum. The readily hydrolysable fraction of the ester-P (10 min. boiling with *N*-acid) is not significantly different from normal. Plasma-phosphatase increases in rickets, declines as healing progresses, but is still > 1 normal when roentgenologic healing is complete.

CH. ABS. (p)

Acid-soluble, mineral, and ultrafilterable phosphorus of the blood. I. POROP (Compt. rend., 1935, 201, 490—492).—The acid-sol. (I), mineral, and ultrafilterable P (II) in the blood-serum and blood-plasma of dogs have been determined. Addition of $CaCl_2$ *in vitro* produces changes in the proportion of (II) in accord with the results of Scholtz (A., 1931, 506) and Grollmann (A., 1927, 584). In normal serum and plasma (II) is entirely mineral and composed of orthophosphates (III). In experimental acidosis the proportion in the serum of (I) and (III) increases, whilst in alkalosis it diminishes.

H. G. M.

Total protein content of plasma and serum. W. LEHMAN and F. H. SCOTT (J. Biol. Chem., 1935, 111, 43—44).—The % of protein in oxalated plasma and defibrinated serum was the same.

H. D.

Alteration of protein distribution, *in vitro*, between corpuscles and plasma caused by isotonic and hyperosmotic solutions. C. J. BELLIS and F. H. SCOTT (J. Biol. Chem., 1935, 111, 17—42).—The increases in the serum-protein content produced by the addition of isotonic solutions of NaCl, $CaCl_2$, and $BaCl_2$ \propto dilution; hypertonic solutions decreased the serum-protein content to a limiting val. and increased the non-protein-N. The changes occur chiefly in the albumin fraction. Although the γ of the hypertonic solutions were $>$ that of H_2O , their addition to serum was without influence of its γ . The electrokinetic potentials of the erythrocytes and serum-proteins were either zero or reversed by treatment with hypertonic solutions. A modified viscosimeter is described.

H. D.

Effect of a low-calorie low-protein diet on blood-proteins. W. C. CUTTING and R. D. CUTTER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1053—1056).—A low-calorie protein-free diet concentrates the blood and increases serum-protein in man, due chiefly to low fluid intake; the increase in serum-protein is not quite \propto that of blood concn., indicating that some protein is lost. Total blood-proteins are lowered,

but their character is unchanged by 2 days of protein deprivation. R. N. C.

Influence of parenteral administration of protein- and non-protein-colloids on blood-proteins. H. HEINLEIN (Arch. exp. Path. Pharm., 1935, 179, 127—144).—Parenteral administration of "caseosan" or horse-serum to rabbits increases blood-fibrinogen and -globulin and decreases -albumin. Non-protein colloids (Cu, Bi, S, trypan-blue, etc.) have a similar but more marked and rapid action, which is therefore not specifically related to the phenomena of anaphylactic shock or antigen-antibody reaction. The hyperproteinæmia is due to increased cellular reaction. F. O. H.

Protein fractions of blood sera. II. Blood sera of opium addicts. R. N. CHOPRA, S. N. MUKHERJEE, and G. S. CHOPRA. **III. Malarial sera during and after the rigour stage.** R. N. CHOPRA, S. N. MUKHERJEE, and B. SEN (Indian J. Med. Res., 1935, 22, 561—570, 571—580).—II. Opium addicts show a lowered blood- p_H , concurrent with an increase of CO_2 tension. Buffer action is reduced, due to lowered alkaline reserve, and its efficiency as a buffer through increased CO_2 tension, σ is increased, and relative η decreased, indicating increased fluid and decreased protein contents. In some cases η of the whole blood increases. Total proteins are diminished. The albumin and euglobulin fractions are increased, whilst the pseudoglobulin fraction is decreased.

III. During the rigour stage in malaria, blood- p_H and buffer action are scarcely changed, whilst σ and η both fall, particularly σ . Total proteins fall, albumins decrease, euglobulin increases, whilst pseudoglobulin remains practically normal. After the rigour subsides the physical properties and protein contents tend to return to normal. R. N. C.

Determination of plasma-fibrin. S. ROSENFELD and A. S. WIENER (Proc. Soc. Exp. Biol. Med., 1935, 32, 788—791).—The fibrin is coagulated with tiger-snake venom, washed with H_2O , dried, and weighed. The results agree closely with those obtained by the micro-Kjeldahl method. R. N. C.

Effect of temperature on hæmolysis by hypotonic solutions. V. V. LEPESCHKIN (Pflüger's Archiv, 1935, 235, 756—763).—Resistance of red corpuscles to hæmolysis by hypotonic NaCl or Na_2SO_4 solutions, unbuffered or lightly buffered with PO_4''' at p_H 7.3, increases with rise of temp. to a max. at 40—50°, afterwards declining through spontaneous hæmolysis at high temp. High PO_4''' concns., or the substitution for hypotonic solutions of pure buffer solutions at the same p_H , shift the max. to 23—25°, probably through increased permeability of the corpuscles to PO_4''' at high temp. In acid solution temp. has no effect. The osmotic pressure of the corpuscles does not play a decisive part in the increased resistance, since the cooling of a corpuscle suspension hæmolysed at high temp. does not intensify hæmolysis. This effect is attributed to increased viscosity of the corpuscular protoplasm.

R. N. C.

Specificity of antivenomous sera with special reference to sera prepared with venoms of

Indian and South African snakes. M. L. AHUJA (Indian J. Med. Res., 1935, 22, 479—484).—Antivenenens of Indian and Cape cobras each exert a protective effect against the venom of either species, but neither protects against the venom of the banded krait. Each antivenenens inhibits the hæmolytic effect of both cobra venoms, which therefore contain the same hæmolytic principle. R. N. C.

Detoxication of snake venom by the photodynamic action of methylene-blue. H. E. SHORTT and S. M. K. MALLICK (Indian J. Med. Res., 1935, 22, 529—536).—*Daboia* venom (I) is rapidly detoxicated by the photodynamic action of methylene-blue (II), the rate of detoxication depending on the time of exposure and the concns. of (I) and (II). The optimum concn. of (II) is approx. 1/50,000. Detoxication of (I) by (II) also destroys its antigenic properties. R. N. C.

Venom of *Lachesis (Bothrops)* snakes. I. Blood-coagulating activity and purification of venom of *L. jararaca*. D. VON KLOBUSITZKY (Arch. exp. Path. Pharm., 1935, 179, 204—216).—Fresh venom (total N, 9.704%; heat-coagulable N, 8.971%; light petroleum extract, 5.296%; inorg. salts, 4.437%; Cl, 0.179% of dry substance) in concn. of 0.005% has a blood-coagulating action; with 0.01—0.02% it inhibits coagulation whilst higher concns. have a hæmolytic action. Pptn., dialysis, etc. of the venom yields a colloidal active product, "bothropotoxin" (I), free from hæmolytic action, from which toxic and blood-coagulating principles could not be isolated. Replacement of Ca and destabilisation of fibrinogen are concerned in the blood-coagulation by (I). F. O. H.

Gelation of blood with nucleated corpuscles and pathological blood. E. BIOCICA (Atti R. Accad. Lincei, 1935, [vi], 21, 666—670).—Blood with nucleated erythrocytes (birds, reptiles, amphibia, fishes) when hæmolysed and treated with neutral salts [$K_2Fe(CN)_6$, $(NH_4)_2SO_4$, $KMnO_4$, NaCl, etc.] gelatinises even when dil. (down to 2%). Drying at room temp. does not prevent the reaction, which is also shown by blood of new-born and leucæmic (but not leucoctytic) persons. The phenomena is due to nucleoproteins of the nuclei. F. O. H.

Effect of anticoagulants on the determination of certain substances in blood. I. BLITSTEIN (Rev. belge Sci. méd., 1935, 7, 69—154).—The effects of $K_2C_2O_4$, Na citrate, NaF, $ZnSO_4$, heparin, hirudin, and "liquoid Roche," in the determination of cell-vol., dry matter, Cl, cholesterol (I), inorg. P, non-protein-N, serine, and globulins were examined. The vals. for serum and plasma were compared. For plasma vals. the first four anticoagulants are not satisfactory, and the last three are not universally applicable. For the determination of cell vol., dry matter, Cl, and (I) all three can be used, but for inorg. P only "liquoid" can be used if equal plasma and serum vals. are to be obtained. For the determination of non-protein-N and the proteins it is better to use serum. NUTR. ABS. (m)

Heparin: a chondroitinpolysulphuric acid. A. SCHMITZ (Z. physiol. Chem., 1935, 236, 1; cf. this

vol., 646, 1024).—Highly purified heparin (I) (1000 units per mg.) contains no H_2SO_4 and yields no hydrochloride. The ash content is $<4\%$. Possibly derivatives of (I) (or other inhibitors of coagulation) occur in the organism or are produced during isolation, but the active principle of (I) appears in all cases to be a monocarboxylic derivative of a polysaccharide.

W. McC.

Immunological reactions and viscosity. L. DU NOUX (Science, 1935, 82, 254).—Certain immunological reactions accompanied by changes in η are summarised.

L. S. T.

Ultra-violet absorption spectra of normal antitoxic and antimicrobial serums and their respective protein fractions. I. PIROSKY (Folia Biol., 1931, Nos. 3—4, 9—10).—Spectrographic differences between normal and antitoxic sera are examined. Clear differences are shown in the spectrograms of euglobulins, pseudoglobulins, and albumins separated by electrodialysis.

CH. ABS. (p)

Heterophile antibodies in infectious mononucleosis. C. A. STUART (Proc. Soc. Exp. Biol. Med., 1935, 32, 861—863).—Emulsions of guinea-pig kidney adsorb the sheep-cell antibodies from rabbit antiginea-pig-kidney serum, but do not adsorb them from infectious mononucleosis serum. Boiled sheep cells adsorb the antibodies from both sera. Injection of guinea-pig emulsion into rabbits produces a high lysis but a low agglutinin content; in infectious mononucleosis the two are of the same order.

R. N. C.

Effects of hyperpyrexia induced by physical means on complement-fixing antibodies. J. G. HADJOPOULOS and W. BIERMAN (J. Lab. Clin. Med., 1934, 20, 227—230).—Exposure of rabbits, after injection of killed bacteria, to radiotherapy sufficient to raise their temp. to $41-42^\circ$ caused a temporary decrease in the concn. of complement-fixing antibodies.

CH. ABS. (p).

Equivalence-point ratio of antibody to antigen in ovalbumin precipitates. S. B. HOOKER and W. C. BOYD (Proc. Soc. Exp. Biol. Med., 1935, 32, 1104—1106).—The mean equivalence-point antibody-antigen ratio in ovalbumin-antiserum ppts. is 9.99 ± 0.13 .

R. N. C.

Antigens for complement fixation in amoebiasis. C. F. CRAIG and L. C. SCOTT (Proc. Soc. Exp. Biol. Med., 1935, 32, 958—960).—EtOH extracts of the mucoid material from the intestines of dogs infected with *Endamoeba histolytica* are excellent antigens for complement fixation in amoebiasis.

R. N. C.

New antigens for the Kolmer modification of the Wassermann test. J. A. KOLMER (Amer. J. Clin. Path., 1935, 5, 55—59).—In the prep. of cholesterolised and lecithinised antigens described, the sensitiveness is increased by addition of COME₂-insol. lipins.

CH. ABS. (p)

Rabies fixed virus as an antigenic agent when inactivated by the photodynamic action of methylene-blue. H. E. SHORTT and A. G. BROOKS (Indian J. Med. Res., 1935, 22, 557—560).—The

antigenic activity of rabies fixed serum is impaired by the photodynamic action of methylene-blue.

R. N. C.

Antigenic fixatives of tubercle bacilli. II. Purification and fractionation of lipins with hapten activity from heat-killed bacilli. M. A. MACHEBOEUF and A. BONNEFOI (Ann. Inst. Pasteur, 1935, 55, 433—440; cf. A., 1934, 564, 929; this vol., 256, 407).—Heat-killed tubercle bacilli are washed with H_2O and dried and freed from extractable lipins with COME₂; the residue is exhaustively extracted with hot 96% EtOH. On cooling, an inactive fraction is pptd.; the solution is then evaporated in vac., and the dried residue taken up with $CHCl_3$. A fraction containing practically the whole hapten activity is pptd. with COME₂ (P 3.8, N 2.36%). Repetition of this COME₂ pptn. leads to no significant change in the hapten activity or in the chemical composition; pptn. is almost quant. Fractional pptn. of the $CHCl_3$ solution with cooled MeOH yields fractions of higher hapten activity and different chemical composition (P 3.32, N 1.43% after 5 ppts.).

E. A. H. R.

Anti-gonadotropic sera. C. BACHMAN (Proc. Soc. Exp. Biol. Med., 1935, 32, 851—854).—Rabbits injected with anterior pituitary-like hormone (I) from pregnancy urine yield sera that give weak complement-fixation reactions with (I) solutions and extracts of male urine *in vitro*; human serum-proteins give stronger and less const. reactions. There is no apparent connexion between these reactions and the sp. (I) inhibition by such sera that can be demonstrated biologically.

R. N. C.

Placental immunity. I. Determination of dosage of placental globulin in measles prophylaxis. S. KARELITZ, C. K. GREENWALD, and A. J. KLEIN. II. Comparison of maternal circulating blood immunity with that of placental fluid. S. KARELITZ and C. K. GREENWALD (Proc. Soc. Exp. Biol. Med., 1935, 32, 1359—1362, 1362—1365).—I. The measles prophylactic vals. of the amounts of human blood-serum and of placental extract that contain one unit of diphtheria antitoxin (I) are equiv. Both the measles antibody and (I) are contained in the globulin extract of placenta, which is effective in measles prophylaxis.

II. The (I) titre of placental fluid is equal to that of the serum of the circulating maternal blood at the time of placental expulsion. Those of the circulating maternal blood and placental blood and tissue fluid are alike in most cases.

R. N. C.

Comparative action of the bile acids on tetanus and diphtheria toxins; special properties of lithocholic acid. L. VELLUZ (Compt. rend., 1935, 201, 432—434).— > 50 mg. of Na glyco- or taurocholate are required to destroy the toxicity of 1000 lethal doses of tetanus toxin (I) at $37-38^\circ$ during 5 days; diphtheria toxin (II) is unchanged. Na cholate, deoxy- and litho-cholate are about 500 times as active in detoxifying (I), and are progressively more capable of destroying (II) because of the no. of OH-groups in the mols.

J. L. D.

Heat-stable agglutinogens in the *Suipestifer* group. P. LEVINE and A. W. FRISCH (Proc. Soc.

Exp. Biol. Med., 1935, **32**, 883—886).—The various strains of *Suipestifer* differ widely from one another in their ability to absorb phage and agglutinins.

Stability of streptofibrinolysin. R. R. MADISON and J. K. VAN DEVENTER (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1041—1043).—The fibrinolytic titre of *Streptococcus* filtrate often shows considerable increase on mixing with normal horse-serum, during neutralisation with sp. immune serum, or when stored at 4°.

R. N. C.

Antifibrinolytic titre of commercial antistreptococcal sera. J. K. VAN DEVENTER (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1117—1118).—Vals. are given for 28 sera. Each species is immunised only against the homologous fibrinolysin.

R. N. C.

Complement titre of the blood in allergic conditions. E. B. TILDEN (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1135—1136).—The complement content of the blood of allergic patients is similar to the average content of general clinical cases.

R. N. C.

Mutual interaction of liquid films.—See this vol., 1317.

Concentration of heavy water within the human organism. G. ORBAN (Orvosi Hetilap, 1935, **79**, 193—194).—No appreciable amount of D₂O was detected in H₂O from brain and liver of old men or from flesh of old oxen. The osmotic function of the kidneys probably prevents accumulation of D₂O.

CH. ABS. (p)

Hydrogen-ion concentration of the digestive tract of the fowl. R. L. MAYHEW (J. Amer. Vet. Med. Assoc., 1935, **39**, 148—152).—*p_H* vals. averaged 5.0 in the crop, increasing to neutrality in the caecum. Acidity of the posterior portion was higher in birds 10—11 weeks old than in older ones.

CH. ABS. (p)

Dust in the organism. II. Technique of determination of siliceous particles and particles of carbon in the lung. E. KAHANE (J. Pharm. Chim., 1935, [viii], **22**, 204—211).—The lung-tissue is digested with H₂SO₄+HNO₃+HClO₄ and the siliceous material collected. The SiO₂ content is determined by treatment with H₂SO₄+HF. In the determination of free C, the tissue is digested first with HNO₃, and the remaining lipid material treated with fuming HNO₃ until sol. in COMe₂.

R. S.

Chemical analyses of the flesh and viscera of slaughterhouse animals. G. BALBONI (Quad. Nutrizione, 1934, **1**, 275—283).—Tables give data for edible portion, solid residue, N, protein, fat, and ash of the ox, calf, horse, pig, and lamb.

NUTR. ABS. (m)

Distribution of choline. J. P. FLETCHER, C. H. BEST, and O. M. SOLANDT (Biochem. J., 1935, **29**, 2278—2284).—The total choline (I) content of tissues is determined by digestion of the tissue with HCl, extraction of the (I) followed by acetylation, and assay of the acetylcholine using the isolated intestine of the rabbit. The results are correct within 10%. The total (I) contents of the various tissues of the white rat and other animals, and of many foods of both animal and vegetable origin, have been determined. Spermatid fluid contains the greatest amount; next in order come the various parts of the central

nervous system and the liver. Fat and blood contain the least (I).

J. N. A.

Iodine contents of various endocrine organs of normal rabbits. A. OHTA (Sei-i-Kwai Med. J., 1934, **53**, No. 8, 1—8).—The I content of organs decreased in the order, thyroid, spleen, adrenal gland, thymus, testicle, liver, male blood, female blood, ovary (trace). Pituitary and pancreas contained none.

CH. ABS. (p)

Mineral constituents of bone. I. Methods of analysis. C. M. BURNS and N. HENDERSON (Biochem. J., 1935, **29**, 2385—2395).—Analysis of bone-phosphate by a method which involves filtering off the ppt. produced by (NH₄)₂MoO₄ gives low results. Extraction of the bones by alkaline glycerol by the method of Morgulis removes some phosphate, so that the remaining salt does not accurately represent the original bone. Methods are described for the analysis of bone-Ca, -P, and -carbonate with an accuracy of 1.5%, 1.5%, and 3%, respectively. Bone probably contains a phosphate which is not tertiary Ca or Mg phosphate.

W. O. K.

Calcium content of bone determined *in vivo*. A. W. ENDTZ (Maandschr. Kindergeneesk., 1934, **4**, 7).—An improvement of the method of de Does *et al.* (1933) is described. The Ca content of the radius in normal children is > that in the radius of children suffering from rickets, osteopsathyrosis, or intestinal infantilism with osteoporosis.

NUTR. ABS. (m)

Normal distribution of calcium between the skeleton and soft tissues. O. A. BESSEY, C. G. KING, E. J. QUINN, and H. C. SHERMAN (J. Biol. Chem., 1935, **111**, 115—118).—Of the total body-Ca of rats, 99.3% is in the skeletal system. In immature growing rats, and in adult rats on a low-Ca diet, the % is less (about 99.0%).

F. A. A.

Chemistry of bone-salts. R. KLEMENT (Z. physiol. Chem., 1935, **235**, 272; cf. this vol., 1004).—Since the nature of the salts in bone cannot be deduced from chemical analysis alone, and since X-ray examination indicates that the Ca is present chiefly as hydroxyapatite (cf. Tromel *et al.*, A., 1932, 707), the conclusions of Marek *et al.* must be rejected.

W. McC.

Distribution of diethylbarbituric acid in brain. E. KEESER and I. KEESER (Arch. exp. Path. Pharm., 1935, **179**, 226—228).—Using better methods of extraction, the preferential absorption of barbitol in the diencephalon after intravenous injection of suitably small doses into rabbits is confirmed (cf. this vol., 525).

F. O. H.

Etiology and histology of dental tartars. J. D. BERKE (Dental Cosmos, 1935, **77**, 134—139).—Deposition of Ca salts is not by crystallisation, but occurs in a matrix of fungi, bacteria, fibrin, haemoglobin, phagocytes, and epithelial cells.

CH. ABS. (p)

Fibre forms in animal hairs. R. O. HALL (Nature, 1935, **136**, 478).—Straightening and steaming certain animal guard hairs with supernormal curvature at the tip results in further contraction. This is opposed to Woods' views (this vol., 1266).

L. S. T.

Rhythmic changes in the foetal liver after feeding. H. A. STUART and G. M. HIGGINS (Amer. J. Physiol., 1935, **111**, 590—595).—Liver-glycogen (I) in the rat foetus increases to a max. 12 hr. after the feeding of the mother, and falls again to the initial level after 24 hr. Foetal (I) is > maternal (I) in proportion to the wt. of the liver, both before and after feeding. Foetal (I) remains fairly high when maternal (I) is lowered by fasting; it begins to rise immediately food is given to the mother. R. N. C.

Glycogen content in the central nervous system of human embryos. O. FUSEJIMA (Sei-i-Kwai Med. J., 1934, **53**, No. 9, 1—79).—Histological analysis. CH. ABS. (p)

Glycogen. II. Occurrence of glycogen in the neoplasma and allied changes in epithelial covering. S. HORIE (Sei-i-Kwai Med. J., 1934, **53**, No. 9, 243—267; cf. this vol., 237).—Histological analysis. CH. ABS. (p)

Determination of muscle-haemoglobin. R. H. WATSON (Biochem. J., 1935, **29**, 2114—2121).—Quant. extraction is achieved by washing the minced unperfused tissue with $M/15\text{-PO}_4'''$ buffer at p_H 6.5, adsorption from the extract by kieselguhr, elution with aq. NH_3 , and clearing of the eluted fluid by $\text{Al}(\text{OH})_3$. The relative concns. of haemoglobin (I) in blood and muscle are then determined from the position of the α -band of the oxyhaemoglobin (reversion spectroscopy) and the total concn. of (I) is determined spectrophotometrically. (I) in muscle extracts is also determined colorimetrically by conversion into acid haematin. Data, mainly from heart-muscle, are compared with those of Whipple (Amer. J. Physiol., 1926, **76**, 693). F. O. H.

Non-protein nitrogenous constituents of fish and lobster muscle. J. CAMPBELL (J. Biol. Board Canad., 1935, **1**, 179—189).—The total non-protein-N in muscle of cod, herring, haddock, and salmon is of the same order; that of skate is higher, mainly as a result of larger proportions of urea, NH_3 , and volatile bases; that of lobster is still higher, due to larger mono- NH_2 -acid and histidine-arginine (I) fractions. Cod muscle is rich in the lysine (II) fraction and low in (I) fraction. Herring has intermediate proportions, but (II) is approx. double (I). In lobster (II) is < in cod, but the N of (I) is extremely high. Relationships between morphology and chemical composition are examined. CH. ABS. (p)

Determination of fermentable sugar in muscle. A. STEINER (Proc. Soc. Exp. Biol. Med., 1935, **32**, 968—971).—The muscle is fixed in $N\text{-H}_2\text{SO}_4$ at -4° , ground up, and extracted with the same solution. Glycogen and hexose monophosphate are removed by pptn. twice with $\text{Fe}_2(\text{SO}_4)_3\text{-HgSO}_4$ reagent in H_2SO_4 solution, the mixture is neutralised with BaCO_3 and filtered. After removal of Fe and Hg with H_2S , and of Ba and excess of H_2S , the filtrate is evaporated in vac., salts are pptd. with EtOH, and the filtrate is again evaporated in vac. The residue is dissolved in H_2O , and total sugar determined by Cu and I in one part of the solution after hydrolysis with $N\text{-H}_2\text{SO}_4$. In other parts glucose is determined by fermentation with Fleischmann's yeast at an alkaline p_H , and glucose and maltose together at an acid p_H . Mannose does not

interfere. Tetanic stimulation of muscle causes an increase in glucose, but not in maltose. R. N. C.

Stony deposits in the gluteal muscles of a horse. A. H. KHAN (Vet. Rec., 1933, **13**, 1134—1135).—Grey deposits in an aged horse consisted mainly of Ca Al silicate. CH. ABS. (p)

Metabolism of the phospholipins. VI. Relative proportions of saturated and unsaturated fatty acids in phospholipins of different degrees of unsaturation. VII. Selection and retention of unsaturated fatty acids by phospholipins of animal tissues. R. G. SINCLAIR (J. Biol. Chem., 1935, **111**, 261—273, 275—284; cf. A., 1932, 643).—VI. By the Twitchell Pb salt-EtOH method it has been shown that the ratio of solid to liquid acids in phospholipins (I) of the liver, skeletal muscle, and kidney of the rat is const., regardless of the degree of unsaturation of the mixed acids. Differences in the degree of unsaturation of tissue-(I) fatty acids are due to differences in the relative proportions of the various unsaturated fatty acids. A micro-method which permits the determination of the relative proportions and the I vals. of solid and liquid acids in 30—40 mg. of mixed acids is described.

VII. The feeding of a fully saturated fat has no effect on the degree of unsaturation of the tissue-(I), and it does not interfere with the effect of small amounts of very unsaturated fat on the unsaturation of the (I). The high degree of unsaturation induced in tissue-(I) by daily feeding of a small amount of highly unsaturated fat is maintained during prolonged fasting. J. N. A.

Relation between the pituitary and lipin content of organs: relationship between the pituitary and adrenaline content of the adrenals. I. T. USUI (Sei-i-kwai Med. J., 1934, **53**, No. 4, 1—103; No. 5, 105—171).—Effects are recorded of injections of pituitrin (I), pituglandol (II), hypophorin, puberogen, and antuitrin (III) on the fatty acid, cholesterol, and unsaponifiable matter of organs of rats. Hypophysectomy induces changes in the lipin content of organs which can be restored, to some extent, by injection of (I), (II), or (III). The coincident change in adrenaline content of the adrenal cannot be so remedied. CH. ABS. (p)

Lipochromes of higher animals and of man. L. ZECHMEISTER and P. TUZSON (Naturwiss., 1935, **23**, 680—685).—A review.

Lipochromes of fats. L. ZECHMEISTER and P. TUZSON (Orvosi Hetilap, 1935, **79**, 115—116).—The fats of the cow and horse contain, respectively, 11 and 6 mg. per kg. of carotene (I) and fowl fat contains 5 mg. per kg. of (I)-free xanthophyll. The lipochromes of human fat are identical with those in the plants from which they originate. NUTR. ABS. (m)

Occurrence of a saturated hydrocarbon, pristane, in sardine, herring, and sperm oils. Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, **38**, 254—258B; cf. A., 1923, i, 890).—An isoparaffin, regarded as pristane, has been recovered in very small amount from the condensates obtained by the steam-distillation in vac. of sardine, small herring, mixed fish (sardine+herring), and sperm oils. E. L.

Gadusene, an unsaturated hydrocarbon occurring in animal and vegetable oils. Z. NAKAMIYA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 16—26).—A detailed account of work already noted (this vol., 1264).

Actiniasterol. E. KLENK and W. DIEBOLD (Z. physiol. Chem., 1935, 236, 141—144; cf. Dorée, A., 1909, i, 152).—The sea anemone, *Anemonia sulcata*, yields a sterol, *actiniasterol* (I), m.p. 145—146°, $[\alpha]_D^{20}$ -42.5° in CHCl_3 (acetate, m.p. 126.0—126.5°). (I) in AcOH with $\text{PtO}_2 + \text{H}_2$ gives the *acetate*, m.p. about 120°, of the H_4 -derivative, m.p. 139—140°.

W. McC.

Reduced-glutathione contents in an incubated egg and in the organ tissues of a chick and the effect of sodium glutamate on their glutathione contents. F. MURATA (Sei-i-Kwai Med. J., 1933, 52, No. 10, 1—34; cf. this vol., 511, 536).—Reduced glutathione (I) is slightly higher in the yolk of the fertilised than in that of the unfertilised egg. During incubation vals. decline to zero at approx. the 15th day. In the embryo (I) increases to a max. on the 18th day. Injection of Na glutamate increases (I) in yolk and embryo. Chicks show a marked increase in (I) in the digestive tract after 1 week, and a further increase after 3 weeks, notably in lungs.

CH. ABS. (p)

Colouring matter of domestic cocoons. IX. Water-soluble colouring matter of yellow cocoons; colouring matter of white, green, and red cocoons. X. Fluorescent colour of cocoons in ultra-violet light and the colouring matters of cocoons. M. OKU (J. Agric. Chem. Soc. Japan, 1934, 10, 1239—1252, 1253—1257; cf. this vol., 883).—IX. Yellow cocoons yield a glucoside, sol. in 80% EtOH, giving an amorphous brown powder and glucose on hydrolysis. The EtOH-extract of white cocoons contains H_2O -sol. pigments resembling flavonol. Green cocoons similarly yield colouring matter resembling bombycetin and bombycin. The red pigment in red cocoons is a xanthophyll. The green colour in *Rhodinia fugax* is chlorophyll.

X. Coloured cocoons give a yellow fluorescence in ultra-violet light. When the colouring matter is extracted a violet fluorescence is observed. This may be due to sericin and fibroin. The isolated pigments, lutein, violaxanthin, carotene, bombycin, bombycetin, etc., give a yellow fluorescence.

CH. ABS. (p)

Behaviour of aqueous solution of the domestic cocoon. XXI. Isoelectric points of sericin and fibroin. H. KANEKO and K. YAMAMOTO. XXII. **Adsorption of colouring matter by sericin**. H. KANEKO and Y. NAKAZAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 1291—1294, 1295—1297; cf. this vol., 511).—XXI. The 3 isoelectric points for each of fresh and dry cocoons and raw and boiled-off silk were determined. Boiling cocoon fibre with H_2O or alkali lowered the first (lowest) isoelectric point in proportion to the boiling-off coeff. It was also lowered by treatment with higher fatty acids or bleaching agents and under the action of air and heat, and was raised by treatment with reducing agents or by dyeing.

XXII. Adsorption of natural pigments and of dyes

by sericin-A was markedly superior to that by sericin-B.

CH. ABS. (p)

Putrefactive decomposition of Bengal silk cocoon. S. DUTT (J. Indian Chem. Soc., 1935, 12, 458—462).—Complete hydrolysis by HCl of the cocoons gave various NH_2 -acids, the relative amounts of which are similar to those found in the hydrolysis of Bengal silk (A., 1909, i, 750), except that this gives rise to much less serine. The products of the putrefaction of the cocoons are CO_2 , NH_3 , NH_2Me , NH_2Et , $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{NH}_2$, $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$, and fibrous matter. The formation of these amines explains why the product of putrefaction of silk acts as a pressor substance for the heart.

H. G. M.

Chemical composition of the crystalline style and of the gastric shield: occurrence of the style oxidase. C. BERKELEY (Biol. Bull., 1935, 68, 107—114).—Acid hydrolysis of the cryst. styles of *Schizothaerus nuttalli*, *Mya arenaria*, *Ostrea gigas*, and *Saxidomus giganteus* yields protein, glucosamine, and H_2SO_4 and approx. the same amounts of glycuronic acid. These are cleavage products of mucin rather than of chondrin. The gastric shield in *S. nuttalli* is chitin. *Panope generosa*, *Pholadidea penita*, and the gastropod *Crepidula fornicata* have an oxidase system in the cryst. style (cf. A., 1933, 297, 1201).

CH. ABS. (p)

Coccids of Japan. VIII. Nitrogenous compounds and mineral constituents of *Iceria purchasi*. Mask. M. KONO and R. MARUYAMA (J. Agric. Chem. Soc. Japan, 1935, 11, 21—28; cf. A., 1934, 1381).—Analytical data.

CH. ABS. (p)

Influence of the physical properties of milk on its rate of digestion *in vivo*. C. Y. CANNON and D. L. ESPE (Iowa Agric. Exp. Sta. Rept., 1933, 35—36; cf. this vol., 379).—Young calves excrete fat even when none is supplied in the diet. Butter-fat renders casein more easily digested by calves. High-fat milk leaves the stomach more quickly than does low-fat milk.

CH. ABS. (p)

Influence of the food of the cow on the nutritional value of the milk. E. SCOTT, L. A. ERF, and C. J. DELOR (Vet. Alumni Quart., 1933, 20, 154—166).—Nutritional anaemia in rats was relieved by feeding milk from cows receiving lucerne-grain rations with CuSO_4 , MnI_2 , Fe sulphate, As, AlCl_3 , and ZnCl_2 , or by supplementing the diet with an EtOH extract of dried lucerne dissolved in olive oil, or by feeding halibut oil. The relationship between the food of the cow and the hæmopoietic properties of the milk is examined.

CH. ABS. (p)

Variations in the fat content of human milk during suckling. D. LUCIGNANI (Riv. Clin. pediat., 1934, No. 4, 412).—During suckling the fat % increased during the first 10 min. and fell slightly in the last 5, whilst the quantity of milk suckled was greatest in the first 5 min., fell in the second 5, and increased in the last 5, although not quite to the level of the first period. Thus the fat content varies inversely with the quantity.

NUTR. ABS. (m)

Spectrographic examination of some Indian milks. N. K. DE (Indian J. Med. Res., 1935, 22, 499—508).—The vitamin-A contents of human, cow,

goat, and buffalo milk are similar, and average 71.3×10^{-6} g., corresponding with 0.15–0.2 g. of cod-liver oil, per 100 c.c. In human milk Cu and Fe are high, and Ca and P low. Cow milk contains Si, unlike the other milks, and is high in Ca and low in Fe and Cu. Fe, Cu, and Mn are low, and Ca, Mg, and Na high, in buffalo milk. Goat milk contains all the above metals in fair proportions. R. N. C.

Colorimetric micro-determination of magnesium in milk. M. SATO and K. MURATA (J. Agric. Chem. Soc. Japan, 1935, 11, 431–434).—Milk (5 c.c.) is deproteinised, freed from Ca, treated with sol. starch, Titan-yellow, and 0.4N-NaOH, and the resulting pink colour is compared with suitable standards. F. O. H.

Properties of human seminal plasma. M. W. GOLDBLATT (J. Physiol., 1935, 84, 208–218).—Human seminal plasma contains a powerful vasodilator and can stimulate plain muscle. The active depressor substance is distinct from other depressors present in tissue extracts. The oxytocic power of seminal plasma is probably due to a sp. substance. The plasma also contains a substance with acetylcholine-like effect on the eserinated rectus abdominus of the rat. The acetylcholine equiv. of seminal plasma is $> 10^{-6}$ g. per c.c. (Cf. this vol., 1006.) R. N. C.

Inorganic constituents of the cerebrospinal fluid. VI. Sulphur. E. WATCHORN and R. A. McCANCE (Biochem. J., 1935, 29, 2291–2296).—In non-nephritic patients serum-inorg. S is 1–4 mg. per 100 ml. Vals. up to 35 mg. were found in chronic interstitial nephritis. The inorg. S in ventricular and cerebrospinal fluids is about $\frac{1}{3}$ — $\frac{1}{4}$ of the serum val. As the whole of the serum-inorg. S is ultrafilterable, these fluids are not serum ultrafiltrates. In tuberculous meningitis the cerebrospinal-fluid-S val. approaches the serum val. The inorg. S vals. of pathological effusions suggest that these fluids have been formed by ultrafiltration. Modifications are introduced into the method of Cuthbertson *et al.* (A., 1931, 1177) for determining inorg. S. E. A. H. R.

Ultra-violet absorption spectrum of cerebrospinal fluid in progressive general paralysis. I. PIROSKY (Rev. especialidades, 1931, 6, 1250–1256).—Differentiation is shown between normal fluids and those of general paralysis, the latter containing small quantities of protein. Variations in the shape of curves and width of absorption bands in paralysis are due to pseudoglobulin. CH. ABS. (p)

Silicotungstic acid reaction of cerebrospinal fluid. M. NAGY (Orvosi Hetilap, 1935, 79, 126–127).—Globulin is quantitatively pptd. by 1% silicotungstic acid solution and may thus be determined nephelometrically. CH. ABS. (p)

Alleged occurrence of acetylcholine in the saliva. O. S. GIBBS (J. Physiol., 1935, 84, 33–40).—Intravenous injection of saliva in the cat induces a fall of blood-pressure, followed by a slight rise. Atropine does not abolish the effect in concns. sufficient to abolish that of acetylcholine (I). Injection of saliva into the artery of the gland reduces the

secretion evoked by added (I). There is no indication that saliva contains (I). R. N. C.

Bile acids of Argentine snakes. V. DEULOFEU (Anal. Asoc. Quim. Argentina, 1935, 23, 22–25).—See this vol., 378.

Total and neutral chlorine contents of gastric juice. L. BERKESY (Orvosi Hetilap, 1935, 79, 183–184).—The total Cl increased continuously to the end of secretion. No consistent relationship was apparent between total Cl' and acid concn., or between neutral Cl' and total acidity. Alkalisalation of gastric juice is probably effected by the mucin produced in the stomach. CH. ABS. (p)

Influence of duodenal secretions on acid gastric contents. C. M. WILHELMJ, L. C. HENRICH, and F. C. HILL (Amer. J. Physiol., 1935, 111, 293–304).—Gastroduodenostomy and gastrojejunostomy, but not pyloroplasty, result in the dog in increased entry of duodenal secretions into the stomach. The average composition of the duodenal secretions is normal. The efficiency of duodenal secretion in lowering the acidity in approx. 0.1N-HCl in the stomach is due rather to dilution than neutralisation, the average distribution of the reduction between the two being 75% and 25%, respectively. The presence of large amounts of duodenal secretion apparently increases HCl secretion in the stomach; the effect is evident only after the stomach has been stimulated by histamine. The Cl content of the mixed gastric secretions depends on the ratio of acid fluid and extra fluid present. R. N. C.

Methylene-blue as a stain for mucus. A. G. LOWNDES (Nature, 1935, 136, 398).—The view that methylene-blue is one of the best stains for mucus is maintained. L. S. T.

Reflector effect on water and sodium chloride excretion. S. JANSSEN (Pflüger's Archiv, 1935, 235, 523–533).—Depressor section, vagotomy, or femoral clamping increases excretion of H_2O and NaCl, and the concn. of NaCl in the urine. R. N. C.

Excessive water-intake and excretion of chloride by dogs. L. WOLFF (Arch. exp. Path. Pharm., 1935, 179, 200–203).— H_2O -diuresis in dogs is accompanied by an excretion of Cl' $>$ the ingested Cl'. The source of this excess Cl' is not only the blood. F. O. H.

Determination of urinary chlorides with mercuric nitrate. C. E. HOLDRIDGE and J. W. CAVETT (J. Lab. Clin. Med., 1934, 20, 303).—The method previously described for plasma-Cl' (A., 1933, 1182) is adapted. Urine is diluted (1:20) and 5–10 c.c. are titrated as for a protein-free blood filtrate. Turbid urine is boiled with 10% aq. sulphosalicylic acid and filtered. CH. ABS. (p)

Is there a racial factor in metabolism? M. DAMODARAN and K. G. ANANTHANARAYANAN (Current Sci., 1935, 4, 96–97).—The N distribution in the urine of vegetarian and meat-eating South Indians is compared with that of Europeans. F. N. W.

Determination of urea in urine with a photo-electric densitometer. New technique. E.

OBERMER and R. MILTON (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 741—752).—Furfuraldehyde, SnCl_2 , and HCl give a blue colour when boiled together, but not at 0° . Addition of urea to the mixture at 0° produces the blue colour, the intensity of which \propto the amount of urea added. Technique and an instrument for the application of this reaction to urine analysis are described.

CH. ABS. (p)

Effect of clamping the large arteries on the composition of the urine. H. HUNGERLAND (Pflüger's Archiv, 1935, 235, 644—654).—Clamping the femoral or saphenous artery in the dog causes a rise in total bases, HCO_3^- , Cl , H_2O , and the basic—acidic ion difference in the urine, whilst NH_3 , PO_4 , and excess acid fall. The effects are similar to those obtained by clamping the carotid, but the max. changes appear after the loosening of the ligature.

R. N. C.

Porphyryns excreted in porphyrinuria. W. HOERBURGER and H. FINK (Z. physiol. Chem., 1935, 236, 136—140; cf. this vol., 776).—By means of p_H -fluorescence curves the coproporphyrin from the urine of a patient suffering from Pb poisoning and that from the urine of a patient to whom salvarsan had been administered was identified as coproporphyrin-III. The urine of another patient contained coproporphyrin-I.

W. McC.

Calcium and phosphorus metabolism in a case of acromegaly showing marked osteoporosis. W. DE M. SCRIVER and A. H. BRYAN (J. Clin. Invest., 1935, 14, 212—219; cf. A., 1934, 680).—The osteoporosis described was probably due to insufficient intake of Ca and P associated with increased excretion. No evidence of hyperactivity of the thyroid or parathyroid was obtained.

CH. ABS. (p)

Sodium chloride and protein changes induced by adrenalectomy and glucose administration. H. SILVERTE and S. W. BRITTON (Amer. J. Physiol., 1935, 111, 305—311).—Adrenalectomy in cats is followed by progressive diminution in the concn. of Na and Cl' in blood-serum, liver, and muscle, together with a slight diminution in serum-protein. A much greater diminution of Na and Cl' in serum and tissues may be caused, without harm to the animal, by intraperitoneal injection of glucose (I). Reductions in Na and Cl' two or three times $>$ those following adrenalectomy must occur to cause death. For <24 hr. muscular tremors and prostration follow intraperitoneal injection of large quantities of (I). This condition seems to be due to excessive salt loss and is different from the severe convulsive (hypoglycaemic) seizures of adrenal insufficiency.

NUTR. ABS. (m)

Ingestion of excess sodium chloride in allergic diseases. (A) B. PAUL and P. VÉGH. (B) L. ROSA (Orvosi Hetilap, 1934, 78, 1015—1016, 1048—1049).—(A) In allergic hepatopathy only part of the NaCl given perorally enters the blood. Most is probably retained by the liver parenchyma.

(B) Retention of NaCl by the liver is not due to parenchymal absorption, but to insufficient function of the liver.

CH. ABS. (p)

Experimental production of loss of hæmatopoietic elements of the gastric secretion and of the liver in swine with achlorhydria and anæmia. D. K. MILLER and C. P. RHODES (J. Clin. Invest., 1935, 14, 153—172).—Achlorhydria and anæmia can be produced by feeding a modified canine-black-tongue-producing diet. Gastric secretions and liver simultaneously lose anti-pernicious anæmia activity. The condition is relieved by administration of liver extract.

CH. ABS. (p)

Spleen, hæmoglobin, and erythrocytes in nutritional anæmia of the rat. C. J. HAMRE and C. D. MILLER (Amer. J. Physiol., 1935, 111, 578—589).—The spleen is disorganised and unable to produce blood-elements in severe nutritional anæmia. It enlarges during recovery when Cu and Fe are fed in adequate quantities, and is actively erythropoietic. Cu, but not Fe, enlarges the spleen and increases erythropoiesis when fed alone as a supplement to milk. Neither metal causes complete recovery of hæmoglobin.

R. N. C.

Azotæmia in acute Bright's disease. J. B. RENNIE (Lancet, 1935, 229, 658—660).—Determinations of non-protein-N of the blood of children suffering from acute nephritis show that azotæmia occurs in most cases at the onset of the disease. No relation occurs between the level of non-protein-N and the height of blood-pressure, the amount of oedema, or the cerebral manifestations. Sufficient protein in the diet has no adverse effect on the disappearance of the azotæmia.

L. S. T.

Biochemistry of burns. I. Blood- and urine-chloride and -non-coagulable nitrogen. II. Creatinine. III. Blood-purines. IV. Oxidation-reduction activity of the blood. G. CICALA (Arch. Farm. speriment., 1935, 60, 312—324, 325—330, 331—336, 337—341).—I. Severe cutaneous burns in rabbits (resulting in death after 7—14 days) decrease blood- Cl' and increase blood-urea-N, especially after 3 days; the variations in the urinary levels are less marked.

II. Blood-creatinine increases whilst the urinary content tends to diminish.

III. Blood-uric acid increases.

IV. Reduced glutathione of the blood markedly increases.

F. O. H.

Carcinogenic action of aromatic hydrocarbons. O. SCHURCH and A. WINTERSTEIN (Z. physiol. Chem., 1935, 236, 79—91).—The carcinogenic action (on mice and rabbits) of highly purified 1:2-benzpyrene (I) has been confirmed. The H_4 - and the 3'(or 2')-Me derivatives of (I) are inactive. Purest chrysene (II) is inactive but 1:2-benzcarbazole, often an impurity in (II), appears to possess activity.

W. McC.

Carcinogenic hydrocarbons and their relationship to the sterols. J. W. COOK (Chem. Weekblad, 1935, 32, 563—566).—A lecture.

Sterols, sex hormones, and cancer. G. BOURNE (J. Cancer Res. Comm. Sydney, 1935, 7, 34—39).—A discussion.

Presence of carotene in ovarian tumours. C. Y. CHU, P. L. LI, and C. S. YANG (Chinese Med. J., 1935, 49, 751—754).—A case of ovarian cyst was

accompanied by large quantities of carotene in the ovaries and in the blood.

H. G. R.

Action of iron-vitamin-C preparations on tumours. F. ARLOING, A. MOREL, and A. J. SERAND (Compt. rend., 1935, 201, 456—458).—The use of intravenous injection of sol. Na derivatives of FeCl_2 and FeCl_3 with normal and oxidised ascorbic acid, respectively, in cancer therapy (rabbit, man) is described (cf. this vol., 775).

F. O. H.

Glutathione and ascorbic acid in tissues of normal and tumour-bearing albino rats. G. E. WOODWARD (Biochem. J., 1935, 29, 2405—2412).—The tissues of rats, bearing Walker no. 256 carcinoma or Philadelphia no. 1 sarcoma, had glutathione (I) and ascorbic acid (II) contents not significantly different from those of normal tissue. The (I) content of the carcinoma tissue was slightly > that of the sarcoma, whilst (II) is lower in the former, although > in any normal tissue except adrenal. Long-continued injections of (II), mannose, glucose, or oxidation-reduction dyes into tumour-bearing rats did not materially affect growth of the tumours or the consens. of (II) or (I) in the tumour-tissue or other tissues of the body. X-Ray treatment lowered the (I) content of the tumours provided the growth rate was also retarded.

W. O. K.

Effects of oxidation-reduction potential indicator dyes on the metabolism of tumour and normal tissues. K. A. C. ELLIOTT and Z. BAKER (Biochem. J., 1935, 29, 2396—2404).—At consens. about $10^{-3}M$, a no. of dyes, the redox potentials of which vary from that of dichlorophenol-indophenol (I) to that of methylene-blue (II), inhibit the respiration of tumour slices in the absence of glucose (III), but accelerate in its presence. Dyes with a potential more positive than that of (I) inhibit the respiration even in presence of (III), whilst cresyl-violet (IV) at the negative end of the series accelerates even in absence of (III). With brain, testis, retina, and kidney, dyes of the main group inhibit respiration even in presence of (III), whilst with liver-tissue they increase the respiration in presence or absence of (III). Thionine, prune, (II), and (IV), besides accelerating the respiration of tumour slices in (III) medium, also increase the aerobic glycolysis. At $10^{-5}M$, the dyes usually give a slight increase in the average rate of respiration in presence of, and some inhibition in absence of, (III). In $10^{-3}M$ concn. 4 : 6-dinitro-*o*-cresol increases the glycolysis of tumour-tissue and of brain, liver, and testis. It inhibits the respiration of liver and of tumour-tissue even in the presence of (III). It markedly inhibits respiration of tumour in the absence of (III) and of other tissues in the absence or presence of (III). In $10^{-5}M$ concn. it accelerates the respiration of tumour, brain, and liver considerably.

W. O. K.

Relation between castration and blood pressure in rabbits. T. IJIMA (Japan J. Med. Sci., IV [Proc. Japan Pharmacol. Soc.], 1933, 7, 119).—Castration of either sex did not alter blood pressure, but increased sensitivity to adrenaline.

CH. ABS. (p)

Ascorbic acid in cataract with special reference to dinitrophenol cataracts. E. M. JOSEPH-

SON (Science, 1935, 82, 222—223).—The toxic effects, especially cataracts, of dinitrophenol, and cataracts of all types have been successfully treated with vitamin-C.

L. S. T.

Allergic factor in the aetiology of non-specific colitis. D. C. HARE (Lancet, 1935, 229, 767—768).—Evidence for the view that allergic factors play a part in the aetiology of sp. colitis is discussed.

L. S. T.

Heat cramps and uraemic cramps with special reference to their treatment with sodium chloride. E. H. DERRICK (Med. J. Australia, 1934, 2, 612—616).—Cramps associated with loss of NaCl in perspiration were prevented by drinking H_2O containing 10 g. of NaCl per gallon.

CH. ABS. (p)

Specific rotation of cystine excreted in cystinuria. B. H. BROWN and H. B. LEWIS (Proc. Soc. Exp. Biol. Med., 1935, 32, 1100—1102).—*l*-Cystine from cystinuric patients differs from protein *l*-cystine in $[\alpha]^{20}$ by approx. 1.5° . There is no evidence that the two α vals. are fundamentally different.

R. N. C.

Diabetes insipidus: treatment with intermedin and pitmelanin. H. H. TURNER (Endocrinol., 1935, 19, 275—283).—Intermedin (I) and pitmelanin contain the antidiuretic factors of the pituitary, and are free from pressor action; they can be used to control the symptoms of diabetes insipidus. The reduction in diuresis from (I) is < that from pituitrin.

R. N. C.

Anti-ketogenic substance and phloridzin diabetes. P. T. BLACK (J. Physiol., 1935, 84, 15—19).—Female rats injected daily with anterior pituitary extracts containing the ketogenic principle develop a resistance to its action in 4 months. Large doses of phloridzin given in such circumstances and while fasting produce only slight ketonuria.

R. N. C.

Hypoglycæmic action of pancreatic diathermy. A. ROBECCI (Minerva med., 1934, II, 905—909).—Changes in the glycaemic curve following diathermy are compared in normal fasting individuals, normal individuals after ingestion of 50 g. of glucose, and in diabetics after ingestion of glucose.

CH. ABS. (p)

Creatinine clearance during the hyperthermia of diathermy and fevers. W. T. GRANT and G. MEDES (J. Lab. Clin. Med., 1935, 20, 345—349).—In dogs hyperthermia caused by diathermy is accompanied by increased creatinine (I) clearance. In patients with fever caused by infection there was no general change in (I) clearance, although urea clearance varied widely.

CH. ABS. (p)

Hæmorrhagic chick disease of dietary origin. H. J. ALMQUIST and E. L. R. STOKSTAD (J. Biol. Chem., 1935, 111, 105—113; cf. this vol., 903).—Details of experiments already reported (*ibid.*, 1148) are given.

F. A. A.

Metabolic criteria of hyperparathyroidism. C. L. ROBBINS and D. M. KYDD (J. Clin. Invest., 1935, 14, 221—227).—Parathyroid glands were normal in cases of multiple myeloma and in Paget's disease in which alleged metabolic criteria of hyperparathyroidism were exhibited. Ca excretion could not be

correlated with its concn. in the serum. Ingestion of $\text{PO}_4^{'''}$ diminished the calcinuria without changing the blood picture. CH. ABS. (p)

Trichogenic action of the thiol group in hereditary hypotrichosis of the rat. G. J. MARTIN and R. E. GARDNER (J. Biol. Chem., 1935, 111, 193—196).—Cysteine (I) through the SH group acts as a stimulant to the hair follicle, causing a trichogenic action in hereditary hypotrichosis of the rat. (I) cannot be replaced by glutathione, and cystine causes only a temporary growth of hair. It is concluded that there is an absence in the hairless rat of an enzyme capable of breaking peptide linkings involving S-containing groups into the constituent NH_2 -acids. J. N. A.

Ionic changes and urea in certain kidney and heart diseases; the acid-base equilibrium. C. P. MAYER and I. TESSIERI (Semana med., 1935, I, 480—488). CH. ABS. (p)

Urea clearance test in children. W. W. PAYNE and H. SHUKRY (Arch. Dis. Childhood, 1934, 9, 335—338).—In diseases involving the kidney, the latter loses the capacity of excreting urea earlier than the capacity to concentrate urea. CH. ABS. (p)

Increased blood pressure in experimental nephritis. H. SAKAMOTO (Japan J. Med. Sci., IV [Proc. Japan Pharmacol Soc.], 1933, 7, 118).—After ingestion of K_2CrO_4 , HgCl_2 , uranyl nitrate, or cantharidin into rabbits, anuria, albuminuria, and hæmaturia developed, with an increase in blood pressure. The sensitivity of the pressure to administration of adrenaline was not increased. CH. ABS. (p)

Glucoproteins in hepatopathy. V. GAUDIO and E. HINRICHSSEN (Minerva med., 1934, II, 909—913).—Following ingestion of glucose (I), the combined (I) in hepatic patients was < in normal subjects. The ratio of combined to free (I) was lower in hepatic cases, and did not return to the initial val. until 4 hr. after the ingestion. CH. ABS. (p)

Plasma-fat acids after adrenaline injection in normal subjects and in patients with liver disease: prognostic significance. C. M. JONES and J. W. FISH (J. Clin. Invest., 1935, 14, 143—152).—Intramuscular injection of adrenaline is followed, in normal subjects, by a sharp rise in blood-fat acids within 0.5 hr. with subsequent return to normal in 2 hr. Abnormal curves are obtained in cases of liver disease. CH. ABS. (p)

Serum-protein precipitated by Hayem's solution, occurring in multiple myeloma. B. M. JACOBSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1257—1258).—An amorphous protein mass is pptd. by Hayem's solution from the blood of multiple myeloma cases in which serum-euglobulin is > pseudoglobulin. The protein is pptd. completely by all globulin precipitants except CO_2 , and is almost completely confined to the euglobulin fraction, pptd. by 14% Na_2SO_4 . It is not the Bence-Jones protein which is not pptd. by Hayem's solution. R. N. C.

Henry's reaction (iron flocculation). C. A. VIDELA, E. SAVINO, and L. M. DALKE (Rev. Assoc. méd. Argentina, 1934, 48, 1385—1389).—The reaction

(flocculation of Fe albuminate by serum from malarial patients) was positive in 76% of malarial cases and in 29% of non-malarial cases examined. CH. ABS. (p)

Flocculation and "super-flocculation" in Henry's reaction. V. CHORINE (Compt. rend. Soc. Biol., 1935, 119, 1323—1326).—"Super-flocculation" and flocculation in presence of melanin involve the same phenomenon, i.e., pptn. of the euglobulin. H. G. R.

Colloidal carbon flocculation test in spinal fluid. P. G. SCHUBE (J. Lab. Clin. Med., 1934, 20, 314—316; cf. A., 1933, 526).—The specificity of the test for neurosyphilis is confirmed. Modifications of the method are described and the mechanism of flocculation is discussed. CH. ABS. (p)

Calcium contents of cerebrospinal fluid, blood-serum, and serum ultrafiltrate: its relation to clinical findings in eighty psychiatric patients. J. J. MICHAELS and O. M. SEARLE (Arch. Neurol. Psychiatry, 1935, 33, 330—341).—The Ca content and the ratio between diffused and non-diffused Ca are normal in neuropsychiatric disorders. CH. ABS. (p)

Edema, especially oedema of renal origin. E. J. KIRK (Amer. J. Clin. Path., 1935, 5, 21—39).—A lowering of the serum-protein, notably of the albumin fraction, accompanied oedema produced in dogs by plasmapheresis. Blood-Cl' increased and Cl' in the gastric contents declined. The total and free acidity of the gastric fluid was lowered. CH. ABS.

Lipase and esterase in blood-serum. Diagnostic value in pancreatic disease. M. W. COMFORT and A. E. OSTERBERG (J. Lab. Clin. Med., 1934, 20, 271—278).—Increased activity of serum-lipase is associated with pancreatitis. The concn. of serum-esterase is unrelated to the condition of the pancreas. CH. ABS. (p)

Urinary excretion of "S-substance" [soluble specific polysaccharide] in lobar pneumonia. D. S. PEPPER (Yale J. Biol. Med., 1934, 7, 13—21).—In many cases of lobar pneumonia the "S-substance" (I) is excreted in urine within 12 hr. after the original chill. Methods of separating (I) are described. In infection types I, II, and III, the amount of (I) excreted is related to the severity of the case. With higher types (I) is usually not detectable. CH. ABS. (p)

Endocrine inter-relations during pregnancy. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Endocrinol., 1935, 19, 151—159).—The placenta probably secretes corpus luteum hormone, but is independent of ovarian hormones. R. N. C.

Glycosuria and lactosuria of pregnant and of lactating women. H. J. BROCK and R. S. HUBBARD (Amer. J. Digest. Dis. Nutrit., 1935, 2, 27—33).—A method for determining < 5 mg. of lactose (I) in 100 ml. of urine is described. (I) is usually absent from the urine of normal women. The urine of most pregnant women contains (I) in very varying amount, but its presence is not inevitable even in the later months of pregnancy. During lactation, especially in the puerperium, lactosuria practically always occurs. NUTR. ABS. (m)

Serum-colloid osmotic pressure in normal pregnancy. W. J. DIECKMANN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1127—1129).—The calc. and determined osmotic pressures of serum at different stages of pregnancy agree, indicating that in normal pregnancy there is no change in the serum-proteins, and that the slight oedema that generally occurs is not due to low colloid osmotic pressure. R. N. C.

Punctate basophilia in rheumatic cases after chrysotherapy. G. J. GRIFFITHS and J. RACE (Lancet, 1935, 229, 714—715).—The effects of Au and Pb preps. on the blood picture are described.

L. S. T.

Incidence of rickets in rabbits. W. K. WILSON (Nature, 1935, 136, 434).

L. S. T.

Egg-yolk and chicken fat as preventives of rickets and "slipped" tendons of chicks. E. W. HENDERSON and T. T. MILBY (Iowa Agric. Exp. Sta. Rept., 1933, 39—40; cf. A., 1933, 1072).—Neither cod-liver oil nor sunlight prevented "slipped tendon," which is attributed to excessive P or an associated factor. The no. of affected cases was reduced by limiting P-rich protein concentrates. Excess of fibre (ground oats) had no effect on the disorder.

CH. ABS. (p)

Influence of protein levels and calcium and phosphorus balance on rachitis of chicks. H. L. WILCKE, E. W. HENDERSON, and C. MURRAY (Iowa Agric. Exp. Sta. Rept., 1933, 42).—In chicks with "slipped" tendon the ash of bones was > normal, and blood-Ca and -inorg. P were normal. In rachitis all three vals. were low. The bone-ash of females was > that of males during the first 8 weeks. Effects of varying proportions of dietary Ca and P are recorded.

CH. ABS. (p)

Adrenaline content of the adrenal glands in scurvy and in inanition. W. DEUTSCH and W. SCHLAPP (J. Physiol., 1935, 83, 478—482).—Adrenaline in the adrenals of guinea-pigs falls in scurvy and inanition. Ascorbic acid does not fall in the adrenals in inanition if the diet contains sufficient green food.

R. N. C.

Dietary protein in relation to sterility. I. J. CUNNINGHAM and C. S. M. HOPKIRK (New Zealand J. Sci. Tech., 1935, 17, 420—432).—Sterility was induced in male rats by feeding high-protein diets and also by giving diets in which a large part of the protein was derived from maize or maize with gelatin. Results are discussed in relation to bull sterility on high-protein pastures, and to the significance of the essential NH_2 -acids, e.g., tryptophan, arginine, and lysine, in the normal activity of the testis.

A. G. P.

Relation of blood-calcium and -phosphorus in sterility of dairy animals. C. Y. CANNON, J. A. SCHULZ, and D. L. ESPE (Iowa Agric. Exp. Sta. Rept., 1933, 35).—No relationship was apparent.

CH. ABS. (p)

Results of treatment in syphilis. M. H. O'CONNOR (Irish J. Med. Sci., 1935, 109, 24—38).—A review of the effects of neoarsphenamine, Bi, and KI.

CH. ABS. (p)

Effect of salts on the Wassermann reaction. R. D. DE LA RIVIERE, N. KOSOVITCH, and H. T.

TRY (Ann. Inst. Pasteur, 1935, 55, 417—432).—The hæmolytic effects of Hg, As, and Bi salts on human and animal erythrocytes are described. Previous treatment of a syphilitic serum with these salts, particularly with novarsenobenzene, frequently leads to a negative Wassermann reaction. E. A. H. R.

Low basal metabolic rates obtained by low-calorie diets in coronary artery disease. A. M. MASTER, H. L. JAFFE, and S. DACK (Proc. Soc. Exp. Biol. Med., 1935, 32, 779—783).—The basal metabolic rate in patients with coronary artery thrombosis is lowered by an 800-cal. diet.

R. N. C.

Prognosis of coronary thrombosis based on the non-protein-nitrogen in the blood. C. LE R. STEINBERG (J. Lab. Clin. Med., 1934, 20, 279—285).—In 20 out of 31 cases non-protein-N was < 40 mg. per 100 c.c.

CH. ABS. (p)

Lipin and hæmorrhagic changes in adrenal cortex following traumatic shock. J. K. DONAHUE and W. M. PARKINS (Proc. Soc. Exp. Biol. Med., 1935, 32, 1249—1253).—Traumatic shock in dogs produces a definite depletion in adreno-cortical lipins, and also hæmorrhages into the cortex, which are more severe if intraperitoneal injection of glucose precedes trauma.

R. N. C.

Physics applied to tuberculosis. P. N. CORYLLOS (J. Franklin Inst., 1935, 220, 287—304).—An essay.

W. R. A.

Basal metabolism in pulmonary tuberculosis. Observations of about 240 cases. L. CHAROSKY (Rev. Assoc. Med. Argentina, 1934, 48, 1256—1261).—Basal metabolism was increased in 63% of the cases, especially in active tuberculosis. In inactive cases metabolism is approx. normal.

CH. ABS. (p)

Methylene-blue in the treatment of urinary tuberculosis with presentation of a purified drug. B. E. GREENBERG, M. L. BORDNY, T. L. DAVIS, and C. ARMSTRONG (J. Urol., 1935, 33, 168—174).—Unfavourable effects are due to impurities in methylene-blue. A method of purification is described.

CH. ABS. (p)

Blood-sugar and blood-urea in trypanosomiasis. E. R. JONES (Vet. Rec., 1933, 13, 1062—1063).—In affected cattle and sheep only one case of hyperglycæmia and none of hypoglycæmia were observed. Blood-urea was high only in one instance, although low vals. were observed in certain cases of *T. congolense* infection.

CH. ABS. (p)

Standards for predicting basal metabolism in the immediate pre-adult years. M. E. STARK (Amer. J. Physiol., 1935, 111, 630—640).

R. N. C.

Effects of heavy water on mammalian metabolism. H. G. BARBOUR (Proc. Soc. Exp. Biol. Med., 1935, 32, 1365—1369).— D_2O depresses metabolism in mice, but the depression is small if the animal is well fed and watered. A certain quantity of D_2O is contained in the insensibly-lost H_2O .

R. N. C.

Water and base balance of the body. P. H. LAVIETES, L. M. D'ESOP, and H. E. HARRISON (J. Clin. Invest., 1935, 14, 251—265).—The total base concn. throughout the body is approx. uniform. Na

and to an almost equal degree Cl' are very largely confined to extracellular H_2O . Formulæ for calculating total and extracellular H_2O exchanges from alterations in body-electrolytes are given.

CH. ABS.

Changes in distribution of body-water accompanying increase and decrease in extracellular electrolyte. D. C. DARROW and H. YANNET (J. Clin. Invest., 1935, 14, 266—275).—Loss of extracellular electrolyte (with little change in total body- H_2O) simulated dehydration and resulted in a decrease of serum- Na and Cl , and an increase in protein concn. and no. of red cells. An increase in electrolytes produced an increase in serum- Na and Cl , a decline in protein concn., and an increase in the protein concn. of red cells due to loss of H_2O . Under these conditions H_2O moved from intra- to extra-cellular spaces.

CH. ABS. (p)

Water studies in obesity. E. C. BARTELS and B. BLUM (J. Lab. Clin. Med., 1935, 20, 401—409).—Disturbances in H_2O balance resulting from low-calorific diets are examined.

CH. ABS. (p)

Relation between metabolism, potential formation, and function of frog's skin. E. HUF (Pflüger's Archiv, 1935, 235, 655—673).—A strip of frog's skin excised 4—5 min. after decapitation and suspended between identical Ringer's solutions induces a potential between the two that falls during the first 5 min., and then rises to 6 times the min. val. The increase depends on O_2 supply, and does not occur if the skin has been placed in KCN for $\frac{1}{2}$ hr. If the frog has been poisoned with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ (I) before decapitation, the potential curve is normal, or falls after a low max., or falls without rising, according to the degree of poisoning. The effects of moderate poisoning are hindered by lactate (II), but not by glucose (III). Strips of abdominal skin from the same frog, moderately poisoned by (I), suspended in Ringer's solutions containing (II) and (III), respectively, develop nearly equal potentials, but whilst that with (III) falls soon after reaching its max., that with (II) remains high for 1 hr.; replacement of (III) by (II) causes a recovery of the potential. With skin from normal frogs the potential persists in both solutions. Normal skin suspended between two identical Ringer's solutions induces a migration of Cl' from the epithelium side to the serosa side; the effect is reduced or abolished by poisoning with KCN or (I), but in the latter case is restored by (II). In normal Ringer's solution H_2O passes from the epithelium side to the serosa; addition of KCN reverses this effect. The permeability to Cl' in the direction serosa \rightarrow epithelium of a strip of skin suspended between Ringer's solution on the serosa side and spring H_2O on the epithelium side is increased by KCN.

R. N. C.

Absorption and excretion in segments of the colon in man. F. S. CURRY and J. A. BARGEN (Surg. Gynecol. Obstet., 1935, 60, 667—674).—Distal segments of the colon absorbed methylene-blue (I), atropine, sucrose (II) (which was excreted in urine), As (as neocarphenamine), and glucose (III). These segments did not excrete (I) (when administered orally) or intravenous (II) and (III). Orally administered As (treparsol) was excreted in amounts

which, at times, were $>$ those appearing in the urine.

CH. ABS. (p)

Certain blood changes associated with physical exhaustion in the normal dog. F. W. SCHLUTZ, A. B. HASTINGS, and M. MORSE (Amer. J. Physiol., 1935, 111, 622—629).—Exhaustive exercise produces a rise in lactate (I) and a fall of HCO_3' of blood in the first 15 min., both tending to return to the initial vals. afterwards; at exhaustion the fall in HCO_3' is often $>$ the rise in (I). The p_{H} at exhaustion usually falls below the previous exercise level. Serum-sugar (II) remains normal or rises in the first 15 min.; it then tends to fall. A relation appears between (II) and serum-(I) in dogs exercised by swimming at 38° , suggesting that at exhaustion (I) is dependent on (II).

R. N. C.

Effect of a diet of pure glucose on the fluid balance of the body. F. B. BYRON (Clin. Sci., 1934, 1, 245—250).—An exclusive glucose- H_2O diet produced immediate loss in body-wt. and parallel losses of Na and K .

CH. ABS. (p)

Role of liver in growth, reproduction, and lactation. H. G. SMITH and W. H. SEEGER (Proc. Iowa Acad. Sci., 1933, 40, 109—110).—EtOH-extracted beef liver as sole source of protein in an otherwise complete ration was inadequate for the growth of rats. Addition of raw liver or substitution of dried whole liver for the extracted material improved growth. A H_2O - and Et $_2\text{O}$ -insol. fraction of liver gives conclusive results.

CH. ABS. (p)

Effect of feeding desiccated thymus on growth. E. M. MACKAY and R. H. BARNES (Proc. Soc. Exp. Biol. Med., 1935, 32, 1309—1312).—Rate of growth of the albino rat is slightly impaired by desiccated ox liver or kidney in the diet, and to a greater extent by ox thymus. The effects of these tissues \propto their purine-N contents, and are probably due to the nuclear material they contain.

R. N. C.

Influence of chicken-liver feeding on depancreatized dogs. F. S. CUTHBERT and A. C. IVY (Proc. Soc. Exp. Biol. Med., 1935, 32, 1209—1210).—Chicken-liver fed to a totally depancreatized dog controlled with insulin causes increase of body-wt. and of glucose (I) excretion in the urine, but the increase is $>$ the calc. (I) equiv. of the liver. Substitution of (I) for liver results in excretion of only $\frac{1}{3}$ of the (I) given. The liver has no insulin-sparing action.

R. N. C.

Influence of diet on the sugar-tolerance of healthy men and its reference to certain extrinsic factors. H. P. HIMSWORTH (Clin. Sci., 1934, 1, 251—264).—Decreased tolerance to glucose and impaired sensitivity to insulin due to a high-fat diet and reverse effects due to a high-carbohydrate diet are not associated with changes in blood- p_{H} . Occurrence of ketosis in normal men or the addition of raw liver or lecithin to a high-fat diet had no effect on insulin-tolerance (see also A., 1934, 1143).

CH. ABS. (p)

Effect of heat and alcohol extraction on the nutritive value of casein. H. W. SCHULTZ, W. H. SEEGER, and H. A. MATTILL (Proc. Soc. Exp. Biol. Med., 1935, 32, 1026—1029).—Extraction of casein

for 4 days with boiling 95% EtOH reduces considerably its val. in supporting lactation in the rat, but the difference is only slightly accentuated in the second generation. The nutritive val. is also reduced by heating, prolonged heating at 120° being more effective than short heating at 150°. EtOH extract of wheat-germ increases the nutritive val. of the extracted casein that has been heated to 120°, but not when it has been heated to 150°. Et₂O extracts of wheat-germ are ineffective. R. N. C.

Biological value of mixed cereal proteins. W. H. ADOLPH and F. W. CHENG (Chinese J. Physiol., 1935, 9, 245—252).—The biological val. of the protein of mixed cereal flour has been determined by measuring the N balance and growth rate of rats. Mixtures show biological vals. > that of any of the single cereals (maize + millet + soya-bean > maize + kaoliang + soya-bean > wheat + cowpea > maize + soya-bean > soya-bean, millet > cowpea > kaoliang). E. P.

Availability of indole derivatives for supplementing diets deficient in tryptophan. L. C. BAUGUESS and C. P. BERG (Proc. Iowa Acad. Sci., 1933, 40, 110—111).—Neither α -oximino- β -3-indolyl-propionic nor β -3-indolylacrylic acid could replace tryptophan for growth purposes (cf. A., 1934, 554, 1252). CH. ABS. (p)

Absorption of carbon particles from gastrointestinal tract. F. S. CUTHBERT and A. C. IVY (Proc. Soc. Exp. Biol. Med., 1935, 32, 1272—1273).—C particles fed to dogs are absorbed from the gastrointestinal tract and deposited in the mesenteric lymph glands, and, after prolonged feeding, in the spleen and Kupffer cells of the liver. R. N. C.

Temperature coefficients and viscosity. J. H. BODINE and V. THOMPSON (J. Cell. Comp. Physiol., 1935, 6, 255—261).—The temp. coeff. val. of O₂ consumption of the normal *Melanoplus differentialis* embryo increases with age. It is not changed by partial or complete dehydration with hypertonic solutions, and not necessarily altered by changes of η . R. N. C.

Influence of electrolytes on respiration in nerve. T. H. CHANG, M. SHAFFER, and R. W. GERARD (Amer. J. Physiol., 1935, 111, 681—696).—The action of ions on nerve respiration is related to their effect on the colloidal structure of nerve. Na⁺ maintains the normal O₂ consumption, which is decreased 10—40% in its absence. K⁺, Rb⁺, and Cs⁺ depress respiration when in excess, but the absence of K⁺ has no effect. Small changes in Ca⁺⁺ affect irritability and respiration, which inversely \propto [Ca⁺⁺]. Mg⁺⁺, but not Ba⁺⁺, can replace Ca⁺⁺ in nerve; neither can in grey matter. The decalcifying Na salts increase nerve respiration, the increase being approx. \propto decalcifying power. Al⁺⁺⁺ depresses respiration and coagulates the colloids. Univalent anions show little or no influence. Isotonic sugar solution depresses respiration to 50%, the effect being decreased or abolished by NaCl and increased by KCl or CaCl₂. Ca⁺⁺ is not antagonised by Na⁺ or K⁺, but cations antagonise anions. Results support the view that the structural nerve-colloids are negatively charged. R. N. C.

Influence of blood-constituents on oxygen consumption in nerve. M. SHAFFER, T. H. CHANG, and R. W. GERARD (Amer. J. Physiol., 1935, 111, 697—710).—O₂ consumption of dog nerve in serum is > in Ringer's solution. The behaviour of other tissues is similar, but quantitatively sp. The increase in the case of nerve is related to the serum-proteins. Respiration in Ringer's solution is increased by glycine, decreased by lecithin and acetylcholine, and unaffected by urea, creatine, lactic acid, or glucose. The role of the proteins is probably physical and concerned with osmotic effects. R. N. C.

Some metabolic effects of clamping visceral arteries, splanchnic vaso-constriction, and adrenal and hepatic stimulation, with special reference to the calorogenic action of adrenaline and sympathin. F. R. GRIFFITH, jun., and F. E. EMERY (Amer. J. Physiol., 1935, 111, 369—381).—Blood-lactic acid in cats is increased by clamping the visceral arteries, stimulation of the splanchnic after adrenalectomy and hepatic nerve section, splanchnic-adrenal stimulation after hepatic nerve section, and stimulation of the nerves to the liver. O₂ consumption is decreased by the two former operations and increased by the two latter, these increases being ascribed to adrenaline or sympathin, which is produced in amounts sufficient to overcome the metabolic-depressive effect of vaso-constriction. R. N. C.

Influence of optically-active amino-acids on tissue metabolism. B. KISCH (Biochem. Z., 1935, 280, 41—54).—The influence of various *dl*-, *d*-, and *l*-NH₂-acids on the respiration and oxidative NH₃ formation by kidney slices is investigated. Using the *d*-series of NH₂-acids, the increase of respiration was for rat-kidney cortex with alanine, isoleucine, and leucine 108, 34, and 24%, respectively, for sheep-kidney 94, 39, and 24%, and for pig-kidney 51, 199, and 94%. The *d*-series of acids always have a greater effect on respiration than the corresponding members of the *l*-series (except with isoleucine with rat and guinea-pig tissue) and always have considerably greater deaminating power. The Henle loop tissue, however, shows no considerable deaminising power. The kidney cortex tissue (ox and sheep) behaves in the same way as does the corresponding tissue of adult animals. P. W. C.

Respiration values of fresh mammalian tissue. B. KISCH (Biochem. Z., 1935, 280, 55—57).—Tables summarise the respiration vals. of a no. of tissues of various animals both fresh and after keeping on ice for several hr. The vals. show individual variations with the same kind of animal and considerable variations with different types of animal. The vals. are greatest with all animals for kidney cortex and decrease with kidney medullary tissue, liver, heart, and diaphragm. After keeping for 3 hr. on ice the respiration of kidney cortex and medullary tissue increases or remains unchanged, but of liver, heart, and diaphragm decreases. P. W. C.

Resting respiration of mammalian tissue in hydrogen cyanide. I. TORRES (Biochem. Z., 1935, 280, 114—117).—The respiration of rat liver, kidney, spleen, and brain in serum is inhibited by >90% by

5×10^{-3} HCN, of diaphragm muscle only by 60%, of liver, kidney, and spleen is increased by methylene-blue by 2–4 times, and is not related to the flavin content. P. W. C.

Significance of fumaric acid in respiration of animal tissues. I. Introduction, summary, and methods. A. SZENT-GYORGYI. II. Influence of C_1 acids on tissue-respiration. I. BANGA. III. Oxidation and reduction of C_4 dicarboxylic acids. K. LAKE. IV. Micro-determination of fumaric acid and its application. F. B. STRAUB. V. Micro-determination of succinic acid and its application. B. GOZSY. VI. Fumaric and malonic acids. E. ANNAU. VII. Experiments *in vivo*. S. HUSZAK (Z. physiol. Chem., 1935, 236, 1–20, 20–31, 31–42, 42–53, 54–58, 58–66, 66–68).—I. The respiration of pigeon's breast-muscle in PO_4''' buffer at p_H 7 (Thunberg-Barcroft technique) in presence of codehydrogenase (A., 1933, 748) indicates a marked dehydrogenase system for succinic (I), lactic, glycerophosphoric, glutamic, and citric acids, glyceraldehydophosphoric ester, and hexose mono- and di-phosphate. (I) dehydrogenase (A., 1934, 807) is differentiated by its reaction const., independence of codehydrogenase, ability to utilise O_2 as H acceptor, etc. Experimental data (see below) indicate that a fumarate (II)-oxalacetate (III) reaction [due to (II) dehydrogenase and codehydrogenase], together with an intermediate product (functioning as H acceptor) derived from the respiratory enzyme-cytochrome complex, forms the basis of the respiratory system. Conversion of (III) into (I) and then into (II) by (I) dehydrogenase also occurs.

II. The rapid decrease in O_2 uptake by normal muscle preps. is due to outward diffusion of (II) and is compensated by addition of (II). This effect is sp. for C_4 dicarboxylic acids. Thus (III), hydroxy-fumarate and -maleate are active, whilst lower mono- or di-carboxylic acids are inactive or inhibitory. (III) rapidly disappears from incubated aerobic or anaerobic muscle excepting when H donator is removed by washing. As_2O_3 -treated muscle readily converts (II) into (III), the reduction of which, however, is markedly inhibited. Aq. extracts of muscle with CO_2 yield a prep. of highly active dehydrogenase of (II), lactate, and citrate, free from donator. The wash-liquor contains a substance [heat-labile and pptd. by half-saturation with $(NH_4)_2SO_4$ or by $COMe_2$] which allows (II)-dehydrogenase to use O as acceptor and is possibly a cytochrome-protein complex; this factor is essential to the respiratory system.

III. (I) shows marked H donation to dyes or O only at concns. $> 10^{-4}M$; H acceptance by (II) follows a parallel course. *l*-Malic acid inhibits (I) dehydrogenase; maleic acid has little action. *l*-Malic acid resembles (II) as H acceptor when activated by washed muscle. Reduction-oxidation potentials of the system maleate-(I), the dependence of (II) dehydrogenase activity on concn. of (II), and the behaviour of allied acids in presence of muscle were investigated.

IV. (II) is extracted from muscle totally by EtOH

and to the extent of 25–40% by 5% CCl_3CO_2H . Extraction of these fluids by Et_2O and removal of Et_2O gives a residue which is titrated by 0.01N- $KMnO_4$. A correction is necessary for oxidisable substances in Et_2O , and approx. the same amount of (II) must be determined on account of continuous oxidation. Pigeon's breast-muscle contains 0.008–0.009% of "(II)." Application of this method to the influence of malonate and (III) on (II)-dehydrogenase is described.

V. Tissue-suspension is treated with 20% CCl_3CO_2H , filtered, and the filtrate treated with 0.5N- $KMnO_4$ at the b.p. just to complete oxidation. The residue after removal of Et_2O from an Et_2O extract is added to suspensions of washed muscle (the small O_2 uptake of which is determined in control experiments) with and without addition of malonate [which inhibits oxidation of (I) (A., 1926, 434)]. The difference in O_2 uptake is due to (I). Standardisation with known amounts of (I) is necessary owing to loss on deproteinisation, incomplete inhibition by malonate, etc. Application of the method indicates aerobic (but not anaerobic) (I) formation from (II) in presence of malonate.

VI. The O_2 uptake of liver and kidney in PO_4''' buffer or Ringer's solution is decreased by malonate and increased by (II); the effects with pulped tissue are $>$ those with sections. (III) can be detected following aerobic incubation in Ringer's solution, but not in PO_4''' buffer. Formation of ketones by liver-tissue alone or in presence of $AcCO_2H$ (cf. A., 1934, 802) is suppressed by (II) and enhanced by malonate; with added butyric or β -hydroxybutyric acid (II) inhibits, but malonate is without effect.

VII. Intravenous administration of malonate to rabbits (0.5 g. per kg.) produces a marked $COMe_2$ reaction in the urine, max. after 30–60 min.; with (II), (III) but not $COMe_2$ is formed. $COMe_2$ formation follows administration of β -hydroxybutyric acid and is markedly diminished by simultaneous injection of (II). Similarly formation of $AcCO_2H$ from injected (III) (0.2 g. per kg.) is enhanced by subcutaneous injection of As_2O_3 (3 mg. per kg.) which retards reduction of (III). Formation of (III) from (II) is also demonstrable in As_2O_3 -treated rabbits. The relative non-toxicity of malonate is related to its *in-vitro* behaviour in PO_4''' and Ringer's solution. F. O. H.

Biological value of the proteins of white, wheat, and rye breads. R. B. FRENCH and H. A. MATILL (Cereal Chem., 1935, 12, 365–371).—The biological vals. for maintenance are given for the proteins of white, whole-wheat (50:50), and rye (25:75) breads. Young rats did not utilise rye bread as well as the protein of milk-supplemented white or whole-wheat bread, nor could they utilise any of the bread-proteins for their maintenance needs as well as could mature rats. The biological vals. of all the breads were of the same order when determined on mature rats or on man. Bread-proteins may be classed with meat-proteins, and are inferior only to proteins of the highest biological val., e.g., those of milk. E. A. F.

Protein-synthesising function of the liver. A. MILELLA (Policlin., 1935, 42, 220—238).—In curarised dogs with artificial respiration, samples of blood were taken from the hepatic veins before and at short intervals after injecting into the portal vein 200 ml. of a 10% solution of the NH_2 -acids of meat, prepared by enzymic digestion of skeletal muscle. 5 min. after injection the albumin (I) content of the blood of the hepatic vein rose and remained above the original val. for 20—30 min. Globulin (II) of the serum fell and remained below the original level, but the ratio (I):(II) after injection was always much > before. In dogs previously poisoned with P, (I) and the (I):(II) ratio fell and in normal dogs injected with 200 ml. of *N*-NaCl (I) fell slightly and (II) was unchanged. Results similar to the above were obtained when 200 ml. of 10% NH_2 -acid solution from meat were placed in the stomach, but the increase in (I) in the hepatic vein appeared later. These results suggest that the liver can synthesise protein from NH_2 -acids. NUTR. ABS. (m)

Nitrogen metabolism of certain invertebrates. R. TRUSZKOWSKI and S. CHAJKINÓWNA (Biochem. J., 1935, 29, 2361—2365).—Aq. extracts of some invertebrates were tested for urease, uricase (I), xanthine oxidase, and uric acid (II), and it is deduced that uricotelic N metabolism is probable in the black-beetle, cockroach, May-beetle, and Roman snail. In the colorimetric determination of (II) blank determinations are made on portions of the solution to be examined after incubation with (I). H. D.

Proteins and carbohydrates: their gastric digestion. M. E. REHFUSS (J. Amer. Med. Assoc., 1934, 103, 1600—1605).—Even in diseased individuals there is no incompatibility between protein and carbohydrate digestion. CH. ABS. (p)

Oxidation of *l*- and *dl*-tyrosine by the livers and kidneys of various animals. F. BERNHEIM (J. Biol. Chem., 1935, 111, 217—224).—Broken cell suspensions of the kidney and liver of the rat, cat, and dog, together with the purified enzyme of the kidney, were used. Kidney suspension and purified kidney-enzyme oxidise *d*-(I) but not *l*-tyrosine (II), and up to 4 O can be taken up for each mol. of (I) oxidised by the suspension. With the purified enzyme only 1 or 2 O are taken up, depending on the degree of purification. Deamination occurs with the suspension when 1 O is taken up, and this is not affected by 0.005*M*-KCN, but the further oxidation is inhibited. Liver suspensions oxidise (I) and (II), in each case 4 O being taken up. 0.005*M*-KCN completely stops the oxidation of (II), whilst that of (I) is unaffected. (I) is and (II) is not deaminated by liver suspension. Neither (I) nor (II) will reduce methylene-blue in presence of liver. J. N. A.

Uric acid synthesis in pigeons. I, II. R. B. FISHER (Biochem. J., 1935, 29, 2192—2197, 2198—2207).—I. The source of C for uric acid (I) synthesis in pigeons is investigated. There is a correlation between the quantity of the food ingested at a given time and the (I) excreted 24 hr. later. The (I) excreted \propto ingested N.

II. 100 mg. of *l*-lactate (II) administered to pigeons

on a normal diet increases the excretion of (I), whilst *d*-lactate does not. A statistical study of the results indicates that the effect of (II) is due to participation in the synthesis of (I). H. D.

Nutritive value of canavanine. M. OGAWA (J. Agric. Chem. Soc. Japan, 1935, 11, 558—563).—The average daily requirement of the $(\text{NH}_2)_2$ -acid, canavanine, for normal growth of young animals is 0.05—0.1 g. per kg. body-wt. P. G. M.

Influence of glycine on excretion of creatine and creatinine. M. ADAMS, M. H. POWER, and W. M. BOOTHBY (Amer. J. Physiol., 1935, 111, 596—610).—Glycine (I) causes an increase in excretion of creatine (II) in the urine by man, but creatinine excretion is generally unaffected. The increase usually occurs within the first week, and generally establishes itself in a few days, but in some cases the increase is gradual. (II) tolerance is reduced by (I). Glutamic acid does not affect (II) excretion. R. N. C.

Utilisation of amides in nitrogen metabolism. M. MEZINGESCO (Ann. Physiol. Physico-Chim. biol., 1934, 10, 1041).—Addition of asparagine, NH_2Ac , or succinamide to a carbohydrate diet on which min. endogenous N excretion has been established reduces N loss by about 30%. Creatinine and S excretions are not affected. There is no increased production of creatine. NUTR. ABS. (m)

Liberation of ammonia by the brain after natural stimulation. J. KAHN and L. CHEKOUN (Compt. rend., 1935, 201, 505).—The brain, removed from the fish, *Carassius*, kept in H_2O of low O_2 content and therefore respiring abnormally quickly, liberates NH_3 more rapidly than a brain similarly removed from the fish kept in well-aerated H_2O . At 15—16°, increase of the respiratory movements from 30 to 75 per min. was associated with an increase of NH_3 production of 43%. Lowering the temp. 10° (without defective aeration) reduces the rate of breathing and also the NH_3 production by about 50%. W. O. K.

Precursors of coprosterol and the bile acids in the animal organism. O. ROSENHEIM and T. A. WEBSTER (Nature, 1935, 136, 474).—Addition of cholestenone (I) to diets poor in cholesterol (II) gives rise to a large increase in the excretion of faecal coprosterol (III) by animals. (I), arising presumably from cholestene-3:4-diol, and coprostanone, and not (II) itself, are regarded as the immediate precursors of (III), which is formed from them by bacterial reduction in the intestine. The possible role of (I) in the conversion of (II) into bile acids and certain sexual hormones is discussed. L. S. T.

Deuterium as an indicator in the study of intermediary metabolism. I. R. SCHOENHEIMER and D. RITTENBERG. II. Methods. D. RITTENBERG and R. SCHOENHEIMER. III. Role of the fat tissues. R. SCHOENHEIMER and D. RITTENBERG. IV. Mechanism of coprosterol formation. R. SCHOENHEIMER, D. RITTENBERG, and M. GRAFF (J. Biol. Chem., 1935, 111, 163—168, 169—174, 175—181, 183—192).—I. The uses and limitations of D as an indicator are discussed. *Tetra-*

deuterostearic acid ("6:7:9:10"), m.p. 69°, prepared by catalytic reduction of linoleic acid with D_2 , has m.p. 69°, not depressed by stearic acid.

II. The prep. of D_2 by electrolysis of dil. D_2SO_4 in D_2O is described. In determining D in org. compounds the water formed by combustion is frozen out by solid CO_2 .

III. A D-containing fat was prepared by partial catalytic reduction of linseed oil by D_2 , and fed to groups of mice as 1%, 4%, and 20% of their diet. The results of *post-mortem* analyses indicate that most of the fat is deposited in the fat tissues before utilisation.

IV. 4:5-*Dideuterocoprostanone* (I), prepared by addition of D_2 to cholestenone (II) (Pd catalyst), has $[\alpha]_D^{25} + 36.9^\circ$, m.p. 62°, not depressed by coprostanone (III). One D is replaced by H by boiling with KOH in EtOH. (II), fed to a dog on a dog-biscuit diet, is converted into cholesterol; on a meat diet, it is converted into coprosterol (IV). (III) [using (I) as indicator] is converted into (IV) by dog or man. F. A. A.

Metabolism of isolated fat-tissue. II. Dependence on body-weight, growth, and nature of food. H. RUSKA and A. QUAST (Arch. exp. Path. Pharm., 1935, 179, 217—225; cf. this vol., 114).—Marked variations in the respiration of fat-tissue (rat) are related to the presence of brown fat-tissue, which has an O_2 uptake and anaerobic glycolysis > and R.Q. < those of white. The vals. for fat-tissue are more dependent on body-wt. and growth than are those of other tissues. The ratio glycolytic activity/respiration is > that of liver or kidney, but < that of retina, brain cortex, or tumour. The possibility of fat-synthesis by fat-tissue *in vitro* is discussed.

F. O. H.

Effect of fat on gastric motility. B. A. MC-SWINEY and W. R. SPURRELL (J. Physiol., 1935, 84, 41—49).—The degree of gastric delay produced by fats \propto their concn. in the diet. The action of the fat occurs directly in the stomach; the effect in the duodenum is governed by intragastric conditions.

R. N. C.

Fat metabolism. I. Oxidation of butyric, crotonic, and β -hydroxybutyric acids in presence of guinea-pig liver slices. II. Oxidation of normal saturated fatty acids in the presence of liver slices. III. Formation and breakdown of acetoacetic acid in animal tissues. M. JOWETT and J. H. QUASTEL (Biochem. J., 1935, 29, 2143—2158, 2159—2180, 2181—2191).—I. Liver slices are incubated with β -hydroxybutyric (I), crotonic (II), and butyric (III) acids in glycerophosphate buffer and the rate of formation (Q_{Ac}) of $CH_3Ac \cdot CO_2H$ (IV) is determined by measuring the CO_2 produced on breakdown with $NH_4Ph \cdot HCl$ as catalyst. In all cases Q_{Ac} increases with the substrate concn.; with (II) a max. occurs. With (II) and (III) optimum concns. of K^+ and Ca^{++} are shown to exist. The optimum p_H for (I) and (III) is 7.4 and for (II) 7.7. The mean Q_{Ac} are in the order (III) > (II) > (I). The Q_{Ac} of (III) may be raised by addition of (I), whilst addition of (II) lowers it. Inhibition of the Q_{Ac} by a no. of unsaturated compounds is shown; that produced by propion-

ate and cinnamate, which inhibit with (II) and (III) but not with (I), shows that (II) and (III) are not intermediates in the oxidation of (I) to (IV). Of the possible modes of formation of (IV) from (II) and (III), that involving the adsorption of (II) and (III) on the same enzyme is favoured.

II. The production of (IV) by liver slices on treatment with straight-chain fatty acids of 2—10 C is investigated. With even nos. of C the order of Q_{Ac} is 4, 6, 8 > 10 > 2; acids containing 5, 7, and 9 C produce small but significant quantities, whilst $EtCO_2H$ produces none. Since the production of (IV) from (III) is <, and its inhibition by NaOBz is >, those of the higher homologues, the β -oxidation theory of the metabolism of fatty acids is discarded and a mechanism based on the oxidation of alternate C atoms is put forward.

III. In the absence of added fatty acids, rat kidney, brain, and spleen do not produce (IV); rat testes give a little. In the presence of added fatty acid all these tissues produce some. With (I) and guinea-pig kidney is greatest in the absence of K^+ and Ca^{++} . The anaerobic destruction of (IV) by kidney is 30—40% of its aerobic rate; the rate is decreased by removal of K^+ and Ca^{++} . Malonate increases Q_{Ac} with rat and guinea-pig livers in the absence of added substrate; with the former liver respiration is decreased and with the latter increased. Atoxyl (V) and quinine inhibit spontaneous formation of (IV) by liver, the action of (V) occurring at concns. which inhibit liver-esterase activity. H. D.

Biology of carbohydrate metabolism. R. P. VAN CALCAR (Chem. Weekblad, 1935, 32, 530—537).—A review comparing and contrasting the degradation of glycogen in muscle and the fermentation of glucose by zymase. S. C.

Role of the nervous system in the regulation of the glycogen metabolism of skeletal muscle. H. M. HINES and G. C. KNOWLTON (Amer. J. Physiol., 1935, 111, 243—249).—The glycogen (I) content of the denervated gastrocnemius muscle of the rat remains normal for 48 hr. after section of the sciatic nerve, and falls considerably on the 3rd day. Administration of glucose (II) produces normal (I) storage in the denervated tissue 24 hr. after nerve section, but not after > 24 hr. Depletion of tissue- (I) by adrenaline (III) or insulin (IV), followed by (II) administration, produces (I) storage up to the level before depletion. (III) and (IV) produce approx. equal decreases in (I) of denervated and control muscle; thyroxine decreases (I) in denervated muscle in doses < those required for normal muscles. Fasting reduces (I) in denervated muscle. The period elapsing before (I) falls in denervated muscle corresponds with the time of loss of viability before atrophy begins; the persistence of the normal (I) content for 24 hr. after section does not suggest that reflexes are involved in (I) metabolism. R. N. C.

Availability of bread carbohydrates. E. P. LAUG, L. A. GARAVELLI, and T. P. NASH, jun. (Cereal Chem., 1935, 12, 356—364).—Assays with phloridzinised dogs and on reducing substances excreted in the urine of normal dogs after bread feeding showed that practically the whole of the non-cellulose carbo-

hydrates of white, whole-wheat, and rye breads are available for nutrition. Whole-wheat bread carbohydrates appear to be absorbed more rapidly than those of white or rye bread, whilst rye-bread carbohydrates appear to be less completely assimilated than those of whole wheat or white bread. Dogs could apparently be maintained indefinitely in a good nutritional state on an exclusively bread diet.

E. A. F.

Sugar utilisation in eviscerated rabbits. D. R. DRURY (Amer. J. Physiol., 1935, **111**, 289—292).—The rate of utilisation of glucose (I) by eviscerated rabbits varies between 45 and 236 mg. per kg. per hr. Pre-operative fasting decreases the need of (I).

R. N. C.

Utilisation of galactose following complete removal of the liver. J. L. BOLLMAN, F. C. MANN, and M. H. POWER (Amer. J. Physiol., 1935, **111**, 483—491).—Galactose (I) injected intravenously in normal dogs is removed from the blood in 2 hr.; 10—30% is excreted in the urine. In hepatectomised animals 50—60% is excreted in the urine. Nephrectomy delays the clearance from the blood; the delay is greater if hepatectomy is also performed. Hepatectomy decreases, but does not abolish, (I) utilisation; the utilised (I) is not converted into glucose, since the hypoglycaemia of hepatectomised animals is unaffected. Partial (50—70%) hepatectomy does not alter (I) excretion in the urine. (I) excretion is increased by acute degenerative lesions of the liver or the histological changes produced.

R. N. C.

Metabolic fate of galactose in adult dogs and rabbits. J. H. ROE and G. R. COWGILL (Amer. J. Physiol., 1935, **111**, 530—538).—Galactose (I) administered intraperitoneally to rabbits is transformed into glucose (II) if the animals have not fasted. In the adult dog, blood-(I) following injections shows no difference in concn. between the afferent and efferent blood of the leg muscles and brain. The portal and hepatic blood show significant falls of (I) and corresponding rises of (II) during the passage through the liver.

R. N. C.

Determination of benzoic acid in biological material. Enzymic transformation of the acid in horse-kidney. H. WAELSCH and G. KLEPETAR [with A. BUSZTIN] (Z. physiol. Chem., 1935, **236**, 92—102).—The acid (liberated by hydrolysis if necessary) is determined by a modification of the method of Grossfeld (A., 1916, ii, 158). In kidney pulp and in glycerol extracts of horse kidney, BzOH undergoes enzymic alteration, being probably converted into OH-derivatives.

W. McC.

Role of the lungs in the removal of lactic acid in physical work. D. ALPERN, E. SIMONSON, G. SIRKINA, and L. TUTKIEWITSCH (Pflüger's Archiv, 1935, **235**, 554—561).—Lactic acid (I) in the arterial blood of the dog after physical work is < in the right heart, whilst glucose (II) is higher, the rise in (II) being > the fall in (I). The removal of (I) in the lungs is probably not a resynthesis of (II), but rather an oxidative process, which accounts for 10—20% of the total O₂ consumption.

R. N. C.

Can ethyl alcohol serve as oxidation material in muscular activity? G. TROSCHKE (Pflüger's

Archiv, 1935, **235**, 785—788).—Ingestion of EtOH and sugar followed by muscular work results in blood-sugar and EtOH attaining their max. at the same time. EtOH indirectly accelerates sugar supply to the muscles by replacing it in the metabolism of non-muscular organs.

R. N. C.

Alcohol injected intravenously: effect of habituation on rate of metabolism. H. W. NEWMAN and W. C. CUTTING (J. Pharm. Exp. Ther., 1935, **54**, 82—89).—A possible acquired tolerance to EtOH is investigated. A daily intake of 5—7 c.c. of EtOH per kg. body-wt. for 3 months causes no increased rate of EtOH metabolism in the dog.

H. D.

Etiology of so-called alveolar pyorrhoea. I. Influence of diet on mineral metabolism. L. I. KAUSHANSKY (Dental Cosmos, 1935, **77**, 69—74).—Base-forming rations ("soda") and acid-forming rations (NH₄Cl) produced changes in the K, Na, Ca, and Mg contents of dogs' blood and in the dental enamel and dentine. The decline in blood-Ca was more marked on the base-forming ration. The K : Ca ratio and the Loeb ionic coeff. of the blood were changed by both rations.

CH. ABS. (p)

Calcium-potassium law of Ehlenberg. I. Y. ISHIZUKA (J. Agric. Chem. Soc. Japan, 1935, **11**, 574—588).—Absorption of K is retarded with increasing concn. of Ca, growth being correspondingly decreased.

P. G. M.

Calcium in nutrition in China. W. M. ADOLPH (Nutrition Notes [China], 1934, No. 2, 8 pp.).—A review.

CH. ABS. (p)

Effects on calcium and phosphorus metabolism in dairy cows of feeding low-calcium rations for long periods. E. B. MEIGS, W. A. TURNER, E. A. KANE, and L. A. SHINN (J. Agric. Res., 1935, **51**, 1—26).—In normal cattle the % of Ca and P and the Ca : P ratio of the whole body and of the bone are substantially const. Differences effected by use of low-Ca rations are much < are usually supposed. After 9 months on low-Ca rations cows utilise approx. 50% of the Ca intake for calf and milk production. Poor reproduction following substitution of hay or straw for lucerne in cows' rations is attributable to deficiency of vitamin-A rather than to that of Ca.

A. G. P.

Phosphorus requirement of dairy heifers. J. G. ARCHIBALD and E. BENNETT (J. Agric. Res., 1935, **51**, 83—96).—Data for 1-, 2-, and 3-year heifers are given. Rowen and legume hays provide sufficient P when fed alone, but ordinary mixed hay may be deficient. Retention and utilisation of N and Ca were similar with low- and high-P rations. The utilisation of ingested P was proportionally higher with low-P rations, but the resulting storage of P in no case equalled that produced by high-P rations.

A. G. P.

Individual variation in response to drugs. A. J. CLARK (Edinburgh Med. J., 1935, **42**; Trans. Med.-Chirurg. Soc. Edinburgh, Session 1934—1935, **114**, 1—14).—Variations in individual response of man and certain animals to a no. of drugs are discussed.

CH. ABS. (p)

Sympathetic dilator fibres in the muscles of the cat and dog. E. BULBRING and J. H. BURN (J. Physiol., 1935, 83, 483—501).—Perfusion of the hind-limb muscles with Ringer's solution containing eserine (I) and adrenaline (II) and stimulation of the sympathetic chain liberates an acetylcholine-like substance in the perfusate. Vaso-dilatation occurs on stimulation when the muscles are perfused with defibrinated blood containing (II) or pituitary extract, or injected with (I) or ergotoxine (III). The effect is increased by (I) and abolished by atropine except after (III) or in Et₂O anaesthesia. R. N. C.

Pharmacological action of the alkaloids of fumaraceous plants. II. Corydine. R. A. WAUD (J. Pharm. Exp. Ther., 1935, 54, 40—45).—Corydine is very similar in action to isocorydine (A., 1934, 325) with a smaller tendency to produce catalepsy. H. D.

Mechanism of morphine hyperglycaemia. II. Action of opium alkaloids on the total carbon dioxide and alkali reserve in blood-plasma of rabbits. III. Influence of opium alkaloids on adrenaline content of blood in normal rabbits. IV. Influence on blood-sugar and plasma alkali reserve of rabbits. H. GYOKU (Folia Pharmacol. Japon., 1934, 19, No. 1, 1—13, 13—25; Japan. J. Med. Sci., IV [Proc. Japan Pharmacol. Soc.], 1934, 8, 111; cf. this vol., 528).—II. The increases in alkali reserve caused by pantapon, morphine, heroin, codeine, apomorphine, thebaine, papaverine, narceine, and narcotine were in the order named. Parallel increases in blood-sugar occurred.

III. Adrenaline was determined by perfusion through the vessels of a frog's leg.

IV. Morphine hyperglycaemia was lessened by cutting the vagus and splanchnic nerves and removing the thyroid glands. CH. ABS. (p)

Mechanism of strychnine action or its combination with various uterus tonics on the isolated rabbit uterus. K. IBA (Folia Pharmacol. Japon., 1934, 19, 51—58).—Strychnine (I) (1 in 20,000—1,000,000) increases the contraction of the isolated uterus. When added to half the min. stimulative doses of tyramine, pilocarpine, histamine, BaCl₂, pituitrin, or quinine (I) exerts an additive effect. With choline chloride, adrenaline, and quinine there is potentiation. CH. ABS. (p)

Non-modification of the sympathicolytic activity of yohimbine by the introduction of a double linking into the molecule. RAYMOND-HAMET (Compt. rend., 1935, 201, 434—436).—*apo*-Yohimbine (1 mg. per kg.) abolishes the rise in carotid pressure and increase in kidney vol. which are produced when adrenaline is injected into a dog under chloralose anaesthesia. 3 mg. per kg. completely reverses the effects, as is the case with yohimbine. J. L. D.

Effect of amytal on pilocarpine-induced sub-maxillary and gastric secretion. M. F. MONTGOMERY (Proc. Soc. Exp. Biol. Med., 1935, 32, 1287—1290).—Amytal depresses both salivary and gastric secretions 6 hr. after administration in dogs; they

fall to a min. in 2—3 days, afterwards returning slowly to normal. R. N. C.

Detoxification of amidopyrine by sodium amytal. C. L. ROSE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1242—1243).—The min. lethal dose of amidopyrine in mice and rats is increased by addition of Na amytal. R. N. C.

Sodium amytal for anaesthesia in studies on mitochondria. J. MCA. KATER (Science, 1935, 82, 256).—Na amytal is suitable for experiments with rabbits on mitochondria of the liver; there is no difference between anaesthetised and unanaesthetised material. L. S. T.

Surface anaesthesia of the outer ear passage of guinea-pigs. S. IKEBE (Folia Pharmacol. Japon., 1934, 19, 62—69).—The anaesthetising power of procaine, tutocaine, tropacocaine, cocaine, and nupercaine increased in the order named. The action of Et, Pr, Bu, amyl, hexyl, and heptyl alcohols increased with mol. wt. MeOH (20% solution) had no action. Paraldehyde, MeCHO, MeOAc, and EtOAc in 10—20% solution were anaesthetics. Menthol (10—20%) produced anaesthesia, but camphor was inactive. *p*-Cresol produced more intense effects than *o*- or *m*-cresol or PhOH. CH. ABS. (p)

Influence of various local anaesthetics on the cornea after extirpation of the superior cervical ganglion. K. ARIMA (Folia Pharmacol. Japon., 1934, 19, 204—210).—The intensity of action of the anaesthetics was in the decreasing order, pantocaine, cocaine, procaine, tutocaine. Simultaneous application of adrenaline and anaesthetic produced an earlier and more prolonged effect on the side having the ganglion still intact. CH. ABS. (p)

Isolation, properties, and pharmacological action of hagarotoxin. K. SAMAA (J. Egypt. Med. Assoc., 1935, 18, 17—31).—An Egyptian product (El Hagar, El Hindi, or Indian stone), apparently a mixture of sand and dried secretion of certain frogs, contains hagarotoxin (I) which has anaesthetic and toxic properties. (I) is obtained by EtOH extraction, has m.p. 161°, and gives a bright red colour with conc. H₂SO₄. CH. ABS. (p)

Sex variation in the ketonuria of ether anaesthesia in rats. G. A. EMERSON (J. Pharm. Exp. Ther., 1935, 54, 90—96).—Female rats show a ketonuria on Et₂O anaesthesia > that of males; feeding of CH₃Ac·CO₂H increases the ketonuria, whereas none is produced by injection of adrenaline alone. H. D.

Ether dosage after pre-anaesthetic medication with narcotics (barbiturates, magnesium sulphate, and morphine). F. A. CALDERONE (J. Pharm. Exp. Ther., 1935, 54, 24—39).—After morphine and sub-anaesthetic doses of Na amytal (I) there is no change in the blood-Et₂O concn. necessary for surgical anaesthesia and respiratory failure in dogs; after anaesthetic doses of (I), Na dial, and Na barbital the Et₂O concn. for respiratory failure is decreased and MgSO₄ influences the surgical anaesthesia concn. only when the doses approach anaesthetic ones. There is an additive effect in the causation of respiratory failure. H. D.

Barbiturates. XII. Factors governing distribution. J. M. DILLE, C. R. LINEGAR, and T. KOPPANYI. **XIII. Analysis of the duration of action.** T. KOPPANYI, C. R. LINEGAR, and J. M. DILLE (J. Pharm. Exp. Ther., 1935, 54, 46—61, 62—71; cf. A., 1934, 1254).—XII. After intravenous injection of barbiturates (I) into dogs and fowls, there is at first a rapid, then a slower, decrease in (I) concn. in the blood. After barbital (II) the brain contains less, and after nembutal (III) more, (I) than the other organs. Injection of (II) in 50% MeOH into carotid increases the concn. in the brain.

XIII. Long-acting (I) such as (II) and phenobarbital are destroyed slowly in the body, whilst (III) is quickly destroyed and rapidly disappears from the central nervous system. H. D.

Effect of nembutal on serum-cholesterol of dogs. E. H. BIDWELL, F. H. SHILLITO, and K. B. TURNER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1235—1236).—Nembutal in amounts sufficient to produce deep narcosis in dogs does not affect total serum-cholesterol. R. N. C.

Pharmacological action of insulin. M. TAMAKI, T. MATSUI, and T. KOBAYASHI (Japan. J. Med. Sci., IV [Proc. Japan Pharmacol. Soc.], 1933, 7, 117—118).—Insulin has no action on smooth muscle, and no antagonistic effect against atropine or ergotamine. CH. ABS. (p)

Control of some ectoparasites of laboratory rats by atomised pyrethrum extracts in oil. E. M. SEARLS and F. M. SNYDER (J. Econ. Entom., 1935, 28, 304—310).—Spraying with a petroleum extract of pyrethrum (2.1% of pyrethrins) was effective against body lice and produced no ill effects on the animals. A. G. P.

Exchanges of water, electrolytes, and heat during phenylethylhydantoin sickness. F. W. ROCKWELL (J. Clin. Invest., 1935, 14, 202—211).—A temporary H_2O retention was followed by retention of Na, Cl, and K in the order named. During the fever acidosis and increased O_2 consumption occurred. The increased heat production was not at the expense of protein. CH. ABS. (p)

Effects of acetyl- β -methylcholine on the gastric acidity of monkeys. J. H. FERGUSON and E. R. B. SMITH (J. Physiol., 1935, 83, 455—458).—Intraventricular, intravenous, or subcutaneous injection of acetyl- β -methylcholine in green monkeys abolishes temporarily the free acidity of the gastric contents. Total Cl is unaltered. The lowest threshold dose is that required intraventricularly. The effect is antagonised by atropine. There is little evidence that the disappearance of acidity is due to simple neutralisation. Posterior pituitary extracts give no anacidity response. R. N. C.

Choline and certain of its derivatives. I. Pharmacological activity of acetylphosphocholine and acetylarsenocholine relative to acetylcholine. A. D. WELCH and M. H. ROEPKE (J. Pharm. Exp. Ther., 1935, 54, 118—126).—The actions of the P and As analogues of acetylcholine (I) on the blood-pressure of the pithed cat, the turtle's and frog's

heart, and the rabbit's intestine are qualitatively the same as that of (I), but quantitatively very much less. H. D.

Effect of methylhistamine and hydroxyethylglyoxaline on gastric secretion and blood-pressure in the dog. J. G. SCHNEDORF and A. C. IVY (Proc. Soc. Exp. Biol. Med., 1935, 32, 777—778).—Methylhistamine is as potent as histamine in its gastro-secretory and depressor actions, but hydroxyethylglyoxaline has neither of these actions. R. N. C.

Non-production of granulocytopenia with an amidopyrine compound in some acute infections. M. M. KUNDE, R. P. HERWICK, A. LEARNER, and M. STERNBACK (Proc. Soc. Exp. Biol. Med., 1935, 32, 1121—1125).—Cibalgine (I) does not reduce the leucocyte count in normal rabbits, nor the leucocytosis in gastro-intestinal infection. Thyroidectomised rabbits receiving (I) develop leucocytosis similarly to normal animals when infected. R. N. C.

Influence of bile salts on the nervous system following intraspinal usage. S. S. LIGHTMAN and E. L. STERN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1201—1204).—Na deoxycholate does not affect the spinal cord when introduced intraspinally in the lumbar region of the cat in minute quantities in aq. solution; larger quantities produce motor and sensory disturbances and respiratory paralysis. In EtOH solution it affects traumatised spinal cord tissue in doses that are harmless in aq. solution. The haemolytic action of bile salt is reduced by spinal cord tissue or fluid protein. R. N. C.

Effects of phenanthrene derivatives on lipid contents of organs. T. USUI (Sei-i-Kwai Med. J., 1934, 53, No. 7, 154—161).—Injection of thebaine and dihydrohydroxycodone hydrochlorides or hydrocodone phosphate into mice causes an increase in the lecithin, cholesterol, and total fat-acid contents of the liver, spleen, kidneys, and heart. CH. ABS. (p)

Action of pyrazolone derivatives on the vascular system. J. BOCK, H. KAUNITZ, and H. POPPER (Arch. exp. Path. Pharm., 1935, 179, 170—179).—Retardation of the diffusion of injected Na fluorescein into the anterior chamber of the rabbit's eye by injection of Ca salts is confirmed. Pyrazolone derivatives (novalgin, melubrin) and ferrum saccharatum oxydatum have a similar action, which is due to decreased permeability of the blood-vessel walls. A related phenomenon is the retardation by these substances of the increase in protein content of the aq. humour replacing that removed from the anterior chamber. F. O. H.

Toxicity and absorption of digilanid. F. ŠVEC (Arch. exp. Path. Pharm., 1935, 179, 157—163).—Digilanid (mixture of -A, -B, and -C) (A., 1933, 877, 1146) has a min. lethal dose (Hatcher-Magnus) of 0.3754 mg. per kg. (cat). The min. lethal dose enterally is approx. twice that intravenously. Following oral administration approx. 3/4 of the lethal dose of the glucoside is absorbed from the intestinal tract in 14 hr. F. O. H.

New agent for stimulating metabolism: di-nitro-o-cyclopentylphenol (preparation 2769/1)

and its action on basal metabolic rate. F. E. C. DEVEGNEY (Brit. J. Exp. Path., 1934, 15, 360—362).—The basal metabolic rate may be increased 25—30% by very small doses (1—2.5 mg. per kg. per 24 hr.) of the prep. in the form of the Na salt. CH. ABS. (p)

Anthelmintic action of *o*-heptylphenol and 6-hexyl-*m*-cresol against *Ascaris lumbricoides*, *Necator americanus*, and *Trichuris trichiura*. P. D. LAMSON, D. M. MOLLOY, and H. W. BROWN (Amer. J. Hyg., 1935, 21, 188—199).—These compounds cause no irritation of the mucous membrane of the mouth. Homologues with smaller alkyl groups are irritating, those with larger groups non-irritating but inactive towards *A. lumbricoides*. CH. ABS. (p)

Acetylsalicylic acid poisoning. S. C. DYKE (Lancet, 1935, 229, 613—614).—Poisoning by 435 grains in a woman resulted in symptoms of profound toxæmia with evidence of hepatic, renal, and cerebral damage. L. S. T.

Some effects of 2:4-dinitrophenol on pregnancy in the white rat. L. M. R. WULFF, L. A. EMGE, and F. BRAVO (Proc. Soc. Exp. Biol. Med., 1935, 32, 678—680).—Fertility is not appreciably affected by intragastric administration of 2:4-dinitrophenol, but the no. of still-births and the mortality rate of the young during the nursing period are increased. R. N. C.

Effect of 2:4-dinitrophenol on calcium, creatinine, and creatinine excretion in the rat. L. I. PUGSLEY (Biochem. J., 1935, 29, 2247—2250).—The feeding of 25 mg. of 2:4-dinitrophenol per rat daily caused approx. 100% increase in the excretion of Ca in the fæces, with marked creatinuria and increased excretion of creatinine. J. N. A.

Physiological activity of some pyrocatechol derivatives. M. G. MULINOS and R. L. OSBORNE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1344—1345).—A no. of *o*-C₆H₄(OH)₂ (I) derivatives show sympathomimetic action, chloroacetylpyrocatechol (II) being the most powerful. (I) shows vasopressor activity, but (II) raises blood-pressure by medullary stimulation. (II) shows midriatic action, and raises blood-sugar in unanæsthetised rabbits. The contributory factors to the chemical constitution of sympathomimetics are stated. R. N. C.

Biological experiments with esters of *p*-hydroxybenzoic acid. H. CREMER (Z. Unters. Lebensm., 1935, 70, 136—150).—The esters (nipagin, nipasol) had no harmful effect on scorbutic or otherwise avitaminose animals in respect of growth, fertility, resistance to infectious diseases, arteriosclerosis (in rabbits), or intermediate oxidative metabolism. The blood picture was unaffected. The activity of vitamins was not impaired, but, on the contrary, they were protected from decomp. E. C. S.

Action of methylglyoxal on acetoacetic acid. V. Effect of the ketol on the respiration of surviving tissue. R. STÖHR (Z. physiol. Chem., 1935, 235, 265—271; cf. A., 1933, 88, 377).—OH·CHAc·CH₂Ac (I) in low concn. (0.0033—0.033*M*) restricts the respiration of surviving tissues. Except when its concn. is high (I) disappears in liver and kidney, but not in diaphragm. Possibly the toxic

action of (I) or of its degradation products (perhaps AcCHO) masks an increased uptake of O₂. W. McC.

Toxicity of calcium cyanamide. F. SCHOOF (J. State Med., 1935, 43, 116—118).—A discussion. CH. ABS. (p)

Effect of alcohol on spleen volume. F. D. MCCREA, D. F. MARION, W. W. TYSON, and W. P. KAVANAGH (J. Lab. Clin. Med., 1935, 20, 350—352).—Intravenous administration of small doses of dil. EtOH to cats anæsthetised with urethane caused contraction of the spleen followed by rhythmic relaxations and contractions. The size of the splenic waves increased with the dosage of EtOH. CH. ABS. (p)

Quaternary ammonium salts and the action currents in nerve. S. L. COWAN and H. R. ING (J. Physiol., 1935, 84, 90—110).—The action current of crab nerve is unaffected by a no. of quaternary NH₄ salts (I) or curarine (II) in low concns. It is slightly depressed by sea-H₂O saturated with AgCl, and abolished under these conditions by addition of (I) or (II). The action current of frog nerve is not affected by (I) or (II), even when the nerve is asphyxiated after treatment and recovered in O₂. The action current is diminished in a (I)-poisoned nerve by solid AgCl, and to a smaller extent by Ringer's solution saturated with AgCl. NEt₄I increases the galvanometer deflexion × time area. R. N. C.

Mechanism of the arsenite action on medullated nerve. F. O. SCHMITT and R. K. SKOW (Amer. J. Physiol., 1935, 111, 711—719).—Nerve oxidase is not inhibited by AsO₃^{'''} in sufficient quantity to inhibit nerve respiration 50—80% and block action potentials. Substrate activation is inhibited by AsO₃^{'''}, the degree of inhibition and the AsO₃^{'''} extinction time of the action potential showing marked seasonal variations. Respiration is scarcely protected by preliminary treatment with cysteine or glutathione, but the action potential extinction time is prolonged, although the eventual extinction is not prevented. ·SH does not restore irritability after AsO₃^{'''} block. R. N. C.

Epithelial cells of the iris in cultures in *in vitro*. VII. Influence of arsenious acid, sodium arsenite, sodium arsenate, and arsenic acid on the growth of cultures: histological changes. VIII. Influence of atoxyl, sodium cacodylate, neoarsphenamine, myoarsphenamine, and sodium salviol. K. SANJO (Folia Pharmacol. Japon., 1934, 19, 151—164, 165—177).—VII In low concns. growth is increased. Larger amounts damage the cells. The activity of the compounds decreased in the order H₃AsO₃, Na₃AsO₃, H₂AsO₄, Na₃AsO₄.

VIII. Similar results are recorded. The (decreasing) order of activity was myoarsphenamine, neoarsphenamine, Na salviol, Na cacodylate, atoxyl.

CH. ABS. (p)

Influence of various arsenic compounds on the growth of cultures of fibroblast *in vitro*: morphological changes in the cultures. II. H. OKADA (Folia Pharmacol. Japon., 1934, 19, 191—198; cf. this vol., 399).—Small concns. of Na

arsphenamine, neo- and myo-arsphenamine increased the growth in cultures. Larger proportions poison the tissue. Tartar emetic produces similar effects.

CH. ABS. (p)

Effect on blood-sugar of some organic compounds with labile sulphur. III. A. C. DE DEGIORGI (Anal. Assoc. Quim. Argentina, 1935, 23, 8—13; cf. A., 1933, 859).—The hyperglycæmia in rabbits due to injection of Na *N*-methyl-, *N*-isopropyl-, *NN*-dipropyl-, *NN*-diisopropyl-, *N*-amyl-, and *N*-isoamyl-dithiocarbamate and NH_2Me *N*-methylidithiocarbamate for the dialkyl is > that for the monoalkyl compounds, that for the isoalkyl is > that for the *n*-alkyl compounds, and that for the NH_2Me is > that for the corresponding Na salt.

F. R. G.

Effect of sulphur on Merino sheep: safe dose of sulphur for cattle. D. G. STEYN (J. S. African Vet. Med. Assoc., 1934, 5, 18—22; cf. A., 1933, 530).—Administration of 30 g. of S daily had no harmful effect over a 14-month period. A dosage of 45 g. had no harmful action on the live-wt. or digestive processes, but breath odour was unpleasant. The ability of S to prevent loss of body-wt. during periods of food scarcity is indicated.

CH. ABS. (p)

Effect of certain bactericides, especially copper sulphate, on the longevity of honey bees. E. M. HILDEBRAND and E. F. PHILLIPS (J. Econ. Entom., 1935, 28, 559—565).—Even in sublethal doses CuSO_4 acts as a repellent to bees and decreases the total food ingested. The min. lethal dose cannot be determined accurately, since amounts > this are ingested prior to death. CaO did not shorten the life of bees, but lowered the food intake. A. G. P.

Pharmacodynamic study of vanadates. A. H. ROFFO, O. CALCAGNO, and R. L. RAMIREZ (Rev. Assoc. med. Argentina, 1932, 46, 1524—1528).—Salts of V are hypertensive irrespective of the anion.

CH. ABS. (p)

Factors affecting the hypotensive action of sodium nitrite in dogs. E. HUG (Rev. Soc. Argentina biol., 1934, 10, 451—452).—The depressive effect on arterial pressure of injections of NaNO_2 into anæsthetised dogs is intensified by addition of acid. If NaNO_2 is injected 2—3 min. after injection of HCN (5 mg. per kg.) it has a hypertensive action and counteracts the hypotensive effect of HCN.

CH. ABS. (p)

Diagnosis of hydrocyanic acid and arsenical poisoning under field conditions. D. G. STEYN (J. S. African Vet. Med. Assoc., 1934, 5, 106—112).—HCN is determined by the Na picrate method. As is converted into AsH_3 and determined by the blackening of AgNO_3 test-paper.

CH. ABS. (e)

Effect of fluorine in natural waters on the teeth of small fish. A. NEFF (Science, 1935, 82, 301—302).—A relationship between the amount of F' in a given H_2O and the condition of the teeth of the fish living in it appears to exist.

L. S. T.

Occurrence of mottled enamel in Iowa. C. T. OSTREM, D. A. GREENWOOD, H. A. WILHELM, and V. E. NELSON (Proc. Iowa Acad. Sci., 1933, 40, 99—

102).—Records of mottling due to F in drinking- H_2O are given.

CH. ABS. (p)

Oxygen compounds of fluorine. J. SURU (Tech. Kurir, 1935, 6, No. 7, 1—2; cf. Ruff *et al.*, A., 1931, 810; 1934, 378; this vol., 715; Cady, *ibid.*, 181).—Sensitivity towards F gases is individual. O_2F_2 behaves physiologically very like $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$ (I). In addition it penetrates the skin and attacks the nerves. Salts of fatty acids (*e.g.*, Mg, Al, Zn, and especially Cd) in vaseline which protect against (I) (*e.g.*, those yielding tetramethylene sulphide) seem to protect also against O_2F_2 .

E. P.

Tissue changes in poultry resulting from ingestion of sodium hydrogen carbonate. G. F. DELAPLANE (Vet. Alumni Quart., 1934, 21, 149—166).—Lesions, resembling those in cases of gout, and deposition of Na urate were caused by continuous feeding of NaHCO_3 (1.6—2% in drinking- H_2O or 3.0—3.3% of the feed). Lesions were not caused by CaCO_3 , KHCO_3 , NaOH, Na_2SO_4 , or NaCl. Urate deposition in birds receiving Na_2SO_4 was > in those receiving KHCO_3 .

CH. ABS. (p)

Survival of salt-treated adrenalectomised rats. R. GAUNT, C. E. TOBIN, and J. H. GAUNT (Amer. J. Physiol., 1935, 111, 321—329).—The life-span of adrenalectomised rats is considerably extended by oral administration of 0.9% NaCl or the Rubin-Krick salt solution, the latter being more effective. Daily intraperitoneal injections of 0.9% NaCl are also beneficial. The rate of growth is sub-normal.

R. N. C.

Effect of carbon dioxide on the beat of the lateral body walls of the grasshopper embryo. J. F. WALKER (J. Cell. Comp. Physiol., 1935, 6, 317—334).—The time of recovery of the beat after exposure to pure CO_2 is > the time required for cessation, and \propto it when the latter is < 10 min. The beat when stopped by 95% CO_2 may be resumed while the embryo is still exposed. Response of the embryo to a given CO_2 tension depends on the tension of the previous environment; acceleration occurs when the CO_2 tension is decreased. The beat is unaffected in an O_2 tension of 6.8%.

R. N. C.

Boron poisoning in dogs. G. W. CLOUGH (Vet. Rec., 1933, 13, 585).—Borax, used in error for H_3BO_3 in ear treatment of dogs, caused severe disorders and death. B was detected in alkaline stomach contents and in urine.

CH. ABS. (p)

Influence of mercury on cultivated tissue. I. (a) Influence of mercuric chloride, bromide, cyanide, and oxycyanide on growth and morphological picture of fibroblast *in vitro*. (b) Influence of neptal, salyrgan, novasurol, and imamicol. K. HIRASHIMA (Folia Pharmacol. Japon., 1934, 19, 219—238, 239—247).—Growth was increased by low and inhibited by higher concns. of the salts. Toxicity decreased in the order HgCl_2 , HgBr_2 , $\text{Hg}(\text{CN})_2$, HgO — $\text{Hg}(\text{CN})_2$.

b. The org. Hg compounds reacted similarly, but concns. > those of inorg. salts were necessary to produce the same effect. The (decreasing) order of activity was imamicol, novasurol, salyrgan, neptal.

CH. ABS. (p)

Lead poisoning in calves. W. P. MOSS (Vet. Rec., 1933, 13, 1099—1100).—Stomach contents of calves suspected of death from Pb poisoning contained approx. 0.022 gram of Pb per oz. CH. ABS. (p)

Reactions of rat and mouse ova to hydrogen ions. B. V. HALL (Proc. Soc. Exp. Biol. Med., 1935, 32, 747—748).—The oolemma swells and then dissolves in Ringer's solution at acid p_H , the time of dissolving decreasing with p_H . The process appears to be similar to that occurring *in utero*. R. N. C.

Hydrogen-ion concentration and the rhythmic activity of the nerve cells in the ganglion of the *Limulus* heart. I. CHAO (Biol. Bull., 1935, 68, 69—73; cf. A., 1934, 1399).—Application of H_2CO_3 to the dorsal median ganglion in sea- H_2O or Ringer's solution rapidly inhibits rhythmic activity at p_H 5.2. HCl increases the heart-rate, and inhibition is first observed near the toxic concn. of 0.001N. In Ringer's solution without Mg 0.001N-NaOH is inhibitory. Smaller concns. of aq. NH_3 cause temporary inhibition not referable to NH_4^+ . The effect of weak acids and bases is attributable to penetration of undissociated mols. into the living cells. The ganglion is relatively resistant to p_H changes in the external medium. CH. ABS. (p)

Physico-chemical theory of [nerve] excitation and inhibition. N. RASHEVSKY (Physical Rev., 1934, [ii], 45, 125). L. S. T.

Physico-mathematical theory of organic form. N. RASHEVSKY (Physical Rev., 1934, [ii], 45, 125).—The general arrangement which cells will assume in early embryonic stages under the influence of the various forces of attraction and repulsion known to exist between them is discussed. L. S. T.

Light intensity as an inhibiting factor in the fixation of atmospheric nitrogen by Manchu soya beans. F. S. ORCUTT and E. B. FRED (J. Amer. Soc. Agron., 1935, 27, 550—558).—Inoculated soya beans grown in N-free sand, with high light intensity, failed to initiate N fixation. The latter commenced after partial shading for 1 week. The effect of light intensity is correlated with the C : N ratio within the plant. An extremely high ratio probably inhibits N fixation. A. G. P.

Lethal action of radiant energy on living cells. F. F. HEYROTH and J. R. LOOFBOUROW (Physical Rev., 1934, [ii], 45, 126; cf. A., 1934, 926; this vol., 120).—The existence of a frequency threshold for the lethal action of radiant energy on living cells is discussed. The destruction of cell-enzymes as a possible mechanism of lethal action appears to be eliminated, but destruction of compounds of the cell-nucleus is of great importance. L. S. T.

Influence of Röntgen treatment on uric acid metabolism. S. OKAUE (Folia Pharmacol. Japon., 1934, 19, 259—268).—Rabbits treated for 80—120 min. excreted less urine, which usually had a lowered N content. Urinary uric acid increased on the following day. Blood-uric acid increased immediately with treatment, returning to normal within 1 hr. of cessation, and subsequently declined. CH. ABS. (p)

Differential effect of radium radiation on the carbohydrate metabolism of normal and tumour tissues irradiated at low temperature. H. G. CRABTREE (Biochem. J., 1935, 29, 2334—2343).—Tumour tissue subjected to $\beta + \gamma$ irradiation at 37.5° suffers a decrease in respiration, although both aerobic and anaerobic glycolysis are unaffected; irradiation after HCN treatment of the tissue has a more marked effect. At 0—10° respiration is decreased, but glycolysis is scarcely affected. The metabolism of normal spleen, liver, kidney, and testis at low temp. is unaffected by irradiation. H. D.

Some factors influencing the heat production of muscle after stretching. U. S. VON EULER (J. Physiol., 1935, 84, 1—14).—The resting heat and the stretch response of frog's sartorius are increased by soaking in Ringer's solution at p_H 8—9, whilst the stretch response is diminished or abolished at p_H 5—6. The stretch response is increased by cocaine and diminished by $C_{16}H_{33}NMe_3Br$ or Na oleate. The extra heat rate resulting from stretch reaches a max. in 10 sec., and then remains high, rising gradually in O_2 and falling in N_2 . The differences in apparent initial heat in the stretch response in O_2 and N_2 are considered to be due to rapid oxidation processes not preceded by non-oxidative breakdown. R. N. C.

Proposition of "T.N.N." equations in the kinetics of enzymes. K. NAKAJIMA and T. KAMATA (J. Fac. Agric. Hokkaido, 1934, 35, 151—291).—Modifications of equations for unimol. reactions are examined in relation to the activity of numerous enzymes. CH. ABS. (p)

Metabolism of tissues growing in culture. VI. **Effect of radium on the lactic dehydrogenase and arginase systems of embryonic tissue.** B. E. HOLMES (Biochem. J., 1935, 29, 2285—2290; cf. A., 1933, 747).—A tissue culture method has the advantage over the manometric technique in studying the effect of irradiation on tissue metabolism in that the conditions are more suitable for the prolonged life of the tissue. The main disadvantage is that the metabolic reactions cannot proceed at their optimum rates if the tissue is not shaken. The lactic dehydrogenase system in the tissue of young embryos is more susceptible to γ -rays than that of older embryos. The co-enzyme is possibly the part of the system affected. Arginase activity of a tissue culture is not impaired by γ -rays. E. A. H. R.

Schardinger enzyme and co-enzymes involved in phosphorylation and oxido-reduction. B. ANDERSSON (Z. physiol. Chem., 1935, 235, 217—225).—The oxidation by the enzyme of xanthine in presence of methylene-blue is not affected by addition of co-enzyme (I), but that of MeCHO is inhibited by addition of active or inactivated (I), adenylypyrophosphate, adenylic acid (from muscle), and adenosine (not by addition of Warburg's co-enzyme). The enzyme inhibits phosphorylation during glycolysis, but does not inhibit some enzymic oxidations which require the presence of (I) as activator. Associated with the enzyme is a non-dialysable, thermolabile substance, possibly identical with the substance which oxidises MeCHO, which inhibits alcoholic fermentation and glycolysis. W. McC.

Peroxidases and cell activity in the developing egg (*Orthoptera*). J. H. BODINE and E. J. BOELL (Proc. Soc. Exp. Biol. Med., 1935, 32, 783—787).—The peroxidase reaction of the developing grasshopper's egg at 25° is negative before and positive after the diapause, becoming negative again in the embryo after hatching. Pre-diapause eggs exposed to temp. 0—5° show a positive reaction, apparently owing to the destruction of a naturally-occurring inhibitor. R. N. C.

Mechanism of catalase inhibitions. H. BLASCHKO (Biochem. J., 1935, 29, 2303—2312).—A manometric method for the study of reversible catalase (I) inhibitions is described. NaN_3 , NH_2OH , N_2H_4 , $\text{NHPh}\cdot\text{NH}_2$, EtO_2H , KClO_4 , resorcinol, *p*- and *m*- $\text{C}_6\text{H}_4(\text{NH})_2$ give reversible, HgCl_2 a partly reversible, and KClO_3 an irreversible inhibition. All substances known to give methæmoglobin compounds act as reversible inhibitors of (I), which supports the theory that (I) is a hæmin compound. E. A. H. R.

Catalase in embryonic development. II. First phase of development of eggs of *Salmo irideus* and *Esox lucius*. U. SAMMARTINO (Arch. Farm. sperim., 1935, 60, 342—352; cf. this vol., 519).—The primary segmentation (4—10 days) of the eggs influences neither the absorption of H_2O from the medium nor the (approx. const.) catalase activity. F. O. H.

Enzymic amylolysis. IV. Action of β -amylase on starch preparations. M. SAMEC [with R. MODIC] (Z. physiol. Chem., 1935, 236, 103—118).—Preps. from potato starch which yield different colours with I differ as regards their behaviour on treatment with β -diastase from wheat and are divided into 3 types: the amyloamyloses, which are relatively slowly but completely degraded; the Lintner and Fouard varieties, with which degradation ceases when about 65% of the calc. amount of maltose (I) has been produced, and the erythroamyloses (and Meyer's dextrin), which are rapidly degraded until 45—50% of the calc. amount of (I) has been produced. The degree of dispersion of the preps. affects the rate, but not the type, of reaction, and the diminution in the intensity of the colour produced with I \propto the extent of saccharification. The material left after saccharification has mol. wt. about 2000 (13—15 glucose residues) and resembles the original material in $[\alpha]$ and in colour produced with I, but has reducing properties and is much more highly dispersed. W. McC.

Specificity of amylases. II. Degradation of the hydroxyethyl ether of potato-starch to non-reducing substances. W. ZIESE (Z. physiol. Chem., 1935, 235, 235—245; cf. this vol., 401).—As regards its behaviour towards α - and β -amylase the ether does not differ from that of Lintner starch. The action of the enzyme reduces the viscosity of the solutions to 0.1—0.05 of its original val., but the degradation products have no reducing power. W. McC.

Yeast amylase. I. Preparation of amylase solution from pressed yeast. K. ONO (J. Agric. Chem. Soc. Japan, 1935, 11, 60—67).—Neutralised aq. extracts of yeast pretreated with EtOAc had poor amylolytic power. Active extracts were obtained by

means of aq. $(\text{NH}_4)_2\text{HPO}_4$ at 5°. Amylase was unstable at room temp. CH. ABS. (p).

Taka-amylase. I. Amount of glucose formed by the action of taka-diastrase on starch. II. Reaction-velocity coefficients for amylase and maltase action. III. Optimum p_H for taka-diastrase action. T. KITANO (J. Soc. Chem. Ind. Japan, 1935, 38, 376—381B, 381—385B, 385—388B).—I. The action of taka-diastrase (I) on starch (II) produces, in addition to dextrin and maltose (III), a polysaccharide sol. in 95% EtOH which possesses strong reducing properties. (III) and glucose (IV) cannot therefore account for the whole reducing powers developed by (II) when incubated with (I). (II) is rapidly hydrolysed to (III) and other polysaccharides, but further hydrolysis to (IV) is slow, although more rapid than if due to the action of maltase (V) alone. This is accounted for by the intermediary formation of a trisaccharide which is hydrolysed further to (III) and (IV). The action of (V) is independent of substrate concn. An enzyme prep. similar to (I) in its action on (II) can be obtained from soya beans by inoculation with *Aspergillus oryzae*.

II. The production of sugars from (II) by very dil. (I) solutions follows a unimol. course. At higher enzyme concn. (V), but not amylase (VI), still gives a unimol. coeff. (VI) activity does not increase correspondingly with concn.

III. The optimum p_H for (V) action is always < that for (VI) action. Both optima increase with rise of temp. E. A. H. R.

Effect of ultra-violet light on enzymic reactions. I. Diastase. S. BANERJEE and H. K. SEN (J. Indian Chem. Soc., 1935, 12, 379—383).—The enzyme action of malt-diastrase (I) on starch at p_H 5.4—5.8 is destroyed by exposure to ultra-violet light, but $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, asparagine, gelatin, tyrosine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and NH_4 citrate exert a protective action. Other catalysts which normally increase the activity of (I) have no protective action. J. W. B.

Determination of pectolytic activity of filtration enzymes. A. MEHLITZ and H. MAASS (Z. Unters. Lebensm., 1935, 70, 180—186).—The original method (A., 1934, 465) is modified. Instructions are given for the prep. of the pectin (I) solution, which should be adjusted to p_H 3.6 by addition of citric or tartaric acid. The % of (I) need not be so rigidly fixed (at 2.0%) as was previously stated. Fermentation is carried out at 37—38° for 15 hr., and is stopped by addition of CH_3CO . E. C. S.

Influence of proteins on the activity of yeast-invertase. E. L. SAUL and J. M. NELSON (J. Biol. Chem., 1935, 111, 95—103).—Yeast-invertase solutions (I), on dilution, lose a disproportionate amount of activity in hydrolysing sucrose at p_H 3. This loss is less in the presence of added protein (II). Irreversible inactivation of (I) in solution at p_H 3 is also reduced by (II). At p_H 4.5, the optimum for this reaction, or in more alkaline solution, the abnormal loss in activity is not found, and (II) has no influence. F. A. A.

Biochemical detection of carbohydrates, polysaccharides, alcohols, glucosides, and other organic compounds. H. DAMM and A. LEMBKE (Naturwiss., 1935, 23, 641).—Enzyme preps. extracted under definite conditions from various micro-organisms are allowed to act on the compound in question. From the course of the reaction, e.g., production of acid, the constitution of the compound is deduced, 10 mg. of substance being usually sufficient.

W. O. K.

Cardiac glucosides. XII. Glucosidases of *Digitalis* leaves. A. STOLL, A. HOFMANN, and W. KREIS (Z. physiol. Chem., 1935, 235, 249—264; cf. this vol., 754).—Fresh and dried leaves of *D. lanata* and *D. purpurea* contain the glucosidases digilanidase and digipurpidase, which hydrolyse the true glucosides of the leaves of these plants liberating digilanids A, B, and C and purpurea glucosides A and B (deacetyldigilanids A and B), respectively. The enzymes, which are desmo-enzymes and cannot be extracted from the leaves, also liberate the terminal glucose residue from deacetyldigilanid C and from scillaren A. Although the enzymes do not exhibit abs. specificity, they act more rapidly on the substrates with which they are associated in the leaves than on other substrates.

W. McC.

Enzymic synthesis of cholesteryl esters. S. V. NEDSVEDSKI (Z. physiol. Chem., 1935, 236, 69—72).—Lipase (from pig pancreas) in presence of CaCl_2 , PhMe, and Na cholate, taurocholate, or glycocholate produces cholesteryl palmitate, stearate, and oleate in good yields (up to 90%) from colloidal aq. solutions of cholesterol and the fatty acid.

W. McC.

Castor-bean lipase. VI. Preparation of highly active *Ricinus* lipase and its properties. E. TAKAMIYA (J. Agric. Chem. Soc. Japan, 1935, 11, 68—76).—Treatment of castor beans with *N*-acid (org. or inorg.) increases lipase activity without hydrolysis of protein. The lipase exists as a protolipase. Beans are treated with $N\text{-H}_2\text{SO}_4$ saturated with CO_2 , and subsequently extracted with Et_2O . To the extract is added light petroleum and the ppt. removed, washed, dissolved in olive oil, and again washed with Et_2O and petroleum. The purified lipase after drying over H_2SO_4 in a vac. showed positive Molisch and sterol tests, but a negative Millon reaction, contained N 7.5% and P 1.48%, and was inactivated by oxidising and reducing agents. The olive oil solution mixed with CHCl_3 and treated with 20% SbCl_3 in CHCl_3 gave a deep blue colour changing slowly to pinkish-violet.

CH. ABS. (p)

Relative choline-esterase activities of serum and corpuscles from the blood of certain species. E. STEDMAN and E. STEDMAN (Biochem. J., 1935, 29, 2107—2111).—Data from gasometric determinations of choline-esterase (I) in various sera agree with those from the titration method (A., 1933, 315, 1081). The absence of (I) from ox, sheep, and goat sera is confirmed; the corpuscles, however, contain appreciable amounts, whilst those of cat, fowl, and duck are inactive. (I) is absent from cerebrospinal fluid (cat, man), but occurs in the basal ganglia and, to a greater extent, cortex of the brain (cat).

F. O. H.

Digestion of digestive enzymes in the herring (*Clupea harengus*, L.). H. I. BATTLE (J. Biol. Board Canad., 1935, 1, 145—157).—Weak lipolytic and amylolytic enzymes are present in gastric juices, and more active ones in pyloric, caecal, and intestinal mucosa. The lipase in the latter is rendered more active by bile. Chitin is not digested. Acid extracts from gastric juice are concerned in the reddening of food organisms containing a chitinous exoskeleton. The acid gastric juice can remove hyalodentine from fish scales, but basic extracts from the pyloric caeca are without effect.

CH. ABS. (p)

Proteolytic enzymes. VI. Specificity of papain. M. BERGMANN, L. ZERVAS, and J. S. FRUTON. VII. Synthesis of peptides of *L*-lysine and their behaviour with papain. M. BERGMANN, L. ZERVAS, and W. F. ROSS (J. Biol. Chem., 1935, 111, 225—244, 245—260).—VI. The action of papain has been investigated on several peptides containing no free $\alpha\text{-NH}_2$ or $\alpha\text{-CO}_2\text{H}$, but having a β - or $\gamma\text{-CO}_2\text{H}$ in the side-chain. These are hydrolysed by papain-HCN and in each case a $\text{CO}\cdot\text{NH}$ next to the end $\text{CO}\cdot\text{NH}$ is hydrolysed. If leucine be situated next to the acyl, however, the site of hydrolysis is moved one NH_2 -acid residue away from the acyl; thus benzoylglycyl-*L*-leucylglycine, m.p. 186°, $[\alpha]_D^{24}$ -35.8° in $\text{H}_2\text{O} + 1$ equiv. of NaOH [*d*-form, m.p. 186°, $[\alpha]_D^{24}$ $+35.2^\circ$ in $\text{H}_2\text{O} + 1$ equiv. NaOH (*Me* ester, m.p. 180°)], yields hippuric acid, whilst carbobenzyloxy-*L*-leucylglycylglycine, m.p. 144°, $[\alpha]_D^{22}$ -12.8° in EtOH (*Et* ester, m.p. 105°; *d*-form, m.p. 144°, $[\alpha]_D^{22}$ $+12.3^\circ$ in EtOH), yields carbobenzyloxy-*L*-leucylglycine, m.p. 115° (*Et* ester, m.p. 103—104°). The free CO_2H of the side-chain is not necessary for papain action, but two $\text{CO}\cdot\text{NH}$ must be present, one of them being hydrolysed and the other probably serving as a point of attachment. Also, if H in the $\text{CO}\cdot\text{NH}$ be replaced by Me the linking becomes resistant to hydrolysis. With optical isomerides of a peptide, the *d*-form is hydrolysed very slowly or not at all. The following compounds are described: *L*-glutamyl- α -glycine *Et* ester, m.p. 151°; carbobenzyloxyglycyl-*L*-glutamyl- α -glycine, m.p. 98—100° (*Et* ester, m.p. 169°); glycyl-*L*-glutamyl- α -glycine; glycyl-*L*-glutamylglycine *Et* ester; glycylglutamic acid-diketopiperazine, m.p. 240°; *L*-asparagyl- α -glycine *Et* ester, m.p. 232°; carbobenzyloxyglycyl-*L*-asparagyl- α -glycine *Et* ester, m.p. 148°; benzoyldiglycyl-*L*-glutamylglycine *Et* ester, m.p. 252°; carbobenzyloxyglycyl-*L*-isoglutamine, m.p. 185°; benzoyl-*L*-isoglutamine, m.p. 158°; carbobenzyloxytriglycine, m.p. 196°; carbobenzyloxytetraglycine, m.p. 230°; carbobenzyloxyglycylsarcosyldiglycine, m.p. 127°; carbobenzyloxyglycyl-*L*-leucylglycine *Me* ester, m.p. 131° (*d*-ester, m.p. 131°); glycyl-*L*-leucylglycine, $[\alpha]_D$ -41.2° in H_2O ; diglycyl-*L*-leucylglycine, $[\alpha]_D$ -43.2° in H_2O (*Bz* derivative, m.p. 195°); triglycyl-*L*-leucylglycine, $[\alpha]_D$ -28.4° in H_2O (carbenzyloxy-derivative, m.p. 225°); benzoyl-*dl*-leucylglycylglycine, m.p. 168°.

VII. The following method for the synthesis of lysine peptides with the lysine coupled as in natural proteins has been devised. $\alpha\epsilon$ -Dicarbenzyloxy-*L*(+)-lysine, m.p. 150° (amide, m.p. 155°), is converted into the acid chloride, which when heated loses *BzCl* giving ϵ -carbenzyloxy- α -carboxy-*L*-lysine anhydride,

m.p. 100° (decomp.), which with dil. HCl yields ϵ -carbobenzyl-oxy-l-lysine, m.p. approx. 255°, $[\alpha]_D^{25} +14.0^\circ$ in $H_2O + 2$ equiv. HCl, and with MeOH-HCl gives the corresponding *Me ester hydrochloride*, m.p. 117° (*amide hydrochloride*, m.p. 203°). This ester is coupled through its $\alpha-NH_2$ with any chloride, followed by conversion into the azide, which is then condensed with an NH_2 -acid ester or peptide ester. The ϵ -carbobenzyl-oxy-group can be removed simultaneously with the terminal α -carbobenzyl-oxy-group, and with an acylated terminal $\alpha-NH_2$, the removal of the ϵ -group does not interfere with the acyl. In simple acylated lysine peptides with the $\epsilon-NH_2$ unsubstituted, papain causes a cleavage next to the $CO-NH$, but if the $\epsilon-NH_2$ be acylated as well, hydrolysis occurs also at the amide linking. Thus α -hippuryl- ϵ -carbobenzyl-oxy-l-lysineamide, m.p. 209°.

$NH_2Bz \cdot CH_2 \cdot CO \cdot NH \cdot CH([CH_2]_{14} \cdot NH \cdot CO_2CH_2Ph) \cdot CO \cdot NH_2$ is hydrolysed at * and †, but the hydrolysis at † will result only if the $\alpha-NH_2$ of the lysine be acylated. The rate of hydrolysis at † is $>$ at *. The specificity of papain is compared with that of other peptidases. The following compounds are described: α -hippuryl- ϵ -carbobenzyl-oxy-l-lysine (*Me ester*, m.p. 145°; *hydrazide*, m.p. 195°); α -hippuryl- ϵ -carbobenzyl-oxy-l-lysylglycine *Et ester*, m.p. about 163°; α -hippuryl-l-lysylglycine *Et ester hydrochloride*, m.p. 123—133°, $[\alpha]_D^{25} -30.5^\circ$ in H_2O ; α -carbobenzyl-oxyglycyl- ϵ -carbobenzyl-oxy-l-lysine (*Me ester*, m.p. 97°; *Et ester*, m.p. 146°; *amide*, m.p. 130—134°; *hydrazide*, m.p. 167°); α -glycyl-l-lysine *Me ester dihydrochloride*, m.p. 177°, $[\alpha]_D^{25} -23.9^\circ$ in H_2O ; α -carbobenzyl-oxyglycyl- ϵ -carbobenzyl-oxy-l-lysylglycineamide, m.p. 90—95°; α -benzoyl- ϵ -carbobenzyl-oxy-l-lysineamide, m.p. 172—173°; α -benzoyl-l-lysineamide hydrochloride; α -benzenesulphonyl- ϵ -carbobenzyl-oxy-l-lysine *Me ester*, m.p. 80°. J. N. A.

Pancreatic proteinase. I, II. Effects of various compounds on activity of the enzyme. L. FARMER and A. M. WYNNE (Biochem. J., 1935, 29, 2313—2322, 2323—2330).—I. The initial rate of proteolysis is measured directly by a determination of the total protein and is $>$ the rate of accumulation of NH_2-N . This latter rate is therefore not a satisfactory index of proteinase (I) activity. Of five proteins investigated, caseinogen (II) was the most rapidly hydrolysed. Initially ovalbumin is hydrolysed at a rate comparable with the other proteins, but subsequent hydrolysis is slow, due perhaps to the liberation of an anti-(I) substance. The initial rate of hydrolysis varies with the substrate concn. in accordance with the theory of Michaelis and Menten, and \propto (I) concn. The reaction rate is linear during the breakdown of sometimes as much as 65% of the protein. The lower p_H limit for (II), fibrin, and haemoglobin decreases with their isoelectric points, supporting the theory that (I) is active only on protein anions. A (I) unit is defined.

II. The influence of various substances on the initial rate of hydrolysis of (II) by (I) was investigated. Inhibitions by mono- and di-saccharides and by glycerol are believed to be due to a disturbance of effective H_2O concn. Higher polysaccharides were less effective inhibitors. Asparagine, aspartic acid, and glutamic acid caused a definite, cysteine a less

marked, activation; other NH_2 -acids were ineffective. Emulsified triacetin, tributyrin, and triolein, fresh ox-bile, and bile salts were inhibitory. Indicators and dyes inhibitory towards fumarase and urease had no effect. $CaCl_2$, $NaCN$, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$ had an activating effect. Heavy metals were without effect, so that CN' activation cannot be due to their removal.

E. A. H. R.

Trypsinogen, enterokinase, and trypsin system. Assay methods for trypsinogen and enterokinase. R. W. BATES and F. C. KOCH (J. Biol. Chem., 1935, 111, 197—215).—Simple methods are described for the prep. of trypsinogen (I) free from trypsin and enterokinase (II), and for the accurate assay of (II). (I) is more stable at p_H 2.5 than at 6.0, and it can be stabilised in neutral solution by 0.05N-KCl. Activation of (I) by (II) occurs in the presence of substrate at p_H 8.2. (II) is rapidly destroyed at p_H vals. of 2.5 and 11.7. The results of a comparative study are not in agreement with the additive compound theory, and it is concluded that (II) acts as an enzyme in the activation of (I).

J. N. A.

Proteolytic enzyme content of latex from the fig tree (*Ficus carica*, L.). Seasonal variation. B. H. ROBBINS (Proc. Soc. Exp. Biol. Med., 1935, 32, 892—893).—The enzyme content shows seasonal variations, being min. in early summer and max. in early winter.

R. N. C.

Proteolytic enzyme in the latex from the fig tree (*Ficus glabrata*). p_H of optimal activity. B. H. ROBBINS (Proc. Soc. Exp. Biol. Med., 1935, 32, 894—896).—The optimum p_H for the enzymic hydrolysis of ficin-gelatin is 5.

R. N. C.

Arginase in skeletal muscle. G. KLEIN and W. ZIESE (Z. physiol. Chem., 1935, 235, 246—248).—An inactive form (activated by 0.005M-MnSO₄, but not by FeSO₄) of arginase occurs in muscle (calf, ox, horse, wether, rat). In rat-muscle, which contains much more arginase than does the muscle of other animals, the content in hot is much $<$ in cold weather.

W. McC.

Enzymes in ontogenesis (*Orthoptera*). I. Tyrosinase. J. H. BODINE and E. J. BOELL (J. Cell. Comp. Physiol., 1935, 6, 263—275).—Tyrosinase (I) activity increases in the grasshopper egg for the first 20 days of development at 25°, afterwards remaining approx. const. until hatching. (I) is confined to the yolk and serosa cells until these are engulfed in the embryo, when it is transferred to the embryonic cells.

R. N. C.

Phosphatase in heterotopic bone formation following transplantation of bladder mucosa. E. M. REGEN and W. E. WILKINS (J. Lab. Clin. Med., 1934, 20, 250—252).—Bone formation around transplants in the sheath of the rectus abdominus muscle in dogs was accompanied by increased phosphatase activity of the implanted tissue.

CH. ABS. (p)

Course of phosphatase activity in healing of fractured bone. W. E. WILKINS and E. M. REGEN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1373—1376).—Fracture in the adult rabbit bone is followed by a

rapid rise in phosphatase activity at the site of the injury, which reaches a max. at the 22nd day and then falls gradually as healing proceeds. R. N. C.

Influence of sodium thioglycollate on the glycolytic enzyme system of muscle extract. L. MICHAELIS and C. V. SMYTHE (Proc. Soc. Exp. Biol. Med., 1935, 32, 825—827).—The positive manometric pressure developed by addition of $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) to inactivated muscle extract is not accompanied by formation of lactic acid, and is due to (I) itself. There is therefore no evidence that (I) regenerates the inactivated enzyme system. R. N. C.

Activated transformation of phosphate during glycolysis. H. VON EULER and R. VESTIN (Svensk Kem. Tidskr., 1935, 47, 231).—Thermally inactivated solutions of cozymase which do not effect alcoholic fermentation accelerate the phosphorylation and the production of lactic acid using muscle extract. E. P.

Enzymic reactions with synthetic phosphopyruvic acid (enolised phosphopyruvic acid). O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 280, 99—109).—The velocity and course of fermentation of synthetic phosphopyruvic acid (I) are identical with those of natural (I). Both acids ferment completely and the acid must have a symmetrical structure. A method is described for the partial separation of the enolase which converts (I) into 2-phosphoglyceric acid (II) from the phosphoglyceromutase which converts 3-phosphoglyceric acid into (II). By addition of AsO_4''' , the velocity of fermentation of natural and synthetic (I) can be increased to that of hexosediphosphoric acid. AsO_4''' has a similar action in the degradation of (I) with formation of lactic acid in muscle extract. P. W. C.

Separation of "enolase" and "phosphoglyceromutase." R. AKANO (Biochem. Z., 1935, 280, 110—113).—Owing to the extreme sensitivity or small amount of phosphoglyceromutase, it is possible by adsorption on various adsorbents, especially animal charcoal, to separate from dialysed yeast maceration extract an enzymic prep. containing chiefly enolase, by use of which the equilibrium 2-phosphoglyceric acid \rightleftharpoons phosphopyruvic acid can be attained without any considerable displacement by the equilibrium 2-3-phosphoglyceric acid. P. W. C.

Adenosinetriphosphoric acid in living yeast. H. VON EULER, E. ADLER, and M. PÉTERSSON (Svensk Kem. Tidskr., 1935, 47, 249—251).—A prep. obtained from fresh top yeast is identical with adenosinetriphosphoric acid from muscle. Possibly the co-enzyme has the same action in the yeast as in the muscle, or is itself the phosphate carrier. E. P.

Preparation of d(—)-3-phosphoglyceric acid. A. VERCELLONE and C. NEUBERG (Biochem. Z., 1935, 280, 161—162).—Details are given for increasing the yield of this acid in fermentations of hexose diphosphate by increasing the amount of yeast used and for its separation as the cryst. Ba salt by pptn. with EtOH. P. W. C.

Phosphorylation with living yeast. C. NEUBERG (Biochem. Z., 1935, 280, 163—166).—Fructose

monophosphate in presence of muscle-adenylic acid is converted by yeast into hexose diphosphate (and adenylypyrophosphate). P. W. C.

Fermentation of trioses by yeasts. C. NEUBERG and E. HOFMANN (Biochem. Z., 1935, 280, 167—172).—A detailed account of the work, the results of which have been already described (this vol., 1164). P. W. C.

Saccharomyces peka, nov. sp. Y. TAKEDA (Agric. Chem. Soc. Japan, 1934, 10, 1280—1282).—The yeast in "peka" (used in the production of "Beishu") ferments glucose, maltose, sucrose, raffinose, mannose, fructose, α - and β -methylglucoside, but not galactose, lactose, rhamnose, dextrin, mannitol, inulin, xylose, arabinose, sorbitol, or dulcitol. Optimum conditions for growth and fermentation, respectively, are 33° and 33—35°, p_{H} 4.0—5.5 and 5.0—6.3. CH. ABS. (p)

Hydrogenation of unsaturated ketones by fermenting yeast.—See this vol., 1367.

Haplophase and diplophase in Saccharomycetes. Ö. WINGE (Compt. rend. Trav. Lab. Carlsberg, 1935, 21, No. 4, 77—112).—A discussion of the facultative alternation of haploid and diploid generations in yeasts. E. A. H. R.

Amino-acid content of wheat-flour dough. L. W. SAMUEL (Biochem. J., 1935, 29, 2331—2333).—The NH_2 -acid content of flour dough increases with time; in dough to which yeast has been added it increases to a limit and then decreases. In a solution containing glutamic acid, sugar, salt, and yeast at p_{H} 5.9 and 29° the NH_2 -acid content decreases slowly, so that in dough the degradation of proteins by yeast is not very important. H. D.

Inhibitor of fermentation in yeast. H. VON EULER, E. ADLER, and G. DAHLGREN (Z. physiol. Chem., 1935, 236, 119—130).—The inhibitor occurs in top, and to a smaller extent in bottom, yeast, but not in yeast maceration juice. It is thermolabile and non-dialysable (high mol. wt.) and is purified by pptn. with EtOH, removal of impurities by dialysis, adsorption on $\text{Al}(\text{OH})_3$, and elution with aq. Na_2HPO_4 . In proportion to its concn. it delays the onset and diminishes the extent of fermentation. KCN does not affect it. Probably its action is reversible (added cozymase or its amount diminishes the action), and it does not destroy any of the components of the fermentation system. It seems not to be a dehydrogenase or protease, nor to affect glycolysis in muscle extract or other processes of carbohydrate degradation. W. McC.

Influence of saponin and other poisons on yeast. W. SCHWARTZ and H. KRETZDORN (Biochem. Z., 1935, 280, 72—87).—The acceleration of fermentation by saponin (I) is accompanied by considerable injury of the cell, but the injury occurs only in presence of fermentable sugar. Similarly injury by NaCl and KNO_3 occurs only during fermentation. This difference between the effect on resting and fermenting cells indicates that the action of (I) is not solely on the permeability of the cells. P. W. C.

Iron in the sea and in marine plankton.—See this vol., 1343.

Effect of skim-milk, lactose, vinegar, and iodine on the quantitative character of a coccidian infection. E. R. BECKER and N. F. MOREHOUSE (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1030—1031).—The numerical increase of the coccidian content of the alimentary tract of the rat is not restrained by skim-milk or lactose in the diet, or I or vinegar in the drinking- H_2O . R. N. C.

Metabolism of protozoa. II. Biochemical reactions in the presence of washed cells of *Glaucoma pyriformis*. N. R. LAWRIE (Biochem. J., 1935, **29**, 2297—2302).—A suspension of *G. pyriformis* can bring about the proteolysis of caseinogen over a wide range of p_H with an optimum at p_H 6.0, but ovalbumin is only slightly affected. Diastase, succinic dehydrogenase, a thermolabile peroxidase, and (probably) glutathione are also present in the protozoon. E. A. H. R.

Effect of low temperature on trypanosomes (*Trypanosoma equiperdum*) in mammals. N. KALABUCHOV and L. LEVINSON (Nature, 1935, **136**, 553).—When bats infected with *T. equiperdum* are kept at 3° or 10° for 3—8 days the micro-organisms disappear from the blood and the animals recover. At room temp., infected animals die within 9 to 13 days. L. S. T.

Diastatic activity of *Aspergillus*. N. S. WEI and K. S. CHIN (Science [China], 1934, **18**, 1193—1198).—Of 10 species examined *A. oryzae* had the greatest activity. CH. ABS. (p)

Effect of ammonium chloride on the growth and production of acid by *Aspergillus niger*. E. L. FULMER, L. M. CHRISTENSEN, and H. SCHOPMEYER (J. Amer. Chem. Soc., 1935, **57**, 1537—1538).— NH_4Cl is an excellent sole source of N for the growth of and production of acid by *A. niger*. On a medium containing sucrose 12.5, $MgSO_4 \cdot 7H_2O$ 0.08, $FeSO_4 \cdot 7H_2O$ 0.01, $ZnSO_4$ 0.01, and KH_2PO_4 0.125% at p_H 3 and 30°, max. production of acid occurs with 0.188% of NH_4Cl (the calc. first optimum for the growth of yeast and the concn. which produces min. hydration of wheat-gluten), but the optimum for formation of mycelium is with 0.275—0.5% of NH_4Cl . R. S. C.

Effect of rice-bran extract on growth of organisms from several genera. A. J. SALLE and R. W. DUNN (Proc. Soc. Exp. Biol. Med., 1935, **32**, 939—942).—Carbohydrate-fermenting organisms are stimulated by EtOH extract of rice-bran, irrespective of species, whilst non-carbohydrate-fermenting organisms are unaffected. The stimulating agent is therefore related to the carbohydrates, and is probably pantothenic acid (cf. this vol., 408). R. N. C.

Enzyme formation and polysaccharide synthesis by bacteria. E. A. COOPER and J. F. PRESTON (Biochem. J., 1935, **29**, 2267—2277).—Mannose and arabinose inhibit polysaccharide (I) formation from sucrose by *B. mesentericus*, *B. megaterium*, and *Ps. pruni*, and also by *Ac. xylinum* from sorbitol; the action is probably due to a toxic effect on the cell, and not to an interference with enzyme action. Glycerol, mannitol, and sorbitol diminish the di-

astatic power of *B. megaterium*, due probably to a depression in the rate of formation of the enzyme in the cell. *B. megaterium* and *Ac. xylinum* do not synthesise (I) from fatty acids. Peptone is not essential for (I) formation by *B. megaterium*, *Ps. pruni*, and *B. syringae*, and can be replaced by asparagine as sole source of N. Bacteria pathogenic to plants synthesise (I) from sucrose; these are of the fructosan type, and no evidence has been obtained of the formation of dextrans or pentosans. Spore-forming organisms related to *B. mesentericus* also form similar products. J. N. A.

Reducing intensity of luminous bacteria in presence of agents affecting oxidations. I. M. KÖRR (J. Cell. Comp. Physiol., 1935, **6**, 181—216).—The limiting reduction E_h of *Achromobacter fischeri* suspensions in beef-peptone broth at p_H 7.6 and 24—28° is -0.214 ± 0.003 volt. Heat treatment of the cultures lowers respiration without affecting reducing intensity, unless the cultures are injured by high temp. Reducing intensity is not affected by urethanes, except when in sufficient concn. to cause cytolysis. It is unaffected by $P_2O_7^{4-}$, KF, KCN, or $CH_2Cl \cdot CO_2H$, but is lowered by AsO_3^{3-} , $CH_2Br \cdot CO_2H$, and $CH_2I \cdot CO_2H$. Rate of E_h change is slackened by most of these agents. R. N. C.

Survival and rate of death of intestinal bacteria in sea-water. P. J. BEARD and N. F. MEADOWCROFT (Amer. J. Publ. Health, 1935, **25**, 1023—1026).—Data are given for the rates of death of *Eberthella typhosa* and *Escherichia coli* in polluted sea- H_2O . The latter is resistant enough to serve as an indicator of pollution. E. A. H. R.

Chemistry and pharmacology of fermented foodstuffs. IV. W. KEIL and F. PÖRTNER (Biochem. Z., 1935, **280**, 61—64).—The ability to produce acetylcholine (I) appears to be characteristic of the strain of organisms (probably identical with Henneberg's *B. cucumeris fermentati*) which was isolated by the authors from cabbage and cucumber fermentations (this vol., 529). (I) can be isolated in the pure state from maize-sunflower silage. P. W. C.

Voges-Proskauer reaction. S. S. EPSTEIN and M. LEVINE (Proc. Iowa Acad. Sci., 1933, **40**, 80; cf. A., 1934, 698).—Methods of procedure are examined. The creatine-KOH reagent may be stored for 3 weeks at room temp. or 6 weeks in ice. When the reaction with 10% KOH was weak, special reagents were advantageous in accelerating colour production, e.g., creatinine (I), $FeCl_3$, or $Cu-NH_3-NaOH$. Best results were given by (I) in 40% KOH. CH. ABS. (p)

Colloidal culture media for bacteria. N. N. KLODNIZKY (Ann. Inst. Pasteur, 1935, **55**, 486—490).—Anaerobic bacteria can be cultivated in the presence of O_2 if the medium is a colloidal solution. This is achieved by adding 0.1% of agar to a bouillon. Most of the ordinary pathogenic bacteria can also grow in this medium, giving typical cultures often different from those obtained in ordinary bouillon. E. A. H. R.

Culture medium for the production of diphtheria toxin. E. M. TAYLOR (Ann. Inst. Pasteur,

1935, 55, 474—485; see this vol., 1003).—The prep. of a bouillon containing only a peptic digest of pig's stomach and 2% of maltose is described. It is best sterilised by passing through a Seitz filter at 32—33°. The highest yields of toxin are obtained with a surface area of 1.2 sq. cm. per c.c. The CH_2O -detoxicated substance retains its efficiency as an immunising agent.

E. A. H. R.

Modified technique for detection of the *Escherichia-Aerobacter* group in milk. A. MOLDAVAN (Amer. J. Publ. Health, 1935, 25, 1032—1033).—An agar plug is introduced immediately above the inoculated medium. Gross contamination can be detected within 8 hr.

E. A. H. R.

Influence of ultra-violet rays on the physiological activity of *Azotobacter*. III. Effect of ultra-violet and monochromatic rays on pigment production. A. ITANO and A. MATSUURA (J. Agric. Chem. Soc. Tokyo, 1935, 11, 564—573).—A short exposure to ultra-violet light stimulates pigment production, the optimum being 10 min. As in the case of growth, black, red, and green rays have more effect than violet and orange.

P. G. M.

Nitrous products in cultures of *Azotobacter chroococcum* and its relation to other soil micro-organisms. D. M. NOVIGRUDSKI (Microbiol. U.S.S.R., 1933, 2, 237—250; cf. B., 1932, 200).—*B. denitrofluorescens*, *B. mycoides*, and *B. mesentericus* which require fixed N for growth, developed on N-free media if cultivated with *A. chroococcum*. Bacteria for which protein is the only possible source of N (*B. mycoides*, *B. subtilis*) were able to reproduce only on old cultures of *A. chroococcum*. Bacteria capable of utilising protein, NH_2 -acids, or NH_3 grew in both young and old cultures of *A. chroococcum*. Production of NH_3 by this organism in the early stages, and of protein after cessation of N fixation, cannot be demonstrated analytically. The temporary formation of small amounts of these compounds is indicated.

CH. ABS. (p)

Influence of nitrogenous compounds on the respiratory quotient of *Rhizobium*. D. A. ANDERSON and R. H. WALKER (Proc. Iowa Acad. Sci., 1933, 40, 73—74; cf. A., 1933, 638).—The R.Q. of the cultures was influenced by the form in which N was supplied. In glucose-yeast media vals. were always < 1. The O_2 consumption with yeast extract was > that with any other N source. In glucose media free from N the R.Q. = 1; with NaNO_3 supplied, vals. were > 1 and with NH_4Cl , < 1.

CH. ABS. (p)

Acidobacteria in the mouth and their decalcifying action on the teeth. D. ANTONIOTTI (Rev. Odontol., 1932, 22, 217).—Cultures of *B. acidophilus* utilise Ca salts from teeth to neutralise acids produced during growth.

CH. ABS. (p)

Sugar dissimilation by *Shigella paradysenteriae*, var. Sonne. H. REYNOLDS, C. S. MCCLESKEY, and C. H. WERKMAN (Proc. Iowa Acad. Sci., 1933, 40, 81—82).—Changes in sugar consumption, acidity, and population associated with the growth of the acid and alkaline types of the organism are examined, together with the effect of aeration.

CH. ABS. (p)

Micro-organism which decomposes the specific carbohydrate of *Pneumococcus* type VIII. G. M. SICKLES and M. SHAW (Proc. Soc. Exp. Biol. Med., 1935, 32, 857—858).—A variety of *B. palustris* that decomposes the sp. carbohydrate of *Pneumococcus* type VIII has been isolated from uncultivated soil. It does not attack the types I, II, and III carbohydrates. The sol. enzyme is conc. by ultra-filtration and protects mice against heavy doses of the *Pneumococcus*.

R. N. C.

Type II *Pneumococcus* specific precipitate. H. O. CALVERY (Proc. Soc. Exp. Biol. Med., 1935, 32, 1099—1100).—Analytical vals. for two samples of the ppt. are given.

R. N. C.

Decomposition of the group-A substance in horse saliva by a myxobacterium. K. LANDSTEINER and M. W. CHASE (Proc. Soc. Exp. Biol. Med., 1935, 32, 713—714).—The group-A substance is decomposed by Morgan and Thaysen's bacterial-polysaccharide-destroying *Myxococcus* (cf. A., 1933, 1207), but not by other types of organisms, which tends to support the view that it is a carbohydrate.

R. N. C.

Decomposition of the group-A substances. K. LANDSTEINER and M. W. CHASE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1208).—The group-A substance in horse saliva is destroyed by the polysaccharide-fermenting organism, *Saccharobacterium ovale*.

R. N. C.

Properties of viantigen of *Eberthella typhi*. A. FELIX, S. S. BHATNAGAR, and R. M. PITT (Brit. J. Exp. Path., 1934, 15, 346—354).—Detection, and conditions of production, of the viantigen together with its thermal stability are examined. Use of formalised extracts in the prep. of antiserum is recommended.

CH. ABS. (p)

Antigenic differences between related bacterial strains: criticism of the mosaic hypothesis. F. M. BURNET (Brit. J. Exp. Path., 1934, 15, 354—359).—A Flexner dysentery bacillus is composed of immunologically similar antigen mols.

CH. ABS. (p)

Horse-sickness. II. Nature of the immunising agents in formalised virus. G. G. KIND (J. S. African Vet. Med. Assoc., 1934, 5, 25—28).—The anatoxin in a formalised virus from spleen pulp was light-sensitive, and destroyed by $\text{Na}_2\text{C}_2\text{O}_4$ or by media made alkaline with NH_3 . The virus was attenuated by exposure to CH_2O but not by $(\text{CH}_2)_6\text{N}_4$.

CH. ABS. (p)

Nature of ultra-viruses. C. ACQUA (Atti R. Accad. Lincei, 1935, [vi], 24, 593—599).—Filterable viruses are considered to be ultra-viruses with autocatalytic action, and not living organisms.

T. H. P.

Stimulatory action of disinfectants. H. KUHLE (Pharm. Ztg., 1935, 80, 1010—1011).—Inhibition of growth by dil. bactericidal preps. varies with the type of bacteria. With basic Al acetate solution (the antiseptic action of which decreases with age) and a virulent strain of *B. coli*, stimulatory, null, and inhibitory actions are shown by approx. concns. of 0.01—0.05, 0.10, and 0.2—0.5%, respectively. The growth of *Penicillium glaucum* in milk is stimulated by 0.0002% of CH_2O . The stimulation is exempli-

fied by the growth of various moulds on rye bread treated with $C_6H_4Cl \cdot CO_2H - BzOH$. F. O. H.

Comparison of the resistance of bacteria and embryonic tissue to germicidal substances. I. Merthiolate. II. Metaphen. III. Mercurochrome. IV. Hexylresorcinol. A. J. SALLE and A. S. LAZARUS (Proc. Soc. Exp. Biol. Med., 1935, 32, 665—667, 937—938, 1057—1060, 1119—1120).—I. The toxicity index for merthiolate (I) is $>$ for PhOH.

II. The toxicity indices of metaphen (II) and PhOH are of the same order as applied to tissue cultures. (II) has a high PhOH coeff. in respect to its effect on *Staph. aureus*.

III. Mercurochrome has a low PhOH coeff., and a high toxicity index compared with PhOH, and is poorer as a germicide than (I) or (II).

IV. The toxicity index of hexylresorcinol is low and the PhOH coeff. high; it is the most efficient of the germicides tested. R. N. C.

Bactericidal action of ketonurine. A. E. OSTERBERG and H. F. HELMHOLTZ (J. Amer. Med. Assoc., 1934, 102, 1831—1832).—Ketonurine having $p_H > 5.5$ and $< 0.5\%$ of β -hydroxybutyric acid (I) is bactericidal toward urinary strains of *Es. coli*. The p_H is conveniently ascertained by chlorophenol-red paper. A fairly const. ratio (1:5) exists between $COMe_2 + CH_2Ac \cdot CO_2H$ and (I). By use of the nitroprusside test for $COMe_2 + CH_2Ac \cdot CO_2H$, the amount of (I) may be calc. CH. ABS. (p)

Continuous oligodynamic action of elements on bacteria. Y. SEUDERLING (Duodecim., 1933, A, 16, No. 8, 1).—In agar-culture tests with 40 species of bacteria Be and Al proved inactive. The effect of Ag, Cu, and Au decreased in the order named. With Cd and Hg and also with As, Sb, and Bi the inhibitory action decreased with increasing at. wt. Te produced a large effective zone free from bacteria. Co had slightly greater activity than elements of group I. The life of the bacteria was shorter as the effective zone increased and was affected most by Cd, Hg, As, and Sb and least by Au and Bi. CH. ABS. (p)

Action of human blood on the meningococcus. N. SILVERTHORNE and D. T. FRASER (Brit. J. Exp. Path., 1934, 15, 362—366).—Most adult blood samples were bactericidal. Samples from infants were more often non-bactericidal. Cases are recorded of infants with meningitis in which the blood, initially non-bactericidal, became active 2 weeks after administration of serum. CH. ABS. (p)

Unsaturated ethers of pyrogallol.—See this vol., 1362.

Germicidal properties and mercuration of alkylresorcinolcarboxylic acids.—See this vol., 1364.

Sulphide analogues of azo-dyes having bactericidal properties.—See this vol., 1360.

Effect of desiccated thyroid, 2:4-dinitrophenol, and cortical hormone extract on the vitamin-C content of some organs of the guinea-pig fed graded doses of ascorbic acid. J. L. SVIRBELY (J. Biol. Chem., 1935, 111, 147—154).—Cortical hormone extract or 2:4-dinitrophenol (I)

has no influence on the survival period of guinea-pigs on a scorbutic diet. The condition of guinea-pigs on a diet including 0.5% of desiccated thyroid is improved by the addition of large amounts of ascorbic acid (II) (5—10 mg. *per diem*). The (II) content of the organs depends on the amount fed; it is diminished when (I) or desiccated thyroid, which increase the metabolic rate, is given. F. A. A.

Potential action of acetylcholine. H. GREMELS and F. ZINNITZ (Arch. exp. Path. Pharm., 1935, 179, 229—233).—Continuous injection of acetylcholine (I) ($< 0.5 \times 10^{-6}$ g. *per min.*) into cats produces a correspondingly continued depression of blood-pressure, the max. effect being equal to that produced by single dosage. The data indicate a "potential" action similar to that of adrenaline and confirm the hormonal character of (I). F. O. H.

Effect of eserine and acetylcholine on gastrointestinal motility in normal dogs. R. FRANK, L. ZIMMERMAN, and H. NECHELES (Proc. Soc. Exp. Biol. Med., 1935, 32, 686—689).—Eserine combined with small quantities of acetylcholine produces peristalsis in doses in which it is ineffective *per se*. R. N. C.

Action of acetyl- β -methylcholine on ventricular rhythms induced by adrenaline. M. H. NATHANSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1297—1299).—Acetyl- β -methylcholine neutralises the effect of adrenaline on the human ventricle. R. N. C.

Adrenal insufficiency in the marmot and opossum, and theories of cortico-adrenal function. S. W. BRITTON and H. SILVETTE (Science, 1935, 82, 230—232).—After adrenalectomy the serum-Na and -Cl of the marmot and opossum show a definite increase, the NaCl content of the muscles appears to be increased, and the muscle- H_2O % is markedly reduced. The animals die from carbohydrate insufficiency and not from NaCl disturbance. The results oppose the theory that NaCl metabolism is regulated by the adrenal cortex and support the carbohydrate theory of cortico-adrenal function (A., 1934, 1144). L. S. T.

Extracellular and intracellular water loss during suprarenal insufficiency in the dog. G. A. HARROP, W. M. NICHOLSON, J. L. SOFFER, and M. STRAUSS (Proc. Soc. Exp. Biol. Med., 1935, 32, 1312—1315).—Adrenal cortex insufficiency induces a diuresis in which Na and Cl excretion are increased, and involves loss of extracellular H_2O . On administration of cortical hormone (I) there occurs a second diuresis in which K, N, and PO_4 are increased, and intracellular H_2O is lost. The action of (I) is to restore and maintain the correct K and Na concns. and osmotic pressure in the plasma. R. N. C.

Mortality of adrenalectomised young rats, with improved technique of operation, and after a period of treatment with cortical hormone. P. SCHULTZER (J. Physiol., 1935, 84, 70—82).—With the improved technique of operation the mortality rate is 100%. Daily injections of cortical hormone prolong life indefinitely. R. N. C.

Chemical principles of the Viale reaction. M. HESS (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 655—666).—Viale's test is not sp. for adrenaline and cannot serve for its determination in blood or urine. Human blood usually gives a negative reaction. The brownish colour sometimes observed is probably due to tyrosine and tryptophan. A positive reaction in urine is due to phenols (cf. A., 1933, 1210).

CH. ABS. (p)

Influence of the oxidation-reduction system on adrenaline action. II. K. TERAT (Folia Pharmacol. Japon., 1934, 19, 248—258; cf. this vol., 1172).—The effects of adrenaline on the pupil of the frog's eye and on blood pressure and blood-sugar in rabbits are removed by benzoquinone and caused to reappear by quinol.

CH. ABS. (p)

Pharmacodynamics of the autonomic nervous system in schizophrenia. I. **Effect of intravenous injections of adrenaline on blood pressure and pulse rate.** H. FREEMAN and H. T. CARMICHAEL (Arch. Neurol. Psychiatry, 1935, 33, 342—352).

CH. ABS. (p)

Effect of trauma on healthy vigorous dogs with or without adrenal glands. W. W. SWINGLE and W. M. PARKINS (Amer. J. Physiol., 1935, 111, 426—439).—Adrenalectomised dogs develop profound and fatal shock following a degree of trauma < that required for normal dogs. Hence the adrenal of the normal animal contains sufficient reserve cortical hormone (I) to prevent shock following trauma. Injection of (I) in adrenalectomised animals prevents shock following slight trauma, and also rapidly restores animals suffering from shock.

R. N. C.

Histamine content of the lungs. I. SIBUL (Pflüger's Archiv, 1935, 235, 742—755).—Perfusion of the lungs of the cat with histamine-free blood does not result in the appearance of histamine (I) in the perfusate. If (I) is added to the blood *in vitro* the effect on the isolated guinea-pig uterus decreases after some hr. (I) introduced into the lung circulation disappears at the rate of 0.3 mg. in 1½ hr.; it induces contraction of the lung vessels, particularly on the venous side.

R. N. C.

Insulin hypoglycæmia. W. DAMESHEK, A. MYERSON, and C. STEPHENSON (Arch. Neurol. Psychiatry, 1935, 33, 1—18).—Changes in glucose and O₂ in vessels supplying the brain and arm are compared before and after intravenous administration of insulin (I). The glucose taken up by the brain decreased during the hypoglycæmic reaction; that by the arm usually increased. The uptake of O₂ increased with the severity of the (I) reaction, but the lactic acid content decreased. The pressure of the spinal fluid increased early in the reaction, but no sugar appeared in the fluid up to 1.5 hr. Injection of adrenaline immediately after (I) diminished the symptoms.

CH. ABS. (p)

Mechanism of the circulatory changes accompanying insulin hypoglycæmia. A. C. ERNSTENE, J. E. F. RISEMAN, B. STERN, and B. ALEXANDER (Amer. J. Physiol., 1935, 111, 440—445).—The cardiac output in cats with denervated hearts during insulin hypoglycæmia is increased if the adrenals are

intact. O₂ consumption is unchanged. The O₂ content of the arterial and mixed venous blood is increased in normal animals and those with denervated hearts, but is decreased if the adrenals are inactivated. The arterio-venous O₂ difference is unchanged in normal animals, decreases if the heart is denervated, and increases if the adrenals are inactivated.

R. N. C.

Stimulation of adrenal medulla by irradiated insulin. J. M. LUCK and G. M. RICHMOND (Proc. Soc. Exp. Biol. Med., 1935, 32, 1056—1057).—Insulin irradiated with soft X-rays causes a reduction of blood-NH₂-acids in normal, but not in adreno-medullated, rabbits. Hence the irradiation does not destroy the ability of insulin to stimulate the adrenal medulla.

R. N. C.

Effect of insulin on the glycogen content of livers of polyneuritic animals. C. Y. CHEN (Ann. Res. Council. Nat. Univ. Peiping [Rept.], Agric. Sci. Ser., 1934, No. 1, 9 pp.).—Injection of insulin lowers the liver-glycogen in pigeons. Vals. for control birds receiving yeast were the same as for those receiving vitamin-B₁ only.

CH. ABS. (p)

Nature of the action of insulin. V. VENDEG (Pflüger's Archiv, 1935, 235, 674—699).—Insulin (I) accelerates glycogen (II) deposition in the liver of the dog at high blood-glucose (III) vals., and (II) breakdown with normal or low (III). Both effects \propto the quantity of (I) given. The (II) content of the liver also affects the action of (I); (II) deposition is more rapid, or breakdown slower, in a (II)-poor liver. The disappearance of much (III) indicates that (I) also increases (III) oxidation. (I) accelerates (II) deposition in muscle in hypoglycæmia; (II) breakdown in hypoglycæmia is less marked than in liver, deposition occasionally occurring. Glucose infusion in freshly depancreatised animals causes deposition of the same amount of (II) in the liver as in fasting normal animals, if the initial (II) val. is low.

R. N. C.

Action of benzylcarbonyl chloride on insulin and other proteins. W. E. GAUNT, G. HIGGINS, and A. WORMALL (Nature, 1935, 136, 438—439).—CH₂Ph·O·COCl (I) readily inactivates insulin (II), and the loss of hypoglycæmic power by (II) is probably due to the blocking of the free NH₂-groups. (I) also reacts smoothly with native proteins at approx. p_H 8 and 5°, with marked diminution in the free NH₂-N of the protein; in many cases, the product, carbobenzyloxy-protein, contains practically no free NH₂-N. On injection into rabbits, the carbobenzyloxy-derivative of serum-globulin produces antibodies which, from precipitin and inhibition tests, appear to be sp. for the new grouping, the carbobenzyloxy-NH₂-acid group, in the protein.

L. S. T.

Action of the melanophore hormone on pigment migration and pupil width of the frog's eye. A. JORES and K. G. CAESAR (Pflüger's Archiv, 1935, 235, 724—732).—The melanophore hormone is generally ineffective in the frog's eye in the light, but in the dark the pupil pigments are deepened. Hypophysectomy has no effect; the hormone can still be detected in the mid-brain. Irritation of the pituitary darkens the retina pigments. The eye-ball is unaffected; the pupil is widened.

R. N. C.

Mechanism of parathyroid hormone action. J. B. COLLIP, L. I. PUGSLEY, H. SELYE, and D. L. THOMSON (Brit. J. Exp. Path., 1934, 15, 335—336).—The characteristic effect of the parathyroid on the bones of rats cannot be ascribed to an action of the hormone on the renal threshold for PO_4''' . It is doubtful whether ergosterol acts merely by stimulating production of the parathyroid hormone.

CH. ABS. (p)

Influence of parathormone on the neuro-muscular system: an experimental analysis. E. GELLHORN (Amer. J. Physiol., 1935, 111, 466—476).—Perfusion of frog muscle with Ringer's solution containing parathormone (I) increases the height of contraction to a degree \propto the concn. of the (I) solution; the effect is reversible. Inactivation of (I) by boiling with 10% HCl or EtOH destroys the effect. The action of (I) is abolished by curare, Ca-deficiency, and degeneration of the nerve-endings, showing that it acts on the neuro-muscular junction. Sr can partly replace Ca. The effect of Ca on the muscle is increased by subliminal concns. of (I), but this synergism is absent in the heart. (I) does not enhance the decrease in imbibition caused by CaCl_2 .

R. N. C.

Possible inter-relationship between the physiological actions of the parathyroid glands and vitamin-D. J. H. JONES (J. Biol. Chem., 1935, 111, 155—161).—A suitable diet + 0.75% BeCO_3 produces Be-rickets in young pups; this condition is not prevented by ultra-violet irradiation or cod-liver oil. Large doses of parathyroid extract (I) do not raise the serum-Ca, but large doses of irradiated ergosterol (II) produce marked hypercalcaemia and toxic symptoms. Hence the failure of rachitic animals to respond to (I) is not due to lack of vitamin-D, or the toxicity of (II) to stimulation of the parathyroid glands.

F. A. A.

Iodine metabolism and thyroid activity. I. BÓNIS (Orvosi Hetilap, 1935, 79, 99—100).—No consistent relationship was found.

CH. ABS. (p)

Hormonic symptomatology of the thyroid: to what extent is it explicable on the basis of altered metabolic rate? J. H. MEANS and J. LERMAN (Endocrinol., 1935, 19, 181—186).—The symptoms of abnormal thyroidism attributable to change of heat production are connected with sweating, skin temp., and body-wt. The remaining symptoms are due to other physiological actions of thyroxine.

R. N. C.

Proliferative activity of the thyroid gland of the female guinea-pig during the sexual cycle. K. S. CHOUKE, H. FRIEDMAN, and L. LOEB (Anat. Rec., 1935, 63, 131—137).—The mitotic activity of the thyroid is low in the follicular and high in the lutein phase of the cycle.

R. N. C.

Anti-thyrotoxic action of ascorbic acid. V. DEMOLE and F. IPFEN (Z. physiol. Chem., 1935, 235, 226—232).—In guinea-pigs the fatal toxic action of subcutaneously administered thyroxine (I) is counteracted by giving approx. proportionate doses of ascorbic acid (II). The (II) content of the liver and adrenals is greatly reduced by giving (I).

W. McC.

Effect of hypothyroidism on antidiuretic action of pressor principle of posterior pituitary. B.

STERN and D. R. GILLIGAN (Proc. Soc. Exp. Biol. Med., 1935, 32, 843—846).—The antidiuretic effect of pitressin injected subcutaneously is the same in normal and thyroid-deficient patients.

R. N. C.

Relation of blood volume to certain glands of internal secretion. Effect of thyroid and gonad ablation. M. FRIEDLANDER, N. LASKEY, and S. SILBERT (Endocrinol., 1935, 19, 342—346).—Thyroidectomy (cat, man) lowers blood vol. in males, but does not affect either blood vol. or chemistry in females. Blood vol. is reduced by bilateral ovariectomy, but not by orchidectomy.

R. N. C.

Effect of iodine and desiccated thyroid on the anterior pituitary of goitrous and thyroidectomised rabbits. D. MARINE, S. H. ROSEN, and C. SPARK (Proc. Soc. Exp. Biol. Med., 1935, 32, 803—810).—KI restores the hypertrophic pituitary to normal in parenchymatous goitre, but not after thyroidectomy, whereas desiccated thyroid restores it to normal in both cases. Hence I is effective only in the form of thyroxine.

R. N. C.

Cytological responses of rat thyroid to treatment with anterior pituitary and potassium iodide. A. C. HALPERN (Proc. Soc. Exp. Biol. Med., 1935, 32, 854—857).—Anterior pituitary and KI both stimulate mitosis in the rat thyroid. Mitochondria tend to become granular. KI does not affect the Golgi material, but pituitary tends to draw it out of the follicle cells into the intercellular regions.

R. N. C.

Basal metabolism and the thyrotropic hormone of the anterior pituitary. F. ZAJÍC (Pflüger's Archiv, 1935, 235, 575—581).—The thyrotropic hormone influences basal metabolism in the dog exclusively through the thyroid. The presence of thyroid hormone is not sufficient to allow its action to occur. The R.Q. is unaltered; the increases of pulse and temp. and the fall of body-wt. are parallel with the rise of basal metabolism. The absence of the effect in thyroidectomised animals is hence an indication of complete thyroidectomy. (Cf. this vol., 541.)

R. N. C.

Hormone affecting metabolism and substance stimulating insulin production of the anterior pituitary. O. STEPPUHN (Wien. Arch. inn. Med., 1934, 26, 87—100).—The anterior pituitary produces a hormone which very rapidly mobilises depot fat, causes hyperlipaemia and acetonæmia, and reduces liver-glycogen. Associated with the hormone there is a substance which stimulates insulin production and counteracts the effect of the fat-mobilising hormone.

NUTR. ABS. (m)

Action of anterior pituitary extract and its effect on blood-sugar. K. VENKATACHALAM and A. N. RATNAGIRISWARAN (Indian J. Med. Res., 1935, 22, 425—431).—Anterior pituitary extract depresses blood-pressure in cats and raises blood-sugar to nearly double the normal val. This increase is enhanced by atropine or vagal section, both of which also increase blood-pressure *per se*. Blood-sugar is reduced by gonad extract (II), which neutralises the effect of (I), this effect being inhibited by atropine or vagal section. (II) sensitises, and (I) desensitises,

the vagal centre to electric stimulation; the hyperglycæmic action of (I) is the result of this action, which is possibly due to thyroid stimulation.

R. N. C.

Glutathione concentration of livers and muscles of rats following injection of pituitary growth-hormone. H. GOSS and P. W. GREGORY (Proc. Soc. Exp. Biol. Med., 1932, 32, 681—683).—A single injection of growth-hormone (I) in normal or spayed female rats reduces liver- and muscle-glutathione (II) considerably. (II) appears to be raised before or after injection by feeding. A series of 5 daily doses of (I) restores liver-(II) to normal, and increases muscle-(II) to vals. > normal.

R. N. C.

Physiological effects of pituitary growth-hormone: growth and efficiency of food utilisation. H. W. NILSON, L. S. PALMER, and C. KENNEDY (Amer. J. Physiol., 1935, 111, 341—351).—The hormone promotes growth and increases the efficiency of dry matter utilisation, but does not increase the relative H_2O consumption.

R. N. C.

Pituitary hormones and the blood-sugar level. M. C. HRUBETZ (Proc. Soc. Exp. Biol. Med., 1935, 32, 842—843).—Blood-sugar in rats is unaffected by antuitrin-S or -G, theelin, or growth-hormone.

R. N. C.

Chemistry of oxytocin (the oxytocic hormone of the pituitary gland). IV. Action of nitric and nitrous acids and sulphur dioxide: extraction with pyridine, ethyl alcohol, chloroform, and acetone. N. DAS and B. C. GUHA (Indian J. Med. Res., 1935, 22, 517—520).—Oxytocin is inactivated to 50—60% by SO_2 , to 75% by conc. HCl, to 85—90% by HNO_3 in presence of AcOH, and completely by HNO_3 and by HNO_2 in presence of HCl; it is unaffected by AcOH alone. It is not dissolved or inactivated by C_5H_5N , EtOH, $CHCl_3$, or $COMe_2$.

R. N. C.

Oxytocic hormone of the posterior lobe of the pituitary gland. VII. (A) Ultra-violet absorption spectra. J. M. GULLAND and N. S. LUCAS. (B) Adsorption and electrodialysis. M. FREEMAN, J. M. GULLAND, and S. S. RANDALL (Biochem. J., 1935, 29, 2208—2220).—(A) There is no correlation between the curves of ultra-violet absorption and the oxytocic activity of posterior lobe extracts; the curves are markedly similar to those of peptides.

(B) Attempts at concn. of the preps. by a no. of adsorbents at different p_H were unsuccessful. The hormone is inactivated by Ac_2O . Electrodialysis of preps. did not effect concn. or separation of the oxytocic and pressor hormones. At $p_H > 8$ the hormone remained in the centre compartment of the cell, whilst at $p_H < 6$ it migrated to the cathode.

H. D.

Effects of pituitrin, pitressin, and pitocin on the copper-reducing substances in the serum and urine of dogs. A. R. MCINTYRE, R. F. SIEVERS, and H. F. ELIAS (Endocrinol., 1935, 19, 298—304).—Injection of pituitrin, pitressin, or pitocin in dogs fasted for 18 hr. increases the Cu-reducing power of the serum; that of the urine varies, and is not related to that of the serum. There is no pro-

portional variation in the fermentable and non-fermentable Cu-reducing substances of the urine.

R. N. C.

Acquired resistance to the thyroid-stimulating and pseudo-luteinising hormone of cattle anterior pituitary. P. MAX, M. M. SCHMECKEBIER, and L. LOEB (Endocrinol., 1935, 19, 329—341).—Prolonged injections of thyrotropic hormone (I) of the anterior pituitary in guinea-pigs produce stimulation of the thyroid and characteristic ovary changes, followed by retrogression and a return to normal. A second series of injections after a rest produces only a transitory stimulation of the thyroid, and the refractory state develops more rapidly. The effect is considered to be due to formation of neutralising substances, and also to the antagonism between (I) and thyroxine.

R. N. C.

Gonad-stimulating activity of pituitary glands from horses of different ages and sex types. A. A. HELBAUM (Anat. Rec., 1935, 63, 147—157).—The pituitaries of young normal mares and geldings show luteinising activity, those of old mares and geldings and of stallions show follicle-stimulating activity, whilst those of colts and fetuses show both types of activity; those of pregnant mares vary.

R. N. C.

Sex comparison of gonadotropic hormone content of anterior pituitaries from rats before and after puberty. M. McQUEEN-WILLIAMS (Proc. Soc. Exp. Biol. Med., 1935, 32, 1051—1052).—The gonadotropic hormone content of the female pituitary is > that of the male in young animals. Both fall very suddenly as maturity is approached, but whilst the potency of the female pituitary remains low, that of the male attains its former val.

R. N. C.

Anterior pituitary hormone content of the hypothalamus of the dog. G. PIGHINI (Endocrinol., 1935, 19, 293—297).—Female rats injected with emulsion of the tuber cinereum tissue from normal dogs show a definite maturation of the ovaries and uterine hypertrophy, similar to that obtained with anterior pituitary hormone (I). Previous injection of the dogs with (I) does not increase the (I) content of the emulsions.

R. N. C.

Anterior-pituitary-gonadal inter-relations. W. O. NELSON (Endocrinol., 1935, 19, 187—198).—The % of basophiles and acidophiles in the male rat anterior pituitary is > in the female, whilst chromophobes are less. Castration of rats injected with œstrin (I) causes a fall of basophiles. The suppressing influence of the gonads on the gonadotropic activity of the pituitary is due to the action of (I) on the secretory cycle of the anterior lobe basophiles. (I) and prolactin control lactation in guinea-pigs. In monkeys (I) abolishes the hyperglycæmia and glycosuria following pancreatectomy.

R. N. C.

Age factor in responsiveness to gonadotropic hormones. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 800—803).—œstrus does not occur in 12-day-old rats injected with pituitary extract, nor in ovariectomised rats implanted with the ovaries of 12-day-old rats.

R. N. C.

Effect of urine from pregnant women on the ovary-stimulating potency of the pituitaries of rabbits and rats. LE R. GOODMAN (Amer. J. Physiol., 1935, 111, 312—320).—Intravenous injection of Et₂O-extracted urine of pregnancy increases the ovary-stimulating potency of the pituitaries of normal male and female and spayed female rabbits, but reduces or does not alter that of normal male and female and castrated male rats. Subcutaneous injection in spayed female rats, or spaying without injection (rabbit or rat), increases the potency. The potency in normal male rats is > in normal females, but in castrated males is < in castrated females. The action of the pregnancy urine on the pituitary appears to be partly direct and partly indirect through the gonads in rabbits, and wholly indirect in rats.

R. N. C.

Prolongation of pregnancy in the rat by injection of human pregnancy urine extract. E. C. HOOPES and J. L. KING (Amer. J. Physiol., 1935, 111, 507—514).—Injection of 75 units of antuitrin-S delays parturition for 3 days and prolongs it over 2 days. Foetuses remain alive.

R. N. C.

Preoperative administration of an extract of pregnancy urine: a study of the ovaries and of the endometria in hyperplasia of the endometrium following such administrations. E. C. HAMBLEN (Endocrinol., 1935, 19, 169—180).—Anterior-pituitary-like luteinising extract of pregnancy urine, affects mature but not early follicles in women; it increases the degenerative changes commonly observed. Recent corpora lutea are produced in mature women with hyperplasia. Endometrial changes are rare.

R. N. C.

Factors to be considered in immature female rat titration of pregnancy urine. L. DAVY (Proc. Soc. Exp. Biol. Med., 1935, 32, 927—931).—Vaginal opening can be prevented by excess of pregnancy urine, which causes luteinisation, and is only an indication of follicular activity. Increase of ovary wt. does not occur with doses of urine that are too excessive for follicle stimulation and insufficient for luteinisation. The uterine reactions are too variable for incorporation into the criteria of the unit dose.

R. N. C.

Reactivity of the uterus to pre-sacral nerve stimulation and to adrenaline, pituitrin, and pilocarpine administered during certain sexual states in the anaesthetised rabbit. J. J. SAUER, C. E. JETT-JACKSON, and S. R. M. REYNOLDS (Amer. J. Physiol., 1935, 111, 250—256).—The uterus is contracted by pilocarpine only after administration of oestrin, and not after castration or in pseudo-pregnancy. In castrated animals it is contracted by adrenaline or pituitrin, and by pre-sacral nerve excitation if corpora lutea are absent; the inhibitory action of the latter lasts only until the 11th day in pseudo-pregnancy.

R. N. C.

Reactions of anterior pituitaries of male rats to administration of anterior pituitary-like substances and to oestrin. J. M. WOLFE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1305—1309).

R. N. C.

Synergism between oestrin and oxytocin. G. F. MARRIAN and W. H. NEWTON (J. Physiol., 1935, 84, 133—147).—The sensitivity of the mouse uterus to pitocin (I) is increased considerably by 400—500 mouse-units of oestrin, so that 1 unit of (I) causes constriction sufficient to kill or expel the foetus. The effect is the same whether oestrone, oestriol, or the Et₂O-sol. phenol of pregnancy urine is used. The reactivity of the uterus returns to normal 15 hr. after cessation of injections.

R. N. C.

Reaction of anterior pituitaries of mature female rats to injections of large amounts of oestrin. J. M. WOLFE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1192—1195).

R. N. C.

Morphological and quantitative reaction of anterior pituitaries of castrated female rats to oestrin injections. J. M. WOLFE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1189—1191).

R. N. C.

Comparatively low levels of oestrin in cases of chorioepithelioma and hydatidiform mole. G. VAN S. SMITH and O. W. SMITH (Proc. Soc. Exp. Biol. Med., 1935, 32, 847—849).—Oestrin (I) was low and anterior pituitary-like hormone (II) high in several cases of chorioepithelioma or hydatidiform mole. Injection of (I) in one case lowered blood- and urinary (II) without raising (I).

R. N. C.

Effect of oestrin on ovaries and adrenals. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1377—1381).—Oestrone (I) injected into late pregnant rats prolongs the life of the corpora lutea and interferes with parturition. (I) injected during lactation maintains diœstrus, and enlarges the ovaries, pituitary, and adrenals; the no. of corpora lutea is not increased. (I) given to young female rats atrophies the ovaries and does not influence the pituitary or adrenals. The enlargements of the ovaries produced by (I) in adult rats disappear after 3 weeks, and œstrus reappears. (I) does not maintain the corpora lutea in lactating rats after hypophysectomy. (I) and anterior pituitary-like hormone may act synergistically or antagonistically to each other in different circumstances.

R. N. C.

Extraction of oestrin from female urine after acidification with various acids. W. K. CUYLER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1352—1357).—Oestrin can be extracted from urine acidified with AcOH, CCl₃-CO₂H, or (best yield) tartaric acid. Extraction after acidification with H₂SO₄ or HCl gives negative results.

R. N. C.

Effect of oestrin on uterine activity and its relation to experimental abortion and parturition. J. M. ROBSON (J. Physiol., 1935, 84, 121—132).—Injections of ketohydroxyoestrin (I) over a period of < 12 hr. in pregnant and ovariectomised mice increase the reactivity of the uterus to oxytocin, which becomes of the same order as in normal parturition if injections are continued over 2—3 days. Abortion occurs 1—3 days after cessation of injections. (I) injections do not increase the spontaneous rhythmic contractions *in vitro*.

R. N. C.

Action of oestrin on the uterus of hypophysectomised and of pregnant rabbits. J. M.

ROBSON (J. *Physiol.*, 1935, **84**, 148—161).—The response of the uterus to oestrin (I) is not qualitatively affected by the absence of the pituitary. (I) does not increase the reactivity of the uterine muscle to oxytocin during pseudo-pregnancy and all but the later stages of pregnancy, but the progestational response of the endometrium is sometimes affected. In the later stages of pregnancy (I) affects the uterine muscle normally in the absence of corpus luteum secretion. R. N. C.

Movements of the uterus. II. Action of extract of corpus luteum on the uterus of the unanæsthetised rabbit. III. Action of gonadotropic extracts on movements of the uterus in unanæsthetised rabbits. T. N. MORGAN (J. *Obstet. Gynaecol. Brit. Emp.*, 1935, **42**, 79—83, 84—87).—Effects on sexually mature and immature rabbits, castrated and normal, are described. CH. ABS. (p)

Concentration of gonad-stimulating hormone in blood-serum and of oestrin in the urine throughout pregnancy in the mare. H. H. COLE and F. J. SAUNDERS (*Endocrinol.*, 1935, **19**, 199—208).—Gonad-stimulating hormone is produced rapidly in the serum after its first appearance and increases to a max. on the 70th day, afterwards disappearing. The curve of increase is sigmoid, the decrease curve resembling that of a unimol. reaction. Oestrin appears in the urine at the 100th day, and rises to a max. between the 200th and 275th days, afterwards decreasing, and disappearing 1—2 days after parturition. R. N. C.

Follicular apparatus of the ovary of the hypophysectomised immature rat and the effects of hypophyseal gonadotropic hormones on it. C. E. LANE and R. O. GREEP (*Anat. Rec.*, 1935, **63**, 139—146).—The follicle content of the ovary rises to a max. at 4 days after hypophysectomy and then falls steadily. Follicle-stimulating hormone increases total follicles and decreases the vesicular %; luteinising hormone increases the latter and does not affect the former. R. N. C.

Failure of theelin and thyroxine to affect plumage and eye-colour of the blackbird. C. H. DANFORTH and J. B. PRICE (*Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 675—678).—Injection of theelin or thyroxine in male birds does not change the plumage and iris colours to those of the female. R. N. C.

Duration of oestrus in ovariectomised and adrenal-ovariectomised rats before and after theelin. F. E. EMERY and E. L. SCHWABE (*Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 910—913).—Total adrenalectomy does not affect the oestrous cycles occurring after ovariectomy, the min. doses of theelin (I) required, the duration following 1—10 rat-units of (I), or the tendency for oestrus to recur after a positive reaction to (I). R. N. C.

Experiments with theelin and galactin on growth and function of the mammary glands of the monkey. E. ALLEN, W. M. GARDNER, and A. W. DIDDLE (*Endocrinol.*, 1935, **19**, 305—313).—Galactin induces lactation only in mature animals with fully developed mammary glands, whether or not theelin has previously been given. R. N. C.

Gross action of prolactin and follicle-stimulating hormone on the mature ovary and sex accessories of fowl. R. W. BATES, E. L. LAHR, and O. RIDDLE (*Amer. J. Physiol.*, 1935, **111**, 361—368).—Prolactin (I) decreases, and follicle-stimulating hormone increases, the wts. of the mature fowl ovary and sex accessories and the oestrin output. The effects of prolactin and corpus luteum hormone on the ovary resemble that of (I). R. N. C.

Prolactin induces broodiness in fowl. O. RIDDLE, R. W. BATES, and E. L. LAHR (*Amer. J. Physiol.*, 1935, **111**, 352—360).—Injection of prolactin induces full or partial broodiness in hens. Other pituitary hormones, oestrin, and corpus luteum hormone are ineffective. R. N. C.

Maternal behaviour induced in virgin rats by prolactin. O. RIDDLE, E. L. LAHR, and R. W. BATES (*Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 730—734).—Administration of prolactin for 5 days to virgin rats, the ovaries of which have been stimulated by prolactin or follicle-stimulating hormone, induces maternal behaviour. R. N. C.

Experiment to produce lactation in castrate women. A. A. WERNER (*Endocrinol.*, 1935, **19**, 144—150).—Injection of amniotin (I) stimulates and induces development of the breasts. Follutein and corporin combined with (I) increase the effect. Prolactin stimulates the breasts, whether or not (I) has been injected previously, but does not cause lactation; in some cases it produces severe anaphylaxis, suggesting that it is protein in nature. R. N. C.

Sex hormones and related substances. IV. Dehydrogenation of equilin to equilenin. W. DIRSCHERL and F. HANUSCH (*Z. physiol. Chem.*, 1935, **236**, 131—135; cf. this vol., 1242).—At 80° in N₂ equilin (I) in EtOH is converted in 16 hr. into equilenin (*picrate*, m.p. 209° corr.) by a large amount of Pd-black. In (I) the double linking is probably at C7:8 and may move to C8:9 before the dehydrogenation. W. McC.

Effects of water-soluble preparations of androsterone and androsteronediol on castrated rats. V. KORENCHESKY, M. DENNISON, and S. L. SIMPSON (*Biochem. J.*, 1935, **29**, 2131—2142).—Comparison of H₂O-sol. (Li salt of monosuccinic ester) preps. of androsterone (I) and androsteronediol (II) with (oil-sol.) (I) and (II) indicates a general similarity [*i.e.*, characteristic differences in growth of certain genital organs and a markedly greater action with (II) than with (I)]. The rat-units of "comb-growth activity" of H₂O-sol. (I) and (II) are 1.60 and 0.067 mg., respectively, the ratios to the units of (I) and (II) being 1:9 and 1:3, respectively. The ratio of activity of H₂O-sol. (I) to that of H₂O-sol. (II) is approx. 2:1 with capons but approx. 1:24 with rats. Other comparative aspects of the action of (I) and (II) are discussed. F. O. H.

Inability of testicular hormone to masculinise plumage and eye-colour of female Brewer's blackbird. C. H. DANFORTH and J. K. FISHER (*Proc. Soc. Exp. Biol. Med.*, 1935, **32**, 1115—1117).—The hormone is ineffective even in doses 10—12 times

as great in proportion to wt. as that producing marked comb-growth in capons. R. N. C.

Assay of fat-soluble androsteronediol. V. KORENCHESKY and M. DENNISON (Biochem. J., 1935, 29, 2122—2130).—The effect of androsteronediol (I) (this vol., 346) on the growth of genitalia of castrated rats indicates a rat-unit of "comb-growth activity" to be approx. 21 and of "whole male sexual activity" approx. 19×10^{-6} g. (A., 1934, 1269; this vol., 1174). The rat- and capon-unit of (I) are therefore approx. $\frac{1}{8}$ and $\frac{1}{3}$ those of androsterone, respectively. (I) is also characterised by preferential stimulation of some of the organs. F. O. H.

The male sexual hormone and its artificial preparation in the laboratory. L. RUZICKA (Bull. Soc. chim., 1935, [v], 2, 1497—1512).—A lecture.

Quantitative assay for the testicular hormone by the comb-growth reaction. II. T. F. GALLAGHER and F. C. KOCH (J. Pharm. Exp. Ther., 1935, 54, 97—117; cf. A., 1930, 118).—In the assay of testicular hormone by the comb-growth method the response after 5 daily doses is measured and corrections are made for the initial size of the comb and body-wt. All assays are expressed in terms of a standard prep. assayed in parallel with each set of unknowns. The age and previous use in assays of capons are without importance. H. D.

Vitamins. I. Fat-soluble. II. Water-soluble. V. E. LEVINE (J. Chem. Educ., 1935, 12, 357—362, 429—435).—A comprehensive summary. L. S. T.

Human requirements for vitamins. D. B. JONES *et al.* (Amer. Publ. Health Assoc. Year Book, 1934—1935, 69—72).—A review. CH. ABS. (p)

Inter-relationship of vitamins and other dietary constituents. I. Their relation to the production of urinary calculi. H. C. HOV (Chinese J. Physiol., 1935, 9, 299—305).—A high dosage of vitamin-D or protein, or a low dosage of phosphate in a diet deficient in vitamin-A, increases the frequency of production of urinary calculi to 100%. The frequency is much lower when the same diet is used without vitamin-D or with low protein and high starch content. When a high-cereal diet is supplemented with cod-liver oil, calculi are not developed. E. P.

Pro-vitamin-A in the food of whales. J. C. DRUMMOND and R. J. MACWALTER (J. Exp. Biol., 1935, 12, 105—107).—The plankton ("krill") which constitutes the main food of Antarctic whales contains small amounts of carotene and (possibly) still smaller amounts of xanthophyll. The main pigment appears in the acid fraction after saponification, and may be astacene (I). (I), mainly in the form of esters, together with a small amount of another pigment resembling that of salmon-muscle, is present in oil extracted from the faeces of whales.

NUTR. ABS. (m)

Oxygen consumption of rats in A-avitaminosis and when fed with carotene. N. TORNBLOM (Skand. Arch. Physiol., 1935, 71, 200—210).—There is no significant difference between the O_2 consumption of rats developing well-marked symptoms of deficiency on a diet deprived of vitamin-A, and that of rats main-

tained in health on the same diet by the daily addition of 0.01 mg. of carotene. NUTR. ABS. (m)

Absorption and utilisation of carotene and vitamin-A in choledochocolonostomised vitamin-A-deficient rats. J. D. GREAVES and C. L. A. SCHMIDT (Amer. J. Physiol., 1935, 111, 492—501).—Female rats with simple avitaminosis-A respond to oral administration of carotene (I) in 4—6 days. Choledochocolonostomised rats do not respond to oral administration of (I), but response is obtained with subcutaneous injections in certain concns., or oral administration together with deoxycholic or glycodeoxycholic acid, indicating that bile acids act as carotene carriers across the intestinal tract. (I) absorption after daily oral administration in small quantities is not appreciably affected by the fat content of the diet. Orally-fed vitamin-A is absorbed by the rat with internal bile fistula in sufficient amounts to correct the vaginal smear picture. R. N. C.

Utilisation of carotene by jaundiced and phosphorus-treated vitamin-A-deficient rats. J. D. GREAVES and C. L. A. SCHMIDT (Amer. J. Physiol., 1935, 111, 502—506).—Administration of carotene (I) by any route to vitamin-A-deficient icteric rats produces little or no conversion into vitamin-A (II). The ability of the rat to transform (I) into (II) is reduced by treatment with P, but not by C_6H_6 , $CHCl_3$, or CCl_4 . Results indicate that the liver is responsible for the conversion. R. N. C.

Determination of carotene and vitamin-A in blood-serum by the alkali-digestion method. M. VAN EEKELLEN and A. EMMERIE (Acta brev. Neerl. Physiol., 1934, 4, 171—172).—10 ml. of serum are heated with 1 ml. of 60% aq. KOH at 100° for 30 min. After cooling, 5 ml. of EtOH are added and the mixture is shaken with 50 and 25 ml. of Et_2O . The combined Et_2O extracts are washed twice with 10 ml. of H_2O , once with 20 ml. of 3% aq. KOH, and twice with 50 ml. of H_2O , dried and evaporated in a CO_2 atm. The residue is dissolved in light petroleum and the carotene content determined colorimetrically. Vitamin-A is then determined by concentrating the solution to 0.2 ml., adding one drop of Ac_2O and 1—2 ml. of $SbCl_3$ reagent, and matching the blue colour produced. The results agree with those obtained by the van den Bergh technique. NUTR. ABS. (m)

Vitamin-A and carotenoid content of human serum and milk. J. G. MENKEN (Maandschr. Kindergeneesk., 1934, 4, 22).—Colorimetric determinations of vitamin-A and carotene (I) gave results as follows: in 60 better-class persons 3.6 ± 2.4 Lovibond blue units of vitamin-A and 0.0043 ± 0.0023 mg. of (I) (no vitamin-A in 3.3% of cases); in 133 persons of both sexes of the labouring class, 2.1 ± 1.6 units and 0.0029 ± 0.0017 mg. of (I) (no vitamin-A in 14.3%); in 74 mothers (*in partu*) of the labouring class, 1.3 ± 1.2 units and 0.0047 ± 0.0026 mg. of (I) (no vitamin-A in 14.9%); in 76 infants (serum from umbilical cord) 1.3 ± 1.6 units and 0.0008 ± 0.0003 mg. of (I) (no vitamin-A in 48.7%); in 49 samples of human colostrum 6.6 ± 3.4 units and 0.0051 ± 0.0037 mg. of (I) (no vitamin-A in 2%); in 42 patients with eczema, 3.3 ± 1.9 units and 0.0030 ± 0.0018 mg. of (I) (no

vitamin-A in 2.4%); in 89 patients with other diseases, 2.5 ± 2.1 units and 0.0025 ± 0.0017 mg. of (I) (no vitamin-A in 21%). The measurements refer to 10 ml. of serum. NUTR. ABS. (m)

Qualitative blood-cell changes in the rat due to vitamin-A. P. D. CRIMM and D. M. SHORT (Amer. J. Physiol., 1935, 111, 397—405).—Avitaminosis-A results in a neutrophil index lag, inhibition of formation of granulocytic cells, and impairment of the protein-fixing function of the reticulo-endothelial system. All these effects are abolished by halibut-liver oil, which after prolonged administration in conc. form produces leucocytosis with a "left shift" of the Arnath index; blood-cholesterol remains within normal limits, and the cholesterol of the fish oil is not responsible for the above hypervitaminosis effects. Desiccated thyroid fed to vitamin-A-deficient rats hastens the onset of xerophthalmia. The -A content of the liver is correlated with the blood-cell and pathological findings. R. N. C.

Effect of diet on the quantity of vitamin-A and -D occurring in hens' eggs. B. H. THOMAS and F. W. QUACKENBUSH (Iowa Agric. Exp. Sta. Rept., 1933, 27).—The vitamin-A content of eggs was increased by supplementary feeding of cod-liver oil, although the increase was not \propto the additional -A intake. The efficiency of transference of dietary -A to the eggs declined as the -A intake increased. CH. ABS. (p)

Nutritional properties of red palm oil. J. L. ROSEDALE and C. J. OLIVEIRO (Malayan Med. J., 1934, 9, 140—145).—Lard and earlnut, gingelly, and coconut oils contain little or no vitamin-A. Red palm oil (0.05% of the diet being the min. prophylactic dose) and king ray, shark, and carp oils are good sources of the vitamin. Coconut, earlnut, gingelly, red palm, and olive oils contain no vitamin-D, but are activated by direct sunlight, exposure for short periods daily causing complete healing of rickets in rats (red palm oil least effective). Red palm oil, in doses of about 50 mg. daily, is effective in promoting growth and preventing or healing xerophthalmia in rats. Heating at 140—160° for 30 min. leaves a substantial fraction of the activity intact, but higher temp. (220°) causes complete inactivation. NUTR. ABS. (m)

Synthetic vitamin-A-free milk suitable for vitamin-A studies in very young puppies. W. O. FROHRING (Proc. Soc. Exp. Biol. Med., 1935, 32, 1021—1024).—The composition is given of a synthetic milk that resembles bitch's milk, but is free from vitamin-A. It can also serve for studying vitamin-B₁, -B₂, and -D. R. N. C.

Spectrographic study of the vitamin-A content of some oils and fats. N. K. DE (Indian J. Med. Res., 1935, 22, 509—516).—Vitamin-A (I) vals. are given for a no. of fats and oils. Vegetable oils contain insufficient (I) to allow spectrographic detection. EtOH washing is suitable for fish oils, but useless for milk fats. R. N. C.

Vitamin-A values of Indian fish-liver oils determined biologically and tintometrically.

A. R. GHOSH and B. C. GUHA (Indian J. Med. Res., 1935, 22, 521—528).—The biological and tintometric vitamin-A vals. of a no. of Indian fish-liver oils do not agree strictly. The biological activity depends on the diluent used, solutions in EtOH, EtOAc, CHCl₃, and arachis oil showing progressively decreasing activities. R. N. C.

"Lovibond unit" of vitamin-A. M. VAN EEKELEN, A. EMMERIE, and L. K. WOLFF (Acta brev. Neerl. Physiol., 1934, 4, 172—175).—The "units" used to express results of vitamin-A determinations by the SbCl₃ method have been converted into international units as follows: 1 cod-liver oil unit (Rosenheim and Webster)=208, 1 blue val. (Drummond and Hilditch)=20.8, 1 Lovibond unit (Wolff)=4.2, and 1 blue unit (Moore)=0.39. NUTR. ABS. (m)

Differential reactions between carotene and oils rich in vitamin-A. V. E. LEVINE and G. E. BIEN (Proc. Soc. Exp. Biol. Med., 1935, 32, 873—876).—Carotene (I) and oils containing vitamin-A (II) give blue colours with SbCl₃, CCl₃·CO₂H (III), and CCl₃·CHO·H₂O (IV), which in the case of (II) oils change to purple on heating; cod-liver oil and butterfat yield the purple colour immediately with (III) or (IV). CH₂O-H₂SO₄ reagent (V) gives a purple colour with (I), whilst with (II) the acid layer is coloured red and the CHCl₃ layer green. (III), (IV), and (V) can be used to distinguish between (I), (II), and sterols; (III) and (IV) also distinguish between cholesterol and ergosterol. R. N. C.

Reaction to differentiate vitamin-A from carotene by means of antimony trichloride. A. C. ANDERSEN and V. E. LEVINE (Proc. Soc. Exp. Biol. Med., 1935, 32, 737—741).—The blue colour of vitamin-A (I) with SbCl₃ is changed on heating to 60° to red, the depth of which \propto the concn. of (I), whereas with carotene the blue is unchanged. Pyrocatechol inhibits the formation of the colours. R. N. C.

Colour reaction of vitamin-A. E. ROSENTHAL and J. ERDELYI (Biochem. J., 1935, 29, 2112—2113).—A reply to Andersen and Levine (see above). Guaiacol (I) ensures the production of a stable and suitable colour in the SbCl₃ test for vitamin-A (this vol., 792), but not in that for carotene. Whilst (I) can be replaced by heating for qual. differentiation, (I) is essential for exact determinations. F. O. H.

Detection of vitamin-A by means of the magneto-optic apparatus. G. M. WISSINK and J. W. WOODROW (Physical Rev., 1934, [ii], 45, 126).—Using a modified Allison apparatus, a characteristic min. has been found for all substances investigated which contained vitamin-A. This min. was not obtained with strongly-irradiated cod-liver oil, pure carotene, peanut and Wesson oils. L. S. T.

Crystalline vitamin-B₁.—See this vol., 1385.

Oryzanin: vitamin-B₁. V. Activity of oryzanin hydrochloride. S. OHDAKE and T. YAMAGISHI (Bull. Agric. Chem. Soc. Japan, 1935, 2, 111—119).—By curative tests on polyneuritic pigeons, 0.0015 mg. of cryst. oryzanin hydrochloride (vitamin-B₁) is equiv. to the standard unit. A. L.

Treatment of human beri-beri with crystalline vitamin-B₁. A. J. HERMANO and F. EUBANAS (Philippine J. Sci., 1935, 57, 277—287).—A report of the successful treatment of a no. of cases.

P. G. M.

Functional studies of the nervous system in experimental beri-beri. C. F. CHURCH (Amer. J. Physiol., 1935, 111, 660—679).—The characteristic neurological symptoms resulting from vitamin-B₁ deficiency are described.

R. N. C.

Properties of blue fluorescent substances formed by oxidation of vitamin-B₁ (quinochromes). H. W. KINNERSLEY, J. R. O'BRIEN, and R. A. PETERS (Biochem. J., 1935, 29, 2369—2384).—At room temp. oxidation of vitamin-B₁ (I) by KMnO₄ or MnO₂ in EtOH produces a strongly fluorescent solution. By comparing the catatorulin activity of these solutions (yielding only non-cryst. oils) with their colour reactions, it is concluded that the blue fluorescent substance is biologically active. The S is removed from (I) as H₂S by a treatment with hot alkali which leaves the N intact. (I) reacts very slowly if at all with HNO₂. The fluorescent compound is probably not identical with thiochrome.

W. O. K.

Vitamin-B₂ requirements of the chick. S. LEPKOVSKY and T. H. JUKES (J. Biol. Chem., 1935, 111, 119—131).—The findings of Elvehjem and Koehn (this vol., 669) that a factor, essential for the normal growth of chicks, not present in the heated diets used, is present in aq. liver extracts are confirmed. This factor is distinct from vitamin-B₂ and, unlike it, is not adsorbed from aq. liver extracts by fuller's earth.

F. A. A.

Structure and synthetic production of vitamin-C. J. DI GLERIA (Kislerlet. Kozl., 1934, 37, 267—269).—Natural and synthetic samples of ascorbic acid showed the same oxidation-reduction potential.

CH. ABS. (p)

Behaviour of l-ascorbic acid and chemically related compounds in the animal body. Influence of generalised ether anaesthesia on their urinary excretion. S. S. ZILVA (Biochem. J., 1935, 29, 2366—2368; cf. this vol., 1036).—The excretion of antiscorbutic compounds by the kidneys is increased by Et₂O anaesthesia; this difference increases with the antiscorbutic activity of the compound used. Anaesthesia does not influence the fixation of the vitamin in the tissues.

H. D.

Effect of ascorbic acid on the work of the isolated surviving frog's heart. L. BILLING (Pflüger's Archiv, 1935, 235, 791—794).—The energy of the action of the surviving heart in serum salt solution is increased by ascorbic acid (I) in concn. 1 in 10⁶. The action is enhanced by lactic acid. With (I) concns. of 1 in 10⁵ arrhythmia occurs.

R. N. C.

Insusceptibility of the rat to a dietary deficiency of vitamin-C. C. T. SUDEN and O. E. MALLEY (Proc. Soc. Exp. Biol. Med., 1935, 32, 753—754).—A diet of bread and boiled whole milk, scorbutogenic to guinea-pigs, was without effect on rats up to 3 generations.

R. N. C.

Inactivation of diphtheria toxin *in vivo* and *in vitro* by crystalline vitamin-C (ascorbic acid). C. W. JUNGBLUT and R. L. ZWEMER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1229—1234).—Vitamin-C (I) in quantities of 0.5—5 mg. inactivates diphtheria toxin (II) *in vitro*: larger quantities are ineffective. (I) also inactivates (II) in guinea-pigs, but the effect is not so precise. Guinea-pigs with large quantities of (I) stored in their organs show a negative or reduced sensitivity to (II).

R. N. C.

Vitamin-C and diphtheria toxin. C. K. GREENWALD and E. HARDE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1157—1160).—Vitamin-C (I) under certain conditions increases the resistance of guinea-pigs to diphtheria toxin (II). The toxicity of (II) solutions is decreased by contact for 1 hr. at room temp. with (I); guinea-pigs that survive injections of the mixture are not immunised. (I) does not destroy the antitoxic properties of diphtheria antitoxin (III), or the slightly toxic (II)-(III) mixture.

R. N. C.

Vitamin-C. VII. Germination of seeds. vi. Effect of light on its production during germination. VIII. Chemical nature. i. Separation from cabbage juice. IX. ii. Vitamin-C and ether. X. iii. Narcotine and vitamin-C. XI. Physiological studies. i. Antiscorbutic value and method of administering. XII. Chemical nature. iv. Vitamin-C in the liver and adrenal of cattle. XIII. v. Extraction and solvents. XIV. vi. Extraction of vitamin-C and *p_H* value of the solution. XV. Physiological studies. ii. Antiscorbutic value and administration. XVI. Enzyme and vitamin-C. i. XVII. Chemical nature. vii. Change of content in barley. T. MATSUOKA (Mem. Coll. Agric. Kyoto, 1935, No. 35, 1—10, 11—23, 25—30, 31—38, 39—47, 49—56, 57—64, 65—70, 71—80, 81—92, 93—108).—VII. Formation of vitamin-C occurs during germination of rice in the dark, but is considerably increased by sun- or artificial light.

VIII. 1.5 g. of raw cabbage or 1.5 c.c. of juice per 100 g. body-wt. is required to protect guinea-pigs from scurvy. By fractionation with EtOH and Pb(OAc)₂, a substance was obtained which protects in a dose of 4 mg. per 500 g. body-wt.

IX. At *p_H* 4, vitamin-C is not extracted with Et₂O, whereas at *p_H* 7—8 approx. 40% is sol.

X. Methylnarcotine does not prevent scurvy in guinea-pigs.

XI. More vitamin-C is required to cure scurvy than to prevent it. The dose may be administered daily, but at 5-day intervals it is not effective.

XII. Crude ascorbic acid has been prepared from ox adrenal by extraction with EtOH-COME₂, MeOH, and Et₂O.

XIII. Vitamin-C is sol. in EtOH, COME₂, wet Et₂O, and wet light petroleum.

XIV. The extraction of vitamin-C by EtOH or COME₂ does not depend on the *p_H*. Destruction during concn. is more rapid in alkaline solution.

XV. In feeding tests the addition should take place on about the 22nd day of feeding with the basal ration; otherwise the scurvy will be too severe.

Animals which have received abundant vitamin-C before the test require a larger quantity in the test.

XVI. Orange juice increases diastatic and decreases peptic action, but does not affect that of pancreatic lipase.

XVII. Vitamin-C is produced by barley, even in the dark, after germination, and reaches a max. at blooming, after which it decreases. Vitamin-C has no auxin-like action on germinated oats.

H. G. R.

Ascorbic acid (vitamin-C) and the germination and growth of seedlings. L. HAVAS (Nature, 1935, 136, 435).—Vitamin-C (I) in concns. of 1–5 parts in 10^4 accelerates the growth and increases the length of wheat seedlings grown under sterile conditions in absence of added nutrients. Compared with controls the wt. of the shoots increased by 25–30% and those of the roots up to 50%. Germination is not stimulated. A concn. of 25 parts in 10^4 has a slight inhibitory effect on germination and a marked one (24–45%) on growth and wt. of the seedlings. A concn. of 50 parts in 10^4 is practically lethal. Oat seedlings are less sensitive than wheat in both respects, but plants with a high natural content of (I) are more sensitive.

L. S. T.

Vitamin-C of Chinese oranges. H. C. HOU (Chinese J. Physiol., 1935, 9, 223–243).—Canton oranges have a slightly higher, Swatow a slightly lower, antiscorbutic activity than Sunkist, whilst Wenchow oranges are definitely inferior. Chemical determination of ascorbic acid gave similar results.

E. P.

Vitamin-C content of Chinese amaranth (Hsien ts'ai). H. C. HOU (Chinese J. Physiol., 1935, 9, 253–260).—Red amaranth (*Amaranthus gangeticus*) has the same antiscorbutic activity as Sunkist orange juice; green amaranth (*A. blitum*) has slightly > double. For the green amaranth the graph of protection from scurvy (guinea-pigs) is not a straight line. Complete protection requires > 3 g. According to chemical titration green amaranth contains 4 times as much ascorbic acid as the red.

E. P.

Differences in values of vitamin-C by chemical and biological methods. H. C. HOU (Chinese J. Physiol., 1935, 9, 291–298).—Vitamin-C contents obtained by Key and Elphick's modification of Hojer's method agree with those found by chemical methods in case of oranges, but give lower vals. with vegetables (lucerne, beet leaves, beetroot, green and red amaranth, and fresh *Capsicum*). The possible presence of interfering substances in the titration and those in biological absorption are discussed.

E. P.

Determination of vitamin-C. V. A. DEVJATNIN and V. M. DOROSHENKO (Biochem. Z., 1935, 280, 118–125).—A no. of substances which possess no antiscorbutic activity reduce 2:6-dichlorophenol-indophenol and so cause high results for the vitamin-C content as determined by the Tillmans method. A modification which is designed to avoid such errors is described.

P. W. C.

Determination of ascorbic acid in urine with phospho-18-tungstic acid. G. MEDES (Biochem. J., 1935, 29, 2251–2255).—Urine is treated with CH_2O and Folin's uric acid reagent and after 20 min.

the colour is compared with known ascorbic acid (I) standards. Phenols and S compounds do not interfere, and the method, which is simple and rapid, gives results within 8% of those obtained with dichlorophenol-indophenol. HgCl_2 and NaHSO_3 may be used in place of CH_2O . If urine be acidified with AcOH and saturated with H_2S , the (I) remains unchanged for < 24 hr.

J. N. A.

Identity of natural vitamin-D from different species of animals. O. RYGH (Nature, 1935, 136, 552–553).—No difference in the antirachitic effect in chicks of vitamin-D (I) obtained from the liver and body fats of a woman, a cow, and numerous species of fish could be detected (cf. this vol., 417). No prep. showed an absorption max. at 260–270 μ , or rotation in EtOH. Esterification with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and $\text{C}_5\text{H}_5\text{N}$ after 10 days was 100%. Maleic anhydride was without effect on the (I).

L. S. T.

Non-identity of vitamin-D, (irradiated ergosterol, calciferol) and the natural vitamin-D from cod-liver oil. O. RYGH (Nature, 1935, 136, 396–397).—The ultra-violet absorption, α , and certain chemical reactions of irradiated ergosterol differ from those of vitamin-D from cod- and tunny-liver oils.

L. S. T.

Supposed identity of artificial antirachitic vitamin (irradiated ergosterol) and the natural vitamin-D of cod-liver oil. M. J. L. DOLS (Diss., Nijmegen, 1935, 139 pp.).—Chickens were protected from rickets by 2% of cod-liver oil in the ration, but not by irradiated ergosterol (I) equiv. to 20% of cod-liver oil, as determined on rats. The unsaponifiable fraction of cod-liver oil was as effective for chicks as the corresponding amount of whole oil. The val. of irradiated (I) for chicks was not enhanced by dissolving it in the saponifiable fraction of cod-liver oil. A tunny-liver oil concentrate was nearly as effective as cryst. calciferol (II) for rats, and as effective, in rat dosage, as cod-liver oil for chicks; it follows that the material having antirachitic potency in the tunny concentrate like that in cod-liver oil is not (II). Irradiated cholesterol (III) in rat dosage was as effective for chicks as cod-liver oil, whence the material activated was probably not (I). 250 international units per 100 g. of ration, in the form of cod-liver oil, tunny-liver oil concentrate, or irradiated (III), sufficed for chicks, whilst 2500 as (II) were insufficient.

NUTR. ABS. (m)

Treatment of low-calcium tetany with calciferol. R. S. STACEY (Lancet, 1935, 229, 656–658).—Administration of large amounts of calciferol maintains freedom from symptoms with normal blood findings. Possible toxic effects are discussed.

L. S. T.

Vitamin-D in the nutrition of calves. O. J. HILL (Proc. 20th Ann. Meet. West. Div. Amer. Dairy Sci. Assoc., 1934, 60–63).—Calves receiving a basal ration without vitamin-D showed lower bone-ash and blood-inorg. P than those directly irradiated or receiving irradiated food or cod-liver oil. Sun-cured lucerne and viosterol induced proper calcification. Direct irradiation prevented further development of rickets.

CH. ABS. (p)

Influence of diet on antirachitic potency of cow's milk. B. H. THOMAS and C. Y. CANNON (Iowa Agric. Exp. Sta. Rept., 1933, 26—27).—Feeding of irradiated moulds increased the vitamin-*D* potency of butter fat after 3 days and continued to do so throughout the experimental period (30 days).

CH. ABS. (p)

Depression of intestinal reduction by vitamin-D. L. YODER (Iowa Agric. Exp. Sta. Rept., 1933, 28).—Viosterol in < the min. effective dose caused a decline in faecal reduced Fe. This may be related to the observation that in rats receiving vitamin-*D*, food passed the intestines in approx. 70% of the time necessary in the case of control animals.

CH. ABS. (p)

Influence of the calcium and phosphorus contents of the diet on the vitamin-D requirements. A. QUERIDO (Acta brev. Neerl. Physiol., 1935, 5, 9—11).—The development of rickets in rats, on a diet with Ca : P ratio of 1 and P content 0.12%, could not be completely prevented by administration of ≥ 0.005 mg. of calciferol (I) daily. On a diet with Ca : P ratio 4 and the same P content, 0.0006 mg. of (I) was an adequate prophylactic dose. The rats did not develop rickets when the Ca : P ratio was 1 and the P content 0.35%. Mild rickets developed with this amount of P and Ca : P ratio 4, but was readily preventable by minute doses of vitamin-*D*.

NUTR. ABS. (m)

Properties of vitamin-E concentrates. H. S. OLCOTT (Proc. Iowa Acad. Sci., 1933, 40, 110).—Preps. from lettuce and wheat-germ oil are obtained by fractional crystallisation of unsaponifiable lipins. Further conc. fractions are separated by fractional distillation in vac., the most active being that having b.p. 190—220°/0.1 mm. The product is resin-like and does not crystallise. The vitamin is not destroyed by acetylation, benzoylation, or mild hydrogenation, but is decomposed by Br.

CH. ABS. (p)

Follicular hormone and the time of blooming of hyacinths. R. HARDER and I. STORMER (Biochem. Z., 1935, 280, 126—136).—The length of leaf and height of bloom were somewhat increased by administration of progynon, but the no. of blooms was not increased.

P. W. C.

Follicular (œstrus) hormone and plant tumours. L. HAVAS (Nature, 1935, 136, 516).—The effect of injecting aq. solutions of cryst. œstrus hormones (I) (from urine of pregnant mares) on the characteristic tumours produced in tomato plants by *Bacillus tumefaciens* has been investigated. The tumours above the site of injection of (I) (the petiole) increase while those below decrease in size. It is uncertain whether the direction of (I) migration is const.

L. S. T.

Accumulation of ions: relations between protoplasm and sap in *Valonia*. S. C. BROOKS (J. Cell. Comp. Physiol., 1935, 6, 169—170).—Protoplasm of coenocytes of *V. ventricosa*, Agardh, in sea- H_2O containing RbCl takes up Rb at the mean rate of 10^{-6} mol. per sq. cm. per hr., and allows it to diffuse into the vacuole at 9×10^{-8} mol. per sq. cm. per hr. The Rb accumulation ratio reaches a max. at the second day, after which the proto-

plasm loses Rb to the sap and the external solution, in both of which [Rb] increases. The accumulation ratio for the protoplasm cannot clearly be deduced, since the exact vol. of the protoplasm is not clear; the solubility limit of RbCl is probably approached.

R. N. C.

Effect of the performance of physical work on mimosa. W. E. BURGE and G. C. WICKWIRE (Science, 1935, 82, 304—305).—The effect is to increase the capacity of the leaves of the plant to do work and to support fatigue.

L. S. T.

Flow and coagulation of latex in *Scorzonera Tau-Sagiz*. N. N. KISELEV and K. A. KUZMINA (Bull. Acad. Sci. U.R.S.S., 1935, 397—412).

Effect of nutritive state on the quantity of vitamin-A present in the leaves of *Coleus blumei*. E. S. HABER and P. P. SWANSON (J. Agric. Res., 1935, 51, 75—81).—Well-nourished plants produced more vitamin-A than did poor stunted plants. When differentiated growth was induced in a single plant, undeveloped branches and luxuriantly growing ones contained similar amounts of -A. Possible relationships between nutrient factors and -A synthesis are discussed.

A. G. P.

Effects of zinc salts on the oxidation process in plant cells. H. S. REED and J. DUFRENOY (Science, 1935, 82, 249—250).—A summary.

L. S. T.

Plant growth substances. XV, XVI.—See this vol., 1351.

Origin, formation, and chemical processing of amber. C. PLONAIT (Angew. Chem., 1935, 48, 605—607; cf. B., 1935, 465).—A lecture. Data are tabulated for the appearance, hardness, d , m.p., and C, H, S, EtOH-sol., and succinic acid contents of 5 types of Baltic ambers.

S. M.

Variations in the mineral and organic substances of *Nicotiana tabacum* during development. I. VLADISCU (Bull. Cult. Ferment. Tutunului, 1934, 23, 231—287, 359—437).—Variations in plant composition can be expressed satisfactorily only in terms of amounts per plant. Results calc. per unit dry matter are misleading, since a no. of constituents are changing simultaneously. Changes in mineral content are determined during the first 30 days after germination. During this period nicotine synthesis proceeds relatively more rapidly than that of protein.

From the age of 30 days until maturity the total dry matter, N, P, Ca, Mg, and K per plant increase to a max. at flowering, subsequently declining until lateral buds develop, when a further increase to a second, and higher, max. occurs. Si, Fe, and Mn increase steadily with the age of the plant, probably accumulating in insol. forms. Nicotine formation increases with primary and secondary growth, declining between flowering and later development. Addition of Mn to soil retards flowering and the associated condition of max. accumulation of org. and inorg. constituents.

CH. ABS. (p)

Seasonal changes of reducing and non-reducing sugars in the upper and under parts of

citrus fruits. K. TAKATA (J. Agric. Chem. Soc. Japan, 1934, 10, 1069—1076).—At all stages of ripening the upper halves of fruit contained more reducing sugars than lower halves. In upper halves vals. increased in winter. Seasonal changes in reducing and non-reducing sugars were approx. parallel.

CH. ABS. (p)

Constituent of *Baomyces roseus*, Pers. G. KOLLER and W. MAASS (Monatsh., 1935, 66, 57—63).—Extraction with Et₂O of soil on which this lichen is growing yields *baomycesic acid*, C₁₉H₁₈O₈ (anilide, decomp. 210°), which is probably 4-6'-hydroxy-5'-aldehydo-4'-methoxy-*o*-toluoyl-2-hydroxy-3:6-dimethylbenzoic acid, since it gives, with AcOH, atranol Me ether, and, with MeOH, the *Me ether*, m.p. 88—90°, of Me hæmatommate, β -orcinol being also formed in each case.

E. W. W.

Chemistry of higher fungi. XXIII. *Geaster fimbriatus*, Fr., and *Polystictus velutinus*, Pers. O. RUTINER and J. ZELLNER (Monatsh., 1935, 66, 76—80).—*G. fimbriatus* contains an ergosterol-fungisterol mixture, fatty acids, mannitol, urea, polysaccharides, and a pigment. The EtOH extract of *P. velutinus*, when fractionated, yields substances, m.p. 98° and 130°, resembling the cerebrin-like substances obtained from *Amanita muscaria* etc. (cf. A., 1923, i, 987); ergosterol; myeose; and a residue extracted with light petroleum and with Et₂O. The former extract contains oleic acid and other fatty acids; the latter, substances resembling tannins. Glucose, choline, and a polysaccharide are present in the aq. extract.

E. W. W.

Chemistry of lichens. IV. *Gyrophora Dillenii* (Tuck.), Mull. Arg., and *Parmelia furfuracea*, L. J. ZELLNER (Monatsh., 1935, 66, 81—86).—*G. Dillenii* contains ergosterol, carotenoid compounds, and fatty acids; a mixture of lichen acids probably containing gyrophoric and lecanoric acids; mannitol, glucose, a polysaccharide, basic substances, lichenin, and a pigment. *P. furfuracea* contains an ergosterol-fungisterol mixture; fatty acids; atranorin; a substance, m.p. 185°, resembling hypogymnol (cf. A., 1934, 570); physodic acid; dark resinous substances; erythritol; and lichenin.

E. W. W.

Chemical examination of *Cuscuta reflexa*, Roxb. I. Constituents. R. R. AGARWAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 384—388).—From the boiling EtOH extract of air-dried *C. reflexa* (contains 9.85% of ash of which 80.88% is H₂O sol.: Na, K, Mg, Ca, NO₃', PO₄''', CO₃'', and SiO₂ present) is isolated (in addition to a wax substance, m.p. 74°) the Δ^2 -lactone, *cuscutalin*, C₁₈H₁₀O₄, m.p. 68° (no CO; reduces Tollens' reagent). After successive extraction of the conc. mother-liquor with C₆H₆ and EtOAc, H₂O extracts *cuscutin*, C₁₅H₁₀O₆, softens 179, m.p. 208—209 (decomp.) (0.2% yield) [Ac₂, m.p. 140°, (CO₂Et)₂, m.p. 151° (decomp.)], and (OMe)₂, m.p. 193°, derivatives; Pb salt], which is acidic.

J. W. B.

Chestnut. E. D. KHARYUZOVA (Bull. Appl. Bot. Genetics, 1934, Ser. 8, No. 3, 3—112).—Biochemical and analytical data are given.

CH. ABS. (p)

Quince. R. Y. KORDON (Bull. Appl. Bot. Genetics, 1934, Ser. 8, No. 3, 3—112).—Analyses are recorded.

CH. ABS. (p)

Composition of raspberries. T. MACARA (Analyst, 1935, 60, 592—595).—The composition of raspberries grown in Cambridgeshire is compared with that of similar fruit grown in Scotland. The influence of climate is apparent only in respect of sol. solids, which were 10.9—12.2 and 6.5—9.2%, respectively. The amount of insol. matter depends on the variety of fruit, the type of soil, and the length of time the fruit is on the cane.

E. C. S.

***Fomes pomaceus* (Pers.), Big and Guill, infecting plum trees.** E. FISHER (Trans. Brit. Mycol. Soc., 1935, 19, 102—113).—In healthy plum wood, cells of the tracheæ have uniform composition, but in the fibres lignin is more conc. near the middle lamella where it is accompanied by certain aldehydes. The remainder of the fibre wall has a relatively higher cellulose content and, usually, no aldehydes. Medullary ray cells are similarly formed. Gum formation characteristic of the early stages of decay is associated with the removal of starch from the ray cells. The characteristic of the "white rot" stage is not a delignification of wood elements but a removal of the lining layer from the walls of wood fibres.

CH. ABS. (p)

Biology of *Fomes pini* (Thone), Lloyd (*Trametes pini* [Thone], Fries). W. C. PERCIVAL (Bull. N.Y. State Coll. Forestry [Tech. Publ. No. 40], 1933, 6, No. 1, b, 72 pp.).—Germination of basidiospores was favoured by a high sugar content in the substrate and by p_H 5.0—6.0. Optimum production of mycelium occurred at 25° in a high-sugar medium, and was not greatly affected by p_H in the range 3.85—7.90. Exposure to light through glass caused darkening of mycelium, which was intensified by direct sunlight.

CH. ABS. (p)

Pollen of some Leguminosæ. J. N. MARTIN (Proc. Iowa Acad. Sci., 1933, 40, 86—87).—The occurrence of starch, sugars, dextrin, proteins, and fats in pollen of 30 species is examined.

CH. ABS. (p)

Constituents of the stems of *Leucothoe Grayana*, Max. M. YAMASHITA (Sci. Rep. Tohoku, 1935, 24, 197—201).—The stems of *L. Grayana*, gathered in October, contained grayanotoxin (I), sucrose (2.5%), and an amorphous substance (II), m.p. 246—248°, whereas those gathered in June contained only (II) and a smaller amount of (I).

R. S. C.

Bitter principles of the columba root. Columbin. F. WESSELY, K. DINJASKI, W. ISEMANN, and G. SINGER (Monatsh., 1935, 66, 87—110).—Columbin as extracted from the root (*Jatrorrhiza palmata*, Miers) has $[\alpha]_D +34^\circ$ to $+42^\circ$, and is not readily purified. It forms an Ac derivative, m.p. 230° (decomp.), $[\alpha]_D +20^\circ$ to $+22^\circ$ (all rotations are in C₅H₅N). When heated at 200—210° in N₂, the product is *decarboxycolumbin*, C₁₉H₂₂O₄, m.p. 149°. This is converted by alkali into *decarboxyisocolumbin*, C₁₉H₂₂O₄, m.p. 210°, also obtained by the action of alkali on *decarboxy-acetylcolumbin*, m.p. 169.5°, $[\alpha]_D -326^\circ$, or by heating *isocolumbin*, C₂₀H₂₂O₆, m.p. 190° (decomp.), $[\alpha]_D$

+68° to +79°. The last is the product obtained by treating columbin with alkali; when acetylated it forms acetylcolumbin. The formula of columbin is established as $C_{20}H_{22}O_6$. The mol. contains a lactone group (possibly two); there is no evidence of CO or alkoxyl groups; hydrogenation leads to acid substances, but gives no definite indication of unsaturation.

E. W. W.

Roots of *Aristolochia indica*, Linn. I. P. R. KRISHNASWAMY, B. L. MANJUNATH, and S. V. RAO. II. Essential oil. U. S. K. RAO, B. L. MANJUNATH, and K. N. MENON (J. Indian Chem. Soc., 1935, 66, 476–485, 494–498).—I. The following substances have been isolated from the crushed roots: an essential oil (I) slightly volatile in steam; the glycerides of stearic, lignoceric, cerotic, oleic, and linoleic acids; sitosterol; a glucoside, m.p. 285–290° (*Ac* derivative, m.p. 162–163°), of a phytosterol, m.p. 146°; an alkaloid aristolochine, m.p. 215° (cryst. from MeOH) or m.p. 158–159° (decomp.) (from PhMe; this probably is a mol. compound containing PhMe) [hydrochloride, m.p. 268° (decomp.)] (cf. Wehmer, "Die Pflanzenstoffe," 1931, Vol. I, p. 263; Hesse, A., 1896, i, 180); allantoin; glucose and unidentified hydrolysable sugars; ceryl alcohol; and isoaristolochic acid (II), $C_{17}H_{11}O_7N$, m.p. 275° (decomp.) (*Na* salt + H_2O ; *Bz* derivative, m.p. 170–171°), isomeric with aristolochic acid (cf. Wehmer, *loc. cit.*). (II) contains 1 active H (Zerevitinov) and with Me_2SO_4 gives a *Me*₁ ether, m.p. 267° (decomp.), unaffected when refluxed with *N*-MeOH-KOH. (II) does not, therefore, contain CO_2H . (II) with $KOH-H_2O_2$ yields a dibasic acid, $C_{16}H_{13}O_9N$, m.p. 164.5°, which loses 1 H_2O at 120° during 3 hr.

II. Repeated fractionation of (I) after the removal of saponifiable matter gave a sesquiterpene *ishwarene*, $C_{15}H_{24}$, b.p. 130–132°/10 mm., $[\alpha]_D^{25} -42.37^\circ$ (monohydrochloride, b.p. 128–130°/1 mm., $[\alpha]_D^{30} -18.7^\circ$ in EtOH), and a pale green fraction from which a ketone *ishwarone*, $C_{15}H_{22}O$, b.p. 118–120°/1 mm., $[\alpha]_D^{30} -46.47^\circ$ [semicarbazone, m.p. 240°; *p*-nitrophenylhydrazone, m.p. 186.5°; 2:4-dinitrophenylhydrazone, m.p. 167.5°; isoxime, m.p. 133°, insol. in alkali but contains 1 active H (Zerevitinov)], and an alcohol *ishwarol*, $C_{15}H_{24}O$, b.p. 126–128°/1 mm., $[\alpha]_D^{30} -7.29^\circ$ in EtOH, were obtained. The alcohol does not react with $PhNCO$ and resinifies when heated with $o-C_6H_4(CO)_2O$. (I) also contains a little camphor. H. G. M.

Original acids in American pine resin.—See this vol., 1372.

Constituents of the Chinese drug hsi-hsin (*Asarum sieboldi*, Miq.). T. Q. CHOU and J. H. CHU (Chinese J. Physiol., 1935, 9, 261–266).—Besides constituents formerly found, the steam-distillate of hsi-hsin contains pinene (cf. Kaku, A., 1932, 663). The C_6H_6 extract of the finely-powdered drug yielded after removal of the volatile oil a neutral substance, m.p. 124°, $[\alpha]_D^{20} -130^\circ$, containing no OMe and not reacting with Ac_2O and $NHPh-NH_2$. E. P.

Digestion of chlorophyll *in vitro*. A. G. CZIMMER (Magyar Orvosi Arch., 1934, 35, 465–471).—Chlorophyll is digested by pepsin-HCl followed by glycerol extract of pancreas. Phæophytin and phæophorbides were produced. CH. ABS. (p)

X-Ray interpretation of denaturation and the structure of the seed-globulins. W. T. ASTBURY, S. DICKINSON, and K. BAILEY (Biochem. J., 1935, 29, 2351–2360).—The X-ray study of denaturation of the seed-globulins in their normal state and on stretching indicates that the process of denaturation involves the liberation of peptide chains which aggregate on coagulation to parallel bundles, so that the roentgenograms of stretched denatured cdestin (I) and ovalbumin (II) are similar to that of β -keratin (III) fibres; in the case of (II) the polypeptide chains must be shorter than those of (I) and (III). The actual transition of cryst. excelsin to an intermediate fibrous form (excelsan?) is observed. H. D.

Basic amino-acids of typical forage-grass proteins. E. J. MILLER (Biochem. J., 1935, 29, 2344–2350).—The proteins of grasses are prepared by the method of Chibnall (A., 1934, 229) and analysed by that of Vickery (A., 1932, 1148). Arginine, histidine, and lysine represented 12.1–13.1%, 1.9–2.7%, and 4.4–5.3%, respectively, of the total N. The basic NH_2 -acids of the isolated proteins and of the proteins extracted by 4% HCl from spring pasturage occurred in approx. the same proportions. H. D.

Alkaloids of mu-fang-chi. T. Q. CHOU (Chinese J. Physiol., 1935, 9, 267–274).—The drug was soaked in 1% AcOH and the alkaloids after pptn. with Na_2CO_3 were dissolved in $CHCl_3$. Two substances were isolated: *menisine*, $C_{19}H_{22}O_3N$, m.p. 152°, $[\alpha]_D^{20} +290^\circ$ in $CHCl_3$ [hydrochloride, non-cryst., m.p. about 260°; phosphate, m.p. 280°; methiodide, m.p. 263° (decomp.); hydrate, m.p. 127°], a *tert*-base containing 2 OMe; *menisidine*, $C_{36}H_{41}O_6N_2$, m.p. 176°, $[\alpha]_D^{20} +260^\circ$ in $CHCl_3$ [dihydrochloride, m.p. 265° (decomp.); phosphate, m.p. 290°; dimethiodide], a *tert*-base containing 3 OMe which forms an additive compound with $2COMe_2$. E. P.

Alkaloids of *Anagyris foetida*. II. H. R. ING (J.C.S., 1935, 1053–1054; cf. A., 1933, 727).—Small amounts of *N*-methyletyisine and *d*-sparteine (hexahydrodeoxyanagyrene), but no *l*-lupanine, have been isolated from the mother-liquors from the crystallisation of cytisine and anagyrene obtained from the seeds of *A. foetida*. H. G. M.

Chemical examination of *Tylophora asthmatica* and isolation of the alkaloids tylophorine and tylophorinine. A. N. RATNAGIRISWARAN and K. VENKATACHALAM (Indian J. Med. Res., 1935, 22, 433–441).—The isolation of two cryst. alkaloids, *tylophorine*, $C_{24}H_{27}O_4N$, decomp. 275°, and *tylophorinine*, $C_{23}H_{27}O_4N + 0.5H_2O$, decomp. 232–233°, is described. The alkaloid content of the leaves, stem, and root is 0.2–0.3%. The plant contains also ceryl alcohol, a phytosterol, m.p. 192–193°, a wax alcohol, m.p. 89–90°, a flavone colouring substance, chlorophyll, glucose, KCl, Ca salts, wax, caoutchouc, resins, and tannin. R. N. C.

Occurrence of phenylethylamine in fungi. W. KEIL and H. BARTMANN (Biochem. Z., 1935, 280, 58–60).—The EtOH extract of *Boletus luteus* and of *B. elegans* contains choline, putrescine, and fumaric acid, but only that of *B. luteus* contains phenylethylamine. P. W. C.

Constituents of kanzantiku (*Arundinaria hindu*, Makino). K. YOSHIMURA and I. YAMASHITA (J. Agric. Chem. Soc. Japan, 1935, 11, 355—356).—3.5 kg. of seed (which resembles unpolished rice in composition) yield (as aurichloride) 0.3 g. of betaine and 0.5 g. of choline. F. O. H.

Chemical composition of sea-weed. P. KLA-SON (Svensk Kem. Tidskr., 1935, 47, 215—220).—The lignin of sea-weed contains no OMe. Instead of CHO it has OH. The formula is possibly $\text{NH}_2\cdot\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ and after losing 1 H_2O $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{OH}$. The sea-weed contains lignin 30%, methylpentose 6.6%, ash and fibre 2%, cellulose 60.4%. The proportion of xylose to hexose is 1:1, whilst in higher plants it is 3:2. Ppts. with naphthylaminesulphonic acid have different structures, for which formulæ are given. E. P.

Caffeic acid in prunes and its behaviour as a laxative principle. E. MRAK, J. FESSLER, and C. SMITH (Science, 1935, 82, 304).—Caffeic acid (I) (0.03% on dried prune), but not chlorogenic acid, has been isolated from Santa Clara prunes. With rabbits, dogs, and human beings (I) shows no significant laxative effect (cf. A., 1934, 692). L. S. T.

Gramine and two concomitants in the leaves of varieties of barley. K. BRANDT, H. VON EULER, H. HELLSTROM, and N. LOFGREN (Z. physiol. Chem., 1935, 235, 37—42; cf. this vol., 1040).—Gramine, possibly identical with donaxine, is detected in 5 further varieties of barley out of 17 examined; the content is approx. const. during the period of development of the plant. The separation of its two concomitants with absorption bands at 330 and 270 $\text{m}\mu$, respectively, is effected by $\text{Pb}(\text{OAc})_2$ in neutral or alkaline solution. The "330 solution" gives a positive Molisch reaction and gives a yellow cryst. ppt. with $\text{NHPh}\cdot\text{NH}_2$. It immediately decolorises KMnO_4 in dil. H_2SO_4 . "Substance 270" is probably a purine derivative. The variations of the amounts of "330" and "270" with the period of development of the leaves are recorded. H. W.

Gramine from Swedish strains of barley.—See this vol., 1386.

Active principle of *Piper Chaba*, Hunter. P. K. BOSE (Sci. and Cult., 1935, 1, 111).—The dried stem of the plant contains 0.38% of piperine. W. MCC.

Plant-phosphatides. H. ARNI (Diss., Zurich, 1933; Bied. Zentr., 1935, A, 5, 444).—Methods for the isolation of phosphatides and the corresponding acids from green plants are described. Wheat-gluten yields a carbohydrate-free phosphatide; unpolished rice, a lysolecithin possessing hæmolytic properties; leaves of *Ricinus* and rhubarb, phosphatides containing only 1.5% P. Stinging-nettle and *Ricinus* contain N-free phosphatide-acids. A. G. P.

Leaf carotenes. G. MACKINNEY (J. Biol. Chem., 1935, 111, 75—84).—Leaf carotenes were isolated from 59 different plant species and the % of α - (I) and β -carotene (II) approx. determined from the $[\alpha]_D$, m.p., and ultra-violet absorption spectra. 24 preps. contained only (II) and in the remaining preps. (I) was present up to 35%. The (II) from different

sources gave no mutual depression of m.p. and had identical ultra-violet absorption spectra. H. D.

Carotene. IX. Carotenes from different sources and some properties of α - and β -carotene. H. H. STRAIN (J. Biol. Chem., 1935, 111, 85—93; cf. A., 1934, 931).—The proportion of α - (I) to β -carotene (II) in preps. from a no. of sources was determined by fractional adsorption from $\text{C}_2\text{H}_4\text{Cl}_2$. The products obtained were contaminated by colourless crystals, some of which remained at the top of the adsorption column, and others were present in such high concn. that they caused the rapid elution of (II). Dipalmitylcarbinol behaves similarly in the adsorption column. The $[\alpha]_D$ and ultra-violet absorption spectra of (I) and (II) were determined in a variety of solvents; (I) and (II) form stable compounds with SbCl_3 in CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$ with max. absorption at identical λ ; they also give an unstable blue colour with $\text{CCl}_3\cdot\text{CO}_2\text{H}$ in CH_2Cl_2 , CHCl_3 , and $\text{C}_2\text{H}_4\text{Cl}_2$. H. D.

Colorimetric determination of carotene in plant-tissue. W. C. RUSSELL, M. W. TAYLOR, and D. F. CHICHESTER (Plant Physiol., 1935, 10, 325—340).—Dry powdered material is extracted with petroleum. Fresh material is triturated with COMe_2 and sand. The pigments are transferred to petroleum solution by shaking the COMe_2 extract with this solvent and removing COMe_2 by washing with H_2O . From the petroleum solution xanthophyll is removed by MeOH (88—89% MeOH avoids emulsification) and chlorophyll is extracted with 25% KOH in MeOH . After appropriate concn. the petroleum solution of carotene is compared colorimetrically with standard aq. $\text{K}_2\text{Cr}_2\text{O}_7$ (0.00206 mg. of carotene per c.c. = 0.036% $\text{K}_2\text{Cr}_2\text{O}_7$ solution). A. G. P.

Constituents of the wax-like coating of the pear, *Pyrus communis*, L. K. S. MARKLEY, S. B. HENDRICKS, and C. E. SANDO (J. Biol. Chem., 1935, 111, 133—146).—Air-dried pear skins, extracted with light petroleum and then Et_2O , yield fractions (I) and (II), corresponding with 1.95% and 2.38% of the dry wt., respectively. About 40% of (I) consists of acids, mainly oleic acid; of these, about 1/3 are unesterified. The hydrolysate from (I) also contains glycerol, a mixture of primary alcohols C_{20} — C_{30} , and hydrocarbons, mostly $\text{C}_{29}\text{H}_{60}$. (II) consists of ursolic and other resinous acids. The results are compared with similar data for the apple. F. A. A.

Total sterol content of cereals and legumes and method for its determination. E. KEDING (Diss., Munich, 1932; Bied. Zentr., 1935, A, 5, 343).—Results of phytosterol analyses depended on the pre-treatment of the material. Alkaline hydrolysis increases the amount obtained (Soxhlet). Vals. for beans and peas were similar, as also were those for maize and wheat. A. G. P.

Oiticica fat [oil].—See this vol., 1350.

Oil of *Berteroa incana* (grey cress-seed oil). C. LUTENBERG and S. IVANOV (Fettchem. Umschau, 1935, 42, 167—168).—The seeds yielded 25% of oil having n_D^{40} 1.4750, I val. 181.0, acid val. 3.22, sap. val. 181.2, ester val. 178.0, CNS val. 109.4, and unsaponifiable matter 1.5%. The fatty acids had mean

mol. wt. 290.7 and yielded 8% of solid acids, m.p. about 50°. Bromination of the liquid fatty acids gave linolenic acid hexabromide, whilst after oxidation di-, tetra-, and hexa-hydroxystearic acids were recognised.

G. H. C.

Oil of *Cassia absus*. Z. AHMED (Z. Unters. Lebensm., 1935, 70, 166—169).—Oil extracted from the whole seed (4%) and from the kernel (6%) with light petroleum of b.p. 60—80° and 30—50°, respectively, had d_{20}^{20} 0.9276, 0.9284, n_D^{20} 1.4840, 1.4735, sap. val. 190.4, 185.6, I val. (Wijs) 130.5, 125.7, Ac val. 12.0, 10.8, acid val. 2.5, 1.4, unsaponifiable matter 8.4%, 4.8%; the fatty acids of the whole seed (mean mol. wt. 282.4, I val. 129.2) consisted of 19.0% saturated and 81.0% unsaturated.

E. C. S.

Supposed occurrence of acids of uneven number of carbon atoms in vegetable oils and fats.
I. Daturic acid from the seeds of *Datura stramonium*, Linn. B. L. MANJUNATH and S. SIDDAPPA (J. Indian Chem. Soc., 1935, 12, 400—404).—The unsaponifiable portion (26%) of the oil (16.3%) extracted by ligroin from the seeds contains a phytosterol, m.p. 134° (Ac derivative, m.p. 129°). The unsaturated acids, separated by Twitchell's method, contain oleic and linoleic acids. By fractionation of their Me esters, palmitic (I), stearic (II), and a little lignoceric acid are isolated from the saturated acids. So-called daturic acid is actually a mixture of (I) and (II).

J. W. B.

Chemistry of the flowers of the mullen (*Flores verbasci*). III. L. SCHMID and C. KEMENY (Monatsh., 1935, 66, 1—5).—The presence of thapsiaic acid, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{14}\cdot\text{CO}_2\text{H}$ (A., 1932, 931), is confirmed by comparison with synthetic material (cf. A., 1926, 499).

E. W. W.

Cellulose resources. I. Composition of Decan hemp and Indian mallow cultivated in Manchuria. M. SHIKATA, K. AKAGI, and N. URANO. II. Properties of α -celluloses from various plants. M. WATANABE. III. Rayon pulp from cotton stalks. M. SHIKATA and K. AKAGI (J. Agric. Chem. Soc. Japan, 1935, 2, 621—623, 624—634, 635—638).—I. Analyses of the basts and stalks of Decan hemp (*Hibiscus cannabifolius*, L.) and Indian mallow (*Abutilon Aircennae*, Gaertn.) are given.

II. The α -celluloses of cotton-seed hairs, cotton bast fibre, Decan hemp, and Indian mallow are compared.

III. Prep. of pulp from cotton stalks is described.

A. L.

Carbohydrates of the bulbs of *Allium*. IV. Hydrolysis of scorodose by enzymes. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 29—33; cf. this vol., 673).—Scorodose (a fructan) was hydrolysed by taka-diastase (optimum p_H 5.5—5.6 and 30°), malt extract, pressed yeast, and germinating *Allium* bulbs. Emulsin, snail extract (*Eulota*), saliva, and dormant bulbs had no action. Treatment of dormant bulbs with KCN did not induce enzymic activity. Germinating bulbs and leaves of *Allium* contained invertase.

CH. ABS. (p)

Wood hemicelluloses. W. G. CAMPBELL (Nature, 1935, 136, 299).—In addition to starch (this vol.,

797), the cell-walls of oak sapwood yield a product which gives with I a purple colour changing to blue on keeping. It is more closely allied to hemicellulose-A than the starch, and appears to consist of uronic and aldobionic anhydride residues (approx. 14%), anhydroxylose (approx. 10%) and anhydroglucose residues (approx. 75%). Hydrolysis of the starch from oak leaves indicates that certain hemicelluloses of oak wood are derived from starch by steps involving the oxidation of primary OH and the subsequent formation of anhydroxylose residues by decarboxylation.

L. S. T.

Hemicelluloses. II. Association of hemicelluloses with lignin. A. G. NORMAN and (in part) J. G. SHRIKHANDE (Biochem. J., 1935, 29, 2259—2266).—Polyuronide hemicelluloses (I) are easily extracted from woods and plant materials by dil. sulphite solution if the material has been previously chlorinated. There is probably some form of combination or association between lignin (II) and (I), since the extraction of (I) depends on a treatment effecting the dissolution of (II).

J. N. A.

Glucosides and minerals in citrus fruits. L. W. GADDUM (Proc. Florida State Hort. Soc., 1934, 83—85).—At certain stages of maturity a grapefruit may contain 0.0004 g. of Cu and 0.1 g. of naringin (I). Citrus glucosides contain glucose and rhamnose with (I) (grapefruit) or hesperidin (orange). No alkaloids or cyanophoric glucosides occur. The bitterness of (I) is not an obstacle to the use of grapefruit cannery refuse as a stock feed. In addition to the customary elements, grapefruit contain spectrographically detectable amounts of Zn, Cu, Ni, Mn, B, Cd, Al, and Pb. Cases of Zn deficiency are recorded. Pulp of the fruit contains more Cu than does the albedo. The reverse is true of the Zn content. The cultural treatment of trees affects the Cu content of fruit > the p_H , sugar, or acid contents.

CH. ABS. (p)

Sugar content of pods of paprika plant types. A. TOMPOS (Kisérlet. Kozl., 1934, 37, 286—288).—Analyses are recorded. During ripening the glucose (I) and sucrose contents increased considerably. Approx. 40% of the dry matter consisted of (I).

CH. ABS. (p)

(A) Chemical analysis of plant tissue. (B) Determination of carbohydrates. (C) Determination of nitrogen in relatively simple compounds. W. E. TOTTINGHAM, Z. I. KERTESZ, W. E. LOOMIS, and T. G. PHILLIPS (Plant Physiol., 1935, 10, 383—386, 387—392, 393—399).—Reports of committees on current methods and recommendations arising therefrom.

A. G. P.

Comparative colour test for coumarin and melilotic acid in *Melilotus* species. J. S. CLAYTON and R. K. LARMOUR (Canad. J. Res., 1935, 13, C, 89—100).—The method is based on the colour intensity produced by coupling diazotised $p\text{-NO}_2\text{C}_6\text{H}_4\cdot\text{NH}_2$ with coumarin (I). Melilotic acid (II) produces a similar colour and is determined simultaneously. Obermayer's method (A., 1913, ii, 353) is subject to error, since there is a partial distillation of (II) with (I) and the subsequent titration with KMnO_4 leads to falsely high vals. for (I). The dis-

tillate also contains a third substance which reduces KMnO_4 but gives no colour with diazonium reagents. Extraction of (I) from sweet clover by Et_2O is incomplete after 20 hr. A tentative method of examining EtOH extracts is described. A. G. P.

Boron status of fruit and leaves in relation to "internal cork" of apples in the Nelson district. H. O. ASKEW (New Zealand J. Sci. Tech., 1935, 17, 388—391).—The B content of apples affected with "internal cork" was approx. 1/3 of that of healthy fruit. The severity of the disease was inversely \propto the % of B in the fruit. A. G. P.

Weeds and poisonous plants of Southern Rhodesia. C. K. BRAIN (Rhodesia Agric. J., 1934, 31, 779—791).—Sorghums, Johnson grass, Sudan grass, and Kafir corn, when wilted in hot dry weather, produce sufficient HCN to poison cattle. HCN disappears when the plants regain turgidity. CH. ABS. (p)

Iodine content of tea. A. ITANO and Y. TUJI (J. Agric. Chem. Soc. Japan, 1935, 11, 545—551).—The I content of dried leaves is 0.45—1.20 mg. per kg.; it is greater in young leaves. 50—60% of the I can be extracted with H_2O . P. G. M.

Iodine content of Chinese marine algæ. P. S. TANG and P. C. WHANG (Chinese J. Physiol., 1935, 9, 285—290).—The I content of 10 species has been determined. The results are doubtful owing to the influence of storage, season, and analytical errors. E. P.

Absorption of sulphur dioxide by lucerne and its relation to leaf injury. M. D. THOMAS and G. R. HILL, jun. (Plant Physiol., 1935, 10, 291—307).—Leaf destruction in lucerne fumigated with SO_2 approaches a linear function of the amount of SO_2 absorbed in a given time. An appreciable amount of gas may be adsorbed without injury, which appears when the rate of absorption exceeds a certain threshold val. These relationships are examined in connexion with smoke injury of plants. A. G. P.

Wave-lengths of radiation in the visible spectrum inhibiting the germination of light-sensitive lettuce seed. L. H. FLINT and E. D. MCALISTER (Smithsonian Misc. Coll., 1935, 94, No. 5, 1—11).—Germination is more markedly inhibited by a band in the region of 760 $\text{m}\mu$ than by those at 420—520 $\text{m}\mu$, previously recorded. In the latter case the relative effect of radiations on germination is similar to that in inducing phototropic response in etiolated oat coleoptiles, max. vals., in each case, corresponding with 440 and 480 $\text{m}\mu$. A. G. P.

Biochemical modifications in phytopathology. R. SALGUES (Compt. rend. Soc. Biol., 1935, 119, 1396—1398).—In *Napel* aconite infected with *Septoria lycottoni macrospora*, only the leaves show any variation in total alkaloid. Leaves of *Prunus lauro-cerasus* infected with *Phyllosticta mathioliolana* show a decrease in HCN, glucosides, and insol. polysaccharides and an increase in sol. sugars. H. G. R.

Phosphatide auto-complex coacervates as ionic systems and their relation to the protoplasmic membrane.—See this vol., 1321.

Causes of immunity to the apple woolly aphis (*Eriosoma lanigerum*, Hausmann). R. M. GREENSLADE, A. M. MASSEE, and W. A. ROACH (East Malling Res. Sta. 21st Ann. Rept. [1933], 1934, 220—224).—Apple bark contains a substance which imparts immunity or susceptibility to attack by woolly aphis. The substance is insol. in EtOH , but sol. in Et_2O . The life of the aphis on apple-bark media is prolonged by the presence of *Torula rubra*. CH. ABS. (p)

Fractional ultrafiltration.—See this vol., 1342.

Fractional electrical transport as a tool in biochemical research. R. J. WILLIAMS (J. Biol. Chem., 1935, 110, 589—597).—Apparatus is described for determining the chemical nature of physiologically active substances and for giving an approx. iso-electric point, if amphoteric. Other uses, e.g., electrolytic purification, separation of lecithins and cephalins, are suggested. H. G. R.

Modification of the apparatus and technique for the micro-determination of ammonia in biological liquids. M. POLONOVSKI and P. BOULANGER (Bull. Soc. Chim. biol., 1935, 17, 944—959).—A modification of the apparatus of Parnas and Heller embodying a water-jacket to prevent the condensation of droplets of liquid between the distillation flask and the absorption tube. A. L.

Micro-determination of halogens in body-fluids and tissues. W. LIPSCHITZ (Arch. internat. Pharmacodyn., 1935, 49, 379—392).—75—200 mg. of material are treated at 100° with HNO_3 (d 1.4) in presence of 1 ml. of 0.02N- AgNO_3 . After oxidation is complete the diluted liquid is titrated with KCNS using Fe alum as indicator. Within limits the method is applicable for Br as well as Cl, but not for I. Sources of error in Bang's method are indicated. NUTR. ABS. (m)

Absorption apparatus for micro-determination of volatile substances. III. Micro-determination of chloride with application to blood, urine, and tissues. E. J. CONWAY (Biochem. J., 1935, 29, 2221—2235).— Cl' , contained in the outer chamber of the apparatus of Conway *et al.* (A., 1933, 654), is oxidised by acid KMnO_4 to Cl_2 , which liberates I from the KI contained in the inner chamber. The I liberated is a measure of the Cl' content, and with amounts of $\text{Cl}' < 0.035$ mg. may be titrated with 0.05N- $\text{Na}_2\text{S}_2\text{O}_3$. Lower amounts, < 0.007 mg., are determined colorimetrically, and still lower amounts can be determined colorimetrically after adding 0.5 ml. of 0.2% starch. The application of the method to the determination of Cl' in protein-free filtrates of blood, undiluted urine, and tissues is described. The method is independent of the presence of I' and of ≥ 1 mg. of protein. E. A. H. R.

Determination of iron in biological materials. G. E. FARRAR, jun. (J. Biol. Chem., 1935, 110, 685—694).—The material is ignited with CaCO_3 , the residue dissolved in HCl, and after oxidation the Fe is determined colorimetrically as $\text{Fe}(\text{CNS})_3$ in amyl alcohol. Sources of error have been eliminated, including interference of pyro- and ortho-phosphates.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1935.

General, Physical, and Inorganic Chemistry.

Slight correction to the Rydberg constant for hydrogen (H^1). R. C. WILLIAMS and R. C. GIBBS (Physical Rev., 1934, [ii], 45, 491). L. S. T.

Triplet $3p$ complex of the hydrogen molecule. G. H. DIEKE (Physical Rev., 1935, [ii], 48, 610—614; cf. this vol., 917).—Many peculiarities in the Fulcher bands of H_2 can be explained by the interaction of the $3p^3\Pi$ with the $3p^3\Sigma$ level (cf. following abstract). N. M. B.

$3p^3\Sigma \rightarrow 2s^3\Sigma$ bands of HD and D_2 . G. H. DIEKE (Physical Rev., 1935, [ii], 48, 606—609; cf. this vol., 555).—Full data for the system in the extreme red and near infra-red are tabulated, and the band consts. are calc. N. M. B.

Vibration and rotation spectrum of the molecule HD. G. C. WICK (Atti R. Accad. Lincei, 1935, [vi], 21, 708—714).—Theoretical and mathematical. O. J. W.

Anomalies in the Zeeman effect of helium. L. E. KINSLER and W. V. HOUSTON (Physical Rev., 1934, [ii], 45, 134). L. S. T.

Photographic record of the resonance line of helium. K. HAIDRICH (Phot. Korr., 1935, 71, 106—107).—The He resonance line at λ 10,830 ($2s-2p$) can be photographed on Ilford I.-R. plates sensitised by neocyanine. The greatest intensity of the line is near the cathode. J. L.

Electric and magnetic effect on the helium lines for perpendicularly crossed fields. W. STEUBING and W. REDEPENNING (Ann. Physik, 1935, [v], 24, 161—182).—The combined Zeeman and Stark effects on the He lines have been investigated. Detailed results are given for the lines $2s-3p$, $2p-nd$ ($n=4, 5, 6$), $2p-n_s$ ($n=4, 5, 6$), $2S-nP$ ($n=3, 4$), $2P-nD$ ($n=4, 5, 6, 7$), and $2P-nS$ ($n=4, 5, 6$). A. J. M.

Perturbations in the second positive nitrogen bands. L. GERO (Z. Physik, 1935, 96, 669—676). A. B. D. C.

Action of hydrogen bromide on the nitrogen afterglow. W. H. RODEBUSH and M. L. SPEALMAN (J. Amer. Chem. Soc., 1935, 57, 1881—1882).—HBr or Br alters the relative intensity of certain transitions in the afterglow, but the band spectrum of Br was not observed. E. S. H.

Electronic and vibrational absorption in O_4 and O_3 molecules. J. W. ELLIS and H. O. KNESER (Physical Rev., 1934, [ii], 45, 133). L. S. T.

Absorption of oxygen in the extreme ultra-violet. G. B. COLLINS and W. C. PRICE (Physical Rev., 1934, [ii], 45, 561).—Absorption bands below

1000 Å. have been photographed and arranged into three progressions for which formulæ are given. They are due to normal O . Other bands at shorter λ and between 1210 and 1000 Å. have also been measured. L. S. T.

Oxygen in the sun's chromosphere. T. ROYDS (Nature, 1935, 136, 606—607).—The observed infra-red O emission lines 7771, 7774, and 7775 show that O_2 is a normal and probably abundant constituent of the sun's chromosphere. L. S. T.

New emission spectrum of sulphur in the photographic infra-red. M. DESIRANT and J. DUCHESNE (Compt. rend., 1935, 201, 597—598).—Bands at 6650—7765 Å., degraded to the violet, and attributed to S_2 , are described. H. J. E.

Deepest terms in ions of the isoelectronic sequence Al—Mn VIII. P. G. KRUGER and S. G. WEISSBERG (Physical Rev., 1935, [ii], 48, 659—663).—Radiations corresponding with the energy differences between the terms $3p^6\ ^1S_0-3p^54s^3P_1^0, ^1P_1^0$ in Ti v, V vi, Cr vii, Mn viii, and $3p^6\ ^1S_0-3p^55s^3P_1^0, ^1P_1^0$ in V vi and Cr vii, and connecting the upper states with the deepest terms in each ion, have been observed. Series limits and vals. of the deepest terms are calc. N. M. B.

Spectrum of the zinc arc in a vacuum. C. W. HETZLER, R. W. BOREMAN, and K. BURNS (Physical Rev., 1935, [ii], 48, 656—659).—Data for 60 lines in the range 2178—7799 Å. are tabulated. Two new solar Zn lines, λ 4292 and 7799, are reported. A source for obtaining weak lines in vac. is described, and data for the stronger lines of Pb, Cu, Cd, Ag, Sn, Na, K, Rb, Cs, Sr, and Be are given. N. M. B.

Spectrum of doubly-ionised zinc. S. BASU (Indian J. Physics, 1935, 9, 537—544; cf. Bloch, A., 1934, 1051).—Data and analyses for 104 lines and 23 new term vals. are tabulated for the region λ 5513—2387. N. M. B.

Hyperfine structure in selenium, palladium, and gold. L. SIBAIYA (Proc. Indian Acad. Sci., 1935, 2, A, 313—319).—Hyperfine structure analysis of some Se and Pd lines shows that none of the levels examined reveals even isotope displacement. The Se 77 and Pd 105 nuclei have very small magnetic moments, and their spin moment is probably $1/2(h/2-)$. The doublet structure ($\Delta\nu=0.224\text{ cm.}^{-1}$) in the resonance lines of Au is confirmed by the redoubling of each component due to self-reversal in the source. Evidence points to a single Au isotope of mass 197, indicating that the accepted at. wt. is too high. The

nuclear spin moment of Au is $3/2$, and the $g(I)$ factor is 0.136, agreeing with Landé's theoretical val.

N. M. B.

Quenching of cadmium resonance radiation by foreign gases. H. C. LIPSON and A. C. G. MITCHELL (Physical Rev., 1935, [ii], 48, 625—630).—The quenching of the Cd resonance line λ 3261 by H_2 , D_2 , CO, NH_3 , N_2 , and CH_4 was measured by comparing line intensity from a cell containing pure Cd vapour and one containing Cd vapour and the foreign gas. Applying the Stern-Volmer formula, the quenching cross-sections are: H_2 0.67, D_2 0.19, CO 0.14, NH_3 0.041, N_2 0.021, CH_4 0.012×10^{-16} sq. cm.

N. M. B.

Wave-length shifts of the spectral lines of Sn due to change of pressure. T. YUASA (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 2, A, 267—277).— λ shifts and modes of appearance of the lines of Sn I, II, III excited at 1 atm. and a few cm. pressure are tabulated. As the inner quantum no. j increased, the shifts and changes in modes of appearance were more marked. Arc lines showed no appreciable shift with pressure increase, but the mode of appearance changed. Effects were comparatively smaller for the principal series in Sn II and Sn III. Results are tabulated also for a no. of unclassified lines.

N. M. B.

Absorption spectrum of diatomic antimony. S. M. NAUDE (Physical Rev., 1934, [ii], 45, 280).—Two band systems obtained at different temp. and v.p. of the Sb are described. Some bands show fine structure, and the head corresponding with the mol. $Sb^{121}Sb^{123}$ is more intense than those corresponding with the mols. $(Sb^{121})_2$ and $(Sb^{123})_2$.

L. S. T.

Perturbations of the higher caesium terms by methane hydrocarbons and measurements for the doublet $1s-3p$ of the potassium principal series. C. FUCHTBAUER and H. J. REIMERS (Z. Physik, 1935, 97, 1—7).— CH_4 , C_2H_6 , and C_3H_8 give red displacement similar to A for the Cs terms, the displacement increasing with perturbing mol. size. Half-width and displacement measurements are given for the K doublet perturbed by these hydrocarbons and inert gases.

A. B. D. C.

Arc and spark spectra of cerium. G. R. HARRISON and W. ALBERTSON (Physical Rev., 1934, [ii], 45, 289).—The Ce arc between 2000 and 5000 Å. has been photographed using a grating of 0.4 Å. per mm.

L. S. T.

Spectrum of singly-ionised europium. W. ALBERTSON (Physical Rev., 1934, [ii], 45, 499—500).

L. S. T.

Emission and absorption from the 2^3P_0 metastable level in mercury. M. L. POOL and O. W. PRASHUN (Physical Rev., 1934, [ii], 45, 124).

L. S. T.

Proportionality of dispersion to field in the Zeeman effect of three mercury levels. G. DUPOUX and P. JACQUINOT (Compt. rend., 1935, 201, 543—544).— $\Delta\nu/H$ is const. for 3P_1 , but increases for 3S_1 and 3P_2 , as the field increases from 30,000 to 50,000 gauss. For 3P_1 $q=1.493$ (cf. this vol., 137).

T. G. P.

Intensity relations in the hyperfine structure of the optically-excited mercury line 5461 Å. E. E. BOGGS and H. W. WEBB (Physical Rev., 1934, [ii], 45, 561).

L. S. T.

Wave-length standards in the extreme ultra-violet. J. C. BOYCE (Physical Rev., 1934, [ii], 45, 289; cf. A., 1934, 1147; this vol., 799).

L. S. T.

Flame and spark-in-flame spectra of rare earths. C. J. RODDEN and O. S. PLANTINGA (Physical Rev., 1934, [ii], 45, 280—281).—Bands given by La, Sm, Pr, Nd, Gd, and Yb when the corresponding rare-earth salts are introduced as a spray in the spark-in-flame method are recorded.

L. S. T.

Current distribution between a small (point) cathode and a large (infinite) anode for glow discharges in different gases. F. KELLER (Z. Physik, 1935, 97, 8—33).—Inert gases give diffusion flow of electrons when electron concn. near the cathode is sufficiently large, and gradient flow when this is small; N_2 belongs to this class. O_2 and H_2O give ionic sheath flow.

A. B. D. C.

Sparking potential of hydrogen at high frequencies. R. ZOUCKERMANN (Compt. rend., 1935, 201, 649—651; cf. A., 1933, 656).—Data are recorded for the effect of Hg vapour on the pressure variation of sparking potential of H_2 in a SiO_2 tube with external electrodes.

H. J. E.

Development of a spark from a glow. E. L. E. WHEATCROFT and H. BARKER (Phil. Mag., 1935, [vii], 20, 562—571).—The transition glow-spark is discussed, and the relations no. of sparks—pressure, crit. pressure—electrode spacing, and crit. pressure—current are examined and plotted.

N. M. B.

Paschen's law at low striking potentials. E. L. E. WHEATCROFT and H. BARKER (Phil. Mag., 1935, [vii], 20, 571—578).—Paschen's law is found to be valid over the glow-spark discharge range. The striking potential curve for air is found. The striking potential is approx. 50—100 volts lower for the spark than for the glow.

N. M. B.

Theory of the glow discharge. E. L. E. WHEATCROFT (Phil. Mag., 1935, [vii], 20, 578—586).—The main features of a glow discharge can be interpreted quantitatively in terms of the breakdown (breakdown potential—pressure \times electrode spacing) curve, and the ionisation conditions.

N. M. B.

Periodic variation of the concentration of neutral atoms in the vapour of an alternating-current sodium lamp. W. UYTERHOEVEN and C. VERBURG (Compt. rend., 1935, 201, 647—649).

H. J. E.

X-Ray line intensities in thick targets of nickel. L. T. POCKMAN, P. KIRKPATRICK, and D. L. WEBSTER (Physical Rev., 1934, [ii], 45, 131).

L. S. T.

Diffuse scattering of X-rays by conduction electrons. C. ZENER (Physical Rev., 1935, [ii], 48, 573—576).

N. M. B.

Soft X-rays and energy states of the conduction electron. H. W. B. SKINNER and H. M. O'BRYAN (Physical Rev., 1934, [ii], 45, 293).—The emission spectra of some lighter metals have been obtained

in the region 40—600 Å. The results are probably characteristic of the pure polycryst. solid. L. S. T.

State of polarisation of continuous X-rays from a thin aluminium anti-cathode. H. P. DE (Indian J. Physics, 1935, 9, 507—516).—A Wilson chamber method of observing the state of polarisation is described, and % polarisations relative to the direction of the cathode particles are given. Results are discussed in relation to available data and theory. N. M. B.

Rotation of the plane of polarisation of a beam of X-rays. R. L. McFARLAN (Physical Rev., 1934, [ii], 45, 292).—Quartz crystals, 0.75 mm. thick, rotate the plane of polarisation through an angle of approx. $2^{\circ} 30'$ when a plane polarised beam of X-rays passes through parallel to the optic axis. L. S. T.

Emission [of subsidiary lines] in the $K\alpha$ spectra of the elements between Cu (29) and Rh (45) inclusive. H. HULUBEI (Compt. rend., 1935, 201, 544—547; cf. A., 1916, ii, 509).—Studies of the $K\alpha_{3,4}$ emission of Cu, Zn, As, Se, Br, Rb, Sr, Y (39), and Rh have been made. T. G. P.

Fine structure of the L_{III} absorption discontinuity of the rare earths. V. DOLEJSEK and H. HYLMAR (Compt. rend., 1935, 201, 600—602).—The specimens were prepared by mixing the material with a solution of cellulose nitrate in amyl acetate, and drying the resulting emulsion on paper. Data for Yb, Gd, Sm, Nd, Pr, and Ce are recorded. H. J. E.

Relative intensities of certain L-series X-ray lines of gold (79). F. K. RICHTMYER and S. W. BARNES (Physical Rev., 1934, [ii], 45, 562; cf. this vol., 138). L. S. T.

L emission spectrum of platinum. (MLLE.) Y. CAUCHOIS (Compt. rend., 1935, 201, 598—600).—Data are recorded and classified. H. J. E.

Ratio of fluorescence yields of the L_{11} and L_{22} sub-series of lead. B. E. FOSTER (Physical Rev., 1934, [ii], 45, 130—131). L. S. T.

New satellites of the X-ray line $L\beta_2$. S. KAUFMAN and F. K. RICHTMYER (Physical Rev., 1934, [ii], 45, 562). L. S. T.

Rate of change of electron temperature in the mercury afterglow. R. H. RANDALL and H. W. WEBB (Physical Rev., 1935, [ii], 48, 544—549).—The behaviour of a plasma in which no new ions are found was studied for electron temp. and concn. The rate of cooling of electrons was very rapid at first, decreasing rapidly below 2500° abs. to a const. val. several hundred degrees above that of the vapour. N. M. B.

Back diffusion of and excitation of secondary radiation by slow cathode rays at thin metallic layers. H. W. LANGENWALTER (Ann. Physik, 1935, [v], 24, 273—296).—Thin foils of Ag, Pt, and Pd were bombarded by slow electrons (<100 volts) at 70° incidence. The distribution of velocity amongst the electrons emitted perpendicularly from the foil, and the effect of heating and absorption of gas, were investigated. The different metals give similar curves. Foils which have not been heated

give electrons of two distinct velocity groups separated by a gap. One group consists of unretarded reflected electrons, the other principally of very slow true secondary electrons. On heating the foils, the gap between the two groups disappears, its place being taken by electrons which have diffused back. Treatment of the Pt and Pd foils with H₂ produced a similar effect to heating but smaller. A. J. M.

Electron grouping by concave glowing cathode surfaces revealed by the electron microscope. G. KEMMNTZ, M. KNOLL, and W. WALCHER (Z. Physik, 1935, 96, 612—619).—The electron microscope shows clearly the grouping of emitted electrons at small hollows in the cathode. A. B. D. C.

Mechanism of unimolecular electron capture. F. BLOCH and N. E. BRADBURY (Physical Rev., 1935, [ii], 48, 689—695).—The formation of negative ions by electron capture in gases in which a dissociation process does not occur is explained by a unimol. process involving the excitation of mol. vibrational levels and subsequent loss of energy by collision or resonance. A change of only one vibrational quantum no. must be assumed; this sets an upper limit to the electron affinity. In the case of O₂ this limit is 0.17 volt. N. M. B.

Electron scattering in mercury vapour. A. P. GAGGE (Physical Rev., 1934, [ii], 45, 288).—Results obtained with the magnetic deflexion method are described. L. S. T.

Emission of positrons from radioactive sources. A. I. ALICHANOV, A. I. ALICHANIAN, and M. S. KOSODAEV (Nature, 1935, 136, 719—720).—Measurements of the positron spectrum emitted by a thin-walled Rn tube have been repeated, and a new determination of the ratio of the positron no. to that of the β -particles of Ra-C has been made. When Pb or Al is submitted to rays from a Rn source most of the positrons produced are due to the γ -rays from Ra-C. L. S. T.

Theory of the positron. G. E. UHLENBECK (Physical Rev., 1934, [ii], 45, 290).—Dirac's theory is discussed. L. S. T.

Energy spectra of positrons ejected by artificially-stimulated radioactive substances. S. H. NEDDERMEYER and C. D. ANDERSON (Physical Rev., 1934, [ii], 45, 498—499). L. S. T.

Relation of the positron energy spectrum to the decay constant and to the energy of the bombarding protons. C. D. ANDERSON and S. H. NEDDERMEYER (Physical Rev., 1934, [ii], 45, 653—654). L. S. T.

[New] Wilson's cloud chamber and determinations of the ratio of positrons to electrons on transformation of γ -rays in matter. T. BENECKE (Z. Physik, 1935, 96, 571—587). A. B. D. C.

Theory of protons and neutrons. G. WATAHIN (Atti R. Accad. Lincei, 1935, [vi], 21, 703—708).—Mathematical. Dirac's equations are modified for the case of protons and neutrons. O. J. W.

Creation of positive and negative electrons by heavy charged particles. Y. NISHINA, S. TOMO-

NAGA, and M. KOBAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 137—178).—Mathematical. Cross-sections for the creation of pairs of positive and negative electrons by charged particles of high velocity on colliding with at. nuclei are calc. by the method of Weizsacker (cf. A., 1934, 712). Vals. for Pb are 5.6×10^{-25} cm.² for 10^8 e.v. electrons, and 3.5×10^{-25} cm.² for 10^{11} e.v. protons. The screening effect of outer electrons is examined (cf. Oppenheimer, this vol., 278). N. M. B.

Energy of formation of negative ions in O₂. L. B. LOEB (Physical Rev., 1935, [ii], 48, 684—689).—An attempt to evaluate the energy of attachment of electrons to mols. in O₂, by determining at what energy the electron is detached from the O₂ ion in impact with mols., leads to the val. 0.34 volt. Phenomena of the Loeb electron filter are discussed (cf. Bradbury, A., 1934, 126). N. M. B.

Acceleration of ions. J. W. BEAMS and L. B. SNODDY (Physical Rev., 1934, [ii], 45, 287).—The method of accelerating electrons (*ibid.*, 1933, 44, 784) has been applied to the acceleration of protons. The increase in velocity corresponded with 6 times the max. applied potential of 15,000 volts. L. S. T.

Isotopes. F. W. ASTON (Science, 1935, 82, 235—240).—Address to the British Association, 1935.

Incompleteness of the system of chemical elements. M. DIERSCHKE (Chem.-Ztg., 1935, 59, 833—834).—The probable nature of elements 61, 85, and 87 and the possible existence of other new elements are discussed. A. G. P.

D. I. Mendeleev's elements "X" and "Y" in the light of new ideas. A. M. VASILIEV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 2, 33—34).—The neutron and neutrino are identified with "X" and "Y," respectively. CH. ABS. (e)

Liberation of radon by radioactive cells in drinking-glasses. J. M. A. HOEFLAKE and A. E. KORVEZEE (Rec. trav. chim., 1935, 54, 768—778).—The apparently irregular production of Rn in commercial drinking-glasses fitted with radioactive cells is due to the diffusion of the Rn through the paraffin surface of the cells, irregularities disappearing when measurements are taken at equal intervals. An expression is deduced for the amount of Rn transmitted to the H₂O under various conditions.

J. W. S.
Branching ratio of the actinium family of radioactive elements. M. FRANCIS and CHENG DA-TCHANG (Phil. Mag., 1935, [vii], 20, 623—632; cf. A., 1934, 387).—The ratio is const. at $4.05 \pm 0.1\%$, as determined for 88.7% U₃O₈ Katanga and 42.3% U₃O₈ Canadian pitchblendes and 49.5% U₃O₈ Colorado carnotite, and is the same whether Ta or Zr is used to ppt. the Pa. N. M. B.

Radioactivity of potassium and rubidium. K. SITTE (Z. Physik, 1935, 96, 593—599).—The active isotopes are a very rare K⁴⁰₁₉ and Rb⁸⁷₃₇.

A. B. D. C.
Radioactivity of samarium. H. J. TAYLOR (Nature, 1935, 136, 719).—Using the new technique (this vol., 910), the range of α -particles emitted by

Sm is 1.13 ± 0.02 cm. standard air. In addition to this short-range group, less numerous tracks of max. range approx. 3.5 cm. in air, due to singly-charged particles, have been observed. L. S. T.

Chemistry of polonium. M. LEMARCHANDS (Bull. Soc. chim., 1935, [v], 2, 1699—1700).—The position in the electromotive series allocated to Po by Guillot and Haissinsky (cf. A., 1934, 735, 855) between Te and Ag is confirmed by the relative effects of reducing agents on Po salts. J. W. S.

Segregation of polonium in a bismuth crystal. W. W. EATON (Physical Rev., 1934, [ii], 45, 647—648).—The groups of ranges in α -particles detected by Focke (A., 1934, 1284) have been checked by direct measurements of tracks formed in a Wilson expansion chamber. L. S. T.

L-Absorption constants of protoactinium (91). V. DOLEJŠEK and J. MAREK (Z. Physik, 1935, 97, 70—72). A. B. D. C.

α -, β -, and γ -Rays of the actinium family. A. E. RUARK (Physical Rev., 1934, [ii], 45, 564).—A discussion. L. S. T.

Determination of the decay constant of ionium from the number of α -particles emitted. F. HERNEGGER (Sitzungsber. Akad. Wiss. Wien, 1935, IIa, 143, 367—377; Chem. Zentr., 1935, i, 1658—1659).—The decay const. found was 8096×10^{-6} per year. A new method is given for separating Io from larger amounts of UO₂(NO₃)₂. H. J. E.

α -Particle spectra and the Geiger-Nuttall law. A. E. RUARK (Physical Rev., 1934, [ii], 45, 564).—A discussion. L. S. T.

β -Radiation of polonium. W. BOTHE (Z. Physik, 1935, 96, 607—611). A. B. D. C.

Double β -disintegrations. M. GOEPPERT-MAYER (Physical Rev., 1935, [ii], 48, 512—516).—Mathematical. N. M. B.

Use of electron lenses for β -rays. O. KLEMPERER (Phil. Mag., 1935, [vii], 20, 545—561).—The magnetic field distributions of various electron lenses have been measured and their optical qualities are discussed. A single-lens β -ray spectrograph giving high intensity, and a spectrograph comprising two "lenses" and a deflecting magnetic "prism" between them, giving high intensity and resolving power, are discussed. N. M. B.

Neutron emission. J. R. DUNNING and G. B. PEGRAM (Physical Rev., 1934, [ii], 45, 295; cf. A., 1934, 714). L. S. T.

Scattering of neutrons by protons. M. BRONSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 75—78).—Mathematical. A. J. M.

Emission of neutrons from radioactive sources. C. Y. CHAO (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 221—225).—Using a Rn source in Au tubes and irradiating EtI from which the active I is afterwards separated, the no. of emitted neutrons detected was approx. 2 per millicurie per sec., probably emitted by the radioactive nuclei. N. M. B.

Absence of appreciable γ -radiation from the impact of fast neutrons on protons. (MME.) T.

GRIVET-MEYER (Compt. rend., 1935, 201, 658—660).—Lea's results were not confirmed (cf. A., 1934, 235). The increase in the no. of particles is attributed to the action of neutrons on Al used in the construction of the counter. H. J. E.

β -Radioactivity of neutrons. L. MOTZ and J. SCHWINGER (Physical Rev., 1935, [ii], 48, 704—705; cf. Konopinski, this vol., 1048).—Mathematical.

N. M. B.

Neutron-like particles accompanying β -ray emission. G. H. DENISON (Physical Rev., 1934, [ii], 45, 557).—An attempt to detect such particles emitted simultaneously with β -rays failed with Ra-D and -E, KCl, and RbCl. L. S. T.

Possible models of an electrostatic neutron. H. MARGENAU (Physical Rev., 1934, [ii], 45, 559).—Theoretical. L. S. T.

Scattering of slow neutrons. A. C. G. MITCHELL and E. J. MURPHY (Physical Rev., 1935, [ii], 48, 653—656).—Using the radioactivity produced in a Ag foil as a detector of neutrons, curves for the % scattering of slow neutrons as a function of thickness by Fe, Cu, Pb, Sn, and Hg were obtained. The calc. relative cross-sections for scattering are 9.9, 7.7, 7.2, 3.8, and 4.4, respectively. N. M. B.

Velocity of slow neutrons by mechanical velocity selector. J. R. DUNNING, G. B. PEGRAM, G. A. FINK, D. P. MITCHELL, and E. SEGRE (Physical Rev., 1935, [ii], 48, 704; cf. this vol., 1186).—A curve is obtained showing the decrease in no. of slow neutrons from a Rn-Be source detected after passing through a Cd-duraluminium two-shutter system as the speed of the sectors changed. N. M. B.

γ -Rays due to absorption of slow neutrons. F. RASETTI (Z. Physik, 1935, 97, 64—69).—Results are given for energy associated with γ -rays emitted from Cl, Co, Y, Ag, Cd, Ir, and Hg. A. B. D. C.

Slow neutrons. P. LUKIRSKY and T. ZAREWA (Nature, 1935, 136, 681—682).—The increased radioactivity induced in Ag irradiated by slow neutrons on cooling the paraffin wax to the temp. of liquid air has been confirmed (cf. this vol., 802). With thick layers of wax, however, no temp. effect is observed owing to loss of neutrons by absorption in the wax. Absorption increases with a decrease in velocity of thermal neutrons. The calc. effective cross-section of neutrons is approx. 10^{-24} cm.² L. S. T.

Application of radioactive bromine to the investigation of the mechanism of chemical reactions. S. ROGINSKY and N. GOPSTEIN (Physikal. Z. Sovietunion, 1935, 7, 672—676).—Org. Br linked to C shows scarcely any interchange with radioactive Br in Br₂, HBr, KBr, or CuBr₂. Passage of radioactive Br vapour over heated aq. KBr, or dissolution and subsequent evaporation of radioactive Br from aq. KBr, leads to complete distribution of the activity. At high temp. HgBr₂ and AlBr₃ show complete interchange of Br with the vapour phase. Heating of CuBr₂ containing radioactive Br, to form CuBr, followed by re-conversion into CuBr₂ in non-radioactive Br causes < theoretical

loss of activity, and after 5 cycles 50% of the activity remains, indicating that the valencies are unequal.

J. W. S.

Proton source for atomic disintegration experiments. S. N. VAN VOORHIS, J. B. H. KUPER, and G. P. HARNWELL (Physical Rev., 1934, [ii], 45, 492—493).—A focussed beam of ions of 20—50 microamp. consisting mainly of protons has been obtained from a modified Lamar-Luhr low-voltage arc (A., 1934, 1052). L. S. T.

Detection of nuclear disintegration products. H. A. BARTON and D. W. MUELLER (Physical Rev., 1934, [ii], 45, 650—651).—An arrangement for detecting disintegration products by means of tracks in a photographic emulsion is described. L. S. T.

Disintegration of Li⁶ by protons and deutons. T. Y. WU and G. E. UHLENBECK (Physical Rev., 1934, [ii], 45, 553—554; cf. A., 1934, 343).—Bombardment of ordinary Li by protons gives, in addition to the 8.4-cm. group, two groups of α -particles with ranges of 6.5 and 11.5 mm. The 6.5-mm. group may be ascribed to ${}^6_3\text{Li}$. Bombardment of ${}^6_3\text{Li}$ with deuterons gives α -particles of 13.2 cm. range and protons of 30 cm. range; the latter are explained by assuming the reaction ${}^6_3\text{Li} + {}^2_1\text{H} \rightarrow {}^7_3\text{Li} + {}^1_1\text{H}$. L. S. T.

Transmutation of lithium by deuterons and its bearing on the mass of the neutron. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 550—552).—Experiments showing that γ -rays are not produced in the disintegration of Li γ deuterons are described. Hence, previous calculations of the mass of the neutron are not invalidated by this assumption. The val. given for this mass is 1.0068. L. S. T.

Artificial radioactivity produced by deuteron bombardment. M. C. HENDERSON, M. S. LIVINGSTON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 45, 428—429).—With the possible exception of C, no radioactivity was induced in Ca and in the elements from Li to Cl (Ne and S not included) by bombardment with 1.5×10^6 volt protons. With 3×10^6 volt deuterons, each element emitted both γ -radiation and ionising particles, presumably positrons, of approx. electronic mass. The half-lives of the radioelements produced in the following targets were: CaF₂ 40 sec., CaCl₂ 13 min., B₂O₃, Na phosphate, Li₂CO₃, and NH₄NO₃, approx. 2 min., Al 3 min., Mg 9 min., Be 9 min. and possibly 3 min., and C 12 min. L. S. T.

Further experiments with artificially-produced radioactive substances. H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 497—498).—When bombarded by protons, C and B₂O₃ show an activity which decays at the same rate as that produced by deuterons (see below). The intensities are approx. 10 and 20%, respectively, of those produced by deuterons. Alternative reactions are discussed. After deuteron bombardment of B₂O₃ the active material appears to be a gas which rapidly diffuses from the target. It is concluded that most of the C¹¹, assumed to be the radio-element formed, exists in the target as CO or CO₂, and little, if any, as C. L. S. T.

Disintegration of boron by deuterons and by protons. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 493—495; cf. A., 1934, 579).—The radiation obtained from B bombarded with a mixed beam of deuterons and protons has been analysed. In addition to neutrons there is a large component of γ -radiation of energy 1.6×10^6 e.v. The γ -rays are probably associated with the same transformation which produces the neutrons. This is assumed to be $B^{11} + H^2 \rightarrow C^{12} + n^1 + \gamma$, and the val. 1.6×10^6 e.v. probably corresponds with an excitation level in C^{12} . L. S. T.

γ -Rays from carbon bombarded by deuterons. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 345—346; cf. A., 1934, 579).

L. S. T.

Radioactivity from carbon and boron oxide bombarded with deuterons and the conversion of positrons into radiation. H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 430—432).—Additional data (cf. A., 1934, 579) are recorded and evidence for the assumption that the γ -rays originate from the annihilation of positrons together with electrons is advanced. C appears to be transformed by deuterons in two ways: ${}_6C^{12} + {}_1H^2 \rightarrow {}_6C^{13} + {}_1H^1 + \gamma$, ${}_6C^{12} + {}_1H^2 \rightarrow {}_7N^{13} + {}_0n^1$ and ${}_7N^{13} \rightarrow {}_6C^{13} + (+\epsilon)$. The first process is 10 times as frequent as the second. With B the supposed transformations are ${}_5B^{10} + {}_1H^2 \rightarrow {}_6C^{11} + {}_0n^1$ and ${}_6C^{11} \rightarrow {}_5B^{11} + (+\epsilon)$.

L. S. T.

Investigation of nuclear disruption of aluminium by the photographic method. M. BLAU and H. WAMBACHER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 401—410; Chem. Zentr., 1935, i, 1658).—Investigation by the photographic method confirmed the presence of particle groups found by Chadwick and Constable, and revealed a new group of range 35—50 cm. J. S. A.

Secondary emission from elements of medium mol. wt. under action of radiation from Po+Be. Z. OLLANO (Ric. sci. Prog. tec. Econ. naz., 1934, 2, 374—376; Chem. Zentr., 1935, i, 1821).—Heavy elements, except Sn and Sb, have a relatively lower absorption per mol. than light elements toward radiation from Po+Be. Sn emits soft radiation of great energy. J. S. A.

Nuclear evolution of iron, cobalt, and nickel. H. J. WATKES (Phil. Mag., 1935, [vii], 20, 738—739; cf. this vol., 427).—The isotopes ${}_{26}Fe^{58}$ and ${}_{26}Fe^{59}$ are missing, and ${}_{26}Fe^{57}$ and ${}_{28}Ni^{58}$ are stable. The schemes proposed are: ${}_{26}Fe^{58} \rightarrow {}_{27}Co^{58} \rightarrow \beta \rightarrow {}_{28}Ni^{58}$, and ${}_{26}Fe^{59} \rightarrow \beta \rightarrow {}_{27}Co^{59}$. N. M. B.

Atomic fragment of short range from heavy inert gases. H. PETTERSSON and J. SCHINTLMEISTER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 385—399; Chem. Zentr., 1935, i, 1657—1658).—Investigation of very short-range particles by means of a tube electrometer reveals the presence of such particles in addition to elastically scattered α -particles from Xe and Kr but not from Ni or I. J. S. A.

Corpuscular theory of primary cosmic radiation. W. F. G. SWANN (Physical Rev., 1935, [ii],

48, 641—648).—A survey co-ordinating available data and theory. N. M. B.

Effect of primary cosmic-ray energy on burst production. W. F. G. SWANN and D. B. COWIE (Physical Rev., 1935, [ii], 48, 649—652).—The intensity of burst-production was much greater for vertical rays than for rays limited to a direction of 45° , in agreement with the corresponding increase with altitude as compared with ray intensity. N. M. B.

Diurnal variation of cosmic-ray intensity and Nova Herculis. J. BARNÓTHY and M. FORRÓ (Nature, 1935, 136, 680—681). L. S. T.

Positive and negative ions in the primary cosmic radiation. H. J. WATKES (Nature, 1935, 136, 681).—Since equal nos. of positive and negative ions probably occur in the cosmic rays, the observed east-west asymmetry of cosmic radiation must be explained in terms other than those of an unbalanced positive component. L. S. T.

Vertical intensity of cosmic rays by threefold coincidences in the stratosphere. E. REGENER and G. PROTZER (Nature, 1935, 136, 718—719).

L. S. T.

Neutrons of high energy from cosmic-ray bursts in aluminium. G. L. LOOHER (Physical Rev., 1934, [ii], 45, 235; cf. A., 1934, 235).

L. S. T.

Secondary photons in cosmic-ray showers. C. D. ANDERSON and S. H. NEDDERMEYER (Physical Rev., 1934, [ii], 45, 295). L. S. T.

Possible explanation of the frequency distribution of the size of Hoffmann Stosse. C. G. MONTGOMERY (Physical Rev., 1934, [ii], 45, 294).

L. S. T.

Further geographic studies of cosmic rays. A. H. COMPTON, J. M. BENADE, and P. G. LEDIG (Physical Rev., 1934, [ii], 45, 294—295). L. S. T.

Comparison of absorption coefficients of different elements for cosmic rays. J. C. STEARNS and C. HEDBERG (Physical Rev., 1934, [ii], 45, 294).—The cosmic-ray energy absorbed by 6 in. of Al, Cu, Pb, and Zn, respectively, has been determined. L. S. T.

Hypothesis of the instability of the deuteron. G. N. LEWIS, M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 45, 497).—An alternative explanation for previous results (A., 1934, 471) is discussed. L. S. T.

Excitation and disintegration of protons and the neutret. R. M. LANGER (Physical Rev., 1934, [ii], 45, 495—496).—Theoretical. L. S. T.

Emission of fast particles. K. C. KAR (Current Sci., 1935, 4, 154—155).—A modification of the wave-statistical formula for the emission of fast particles from radioactive elements is proposed. W. R. A.

Collisions of very fast heavy particles. W. BRAUNBEK (Z. Physik, 1935, 96, 600—606).—Theoretical. A. B. D. C.

Theory of elementary particles. II. Electromagnetic whirls and elementary particles. N. S. JAPOLSKY (Phil. Mag., 1935, [vii], 20, 641—706; cf.

ibid., 417).—Mathematical. It is suggested that the elementary particles electrons, protons, positrons, light quanta, etc. can be considered as "whirls" or certain systems of Maxwell electromagnetic waves. In this way the quantum and relativity relationships, the de Broglie formula, and gravitation can be explained on classical electrodynamics. The theory leads to a proton-electron mass ratio agreeing with experiment. N. M. B.

Ionising effects of meteors. A. M. SKELLET (Proc. Inst. Radio Eng., 1935, 23, 132—149).—A meteor of average velocity has sufficient velocity to cause ionisation of atm. gases by impact. CH. ABS. (e)

Nuclear energies of aluminium and beryllium. H. A. WILSON (Physical Rev., 1934, [ii], 45, 430).—Bombardment data for Al and Be indicate that the nuclei of the atoms of the elements have possible energies equal to $3.85n$ or $3.85n + a$ const., where n is 0 or an integer. L. S. T.

Energy levels of inert gas configurations. C. L. BARTBERGER (Physical Rev., 1935, [ii], 48, 682—683).—A more accurate calculation of the energy levels for the configuration n^2p^2np is made (cf. Shortley, A., 1933, 1226; this vol., 556), taking account of the electrostatic interaction between groups. N. M. B.

Values of Planck's constant. K. SHIBA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 897—908).—The most probable vals. of e , e/m , and h are recalculated to be (cf. A., 1933, 884) $(4.803_2 \pm 0.02\%) \times 10^{-10}$ e.s.u., $(1.758_2 \pm 0.02\%) \times 10^7$ e.m.u., and $(6.627_1 \pm 0.04\%) \times 10^{-27}$ erg/sec., respectively. R. S. B.

Field between an α -particle and an atomic nucleus. L. SCHAMES (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 102—103).—Mathematical. The field is expressed in terms of the mass and radius of the neutron and the elementary charge. Up to a distance of 3×10^{-13} cm. the difference between the fields of H and of D is calc. to be negligible, in accordance with experiment. S. J. G.

Fundamental difference between material mass and electromagnetic mass. L. SCHAMES (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 103—104).—The mass of both positron and electron is electromagnetic and is annihilated when the two particles collide. The mass of the neutron is material and cannot be destroyed, but obeys the law of conservation of mass. S. J. G.

Bands in the neighbourhood of spectral lines in the ultra-violet. F. DUSCHINSKY (Compt. rend., 1935, 201, 542—543).—Bands described by Hulubei (A., 1931, 993) are due to interference. T. G. P.

Green flame of phosphorus hydride. E. B. LUDLAM (J. Chem. Physics, 1935, 3, 617—620).—The spectrum of the green flame of burning P has been photographed. The moment of inertia of the emitter calc. from the rotational structure of the bands (Σ — Σ) indicates that it is PH. T. G. P.

Absorption spectra of solutions in liquid ammonia. I. Solutions of metallic complex salts. H. SHIBA and T. INOUE (J. Chem. Soc.

Japan, 1935, 56, 213—220).—Solutions of complex salts of Co, Ni, and Cr in liquid NH_3 show absorption bands similar to those in aq. solution. CH. ABS. (e)

Ultra-violet absorption and colour centre formation of alkali halide crystals. E. REXER (Physikal. Z., 1935, 36, 602).—Pressure-deformation of pure KBr with 800 g. per sq. mm. raises the absorption coeff. at 203 $\text{m}\mu$ from 0.250 to 0.750 mm^{-1} . A. B. D. C.

Spectra of strontium hydride. W. R. FREDERICKSON, M. E. HOGAN, jun., and W. W. WATSON (Physical Rev., 1935, [ii], 48, 602—606).—Full data and quantum analyses of the SrH band systems, photographed at high dispersion, are reported. N. M. B.

Emission band spectrum of the OD molecule. Y. OTA (Mem. Fac. Sci. Agric. Taihoku, 1935, 15, 181—191).—The spectrum excited by an electrical discharge through H_2O vapour containing 65% of combined D was photographed, and full data for the (0,0) OD band of the $2\Sigma^+ \rightarrow 2\Pi$ transition are tabulated. From the relative intensity of lines in the P_1 , P_2 , Q_1 , and Q_2 branches the nature of the abnormal rotation of the excited OD mol. is discussed in comparison with the corresponding OH band. N. M. B.

Absorption spectra of iodine solutions and the influence of the solvent. O. J. WALKER (Trans. Faraday Soc., 1935, 31, 1432—1438).—The mol. extinction coeff. for violet solutions of I in eight chlorinated hydrocarbons has been measured. In non-polar solvents λ_{max} is at 516—518 $\text{m}\mu$, and in others is displaced towards shorter λ to an extent which increases with the dipole moment. The types of interaction between I and the solvent are discussed. F. L. U.

Absorption spectrum of Eu^{+++} in crystalline $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. E. J. MIEHAN (J. Chem. Physics, 1935, 3, 621—627; cf. Spedding *et al.*, this vol., 144).—The absorption has been studied from 14° to 290° abs. Variations in intensity with temp. establish levels 21 cm^{-1} and 41 cm^{-1} above the basic one, and indicate others of 67 cm^{-1} , 86 cm^{-1} , and higher levels. Unusual const. energy differences exist between lines at the lowest temp. T. G. P.

Absorption spectrum of selenium dioxide. L. BLOCH, E. BLOCH, and C. S. PIOW (Compt. rend., 1935, 201, 654—655).—A series of absorption bands, degraded to the red, was observed at λ 2400—3200 Å. in the vapour of SeO_2 heated in vac. to 250°. With rise in temp. other bands were observed at approx. λ 3700—4300 Å. H. J. E.

Optical absorption and double linking. V. Absorption at low temperatures of compounds with conjugated doubly-linked carbon atoms. K. W. HAUSER, R. KUHN, and G. SEITZ. VI. Fluorescence of diphenylpolyenes. K. W. HAUSER, R. KUHN, and E. KUHN (Z. physikal. Chem., 1935, B, 29, 391—416, 417—454; cf. this vol., 1300).—V. The position of the absorption bands of the diphenylpolyenes (I), polyenecarboxylic acids, and lycopene in solution at -196° is given by $\nu = (\nu_0 + 37.0l + 47.1m) \times 10^{12} \text{ sec}^{-1}$, where l , m =

0, 1, 2. . . (I) have other bands at shorter $\lambda\lambda$, which are similar to bands of Ph_2 in position and structure and are attributed to the Ph groups; the height of the max. do not vary with the no. of C:C linkings. The spectra of diphenylacetylenes differ in type from those of (I). Fundamentally the spectra of the porphyrins are similar to those of the aliphatic polyenes, but on these bands other vibrations are superimposed.

VI. The absorption and fluorescence spectra of the diphenylpolyenes, $\text{Ph} \cdot [\text{CH}:\text{CH}]_n \cdot \text{Ph}$, are in the relation of object to mirror image in respect of the position, but not of the height, of the bands. With increase in n the fluorescence bands shift more than the absorption bands and the heights of the max. fall. At -196° the positions of the fluorescence bands are given by ν (cm^{-1}) $= \nu_0 - 1550\nu_1'' - 1160\nu_2''$, where ν_0 is the position of the band of shortest λ and ν_1'' , $\nu_2'' = 0, 1, 2, 3, \dots$. The band separations 1550 and 1160 cm^{-1} correspond with the strongest lines in the Raman spectra and represent frequencies of the C:C linking. The variation of fluorescence with concn., solvent, temp., and state of aggregation agrees with the theory of quenching collisions (cf. A., 1925, ii, 474). The fluorescence of dodecapentanoic acid and isomethylbixin proves that ring closure is not essential for fluorescence; they have almost the same fluorescence spectra. R. C.

Optical absorption of porphyrins. II. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1935, 174, 81—103; cf. this vol., 10).—Absorption in dioxan solution has been determined. Comparison of the absorption spectra of porphyrins with those of the corresponding chlorins supports the view that in the latter the porphin framework has changed into a dihydroporphin (cf. *ibid.*, 871). Substances with a structure based on dihydroporphin, such as chlorins, pyroporphorbide-a, and methylphæophorbide-a, have very similar visible absorption spectra. Uroporphyrin Petry, uroporphyrin Pteris, and Me_8 1:3:5:7-tetramethylporphyrin-2:4:6:8-tetrasuccinate are spectroscopically identical. The absorption curve of hæmin solution has been determined. R. C.

Absorption spectra of tervalent halides dissolved in ether and their dissociation products. S. KATO and F. SOMENO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 95—111).—The absorption spectra in range 2000—7000 Å. of solutions of trihalides of As, Sb, Bi, Fe, and Tl in Et_2O , and of the vapours of As, Sb, and Bi trihalides, have been determined. The Raman spectra of AsCl_3 , AsBr_3 , and SbCl_3 in Et_2O are similar to the spectra with the liquid salts, but differ from those with the crystals. Photo-dissociation with light from a Hg-vapour lamp or C arc has been studied chemically, the products being lower halides or metal, except with AsI_3 (As_2O_3), SbI_3 (SbOI), and BiI_3 (BiOI). The mols. of salt in Et_2O are in the ground state, but are deformed by the solvent. R. S. B.

Ultra-violet absorption spectra of certain compounds derived from living cells. F. F. HEYROTH and J. R. LOOFBOUROW (Physical Rev., 1934, [ii], 45, 126; cf. A., 1934, 1112). L. S. T.

Two new bands of CO_2 in the photographic infra-red. G. HERZBERG and H. VERLEGER (Physical Rev., 1935, [ii], 48, 706).—New bands at 1.2031 and 1.2178 μ , showing fine structure, have been photographed. Results agree with the predictions of Adel (cf. A., 1933, 661, 885). N. M. B.

Rotation spectra of ammonia and ND_3 . R. B. BARNES, W. S. BENEDICT, and C. M. LEWIS (Physical Rev., 1934, [ii], 45, 347; cf. this vol., 806). L. S. T.

Absorption spectra, in the near infra-red, of amines and amides. Use of the phenomenon of "dissimulation" in studying amphoteric ions. Influence of neighbouring groups. (MME.) M. FREYMAN and P. RUMPF (Compt. rend., 1935, 201, 606—608; cf. this vol., 563).—The NH absorption band at approx. 1.04 μ is not observed in a 20% aq. solution of glycine, or in saturated aq. taurine, but is observed in solutions of the Na and Li salts, respectively. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ does not show the band, but its Na derivative does. N has a co-ordination no. of 4 when the band is not observed. Data for the position of this NH band in various amides are recorded. The structure of these compounds is discussed. H. J. E.

Absorption of simple substituted hydrocarbons in the near infra-red. I. Influence of state of aggregation. (Gas-liquid comparison.) R. MECKE and O. VIERLING (Z. Physik, 1935, 96, 559—570).—Absorption spectra of the third CH overtone were obtained for MeCl, MeBr, EtCl, vinyl chloride, and $(\text{CH}_2)_2\text{O}$ in the gas and liquid phases, and data are summarised for $n\text{-C}_6\text{H}_{14}$, cyclo-hexane and -hexanol, C_6H_6 , and dioxan. Condensation to the liquid state always lowers the frequency of vibration in a series of overtones by the amount $\Delta\nu$, where $\Delta\nu/\nu$ is a const. Closure of a ring also decreases the frequency, as does an increase in ring size. A. B. D. C.

Infra-red spectrum of hexadeutero benzene and the structure of benzene. W. R. ANGUS, C. R. BAILEY, C. K. INGOLD, A. H. LECKIE, C. G. RAISIN, J. W. THOMPSON, and C. L. WILSON (Nature, 1935, 136, 680; cf. this vol., 914).—The principal frequencies of the infra-red spectra of C_6D_6 and C_6H_6 are compared. The new measurements for C_6D_6 agree, on the whole, with those of Barnes and Brattain (this vol., 1189). Coincidences between certain frequencies of the Raman and infra-red spectra of C_6H_6 and of C_6D_6 , which led to the rejection of the plane hexagonally symmetrical C_6H_6 model, are now regarded as accidental; the model is retained. L. S. T.

Structure and interpretation of the infra-red absorption spectra of crystals. R. B. BARNES, R. R. BRATTAIN, and F. SEITZ (Physical Rev., 1935, [ii], 48, 582—602).—A detailed investigation of the absorption spectrum of MgO in the near infra-red is reported; the fundamental absorption is accompanied by much secondary structure. Results are interpreted on the basis of a quantum-mechanical treatment of anharmonic potential forces, and show that the absorption spectra of a MgO-type cubic crystal should have a very complicated secondary structure. N. M. B.

Infra-red absorption by Rochelle salt crystals. J. VALASEK (Physical Rev., 1934, [ii], 45, 654—655).—Optical measurements indicate that the unusually large ϵ of these crystals is not due to the polarisation of the H_2O mols. L. S. T.

Rayleigh scattering in crystals. F. MATROSSI (Z. Physik, 1935, 96, 698).—Corrections (cf. this vol., 146). A. B. D. C.

Doppler effect in light scattering in liquids. II. Polarisation of the transversely scattered radiations. B. V. R. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 236—241; cf. this vol., 1053).—For light scattered transversely by CCl_4 , PhMe, and CS_2 , the two Doppler components are completely polarised, and the central component is almost completely polarised. N. M. B.

Bibliography of the Raman effect. III. S. C. SIRKAR and D. CHAKRAVARTY (Indian J. Physics, 1935, 9, 553—622; cf. A., 1933, 445).—A complete list of papers classified under subject headings, authors, and substances studied is given. N. M. B.

Intensity of Raman effect. A. CARELLI (Rend. Accad. Sci. Napoli, 1933, [iv], 3, 156—160; Chem. Zentr., 1935, i, 1827).—The ratio of intensity of the Raman line of CCl_4 , $\Delta\nu$ 1550 cm^{-1} , to its first overtone is 1 : 10. An explanation is advanced. J. S. A.

Raman spectrum of (A) deuterium and (B) hydrogen deuteride. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 303—309, 310—312).—(A) Using the λ 4358 Hg line as incident radiation, and 17 atm. pressure, rotation lines ± 179.5 , ± 297.4 , 415.2, 530.8, and 643.5 cm^{-1} , and a vibration line of shift 2992.7 were observed. Results agree with available mol. const. data. Relative rotational intensities agree with a nucleus of one unit spin and obeying the Bose-Einstein statistics. Intensity distribution agrees qualitatively with the theory of rotational Raman scattering in diat. mols.

(B) With λ 4358, HD showed a spectrum containing 267, 442, and 618 cm^{-1} , arising respectively from the rotational transitions $0 \rightarrow 2$, $1 \rightarrow 3$, and $2 \rightarrow 4$, and agreeing with calc. vals. The anti-Stokes line due to the transition $2 \rightarrow 0$ was found. Alternating intensities were not observed, and the line corresponding with $1 \rightarrow 3$ is the most intense. N. M. B.

Raman spectrum of heavy water. R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 291—302).—The spectrum shows a strong band with three imperfectly resolved components of frequency shifts 2363, 2515, and 2662 cm^{-1} , and a sharp band with frequency shift 1235 cm^{-1} with a feeble companion at about 1110 cm^{-1} , and a strong low-frequency band 175 cm^{-1} . Comparison of H_2O and D_2O spectra shows many similarities. The valency angles and force consts. do not alter much in passing from H_2O to D_2O . The triple structure of the principal band indicates polymerisation similarly to H_2O . The low-frequency band is connected with the nature of the liquid state. N. M. B.

Raman spectrum of liquid heavy water. E. BAUER and M. MAGAT (Compt. rend., 1935, 201,

667—669).—The Raman shifts observed for D_2O were 170, 350, approx. 500, 1207, 2389, and 2509 cm^{-1} , the corresponding vals. for H_2O being 176, 500, 700, 1659, 3221, and 3435 cm^{-1} . H. J. E.

Constitution of water in solutions of non-electrolytes. I. Acetone. C. S. S. RAO (Phil. Mag., 1935, [vii], 20, 587—594; cf. this vol., 295).—The intensity distribution along the Raman H_2O band was investigated in solutions of 0, 25, 50, and 75% $\text{C}_2\text{H}_5\text{O}$. The band becomes sharper with increasing concn. of dissolved substance; the intensity max. does not shift with change of concn. as in the case of strong and weak electrolytes; the smaller frequency branch of the intensity curve shifts and changes in shape with increasing concn. of $\text{C}_2\text{H}_5\text{O}$. Results indicate a preponderance of double H_2O mols. and double hydrates over the other types, especially at high concns. of the dissolved substance. N. M. B.

Molecular clustering in binary liquid mixtures. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 221—231; cf. this vol., 11).—A comparative study of the intensity, by the photo-electric method, and the depolarisation of light scattered transversely by mixtures of PhOH and H_2O in different proportions and at different temp. was made. The lowest vals. for the depolarisations of light unpolarised, and perpendicularly and horizontally polarised, were found with the crit. composition mixture (34% PhOH) at the crit. solution temp. The intensity of scattering increases considerably for the 34% mixture as the crit. temp. is approached. The tendency for the formation of, and size of, clusters depend on the temp. and composition of the mixture. These phenomena are most pronounced for the crit. mixture at the crit. temp. The relation of results to anomalies of viscosity, magnetic birefringence, etc. is examined. N. M. B.

Raman spectrum of phosphorus. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 260—264).—Data for solid, liquid, vapour, and solution in CS_2 are given. Only small changes in frequency are found in passing from one state to another, indicating the non-polar character of the mol. In all cases a strong fluorescence band extends from 6230 to 6550 Å. N. M. B.

Raman spectra of heavy and light phosphine. M. DE HEMPTINNE and J. M. DELFOSSE (Bull. Acad. roy. Belg., 1935, [v], 21, 793—799).—The Raman spectra of PH_3 and PD_3 in the liquid and solid state have been investigated. Liquid PD_3 gave lines 1664, 807, and 740 cm^{-1} . The most intense lines are: PH_3 (liq.) 2306, (gas) 2327; PD_3 (liq.) 1664, (gas) 1684; PHD_2 , 1825; PDH_2 , 1755 cm^{-1} . A. J. M.

Raman spectrum of nitrogen pentoxide. J. CHEDIN (Compt. rend., 1935, 201, 552—554).—Raman spectra of N_2O_5 in HNO_3 , H_2SO_4 , CCl_4 , and CHCl_3 are recorded. T. G. P.

Raman spectrum and constitution of fuming sulphuric acid. N. G. PAI (Phil. Mag., 1935, [vii], 20, 616—623).—Raman data obtained for four concns. of fuming H_2SO_4 indicate that at low concn. all the SO_3 mols. go into combination, forming $\text{H}_2\text{S}_2\text{O}_7$, and the H_2SO_4 lines weaken in intensity;

at higher concn. much free SO_3 and S_2O_6 are present; in 71% acid their relative proportions are approx. as in a SO_3 - S_2O_6 mixture in equilibrium; in 80% acid a small concn. of free H_2SO_4 mols. exists.

N. M. B.

Influence of intermolecular action on the Raman effect for liquids. W. BUCHHEIM (Physikal. Z., 1935, 36, 694—711).—The theoretical effect of an electric field on Raman scattering is considered. The Raman lines should increase in width with increasing field strength, owing to alteration of mol. vibrations by the effect on the electron charge cloud. A displacement of the lines is also to be expected. Lines forbidden by mol. symmetry may appear on application of a field. The widening of the lines due to infra-red active vibrations by electrodynamic interaction is considered. The variation in intensity of the Raman spectrum of a substance on mixing with another was investigated in the following cases: C_6H_6 mixed with C_6H_{14} and with CHCl_3 ; CCl_4 in COme_2 mixed with C_6H_6 ; CHCl_3 in C_6H_6 mixed with C_6H_{14} .

A. J. M.

Raman spectra of methyl deuteride. G. E. MACWOOD and H. C. UREY (J. Chem. Physics, 1935, 3, 650—651).—Vibrational frequencies of MeD in the Raman spectra have been measured. They are higher (max. +30 cm^{-1}) than those calc. by Dennison and Johnston (Physical Rev., 1935, [ii], 47, 93). No rotational structure was observed.

T. G. P.

Raman spectrum of neopentyl deuteride. D. H. RANK, E. R. BORDNER, and K. D. LARSEN (Physical Rev., 1934, [ii], 45, 566).—The results show that the vibrational degeneracy of the neopentane mol. is partly removed by the substitution of a D for a H. The C-D vibration becomes evident through the appearance of a line at 2179 cm^{-1} .

L. S. T.

Raman spectra of dioxan and tetralin. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 279—290).—Full data, obtained with the filters used, are tabulated. The spectrum of dioxan consists of 24 lines, 14 being new, and closely resembles that of *cyclohexane*. Tetralin gave 11 new lines. Results are discussed with reference to mol. structure.

N. M. B.

Raman spectra of *cis*- and *trans*-decalins. S. K. K. JATKAR (Indian J. Physics, 1935, 9, 545—551).—Using a sample containing 36% of *cis*-form prepared by fractional distillation, and a sample containing mostly *trans*-form prepared by keeping ordinary decalin in contact with AlCl_3 for 24 hr., Raman data are tabulated, and results are discussed in relation to mol. structure.

N. M. B.

Chemical reactivity and Raman spectra of the eugenols, vanillins, and saftroles, and of piperonal, estragol, and anethole. B. SUSZ, E. PERROTTET, and E. BRINER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 133—134).—The oxidation of the above compounds by O_3 has been studied and their Raman spectra have been determined. All show the characteristic frequencies of the C_6H_6 nucleus, and C:O and C:C linkings where present.

S. J. G.

Raman spectra of solutions of pyrogallol, gallic acid, and tannin. E. BRINER, S. FRIED, and B. SUSZ (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 178—180).—Raman frequencies of pyrogallol and of gallic acid in EtOH solution and of tannin in aq. solution are recorded.

S. J. G.

Coloration of compounds of different elements by cathode rays. H. NAGAOKA and T. MISHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 77—94).—The intensity of the coloration produced when cathode rays of 0—10⁴ volts impinge on various metallic salts has been determined. It is inferred that the colours are due to dissociation of mols. near the surface, the metallic atoms produced being protected by a surface layer of undissociated salt.

R. S. B.

Phosphorescent beryllium nitride. S. SATOH (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 920—924).—Phosphorescent Be_3N_2 , activated by Al, gives a cathode-ray spectrum with a continuous band at 4200—4900 Å., max. at 4650 Å.

R. S. B.

Fluorescence in *cyclohexane*. R. PADMANABHAN (Proc. Indian Acad. Sci., 1935, 2, A, 209—212).—Using an improved continuous distillation apparatus, pure *cyclohexane* has no fluorescence; that reported by Haberl (cf. this vol., 11) is due to photochemical decomp. in which the region λ 2400—2600 is active.

N. M. B.

Comparison of effect of ordinary and *geno*-alkaloids on the fluorescence of uranine solutions. C. ACHARD, A. BOUTARIC, and J. BOUCHARD (Compt. rend., 1935, 201, 629—631).—The *geno*-alkaloids (e.g., *geno*-strychnine hydrobromide) do not inhibit the fluorescence of aq. uranine in the same way as the normal alkaloid.

H. J. E.

Spray electrification of liquids. S. CHAPMAN (Physical Rev., 1934, [ii], 45, 135—136).—Data correlating drop size, sign and magnitude of the charge, γ , and ϵ are given for H_2O , glycerol, NH_2Ph , PhNO_2 , and "ameroil." In general, larger drops ($4\text{--}5 \times 10^{-4}$ cm. radius) have the greater charges, and the greater is ϵ the higher is the charge val.

L. S. T.

Contact potential difference between clean and oxygenated tungsten. A. L. REIMANN (Phil. Mag., 1935, [vii], 20, 594—607).—The contact p.d. at room temp. between slightly electronegatively contaminated W and W when O_2 -covered, for most effectively raising the work function was 1.70 volts. The calc. p.d. at 1500° abs. between clean W and W less effectively O_2 -covered than above is 1.75 volts. Loss of electronegateness of oxygenated W by evaporation of O_2 was detected at 1300° abs., and beyond this the rate of evaporation increased rapidly with rise of temp. A clean W surface oxygenated when hot or cold showed no difference in electronegateness or volatility of O_2 . The most complete O_2 -covering (of the degrees of covering stable in vac.) most effectively raises the work function.

N. M. B.

Photo-electric properties and electrical resistance of metallic films. D. ROLLER and D. WOOLDRIDGE (Physical Rev., 1934, [ii], 45, 119—120).—As the average thickness of a Cd film decreases, the electrical resistivity increases from the val. charac-

teristic of the metal in bulk at first slowly and then more rapidly, until just beyond a crit. thickness it rapidly approaches an infinite val. L. S. T.

Photosensitive layers of the photo-electric conductive thallium cell. (MISS) C. ASAI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 797—832).—Heating of a film of Tl in air yields Tl_2O , Tl_2O_3 , etc. Distillation of Tl_2S gives the amorphous or cryst. form according to conditions of distillation, the former being converted into the latter by annealing. The photo-electric sensitivity is high when Tl_2O and Tl are disseminated in cryst. Tl_2S , so the conductivity is explicable on the impurity theory of semiconductors. J. W. S.

Spectral photo-electric poly-selectivity of various surface layers. W. KLUGE (Z. Physik, 1935, 96, 691—697).—Decrease in sensitivity due to adsorption of O_2 has been studied at λ from 200 to 1100 $m\mu$ for the layers $Ag-Cs_2O-Cs$, $Cu-Cs_2O-Cs$, and Cs . A. B. D. C.

Dielectric loss in electrolytic barrier layers at high field intensities to 10^7 volts per cm. A. GUNTHER-SCHULZE and H. BETZ (Z. Physik, 1935, 96, 686—690).—The loss angle for Al_2O_3 is 0.02, and for Ta_2O_5 is 0.075, both at 50 cycles; its variation with time of measurement, formation voltage, field intensity, time of formation, age, and frequency is also given. A. B. D. C.

Measurement of the variation of the dielectric constant of water with extent of adsorption. G. H. ARGUE and O. MAASS (Canad. J. Res., 1935, 13, B, 156—166).—Apparatus and technique for determining the dielectric const. of cellulose containing various amounts of adsorbed H_2O are described. Dielectric consts. of the adsorbed H_2O have been calc. for the concn. range 0—18%. The dielectric const. of H_2O initially adsorbed is > 0.25 of that of liquid H_2O , but increases with increasing amount of adsorption until it approximates to that of liquid H_2O as the fibre becomes saturated. E. S. H.

Structure of the naphthalene nucleus. N. NAKATA (Bull. Chem. Soc. Japan, 1935, 10, 318—323; cf. A., 1931, 1281).—Dipole moments of a no. of $C_{10}H_8$ derivatives are given. Only the α -positions appear to be aromatic, and centrosymmetry is indicated. R. S.

Dipole moment of tetralin. M. A. G. RAO and S. S. RAO (Proc. Indian Acad. Sci., 1925, 2, A, 232—235).—The val. as measured in C_6H_6 as solvent is $0.4-0.5 \times 10^{-18}$. N. M. B.

Physical chemistry of betaines and related substances. I. Dielectric constants and apparent molal volume. J. T. EDSALL and J. WYMAN, jun. (J. Amer. Chem. Soc., 1935, 57, 1964—1975).—Data are recorded for betaines and for *N*-dimethylantranilic acid (I) and its Me ester (II) in H_2O , EtOH, C_6H_6 , and their mixtures. Approx. dipole moments have been calc. for the relatively rigid benzbetaines. In solvents of low dielectric const., the dielectric increments (and probably the moments) of all the betaines studied are much $<$ their vals. in H_2O , an effect which appears to be

due to deformation rather than association. (I) exists largely as a zwitterion in all the solvents; in C_6H_6 its dipole moment is 3 times that of (II). The electrostriction of the solvent produced by betaines in H_2O is $<$ that produced by similar NH_2 -acids; the electrostriction in solvents of low dielectric const. is much $>$ in H_2O . E. S. H.

Electric moments of organic compounds. J. N. PEARCE and L. F. BERHENKE (J. Physical Chem., 1935, 39, 1005—1010).—The dielectric consts. and d of dil. solutions of *p*-bromo-, *p*-hydroxy-, and *p*-methoxy-benzaldehyde, *p*-tolualdehyde, β -ethylhexan- α -ol, α -ethylhexaldehyde, tri-, di-, and mono-hydroxyethylamine in C_6H_6 and dioxan have been determined at 25°. The total polarisation and dipole moments have been calc. E. S. H.

Constitution of [alkyl] polysulphides. I and II. S. BEZZI (Gazzetta, 1935, 65, 693—703, 704—723).—I. Measurements of d , b.p., refractive index, and of mol. wt. in C_6H_6 have been made for Et, Pr, Bu, and isohexoyl mercaptides, sulphides, disulphides, and tetrasulphides. The at. refraction of S increases from 7.95 in the mercaptides to 8.76 in the tetrasulphides.

II. Viscosity measurements for the above-mentioned substances are recorded. The viscosity of the pure substances is a function of the mol. wt., and is independent of the constitution. From the viscosities of dil. solutions of these substances in $CHCl_3$ and in Et_2O it is shown that the length of the mol. is the same (for a given alkyl radical) in the mono-, di-, and tetra-sulphides, and that, therefore, chains of S atoms are not present. O. J. W.

Behaviour [rotation] of benzylamine tartrate in acetic acid. E. DARMOIS and I. PEYCHES (Bull. Soc. chim., 1935, [v], 2, 1656—1668).— $[\alpha]$ was determined, using Hg lines, for benzylamine tartrate (I) and tartaric acid (II) at different concns. in AcOH. $[\alpha]$ for the tartrate ion is independent of concn. for (II), but increases linearly with the (concn.) $^{1/3}$ for (I). The effect of the addition of H_2O on the val. of $[\alpha]$ is discussed. Vals. of electrical conductivity for solutions of (I) and NMe_4 tartrate in AcOH and with added H_2O are also given. F. R. G.

Anomalous rotatory dispersion of *l*- β -pinene. I. R. PADMANABHAN and S. K. K. JATKAR (J. Indian Chem. Soc., 1935, 12, 518—526).—Tests on samples of purified β -pinene indicate that the anomaly in rotatory dispersion at about 2800 Å. is due to a closely associated impurity which is difficult to remove. The anomaly in the ultra-violet region is a characteristic of β -pinene. This is confirmed by the Raman spectra of the fractions on distillation. As there is no evidence of absorption in the region of anomaly, the latter is not due to a Cotton effect, but is attributable to a superposition effect caused by a second rotation of opposite sign and different dispersion. This second rotation is not due to induced dissymmetry of the semicyclic double linking, because camphene, of similar structure, has normal dispersion. J. W. S.

Magneto-optical rotation of uranyl salts. S. S. BHATNAGAR, P. L. KAPUR, and N. R. VERMA (J.

Indian Chem. Soc., 1935, 12, 514—518).—The mol. rotation of UO_2^{++} , determined from the magneto-optical rotations of $\text{UO}_2(\text{NO}_3)_2$ and UO_2Cl_2 solutions, is about -8 , whereas the val. from measurements on UO_2SO_4 solutions is about -11 , the difference being attributed to the formation of complexes between UO_2^{++} and H_2SO_4 . J. W. S.

Magnetic double refraction and light scattering in fused nitrates. V. N. THATTE (Proc. Indian Acad. Sci., 1935, 2, A, 244—248; cf. A., 1934, 942).—Data for $\text{Zn}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ are given. The calc. magnetic and optical anisotropies of the NO_3 are the same as for the NO_3 in HNO_3 and in cryst. nitrates. N. M. B.

Influence of substituents in bases and anions on the co-ordination number of a metal. VII. **Influence of electric moment on the number of molecules of base fixed by a salt.** A. ABLOV (Bull. Soc. chim., [v], 2, 1724—1736; cf. A., 1934, 755).—If the dipole moment of a negative group substituted in the *p*-position in NH_2Ph is $\pm 1.5 \times 10^{-18}$ it increases the no. of mols. of base co-ordinated by $(\text{CCl}_3\text{CO}_2)_2\text{Ni}$ and $(\text{CHCl}_2\text{CO}_2)_2\text{Ni}$, whilst the same group in the *o*-position has the reverse effect. The results are discussed with reference to the electrostatic theory of valency. J. W. S.

Concentration of H^3 and O^{18} in heavy water. W. BLEAKNEY and A. J. GOULD (Physical Rev., 1934, [ii], 45, 281—282).—Results obtained with heavy water containing 70—98% D show that the ratio $\text{H}^3 : \text{D}$ is < 1 in 10^5 . Hence, in ordinary H_2 the ratio $\text{H}^3 : \text{H}^1$ is probably < 1 in 5×10^8 . In O_2 obtained by electrolysis of nearly pure D_2O yielding 98% D_2 , no increase in the ratio $\text{O}^{18} : \text{O}^{16}$ was detected. L. S. T.

H^3 in heavy hydrogen. W. W. LOZIER, P. T. SMITH, and W. BLEAKNEY (Physical Rev., 1934, [ii], 45, 655).—Measurements with a more sensitive apparatus give an abundance ratio $\text{H}^3 : \text{D}$ of $5 : 10^6$ in 99% D_2 obtained by electrolysis of D_2O . The ratio $\text{H}^3 : \text{D}$ in natural H is probably $\approx 1 : 10^9$. L. S. T.

Stable hydrogen isotope of mass three. M. A. TUVE, L. R. HAFSTAD, and O. DAHL (Physical Rev., 1934, [ii], 45, 840—841).—Range measurements indicating H^3 nuclei from stable H^3 atoms present in the order of 1 in 10^6 in 98% D_2 are described. L. S. T.

Wandering of adsorbed atoms along the surface of solid bodies. A. GEHRTS (Z. tech. Phys., 1934, 15, 456—461; Chem. Zentr., 1935, i, 1344).—Activation and deactivation processes are interpreted in terms of Volmer's conception of atom wandering. J. S. A.

Affinity factors in molecular collisions. A. EUCKEN (Oesterr. Chem.-Ztg., 1935, 38, 162—166).—A lecture. F. L. U.

Calculation of vibrational isotope effect in polyatomic molecules by a perturbation method. E. B. WILSON, jun. (Physical Rev., 1934, [ii], 45, 427).—Mathematical. L. S. T.

Proper vibrations of heavy acetylene and ethylene halides. Y. MORINO and S. MIZUSHIMA

(Physikal. Z., 1935, 36, 600—602).—Assuming the C-H equilibrium separation 1.01 \AA . and the C-C 1.226 \AA ., together with two observed valency and deformation frequencies for C_2H_2 , frequencies are calc. for C_2HD , and C_2D_2 . Similar calculations are made for $\text{C}_2\text{H}_4\text{Cl}_2$ and $\text{C}_2\text{H}_4\text{Br}_2$, and compared with Raman displacements. A. B. D. C.

Analytical representation of the potentials of diatomic molecules and their determination from spectroscopic data. I. General theory. II. Application to CdH and N_2 . E. A. HYLLEBRAS (Z. Physik, 1935, 96, 643—660, 661—668).—I. A general expression for the potential-nuclear separation curve is given; it includes those of Morse and of Rosen and Morse as particular cases, and is determined from D , $h\nu_e$, and rotation consts. An energy formula for vibrational levels is deduced.

II. The above formula is applied to the $^2\Sigma$ -state of CdH and gives excellent reproduction of Rydberg's curve (cf. A., 1932, 104). It also gives improved results for the $1^1\Sigma$ -state of N_2 . A. B. D. C.

Potential curve for diatomic homopolar molecules. Application to CdH and N_2 . E. A. HYLLEBRAS (Physikal., 1935, 36, 599—600).—Preliminary notes (cf. preceding abstract). A. B. D. C.

(C·C)_{diat.} linking energy. H. GERSHINOWITZ (J. Physical Chem., 1935, 39, 1041).—A criticism (cf. this vol., 1058). E. S. H.

Moments of inertia and the shape of the ethylene molecule. R. M. BADGER (Physical Rev., 1934, [ii], 45, 648).—Available spectroscopical data agree with a plane symmetrical structure, and the moments of inertia calc. are 33.2×10^{-40} , 27.5×10^{-40} , and $5.70 \times 10^{-40} \text{ g. cm}^2$, respectively, in the ground state. Vals. for the C-C and C-H distances and for the angle between the C-H linkings consistent with these moments are 1.37 \AA ., 1.04 \AA ., and 126° , respectively. L. S. T.

Periodic unequal potential minima and torsion oscillation of molecules. T. Y. WU (Physical Rev., 1934, [ii], 45, 66—67).—The torsion oscillation of mols. of the *cis*- and *trans*-forms of $\text{C}_2\text{H}_2\text{Cl}_2$ is discussed. L. S. T.

Suggested improvements of Morse's rule. C. H. D. CLARK and J. L. STOVES (Nature, 1935, 136, 682).—The modification of Morse's rule previously suggested (A., 1934, 833) gives better approximations to experimental vals. than those of other workers (cf. this vol., 685). L. S. T.

Potential energy curves and structure of the alkaline-earth oxides. P. C. MAHANTI (Indian J. Physics, 1935, 9, 517—536).—Curves for the different electronic states of BeO , MgO , BaO , CaO , and SrO are drawn according to Morse's function. The electronic configuration, dissociation energy, and the products of dissociation in each state are discussed, and similarities in the spectra of the different members are traced. N. M. B.

Extra negative term in the incoherent part of the diffuse scattering of X-rays from neon-like crystals. G. E. M. JAUNCEY and J. H. DEMING

(Physical Rev., 1935, [ii], 48, 577—581; cf. A., 1934, 1148).—Measurements of the scattering vals. of NaF, MgO, and SiC at 295° abs. lead to results in good agreement with the Waller-Hartree theory of the extra negative term, and give evidence for the operation of the Pauli exclusion principle on the outer shell electrons. N. M. B.

Stress analysis by X-ray diffraction. C. S. BARRETT and M. GENSAMER (Physical Rev., 1934, [ii], 45, 563).—Mathematical. L. S. T.

Selective X-ray diffraction from artificially stratified metal films deposited by evaporation. J. W. M. DuMOND and J. P. YOUTZ (Physical Rev., 1935, [ii], 48, 703).—Stratified films deposited on glass consisting of 100 layers of Au alternating with 100 layers of Cu, and giving selective X-ray diffraction of Mo K radiation in the first order, have been produced. The total thickness is approx. 10,000 Å. and the "grating const." 100 Å. N. M. B.

Ultra-soft Rontgen radiation and lattice binding forces. H. BROILI, R. GLOCKER, and H. KIESSIG (Ergeb. Tech. Rontgen., 1934, 4, 94—99; Chem. Zentr., 1935, i, 1500).—The K α line of graphite differs from that of diamond in the distribution of intensity amongst its 4 components. The difference is attributed to the lattice forces, four homopolar linkings being present in diamond, and three homopolar and one very loose quasi-metallic linking in graphite. SiC resembles diamond, but the C line of Be carbide shows a typical heteropolar linking. The structure of the Be line indicates complete mobility of the conductivity electrons (electron gas state). J. S. A.

Precipitation-hardening and secondary structure. K. H. MOORE (Physical Rev., 1934, [ii], 45, 296).—A preliminary report on the use of polarised light in investigating a possible connexion between pptn.-hardening and the secondary or mosaic structure of crystals, with special reference to a Cu-Be (2.5% Be) alloy. L. S. T.

Bitter's powder patterns. K. J. SIXTUS (Physical Rev., 1934, [ii], 45, 565).—Three different types are distinguished in the Bitter powder patterns (A., 1932, 1077) of single crystals of Si-Fe (3.5% Si). The different directions of the patterns can be explained by the present theory of the magnetisation process. L. S. T.

Molecular field of liquids. J. WEIGLE (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 105—107).—Mathematical. An expression is derived on the assumption that a liquid has a pseudo-cryst. structure, one mol. being imagined fixed and the others arranged somewhat as in a crystal lattice blurred by thermal agitation. S. J. G.

Crystallisation of melts. III. J. MEYER and W. PROFF (Z. anorg. Chem., 1935, 224, 305—314; cf. this vol., 811).—Supercooling of H₂O and C₆H₆ is shown to depend on the presence of nuclei, the nature of the surface of the containing vessel, and purity. Distilled H₂O, filtered through collodion into a quartz vessel and covered with paraffin, was kept liquid at -33°. The growth of single crystals

of ice from the surface of supercooled H₂O into the air-free space above is discussed. T. G. P.

Sub-boundaries in a crystal grown by the Bridgman method. W. H. GEORGE (Nature, 1935, 136, 392).—A photomicrograph of a single crystal of Cu grown by the Bridgman method and etched with HNO₃ suggests that the crystal has broken down into a large no. of smaller ones, the outlines of which appear as curved lines. The markings are similar to the "sub-boundary" or "veined" structures observed in many metals. L. S. T.

Polymorphism from viewpoint of Rontgen investigation II. Polymorphism and atomic structure of elements. Polymorphism of inorganic compounds. H. STINTZING (Ergeb. tech. Rontgen., 1934, 4, 113—129; Chem. Zentr., 1935, j, 1814—1815).—Elements with crystal lattices other than cubic face- or body-centred, or hexagonal close-packed, and particularly those with lattices of low co-ordination no., are especially prone to polymorphism. Only elements for which $\log d/(n-1)$ is $<$ that for the inert gases exhibit polymorphism (d —interat. lattice distance and $n-1$ =principal quantum no. of the highest filled electron shell). Polymorphism in inorg. compounds is a constitutive property, and occurs only when one element is highly polymorphic, especially with O or S. J. S. A.

Stereochemistry of solid substances. W. BILTZ (Ber., 1935, 68, [A], 91—108).—A lecture. H. W.

Large artificial crystals of graphite. K. S. KRISHNAN (Physical Rev., 1934, [ii], 45, 115).—The crystal flakes composing the large artificial crystals prepared by Goetz *et al.* are not necessarily parallel to one another (cf. A., 1933, 1128). L. S. T.

Production of "colloidal single crystals." A. GOETZ (Physical Rev., 1934, [ii], 45, 282—283).—A reply to criticism (see above). L. S. T.

Attempts to produce relief patterns by the direct electrographic effect. E. WILCOX and P. H. CARR (Physical Rev., 1934, [ii], 45, 286).—Partial success in producing relief patterns by taking advantage of the direct electrographic effect, i.e. the partial inactivity in metallic surfaces towards corrosive vapours produced by exposure to cathode rays, is described. L. S. T.

X-Ray determination of the chemical composition of oxide-coated cathodes. W. P. JESSE (Physical Rev., 1934, [ii], 45, 563; cf. A., 1933, 345).—The changes which occur on heating mixtures of BaCO₃+SrCO₃ coated on a Ni ribbon cathode have been followed by means of X-ray photographs. At 800°, the mixed carbonates are converted into the individual oxides, and at 960° a slow transformation into a solid solution, BaO-SrO, occurs. L. S. T.

Structure and physical properties of thin films of metal on solid surfaces. E. N. DA C. ANDRADE and J. G. MARTINDALE (Phil. Trans., 1935, A, 235, 79—100).—Uniform and reproducible films of Ag and Au (30—100 atoms thick) have been obtained by slow cathodic sputtering on a cooled surface. With films of 50 atoms thickness the first

stage of crystallisation, observed at 230° for Ag and $> 230^\circ$ for Au, consists in the formation of small aggregates, which show a characteristic figure in polarised light. This change is independent of the nature of the non-metallic surface supporting the film. The aggregates are formed by the motion of the upper layers of the film only, which must move freely at a temp. 700° below the m.p. Rapid growth of the aggregates follows prolonged heating at about $100^\circ >$ the temp. at which they are formed, leading to the formation of well-defined, cubic crystals, which are arranged with their (111) faces parallel to the supporting surface. The thinner is the film of metal the higher is the temp. required to initiate crystallisation. Variations of colour and other properties found by previous observers under apparently identical conditions are ascribed to uncontrolled heating of the film during prep. E. S. H.

Recrystallisation of thin metallic layers. A. B. C. ANDERSON and A. GOETZ (Physical Rev., 1934, [ii], 45, 293).—Resistivity measurements of thin layers of Ag deposited on amorphous and cryst. surfaces (calcite) by evaporation in a vac. are discussed. The tendency of the isolated atoms to form aggregates is independent of the no. of atoms present. The resistance per layer decreases suddenly when a definite statistical thickness is reached, indicating the formation of cryst. groups of 10^{-5} – 10^{-4} cm. in diameter. L. S. T.

Lattice constants of five elements possessing hexagonal structure. E. A. OWEN, L. PICKUP, and I. O. ROBERTS (Z. Krist., 1935, 91, 70–76).—Precision measures are given for Zn, Mg, Be, Ru, and Os. The annealing technique necessary for undistorted crystals and hence for good X-ray definition is described. B. W. R.

Energy bands in copper. H. M. KRUTTER (Physical Rev., 1935, [ii], 48, 664–671).—The general method of obtaining energy bands and wave functions for a face-centred lattice is applied to a Cu lattice using a corr. Hartree potential field, and energy bands are calc. as a function of internuclear distance. Electron assignment to the lowest energy bands explains the good conductivity of Cu. The various energy bands in the directions 100, 110, and 111 are correlated. N. M. B.

Structure of solid oxygen. L. VEGARD (Nature, 1935, 136, 720–721).—X-Ray powder diagrams of γ -O₂ indicate a lattice with rotating mols. The cryst. structure may be represented by a cubic cell, a 6.83 Å., containing 8 mols. grouped into pairs (O₂–O₂); space-group T_h^6 . The distance between the 2 mols. of a rotating pair, 3.48 Å., is slightly $<$ the min. distance, 3.68 Å., between neighbouring pairs. The centres of the O₂–O₂ pairs form a face-centred lattice, and γ -O₂ thus forms a closest cubical packing of pairs of O₂ mols. Its structure is similar to that of α -N₂ and α -CO. L. S. T.

Structure of electrolytic chromium. L. WRIGHT, H. HIRST, and J. RILEY (Trans. Faraday Soc., 1935, 31, 1253–1259).—The existence of hexagonal Cr in deposits obtained from aq. HCrO₄ + H₂SO₄ has been confirmed. The at. distance is

2.717 Å. and $c/a=1.626$. The hexagonal form is converted into the body-centred cubic form by heating in vac. at 800° for 1.5 hr. The factor influencing the formation of the hexagonal allotrope is the amount of Cr existing in the cation in the reduced solutions. E. S. H.

Crystal structure of γ -Fe₂O₃ and γ -Al₂O₃. E. J. W. VERWEY (Z. Krist., 1935, 91, 65–69).—Powder photographs of Fe₂O₃ and γ -Fe₂O₃, and MgAl₂O₄ and γ -Al₂O₃ (the former of each pair having the known spinel structure), are compared. In the γ -oxides, 21 $\frac{2}{3}$ cations, 32 O atoms, and 2 $\frac{1}{3}$ vacant spaces form statistically a spinel structure. B. W. R.

Structure of silicon disulphide. W. BUSSEM, H. FISCHER, and E. GRUNER (Naturwiss., 1935, 23, 740).—SiS₂ is rhombic (a 9.57, b 5.65, c 5.54 \pm 0.01 Å.), 4 mols. in the unit cell. The Si are surrounded by S atoms at the apices of a tetrahedron, the tetrahedra having two S in common. In the c -direction the crystal forms a unidimensional, infinite chain mol. The structural principle for silicates, viz., that the anionic tetrahedra can only have apices in common, is broken in this case owing to the large diameter of S²⁻. A. J. M.

Crystallography of magnesium sulphite. H. A. KLASSENS, W. G. PERDOK, and P. TERPSTRA (Rec. trav. chim., 1935, 54, 728–732).—MgSO₃·6H₂O has a rhombohedral lattice; unit cell contains 1 mol. J. W. S.

Triphosphonitrilic chloride. K. H. MEYER and G. W. PANKOW (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 139).—(PNCl₂)₃ when heated polymerises to a rubbery product. Stretching makes it birefringent and yields an X-ray diagram, which disappears on releasing the tension. It crystallises in a rhombic elementary cell, period 5.16 Å. A chain structure is suggested. S. J. G.

Structure of potassium hexachlorothallate dihydrate. J. L. HOARD and L. GOLDSTEIN (J. Chem. Physics, 1935, 3, 645–649).—X-Ray data show that K₂TlCl₆·2H₂O has compact, body-centred tetragonal lattice unit with a_0 15.841, c_0 18.005 (\pm 0.020) Å., containing 14 mols. Rb₃TlBr₆·2H₂O has a similar structure. T. G. P.

Crystal structures of rubidium and ammonium fluoborates. J. L. HOARD and V. BLAIR (J. Amer. Chem. Soc., 1935, 57, 1985–1988).—X-Ray data show that RbBF₄ has a 9.07, b 5.60, c 7.23 Å.; NH₄BF₄ has a 9.06, b 5.64, c 7.23 Å. These compounds crystallise with the BaSO₄ type of structure, space-group V_h^2 - $Pnma$, and are aggregates of BF₄ tetrahedra and Rb⁺ or NH₄⁺ ions. E. S. H.

Crystal structure of ammonium uranyl acetate. I. FANKUCHEN (Physical Rev., 1934, [ii], 45, 563).—NH₄ uranyl acetate, tetragonal, a 13.79, c 27.60 Å., body-centred, has 16 mols. in the unit cell; d (calc.) 2.33 (lit. 2.219); space-group probably $I4_12$ (D_{4h}^{10}). L. S. T.

Possibility of a secondary structure in calcite. S. HARRIS (Physical Rev., 1934, [ii], 45, 646–647).—A discussion. L. S. T.

Lattice constants and m.p. of herzeliites. W. BUBECK (Geol. Fören. Stockholm, 1934, 56, 525—530; Chem. Zentr., 1935, i, 1677).— a varied with the Mn content from 12.35 Å. with 2.3% MnO to 12.46 Å. with 19.4% Mn. Corresponding m.p. were 1090° and 1180°, respectively. Vegard's rule is not obeyed.

J. S. A.

Atomic arrangement in vitreous silica and germanium dioxide. B. E. WARREN (Physical Rev., 1934, [ii], 45, 292).—The at. arrangement in the two glasses is the same: each cation is tetrahedrally surrounded by 4 O and each O is shared between two tetrahedral groups. The orientation about the direction of linking is random, and the resulting network non-repeating, distinguishing the vitreous from the cryst. state. The interat. distances in the glass and crystal are equal.

L. S. T.

Orientation of the oxalate group in oxalic acid and some of its salts. S. B. HENDRICKS (Z. Krist., 1935, 91, 48—64).—Lattice consts. and optical properties are determined for α and β anhyd. $\text{H}_2\text{C}_2\text{O}_4$, and for several Na, Rb, and K oxalates; complete structure determinations are made for the acids, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, KHC_2O_4 , and RbHC_2O_4 . The C_2O_4 group has coplanar atoms, and when perfect cleavage occurs it is in planes not cutting C_2O_4 groups or O·H·O linkings.

B. W. R.

Structure of cyanuric triazide. E. W. HUGHES (J. Chem. Physics, 1935, 3, 650).—A reply to Knaggs (this vol., 434).

T. G. P.

Structure of benzil. K. BANERJEE and K. L. SINHA (Sci. and Cult., 1935, 1, 301).—Rotation photographs show 3 mols. per unit cell, confirming a hexagonal basic lattice; space-group D_{3h}^{21} . Reflexion intensity measurements indicate that the mol. has its two C_6 rings in parallel planes.

N. M. B.

Crystal structure of ergotamine. H. BRASSEUR (Bull. Soc. Chim. biol., 1935, 17, 1462—1464).—By means of the polarising microscope and the X-ray diffraction method ergotamine cryst. from aq. COMe_2 is shown to be monoclinic, with negative birefringence. Lattice dimensions are a 20.30, b 18.65, c 10.11 Å., β 90°.

A. L.

X-Ray examination of the transformation of sodium cellulose by the action of carbon disulphide.—See this vol., 1486.

X-Ray examination of the effect of removing non-cellulosic constituents from vegetable fibres. W. T. ASTBURY, R. D. PRESTON, and A. G. NORMAN (Nature, 1935, 136, 391—392).—X-Ray examination of the effect of the progressive removal of the xylan (I) of cellulose fibres from Manila hemp reveals no fundamental change; only a more perfect state of crystallisation is indicated, supporting the view that the incorporation of (I) is a kind of mixed crystallisation. Removal of lignin and enercusting hemicelluloses clarifies the X-ray photograph and leads to improved definition through a sharpening of the crystallite orientation.

L. S. T.

Structure of humic acid and its relation to lignin and coal. J. SEDLETZKI and B. BRUNOVSKI (Kolloid-Z., 1935, 73, 90—91).—The X-ray diagram

of humic acid is compared with those of lignin, coal, and graphite. The genetic relation of these substances is discussed.

E. S. H.

Structure of seed-globulins.—See this vol., 1433.

Process of stretching of highly polymerised substances. H. MARK (Ergeb. tech. Röntgen., 1934, 4, 75—79; Chem. Zentr., 1935, i, 1852).—On the basis that long-chain polymerides exhibit mobility corresponding with all the degrees of freedom of oscillation and rotation present, and that in a swollen gel the polymeride chains, or bundles thereof, are slowly oriented on deformation, a quant. statistical theory of elastic extension is derived. In the most probable orientation, the chain length is $<$ total length of the constituent units, corresponding with bent chains. Alteration of the most probable state involves work of extension or compression.

J. S. A.

Electron diffraction by highly polymerised substances. H. MARK and J. J. TRILLAT (Ergeb. tech. Röntgen, 1933, 4, 69—74; Chem. Zentr., 1935, i, 1852).—Thin films (10^{-5} to 10^{-6} cm.) of unstretched caoutchouc gave an "amorphous" diagram which changed to that of an orthogonal lattice, periods 8.1 and 12.4 Å., on 100% extension, in agreement with X-ray results. Cellulose acetate and nitrate give diffraction rings when fresh due to small crystallites of size 30—60 Å. On ageing, growth of crystallites occurs. For the nitrate, periods a 4.7, b 7.1, c 5.0 Å. were obtained.

J. S. A.

New interference phenomenon on the passage of rapid electrons through crystals. F. KIRCHNER and H. LASSEN (Ann. Physik, 1935, [v], 24, 113—123).—When rapid electrons fall on very thin Ag layers (approx. 10^{-6} cm.) the interference spots at the edges of the zero principal max. resolve themselves into cross-like patterns, which are due to a surface lattice effect. The same effect is obtained with reflexion photographs, and it is deduced that the interference is due to very small Ag crystals with exactly parallel orientation, on the surface.

A. J. M.

Crystal structure and electron configuration of transition and univalent metals. U. DEHLINGER (Z. Physik, 1935, 96, 620—633).—The crystal structures of transition metals are arranged symmetrically about the column Cr, Mo, W; only the last three metals have cube-centred lattices, the others having cubic or hexagonal lattices of closest spherical packing. The structures of the transition metals are therefore due to a gradual building up of the d -shell, all having only one s outer electron. The exception of ferromagnetic Fe is due to preponderance of spin valency over orbital valency to produce the cube-centred lattice at low temp.

A. B. D. C.

Electron-optical observation of transformations of iron between 500° and 1000°. E. BRUCHE and W. KNECHT (Z. tech. Phys., 1934, 15, 461—463; Chem. Zentr., 1935, i, 1336).—The electron emission at 1050° was employed (cf. A., 1934, 859), using Fe specimens annealed at 1050°, heat-treated at temp. between 500° and 1000°, and then rapidly reheated to 1050°. Structural changes were

observed between 665° and 725° , and between 615° and 665° . J. S. A.

Intensity of diffraction of electrons by ZnO. H. J. YEARIAN (Physical Rev., 1935, [ii], 48, 631—639).—Electron diffraction patterns of ZnO powder were obtained in the range 10—80 kv. The intensity distribution shows marked deviations from that of the corresponding X-ray pattern. Numerous considerations fail to explain the anomaly. Agreement between experimental and calc. curves for the scattering factor is obtained by assuming a distortion of the electron cloud (M shell of the Zn and L shell of the O) resulting in a different parameter for the distances Zn nucleus—O nucleus, and Zn electrons—O electrons. An expression for the structure factor is found. N. M. B.

Diffraction of electrons by metals and organic polymerides. J. J. TRILLAT and H. MOTZ (Ann. Physique, 1935, [xi], 4, 273—304).—The electron diffraction patterns obtained with cellulose nitrate and acetate, polyoxymethylenes, synthetic resins, rubber, etc. are closely similar and are attributable to thin oriented surface films of fatty materials (fatty acids, waxes, or paraffins). The same phenomenon with metallic surfaces is due to the presence of long aliphatic mols. oriented perpendicular to the surface. J. W. S.

"Extra" rings in electron diffraction patterns. G. I. FINCH and A. G. QUARRELL (Nature, 1935, 136, 720).—The spacings of extra rings due to grease are found to be independent of the nature of the metal, confirming the results of Mark *et al.* (this vol., 813). Measurements recorded for Au show that the rings obtained by heating a metal in a gas depend on the metal, the gas, and the nature of the heat-treatment. Amalgamation also produces extra ring systems which have spacings dependent on the metal. L. S. T.

Electronic structures of molecules. XIII. Diborane and related molecules. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 635—645; cf. this vol., 1306).— B_2H_6 is shown to have 11 low-energy electron states within an energy range of 1.5 volts, belonging to three electron configurations, in general agreement with the suggestions of Sidgwick *et al.* (A., 1931, 1356). The three H atoms in each BH_3 are held by two [S] and three [$-$] electrons shared equally. The same equal sharing occurs, *e.g.*, in $B_2H_5Me_4$. The absence of dimeric BCl_3 is discussed. T. G. P.

Fundamental problems of the modern theory of metals. L. E. GUREVITSCH (Trans. Lenin. Ind. Inst., 1934, 5, No. 3, 125—147).—A review.

Refinement of the Heisenberg theory of ferromagnetism applicable to simple cubic crystals. C. H. FAX (Proc. Nat. Acad. Sci., 1935, 21, 537—542).—A new method gives results in agreement with the simple Heisenberg theory, but at variance with the approx. method of Heisenberg using Gaussian distribution of coupling energies. A. J. M.

Negative hysteresis in nickel. S. SHARAN (Current Sci., 1935, 4, 157).—The influence of an alternating circular or longitudinal field on the

intensity of magnetisation of soft Fe and Ni under const. magnetic field is examined. Ni exhibits negative hysteresis under the influence of an alternating circular field but not with an alternating longitudinal field. W. R. A.

Validity of Becker's relation for initial permeability of highly strained nickel wires. G. SCHARFF (Z. Physik, 1935, 97, 73—82).—Temp. variation of initial permeability of Ni under load confirms Becker's theory of magnetisation (A., 1930, 844). A. B. D. C.

Negative Matteucci effect. E. ENGLERT (Z. Physik, 1935, 97, 83—93).—Results are given for wires of Ni and of Fe-Ni (92:8%). A. B. D. C.

Displacement of the Curie point by tension. E. ENGLERT (Z. Physik, 1935, 97, 94—96).—No such effect could be found (cf. Ray-Chaudhuri, A., 1931, 1216). A. B. D. C.

Interior magnetic field in iron. L. ALVAREZ (Physical Rev., 1935, [ii], 45, 225—226, 566).—Data obtained from the passage of β -rays from Ra-C through Fe after focussing in a magnetic field disagree with the classical theory of magnetisation. L. S. T.

Comparison of theoretical and measured Hall coefficients. K. K. SMITH and N. A. HEDENBURG (Physical Rev., 1934, [ii], 45, 122). L. S. T.

New substance with the electrical properties of Rochelle salt. G. BUSCH and P. SCHERRER (Naturwiss., 1935, 23, 737).— KH_2PO_4 shows a variation of dielectric const., ϵ , with temp. similar to Na K tartrate (I), although ϵ is $<$ for (I). The principal dielectric const., ϵ_{33} , increases with decrease of temp. attaining a max. of 155 at -130° . Like (I) it has two Curie points (-130° and -195°). Qual. investigation of the piezo-electric activity shows that this varies with temp. in an analogous manner to ϵ . X-Ray analysis indicates no structural change at the upper Curie point. A. J. M.

Dielectric anomalies of Rochelle salt. H. STAUB (Naturwiss., 1935, 23, 728—733).—A review. A. J. M.

Further studies on the double refraction of interfacial layers of the normal aliphatic acids. A. KING (Physical Rev., 1934, [ii], 45, 562).—Measurements on tridecoic and palmitic acids confirm previous results (cf. A., 1933, 889, 1104). L. S. T.

Effect of photochemical coloration on the elastic limit and strength of single crystals of rock-salt. M. PODASCHEVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 71—74).—Uniformly coloured crystals show a considerable increase in the elastic limit and strength. A. J. M.

Cinematographic record of the $\alpha \rightleftharpoons \gamma$ iron transition, as seen by the electron microscope. W. G. BURGERS and J. J. A. PLOOS VAN AMSTEL (Nature, 1935, 136, 721).—The growth of crystals of α -Fe in the original γ -Fe near the transition temp. 900° has been recorded by means of an electron microscope with one magnetic lens. L. S. T.

Allotropy investigations with very pure calcium. A. SCHULZE (Physikal. Z., 1935, 36,

595—598).—Cooling curves, electrical resistance, thermal expansion, and X-ray data all show the presence of two allotropic forms of Ca. The α - β transition lies near 300°, and the β - γ near 450°.

A. B. D. C.

Syntax and polytypy. H. UNGEMACH (Z. Krist., 1935, 91, 1—22).—Special forms of polymorphism are discussed in relation to coquimbite, carborundum, parasite, and other minerals.

B. W. R.

Pressure effect of electrical resistance of metals. N. K. SAHA (Indian J. Physics, 1935, 9, 623—635).—The pressure coeff. of electrical resistance and the change in resistance at different pressures are calc. on the rigid ionic model of Nordheim, using a screened Coulombian form of potential. Good agreement is found for metals having low compressibility. Results are compared with those of Kroll using Fermi's statistical form of ionic potential. The sp. resistances of Au, Ag, Cu, Na, K, and Li are calc. using the two forms of potential on the rigid ionic model. Results on Fermi's potential are less consistent. For the highly compressible alkali metals neither form is satisfactory.

N. M. B.

Diamagnetism of the tervalent bismuth ion. S. S. BHATNAGAR and B. S. BAHL (Current Sci., 1935, 4, 153—154).—Experimental vals. for the diamagnetic susceptibilities of 10 salts of Bi⁺⁺⁺ are recorded. From known vals. for the susceptibilities of the anions the val. 41.24 for Bi⁺⁺⁺ is obtained, compared with 43.8 calc. from theory.

W. R. A.

Magneto-chemical investigations. XVII. Magnetic behaviour of chalcogenides of bivalent chromium. H. HARALDSEN and E. KOWALSKI (Z. anorg. Chem., 1935, 224, 329—336; cf. Henkel *et al.*, this vol., 436).—The susceptibilities of CrS, CrSe, and CrTe have been measured. CrS and CrSe are paramagnetic between 90° and 600°. CrTe is ferromagnetic below 70°. The results confirm the presence of at. linkings between the metallic ions (A., 1934, 1294) in certain compounds of the transition elements.

T. G. P.

Diamagnetism of alkyl acetates. D. B. WOODBRIDGE (Physical Rev., 1935, [ii], 48, 672—682).—Susceptibility measurements on the first five primary alkyl acetates and on MeOH for the range 5—70° show very slight variation of susceptibility with temp. and indicate increasing temp. dependence for higher members of the series. The mol. susceptibility of CH₃ is additive, in agreement with Pascal's law. The magnetic properties of NiCl₂ solutions are discussed.

N. M. B.

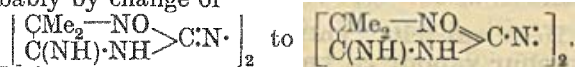
Magneto-chemical investigations of organic substances. IV. Magnetic behaviour of free radicals. E. MULLER, I. MULLER-RODLOFF, and W. BUNGE (Annalen, 1935, 520, 235—255; cf. this vol., 689, 1116).—Susceptibilities of the following paramagnetic substances have been determined at temp. down to —183°: C₁₈H₂₁O₂N₂ (I) (cf. A., 1932, 324); (*p*-OMe·C₆H₄)₂N·O (II); NPh₂·N·C₆H₄(NO₂)₃ (III); C(C₆H₅Ph)₃ (IV). (I) and (II) obey Curie's law exactly, whilst (II) shows a slight, and (IV) a somewhat larger, deviation at

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low temp. The calc. magnetic moments correspond with one unbalanced electron in each of the substances. (I) and (II) are entirely, and (III) is preponderantly, monomeric both in the solid state and in solution at all temp., whilst (IV) may be slightly associated at low temp.

F. L. U.

Magneto-chemical investigations of organic substances. V. Magnetic behaviour of porphyrexide and porphyrindin. VI. Determination of the degree of dissociation of hexa-aryl substituted ethanes. E. MULLER and (FRL.) I. MULLER-RODLOFF (Annalen, 1935, 521, 81—89, 89—94; cf. preceding abstract).—V. Porphyrexide shows the expected (Σ -condition) magnetic behaviour. Porphyrindin is a mixture of dia- and para-magnetic mols., the former being favoured by lower temp., probably by change of



VI. Free radicals should have a paramagnetic susceptibility, $\chi_{\text{mol.}}, +2.1270 \times 10^{-6}$ at 20°. Differences are due to incomplete dissociation, the degree of which can be calc. The method is applicable only for highly dissociated compounds or for high concns. of those slightly dissociated, e.g., for C₂Ph₆ at > 4%. C₂Ph₆ is found to be 2.1% dissociated at 20° in 4% solution, the heat of dissociation being —11.6+1.7 g.-cal.

R. S. C.

Change of magnetic susceptibility of metals during melting and allotropic transformation. K. HONDA and Y. SHIMIZU (Nature, 1935, 136, 393).—New measurements, in a vac., of the change in magnetic susceptibility during the melting of Sn, Cu, Ag, and Au, and the allotropic change of Sn, are recorded.

L. S. T.

Diamagnetism of copper. S. R. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 249—259; cf. this vol., 19).—Colloidal Cu was prepared in vac. by an electrical method in a dispersing medium of C₆H₆ or PrOH. The diamagnetic susceptibility, determined by a sensitive Curie method, was 0.080 for mass Cu, and increased as the size of the particles was reduced, the crit. diameter below which large changes occurred being 0.8 μ . The conclusions of Honda (cf. this vol., 287) are confirmed. The thickness of the surface layer is approx. 300 Å., and its diamagnetic susceptibility 0.200. The density of the surface layer is 8.404 as against 8.943 for mass metal.

N. M. B.

Magnetic anisotropy of crystals of Sn, and of Sn with added Sb, Cd, or Ga. H. J. HOGE (Physical Rev., 1935, [ii], 48, 615—619).—The principal magnetic susceptibilities of single crystals of white (tetragonal) Sn, grown by the travelling furnace method, were measured. Relative to the tetragonal axis the susceptibilities per unit vol. were: k_{\perp} 0.197×10^{-6} and k_{\parallel} 0.176×10^{-6} . The ratio k_{\perp}/k_{\parallel} is strongly influenced by the addition of traces of certain elements; for pure Sn the val. is 1.120, 0.6% Sb gives 1.200, 0.76% Cd gives 0.923, and 0.89% Ga gives 0.897. The relation between the change in this ratio and the no. of valency electrons of the added element is compared with data for Bi (cf. Goetz, A., 1934, 353).

N. M. B.

Paramagnetism of metallic gadolinium above its Curie point. F. TROMBE (Compt. rend., 1935, 201, 652—653).—Measurements of χ are recorded from 16° to 360°. The ferromagnetic and paramagnetic Curie points are at 16° and 29.5°, respectively.

H. J. E.

Absolute temperature of the normal freezing point of water. The ψ_0 -limiting value. W. JACYNA (Z. Physik, 1935, 97, 107—112).—This is 273.22° abs.

A. B. D. C.

Anomaly in specific heat of lithium. G. W. PANKOW and P. SCHERRER (Helv. phys. Acta, 1934, 7, 644—647; Chem. Zentr., 1935, i, 1832).—Between room temp. and -190° the energy supplied to Li goes entirely to at. vibration, and not to a quantum jump. The characteristic temp., θ , is given by three methods as 350—370°.

J. S. A.

Heat capacity, entropy, and free energy of sulphur vapour S_2 between 100° and 5000° abs. I. GODNEV and A. SVERDLIN (Z. Physik, 1935, 97, 124—130).—Heat capacity, entropy, and free energy are deduced from spectroscopic data.

A. B. D. C.

Specific heats of liquid deuterium oxide. R. S. BROWN, W. H. BARNES, and O. MAASS (Canad. J. Res., 1935, 13, B, 167—169).—The mean sp. heats over the ranges 4—26°, 26—45°, and 26—65° are 1.018, 1.003, and 1.008, respectively.

E. S. H.

Anomaly of specific heat of Seignette salt. A. A. RUSTERHOLZ (Helv. phys. Acta, 1934, 7, 643—644; Chem. Zentr., 1935, i, 1832).—The dielectric behaviour is abnormal below 25°, ϵ being very high. The variation of mol. heat with temp. in that region resembles that of ferromagnetic substances, corresponding with a work of electrification of 2.1 g.-cal. per mol.

J. S. A.

Latent heat of vaporisation of water in the pressure range 100—200 kg. per sq. cm. W. KOCH (Forsch. Ing., 1934, A, 5, 257—259; Chem. Zentr., 1935, i, 1672).—The latent heat for H_2O between 100 and 200 atm. is given by $r=59.5(374.11-t)^{0.4}+0.025(374.11-t)$.

J. S. A.

Heat of vaporisation of water and specific volume of saturated vapour up to 200 kg. per sq. cm. (365°). M. JAKOB and W. FRITZ (Physikal. Z., 1935, 36, 651—659).—The heat of vaporisation of H_2O has been determined calorimetrically up to 202 kg. per sq. cm. pressure (365°). An empirical formula for the heat of vaporisation and sp. vol. embodying these results and those of previous workers is deduced.

A. J. M.

Latent heat of condensation of metals. D. S. KOTHARI and N. K. SAHA (Sci. and Cult., 1935, 1, 300—301).—The electron gas theory is extended to calculate the latent heat of fusion of metals. Results for Li, Na, K, Rb, Cs, Ag, Cu, Au, and Cd agree with experimental data only in order of magnitude; those for Hg and Zn diverge widely.

N. M. B.

Expression of the second law of thermodynamics in terms of Clifford's numbers. A. MERCIER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 112—113).—Mathematical.

S. J. G.

I-T diagram for methane. A. EUCKEN and W. BERGER (Z. ges. Kalte-Ind., 1934, 41, 145—152; Chem. Zentr., 1935, i, 1346).—The complete enthalpy-temp. diagram of CH_4 is given between 110° and 290° abs. C_p and the molar heat of evaporation are given as functions of T .

J. S. A.

Vapour pressure of deuterium. F. G. BRICK-WEDDE, R. B. SCOTT, H. C. UREY, and M. H. WAHL (Physical Rev., 1934, [ii], 45, 565: cf. A., 1934, 1164).

L. S. T.

Pressure-volume-temperature relations of the liquid, and the phase diagram of heavy water. P. W. BRIDGMAN (J. Chem. Physics, 1935, 3, 597—605).—Pressure-vol.-temp. relations of liquid D_2O and H_2O have been measured between -20° and 95° and up to 12,000 kg. per sq. cm., and the transition parameters of the liquid and solid modifications of D_2O in the range -60° to 20° and up to 9000 kg. per sq. cm. An unstable modification IV of solid D_2O occurs in the field of stability of V, which confirms the existence of the corresponding modification in solid H_2O (A., 1913, ii, 39). D_2O and H_2O behave similarly, and differ in the direction suggested by the greater zero-point energy of H_2O : the mol. vol. of D_2O is > of H_2O at the same temp. and pressure; the transition lines of D_2O always run at higher temp. In detail the differences are irregular, and considerations other than zero-point energy are necessary for complete explanation.

T. G. P.

Baur and Brunner's measurements of vapour pressure of high-boiling metals. J. FISCHER (Helv. Chim. Acta, 1935, 18, 1028—1029; cf. A., 1934, 1301).—Baur and Brunner's vals. for the b.p. of Pb and Ag disagree with accepted vals. Defects in the method are pointed out.

H. J. E.

Measurements of vapour pressure of high-boiling metals. E. BAUR and R. BRUNNER (Helv. Chim. Acta, 1935, 18, 1030; cf. preceding abstract).—A reply.

H. J. E.

Vapour pressure of barium. E. RUDBERG and J. LEMPET (J. Chem. Physics, 1935, 3, 627—631; cf. this vol., 22).—The v.p. of Ba, determined between 525° and 750° by mol. effusion, gives $\log p(\text{mm.})=6.99-8980/T$, and $L=40.9$ g.-cal. per mol.

T. G. P.

Ratio of the thermal coefficient of expansion to the specific heat at constant pressure for tungsten. W. J. JACKSON (Physical Rev., 1934, [ii], 45, 285).—The ratio is const. for only a limited temp. range; above 200°, it increases with rise of temp. up to 500°, where the validity of the empirical relationships ceases.

L. S. T.

Principal expansion coefficients of single crystals of mercury. D. M. HILL (Physical Rev., 1935, [ii], 48, 620—624).—Expansion coeffs. measured at 5° intervals from -115° to -160°, and mean vals. found from -160° to -190°, are tabulated and plotted. A recrystallisation process sets in between -115° and -110°. Relative to the trigonal axis, α_{11} is larger and increases more rapidly with rise of temp. than α_1 . The vol. coeff. is given from the m.p. to -160°, where the coeff. decreases rapidly with fall of temp.

N. M. B.

Thermal conductivity of carbonic acid. R. PLANK and O. WALGER (Forsch. Ing., 1934, A, 5, 289; Chem. Zentr., 1935, i, 1670).—Sellschop's val. (this vol., 574) is confirmed. J. S. A.

Thermal conductivity of various liquids. R. PLANK (Z. ges. Kalte-Ind., 1934, 41, 214; Chem. Zentr., 1935, i, 1506).—The val. of Kardes (A., 1934, 1300) for CO₂ is too high, due to convection effects. Data for other liquids are not so affected. J. S. A.

Thermal expansion of calcite. H. SAINI (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 108—109).—Determinations of coeff. of expansion of the same crystal of calcite by an optical interference method and by an X-ray method agreed between 25° and 100°. S. J. G.

Density and compressibility of silicane and silicoethane. K. L. RAMASWAMY and G. G. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 213—220).—Using an apparatus for the simultaneous measurements of density and approx. compressibilities, vals. were obtained for SiH₄ at room temp. and -79.8°, and for Si₂H₆ at room temp. The calc. mean mol. wts. are 32.13 and 62.74, respectively. Corresponding at. wts. of Si are compared with those of other authors. N. M. B.

Variation of the viscosity of gases with temperature over a large temperature range. A. B. VAN CLEAVE and O. MAASS (Canad. J. Res., 1935, 13, B, 140—148).—Data are recorded for NH₃, C₃H₈, C₂H₄, and Me₂O between 23° and -80°, with a relative accuracy of 0.1%. The validity of different viscosity-temp. relations has been tested with the present data; an empirical equation, which adequately represents the results, is suggested, but it fails at high temp. for all gases and at low temp. for H₂, air, and C₂H₄. The viscosity-temp. curves for CO₂, SO₂, NH₃, Me₂O, and C₃H₈ show an inflexion point, which is related to the polarity of the mol. and the crit. temp. E. S. H.

Viscosity of air and the electronic charge. G. KELLSTRÖM (Nature, 1935, 136, 682—683).—For dry air η_{20} , determined by the rotating-cylinder method, is $(1820.0 \pm 3.0) \times 10^{-7}$, corresponding with $\eta_{23} = (1834.8 \pm 3.0) \times 10^{-7}$, a val. different from that used by Millikan in determining *e*. The new val. gives $(4.818 \pm 0.012) \times 10^{-10}$ e.s.u. for *e*, the same val. as calc. from X-ray measurements. L. S. T.

Influence of a magnetic field on the coefficient of viscosity of liquids. H. S. VENKATARAMIAH (Current Sci., 1935, 4, 156).—The results of experiments (in 1932) on the influence of a magnetic field on the viscosity of C₆H₆ are published (cf. Raha *et al.*, this vol., 1198). W. R. A.

Influence of the proximity of a solid wall on the consistency of viscous and plastic materials. IV. R. K. SCHOFIELD and G. W. S. BLAIR (J. Physical Chem., 1935, 39, 973—981; cf. B., 1930, 844; 1931, 825).—The rate of flow of an aq. paste of BaSO₄ through tubes of the same radius under the same pressure gradient is independent of the length of the tube, but with tubes of different radii the velocity gradient does not appear to depend only on the shearing stress. The proximity of the tube wall

apparently causes a sheath of material to shear more easily than does the bulk of the material. E. S. H.

Mixed crystal formation with tin oxide. E. HAYEK (Monatsh., 1935, 66, 197—200).—Pptn. of SnO in presence of salts of Pb, Mn, Fe, Zn, Cd, and Ca gives mixed crystals, but Co, Ni, Mg, Sr, and Ba do not enter the SnO lattice. The mixed crystals have characteristic colours. Their homogeneity has been confirmed by X-ray photographs. SnO shows passivity. T. G. P.

Nature of a solid solution. K. HONDA (Metal Progr., 1934, 26, No. 3, 42—43).—Experimental vals. of *d* for a 4.5% Al-Ag alloy agree within 0.3% with the val. calc. from the displacement of the Ag lattice by Al in solid solution. CH. ABS. (e).

Equilibrium diagram of the system magnesium-lithium. P. SALDAU and F. SCHAMRAY (Z. anorg. Chem., 1935, 224, 388—398).—Thermal analysis of Mg-Li mixtures, supported by microscopical observations, indicates the formation of three solid solutions, the limits of which have been established. The compound LiMg₂ (not Li₂Mg₅; cf. this vol., 591) melts without change. F. L. U.

X-Ray study of aluminium-zinc alloys at elevated temperatures. E. A. OWEN and L. PICKUP (Phil. Mag., 1935, [vii], 20, 761—777; cf. A., 1934, 356).—Arrangements are described for obtaining rotation powder photographs of metals and alloys at high temp. in vac., with special reference to the β -phase in Al-Zn alloys which decomposes spontaneously below 270°. Equilibrium diagrams and accurate measurements of parameter vals., temp., and phase-boundaries above the eutectoid temp. are given, and results compared with previous data. The γ -phase parameter in the $\beta + \gamma$ region decreases with rising temp.; the transformation temp. (272°), and the $(\beta + \gamma) - \gamma$ boundary are derived from the thermal "expansion" curves of the γ -phase in certain alloys. N. M. B.

X-Ray investigation of the system iron-chromium-nitrogen. S. ERIKSSON (Jernkont. Ann., 1934, 118, 530—543; Chem. Zentr., 1935, i, 2069—2070).—The existence of an intermediate α' -phase in the Fe-Cr system (approx. formula FeCr) is confirmed (cf. Wever, B., 1932, 469). In the system Cr-N the hexagonal β -phase has a "superstructure," the cell vol. of which is three times as large as that of the hexagonal close-packed lattice. The upper and lower limits of the region of homogeneity of the β -phase are 11.9% N (Cr₂N) and 9.3% N, respectively. Lattice dimensions are recorded. Results are given for the chief phases in the Fe-Cr-N diagram at 700° and 400°. H. J. E.

Metals and alloys. XV. X-Ray analysis of lithium-zinc alloys. E. ZINTL and A. SCHNEIDER. XVI. Structure of platinum-thallium alloys. E. ZINTL and A. HARDER. XVII. X-Ray analysis of lithium amalgams. E. ZINTL and A. SCHNEIDER (Z. Elektrochem., 1935, 41, 764—767, 767—771, 771—774; cf. this vol., 692).—XV. Examination of the phases existing at room temp. confirms the results obtained by thermal analysis and electrical conductivity measurements (cf. A., 1934, 21).

XVI. Pt dissolves up to 1.5% of Tl with widening of the space lattice. The solid solubility of Pt in Tl is very small. The system includes the compound PtTl, the structure of which has been determined.

XVII. The results confirm the existence of the compounds LiHg_3 , LiHg_2 , LiHg , Li_2Hg , and Li_3Hg , the structures of which are discussed. E. S. H.

Irreversibility of iron-nickel alloys and their equilibrium diagram. E. SCHEIL (Arch. Eisenhüttenw., 1935—1936, 9, 163—166).—The irreversible range of Ni steels has an appreciable width for the temp. interval in which place interchange of the atoms takes place, and in this interval the α - γ transformation occurs throughout the irreversible range, provided that the time of annealing is sufficiently prolonged. Transformation in the irreversible range requires not only a change in the lattice structure, but also a diffusion of the Ni atoms to produce a γ -phase which is richer in Ni than the still unconverted α ; the first occurs with great rapidity, but the second only very slowly. Measurements of the Acl, Ar1, and Ar2 points of a 4.8% Ni steel after annealing at 665—725° and of the resulting degree of transformation show that the α - γ range in Fe alloys containing up to 10% Ni is probably bounded by two curved lines convex to the origin, one joining the points 900°, 0% Ni; 725°, 4.8% Ni; and 630°, 10% Ni, and the other the points 900°, 0% Ni; 600°, 4.8% Ni, and 520°, 10% Ni. A. R. P.

Alloys of palladium with manganese. A. T. GRIGORIEV (Ann. Inst. Anal. phys.-chim. U.S.S.R., 1935, 7, 75—88; cf. A., 1933, 18).—Pd-Mn alloys (5—95% Pd), cast or tempered at 900° for 16 hr., and at 300° for 7 days, form on cooling a continuous series of solid solutions. Alloys with 39.3—45% of Pd have a min. m.p. With fall in temp. the solid solution is converted into the compound PdMn. The thermal changes shown by alloys rich in Mn at 1040—1089° and 730—797° are conditioned, respectively, by the Mn transformations $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$. CH. ABS. (c)

Alloys of praseodymium and copper. G. CANNERI (Met. ital., 1934, 26, 869—871; Chem. Zentr., 1935, i, 1816).—The following compounds were found: PrCu_6 , m.p. 962°; PrCu_4 , transition point 824°; PrCu_3 , m.p. 841°; PrCu , transition point 563°. Eutectics occur at 891°, 15% of Pr; 792°, 45% Pr; 472°, 82.5% Pr. The alloys are hard and brittle. J. S. A.

X-Ray and electrical investigation of Pd-Ag-H alloys. G. ROSENHALL (Ann. Physik, 1935, [v], 24, 297—325).—Errors in deducing the [H] of Pd-H alloys from the current passed during electrolysis of aq. KOH, using the Pd as cathode, are discussed. Addition of > 27% of Ag to the Pd leads to the production of single-phase alloys at all [H]. The resistance of such alloys decreases for about four days after prep., this representing the time required to reach equilibrium. The Pd-Ag-H alloys have in all cases face-centred cubic lattices of which the const. varies with composition. The solubility of H_2 in Pd-Ag alloys (30—100% Pd) shows a max. only at pure Pd. X-Ray data can be explained on

either the hydride or the absorption hypothesis, but resistance min. observed favours the PdH hypothesis. J. W. S.

Theory of superlattice structures in alloys. W. HUME-ROTHERY and H. M. POWELL (Z. Krist., 1935, 91, 23—47).—Superlattices of various types are defined, which are intermediate between the random solid solution of A and B and the normal intermetallic compound A_mB_n . The concept of "zones" characterised by different distances between the atoms A and their nearest B neighbours is used to discuss the stability and formation of different superlattices, the lattices FeAl and CuAu being examined in detail. B. W. R.

Diffusion coefficients in alcohol-water mixtures. H. MOUQUIN and W. H. CATHCART (J. Amer. Chem. Soc., 1935, 57, 1791—1794).—Apparatus and technique are described, and results given for crystal-violet. A break in the composition curve occurs at 65% EtOH. E. S. H.

Apparent volumes and apparent compressibilities of solutes in solution. II. Concentrated solutions of lithium chloride and bromide. A. F. SCOTT and G. L. BRIDGER (J. Physical Chem., 1935, 39, 1031—1039; cf. this vol., 31).—Irregularities are discussed in the light of the data recorded and previous measurements. E. S. H.

Volume changes in mixtures of benzene and chloroform. G. BOTECHIA (Atti R. Ist. Veneto Sci., Lett. Arti, 1934, 93, 567—572; Chem. Zentr., 1935, i, 1688; cf. A., 1933, 1110).—The vol. increase shows a max. at 20 mol.-% CHCl_3 . A pressure of 76 atm. is required to restore the vol. to the sum of the vols. of the components. H. N. R.

Variation of vapour pressure of the isotopic mixture of hydrogen with time at 20.38° abs. K. STEINER (Physikal. Z., 1935, 36, 659—660).—The v.p. at 20.38° abs. of samples rich in D_2 decreases with time. The results are discussed. A. J. M.

Critical data of light and heavy water and their density-temperature diagram. E. H. RIESENFELD and T. L. CHANG (Z. physikal. Chem., 1935, B, 30, 61—68).—The crit. temp., t_c , of mixtures of H_2O and D_2O can be calc. with considerable exactness by the mixture rule, being given by $t_c = 374.2 - 2.7n$, where n is the mol. fraction of D_2O . The crit. data for D_2O are t_c 371.5°, p_c 218.6 atm., d_c 0.363 g. per c.c. H_2O and D_2O have the same d at 49.5° (saturated vapour) and also at 370.0° (liquid). R. C.

Mixed m.p. in eutropic series. H. D. K. DREW and J. K. LANDQUIST (J.C.S., 1935, 1480—1482).—The series CPh_3 , SiPh_4 , GePh_4 , SnPh_4 , and PbPh_4 show a continuous fall in m.p., viz., 285°, 237.5°, 233.4°, 229.2°, and 227.8°, respectively. A mixture containing equimol. proportions of each has m.p. 220—221°. The m.-p. depression of binary mixtures suggests a change in some function, possibly in the valency angle, on passing from Ge to Sn. The m.-p. depressions for binary mixtures of NPh_3 , PPh_3 , AsPh_3 , SbPh_3 , and BiPh_3 indicate that N and Bi diverge from the other elements, and that only P and As are compatible with one another. Austin's

formula for m.p. in org. homologous series (A., 1930, 675) is inapplicable to the eutropic series. J. W. S.

Mutual solubility of heavy water and organic liquids in systems with a negative saturation curve. J. TIMMERMANS and G. POPPE (Compt. rend., 1935, 201, 608—610; cf. this vol., 1314).—Replacement of H_2O by D_2O extends the region of non-miscibility of a H_2O - α -picoline mixture. With 33.2% of α -picoline the lower and upper crit. solution temp. are 92° and 112.5° , respectively. With increasing pressure these limits approach one another, the liquids being miscible at all temp. for pressures > 90 kg. per sq. cm. For D_2O - Bu^iOH mixtures a smaller KCl addition is needed to produce two phases than with H_2O . H. J. E.

Ternary system isoamyl alcohol-propyl alcohol-water. J. COULL and H. B. HOPE (J. Physical Chem., 1935, 39, 967—971).—Miscibility, d , and n have been determined at 25° . E. S. H.

Solubility of barium iodate in salt solutions. G. MACDOUGALL and C. W. DAVIES (J.C.S., 1935, 1416—1419).—Conductivity measurements on aq. $Ba(IO_3)_2$, and solubility measurements at 25° for $Ba(IO_3)_2$ in aq. KCl, KNO_3 , $KClO_4$, $CaCl_2$, and $KClO_3$ solutions are recorded. The results, when corr. for ionic association, are in accord with the Debye-Hückel limiting formula. The dissociation const. of $BaIO_3^+$ is 0.083, and that of $BaClO_3^+$, deduced from solubility measurements of $Ba(IO_3)_2$ in $KClO_3$, is about 0.2. J. W. S.

Nitrates of neodymium and praseodymium and their solubilities in water. J. N. FRIEND (J.C.S., 1935, 1430—1432; cf. this vol., 928).— $Nd(NO_3)_3 \cdot 6H_2O$ exists in α - and β -forms, the latter having m.p. 67.5° . The transition point is about 22° . $Pr(NO_3)_3 \cdot 6H_2O$, like the La and Nd salts, is probably isodimorphous with $Bi(NO_3)_3 \cdot 5H_2O$, and has m.p. 56° . The solubilities of $Nd(NO_3)_3 \cdot 6H_2O$ between 0° and the m.p. and of $Pr(NO_3)_3 \cdot 6H_2O$ between 15.8° and the m.p. are recorded. The solubilities of the Nd, Pr, and La salts are all too close to permit good separation in neutral solution. J. W. S.

"Salting-in" of hydrogen peroxide by electrolytes. M. H. GORIN (J. Amer. Chem. Soc., 1935, 57, 1975—1978).—The solubility of H_2O_2 , as determined by its distribution between H_2O and amyl alcohol, is increased in the aq. phase by addition of NaCl, NH_4Cl , KCl, $NaNO_3$, NH_4NO_3 , KNO_3 , and NH_4ClO_4 , but decreased by H_2SO_4 . The apparent displacement of H_2O of hydration by H_2O_2 mols. can be explained if the H_2O_2 mol. has a higher dipole moment than that of H_2O in the neighbourhood of the ion. A structure for H_2O_2 , which would yield the necessary high dipole moment, is discussed. E. S. H.

Systems naphthalene-acetone and diphenylacetone and the solubility of a third substance in them. P. SPINOGLO and G. RAVENNA (Gazzetta, 1935, 65, 668—678).—For a given sample of $COMe_2$, the solubility of CdI_2 in $C_{10}H_8$ - $COMe_2$ and in Ph_2 - $COMe_2$ mixtures of various concns. is const. when referred to a fixed wt. of $COMe_2$. The

actual val. of the solubility varies with the small amounts of H_2O present even in carefully distilled $COMe_2$. O. J. W.

Densities of adsorbed gases. I. Carbon dioxide on charcoal. T. DE VRIES (J. Amer. Chem. Soc., 1935, 57, 1771—1774).—He has been used as the displaced fluid to determine, before and after CO_2 adsorption, the unoccupied vol. in a tube containing C at 30° . He does not penetrate the CO_2 layer when d is > 0.09 mg. per ml. Polanyi's theory gives d for the adsorbed layer equal to the observed vals. if it is assumed that He penetrates the outer portion of the adsorbed layer. E. S. H.

Active charcoal. IX. Curves of sorption isotherms and their properties. X. Non-reducible sorption equilibrium, hysteresis, drift, and residual sorption. XI. Sorption and capillary condensation; their mechanism. O. KAMIKE. **XII. Preparation of active charcoal by the zinc chloride process.** Y. IMAI. **XIII. Velocity of sorption of vapour in a dilute current of inert gas.** S. TAMARU and Y. IMAI (J. Chem. Soc. Japan, 1935, 56, 114—123, 124—132, 133—141, 142—152, 153—177).—IX. A summary of previous work.

X. Hysteresis and drift are different phenomena. The former can be observed at relatively high vals. of v.p.

XI. Org. substances, notably AcOH, are the more readily adsorbed by active C. The radius of the capillary is calc.

XII. Active C of good quality is obtained by dipping a specimen of *Quercus glandulifera* in 30% aq. $ZnCl_2$, treating with HCl at 90° (16 hr.), and igniting at 700° .

XIII. Relations between the amount of gas absorbed, time of contact, and dilution are examined.

CH. ABS. (p)

Adsorption of methane by coal. J. B. SUTTON and E. C. H. DAVIES (J. Amer. Chem. Soc., 1935, 57, 1785—1787).—The Freundlich equation is applicable to the results obtained at 10.94° , 17.77° , and 24.60° . The calc. heats of adsorption are 4700—5200 g.-cal. per mol. for x/m vals. between 1.5 and 3.5.

E. S. H.

Sorption of dimethyl ether on alumina. J. EDWARDS and O. MAASS (Canad. J. Res., 1935, 13, B, 133—139).—The investigations cover the ranges 0.5 — 52 atm. and 25 — 135° . No discontinuity in sorption accompanies the transition of sorbate from vapour to gas at the crit. temp. With increasing pressure the initially-formed unimol. layer is followed by a multimol. layer; it is, however, unlikely that condensation to liquid occurs in the pores, except at high pressures. The increase in crit. temp. of such a liquid must be very great to account for the continuous form of the isobars up to 135° . E. S. H.

Heat of adsorption of gases on zinc oxide and ZnO - Cr_2O_3 at low pressures and room temperatures. W. E. GARNER and F. J. VEAL (J.C.S., 1935, 1487—1495; cf. A., 1931, 904).—The heats of adsorption on oxidised or reduced surfaces of ZnO and ZnO - Cr_2O_3 catalysts decrease as the surfaces become covered with gas, particularly with oxidised surfaces. The adsorption of CO and H_2 on oxidised

$\text{ZnO-Cr}_2\text{O}_3$ occurs irreversibly, and with liberation of 45 kg.-cal. per mol. The surface undergoes simultaneous reduction, the gases being adsorbed on the reduced areas with heats of 10–15 kg.-cal. per mol. O_2 is also adsorbed on the reduced areas, a 2:1 CO-O_2 mixture being adsorbed completely by oxidised $\text{ZnO-Cr}_2\text{O}_3$. CO , H_2 , C_2H_4 , and C_2H_6 are adsorbed reversibly on the reduced surface with heats of 10–25 kg.-cal. per mol., but only when no penetration of capillaries occurs can desorption be completed in a short time at room temp. The behaviour on desorption is discussed with reference to the energies of activation of the adsorption process. It is suggested that the adsorption on the reduced surface is chemisorption. J. W. S.

Kinetics of absorption of oxygen by pyrocatechol. M. A. JOSLYN and G. E. K. BRANCH (J. Amer. Chem. Soc., 1935, 57, 1779–1785).—The dependence of reaction rate on p_{H} , pyrocatechol concn., partial pressure of O_2 , temp., and surface has been studied in buffered and unbuffered solutions. The heats of activation in NaOH solutions and in phosphate buffers have been determined at 20–35°. E. S. H.

Special cases of propagation of capillary action. C. E. GUYE (Helv. phys. Acta, 1934, 7, 850–855; Chem. Zentr., 1935, i, 1987; cf. this vol., 581).—Mathematical. J. S. A.

Dimensions of soap molecules as supposedly deduced from surface tension measurements. H. M. CASSEL (J. Amer. Chem. Soc., 1935, 57, 2009).—A criticism (cf. du Noüy, A., 1925, ii, 109). E. S. H.

Properties of detergent solutions. I. Influence of hydrogen-ion concentration on the surface tension of soap solutions. J. POWNEY (Trans. Faraday Soc., 1935, 31, 1510–1521).—Surface tensions of Na and K laurate, myristate, and oleate have been measured at 20° in presence of atm. CO_2 and of different concns. of added alkali. The effect of the latter is most marked with the laurate, and in all cases depends on soap concn. The results are discussed. F. L. U.

Inter-phase energies in systems of pure electro-neutral phases. H. HOHN and E. LANGE (Physikal. Z., 1935, 36, 603–624).—A discussion of thermodynamic and empirical relations shown by inter-phase energies in phenomena such as wetting, spreading, and cohesion. A. B. D. C.

Surface potential differences of unimolecular films of fatty acids. Y. YAMAGUCHI and S. MIZUNO (Bull. Chem. Soc. Japan, 1935, 10, 453–464).—The p.d. between air and 0.1N-KCl or 0.1N-HCl with a thin film of fatty acid on the substrate has been measured at 17–20° using X-rays to ionise the air gap. The p.d. rises with surface concn. to a const. val. of approx. 350 mv. for $\text{Me}[\text{CH}_2]_n\text{-CO}_2\text{H}$, where $n=12, 14$, and 16, and a const. val. of approx. 240 mv. for $\text{Me}[\text{CH}_2]_7\text{-CH:CH}[\text{CH}_2]_n\text{-CO}_2\text{H}$ (I), the change to a condensed film occurring at an area per mol. of approx. 27 \AA^2 for all acids. The mean vertical component of the dipole moment is 1.89, 1.37, 2.68, and 1.27×10^{-18} e.s.u. for the acids in the order given. It is suggested that (I) is folded at C'C. R. S. B.

Properties of thin layer of clay-water solution interposed between solid surfaces. H. TAKO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 909–919).—The coeff. of friction between a rubber plate (wetted with an aq. suspension of clay) and a plane surface decreases with concn. (c) of clay. With moving surfaces separated by a clay- H_2O film the resisting force is a min. for a velocity (v_0) approx. $\propto c^{3/4}$ (η apparent viscosity). ηv_0 is approx. insensitive to the addition of CuSO_4 and AlCl_3 , although η increases considerably. R. S. B.

Physical chemistry of flotation. VI. Adsorption of amines by sulphide minerals. E. E. WARK and I. W. WARK (J. Physical Chem., 1935, 39, 1021–1030; cf. B., 1935, 671).—The contact angle between the mineral and aq. solutions of several amine hydrochlorides is the same (about 60°) for all the amines investigated. The Cu minerals respond most readily and the quaternary NH_4 salts are most readily adsorbed. Using hexylamine, sphalerite can be floated away from galena. In a homologous series of amines the efficiency at a given concn. increases with increasing no. of C atoms; the activity increases in the order primary, sec., tert. Contact tests are closely parallel to flotation tests in the same solutions. The contact induced at certain mineral surfaces by some amines is prevented by addition of alkali or acid. E. S. H.

Electro-osmosis with some ceramic diaphragms. A. VASIČEK (Sborn. Škol. Tech. Brne, 1934, 8, No. 32; Chem. Zentr., 1935, i, 1350).—Electro-osmotic properties of ceramic diaphragms in aq. KCl have been examined. Surface conduction and electro-osmosis take place in solutions $\geq 0.02\text{--}0.05N$. Electrokinetic potential and surface conduction are dependent on the structure of the diaphragm. J. S. A.

Application of an empirical correction to the Donnan effect in the determination of mol. wts. of proteins by osmotic pressure measurements. D. R. BRIGGS (J. Physical Chem., 1935, 39, 983–995).—The relation between the observed osmotic pressure, P_o , and that calc. on the basis of unequal distribution of diffusible ions, P_c , is given by $E\alpha'([+])^x/(P_o - P_o - P_p) = \text{const.}$, where P_p is the osmotic pressure (calc.) due to protein of mol. wt. M , $E=59.1$ ($p\text{H}_o - p\text{H}_i$) = the membrane potential, α' = equiv. of diffusible ion derived from unit mass of the protein, $[+]$ = concn. of all ions bearing the same sign of charge as the protein, in the colloid-containing solution, and x is const. for a given colloid. Calculations of M gave 35,000, 60,000, and 80,000 (\pm about 15%) for cryst. ovalbumin, non-cryst. cow-serum albumin, and cryst. horse-serum albumin, respectively. E. S. H.

Cryoscopic study of trichloroacetic acid and its hydrate in benzene and in dioxan solution. R. P. BELL and M. H. M. ARNOLD (J.C.S., 1935, 1432–1435).—Cryoscopic measurements have been made with solutions of $\text{CCl}_3\text{-CO}_2\text{H}$ (I) and $\text{CCl}_3\text{-CO}_2\text{H.H}_2\text{O}$ (II) in C_6H_6 . The solid phase contains a little (I), probably adsorbed, but insufficient to prevent interpretation of the results. (I) is present in C_6H_6 solution as double mols. throughout the concn. range investigated

(0.01—1.5 mol.). (II) occurs entirely as single mols. in dil. solution, but probably forms double mols. at higher concn. Structures are proposed for single and double mols. (I) occurs entirely as single mols. in dioxan solution, probably owing to association with solvent mols. On addition of an equiv. amount of H_2O only incomplete formation of (II) occurs.

J. W. S.

Cryoscopic study of the total hydration of the ions of sodium bromide. (MLLE.) O. HUN (Compt. rend., 1935, 201, 547—549; cf. A., 1933, 460).—The total hydration in N and in $0.5N$ solution corresponds with 12.9 and 15.3 mols. H_2O , respectively.

T. G. P.

Cryoscopic determination of the total hydration of ions of sodium nitrate. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1935, 201, 660—662; cf. A., 1934, 728).—Hydration corresponds with $NaNO_3 \cdot 9.3H_2O$ and $NaNO_3 \cdot 11.1H_2O$ in $1.0M$ and $0.5M$ solutions, respectively.

H. J. E.

Effect of light on Brownian motion. R. FURTH and O. ZIMMERMANN (Ann. Physik, 1935, [v], 24, 183—208).—Unpolarised light of intensity 0.00062—2.6 watt per sq. cm. has no effect on particle size or Brownian motion, irrespective of the material, particle size, or λ of light. The Brownian motion is the same in the direction of the light and perpendicular to it. When linearly polarised light is used, the mean square of the displacement in the direction of the magnetic vector of the light vibration is independent of the particle size and material, but is 7—11% > in the direction of the electric vector or in the direction of propagation of the light. The effect disappears if the short-wave part of the light is filtered out. The results disagree with those of Pospíšil (A., 1927, 823; 1930, 412), and a systematic error in his work is suggested. An explanation of the effect is attempted on the basis of photo-electric theory.

A. J. M.

State of aggregation of colloids and calculation of mol. wt. F. F. NORD and F. E. M. LANGE (Naturwiss., 1935, 23, 722).—When solutions of lyophilic and lyophobic colloids of concn. 10^{-6} —5% are submitted to temp. $< 0^\circ$, the particles are either condensed or further dispersed according to the concn. The size of the particle depends on the previous physical treatment of the solution, and hence the mol. wt. of a colloid has little chemical significance.

A. J. M.

Colloidal systems of three components. I. Colloidal behaviour of the critical mixture of three fluids. N. SATA and O. KIMURA (Bull. Chem. Soc. Japan, 1935, 10, 409—420).—The crit. blue opalescence with 3-component mixtures of H_2O and various org. fluids has been studied at 30° . The system C_6H_6 — H_2O —EtOH or MeOH gives emulsoids with the greatest range of stability. When C_5H_{12} or C_6H_{14} replaces C_6H_6 , or when $COMe_2$ replaces EtOH, no opalescence occurs. With C_6H_6 — H_2O —EtOH at approx. 20 — 40° opalescence is stable for an interval of approx. 10° . Mixtures poor in H_2O are stable at a lower temp. than those rich in H_2O . The disperse phase is rich, and the dispersion medium poor, in C_6H_6 .

R. S. B.

Hydrous thorium hydrosols considered as polynuclear basic thorium complexes. A. W. THOMAS and C. B. KREMER (J. Amer. Chem. Soc., 1935, 57, 1821—1824).—The of $Th(OH)_4$ sols is raised by adding K salts. The effect is ascribed to displacement of co-ordinated OH groups by the anion of the added salt, the anion then becoming co-ordinately bound. The dialysed sols rapidly become more acid when kept at room temp., the rate increasing at higher temp. The heated sols are less sensitive to p_H change on addition of salts. A polyolated or oxolated structure of the micelle is assumed.

E. S. H.

Basic zirconium chloride hydrosols. A. W. THOMAS and H. S. OWENS (J. Amer. Chem. Soc., 1935, 57, 1825—1828).—The of the sols is raised on adding K salts by a process similar to that observed with $Th(OH)_4$ sols (cf. preceding abstract).

E. S. H.

Absorption spectra of metallic and organic colloidal solutions and the absorption of metal films. A. T. WILLIAMS (Compt. rend., 1935, 201, 665—667; cf. A., 1932, 691).—Data are recorded for colloidal solutions of Ag, Au, and Pt. The ultraviolet absorption band (2270—2820 Å.) is independent of the method of preparing the colloid. The absorption spectra of colloidal solutions of org. mols. resemble those of true solutions.

H. J. E.

Viscosity of titanium dioxide sol in presence of electrolytes. S. M. MEHTA and (MISS) O. JOSEPH (J. Indian Chem. Soc., 1935, 12, 552—559).—The change of viscosity of TiO_2 sol. dialysed and diluted to different extents, on the addition of salts, has been studied by the method described previously (A., 1932, 693). The viscosity of the sol increases with time, and the viscosity-time curves are periodic or discontinuous in the slow region (cf. A., 1934, 1171). The sp. conductivity and $[H^+]$ of the sol diminishes on dilution and on dialysis, and the increased rapidity of coagulation is attributable to decrease of peptising ions. The autocatalytic nature of the coagulation process disappears as the sol is dialysed.

J. W. S.

Viscosimetric investigation of benzene solutions of ethyl- and benzyl-cellulose. S. LEE and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 436—438B).—Vals. are recorded for η_{sp}/c (when $c=0$), the form and charge factor, and the sp. vol. for solutions of ethyl- (I) and benzyl-cellulose (II) in C_6H_6 at 10 — 60° . η/c for (I) is 0.885 at 20° and 0.74 at 50° , and for (II) is 1.2 at 10° and 0.77 at 60° .

A. G.

Influence of gases on silver sols. T. I. TAYLOR and W. H. CONE (J. Physical Chem., 1935, 39, 997—1003).—The effect of O_2 , N_2 , H_2 , CH_4 , and C_2H_4 on the pptn. vals. (for $NaNO_3$), electrophoretic velocities, and conductances of Ag sols has been investigated. The gases have a stabilising effect on those sols which are on the border line of stability and apparently contain secondary particles. The electrophoretic measurements show no increase in the average charge of the particles.

E. S. H.

Properties of silver halides peptised by ultrasonic waves in gelatin. H. W. DANGERS (Z. Physik, 1935, 97, 34—45).—Peptisation under varied

conditions has been studied, and it is shown that this treatment can produce a max. colour-sensitivity.

A. B. D. C.

Comparative investigations on caramel and molasses colloids.—See this vol., 1485.

Relations between colloid and constitutive changes of proteins. IV. Heat-coagulation and colloid structure of albumins. W. PAULI and J. WEISSBROD (Kolloid-Beih., 1935, 42, 429—462; cf. this vol., 823).—Neutral salts raise the coagulation temp. of serum albumin. The effect is detectable at a concn. of 0.001*N*, and varies with the anion according to the Hofmeister series; SCN has the greatest effect. Sucrose and CO(NH₂)₂ at high concns. have a similar effect. The coagulation temp. of ovalbumin is raised by electrolytes only at low concns. (<0.001*N*); at higher concns. the coagulation temp. is lowered. The order of effectiveness of different anions is that usually observed with positively-charged colloids; sucrose and CO(NH₂)₂ act as with serum albumin, but the effect of glycine is similar to that of a neutral salt. Complex relations are observed with mixed albumin sols. The mechanism of these phenomena is discussed.

E. S. H.

Combination of bivalent manganese with certain proteins, amino-acids, and related compounds. R. K. MAIN and C. L. A. SCHMIDT (J. Gen. Physiol., 1935, 19, 127—147).—Partition, electrophoretic, and anomalous titration data show that Mn⁺⁺ forms complexes with H₂SO₄, H₃PO₄, nucleic and glycerophosphoric acids, with dicarboxylic, hydroxy-mono-, -di-, and -tri-carboxylic acids, dicarboxylic NH₂-acids, and certain enol sulphonic acids; also with certain proteins (casein, edestin, gelatin).

F. A. A.

Lecithin as a dispersing agent for dibenzanthracene. H. D. BARNES (Nature, 1935, 136, 756).—Two methods for obtaining colloidal dispersions of dibenzanthracene using lecithin as dispersing agent are described.

L. S. T.

Swelling of structured proteins.—See this vol., 1522.

Electrophoresis of sterols.—See this vol., 1523.

Factors influencing electrophoretic mobilities and apparent critical potentials. H. L. WHITE and B. MONAGHAN (J. Physical Chem., 1935, 39, 925—934).—In very dil. electrolyte solutions the electrophoretic mobility of small glass particles is < the electro-osmotic mobility at a glass surface, but at 0.01*M* the mobilities are identical. The same holds for gelatin surfaces. The effect is traced to a retardation of the particles in very dil. solutions, chiefly through polarisation of the double layer by the applied field. The apparently lower crit. potential obtained with electrolytes which coagulate in low concns., and kindred phenomena are explained.

E. S. H.

Comparison of the electrokinetic potentials at fused and unfused glass surfaces. B. MONAGHAN and H. L. WHITE (J. Physical Chem., 1935, 39, 935—939).—The prep. of glass spheres 3 μ or less in diameter is described. The electrophoretic velocity of Pyrex glass spheres in aq. KCl is the same as that

of unfused Pyrex particles and < the electro-osmotic velocity at a fused Pyrex surface.

E. S. H.

Thermal equilibrium between ethylene iodide, ethylene, and iodine. G. R. CUTHBERTSON and G. B. KISTIAKOWSKY (J. Chem. Physics, 1935, 3, 631—634).—Results obtained between 50° and 125° agree with the extrapolation of Mooney and Ludlam's data (A., 1929, 766) for lower temp., but disagree with their high-temp. data. The heat of dissociation of C₂H₄I₂ is 13.4 \pm 0.5 kg.-cal. per mol. The position of equilibrium is given by log *K* (atm.) = 8.17—13,400/4.58*T*.

T. G. P.

Exchange of heavy hydrogen atoms between hydrogen and ammonia. K. WIRTZ (Naturwiss., 1935, 23, 721—722).—*K* for the reaction NH₃ + HD = NH₂D + H₂ is 1.9 at 300°.

A. J. M.

Fourth ionisation constant of ferrocyanic acid. I. M. KOLTHOFF and W. J. TOMSICEK (J. Physical Chem., 1935, 39, 955—958).—The val. 5.6 \times 10⁻⁵ at 25° has been derived from a study of the effect of H⁺ on the oxidation potential of a mixture of K₄Fe(CN)₆ and K₃Fe(CN)₆ at known ionic strengths.

E. S. H.

Titration curves and dissociation constants of *l*-ascorbic acid (vitamin-C) and diethyl dihydroxymaleate. W. D. KUMBLER and T. C. DANIELS (J. Amer. Chem. Soc., 1935, 57, 1929—1930).—The results show that *l*-ascorbic acid is 1000 times as strong as Et₂ dihydroxymaleate.

E. S. H.

Interaction of amino-acids and salts. I. Zinc chloride. II. Sodium chloride and thallous chloride. N. R. JOSEPH (J. Biol. Chem., 1935, 111, 479—487, 489—499).—The addition of various NH₂-acids decreases the activity coeffs. of ZnCl₂, TlCl, and NaCl in concn. cells without liquid junction. Comparison is made with results obtained by other methods. These indicate that "salting-out" forces of opposite sign are present, which become relatively greater with increase in the length of the hydrocarbon chain of the NH₂-acid and the dielectric const. of the solvent.

F. A. A.

Association in the dissociation of simple straight-chain sulphonic acids in water. I. Conductivity. II. F.p. III. Electromotive force. J. W. MCBAIN and M. D. BETZ. IV. Comparison of results, and so-called "Hammarsten effects." J. W. MCBAIN (J. Amer. Chem. Soc., 1935, 57, 1905—1909, 1909—1912, 1913—1916, 1916—1920).—I. In very dil. solutions the straight-chain sulphonic acids behave as simple, partly dissociated electrolytes. Conductivity is at a min. in 0.05*N* solutions and increases greatly at higher concns. This is explained by the association of like ions to form ionic micelles, the equiv. conductivity of which in conc. solutions attains that of OH⁻. This effect predominates over the ordinary features of interionic attraction.

II. F.-p. data support the above results.

III. E.m.f. data for sulphonic acids and their mixtures with HCl show that the ionic micelles of the sulphonic acids cannot be regarded as equiv. to multivalent ions in which the charges are conc. at

one point. The degree of dissociation of sulphonic acids in conc. solution remains const. or tends to increase.

IV. The above results are discussed. The dissociation of the colloidal electrolyte is about 50%. An explanation of the Hammarsten effect, based on steric hindrance to close packing, is given.

E. S. H.

Thermodynamic properties of methylbromide. S. SUGAWARA (J. Inst. Mech. Eng. Tokyo, 1935, 38, 87—88).

CH. ABS. (e)

Thermodynamic properties of uni-univalent halide mixtures in aqueous solution. H. S. HARNED (J. Amer. Chem. Soc., 1935, 57, 1865—1873).—E.m.f. of the cells $H_2|HCl(0.01), NaCl(m)|AgCl|Ag$ have been determined at 5° intervals from 0° to 60°. The results are considered in relation to the law of linear variation of the logarithm of the activity coeff. at const. ionic strength for such halide mixtures.

E. S. H.

Thermodynamics of ionised water in sodium chloride solutions. H. S. HARNED and G. E. MANNWEILER (J. Amer. Chem. Soc., 1935, 57, 1873—1876).—The ionic activity coeff. product of H_2O in aq. $NaCl$ has been calc. from e.m.f. measurements of the cells $H_2|NaOH(0.01), NaCl(m)|AgCl|Ag$ and $H_2|HCl(0.01), NaCl(m)|AgCl|Ag$ from 0° to 60°. The logarithm of the ionisation in alkaline halide solutions at a given concn. varies nearly linearly with the sum of the reciprocal of the ionic radii. The total heat change for the ionisation of H_2O and the relative partial mol. heat content of H^+ and OH^- in aq. $NaCl$ have been determined from 0° to 60°.

E. S. H.

Neutral salt action in non-aqueous solutions. P. P. KOZAKEVITSCH (Bull. Soc. chim., 1935, [v], 2, 1631—1655).—The thermodynamic activity of CO_2 , CCl_4 , $CHCl_3$, NH_4Et_2 , $C_{10}H_8$, and camphor in $MeOH$ solution is increased by addition of salts to almost the same extent as in aq. solution. The distribution coeff. of these substances between vaseline oil and $MeOH$ is independent of their concn. but varies with the neutral salt concn. Setschenov's equation holds for $MeOH$ solutions of most metal halides except Li salts. The relative effects vary with the nature of the ions present and are discussed with reference to the action of undissociated mols. and the structure of the solvent. The electrostatic effect of the ions extends probably only to a unimol. layer of $MeOH$ mols. The anomalous behaviour of $HgCl_2$ and CdI_2 in presence of camphor indicates the existence of compounds $C_{10}H_{16}O.HgCl_2$ and $C_{10}H_{16}O.CdI_2$. There is also evidence of complex formation between several salts and $C_{10}H_8$.

J. W. S.

Application of equations for the chemical potentials to partially miscible solutions. G. SCATCHARD and W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 1805—1809).—Equations for the free energy of mixing are computed from the mutual solubilities of partly miscible substances; the vapour compositions and pressures calc. from these equations agree satisfactorily with experiment.

E. S. H.

Application of equations for the chemical potentials to equilibria between solid solution

and liquid solution. G. SCATCHARD and W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 1809—1811).—Theoretical. Simple equations for the change in chemical potentials on mixing are applied to the equilibria between solid and liquid solutions of the $Ag-Pd$ and $Au-Pt$ systems.

E. S. H.

Vapour pressure and thermal dissociation of orthoboric acid. S. BEZZI (Gazzetta, 1935, 65, 766—772; cf. A., 1933, 120).—The v.p. of H_3BO_3 , measured at various temp. by a dynamic method, is independent of the partial pressure of H_2O in the transporting gas and equal to the v.p. of its saturated solutions. H_3BO_3 is therefore volatile in steam on account of its own v.p., and not because it forms volatile compounds with H_2O . The equilibrium pressures of the system $H_3BO_3 \rightleftharpoons HBO_2 + H_2O$ have been determined.

O. J. W.

Two compounds of titanium tetrachloride and hydrogen chloride. A. CHRETIEN and G. VARGA (Compt. rend., 1935, 201, 558—560).—Thermal analysis of the system $TiCl_4-HCl$ reveals $TiCl_4.6HCl$, m.p. -86° , and $TiCl_4.2HCl$, m.p. -30.8° , and the corresponding three eutectics.

T. G. P.

System water-sulphuric acid-nickel sulphate. R. ROHMER (Compt. rend., 1935, 201, 672—674).—Equilibrium data at 25° and 50° are recorded. In presence of H_2SO_4 , both $NiSO_4.H_2O$ (I) and $NiSO_4$ (II) may be prepared at 25°. $NiSO_4.4H_2O$, which is metastable, exists at 25° in contact with solutions containing <43% of H_2SO_4 . Above 84.8° only (I) and (II) occur as stable solid phases.

H. J. E.

Ternary system $K_2SO_4-(NH_4)_2SO_4-H_2O$. E. BOVALINI and E. FABRIS (Gazzetta, 1935, 65, 617—623).—The isotherms at 0°, 35°, 50°, 70°, and 96.5° have been studied. At all temp. the salts form a continuous series of mixed crystals.

O. J. W.

Singular elements in the ternary system: lithium oxide-nitric anhydride-water. Effect of hydration. M. I. RAVITSCH (Ann. Inst. Anal. phys.-chim. U.S.S.R., 1935, 7, 235—244; cf. A., 1932, 469).—Isotherms have been determined at 0°, 15°, 25°, 28.5°, 65°, and 130°.

CH. ABS. (e)

Singular fold in the ternary system: sodium chloride-platinum chloride-water. N. S. KURNAKOV and M. I. RAVITSCH (Ann. Inst. Anal. phys.-chim. U.S.S.R., 1935, 7, 225—233; cf. A., 1933, 1013).—The singular points of the ice field and the cryohydric lines are described. The results are compared with other ternary systems. Na_2PtCl_6 behaves as a complex salt.

CH. ABS. (e)

System $K_2SO_4-MgSO_4-CaSO_4$. L. S. RAMSDELL (Amer. Min., 1935, 20, 569—574).—X-Ray examination of fused mixtures of K_2SO_4 , $MgSO_4$, and $CaSO_4$ show the existence of a continuous isomorphous series with $K_2Mg_3(SO_4)_3$ (langbeinite) and $K_2Ca_2(SO_4)_3$ as end-members, no other compounds being formed. The lattice is a simple cube, 4 mols. per unit cell; the cube edge varies from 9.96 Å. for the Mg to 10.37 Å. for the Ca end-member. Polyhalite (I) calcined at approx. 475° for a short period gives a product of low d from which practically complete extraction of K_2SO_4 and $MgSO_4$ is obtained by hot

H₂O. The CaSO₄ residue is rapidly converted into gypsum by cold H₂O, but X-ray photographs show that it is normal anhydrite. Calcination at higher temp. or for longer periods reduces the yield. The mechanism of dehydration of (I) is discussed.

L. S. T.

Alkali aluminium silicates. X. System ultramarine silicate-sulphur. E. GRUNER and J. FORSTER (Z. anorg. Chem., 1935, 224, 369—387; cf. this vol., 1470).—Pressure-S content curves representing the isothermal decomp. of blue and green ultramarine between 600° and 1050° have the same form as those of substances containing "zeolitic" H₂O. The residue left when all S has been expelled by heat shows the lattice of nephelite. The constitution of ultramarine is discussed.

F. L. U.

Dissociation energy of carbon monoxide and the heat of sublimation of carbon. H. LESSHEIM and R. SAMUEL (Nature, 1935, 136, 606).—The val. calc. for the heat of dissociation of CO is 10.45 v.e. (cf. this vol., 925), giving 155.7 kg.-cal. per mol. for the heat of sublimation of β -graphite at 25°.

L. S. T.

Heat of dilution of cadmium chloride. (MILLER.) M. QUINTIN (Compt. rend., 1935, 201, 549—550).—Calculations are made from previous data (this vol., 826).

T. G. P.

Free energy change that accompanies hydrogenation of pyridine to piperidine. G. H. BURROWS and L. A. KING, jun. (J. Amer. Chem. Soc., 1935, 57, 1789—1791).—The equilibrium between C₅H₅N, C₅H₁₁N, and H₂ at 150°, 170°, and 180° has been determined; the heat of reaction and accompanying free energy changes have been calc.

E. S. H.

Conductivities of acids and other solutes in pyridine. M. M. DAVIES (Trans. Faraday Soc., 1935, 31, 1561—1567).—Conductivities of HClO₄, HNO₃, and HI in C₅H₅N at 25° have been measured. The dissociation const. are, respectively, 7.55×10^{-4} , 4.96×10^{-5} , and 5.9×10^{-4} . Results obtained by addition of C₅H₅N to solutions of CPh₃Cl and of C₆H₂Cl(NO₂)₃ in PhNO₂ indicate the formation of complexes with C₅H₅N. C₆H₃(NO₂)₃ behaves as a weak acid in C₅H₅N, whilst C₆Me₃(NO₂)₃ does not.

Conductance of non-aqueous solutions. I. Sodium triphenylboron and disodium tri- α -naphthylboron in diethyl ether. H. E. BENT and M. DORFMAN (J. Amer. Chem. Soc., 1935, 57, 1924—1927).—Equiv. conductances have been determined at 0° and 25° from 10^{-1} to 10^{-7} mol. per litre. The structure of B(C₁₀H₇- α)₃ is discussed in the light of the results.

E. S. H.

Transport number and valency of silver in silver amalgam. K. SCHWARTZ (Monatsh., 1935, 66, 218—219).—Ag in Ag amalgam is a bivalent anion for which transport no./concn. = 4.0×10^{-4} and diffusion const. = 1.0×10^{-5} cm. per sec.

T. G. P.

Cathode-ray oscillograph method of investigating the Wien effect in electrolytes. W. HUTER (Ann. Physik, 1935, [v], 24, 253—272).—The oscillographic method clearly indicates the Wien effect, and

allows the varying magnitude of the effect with field strength to be rapidly determined.

A. J. M.

Behaviour of oxygen electrodes in carbonate melts. E. BAUR and R. BRUNNER (Z. Elektrochem., 1935, 41, 794—796).—The construction of O₂ electrodes for use at 450—1000° is described. C.d.-p.d. curves covering this temp. range have been determined.

E. S. H.

Oxidation potential of the system potassium ferrocyanide-potassium ferricyanide at various ionic strengths. I. M. KOLTHOFF and W. J. TOMSICEK (J. Physical Chem., 1935, 39, 945—954).—The normal electrode potential is 0.3560 volt at 25°. In very dil. solution the variation of potential with increasing ionic strength is > calc. on the basis of the simple Debye-Hückel expression. For the same valency type of salts the anion effect on the potential is the same for different anions at the same ionic strength. The cation effect of the alkaline-earth ions is > that of the alkali ions, which decreases in the order Ca > Rb > K = NH₄ > Na = Li.

E. S. H.

Junction potentials between solutions of sugars and potassium chloride. J. M. ORT and M. H. ROEPKE (J. Physical Chem., 1935, 39, 941—943).—A saturated aq. KCl bridge eliminates all significant liquid junction potentials, even in the most conc. sugar solutions, if the sugar solution has $p_H > 10$ and does not contain a large amount of ionised decomp. products.

E. S. H.

Electromotive forces due to the combination of metal [electrodes] in gelatin and the importance of the Volta effect in cells. S. VEIL (Compt. rend., 1935, 201, 551—552).—The p.d. between electrodes of Zn, Cd, Fe, Pb, Ni, and Cu and a Pt wire in gelatin have been measured with a quadrant electrometer (cf. this vol., 822).

T. G. P.

Polarographic studies with the dropping mercury cathode. LII. Electro-reduction of benzaldehyde. M. TOKUOKA. LIII. Electro-reduction of ferric-mannitol complexes in alkaline solutions. K. KOMARAK. LIV. Electro-reduction of formaldehyde. F. G. JAHODA (Coll. Czech. Chem. Comm., 1935, 7, 392—403, 404—414, 415—423).—LII. Polarographically recorded current-voltage curves show that the reduction occurs in two stages, each of which requires one F per mol. of PhCHO. The first stage of reduction probably yields free radicals, $\cdot\text{CHPh}\cdot\text{OH}$, which may subsequently form hydrobenzoin; the second stage leads to CH₂Ph-OH and does not involve the deposition of H⁺ or an alkali metal. As the p_H is increased, the potential for the first stage becomes more negative and that for the second stage slightly more positive. The potentials coincide at $p_H > 6$ and decrease by approx. -0.025 volt per unit rise of p_H . These results are, in general, independent of the type of buffer solution used. The reduction potential is approx. -1.5 volt, with respect to the $N\text{-Hg}_2\text{Cl}_2$ electrode in neutral aq. MCl (M = Na, K, NMe₄), but is raised slightly by Sr²⁺, Ca²⁺, NH₄⁺, NH₄Me₃⁺, NH₂Me₂⁺, and NHMe₃⁺, which also increase the

diffusion current. Electro-reduction of BzOH in presence of NMe_4^+ occurs at -2.3 volt.

LIII. Mannitol does not affect the current-voltage curve obtained with slightly acid solutions of Fe^{III} , but in alkaline solutions, especially in absence of O_2 , two saturation currents ("waves") are observed. Glycerol, sucrose, lactic and citric acids give similar results if added before the solution is made alkaline. The "waves" correspond with the successive electro-reductions: Fe^{III} -org. mol. complex $\rightarrow \text{Fe}^{\text{II}}$ -org. mol. complex $\rightarrow \text{Fe}$, and the ratio of the heights of the waves decreases from 1:2 to 1:1 as the alkali is neutralised. The origin of the last phenomenon is discussed. The affinity of the Fe^{III} -mannitol complex is small.

LIV. The saturation current, i , is a linear function of $[\text{CH}_2\text{O}]$ and the "mol. reduction potential" is -1.50 volt. Reduction of 1 mol. of CH_2O requires $2F$. i is increased in alkaline solutions and by rise of temp., indicating dissociation of polymerisation products. The max. of current-voltage curves and i decrease with increasing age of CH_2O solutions. At 90° , 7×10^{-8} g. of CH_2O in 1 c.c. can be determined polarographically to within 10% in presence of other aliphatic aldehydes, ketones, esters, and org. acids. Minute traces of CH_2O in coal gas are inferred.

J. G. A. G.

Electrolytic reduction potential of organic compounds. XXII. Mechanism of electrolytic reduction. I. TACHI (J. Agric. Chem. Soc. Japan, 1935, 11, 734—740).—Small drops of H_2O -insol. org. compounds placed on a Hg cathode having a small surface at first become flat owing to polarisation, but further polarisation tends to restore the original form. The angles of contact between drop and Hg and the changes which these undergo when polarisation occurs vary with the compound used and with the nature of the dissolved electrolyte. Camphor oil drops become flatter than do those of PhNO_2 and CCl_4 . PhNO_2 drops become flatter in alkaline than in acid media.

W. McC.

General properties of electrodes of photo-sensitive organic substances. (Miss) H. T. NEA (J. Chim. phys., 1935, 32, 564—584).—Electrodes were prepared by immersing Cu (or Pt) in collodion and then in aq. solutions of various coloured substances. The photo-potential (E_p) varies with the nature, and diminishes to a steady val. with increasing concn., of the electrolyte. Oxidising or reducing agents diminish E_p irreversibly. The temp. coeffs. of the electrodes are generally negative; for pyronine it is positive, and for crystal-violet zero. The log. variation of E_p with light intensity has been confirmed. The variations of E_p (for different λ) with the polarisation of the electrodes indicate that photo-electric and not electronic processes play the major part. E_p bears no discernible relation to photo-conductivity, is sensibly zero in non-aq. solvents, and \propto the % of H_2O in aq. glycerol. The properties of org. and inorg. photo-electrodes are thus very similar.

T. G. P.

Dependence of the electrochemical properties of an element on the state of aggregation. II. Polarisation relations in the electrolytic de-

position and dissolution of gallium and their dependence on temperature near the m.p. O. STELLING (Z. Elektrochem., 1935, 41, 779—789; cf. this vol., 1325).—Further studies of the anodic and cathodic behaviour of Ga in dil. HCl and NaOH confirm that liquid Ga behaves as a nobler metal than solid Ga.

E. S. H.

Electrode dispersion of noble metals. A. VOET (Trans. Faraday Soc., 1935, 31, 1488—1491).—Anodic disintegration of Au, Pt, and Pd is observed when acid, alkaline, or neutral solutions are electrolysed at 100 volts and high c.d. It is always accompanied by periodicity of the current, and is not due to the Wehnelt effect. An explanation based on the formation and disruption of an oxide layer is given.

F. L. U.

Passivity of iron and steel in nitric acid solution. VII. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan 1935, 14, 925—964; cf. this vol., 827).—The passivation of Fe in conc. HNO_3 is more difficult to effect when the test piece has suffered internal stress by twisting.

R. S. B.

Quantum mechanics and kinetics of reactions in organic chemistry. C. N. HINSHELWOOD (Bull. Soc. chim., 1935, [v], 2, 1786—1799).—A lecture.

General method of statistics and its application to chemical energetics. G. ALLARD (Ann. Physique, 1935, [xi], 4, 305—377).—Mathematical.

J. W. S.

Kinetics of slow reactions and their entropy changes. F. G. SOPER (J.C.S., 1935, 1393—1395).—On the hypothesis that the decomp. of the crit. complex into the products and reagents \propto the relative thermodynamic probabilities of the three states, a factor representing the fraction of crit. complexes which decompose to reaction products has been introduced into the velocity equation. The modified equation is of correct thermodynamic form, and reduces to $k = Ze^{-E/RT}$ when the reaction is attended by an increase of entropy, but gives greatly diminished rates when the entropy change is negative. Existing data show that, with one exception, the classification of reactions as "normal" and "slow" is in general agreement with that based on the sign of entropy change. The factor affects only slightly the existing agreement between observed and calc. velocities of reactions associated with small decreases of entropy, e.g., $2\text{HI} \rightarrow \text{I}_2 + \text{H}_2$; $\text{NH}_4\text{CNO} \rightarrow \text{CO}(\text{NH}_2)_2$.

J. G. A. G.

Photographic investigation of flame movements in gaseous explosions. VII. Phenomenon of spin in detonation. W. A. BONE, R. P. FRASER, and W. H. WHEELER (Phil. Trans., 1935, A, 235, 29—68; cf. A., 1932, 232).—The spiral track formed by the rotation of the "head" of detonation in the system moist $2\text{CO} + \text{O}_2$ has been studied in relation to the influence of dimensions and shape of the explosion tube and the addition of small amounts of H_2 or $\text{Fe}(\text{CO})_5$. Driving the mixture with P_2O_5 increases the flame speed and stabilises the spin. In a moist mixture the flame speed is reduced in passing through a powerful axial magnetic field, and both spin and detonation can be suppressed when

the detonation traverses a sufficiently strong electric field in a negative to positive direction. A new view of the detonation wave is advanced. It is viewed as two separable components, an intensively radiating flame-front with an invisible shock wave immediately ahead of it; whether persistent spin is developed or not depends on the stability of their association.

E. S. H.

Ignition of gases. IX. Ignition by a heated surface. Mixtures of methane and air at reduced pressures. C. A. NAYLOR and R. V. WHEELER (J.C.S., 1935, 1426—1430).—In general, the upper ignition temp., T , of CH_4 -air mixtures in a SiO_2 vessel rises as the proportion of CH_4 is raised from 5.3 to 12.5%, but the variation of T with total pressure ($P=263$ —760 mm.) is not uniform. With $> 10.7\%$ of CH_4 , T decreases progressively as P increases, but with less CH_4 , two pressure limits are found for each val. of T (cf. A., 1933, 129). The data do not conform to the Semenov relation between T and P . The lag before ignition decreases as P is raised and as the % of CH_4 is decreased. The results accord with earlier work (A., 1931, 1240) and an interpretation is suggested.

J. G. A. G.

Kinetics of the thermal decomposition of acetaldehyde. H. W. THOMPSON and J. J. FREWING (J.C.S., 1935, 1443—1451).—The thermal decomp. of 5—650 mm. of acetaldehyde at 490—570° is essentially homogeneous and affords C_4H_8 , C_2H_4 , CO , C_2H_6 , CH_4 , and H_2 . The proportion of C_4H_8 increases with increase of initial pressure and decreases during the course of a run. C_2H_6 , CH_4 , and H_2 are also primary products. The plot of the reciprocal of the period of half change against the initial pressure, P_0 , is segmented and the reaction probably consists of several independent quasi-unimol. processes superposed on a bimol. reaction. The energy of activation increases with decrease of P_0 .

J. G. A. G.

Velocity of thermal decomposition of chloropicrin. D. RADULESCU and G. ZAMFIRESCU (Bull. Soc. Chim. Romania, 1935, 17, 87—92).—The decomp. is unimol. up to 160° and has a large temp. coeff. Photodecomp. is inhibited by the NOCl produced, which absorbs the light.

R. S.

Diabatic reactions and primary chemiluminescence. R. A. OGG, jun., and M. POLANYI (Trans. Faraday Soc., 1935, 31, 1375—1384; cf. this vol., 452).—An outline of the theory of ionogenic reactions and a list of its applications are given. Luminescence accompanying a primary chemical change is described as the inverse of predissociation.

F. L. U.

Mechanism of ionic reactions. Heat of ionic substitution reactions. R. A. OGG, jun. (Trans. Faraday Soc., 1935, 31, 1385—1392; cf. preceding abstract).—Estimates of the heat (H) involved in reactions between MeX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) and a negative ion other than halogen show that ionic interchange reactions having large positive H are characterised by small energies of activation. Examples are given and discussed.

F. L. U.

Steric factor of bimolecular association reactions. C. E. H. BAWN (Trans. Faraday Soc., 1935, 31, 1536—1547).—Consideration of the reaction

velocity coeff. by means of the transition state method indicates that the steric factor of bimol. association reactions is related to the probability of the transition state. The theoretical results are applied to the cracking of long-chain hydrocarbons.

F. L. U.

Velocity of oxidation of sulphides and sulphoxides by peracetic acid. J. BÖESEKEN and (Mlle.) E. ARRIAS (Rec. trav. chim., 1935, 54, 711—715).—The reaction between Ph_2SO and AcO_2H in AcOH is bimol. and its velocity coeff. increases considerably with increasing $[\text{AcO}_2\text{H}]$, possibly owing to spontaneous decomp. of the AcO_2H and an accelerating influence of the change of medium. The oxidation of Ph_2S by AcO_2H occurs in two stages, the bimol. oxidation to Ph_2SO being complete in 3 min. and being followed by oxidation of the Ph_2SO to Ph_2SO_2 . Oxidation of $(p\text{-C}_6\text{H}_4\text{Br})_2\text{S}$ is similar, but the velocity of reaction is less. The results are compared with those for the oxidation of unsaturated hydrocarbons.

J. W. S.

Decomposition of polythionate solutions. A. KURTENACKER, A. MUTSCHIN, and F. STASTNY (Z. anorg. Chem., 1935, 224, 399—419; cf. A., 1934, 160).—The different modes of decomp. of aq. solutions of $\text{K}_2\text{S}_n\text{O}_6$ ($n=3$ —6) are discussed. Velocities of decomp. have been measured, mostly at 50°, and the influence of $[\text{H}^+]$ has been studied. All the decomp. can be represented by a unimol. coeff., except for tetra-, penta-, and hexa-thionates within the range $p_{\text{H}} 4$ —9, where they may be markedly autocatalytic.

F. L. U.

Critical increment of ionic reactions. Influence of dielectric constant and ionic strength. W. J. SVIRBELY and J. C. WARNER (J. Amer. Chem. Soc., 1935, 57, 1883—1886).—Assuming that the rates of ionic reactions are functions only of temp., dielectric const., and ionic strength, equations are derived which predict the influence of dielectric const. and ionic strength on crit. increments. Experimental data for the reaction between NH_4^+ and CNO^- in H_2O and $\text{EtOH-H}_2\text{O}$ are in agreement with the theory.

E. S. H.

Mechanism and thermal effect of fulminic acid polymerisation. K. SENNEWALD and L. BIRCKENBACH (Annalen, 1935, 520, 201—234; cf. A., 1934, 994).—The heat of polymerisation of fulminic acid (I) in 0.4*N* aq. solution has been measured in presence of H_2SO_4 at various concns. When the $[\text{H}_2\text{SO}_4] \geq 0.01*N*$ the heat produced is 20% $>$ when $[\text{H}_2\text{SO}_4]$ is $> 0.15*N*$. In the latter case the reaction is bimol., whilst in the former it is of no simple order. These results, in conjunction with chemical observations, indicate that in neutral ($< 0.01*N*$ -acid) solution cyano-oximinoacetohydroxamic acid is formed as the final, with metafulminuric acid as an intermediate, product. In acid ($> 0.15*N*$) solution the primary product is dicarbonyldioxime (II), a small part of which combines with a mol. of (I) to form a trimeride, whilst a larger part undergoes polymerisation to isocyanilic acid. The following [from (II) and aq. halogen acid] are described: bromoglyoxime, m.p. 173° (decomp.); iodoglyoxime, m.p. 163° (decomp.); also bromoglyoxime anti-diacetate, m.p. 100°. F. L. U.

Reactivity of halogen compounds. III. Velocities of reaction, energies of activation, and probability factors for the reaction between 2:4-dinitrobromobenzene and aromatic primary amines. IV. Effect of addition of inactive substances on the rate of reaction, energy of activation, and probability factor. A. SINGH and D. H. PEACOCK (J.C.S., 1935, 1410—1411, 1411—1412).—III. Velocity coeffs. of the reaction between 1:2:4- $C_6H_3Br(NO_2)_2$ (I) and NH_2Ph , *m*- and *p*-toluidine in EtOH at 35° and 45° are > with 1:2:4- $C_6H_3Cl(NO_2)_2$ (II), probably owing to a higher probability factor (J.C.S., 1923, 123, 3099).

IV. The rate of reaction of NH_2Ph with (I) and (II) is retarded by added C_6H_6 derivatives, but cyclohexane has no effect. The results negative an earlier hypothesis (A., 1926, 691). J. G. A. G.

Influence of substituents on the additive reactivity of ethylene derivatives. III. Addition of bromine in solution. S. V. ANANTAKRISHNAN and C. K. INGOLD (J.C.S., 1935, 1396—1398; cf. this vol., 1103).—Data are recorded concerning the effect of substituting Me, Ph, and CHO in C_2H_4 on the rate of addition of Br in CH_2Cl_2 solution. The rate is increased with the no. of Me groups, in agreement with the theory (A., 1931, 1267), but in each case the CHO increases the rate, indicating an enforced reversal of the anticipated functions of the reagent.

J. G. A. G.

Steric course of two diene syntheses.—See this vol., 1500.

Hydrolysis of phenylalanine. E. BAUR and G. SCHINDLER (Biochem. Z., 1935, 281, 238—248; cf. A., 1934, 1314).—Results of experiments at 110° confirm those obtained at 80°. The unilateral equilibrium follows the mass action law, the reaction being of the first order. The val. for the heat of reaction deduced from the shift of the equilibrium with temp. change differs considerably from that deduced from calorimetric results, although there is qual. agreement.

W. McC.

Velocity of hydrolysis of cyclic acetals. II. R. LEUTNER (Monatsh., 1935, 66, 222—248; cf. A., 1932, 932).—The velocity of acid hydrolysis of the formal, acetal, and acetonal of $\alpha\gamma$ -butylene glycol, and the formal and acetal of pinacol have been measured. The relative ease of rupture of the 6-ring of the $\alpha\gamma$ -butylene glycol acetals of CH_2O , $MeCHO$, and $COMe_2$ is $1.4 \times 10^3 : 7 \times 10^6$. The relationship between hydrolysis and constitution is discussed.

T. G. P.

Aliphatic substitution and the Walden inversion. I. E. D. HUGHES, F. JULIUSBURGER, S. MASTERMAN, B. TOPLEY, and J. WEISS (J.C.S., 1935, 1525—1529).—The abs. rate in $COMe_2$ solution of the exchange of I between NaI and *sec*-octyl iodide, determined by means of the radioactive isotope of I, equals, within the limits of experimental error of the measurements of radioactivity (10%), the abs. rate of racemisation of *d-sec*-octyl iodide by NaI in $COMe_2$ solution. The result confirms that in this reaction inversion is directly caused by substitution.

J. G. A. G.

Kinetics of the interactions of sodium hydroxide with the bromoethanes in ethyl-alcoholic

solution. Mechanism of olefine formation in such systems. W. TAYLOR (J.C.S., 1935, 1514—1524; cf. this vol., 173).—Under the conditions of the kinetic experiments at 25° and 55°, the reactions with EtOH-NaOH are: (i) $CH_2Br.CBr_3$ gives $CHBr.CBr_3$, (ii) $CH_2Br.CHBr_2$ gives $CH_2.CBr_2$, (iii) $CMeBr_2$ yields NaOAc and 2.8% of bromo-olefine, (iv) $CHMeBr_2$ affords $MeCHO$ and a very small proportion of bromo-olefine, (v) $(CH_2Br)_2$ gives 79.5% of $CH_2.CHBr$ and 18.5% of $(-CH_2.OH)_2$, and (vi) EtBr yields EtOH and 1.3% of C_2H_4 . The reactions with measurable rate are bimol.; the velocity increases with dilution of NaOH, is independent of the concn. of the bromoethane, and is decreased by H_2O and large proportions of NaBr. There is a clear distinction between (a) reactions involving OH substitution of Br and (b) those involving complete or nearly complete conversion into olefine. In (a) two Br are displaced either simultaneously or consecutively at rates which are of the same order of magnitude, whilst in (b) one Br is displaced almost, if not quite, instantaneously and the second is displaced relatively slowly. Existing theories are criticised (A., 1933, 470; this vol., 452), and the data are interpreted by a mechanism involving a primary mutual attraction of OH' and an initially positively charged H, followed by simultaneous extension and rupture of the C-H and C-Br linkings of the two C of the ethane mol., whereby H_2O , Br', and olefine are formed. The consequences of the theory are discussed.

J. G. A. G.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. VII. *cyclopentanedicarboxylic* esters. Attempted check on the calculation of molecular dimensions. C. K. INGOLD and H. G. G. MOHRHENN (J.C.S., 1935, 1482—1486; cf. this vol., 1076).—From the velocity coeffs. at 20° of the first and second stages of the alkaline hydrolysis of Me_2 *cis*- and *trans*-1:2- and -1:3-*cyclopentanedicarboxylate*, the distances between the CO_2H have been deduced on certain assumptions. In general, the results conform more closely to the requirements of the mol. model when corr. for local dielectric effects in the aq. medium. The causes of the deviations are discussed.

J. G. A. G.

Constitution and reactivity. XIV. Kinetics of sulphonation with oleum and the properties of fuming sulphuric acid of different concentrations. K. LAUER and R. ODA (J. pr. Chem., 1935, [ii], 144, 32—40).—Vals. of q and $\alpha \times 10^{-10}$ (cf. A., 1933, 69) for the sulphonation of anthraquinone using H_2SO_4 with added SO_3 are determined and plotted against $[SO_3]$. The vals. of q and $\alpha \times 10^{-10}$ for sulphonation with SO_3 are 22,000 and 0.1, respectively. These are < the vals. for sulphonation with H_2SO_4 (cf. this vol., 863).

F. R. G.

Application of the law of mass action to the synthesis of β -glucosides.—See this vol., 1485.

Effect of substituents on organic reactions: a quantitative relationship. G. N. BURKHARDT (Nature, 1935, 136, 684).—Using the logarithms of the dissociation consts. of various *m*- and *p*-substituted $BzOH$ as an arbitrary reference series, linear relationships are obtained when the logarithms of the velocity

coeffs. of a no. of side-chain reactions involving substances containing the same *m*- and *p*-substituents are plotted against them. Thus, a straight line is obtained for the alkaline hydrolysis of substituted EtOBz and substituted NH₂Bz, and the solvent hydrolysis of the benzyl chlorides, etc. The linear relationships are discussed in terms of the transition state conception of Evans and Polanyi. L. S. T.

Measurement of the velocity of rapid reactions. M. WYGAERTS and J. ECKHOOT (*Natuurwetensch. Tijds.*, 1935, **17**, 163—189).—The course of reactions in solution involving a change in absorption spectrum is followed by taking a photographic record of the galvanometer reading of a photo-electric cell registering the intensity of light of given λ transmitted by the solution. The decolorisation of malachite-green by a large excess of NaOH (such that [NaOH] is effectively const.) is unimol., with k 0.94 at 19.85° and 1.6 at 29.65°. The decolorisation of reddened phenolphthalein by a large excess of NaOH is reversible, the reaction in both directions being unimol., with k_1 1.14×10^{-2} at 19.85° and 2.23×10^{-2} at 29.80°, and k_2 7.1×10^{-5} at 19.85° and 3.87×10^{-4} at 29.80°. The absorption spectra of *m*-NO₂·C₆H₄·CH₂·NO₂ and its Na salt (I) have been determined. The action of HCl on excess of (I) in 70% aq. EtOH at 13.9° is a bimol. reversible reaction (*i.e.*, the velocity of both forward and back reactions \propto the concn. of each reactant); $k_1 = 7.49$, $k_2 = 2.63$. D. R. D.

Corrosion of iron and steel.—See B., 1935, 1048.

Atmospheric corrosion and tarnishing of tin.—See B., 1935, 996.

Kinetics of the oxidation of metal filaments. G. VALENSI (*Compt. rend.*, 1935, **201**, 602—604; cf. this vol., 1328).—A general expression is derived from diffusion considerations for the rate of oxidation of filaments of bivalent metals. The result accords with experimental vals. for Ni. H. J. E.

Kinetics of heterogeneous organic reactions: reaction between benzyl chloride and solid silver nitrate. M. V. NABAR and T. S. WHEELER (*Proc. Indian Acad. Sci.*, 1935, **2**, A, 265—278).—The reaction, studied in the absence of solvents and diluents, is independent of the amount of CH₂PhCl (I), but \propto the surface of AgNO₃ present. Results, with particles of three different sizes, can be reproduced by the kinetic equation derived on the assumption that the rate of reaction depends only on the surface of AgNO₃. The velocity of the reaction is independent of the speed of shaking. H₂O inhibits the reaction; the effect of 0.18 wt.-% of (I) is marked, and this effect increases with the amount of H₂O added. N. M. B.

Rate of formation of fully-saturated glycerides during hydrogenation of different natural fats.—See B., 1935, 1053.

Catalytic effect of ozone in the oxidation of hydrocarbons. E. BRINER and J. CARCELLER (*Arch. Sci. phys. nat.*, 1935, [v], **17**, Suppl., 85—86).—Oxidation of *n*-C₄H₁₀ by O₃ is greatly accelerated by small amounts of O₃ at \leq room temp. Products formed include aldehydes, acids, COMe₂, H₂, CO₂,

and peroxides. 1 part in 10,000 of O₃ in air causes knocking in an internal-combustion engine by promoting the formation of peroxides. S. J. G.

Decomposition of chloral catalysed by nitric oxide. F. H. VERHOEK (*Trans. Faraday Soc.*, 1935, **31**, 1521—1526; cf. A., 1934, 1314).—The thermal decomp. of both CCl₃·CHO and CHCl₃ vapour is catalysed by NO. The catalysed reaction is of the first order with CCl₃·CHO, and approx. so with CHCl₃. The mechanism is discussed. F. L. U.

Decomposition of acetaldehyde catalysed by nitrous oxide. F. H. VERHOEK (*Trans. Faraday Soc.*, 1935, **31**, 1527—1533; cf. preceding abstract).—Study of the thermal decomp. of MeCHO vapour in presence of N₂O indicates the occurrence of a reaction between the MeCHO and N₂O giving rise to a substance which acts as a catalyst or initiates a chain. In a clean SiO₂ bulb the catalysed reaction is of the first order with respect to MeCHO. F. L. U.

Decomposition of acetaldehyde catalysed by nitric oxide. F. H. VERHOEK (*Trans. Faraday Soc.*, 1935, **31**, 1533—1536; cf. preceding abstract).—The decomp. of MeCHO catalysed by NO at 480° is approx. 3/2 order with respect to MeCHO, and the rate \propto [NO] when NO is in excess. An explanation of the mechanism is offered. F. L. U.

Catalytic decomposition of hydrogen peroxide in presence of mixtures of salts of manganese and copper. M. BOBTELSKI and (MME.) L. BOBTELSKI-CHAJKIN (*Compt. rend.*, 1935, **201**, 604—606).—The unimol. velocity coeff. increases with increasing [Cu^{II}] to a max., and then diminishes. The max. val. increases with the [Mn^{II}]. Zn^{II} and Cd^{II} increase the catalytic activity of Cu^{II}—Mn^{II} mixtures. A mechanism, involving intermediate compound formation between Mn^{II} or Cu^{II} and H₂O₂, is suggested. H. J. E.

Catalytic decomposition of nitroamide in acid and salt solutions. C. A. MARLIES and V. K. LA MER (*J. Amer. Chem. Soc.*, 1935, **57**, 1812—1820).—The rate of decomp. has been measured in aq. acid and salt solutions over a wide concn. range with an error of about 1%. A negative primary salt effect, which has been observed, is ascribed to the effect of the salt on the catalytic properties of H₂O. Acid catalysis has also been observed and a mechanism proposed. D₂O decreases the velocity of decomp., whilst HgCl₂ increases it. E. S. H.

Conditions of formation of the chloride of tervalent manganese in hydrochloric acid solutions, and its decomposition in presence of complex catalysts. M. BOBTELSKI and (MLLE.) R. COHEN (*Compt. rend.*, 1935, **201**, 662—664).—The catalytic activity of metals in the decomp. of MnCl₃ in presence of HCl was in the order Ag^I > Pt^{IV} > Pb^{II} > Cu^{II}. Increase in [HCl] in presence of Cu^{II}, Pb^{II}, or Pt^{IV} increases the rate of decomp. The temp. coeff. of the decomp. decreases with increasing [HCl]. In presence of Ag^I it is independent of [HCl], and approx. unity. H. J. E.

Catalytic polymerisation of gaseous olefines by liquid phosphoric acid.—See B., 1935, 1035.

Physical chemistry of amino-acids, peptides, and related substances. V. Influence of amino-acids, carbamide, and alcohol on the velocity constants of chemical reactions. D. STRAUP and E. J. COHN (J. Amer. Chem. Soc., 1935, 57, 1794—1800; cf. this vol., 695, 696).—The rate of reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with alkyl iodides is increased by EtOH, slightly increased by $\text{CO}(\text{NH}_2)_2$, and decreased by ions or amino-acids. The rate of reaction between $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{CH}_3\text{Br}\cdot\text{CO}_2'$ is increased by salts, NH_4 -acids, and $\text{CO}(\text{NH}_2)_2$, and but slightly influenced by EtOH. $\text{CO}(\text{NH}_2)_2$ and NH_2 -acids increase the dielectric const. of H_2O in proportion to their concn., but this factor does not entirely explain the influence on reaction rate. An extension of Kirkwood's equation for the activity coeffs. of the NH_2 -acids has been applied satisfactorily to the results.

E. S. H.

Catalytic decomposition of hydrogen peroxide on metals. J. WEISS (Trans. Faraday Soc., 1935, 31, 1547—1557; cf. A., 1935, 174).—The initial process in the catalytic decomp. of H_2O_2 by metals involves the transfer of an electron from the metal to the H_2O_2 , with the consequent formation of free radicals, thus: $\text{H}_2\text{O}_2 + e = \text{OH} + \text{OH}'$. This leads to the initiation of chain reactions, $\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2$ and $\text{O}_2' + \text{H}_2\text{O}_2 = \text{OH}' + \text{OH} + \text{O}_2$. The ease with which the primary electron transfer occurs depends on the electronic work function of the metal, and if this is decreased by cathodic polarisation catalytic decomp. becomes considerably greater, Hg and bright Pt, e.g., being effective catalysts under these conditions. The action of Ag, Pt, Au, Pd, and Zn on H_2O_2 has been studied in detail, and the observations support the theory, which also provides a simple explanation of the action of poisons such as H_2S and KCN.

F. L. U.

Mechanism of sulphur dioxide oxidation in presence of vanadium catalysts.—See B., 1935, 991.

Effect of the ferromagnetic transformation on the catalytic power of nickel for the reaction $2\text{CO} = \text{CO}_2 + \text{C}$. J. A. HEDVALL and F. SANDFORD (Z. physikal. Chem., 1935, B, 29, 455—463; cf. this vol., 153).—The catalysis by Ni of the above reaction in and near the Curie interval and the effect of impurities in Ni on the relation between its ferromagnetism and its catalysis of the reaction $\text{N}_2\text{O} = \text{N}_2 + 0.5\text{O}_2$ have been studied. The yield curves exhibit changes in direction corresponding with the characteristic temp. of ferromagnetic transformation of the catalysts.

R. C.

Active oxides. CXII. Interaction between solid substances. G. F. HUTTIG [with T. MEYER, H. KITTEL, and S. CASSIRER] (Z. anorg. Chem., 1935, 224, 225—252; cf. this vol., 1204).—The catalytic activity towards N_2O decomp. of $\text{CuO}\text{--}\text{Fe}_2\text{O}_3$ and $\text{CuO}\text{--}\text{Cr}_2\text{O}_3$, the magnetic susceptibility, bulk d , and colour of $\text{Fe}_2\text{O}_3\text{--}\text{Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--}\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--}\text{SiO}_2$, $\text{Fe}_2\text{O}_3\text{--}\text{TiO}_2$, $\text{Cr}_2\text{O}_3\text{--}\text{TiO}_2$, $\text{Cr}_2\text{O}_3\text{--}\text{Al}_2\text{O}_3$, and $\text{Cr}_2\text{O}_3\text{--}\text{SiO}_2$, and the rate of sorption of H_2O by $\text{MgO}\text{--}\text{Fe}_2\text{O}_3$, $\text{BeO}\text{--}\text{Fe}_2\text{O}_3$, $\text{ZnO}\text{--}\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{--}\text{Fe}_2\text{O}_3$, $\text{ZnO}\text{--}\text{Cr}_2\text{O}_3$, and $\text{CuO}\text{--}\text{Al}_2\text{O}_3$ have been measured and are discussed. The relationship between H_2O sorption,

catalytic activity, and internal and surface migration of the lattice units of the catalyst are considered.

T. G. P.

[Catalytic] synthesis of methane.—See B., 1935, 1035.

Adsorption and oxidation of succinic acid on carbon. B. TAMAMUSHI and H. UMEZAWA (Z. Elektrochem., 1935, 41, 761—764).—The catalytic activity of different kinds of C in the oxidation of succinic acid by O_2 has been studied by gravimetric determination of fumaric acid, and compared with the adsorptive power of the C. The influence of the relatively greater adsorption of fumaric acid is discussed.

E. S. H.

Electrolytic preparation of deuterium from heavy water. F. NORLING (Physikal. Z., 1935, 36, 711—713).—The apparatus is described. A. J. M.

Concentrating the hydrogen isotope D by electrolysis of water. II. Production of heavy water and its apparatus. Y. OTA (Mem. Fac. Sci. Agric. Taihoku, 1935, 15, 165—170). T. G. P.

Hydrates of lithium perchlorate. K. N. MOCHALOV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 21—25).— LiClO_4 was prepared electrolytically from aq. LiClO_3 (c.d. 0.2 amp. per sq. cm.; temp. $< 20^\circ$). $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ loses $2\text{H}_2\text{O}$ at $98\text{--}100^\circ$ and becomes anhyd. at $130\text{--}150^\circ$. CH. ABS. (e)

Electrolysis of aqueous solutions of alkali sulphates.—See B., 1935, 1000.

Electrochemical anodic behaviour of alloys. W. J. MULLER [with H. FREISSLER and E. PLETINGER] (Z. Elektrochem., 1935, 41, 774—778).—The anodic dissolution of Cu-Zn alloys in $N\text{--HCl}$ and $N\text{--H}_2\text{SO}_4$ has been studied by determining the loss of wt. of the anode and the amount of Cu dissolved from alloys of different compositions after the same time interval. No Cu was dissolved from alloys containing $< 40\%$ of Cu; with increasing Cu content the ratio of Cu to Zn in solution approaches more and more to that in the alloy. In HCl Cu enters solution as Cu^+ , in H_2SO_4 as Cu^{++} .

E. S. H.

Electrochemical behaviour of lead, lead-antimony, and lead-calcium alloys in storage cells.—See B., 1935, 1001.

Inorganic addition salts in the nickel-plating solution.—See B., 1935, 998.

Effect of oxidising agents on nickel deposition. II. Chromic acid. A. W. HOTHERSALL and R. A. F. HAMMOND (Trans. Faraday Soc., 1935, 31, 1574—1582; cf. A., 1930, 1134).—The effects of CrO_3 on cathode efficiency, cathode potential, rate of gas discharge, and appearance of deposits in the deposition of Ni from a NiSO_4 bath containing H_3BO_3 and KCl have been studied. The results suggest that at low $[\text{CrO}_3]$ initial depolarisation leads to pptn. of basic Ni compounds containing Cr, with resulting decrease of $[\text{Ni}^{++}]$, increased discharge of H^+ , and reduced cathode efficiency. At higher $[\text{CrO}_3]$ chemical interaction with the cathode metal leads to the formation of a selectively permeable film and consequent complete inhibition of Ni deposition.

F. L. U.

Concentrated copper cyanide plating baths.—See B., 1935, 997.

Copper plating of iron.—See B., 1935, 1050.

Electrodeposition of zinc from acid solutions.—See B., 1935, 1051.

Electrochemical purification of phosphoric acid.—See B., 1935, 1042.

Preparation of litharge by electrolysis.—See B., 1935, 1043.

Preparation of potassium persulphate by electrolysis.—See B., 1935, 1042.

Electrolytic reduction of nitro-compounds.—See B., 1935, 984.

Inversion of solutions of sucrose in contact with regions traversed by an electric current. P. FABRE (Compt. rend. Soc. Biol., 1935, 120, 179—181).—Sucrose solution in both compartments of a Daniell cell vessel is inverted by passing an electric current through the entire vessel. R. N. C.

Electrolytic preparation of nitrosonaphthols.—See B., 1935, 1036.

Photo-oxidation of hydrogen and deuterium iodides. G. A. COOK and J. R. BATES (J. Amer. Chem. Soc., 1935, 57, 1775—1778).—The reaction of HI or DI with O₂ at 0° under the influence of a low-voltage Hg-A lamp has been followed by pressure measurements and analysis of the products. The reaction between H and O₂ is a 3-body process. The results are: $k_{H+O_2+M}/k_{H+HI} = (2.11 \pm 0.29) \times 10^3$ c.c. per mol.; $k_{D+O_2+M}/k_{D+DI} = (3.98 \pm 0.15) \times 10^{-3}$ c.c. per mol.; $k_{H+O+O_2} \approx k_{D+O+O_2} \approx 1.2 \times 10^{14}$ cm.² mol.⁻² sec.⁻¹ E. S. H.

Use of the ortho-para-hydrogen conversion in the detection of free radicals produced in photodissociation. W. WEST (J. Amer. Chem. Soc., 1935, 57, 1931—1934).—Conversion is produced by MeI or COMe₂ vapour illuminated by radiation of frequency in their continuous absorption regions, but not by propaldehyde or C₆H₆. The results indicate the production of paramagnetic free radicals on illuminating MeI or COMe₂. E. S. H.

Photolysis of azomethane. G. S. FORBES, L. J. HEIDT, and D. V. SICKMAN (J. Amer. Chem. Soc., 1935, 57, 1935—1938).—Quantum yields, ϕ , for the photolysis of Me₂N₂ at 181, 184, 377, and 665 mμ, using six monochromatic radiations, have been determined. ϕ approaches 1 as its upper limit for initial decomp. at low pressure; variation of temp. between 20° and 226° has no effect on ϕ ; with increasing pressure ϕ falls rapidly. In the region 366—335 mμ approx., ϕ passes through a max., apparently corresponding with max. absorption by N.N. E. S. H.

Photographic detection of H-rays. M. BLAU and H. WAMBACHER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 285—301).—The effect of various baths in sensitising plates for the detection of H-particle tracks was examined. Optimum results were obtained with a mixture of pinakryptol and induline-scarlet. The action was not related to the desensitisation of this mixture for the action of light. The density of

grains in the H-particle track was of the same order as that in an α-particle track. H. J. E.

Simple method for determining the colour temperature of flashlights. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Z. wiss. Phot., 1935, 34, 237—240).—A colour chart (cf. Phot. Ind., 1930, 23, 629) was photographed by the flashlight on to panchromatic plates, and the result compared with sources of known colour temp. (C-filament, vac., gas-filled, and arc lamps). The val. for "Photoflux" flashlight [Al-Mg alloy (5—10% Mg) wire burning in pure O₂], as also for Mg or Al foil burning in O₂, was estimated to be about 4000° abs. J. L.

Case of negative photocatalysis. J. MILBAUER (Phot. Korr., 1935, 71, 94—95).—The action of photographic desensitisers on the photochemical decomp. of "Aktivin" (Na *p*-toluenesulphonchloroamide) in MeOH solution has been studied. Nile-blue, brilliant-green, Capri-blue, phenosafranin, fuchsin, and pinakryptol-green are negative catalysts. Malachite-green had no effect. Pinakryptol-yellow and methylene-blue are positive catalysts, even in the dark. J. L.

Free radicals in photodissociation of gaseous metal alkyls. N. PRILESHAIEVA and A. TEREININ (Trans. Faraday Soc., 1935, 31, 1483—1487; cf. A., 1935, 1052).—The decomp. of COMe₂, HgMe₂, and PbEt₄ vapours at low pressure by ultra-violet light has been studied by photometric determination of the progressive thinning of films of Sb under attack by the free radicals produced. F. L. U.

Primary photochemical reactions. VII. Photochemical decomposition of isovaleraldehyde and di-*n*-propyl ketone. C. H. BAMFORD and R. G. W. NORRISH (J.C.S., 1935, 1504—1511).—The proportions of the products of decomp. in the full light of the Hg lamp correspond with the following primary processes: (i) Bu²CHO (I) → *iso*-C₄H₁₀ + CO (47%) and (I) → C₃H₆ + MeCHO (53%) and (ii) COPr^α₂ (II) → C₆H₁₄ + CO (37%) and (II) → C₂H₄ + COMePr (63%). The products containing :CO are further decomposed photochemically. Two types of primary photochemical change are distinguished in carbonyl compounds. In type (i) CO is eliminated and a saturated hydrocarbon is produced, and in type (ii) there is a rupture between the α- and β-C of the hydrocarbon chain, producing an olefine and a simpler CO-compound. Type (ii) occurs more readily with ketones than with aldehydes and is facilitated by increasing the length of the hydrocarbon chain. The mechanism of the processes is discussed. J. G. A. G.

Photochemical reaction of chlorophyll.—See this vol., 1510.

Decomposition of water by X-rays in presence of the iodide or bromide ion. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 596).—Br' or I' catalyses the decomp. of H₂O on irradiation with X-rays, no decomp. occurring in its absence. The concn. of the added ion remains unchanged. In presence of H₂SO₄ (*p*_H 3—4), H₂ and H₂O₂ are formed. In unbuffered solutions, or in presence of NaOH (*p*_H 11.0), the same amount of H₂ is formed, but H₂O₂ is replaced by its equiv. of O₂. The decomp. is

independent of $[\text{Br}']$ or $[\text{I}']$ from 1.0—0.01 millimole per litre. At higher $[\text{KI}]$ free I is formed. No effect was found with Cl' . H. J. E.

Oxidation of ferrocyanide, arsenite, and selenite ions by irradiation of their aqueous solutions with X-rays. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 596).—The $[\text{Fe}(\text{CN})_6]^{4-}$ was oxidised to $[\text{Fe}(\text{CN})_6]^{3-}$, an equiv. amount of H_2 being liberated. The no. of equivs. oxidised was independent of concn. (0.1—100 millimoles per 1000 c.c.) and of p_{H} (2.0—11.0). AsO_3^{3-} and SeO_3^{2-} gave AsO_4^{3-} and SeO_4^{2-} together with an equiv. amount of H_2 . H. J. E.

Kinetic interpretation of the colouring of glass by X-rays. R. LIVINGSTON and C. E. NURNBERGER (J. Physical Chem., 1935, 39, 1011—1019).—The rate of colouring of Pyrex glass by irradiation with hard X-rays, and the distribution of relative absorption of the coloured glass as a function of λ for visible light, have been investigated. The analogous effects of Rn are discussed. E. S. H.

Ring deposits on glass by positive-ray bombardment. B. DASANNACHARYA, V. T. CHITPLONKAR, and L. G. SAPRE (Nature, 1935, 136, 642).—Brown rings are formed. L. S. T.

Chemical action of penetrating radium radiations. XX. Action on aqueous solutions of glycerol, isobutyl and ethyl alcohols, and benzene. A. KAILAN (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 163—174; Chem. Zentr., 1935, i, 1968—1969).—Prolonged action of Ra radiation, filtered through 1 mm. of glass, on aq. glycerol and EtOH produced AcOH and some HCO_2H , + aldehyde. With aq. Bu^nOH , non-volatile acids resulted. The effect is ascribed to H_2O_2 produced from the H_2O by the action of the radiation. C_6H_6 was unaffected. J. S. A.

Preparation of deuterium.—See this vol., 1407.

Concentration of heavy isotopes in cellulose. K. OKABE and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 465—466).—Purified H_2O prepared by burning filter-paper, cotton-wool, cedar wood, and bamboo is 6.3, 5.7, 4.5, and 4.4 p.p.m., respectively, heavier than normal, owing to concn. of D. Purified H_2O from the skin, internal solid, and juice of a bamboo shoot is 4.4, 0.6, and 1.0 p.p.m., respectively, heavier than normal; the concn. is not due to the rapid growth, but is a general effect with carbohydrates. R. S. B.

Chemiluminescence of 3-aminophthalhydrazide. L. HARRIS and A. S. PARKER (J. Amer. Chem. Soc., 1935, 57, 1939—1942).—Under conditions of max. light intensity the quantum efficiency of the oxidation of the Na salt of 3-aminophthalhydrazide is about 0.3%. There is evidence of compound formation with H_2O_2 . E. S. H.

Oxidation of metals. II. Copper, brass, aluminium-brass, aluminium-bronze, magnesium, and some magnesium alloys. G. D. PRESTON and L. L. BIRCUMSHAW (Phil. Mag., 1935, [vii], 20, 706—720).—Investigations were made at temp. $>400^\circ$, and the nature, crystal structure, and orientation of the oxide film were determined by

electron diffraction. The film on Cu, formed at room temp. and 100° in air, and at 183° in O_2 at atm. pressure, consists of ordinary cubic-structure Cu_2O , with a (111) plane parallel to the polished metal surface; there was no indication of CuO . A Cu—Zn brass containing 70% Cu oxidised at temp. $>183^\circ$ acquires a Cu_2O film; at 400° the film is ZnO . Al brasses (22% Zn, 2% Al) show Cu_2O after oxidation at 183° for 10 min.; at 400° ZnO is present. Al_2O_3 was not found. Mg and Mg alloys, oxidised at 400° , acquire a film of cubic MgO . The orientation of oxide films on polished surfaces is discussed; it is probable that the plane in the oxide having the highest density of metal atoms per unit area tends to lie on the polished surface. N. M. B.

Influence of temperature on the formation of additive compounds. M. RAGNO and L. VADALA (Gazzetta, 1935, 65, 686—689; cf. this vol., 182).—From solutions of Cu salts in $\text{C}_5\text{H}_5\text{N}$, which have been kept at 70 — 80° for several hr., there crystallise out compounds which contain fewer mols. of $\text{C}_5\text{H}_5\text{N}$ per mol. of Cu salt than the corresponding compounds which are obtained at lower temp. O. J. W.

Reaction between calcium hydride and water. H. FLOOD (Kong. Norske Vid. Selsk. For., 1934, 7, 66—69; Chem. Zentr., 1935, i, 1516).—The primary reaction between CaH_2 and H_2O is to give CaO , but at low temp. <2 mols. of H_2 per mol. of CaH_2 is evolved, owing to the low v.p. of $\text{Ca}(\text{OH})_2$. Above 350° reaction proceeds directly to CaO , and the drying effect of CaH_2 is most intensive. J. S. A.

Calcium chloroarsenate. C. M. SMITH (J. Washington Acad. Sci., 1935, 25, 435—436).—The compound $(\text{CaCl})_2\text{HAsO}_4 \cdot 2\text{H}_2\text{O}$ has been prepared by addition of $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ to aq. CaCl_2 . R. S.

Hydrates of monocalcium silicate. J. LEFOL (Compt. rend., 1935, 201, 669—672).—V.-p. and dehydration measurements proved the existence of the hydrates $\text{SiO}_2 \cdot 1.2\text{CaO} \cdot 2\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot 1.2\text{CaO} \cdot \text{H}_2\text{O}$. H. J. E.

Formation of barium aluminates from barium carbonate and alumina in the solid state. G. GRUBE and G. HEINTZ (Z. Elektrochem., 1935, 41, 797—804).—At 900 — 1050° the sole reaction product is $\text{BaO} \cdot \text{Al}_2\text{O}_3$, independently of which of the reagents is in excess. At higher temp. $2\text{BaO} \cdot \text{Al}_2\text{O}_3$ is formed; the equilibrium conditions have been determined. E. S. H.

Complex salts of mercury cyanide. R. UZEL (Lekarn., 1934, 14, 335—343; Chem. Zentr., 1935, i, 1353).—Salts of Cu, Ni, Zn, and Cd in aq. NH_3 solution react with $\text{Hg}(\text{CN})_2$ + excess of I' , Br' , CNS' , or N_3' to give complex salts of the general type, $[\text{M}(\text{NH}_3)_4][(\text{CN})_2\text{Hg} \leftarrow \text{X} \rightarrow \text{Hg}(\text{CN})_2]$. The following compounds were obtained: $[\text{Cu}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2 \cdot \text{X}]$; $[\text{Cd}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2 \cdot \text{X}]_2$; $[\text{Ni}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2 \cdot \text{X}]_2$ ($\text{X} = \text{I}$, Br , CNS , or N_3); $[\text{Zn}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2 \cdot \text{Y}]_2$ ($\text{Y} = \text{I}$, Br , or CNS). J. S. A.

Ammonium mercury sulphites. Potentiometric investigations. G. SPACU and C. DRAGULESCU (Z. anorg. Chem., 1935, 224, 273—279; cf. A., 1932, 1216).—Potentiometric titration of aq. HgCl_2

with aq. $(\text{NH}_4)_2\text{SO}_3$ confirms the existence of $[\text{HgCl}(\text{SO}_3)]\text{NH}_4$ and $[\text{Hg}(\text{SO}_3)_2](\text{NH}_4)_2$, which were isolated as stable, cryst. compounds. The substance $3\text{HgCl}_2 \cdot 2(\text{NH}_4)_2\text{SO}_3$, is probably a mixture.

T. G. P.

Alkali aluminium silicates. IX. Silicate component of ultramarine. E. GRUNER (Z. anorg. Chem., 1935, 224, 351—368; cf. this vol., 168).—Repeated fusion with KCN completely removes S from ultramarines (I). KCNS and K_2S_x are formed in the earlier, and KCNS and K_2S in the later, fusions. The residue has the composition KAlSiO_4 . The lattice of (I) with the ratio $\text{Al}_6 : \text{Si}_6$ remains unchanged, but that of (I) with higher proportions of Si is modified by the fusion. Jaeger's determinations of the dimensions of the unit cell have been confirmed and extended. A scheme showing relations between permutites, zeolites, nephelite, and kaolin is given.

F. L. U.

Purification of gallium by fractional crystallisation of the metal. J. I. HOFFMAN and B. F. SCRIBNER (J. Res. Nat. Bur. Stand., 1935, 45, 205—209).—If impure Ga is fractionally crystallised under aq. HCl, Ag, Hg, In, Pb, and Sn are conc. in the molten residue, Cu and Tl remain about equally divided between crystals and residue, Zn is dissolved by the HCl, whilst Sb, Bi, Cr, Co, Cb, Au, Fe, Mn, Mo, Ni, Os, Pd, Pt, Rd, Ru, and V concentrate in the crystals. It is impossible to separate Ga from $> 0.001\%$ Fe or Pt, from $> 0.01\%$ In or Pb, or from $> 0.02\%$ Sn by fractional crystallisation.

J. W. S.

Mixed polyhalides of titanium. G. P. LUTSCHINSKI [with A. I. LICHATSHEVA] (Z. anorg. Chem., 1935, 224, 420—426).—F.-p.-composition curves have been determined for mixtures of TiCl_4 and Br. The existence of compounds, TiCl_4Br (I) and TiCl_4Br_4 (II) is established. Eutectics are formed from TiCl_4 and (I), (I) and (II), and (II) and Br. Br is completely eliminated from (I) and (II) by the action of heat or of H_2O .

F. L. U.

Extraction of germanium and gallium from germanite. I. Removal of germanium by distillation of germanous sulphide. W. C. JOHNSON, L. S. FOSTER, and C. A. KRAUS. II. Acid extraction of germanium. L. S. FOSTER, W. C. JOHNSON, and C. A. KRAUS (J. Amer. Chem. Soc., 1935, 57, 1828—1831, 1831—1835).—I. Finely-ground germanite is heated in a stream of dry N_2 at 800° to remove As_2S_3 and S. NH_3 is passed over the residue at 825° , when GeS_2 is reduced to GeS , which distills and is collected. 99% of the original Ge is thus removed.

II. Ga is obtained from the residue of the above process by boiling with HCl, pptg. sulphides of heavy metals, and separating Ga and Al from large quantities of Fe and Zn by boiling the solution with NH_4HSO_3 , leaving Fe and Zn in solution. Al is separated as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ from a HCl-saturated $\text{Et}_2\text{O}-\text{H}_2\text{O}$ mixture in which Ga and traces of Fe remain dissolved. After removing the remaining Fe, Ga is pptd. as hydrated oxide; the metal is obtained by electrolysis of a solution of the oxide in aq. KOH.

E. S. H.

Allotropy of phosphoric oxide. A. N. CAMPBELL and A. J. R. CAMPBELL (Trans. Faraday Soc., 1935, 31, 1567—1574).—Amorphous P_2O_5 (I) has

$d_4^{20^\circ}$ 2.317, and solubility in CHCl_3 (S) 0.099 g. per 100 g. Heating (I) for not too long at $350-600^\circ$ yields a cryst. variety, $d_4^{20^\circ}$ 2.195, which has not been obtained pure, but is contaminated with a vitreous form which is the sole product when (I) is heated at 450° for 3 weeks. This latter is the stable form, and has $d_4^{20^\circ}$ 2.737, S 0.0015 wt.-%.

F. L. U.

Formula of sodium antimonate. L. A. VASILEVA (Trans. Butlerov Inst. Chem. Tech., 1934, No. 2, 41—49).—Dissociation vals. agree with Tomula's results (A., 1922, ii, 74), showing the formula to be NaSbO_3 and not $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$.

CH. ABS. (e)

Reactions with oxygen. A. H. BELINFANTE (Chem. Weekblad, 1935, 32, 611—615).—Theoretical. The different types of reaction involving direct oxidation by O_2 are briefly reviewed.

D. R. D.

Reaction of sulphur with water at temperatures below 100° , and its geochemical significance. E. CHERBULIEZ and R. WEIBEL (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 87—88).—Appreciable quantities of H_2S and of S_2O_3 were detected after boiling S with SO_2 buffered at p_{H} 7—6.1 for 24 hr.: $3\text{S} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{S} + \text{SO}_2$; $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$; $\text{H}_2\text{SO}_3 + \text{S} \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3$. The presence of H_2S and S_2O_3 in mineral waters is explained in this way, these waters being buffered by H carbonates.

S. J. G.

Action of hydrogen sulphide on the chromates of hydrogen, ammonium, sodium, and potassium. M. A. HAMID, G. SINGH, and H. B. DUNNICLIFF (J. Indian Chem. Soc., 1935, 12, 595—600; cf. A., 1932, 133).—In the action of H_2S on solutions of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, of $\text{K}_2\text{Cr}_2\text{O}_7$, and of H_2CrO_4 the formation of SO_4^{--} is favoured by increased temp. at the expense of $\text{S}_2\text{O}_3^{--}$. Formation of SO_4^{--} is suppressed by an alkaline medium. Analyses of the products of the reaction of H_2S with $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and with $(\text{NH}_4)_2\text{CrO}_4$ solutions under varying conditions are recorded.

O. J. W.

Action of hydrogen sulphide on insoluble chromates. I. Lead chromate and silver chromate. H. B. DUNNICLIFF and B. PRAKASH (J. Indian Chem. Soc., 1935, 12, 505—513).—Treatment of a suspension of PbCrO_4 with H_2S leads to 90—95% attack with production of PbS , $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{S}_2\text{O}_3)_3$ (partly co-ordinated), and $\text{Cr}(\text{OH})_3$, together with some S, probably due to oxidation of H_2S by atm. O_2 . The reaction occurs much more rapidly at higher temp., but with less tendency to form $\text{Cr}_2(\text{S}_2\text{O}_3)_3$. No H_2SO_3 or thionic acids are formed. Ag_2CrO_4 under similar conditions yields Ag_2S , $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_3)_3$, $\text{Cr}_2(\text{S}_2\text{O}_3)_3$ and S.

J. W. S.

Preparation of phosphorescent substances. IX. X-Ray luminophores. N. F. SHIROV, T. E. GETMAN, and E. J. MATENKO (J. Appl. Chem. Russ., 1935, 8, 848—863).—The X-ray luminescence of the following rises in the order $\text{UO}_2\text{F}_4\text{NaF} < \text{UO}_2\text{F}_2 \cdot 4\text{KF} < \text{UO}_2\text{F}_2 \cdot 4\text{NH}_4\text{F} < \text{BaPt}(\text{CN})_4 < \text{Zn}_2\text{SiO}_4$. Directions for the prep. of these substances are given, and the theoretical aspect of the problem of X-ray luminophores is discussed.

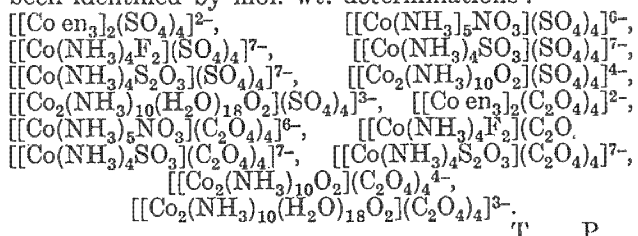
R. T.

Triple sulphates containing water. B. GOSSNER and J. BESSLER (Zentr. Min., 1934, A, 358—364; Chem. Zentr., 1935, i, 1352).—A series of sulphates analogous to voltaite has been prepared, having the general formula $\text{Fe}^{III}\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, in which Fe is partly replaced by Al. The Zn K, Co NH₄, Co Rb, and Mg Rb compounds are described. Mn forms with Li and Na compounds of type $\text{FeMn}_4\text{M}(\text{SO}_4)_6 \cdot 8\text{H}_2\text{O}$, either with or without partial replacement of Fe by Al. J. S. A.

Effect of dehydrated product on the course of dehydration. S. ŠKRAMOVSKY (Lekarn., 1934, 14, 317—322; Chem. Zentr., 1935, i, 1331).— $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$ dehydrate at 60—80° to a product with $1.5\text{H}_2\text{O}$. Addition of dehydrated salt increases the rate of dehydration, and brings about initial formation of tetrahydrate, which then dehydrates further. J. S. A.

Complex ammines of trivalent metals. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 224, 280—282; cf. this vol., 1091).—Mol. wts. of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$, $[\text{Co}(\text{NH}_3)_4\text{S}_2\text{O}_3]^{+}$, $[\text{Co}(\text{NH}_3)_4\text{F}_2]^{+}$, $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, and $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{O} \cdot \text{Cl}]^{2+}$ have been determined by dialysis. The triethylenediamine cobaltic ion is dimeric; the remainder are normal. T. G. P.

Complex compounds of which the central ion is [itself] a complex cation. II. Complex sulphato- and oxalato-compounds with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 224, 283—288; cf. preceding abs.).—The following ions have been identified by mol. wt. determinations:



Composition and properties of precipitated nickel and cobalt sulphides. I. A. W. MIDDLETON and A. M. WARD (J.C.S., 1935, 1459—1466).—The ppts. obtained from aq. solutions of the salts by means of H_2S in the absence of O_2 are probably $\text{Ni}(\text{SH})_2$, $\text{Co}(\text{SH})_2$, and $\text{Co}(\text{SH})_3$. In general, the ratios of combined S to metal in the ppts. dried in N_2 slightly exceed the vals. required by the formulæ NiS , CoS , and Co_2S_3 . The undried sulphides dissolve rapidly and extensively in $2N\text{-HCl}$ (but age to less sol. forms) and H_2S is evolved, but Co^{III} changes into Co^{II} , leading to partial oxidation and lower solubility. With aq. and C_6H_6 solutions in presence of O_2 , the sulphide ppts. contain combined S exceeding the at. ratios corresponding with the simple formulæ and, in general, somewhat greater at. ratios of H and O. Drying removes H_2O and H_2S and may cause further oxidation. The portions of these sulphides sol. in acids afford SO_4^{II} , and only traces of H_2S are produced. The dry sulphides are slowly oxidised to sulphates in the air. J. G. A. G.

Bromo-salts of trivalent iridium. (MME.) M. DELEPINE-TARD (Ann. Chim., 1935, [xi], 4, 282—291; cf. this vol., 868).—The following compounds are described: $\text{K}_4[\text{IrBr}_6] \cdot 4\text{H}_2\text{O}$; $\text{K}_2[\text{Ir}(\text{H}_2\text{O})\text{Br}_5] \cdot \text{H}_2\text{O}$; $\text{Rb}_3[\text{IrBr}_6] \cdot \text{H}_2\text{O}$; $\text{Rb}_2[\text{Ir}(\text{H}_2\text{O})\text{Br}_5]$; $\text{Cs}_3[\text{IrBr}_6] \cdot \text{H}_2\text{O}$; $\text{Cs}_5\text{Ir}_3\text{Br}_{14} \cdot 2\text{H}_2\text{O}$. F. L. U.

Double ammines of platinum. G. SPACU and V. ARMEANU (Bul. Soc. Științe Cluj, 1934, 7, 610—617; Chem. Zentr., 1935, i, 1354).—The following compounds are described: $[\text{Cu en}_2][\text{Pt}(\text{SCN})_6]$; $[\text{Co}(\text{NH}_3)_6][\text{Pt}(\text{SCN})_6]\text{Cl}$; $[\text{Co}(\text{NH}_3)_6][\text{Pt}(\text{SeCN})_6] \cdot 6\text{H}_2\text{O}$; $[\text{Co en}_3]_2[\text{Pt}(\text{SeCN})_6]_3$; $[\text{Ni en}_3][\text{Pt}(\text{SeCN})_6]$. J. S. A.

Spectrum analysis. H. DINGLE (Nature, 1935, 136, 684—685).—Definitions are discussed. L. S. T.

Sensitivity of chemical analysis with X-rays. I. Emission methods. II. Absorption methods. L. MAZZA (Gazzetta, 1935, 65, 724—730, 730—734).—I. The use of X-ray emission spectra in chemical analysis is discussed with particular reference to the rare-earth elements. In the K spectra it is possible to detect 1 : 1000, in the L spectra 1 : 25,000 parts of an element in a mixture. With elements in the metallic state the sensitivity can be extended to 1 : 50,000.

II. In absorption methods the sensitivity is greatly dependent on the at. no. of the element which has to be detected. This practically limits the method to the detection of heavy elements in presence of lighter ones. O. J. W.

Rapid determination of water in small quantities of material. J. ERDOS (Mikrochem., 1935, 18, 256—260).—The sample is distilled with xylene and the distillate centrifuged in a calibrated tube in which the H_2O is measured. The % of H_2O obtained after suitable corrections is < that obtained by the drying method. R. S.

Conductometric determination of water in acetone.—See B., 1935, 1036.

Determination of chloride with adsorption indicators. F. H. C. KELLY (J. Proc. Austral. Chem. Inst., 1935, 2, 250—254).—A review. The addition of 1% starch solution as protective colloid is advantageous. J. S. A.

Determination of the chlorate content of potassium and sodium chlorates.—See B., 1935, 990.

Determination of residual chlorine [in water].—See B., 1935, 1024.

α -Naphthoflavone as a reversible bromometric indicator. R. UZEL (Coll. Czech. Chem. Comm., 1935, 7, 380—387).—Colloidal α -naphthoflavone (I) forms reversibly an orange adsorption compound with free Br in solution. The indicator, 0.5—1 ml. of 0.1% (I) in EtOH or AcOH added to 50—100 ml. of solution, is used with KBrO_3 in determining, in HCl solution, As^{III} , Sb^{III} , Sb in tartar emetic, Sn^{II} , N_2H_4 , NH_2Ph , and NHPhAc after boiling with 20% aq. HCl, diluting and adding Br^+ . Fe^{II} , Ti^{II} , finely-divided Hg, Hg^I , PhOH, and salicylic acid

gave unsatisfactory results. When Br' is titrated with AgNO_3 in presence of 1—2 drops of 0.1N-KBrO₃ and 1 c.c. of 0.1% (I), the end-point is orange \rightarrow green. Small proportions of Cl' do not interfere.

J. G. A. G.

Micro-determination of iodine in common salt.—See B., 1935, 990.

Determination of fluorine in potable waters.—See B., 1935, 1024.

Colorimetric determination of dissolved oxygen [in water].—See B., 1935, 1072.

Determination of atmospheric ozone. Comparison of spectrographic and chemical methods. A. DAUVILLIER (Compt. rend., 1935, 201, 679—680).—The two methods gave approx. the same mean vals. (4.1, 3.3 mg. of O₃ per cu. m. of air, respectively).

H. J. E.

Determination of stibnite-sulphur in ores and minerals.—See B., 1935, 1049.

Volumetric determination of sulphate and barium ions. V. N. SKVORTZOV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 164—167).—SO₄'' is titrated with BaCl₂ in a buffered solution containing CrO₄'''. To determine Ba'' an excess of standard H₂SO₄ is added before titrating with BaCl₂.

CH. ABS. (e)

Use of lead nitrate as precipitant in the titrimetric determination of certain ions. A. RINGBOM (Acta Acad. Aboensis, Math. Phys., 1934, 8, No. 5, 142 pp.).—The potential of a Pt electrode in a solution of Pb₂Fe(CN)₆ containing a small const. [Fe(CN)₆]''' changes when an excess of Pb(NO₃)₂ is added. Using this electrode, SO₄'' may be titrated in 0.025N-Pb(NO₃)₂ solutions in presence of moderate amounts of neutral salts. In more dil. solutions, or with large amounts of neutral salts, the end-point is improved by adding EtOH. Carbonate may be titrated with Pb(NO₃)₂ by adding excess of precipitant and titrating back, or by using hot solutions. SO₃'' may be titrated at $p_H > 6$. CrO₄''' cannot be titrated. Tungstate and molybdate can be titrated in presence of a moderate concn. of neutral salt. Pb(NO₃)₂ may be titrated with Na₂CO₃ (phenol-red indicator). Oxalate may be titrated at an initial p_H of 8—8.5 (phenol-red). For SO₄'' the initial p_H should be 9—9.5 (bromocresol-purple). The same indicator is also used for SO₃'' and CrO₄'''. With tungstate the initial p_H should be 8.5—9 (bromothymol- or bromocresol-blue). Phenol-red is suitable for molybdate.

CH. ABS. (e)

Detection of the use of azides in the preparation of electron tubes. H. FRITZ (Mikrochem., 1935, 18, 162—168; cf. this vol., 837).—The total N content of the mirror gives an indication of the amount of azide used. A further test is the appearance of a permanent brown coloration when the mirror is heated, owing to the presence of Ba etc. R. S.

Detection of very small amounts of phosphorus and phosphine. L. WOLF, W. DUSING, and A. MARTOS (Mikrochem., 1935, 18, 185—192).—Gas containing P or PH₃ is passed through a capillary tube immersed in 1% AgNO₃ in aq. NH₃ and having the lower end turned up. The gas stream is adjusted

so as to impart an oscillatory motion to the liquid in the U, when a black ppt. is formed on the wall. 4×10^{-4} mg. P and 6×10^{-5} mg. PH₃ can be detected when a capillary of 0.83 mm. diameter is used.

R. S.

Elimination of phosphoric, oxalic, fluoride, silicate, and silicofluoride ions in group III. S. AUGUSTI (Annali Chim. Appl., 1935, 25, 448—451).—The method is based on the pptn. of these anions as Pb salts by treating with Pb(OAc)₂ in AcOH solution.

T. H. P.

Determination of arsenic and phosphoric acids and iron in presence of one another. G. BALANESCU and V. IONESCU (Bull. Soc. Chim. Romania, 1935, 17, 93—102).—The As is pptd. by H₂S and PO₄''' obtained as molybdate, whilst Fe''' is determined iodometrically after evaporation and treatment with HNO₃. As is obtained more accurately if titrated iodometrically with the Fe''' and determined by difference.

R. S.

Step-photometric determination of silicic acid and its application to water and mineral water. R. STROHECKER, R. VAUBEL, and K. BREITWIESER (Z. anal. Chem., 1935, 103, 1—12).—50 c.c. of H₂O are treated with H₂SO₄ and 2 c.c. of 10% aq. (NH₄)₂MoO₄. The yellow NH₄ silicomolybdate (I) formed is determined by comparison with aq. picric acid (II) or aq. K₂CrO₄ (III) in filtered blue light using the step photometer. Fe and PO₄''' must be removed by pptn. with Na₂HPO₄ + CaCl₂ + CaCO₃. Solutions of (I) with > 10 mg. of Si per litre deviate from Bell's law. (II) and (III) behave similarly in the same region of colour intensity. At low [SiO₂], the intensity of Mo-blue formed by reduction of (I) is $>$ corresponds with [SiO₂].

J. S. A.

Micro-analysis of silicates. I. Determination of silicic acid. K. SCHOKLITSCH (Mikrochem., 1935, 18, 144—153).—The indirect method, using HF (A., 1933, 687), has been adapted for micro-determinations. Correction must be made for the loss of HPO₃ during the fusion.

R. S.

Rapid test for silica in hydrogen peroxide solutions.—See B., 1935, 1043.

Sensitive test for non-metallic impurities in metals.—See B., 1935, 1051.

Micro-determination of hydrogen cyanide. M. T. FRANCOIS and M. N. LAFFITTE (Bull. Soc. Chim. biol., 1935, 17, 1088—1096).—A method employing "picro-soda" paper for the determination of 2×10^{-6} — 1×10^{-5} g. HCN is described. EtOH, oil, and starch do not interfere.

A. L.

Dipicrylamine as a micro-reagent for potassium, rubidium, and caesium. C. J. VAN NIEUWENBURG and T. VAN DER HOECK (Mikrochem., 1935, 18, 175—178).—Cs can be distinguished from K and Rb by recrystallising the dipicrylamine in presence of glycerol. Photomicrographs are given.

R. S.

Gravimetric micro-determination of potassium in presence of sodium by chloroplatinic acid. P. WENGER, C. CIMERMAN, and C. J. RZYMOWSKA (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 89—93).—Details are given for the determination of K' in

presence of 50 times as much Na^+ by converting into perchlorates and pptg. as K_2PtCl_6 . S. J. G.

Triple nitrites of the rare earths and a new micro-test for caesium. H. C. GOSWAMI and P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 608—610).—By crystallising a mixture of aq. solutions of the rare-earth nitrate, NaNO_2 , and CsNO_3 , the following compounds have been prepared; $\text{Cs}_2\text{CaCe}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaLa}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaPr}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaNd}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaSm}(\text{NO}_2)_6$, and $\text{Cs}_2\text{NaGd}(\text{NO}_2)_6$. A drop of a solution of $\text{Pr}(\text{NO}_3)_3$ (3 g.) and NaNO_2 (10 g.) in H_2O (110 g.) yields octahedral crystals with a drop of CsNO_3 solution. The test is not affected by presence of K or Rb and its limit of sensitivity is 4×10^{-8} g. Cs. J. W. S.

Determination of ammonium salts.—See B., 1935, 1043.

Electrolytic determination of silver. F. FRIEDRICH and S. RAPOPORT (Mikrochem., 1935, 18, 227—234).—Electrolysis is carried out in a micro-apparatus in presence of H_2SO_4 and tartaric acid, at 1.3—1.8 volts. R. S.

Electrolytic drop analysis. I. Theoretical principles. H. FRITZ (Mikrochem., 1935, 19, 6—16; cf. A., 1929, 1414).—(a) Relatively noble metals (e.g., Ag) in a drop of liquid may be detected by their deposition on a strip of base metal (e.g., Cu). By absorption of the drop in filter-paper, the baser metals may then be detected as usual. (b) Electrolysis of a drop absorbed in filter-paper and carried on an insulating support avoids interference due to dissolution of the electrodes. J. S. A.

Direct titration of barium salts with potassium chromate in pressure of rosolic acid as indicator. Application to determination of sulphates, especially of sulphur in pyrites and slags. A. V. VINOGRADOV (Ann. Chim. Analyt., 1935, [iii], 17, 285—288).—The use of rosolic acid (I) as indicator in the titration of Ba by the method of Jellinek (A., 1923, ii, 878) gives a clearly visible, sharp end-point. The solution is first neutralised towards (I), acidified with HCl, and finally exactly neutralised by boiling with CaCO_3 . SO_4^{--} is determined by adding BaCl_2 and titrating back the excess of Ba. Pyrites is oxidised by fusion with $\text{Na}_2\text{CO}_3 + \text{KClO}_3$, and SO_4^{--} is determined in the aq. extract. J. S. A.

Precipitation of barium sulphate in presence of chloride and bromide ions. N. A. RUDNEV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 143—156).—The effect of HCl or HBr on the wt. of BaSO_4 obtained in determining Ba^{++} or SO_4^{--} is explained. Cit. Abs. (e)

Closed titration flask for use in the bromometric determination of magnesium with 8-hydroxyquinoline. Application to determination of magnesium in tissue and urine. D. M. GREENBERG, C. ANDERSON, and E. V. TUFTS (J. Biol. Chem., 1935, 111, 561—565).—Loss of Br in the determination of Mg (A., 1932, 764) is avoided by mixing the solutions in a filter flask provided with a funnel with a long stem which projects below the surface of the liquid. The side-arm is plugged with

glass wool saturated with 20% KI. For the determination of Mg in biological material dry ashing in a muffle and the removal of Fe by the Alten method (A., 1933, 1262) are recommended. H. D.

Determination of small quantities of magnesium sulphate. M. MÖLLER and G. SCHLEGEL (Mikrochem., 1935, 18, 159—161).—The method of repeated pptn. of MgSO_4 by $\text{Ba}(\text{OH})_2$ has been carried out in an atm. of H_2 using a special apparatus. R. S.

Indirect volumetric determination of zinc. G. SPACU and C. G. MACAROVICI (Bul. Soc. Ştiinţe Cluj, 1934, 8, 129—139; Chem. Zentr., 1935, i, 1422—1423).—Zn is pptd. as $[\text{Zn}(\text{CNS})_2(\text{C}_5\text{H}_5\text{N})_4]$ by addition of excess of 0.1N- $\text{NH}_4\text{CNS} + \text{C}_5\text{H}_5\text{N}$. An aliquot part of the filtered solution is neutralised (indicator: dinitrophenol), and excess of 0.1N- AgNO_3 is added. The excess of Ag is then titrated back with NH_4CNS , using diphenylcarbazone as indicator. J. S. A.

Micro-determination of zinc by anthranilic acid. C. CIMERMAN and P. WENGER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 94—98).—To 2 c.c. of solution at p_H 5.5—7 containing 1—3 mg. of Zn^{++} , freshly prepared Na anthranilate (I) is added dropwise, using 0.3 c.c. excess. After an interval the ppt. is collected, washed once with 1—2 c.c. of 0.1% (I) and 5 times with 1 c.c. of EtOH, dried at 110° , and weighed. An accuracy of $\pm 0.3\%$ is claimed. Details of a second method are also given. S. J. G.

Modification in the confirmatory test for zinc ion. M. W. KELLY and E. L. JOHNSON (J. Chem. Educ., 1935, 12, 481—483).— Zn^{++} (≤ 50 mg.) as the nitrate is fused to deflagration with NH_4NO_3 ; a rose-coloured residue, changing in colour to yellow on further heating, is obtained. L. S. T.

Iodometric determination of zinc by Lang's method. C. W. RAADSVELD (Chem. Weekblad, 1935, 32, 655—657).—The amount of I liberated when Zn^{++} reacts with $\text{Fe}(\text{CN})_6^{--}$ and I^- is not const. The method described by Lang (A., 1933, 799) is excellent for rough determinations, but is not sufficiently accurate for exact work. S. C.

Use of styryl dyes in quantitative micro-analysis. P. KRUMHOLZ and E. KRUMHOLZ (Mikrochem., 1935, 19, 47—54).—The styryl dyes formed by $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$ with quinaldines and benzthiazoles give in neutral or acid solution sensitive red to violet colorations with Zn, Au, Pd, Cu, and Mg; less sensitively with Ag, Sn, Co, Cd, and Fe. $p\text{-dimethylaminostyryl-}\beta\text{-naphthothiazole}$ will detect Zn at a concn. of 10^{-7} . J. S. A.

Micro-determination of cadmium by means of 8-hydroxyquinoline. P. WENGER, C. CIMERMAN, and M. WYSZEWIANSKA (Mikrochem., 1935, 18, 182—184, and Arch. Sci. Phys. nat., 1935, [v], 17, Suppl., 125—126).—8-Hydroxyquinoline is added to the Cd solution buffered at p_H 6—7 and the ppt. is washed, dried, and weighed, using the Emich micro-filter technique. The accuracy is 1 in 1000. R. S.

Volumetric determination of lead. S. N. ROX (J. Indian Chem. Soc., 1935, 12, 584—585).—Neutral solutions of Pb salts (free from other metallic ions) can

be titrated with standard K_2SO_4 solution, using fluorescein as external indicator. The method can also be applied to the determination of SO_4^{2-} . O. J. W.

Quantitative emission-spectrum analysis of lead and cadmium contained in zinc oxide.—See B., 1935, 1043.

Identification of the copper ore minerals by means of X-ray powder diffraction patterns. A. W. WALDO (Amer. Min., 1935, 20, 575—597).—X-Ray data for 48 minerals are indexed in a form which permits ready identification of the mineral from its X-ray diffraction lines. L. S. T.

Determination of mercury. S. AUGUSTI (Gazzetta, 1935, 65, 689—693).—To a solution of the Hg^{II} salt an ammoniacal solution of K_2CrO_4 is added, giving a ppt. of $(Hg_2N)_2CrO_4 \cdot 2H_2O$. When this is dissolved in a solution of KI or of $Na_2S_2O_3$, for every atom of Hg, 2 mols. of NaOH, which can be titrated with a standard acid solution, are liberated. The complete determination requires 40—50 min. O. J. W.

Determination of mercury in iodinated organic mercury compounds.—See B., 1935, 1068.

Microchemical contributions. XII. L. ROSENTHALER (Mikrochem., 1935, 19, 17—22; cf. A., 1934, 791).—Yellow, but not red, HgO reacts with NH_3 , aq. $NaHSO_3$, and aq. $KHSO_4$. Vanillin gives characteristic cryst. ppts. with $Ba(OH)_2$ and $MgSO_4 + NH_4Cl$. Phenols give sensitive, in some cases cryst., orange to red ppts. with *p*-diazonitroaniline. Phloroglucinol and pyrocatechol give characteristic ppts. with Zwikker's $Cu-C_5H_7N$ reagent. Protosil gives characteristic ppts. with $[Co(NO_3)_4(NH_3)_2]K$, $AgNO_3$, $HgNO_3$, $Cu(OAc)_2$, and anthraquinone-1-sulphonic acid. J. S. A.

Volumetric determination of aluminium, $p_H > 10$. V. N. SKVORTZOV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 156—164).—Results in the determination of Al by titration with KOH with malachite-green as indicator depend on the temp., concn. of indicator, concn. of solutions, and absence of CO_2 . The method is untrustworthy.

CH. ABS. (e)

Quantitative separation of metals by hydrogen sulphide. VIII. Separation of aluminium from iron, nickel, and cobalt. H. KATÔ (J. Chem. Soc. Japan, 1935, 56, 210—212; cf. this vol., 719).— FeS , NiS , and CoS are pptd. with H_2S at a suitable p_H , basic Al acetate being pptd. from the filtrate by boiling with $NaOAc$. CH. ABS. (e)

Spectrophotometric determination of manganese in steel.—See B., 1935, 1047.

Mixed perchloric and sulphuric acids. III. Determination of chromium in chromic oxide. G. F. SMITH, L. D. McVICKERS, and V. R. SULLIVAN (J.S.C.I., 1935, 54, 369—372; cf. A., 1934, 982).—The oxidation of Cr_2O_3 by $HClO_4$ alone is incomplete owing to the production of a small amount of H_2O_2 . Rapid cooling minimises this and quant. results may be obtained with a mixture of 1 vol. of aq. $HClO_4$ (72%) + 2 vols. of aq. H_2SO_4 (80%). R. S.

Conductometric titration of molybdate with silver nitrate. C. CANDEA and I. G. MURGULESCU

(Bull. Soc. Chim. Romania, 1935, 17, 103—105).— NH_3 must be removed by NaOH and the solution neutralised with HNO_3 before titration. Accurate results are obtained only when $[MoO_4^{2-}] > 0.002N$. R. S.

Use of induced precipitation for detection of small amounts of titanium and zirconium. F. FEIGL and E. RAJMANN (Mikrochem., 1935, 19, 60—63).—To a solution containing < 1 pt. of Ti in 50,000, a few drops of Zr solution are added, and Zr then pptd. with H_3AsO_4 . Ti is co-pptd. and may be detected with H_2O_2 in the ppt. after dissolution in H_2SO_4 . The sensitivity is lowered in presence of Fe, V, W, or Mo. Conversely, Ti may be added to a Zr solution, co-pptg. Zr, which is detected with azoarsinic acid. J. S. A.

Determination of vanadium in the field. V. A. SILBERMINTZ and K. P. FLORENZKI (Mikrochem., 1935, 18, 154—158).—A spot method depending on the oxidation of NH_2Ph is used. HCl and H_3PO_4 are added when Fe is present. R. S.

Relation between sensitivity and mol. wt. (Weighting effect.) P. KRUMHOLZ and H. WATZEK (Mikrochem., 1935, 19, 55—59).—The sensitivity of cyclic N bases as precipitants for $HBiI_4$ is raised by progressive weighting of the ring system, by replacement of S by Se, or by conversion into the corresponding ethiodide. J. S. A.

Micro-determination of bismuth as oxyiodide. F. HECHT and R. REISSNER (Mikrochem., 1935, 18, 283—288).—The method (A., 1928, 388) is inexact. R. S.

Micro-analytical determination of platinum metals in simple and complex salts. J. MEYER and K. HOEHNÉ (Mikrochem., 1935, 19, 64—71).—Pt may be determined by cautious ignition in air. Rh, Ir, Ru, and Pd salts may be ashed in air and finally reduced in H_2 . Only with Pd is cooling in CO_2 essential. Os salts must not be heated in air. Au invariably gives losses due to volatilisation of Au halides. The method is applicable only in the absence of other metals. J. S. A.

Water thermostat. (MME.) S. LALLEMAND (Bull. Soc. Chim. biol., 1935, 17, 1470—1471).—An arrangement for maintaining a water-bath at a temp. $<$ that of the room is described. A. L.

Temperature measurement with photo-electric cells. H. J. ZETZMANN (Arch. tech. Mess., 1934, 4, 1, 116—117; Chem. Zentr., 1935, i, 1420).—Temp. and very rapid fluctuations of temp. above 550° may be measured by determining photo-electrically the intensity of some definite filtered spectral region of the emitted thermal radiation. J. S. A.

Errors in the measurement of temperatures with thermocouples.—See B., 1935, 1025.

Thermocouple vacuum calorimeter [for determining heats of adsorption]. W. E. GARNER and F. J. VEAL (J.C.S., 1935, 1436—1443).—The factors affecting the trustworthiness of several designs of thermocouple calorimeters for determining heats of adsorption of gases on oxides, whereby the adsorbent is placed in a glass vessel surrounded by a high vac., have been investigated. Total heats of slow and

rapid adsorption processes and differential heats of slow adsorption processes are determined accurately, but untrustworthy data for differential heats of rapid processes may be obtained owing to uneven distribution of gas throughout the adsorbent and low grain conductivity in the absence of sufficiently high mobility of the adsorbed mols. in the capillaries. J. G. A. G.

New optical method for the determination of elastic constants of crystals. C. SCHAEFER and L. BERGMANN (*Atti R. Accad. Lincei*, 1935, [vi], 21, 701—702).—Examples are given of the diffraction figures obtained when a beam of monochromatic light is passed through rapidly oscillating crystals of quartz and other substances. From a study of these figures the elastic constns. of the crystal may be calc.

O. J. W.

Simple process for absolute calibration of photo-cells. H. THEISSING (*Physikal. Z.*, 1935, 36, 683—684).—The Hefner lamp, of which the spectral energy distribution closely follows Wien's law, is used to obtain a calibration curve.

A. J. M.

Standardisation of photo-electric cells for the measurement of visible light. H. H. POOLE and W. R. G. ATKINS (*Phil. Trans.*, 1935, A, 235, 1—27).—Representative types of vac. emission and rectifier photo-electric cells have been standardised in light from (a) open solid C arc, (b) vac. sub-standard filament lamp at 2360° abs., (c) artificial "mean noon sunlight" derived from the latter by interposing special filters. The cells were also compared in mixed daylight. Consts. relating to 19 such cells are recorded.

E. S. H.

Modified photographic method for substances of small rotatory dispersion. R. PADMANABHAN (*J. Indian Chem. Soc.*, 1935, 12, 559—565).—The usual method is unsatisfactory for substances of which the optical activity does not vary very much with λ , but by determining the rotatory dispersion of such a substance in a column which also contains another substance of normal dispersive power and high initial rotation, e.g., quartz plates, better results can be obtained. Measurements for β -pinene are recorded.

J. W. S.

Gaseous discharge tube designed as an intense source of continuous ultra-violet radiation. R. H. MUNCH (*J. Amer. Chem. Soc.*, 1935, 57, 1863—1865).—A low-voltage H_2 discharge tube, requiring no H_2O cooling, is described.

E. S. H.

Rapid measurement of optical absorption for small light intensities. M. VON ARDENNE and E. HAAS (*Z. physikal. Chem.*, 1935, 174, 115—121).—The current from a photo-electric cell creates a p.d. in a coupling resistance which is amplified to work a pointer galvanometer. By using a carrier frequency of ~ 20 hertz, produced by periodic cutting off of the incident light, it is possible to use an a.c. amplifier. Light intensities as low as 7×10^{-11} g.-cal. per sec. may be measured in 1 sec. with an accuracy of $\pm 1\%$. The method is suitable for measuring the absorption of light in living cells by the pigments involved in O transfer.

R. C.

New method of focussing in X-ray spectrography. V. KUNZL (*Compt. rend.*, 1935, 201, 656—658).

H. J. E.

Photographic measurement of intensities of spectral lines. E. W. MULLER (*Z. Physik*, 1935, 97, 97—106).—A subjective method applicable to comparison of heterochromatic lines is described.

A. B. D. C.

Compensating photo-electric colorimeter.—See B., 1935, 1001.

Variable layer photo-electric comparison photometer. New type of photo-electric colorimeter. A. GOUDSCHMIDT, jun., and W. H. SUMMERSON (*J. Biol. Chem.*, 1935, 111, 421—433).—The light beams, after passing through the tubes of the colorimeter, fall on two photo-electric cells, arranged to give a differential deflexion on a galvanometer, used as a null instrument. A sensitivity of about 0.5% is attained.

F. A. A.

[Colorimetric technique.] R. VLADESCO (*Compt. rend. Soc. Biol.*, 1935, 120, 221—223).—For colorimetric determinations in complex solutions, equal vols. of the unknown solution are introduced into both colorimeter vessels, a known vol. of the standard is added to one, and the concn. of the unknown determined by difference.

R. N. C.

Colour analysis and specification. J. RAZEK (*Paper Trade J.*, 1935, 101; T.A.P.P.I. Sect., 187—191).—A general outline of the spectrophotometric method of colour analysis is given, and the method of reduction to trilinear co-ordinates in accordance with the procedure suggested by the International Committee on Illumination is described. The significance of dominant λ , colorimetric purity, and relative brightness is discussed. In the case of white samples, it is possible from the co-ordinates to calculate the degree of whiteness in accordance with Judd's formula (B., 1935, 719).

H. A. H.

Errors in colorimetric determinations. R. DOLIQUE (*Bull. Soc. Chim. biol.*, 1935, 17, 1304—1317).—Errors in colorimetric determinations are attributed to the effects of eye-strain. These effects are reduced to a min. by systematic movements of the plungers alternating with periods of rest.

A. L.

Microscopical methods for determining refractive index by immersion. C. P. SAYLOR (*J. Res. Nat. Bur. Stand.*, 1935, 15, 277—294).—The sensitivity of the criterion of match, which limits the immersion method of determining n , has been studied as a function of the method, objective aperture, and size and shape of particle. Objectives of low numerical aperture lead to greater sensitivity. The effect of birefringence has also been studied.

J. W. S.

Mass spectrometer. S. H. BAUER (*J. Physical Chem.*, 1935, 39, 959—965).—The principles of a simple instrument are discussed.

E. S. H.

Measurement of dielectric constants. A. BUCHNER (*Z. tech. Phys.*, 1935, 16, 10—12; *Chem. Zentr.*, 1935, i, 1828—1829).—A valve circuit for dielectric const. measurements which permits the simultaneous determination of dielectric losses is described.

J. S. A.

Simultaneous determination of dielectric constants and conductivity of conductors at high frequency (two-phase bridge). H. GROSS and I. HAÜSSER (Ann. Physik, 1935, [v], 24, 127—160).—Apparatus for a new bridge method which allows the determination at high frequency of the magnitude and angle of loss of a resistance without the use of compensating resistances is described. A. J. M.

Camera for electron diffraction. R. MORGAN and N. SMITH (Rev. Sci. Instr., 1935, [ii], 6, 316—319).—Full constructional details are given. C. W. G.

Transmission photographs of single crystals with fast electrons, and their use in structure determination. G. AMINOFF and B. BROOME (Z. Krist., 1935, 91, 77—94).—Apparatus and technique for obtaining diffraction photographs with thin crystal flakes and also with thicker specimens are discussed. B. W. R.

Micro-cell for the measurement of electrolytic conductivities. A. FINK and P. GROSS (Mikrochem., 1935, 18, 169—174).—A cell having a vol. of 0.45—0.8 c.c. is described. The equiv. conductivity of DCl in D₂O is 250. R. S.

Applicability of conductometric methods with visual observation to titrations in presence of much indifferent electrolyte. G. JANDER and A. EBERT (Z. Elektrochem., 1935, 41, 790—794).—With good apparatus and technique, satisfactory results can be obtained when a 500-fold excess of foreign electrolyte is present. E. S. H.

Antimony electrode for p_H measurement. A. HOLMQUIST (Z. Elektrochem., 1935, 41, 807).—A claim for priority (cf. this vol., 1218). E. S. H.

[Antimony electrode for p_H measurement.] P. WULFF and W. KORDATZKI (Z. Elektrochem., 1935, 41, 807).—A reply (cf. preceding abstract). E. S. H.

Micro-analytical notes. I. Methods of dealing with small quantities of liquids and precipitates. B. L. CLARKE and H. W. HERMANOE (Mikrochem., 1935, 18, 289—298).—Various micro-pipettes, a steam-jacketed capsule, and a micro-distillation apparatus are described. The distillation flask is flat and contains sand to prevent frothing. Sulphides are best pptd. in sealed tubes under pressure by H₂S produced from AcSH. R. S.

Prevention of frothing in Arndt's determination of nitrogen. W. CLASSEN (Chem.-Ztg., 1935, 59, 857).—Froth produced on distilling nitrates according to Arndt's method may be removed by adding sulphate, e.g., 0.5% of MgSO₄ to MgCl₂ lye. Distillation is rapid and the flask is more easily cleaned. R. S. B.

Improved screw plunger for use with mercury piston micro-burettes. S. J. FOLLEY and E. A. ROWSELL (Mikrochem., 1935, 18, 303—304).—A cotton-wool gland is fitted. R. S.

Simple micro-burette without stopcocks. K. SCHWARZ (Mikrochem., 1935, 18, 309—311; cf. A., 1933, 586).—Further details are given. R. S.

Pregl micro-analysis. J. UNTERZAUCHER (Mikrochem., 1935, 18, 312—315).—A stopcock on the inlet tube of the Mariotte flask allows the experiment to be interrupted without interfering with the adjustment of the gas flow. Carius tubes can be opened with the blowpipe flame, thus avoiding contamination of the material by glass. R. S.

Analysis of small volumes of gas by means of the usual micro-analytical apparatus. W. F. BRUCE (Mikrochem., 1935, 18, 261—265).—The Pregl combustion train has been adapted to the analysis of small vols. of gas obtained from *B. aertrycke* in synthetic citrate medium. R. S.

Compact vacuum gauge for measuring pressures from 0.2 mm. to 0.0001 mm. of mercury. C. T. KNIPP (Trans. Illinois State Acad. Sci., 1935, 27, 127—128).—A small McLeod gauge, requiring 10 c.c. of Hg, and connected to the apparatus by a ground joint, is described. CH. ABS. (e)

Improved method of extraction. C. A. MARLIES and V. K. LAMER (J. Amer. Chem. Soc., 1935, 57, 2008).—Extraction of a H₂O-sol. substance, e.g., NH₂NO₂, by Et₂O is more complete and rapid if the H₂O is frozen in solid CO₂. R. S. C.

Dynamic methods for determination of Young's modulus. J. M. IDE (Rev. Sci. Instr., 1935, [ii], 6, 296—298).—The specimen is set in vibration by electric traction and the frequency determined by the use of a piezo-electric detector. C. W. G.

Hydrogenation apparatus for small quantities of material. J. ERDOS (Mikrochem., 1935, 18, 305—308).—H₂ is admitted to the catalyst before addition of 0.5—1 c.c. of the solution. The vol. change is measured in a gas burette. R. S.

High-vacuum micro-desiccator. J. UNTERZAUCHER (Mikrochem., 1935, 18, 315—318).—The boat is contained in a stoppered vessel in the desiccator. Hygroscopic substances can be weighed without contact with the atm. R. S.

New methods of determining mol. wt. K. RAST (Chem.-Ztg., 1935, 59, 853—857).—A review, including micro-methods. R. S. B.

Camphor as cryoscopic solvent and mol. wt. determination by Rast's method. C. F. CAPELLO (Giorn. Farm. Chim., 1934, 83, 336—342, 345—347; Chem. Zentr., 1935, i, 1421).—The cryoscopic const. of camphor is taken as 400. J. S. A.

Micro-determination of mol. wt. M. AF HALLSTRÖM (Ann. Acad. Sci. fenn., 1934, 41, A, No. 6; Chem. Zentr., 1935, i, 1421).—Isotonic solutions of the substance under examination and of a reference substance are prepared by dropping solvent into an evacuated desiccator within which the two solutes are in similar open weighing bottles. The mol. wt. is calc. from the cons. of the solutions as determined from their increase in wt. J. S. A.

Apparatus for the determination of mol. wt. by the camphor method. C. TIEDCKE (Mikrochem., 1935, 18, 223—226).—The H₂SO₄ bath is enclosed by a glass cap carrying the thermometer, stirrer, and a hook for the m.p. tube. R. S.

Micro-filtration apparatus. H. YAGODA (Mikrochem., 1935, 18, 299—302).—The use of a micro-filter of the Buchner type for the detection of Fe etc. is described. R. S.

Fractional ultrafiltration. P. GRABAR (Bull. Soc. Chim. biol., 1935, 17, 1245—1303).—A review of recent work.

Fractional distillation of extremely small volumes of liquids. A. A. BENEDETTI-PICHLER and J. R. RACHELÉ (Mikrochem., 1935, 19, 1—5).—Apparatus is described for the evaporation of 5—15 cu. mm. of liquid below its b.p., condensation taking place on a cold point. J. S. A.

Sealing metals to glass. A. W. HULL (Physical Rev., 1934, [ii], 45, 285—286).—The differential thermal expansion between glass and metal has been measured for the common sealing materials and for some new alloys and glasses. A new alloy the expansion of which matches that of a particular glass from 0° to the softening point has been used to confirm the hypothesis that properly annealed seals will be strain-free to exactly the degree indicated by expansion data. L. S. T.

Adolf von Baeyer, 1835—1917. J. R. PARTINGTON (Nature, 1935, 136, 669—670).—Historical. L. S. T.

Geochemistry.

Helium content of the stratosphere. F. A. PANETH and E. GLUCKAUF (Nature, 1935, 136, 717—718).—The % of He in the air of England remains practically const. ($5.27—5.35 \times 10^{-6}$ c.c. per c.c.) up to a height of 18 km., but at 21 km. an 8% increase has been observed. L. S. T.

Proportion of heavy water in the water of crystallisation of minerals. E. H. RIESENFELD and M. TOBIANK (Ber., 1935, 68, [B], 1962—1969; cf. A., 1934, 1327).—The enrichment in D₂O of the crystal water of rasorite, tincal, carnallite, polyhalite, and gypsum is < that recorded by other authors for natural waters of differing origin. Since similar results have been recorded by other workers, enrichment in D₂O by crystallisation of salts and minerals has never been observed. This is attributed to the rate of crystal formation being small in comparison with the rate of exchange reaction in the D₂O content of the aq. and cryst. phase. The solubility of hydrated salts in D₂O and that of salts containing D₂O of crystallisation in H₂O are therefore not consts. at const. temp., but depend on the amount of salt employed in determining the solubility and other factors. Both must lie between the solubility of hydrates in H₂O and that of D₂O-containing compounds in D₂O, both of which are true consts. H. W.

Occurrence of radium in north- and middle-German deep waters. O. HAHN and H. J. BORN (Naturwiss., 1935, 23, 739—740; cf. A., 1934, 505).—The high He content of sylvine indicates that it was deposited from H₂O more highly radioactive than sea-H₂O. The Ra content of H₂O from oil-borings and elsewhere in the neighbourhood of the north German salt deposits is > that of any previously investigated German H₂O. The Ra content increases with Ca content of the H₂O, and in the stronger Ra-containing H₂O, Li is present. A. J. M.

Chemico-physical analysis of waters of Lurisia and Mondovi. Presence of lithium in besimaudite, quartziferous porphyry, of the same locality. L. FRANCESCONI and R. BRUNA (Annali Chim. Appl., 1935, 25, 460—470).—These waters (cf. A., 1934, 273) are radio-active and contain P₂O₅ and Li₂O in appreciable amounts. T. H. P.

Travertine-depositing waters near Lexington, Virginia. E. STEIDTMANN (Science, 1935, 82, 333—334).—These waters are supersaturated with Ca(HCO₃)₂ throughout the year, the excess ranging from approx. 68 to 76 p.p.m. of CaCO₃. The largest excess appears in winter. The annual range of p_H, temp., free CO₂, and other constituents are recorded. The marked deposition of calcite (I) in the summer is due mainly to a rise in temp., but adjustment is also hastened by aeration and close contact of the H₂O with (I). Travertine grows from the base of the plants upwards by addition of (I) to (I), which may be a result of the catalytic action of (I) on unstable CaCO₃ solutions. L. S. T.

[Electrical conductivity of] salts dissolved in waters of the Autonomous Sandjak of Alexandria. V. FROLOW (Compt. rend., 1935, 201, 613—615).—Conductivity data are recorded. H. J. E.

Plate-like crystals of native silver from "Gottes Hülfe in der Not" mine, Kongsberg-feltet [Norway]. R. STØREN (Tids. Kjemi, 1935, 15, 124—126).—Their occurrence (in a cavity), form, and habit are described. The crystals contain > 3% Hg, whilst no trace of this has been detected in the ordinary ZnS and PbS ores of the mine. It is concluded that the crystals represent a primary deposition from magmatic H₂O. M. H. M. A.

Genetic significance of biotite-pyroxenite and hornblendite. D. L. REYNOLDS (Tsch. Min. Petr. Mitt., 1935, 46, 447—490).—The biotite-pyroxenite of the Newry igneous complex in Co. Down, Ireland, is believed to represent the parent magma from which the other rocks (monzonite, syenite, diorite, granodiorite) have originated by its action on the surrounding sedimentary rocks. Emanations rich in alkalis first gave rise to a feldspathisation of the sediments, which were then soaked with the highly fluid magma. Similar occurrences of biotite-pyroxenite or hornblendite in other regions are compared. L. J. S.

Petrochemistry of the Middle Bohemian pluton. A. ORLOV (Tsch. Min. Petr. Mitt., 1935, 46, 416—446).—43 analyses (8 new) are tabulated of rocks ranging from granite to gabbro from this

plutonic complex (the so-called Middle Bohemian granite massif). The relation of the intrusion to the tectonics of the district is discussed. Differentiation of the magma took place both before and after the intrusion. L. J. S.

Biogenic migration of rare elements. A. P. VINOGRADOV (Trans. Internat. Soc. Soil Sci., Sov. Sect., 1935, A, 64—69).—There appears to be a tendency towards the accumulation of elements of uneven at. no. in soil compared with the composition of the earth's crust. Elements which show greatest biogenic migration are those which most easily form sol. compounds. A. M.

Pyroxene group. A. N. WINCHELL (Amer. Min., 1935, 20, 562—568).—Variations in optical properties and composition, expressed as mol. %, are diagrammatically represented for the following series: clinoenstatite (I)—diopside (II), (II)—hedenbergite (III), (III)—clinohypersthene, MgSiO_3 — FeSiO_3 monoclinic pyroxenes, and clinoenstatite—(II)—(III). Minerals should no longer be regarded as compounds which can be expressed by simple formulæ, but as a series varying in composition through a considerable range. L. S. T.

Genesis of the ore at the Flathead Mine, N.W. Montana. P. J. SHENON (Econ. Geol., 1935, 30, 585—603).—The ore minerals are divided into hypogene and supergene sulphides and oxidation products. The former include pyrite, galena, antimonial matildite, and small amounts of enargite, and the latter, argentite, small amounts of covellite, and possibly marcasite. The associated gangue minerals are mainly quartz, barite, clay minerals, and alunite. The more common oxidation products are anglesite, melanterite, siderotil, malachite, and a yellow amorphous powder containing Pb, Sb, and Bi. Two stages of mineralisation are described, and the genesis of the deposit is discussed. L. S. T.

Red copper ore and plagihedral hemihedry. R. SCHROEDER (Zentr. Min., 1934, A, 353—358; Chem. Zentr., 1935, i, 1354).—Crystals of red Cu ore from Cornwall exhibited plagihedral hemihedry. Only right-handed forms were observed. J. S. A.

Copper ores of Kisenda (Belgian Congo). II. Presence of two varieties of chalcocite. III. Presence of a hypogene covellite and a supergene covellite. M. GYSIN (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 82—85, 116—119).—The varieties are described and explanations of their origin are offered. S. J. G.

Paragenesis of the Colorado copper sulphides, Cananea, Mexico. V. C. KELLEY (Econ. Geol., 1935, 30, 663—688).—The Colorado ore body is located within and along the contacts of a quartz porphyry stock which has been intruded into a series of massive, fine-grained, volcanic rocks. The early gangue minerals form an irregular, pegmatitic ring-dike and the subsequent sulphide mineralisation is localised within and along the pegmatite ring. The ore minerals consist chiefly of Cu sulphides, molybdenite, and sulpho-salts of Cu, mainly luzonite (I) and tennantite (II). They are of hypogene origin

with the exception of minor quantities of "sooty" chalcocite (III). Blue (III) and covellite (IV) replace an earlier chalcopyrite and bornite intergrowth, the latter being more susceptible to replacement. Deposition of (III) and (IV) has been followed by a later sulphide replacement, represented chiefly by (I) and (II). Alunite is abundant throughout the ore body, and its close association with (I) and (II) indicates that they were carried and deposited by acid solutions. L. S. T.

Grunerite from Rockport, Massachusetts, and a series of synthetic fluor-amphiboles. N. L. BOWEN and J. F. SCHAIRER (Amer. Min., 1935, 20, 543—551).—The occurrence of grunerite (I), d 3.597, α 1.686, β 1.709, γ 1.729 (all ± 0.002), as shells surrounding fayalite from Rockport is described. This (I) provides the nearest approach to pure $\text{Fe}_2\text{H}_2(\text{SiO}_3)_8$ yet encountered. The analysis is SiO_2 47.54, Al_2O_3 0.20, Fe_2O_3 0.71, FeO 47.25, MnO 2.14, MgO 0.04, CaO none, Na_2O 0.29, K_2O 0.11, H_2O 1.55, F 0.01, total 99.84%. Regarded as an end-member of the cummingtonite-grunerite series the properties of this (I) are compared with those of other members of the series. The optical properties of synthetic fluor-amphiboles, prepared from pyroxenes in closed tubes at atm. pressure in presence of NaF, are also compared with those of Mg-Fe amphiboles and pyroxenes. The amphibole obtained by this method is always more magnesian than the pyroxene from which it is produced, and in the typical discontinuous reaction series olivine, pyroxene, amphibole the general relation that each phase is more magnesian than the member of the preceding phase with which it is in equilibrium, appears to hold. L. S. T.

Occurrence of narsarsukite in Montana. W. A. P. GRAHAM (Amer. Min., 1935, 20, 598—601).—Optical and chemical data for narsarsukite occurring at East Butte, Sweet Grass Hills, Montana, associated with quartz veins cutting a green syenite are recorded and compared with similar data of the same mineral from the type locality in Greenland. L. S. T.

Study of opaque minerals by the method of imprints. Improvements in the technique of electrolytic attack. T. HILLER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 119—122).—A piece of gelatinised paper is pressed on the polished surface of the grain by a metal spatula, plate of a press, etc., which is connected to the negative pole of an 8-volt battery. The positive pole is connected to a needle touching the free part of the grain. The various elements of the ore suffer anodic dissolution and are tested for in the gelatin by "developing" with suitable reagents. S. J. G.

Examination of linnaeites of N. Rhodesia and Katanga by the method of imprints. T. HILLER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 122—125).—The method described above is applied to the examination of certain linnaeites. S. J. G.

Stainierite. II. L. DE LEENHEER (Natuurwetensch. Tijds., 1935, 17, 148—156; cf. this vol., 725).—Further data are given. D. R. D.

Schoepite and becquerelite. V. BILLIET and W. F. DE JONG (*Natuurwetensch. Tijds.*, 1935, 17, 157—162).—Schoepite is $4\text{UO}_3 \cdot 9\text{H}_2\text{O}$ and has a 14.40, b 16.89, c 14.75 Å., and d 4.83. Becquerelite is $2\text{UO}_3 \cdot 3\text{H}_2\text{O}$ and has a 13.9, b 12.55, c 14.9 Å., and d 5.20. D. R. D.

Fluorescence experiments on natural sulphates. A. KOHLER and H. LEITMEIER (*Zentr. Min.*, 1934, A, 364—375; *Chem. Zentr.*, 1935, i, 1354).—Data are given for barytes, celestine, anhydrite, anglesite, and other sulphates at room temp. and elevated temp. J. S. A.

Zaratite: synthetic zaratite. M. FENOGLIO (*Period. Min.*, 1934, 5, 265—274; *Chem. Zentr.*, 1934, i, 1851).—Material identical with zaratite in composition, properties, and crystal structure is obtained by the action of dil. aq. NiCl_2 on $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite). J. S. A.

Orientation of mica microliths in plagioclases from eruptive rocks. C. ANDREATTA (*Period. Min.*, 1934, 5, 217—235; *Chem. Zentr.*, 1935, i, 1851).—Tonalites, diorite, etc. frequently show partial conversion of plagioclase crystals into preferentially oriented mica microliths. J. S. A.

Natural mineral gel from Vashegy. L. VON ZOMBORY (*Földtani Kozlony*, 1933, 63, 219—220; *Chem. Zentr.*, 1935, i, 1851—1852).—A mineral gel consisting essentially of mixed Fe and Al sulphates + SiO_2 and P_2O_5 is described. J. S. A.

Composition of sky-blue diopside from 1906 Vesuvius eruption. S. RESTAINO (*Rend. Accad. Sci. Napoli*, 1934, [iv], 4, 32—35; *Chem. Zentr.*, 1935, i, 1852).—The diopside has less SiO_2 and more CaO than corresponds with $\text{CaMg}(\text{SiO}_3)_2$, + MnO , CuO , Fe_2O_3 , Al_2O_3 etc. J. S. A.

Minyulite, a new phosphate mineral from Dandaragan, W.A. E. S. SIMPSON and C. R. LE MESURIER (*J. Roy. Soc. W. Australia*, 1932—1933, 19, 13—16).—The formula is $\text{KAl}_2(\text{OH}, \text{F})(\text{PO}_4)_2 \cdot 3.5\text{H}_2\text{O}$. The occurrence and properties are described. CH. ABS. (e)

Role of certain riparian plants in the formation of argillaceous concretions. J. ROUSSEAU (*Natural. Canad.*, 1935, 62, 99—105). CH. ABS. (e)

Shungite. N. A. ORLOV, V. A. USPENSKI, and I. N. SHACHOVITZEV (*Khim. Tverd. Topl.*, 1934, 5, 601—619).—Shungite, a natural cryst. C of very low electrical resistance, contains H_2O 7.76, ash 1.09, C 98.11, H 0.43, O+S 1.03%. An ash analysis is given. CH. ABS. (e)

Igneous assimilation and associated contact metamorphism in the Virginia mining district, New Mexico. S. G. LASKY (*Amer. Min.*, 1935, 20, 552—561).—The rocks consist mainly of basalt of probably Comanche age intruded by late Cretaceous or early Tertiary porphyritic granodiorite (I). (I) generally has a dark border which contains much augite as well as a more calcic plagioclase and more magnetite than the main mass. The differences are attributed to partial assimilation of the adjacent basalt in accordance with Bowen's reaction principle. In addition, the basalt adjacent to the contact is metamorphosed to a rock mineralogically similar to the invading (I). L. S. T.

Some properties of opal. N. L. TALIAFERRO (*Amer. J. Sci.*, 1935, [v], 30, 450—474).—Vals. of d and n for opals and opaline cherts show ranges d 1.983—2.111, n 1.441—1.456, H_2O 4.75—2.70%, but they show no regular variation with H_2O ; when plotted, they lie scattered between the theoretical curves for SiO_2 glass + H_2O and cristobalite + H_2O . On slow dehydration at 120—350°, there is first an increase in d and n up to a transition point (1.6—2.8 mols. H_2O), after which they decrease, and in the completely dehydrated material d and n are < in the original material. X-Ray powder photographs show faint patterns of high-temp. β -cristobalite, but no actual crystals are present. L. J. S.

Conglomerates and grits of Kaldurga, Kadur district, Mysore. C. S. PICHAMUTHU (*Proc. Indian Acad. Sci.*, 1935, 2, B, 254—279).—Geological characteristics are described. F. O. H.

Chemical analyses of Finnish rocks. L. LOKKA (*Bull. Com. géol. Fin.*, 1934, No. 105; *Chem. Zentr.*, 1935, i, 1354).—A summary of published data. J. S. A.

Geology of St. Kilda. A. M. COCKBURN (*Trans. Roy. Soc. Edin.*, 1935, 58, 511—547).—The rocks, all of them of igneous origin, are described with chemical analyses of eucrite, gabbro, pitchstone, and basalt. L. J. S.

Geology of Raasay, Inner Hebrides. C. F. DAVIDSON (*Trans. Roy. Soc. Edin.*, 1935, 58, 375—407).—The igneous rocks of Tertiary age are described with chemical analyses of gabbroid teschenite, riebeckite-granophyre, peridotite, and andesitic pitchstone. L. J. S.

Rare elements in (A) coal ashes, (B) German brown coal ashes.—See B., 1935, 978.

Organic Chemistry.

Evaluation of the structural theory of organic chemistry. II. J. K. SENIOR (*J. Chem. Educ.*, 1935, 12, 465—472; cf. this vol., 1305).—A lecture. L. S. T.

Investigation of different types and isomerides of non-dissociated organic compounds with the help of the dialysis method. H. BRINTZINGER and H. G. BEIER (*Z. anorg. Chem.*, 1935, 224, 325—

328; cf. this vol., 1335).—Data obtained for 17 compounds shew that the diffusion velocity of non-ionised org. mols. depends on structure. T. G. P.

Specific refraction in predicting the composition of saturated synthetic hydrocarbon mixtures. H. I. WATERMAN and J. J. LEENDERTSE (*Rec. trav. chim.*, 1935, 54, 725—727).—The sp.

refraction gives vals. for the C : H ratio of the hydrogenated polymerides of unsaturated hydrocarbons of low mol. wt. in good agreement with analytical vals. (cf. B., 1932, 536). H. G. M.

Catalytic effect of ozone in the oxidation of hydrocarbons.—See this vol., 1466.

Influence of substituents on the addition reactivity of ethylene derivatives. III.—See this vol., 1465.

Addition of hydrogen sulphide to isoprene catalysed by ferrous sulphide. J. BOESEKEN and N. v. D. LINDE (Rec. trav. chim., 1935, 54, 739—744).—Isoprene and H_2S when heated to 96° under pressure in presence of Fe_2O_3 or FeS yield a mixture, probably mainly β -thiol- β -methyl- Δ^2 -butene (I), b.p. $67^\circ/100$ mm. (red Hg salt; oxidised by I to a disulphide, b.p. 87° /high vac.), and, probably, β -dithiol- β -methylbutane, b.p. $135^\circ/20$ mm. (I) rapidly adsorbs SO when oxidised with AcO_2H . Further oxidation to H_2SO_4 also occurs (cf. A., 1934, 1307). H. G. M.

Dimerisation of Δ^2 -butadiene. S. LEBEDEV and S. SERGIENKO (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 79—82).—Thermal polymerisation of butadiene affords a monocyclic product, probably vinyl- Δ^1 -cyclohexene, which yields a trans-, m.p. 101.5 — 102.5° and a cis-tetrabromide, m.p. 74 — 75° , both of which can be reconverted into the original dimeride. No open-chain dimerides are formed, and there is no tendency to further polymerisation, which brings the probable mechanism of this reaction into line with the polymerisation of isoprene and diisoprenyl (cf. A., 1922, i, 1043). J. L. D.

Preparation of butadiene from *s*-dimethylethylene. B. A. KAZANSKI and I. A. RAFILZON (Sintet. Kauchuk, 1934, No. 1, 31—34).—3—4% of $CHMe:CHMe$ (I) is formed in the prep. of butadiene (II) from EtOH. Addition of Cl_2 to (I) affords $(\cdot CHMeCl)_2$ (III), removal of $2HCl$ from which yields (II); the latter process is best carried out by passing (III) over $BaCl_2$ at 360 — 400° [30—40% yield of (II)]. $NiCl_2$ and Al_2O_3 are much less efficient as catalysts. CH. ABS. (r)

Addition of methyl alcohol to dialkylacetylenes. G. F. HENNION and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 2006—2007).—Acetylenes and OH-compounds react to produce successively compounds of the types, $CH_2:CH:OR$ and $CHMe(OR)_2$. Hg acetylides are not essential to the mechanism, since, in presence of a catalyst prepared from HgO , Et_2O , BF_3 , $CCl_3 \cdot CO_2H$, and $MeOH$, Δ^2 -octene, b.p. 132 — 136° (from MeI and $C_5H_{11} \cdot C \cdot CNa$ in liquid NH_3), and $MeOH$ give $\gamma\gamma$ -dimethoxyoctane, b.p. 90 — $92^\circ/26$ mm. (hydrolysed to $COPr \cdot C_5H_{11}$), and $OMe \cdot CH_2 \cdot C:CMc$ gives similarly $(OMe)_2CMc \cdot [CH_2]_2 \cdot OMe$, b.p. 67 — $69^\circ/30$ mm.

R. S. C.

Acetylene polymerides and their derivatives. XXII. α -Dialkylaminomethyl- β -vinylacetylenes. XXIII. δ -Cyano- Δ^2 -butadiene [Δ^2 -pentadienonitrile]. D. D. COFFMAN (J. Amer. Chem. Soc., 1935, 57, 1978—1980, 1981—1984; cf. A., 1934, 990).—XXII. $CH_2:CH:C:CH$ (I), paraformaldehyde, and the requisite *sec.*-amine in dioxan at 100 — 105°

give smoothly ϵ -dimethylamino- (II), b.p. 133 — $135^\circ/752$ mm., -diethylamino- (III), b.p. 166 — $167^\circ/766$ mm., -*N*-piperidino- (IV), b.p. 207 — $209^\circ/766$ mm., and -dihexylamino-pent- α -en- γ -inene, b.p. 138 — $140^\circ/0.5$ mm., which are stable and have characteristic odours. Hydrogenation of (III) and (IV) in EtOH (PtO_2) gives diethyl-*n*-amylamine and *N*-*n*-amylpiperidine, respectively. (II), (III), and (IV) add HCl in presence of aq. $CuCl_2$ at 60° [less readily than does (I)] to give γ -chloro- ϵ -dimethylamino-, - ϵ -diethylamino-, and - ϵ -*N*-piperidino- Δ^2 -pentadiene, which are fairly stable (do not give rubbery polymerides) and with naphthaquinone and $(\cdot CH \cdot CO)_2O$ give black, resinous additive compounds. (II) adds p - $C_6H_4Me \cdot SH$ in ultra-violet light to give α -dimethylamino- ϵ -*p*-tolylthiol- Δ^2 -pentene, b.p. 156 — $158^\circ/0.5$ mm., adds $MeOH$ in presence of $NaOMe$ at 100° to give a substance, $C_6H_{15}ON$, b.p. 69 — $71^\circ/1$ mm. (destroyed by $KMnO_4$), and by exhaustive methylation ($Ag_2O \cdot H_2O$ at 45°) gives a hydrocarbon, C_5H_4 , b.p. 80 — 90° , unstable to heat and O_2 . Physical data are given.

XXIII. $CH_2:CH:CH \cdot CH_2Cl$ and $NaCN$ in hot $MeOH$ react with shift of the ethylenic linking to give a poor yield of Δ^2 -pentadienonitrile (δ -cyano- Δ^2 -butadiene) (V), b.p. 49 — $53^\circ/30$ mm., and δ -methoxy- Δ^2 -pentenenitrile (VI), b.p. 65 — $67^\circ/7$ mm., $\beta\delta$ - or $\gamma\delta$ -dimethoxyvaleronitrile (VII), b.p. 70 — $73^\circ/1$ mm., and a substance, $C_5H_{12}ON_2$, b.p. 131 — $134^\circ/0.5$ mm. Structures are proved by the reactions described below. (V) with conc. $HCl \cdot Et_2O$ at room temp. yields $CH_2:CH:CH:CH \cdot CO_2H$, m.p. 71° (Et ester, b.p. 65 — $67^\circ/30$ mm.; polymerises slowly at 100° and does not add naphthaquinone), with H_2 - PtO_2 in Ac_2O gives n - $C_5H_{11} \cdot NH_2$, with $KMnO_4$ - KOH gives $H_2C_2O_4$, and with $HCl \cdot EtOH$ affords by 1:4-addition and hydrolysis Et δ -chloro- Δ^2 -pentenoate, b.p. 72 — $74^\circ/1$ mm., oxidised by $KMnO_4$ to $CH_2Cl \cdot CO_2H$. (VI) and $KMnO_4$ give $OMe \cdot CH_2 \cdot CO_2H$. (VII), obtained also in 23% yield from (VI) and $NaOMe \cdot MeOH$ at 60° , with H_2SO_4 gives a dimethoxyvaleric acid, b.p. 119 — $122^\circ/1$ mm., hydrolysed by HBr to an unsaturated lactone, b.p. 83 — $85^\circ/3$ mm., 226 — $228^\circ/760$ mm. (solid polymeride formed at 150°), which is hydrogenated (PtO_2) in EtOH to δ -valerolactone [gives δ -hydroxyvaleric hydrazide, m.p. 105° (block)]. In light at 40 — 50° (V) gives a rubbery polymeride, resembling ω -polychloroprene. In 3 weeks at room temp. (V) gives 5% of an α -polymeride (VII), 14% of which is formed in 13 hr. at 100° with 42% of a dimeride. (VIII) can be compounded and partly vulcanised by heat. With hot $NaOH$ (V) gives a brittle polymeride. Physical data are given.

R. S. C.

Kinetics of interactions of sodium hydroxide with bromoethanes.—See this vol., 1465.

Isolation of crotonyl [bromide] and methylvinylcarbinyl bromide [γ -bromo- Δ^2 -butene]. W. G. YOUNG and S. WINSTEIN (J. Amer. Chem. Soc., 1935, 57, 2013).— $CHMe:CH \cdot CH_2Br$ or $CH_2:CH \cdot CHMe \cdot OH$ with HBr and PBr_3 gives mixtures of $CHMe:CH \cdot CH_2Br$, b.p. $107^\circ/760$ mm., $49^\circ/93$ mm., and $CH_2:CH \cdot CHMeBr$ (I), b.p. $86.5^\circ/760$ mm., which equilibrate in a few days at room temp., 1 hr. at 75° ,

and <5 min. at 100° to a mixture containing 14% of (I). Distillation/760 mm. of a mixture through a column gives pure (I). Physical data are given.

R. S. C.

Aliphatic substitution and Walden inversion. I.—See this vol., 1465.

Nitroso-compounds. III. Reactions of organo-metallic compounds with α -halogenonitroso-compounds. J. G. ASTON and D. F. MENARD.

IV. Reaction of ethyl nitrite with isopropyl and cyclohexyl ketones. J. G. ASTON and M. G. MAYBERRY (J. Amer. Chem. Soc., 1935, **57**, 1920—1924, 1888—1891; cf. A., 1934, 868).—III. $\text{CMe}_2\text{Br}\cdot\text{NO}$ (I) (modified prep.; 90% pure) and $\text{CMe}_2\text{Cl}\cdot\text{NO}$ (II) react with organo-metallic compounds by loss of halogen hydride to give $\text{CH}_3\cdot\text{CMe}\cdot\text{NO}$ (III) [leading to $\text{CMe}_2\cdot\text{N}\cdot\text{OH}$ (IV)] or by addition at the NO. (I) and $\text{NH}_3\cdot\text{Et}_2\text{O}$ give only NH_4Br and (IV) [by way of (III)]. (II) and ZnMe_2 (1 mol.) give CH_4 (1 mol.), (IV), COMe_2 , and $\text{NHMe}\cdot\text{OH}$; the last two arise thus: (I) + $\text{ZnMe}_2 \rightarrow \text{CMe}_2\text{Cl}\cdot\text{NMe}\cdot\text{OZnMe}$

$\text{CH}_4 + \text{CH}_3\cdot\text{CMe}\cdot\text{NMe}\cdot\text{OZnCl} \rightarrow \text{COMe}_2 + \text{NHMe}\cdot\text{OH} + \text{ZnCl}\cdot\text{OH}$, although at least some loss of HCl occurs prior to addition. (I) and ZnEt_2 react similarly to the extent of about 70%, giving COMe_2 and $\text{NHMe}\cdot\text{OH}$, but the formation of C_2H_6 shows 30% of reaction thus: (I) + $\text{ZnEt}_2 \rightarrow \text{C}_2\text{H}_6 + \text{CMe}_2\text{Br}\cdot\text{NH}\cdot\text{OZnEt} \rightarrow \text{C}_2\text{H}_6 + \text{CMe}_2\cdot\text{N}\cdot\text{OZnBr} \rightarrow$ (IV). (I) and (II) react with MgEtBr (2 mols.) as with ZnEt_2 , giving C_2H_6 , C_2H_4 , COMe_2 , NH_2OH , and (IV), but formation of an excess of C_2H_6 shows also some reaction thus: (I) + $\text{MgEtBr} \rightarrow$ (III) + $\text{MgBr}_2 + \text{C}_2\text{H}_6$. (II) and MgMeCl (1 mol.) react by addition at the NO, giving $\text{NHMe}\cdot\text{OH}$. 2 mols. of MgMeCl give also replacement of the Cl, thus: (I) + $2\text{MgMeCl} \rightarrow \text{CHMeEt}\cdot\text{NMe}\cdot\text{OMgCl} \rightarrow \text{MgCl}\cdot\text{OH} + \text{CHMeEt}\cdot\text{NMe}\cdot\text{OH}$, the resultant *N-methyl-N-sec-butylhydroxylamine*, b.p. 85—93°/115 mm. (hydrochloride, hygroscopic), being identified by reduction by SnCl_4 to *N-methyl-sec-butylamine* (hydrochloride, m.p. 242—244°; oxalate, m.p. 109—110°; also obtained from $\text{CMeEt}\cdot\text{N}\cdot\text{OH}$ by reduction and methylation). (I) and MgMeCl react similarly, but lead also to a little *N-methyl-N-tert-butylhydroxylamine* [oxalate, m.p. 166—167° (decomp.)]. (I) and MgPhBr give 20% of C_6H_6 by loss of HBr .

IV. NO·OEt reacts with COPr^2 , or cyclohexyl ketone in presence of aq. or, better, dry HCl or AcCl at the $\alpha\text{-CH}_2$ or $\alpha\text{-CH}$ or both, but the relative amounts of the two reactions cannot be correlated with the structure of the second alkyl. The following are incidentally described: *1-nitrosocyclohexyl Me*, m.p. 114—115°, and *Et ketone*, m.p. 119.5—120°; *cyclohexyl α -oximinoethyl*, m.p. 78—78.2°, and *Bu² α -oximinoisopropyl ketone*, m.p. 89.2—90°; *ethylisopropyl-*, m.p. 148.5—149°, and *propylisopropyl-glyoxime*, m.p. 140—140.3°.

R. S. C.

Chemical action of penetrating radium radiations. XX.—See this vol., 1469.

Reactivity of atoms and groups in organic compounds. XVI—XVIII.—See this vol., 1206.

Isomeric branched hexadecanols. W. M. Cox, jun., and E. E. REID (J. Amer. Chem. Soc., 1935,

1801—1802).—All the isomeric C_{16} -alcohols, $\text{CHRR}\cdot\text{CH}_2\cdot\text{OH}$, are prepared by reduction of the corresponding esters, prepared by the $\text{CH}_2(\text{CO}_2\text{Et})_2$ synthesis. The following are described, yields being stated in parentheses: *Et pentadecane- β -*, b.p. 185—187°/12 mm., γ -, b.p. 191—199°/15 mm., δ -, b.p. 181—183°/14 mm., ϵ -, b.p. 180—185°/15 mm., ζ -, b.p. 180—182°/14 mm., η -, b.p. 181—183°/14 mm., and *-o-carboxylate*, b.p. 182—183°/14 mm.; *cetyl alcohol*, m.p. 49.3°; *pentadecyl- β -*, m.p. 12—13°, b.p. 185—187°/15 mm. (66%), γ -, m.p. -0.2° , b.p. 186—188°/15 mm. (53%), δ -, m.p. 5.5° , b.p. 181—184°/15 mm. (32%), ϵ -, m.p. -14.5 to -14° , b.p. 181—183°/15 mm. (30%), m.p. -9 to -8° , b.p. 181—182°/15 mm. (33%), η -, m.p. -30 to -26° , b.p. 181—183°/15 mm. (27%), and *-o-carbinol*, m.p. -25 to -18° , b.p. 181—182°/15 mm. (28%). *n* and *d* are given for the alcohols and their acetates.

R. S. C.

Velocity of hydrolysis of cyclic acetals.—See this vol., 1465.

Benzyl ethers of ethylene glycol and glycerol. S. DANILOV [with V. DRIABCHLITZIN and O. MANOCHINA] (Rev. gen. Mat. plast., 1934, 10, 364—367; Chem. Zentr., 1935, i, 1860).—Treatment of the Na_2 derivative of glycerol with CH_2PhCl affords *glyceryl benzyl*, b.p. 173—175°/9 mm., and *dibenzyl ether*, b.p. 214—216°/9 mm. These are also obtained from glycerol (46 g.), NaOH (60 g.), and CH_2PhCl (200 g.) at 130°. *Ethylene glycol mono-*, b.p. 134—135°/13.6 mm., and *di-*, b.p. 154°/2 mm. *-benzyl ethers* are prepared similarly.

H. N. R.

Synthesis of glycerides by means of triphenylmethyl compounds. I. Mono-acid diglycerides. P. E. VERKADE, J. VAN DER LEE, and (Miss) W. MEERBURG (Rec. trav. chim., 1935, 54, 716—724).—Glycerol $\alpha\text{-CPh}_3$ ether in quinoline and the requisite acid chloride in CHCl_3 yield the $\beta\gamma$ -distearate (I) and $\beta\gamma$ -dibenzoate in 82 and 84% yield, respectively (cf. A., 1933, 374). (I) with $\text{HBr}\cdot\text{Et}_2\text{O}$ affords $\alpha\gamma$ -distearin in 82% yield. Details are given for the determination of CPh_3 as $\text{CPh}_3\cdot\text{OH}$ in compounds which contain higher fatty acids.

H. G. M.

Preparation of *d*(-)-3-phosphoglyceric acid. See this vol., 1418.

Simplexes of lecithin with polysaccharides. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1935, 280, 413—415).—The prep. is described of sol. simplexes containing lecithin (I)—starch (II) [about 50 mols. (I) to 1 mol. (II)], of (I)—glycogen and of (I)—dextrin [about 4 mols. (I) to 1 mol. dextrin].

P. W. C.

Partial synthesis of ribose nucleotides. II. Muscle inosinic acid. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1935, 111, 313—323).—Inosine (modified prep. from adenosine; 100% yield), $[\alpha]_D^{25} -38.3^\circ$, with COMe_2 and ZnCl_2 gives the 2:3-isopropylidene derivative (I), m.p. 240—245° (decomp.) after softening at 225°, $[\alpha]_D^{25} -69.2^\circ$ in dry MeOH, $[\alpha]_D^{25} -88^\circ$ in $\text{C}_5\text{H}_5\text{N}$, the structure of which is proved by ready reaction of its 5-p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative, m.p. 185—186°, $[\alpha]_D^{25} +35.9^\circ$ in $\text{C}_5\text{H}_5\text{N}$, with NaI in COMe_2 . (I) and POCl_3 in $\text{C}_5\text{H}_5\text{N}$ at -40° to -10°

give *Ba* 2:3-isopropylideneinosine-5-phosphate, +3.5H₂O, hydrolysed by 0.05N-HCl to *Ba* inosine-5-phosphate, +7.5H₂O, $[\alpha]_D^{27} -36.8^\circ$ in 0.1N-HCl, identical with the salt of natural inosinic acid.

R. S. C.

Mechanism of reactions of diacyl peroxides with other organic substances and their thermal decomposition. P. H. HERMANS (Rec. trav. chim., 1935, 54, 760—767).—A review. Acyl peroxides when heated alone or with aromatic and aliphatic hydrocarbons (or their substituted derivatives) react according to one or more of the following schemes: $R\cdot CO\cdot O\cdot O\cdot CO\cdot R \rightarrow R\cdot R + 2CO_2$ (a) and $R\cdot CO\cdot O\cdot R + CO_2$ (b), $Ph\cdot CO\cdot O\cdot O\cdot CO\cdot R \rightarrow R\cdot C_6H_4\cdot CO_2H + CO_2$ (c), $R\cdot CO\cdot O\cdot O\cdot CO\cdot R + R'\cdot H \rightarrow R'\cdot CO\cdot O\cdot O\cdot CO\cdot R + RH$ (d) and $R\cdot CO\cdot O\cdot O\cdot CO\cdot H$ (decomp. to $R\cdot CO_2H + CO_2$) + $R\cdot R'$ (e). Thermal decomp. is represented by (a) and (b). Purely aliphatic peroxides react mainly according to (a), but mixed aliphatic and aromatic peroxides react mainly according to (b) and (c), although, as with purely aromatic peroxides, all types of reaction are possible according to the conditions.

H. G. M.

Iodo-fatty acids. I. Additive products of lower unsaturated acids with hydriodic acid. E. MASUDA and K. NISHIDA (J. Pharm. Soc. Japan, 1934, 54, 1091—1100).—Addition of HI to $CH_3\cdot C\cdot CO_2H$ affords β -iodoacrylic acid (I), m.p. 147° , and $\beta\beta$ -diiodopropionic acid (II), m.p. 87° . Addition of HI to $Cl_2\cdot C\cdot CO_2H$ yields $\beta\beta$ -triiodopropionic acid (III), m.p. 131° , $\beta\beta$ -diiodoacrylic acid, m.p. 133° , and (II). Addition of HI to $Cl_2\cdot CH\cdot CO_2H$ (IV) gives (III), whilst $CHI\cdot Cl\cdot CO_2H$ and HI afford no I₂-acid, but only (II). (II) may also be obtained by the reduction of (IV) with HI. (II) with 10% NaOH yields (I).

CH. ABS. (r)

Vinylacetic [Δ^2 -butenoic] acid. C. MANNICH (Arch. Pharm., 1935, 273, 415—417).—This acid is readily obtained in 65—75% yield from $CH_2\cdot CH\cdot CH_2\cdot CN$ and conc. HCl at 100° (75 min.). With O₃ it gives only MeCHO, CO₂, and a little CH₂O and $CH_2\cdot (CO_2H)_2$, and with BzO₂H β -hydroxybutyrolactone. With SOCl₂ at 45° , followed by EtOH, or by way of the Ag salt and EtI it gives the *Et* ester, b.p. 118 — 120° , which with O₃ gives probably Et γ -formylglutaconate.

R. S. C.

Configurative relationship of acids of the isopropyl and isobutyl series to those of the normal series. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 111, 299—312).—Significant differences in $[M]_D^{25}$ between $Pr^a\cdot [CH_2]_m\cdot CHMe\cdot [CH_2]_n\cdot X$ and $Pr^b\cdot [CH_2]_m\cdot CHMe\cdot [CH_2]_n\cdot X$ exist only if $m=0$ or 1. *dl*- $CHMePr^b\cdot CO_2H$, b.p. $90^\circ/16$ mm., is resolved by quinine to give the *l*-form, $[\alpha]_D^{25} -18.9^\circ$. The *d*-acid, $[M]_D^{25} +6.7^\circ$, gives the *d*-*Et* ester, b.p. 146° , $[\alpha]_D^{25} +8.1^\circ$, and thence *d*- β -dimethylbutan- α -ol, b.p. 142° , $[\alpha]_D^{25} +1.9^\circ$ (acetate, b.p. 147° , $[\alpha]_D^{25} +2.7^\circ$), *d*- α -bromo- $\beta\gamma$ -dimethylbutane, b.p. 140° , $[\alpha]_D^{25} +1.9^\circ$, *d*- $\beta\gamma$ -dimethylvaleric acid, b.p. $109^\circ/14$ mm., $[\alpha]_D^{25} +1.3^\circ$ (*Et* ester, b.p. 165° , $[\alpha]_D^{25} +1.3^\circ$), $\beta\gamma$ -dimethylpentan- α -ol, b.p. 164° , $[\alpha]_D^{25} +2.8^\circ$, *d*- α -bromo- $\gamma\delta$ -dimethylpentane, b.p. 162° , $[\alpha]_D^{25} +3.3^\circ$, and $\beta\gamma$ -dimethylpentane, b.p. 90° , $[\alpha]_D^{25} +2.1^\circ$. $CHMePr^a\cdot [CH_2]_2\cdot Br$, $[\alpha]_D^{25} -4.7^\circ$, gives (Grignard) $\gamma\delta$ -dimethyl-*n*-hexoic

acid, b.p. $92^\circ/1$ mm., $[\alpha]_D^{25} -1.26^\circ$. 1- $\alpha\gamma$ -Dimethylvaleric acid (obtained by the cinchonine salt in COMe₂ at -10°), b.p. $117^\circ/17$ mm., $[\alpha]_D^{25} -13.8^\circ$, gives the *Et* ester, b.p. 164° , $[\alpha]_D^{25} +1.5^\circ$, 1- $\beta\delta$ -dimethylpentan- α -ol, b.p. 157° , $[\alpha]_D^{25} -1.1^\circ$, 1- α -bromo- $\beta\delta$ -dimethylpentane, b.p. $68^\circ/30$ mm., $[\alpha]_D^{25} -0.44^\circ$, and $\beta\delta$ -dimethylhexoic acid, b.p. $91^\circ/1$ mm., $[\alpha]_D^{25} -0.75^\circ$. $[\alpha]$ are for the homogeneous liquids, but are not necessarily max.

R. S. C.

Tetradesterostearic acid.—See this vol., 1407.

Fatty acids and glycerides of partly hydrogenated rape oil.—See B., 1935, 1054.

Polymerisation of fatty oils. IX. Hydrogenation of polymerised ethyl linolenate. X. Polymerisation of ethyl linoleate. A. STEIGER and J. VAN LOON (Rec. trav. chim., 1935, 54, 750—756, 756—759).—IX. Polymerisation of *Et* linolenate (I) at 300° in CO₂ is accompanied by the formation of a compound, b.p. 95 — 100° /high vac. (30.7%), incapable of polymerisation and hydrogenated (Pd, H₂, 1 atm., room temp.; Ni, H₂, 50 atm., 170°) to a monocyclic acid C₁₈H₃₄O₂, slowly oxidised by cold, alkaline KMnO₄. A little stearic acid is also formed, probably from unchanged (I), during hydrogenation. The main product from (I) is not completely hydrogenated by Pd (H₂, 1 atm., 15°) or by Ni (H₂, 100 atm., 170°). The resulting products have different I vals. and are oxidised by cold, alkaline KMnO₄ to products considered to consist of unsaturated compounds.

X. *Et* linoleate when heated (300° , 6—14 hr.) in CO₂ yields two main polymerisation products, b.p. $<100^\circ$ /high vac. and b.p. $>150^\circ$ /high vac. (some decomp.). The proportion of the latter increases with increase in the time of heating. The sap. and I vals., n_D^{20} , and mol. wt. of these fractions are given.

H. G. M.

Highly unsaturated acids in sardine oil. VII. Separation of highly unsaturated C₂₂-acids. VIII. Constitution of clupanodonic acid. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 433—440, 441—453).—VII. Fractionation of the highly unsaturated acids by pptn. as Na salts from COMe, affords clupanodonic acid, a more highly unsaturated fraction, chiefly docosahexaenoic acid, and a less unsaturated fraction containing cetoleic acid, C₂₂H₄₀O₂. Docosatetraenoic acid may be present.

VIII. Ozonolysis of amyl clupanodonate affords EtCHO, MeCHO, CO₂, ($\cdot CH_2\cdot CO_2H$)₂, amyl H succinate, and lower fatty acids. Ozonolysis of *di*-bromoclupanodonic acid affords a Br-compound converted by debromination and subsequent hydrogenation into C₆H₁₃CO₂H. This procedure applied to *tetrabromo*- and *hexabromo*-clupanodonic acids affords decaoic and myristic acids, respectively. On the above results clupanodonic acid is $\Delta^{7,11,15}$ -docosapentaenoic acid.

P. G. C.

Migration of allyl groups in the ethyl acetoacetate series. E. BERGMANN and H. CORTE (J.C.S., 1935, 1363—1365).—*Et* sodioacetoacetate with cinnamyl chloride in boiling C₆H₆ gives *Et* *dicinnamyl*-, b.p. $258^\circ/14$ mm., and *Et* *C-cinnamyl*-acetoacetate (I), b.p. $200^\circ/14$ mm., which is hydrolysed (EtOH-10% KOH) to γ -benzylidenebutyric acid and

α -phenyl- Δ^6 -hexen- ϵ -one. Cinnamyl alcohol, Et β -ethoxycrotonate, and NH_4Cl at 150° give Et β -cinnamylcrotonate (II); b.p. $162^\circ/12$ mm., and Et β -cinnamylcrotonate (III), b.p. 200 — $210^\circ/5$ mm. (cf. A., 1919, i, 266). (II) with boiling EtOH-10% KOH gives cinnamyl isopropenyl ether, b.p. 120 — $122^\circ/12$ mm., and β -phenyl- β -vinylpropionic acid, b.p. $162^\circ/12$ mm., which involves a re-arrangement analogous to the changes in the Ph allyl ether series. (II) at 260° gives (I), the enolic form of which reacts with cinnamyl chloride to give (III).

J. L. D.

Detection of organic compounds with the help of spot reactions. X. F. FEIGL and O. FREUDEN (Mikrochem., 1935, 18, 272—276).— $\text{H}_2\text{C}_2\text{O}_4$ reacts directly with NHPh_2 to give aniline-blue, whilst the supposed intermediate HCO_2H does not. Insol. oxalates are treated with NHPh_2 and H_3PO_4 . The test is sp. and is affected only by conc. H_2SO_4 .

R. S.

New tetrahydroxyadipic acid. T. POSTERNAK (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 184—185; cf. this vol., 846).—By oxidation of *d*-allonolactone with HNO_3 , a tetrahydroxyadipic acid, m.p. 197 — 198° (monolactone, m.p. 196° ; Et₂ ester, m.p. 153 — 154°), has been obtained.

H. G. R.

Determination of ascorbic acid. A. L. BACHARACH and H. E. GLYNN (Nature, 1935, 136, 757).—*l*-Fructose and *l*-arabinose have no reducing action on 2 : 6-dichlorophenol-indophenol, the val. of which as a reagent for the determination of ascorbic acid is emphasised.

L. S. T.

Derivatives of glycuronic acid. VI. Preparation of methyl α -chloro- and α -bromo-triacetyl-glycuronate. Synthesis of β -glycuronides. W. F. GOEBEL and F. H. BABERS (J. Biol. Chem., 1935, 111, 347—353; cf. this vol., 1352).—Me β -tetraacetylglucuronate (modified prep. from glycuronolactone) and TiCl_4 in CHCl_3 at 40 — 45° afford Me α -triacetylchloroglycuronate, m.p. 99 — 100° , $[\alpha]_D^{25} +168.7^\circ$ in CHCl_3 , which with MeOH and Ag_2CO_3 gives the β -methylglucoside, m.p. 149 — 150° , $[\alpha]_D^{25} -28.9^\circ$ in CHCl_3 , stable to Fehling's solution and completely hydrolysed by 0.1*N*-HCl. Me α -tetraacetylglucuronate and HBr -AcOH give Me α -triacetyl bromoglycuronate, m.p. 104 — 105° after sintering at 85° , which with *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ and Ag_2CO_3 affords the *p*-nitrobenzyl- β -glucoside, deacetylated by $\text{Ba}(\text{OMe})_2$ to Me glycuronate *p*-nitrobenzylglucoside, m.p. 167 — 168° , $[\alpha]_D^{25} -63.2^\circ$ in H_2O .

R. S. C.

Catalytic decomposition of chloral and acetaldehyde.—See this vol., 1466.

Kinetics of thermal decomposition of acraldehyde.—See this vol., 1464.

Photochemical decomposition of isovaleraldehyde and di-*n*-propyl ketone.—See this vol., 1468.

Reaction of periodic acid with α -ketols, α -diketones, and α -ketonealdehydes. P. W. CLUTTERBUCK and F. REUTER (J.C.S., 1935, 1467—1469; cf. A., 1934, 1090).—Many α -ketols, -diketones, and -ketonealdehydes are oxidised with the theoretical amount of HIO_4 (cf. A., 1928, 269), the amount of

acid to be used being determined in a separate experiment. Acetoin and benzoin give $\text{MeCHO} + \text{AcOH}$ and $\text{PhCHO} + \text{BzOH}$, respectively. Ac_2 and Bz_2 give 2 mols. each of AcOH and BzOH . *p*-Toluoyl-phenylcarbinol (A., 1930, 475) gives $\text{p-C}_6\text{H}_4\text{MeCO}_2\text{H}$ and PhCHO , which indicates that $\cdot\text{CH}\cdot\text{OH}$ gives rise to CHO , and $\cdot\text{CO}$ to CO_2H . 3 : 5-Dihydroxy-2-carboxybenzoyl Me ketone and -2-carboxyphenyl-acetylcarbinol with HIO_4 give AcOH and, respectively, 3 : 5-dihydroxyphthalic acid and 6-aldehydo-2 : 4-dihydroxybenzoic acid [dinitrophenylhydrazones + H_2O , m.p. 270° (decomp.)], thereby confirming the structures assigned to these compounds (A., 1933, 949). Benzofuroin (A., 1882, 499) gives 1 mol. each of PhCHO and furoic acid, and is therefore furoylphenylcarbinol.

J. L. D.

Preparation of *N*-carbethoxyketimines, $\text{CRR}'\text{N}\cdot\text{CO}_2\text{Et}$. J. HOCH (Compt. rend., 1935, 201, 560—562).—Et₂ acetals of ketones (1 mol.) with $\text{NH}_2\cdot\text{CO}_2\text{Et}$ (1.5 mols.) and a little $\text{NH}_2\text{Ph}\cdot\text{HCl}$ at 190° afford *N*-carbethoxyketimines, which are prepared (b.p. in parentheses) from the following ketones: COPr^a_2 (105 — $106^\circ/20$ mm.); COBu^a_2 (122 — $124^\circ/18$ mm.); Me nonyl ketone (170 — $172^\circ/15$ mm.); cyclohexanone ($138^\circ/51$ mm.); 2-methylcyclohexanone (144 — $145^\circ/17$ mm.); COPhMe (162 — $163^\circ/17$ mm.). COMe_2 affords isopropyl bisdiethylcarbamate, b.p. 145 — $155^\circ/15$ mm. The ketimines are decomposed instantly by dil. HCl. Et β -ethoxycrotonate with $\text{NH}_2\cdot\text{CO}_2\text{Et}$ gives Et *N*-carbethoxy- β -aminocrotonate, b.p. $133^\circ/17$ mm. The acetals of aldehydes similarly treated yield exclusively bisdiethylcarbamates.

d-Xylomethylose and [its] derivatives. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1935, 111, 325—333).—5-Iodoisopropylidene-*d*-xylose (improved prep.) with H_2 -Raney Ni in MeOH- NaOH affords isopropylidene-*d*-xylomethylose (I) [$\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative, m.p. 41 — 42° , $[\alpha]_D^{25} -18.02^\circ$ in CHCl_3 , hydrolysed by hot KOH-aq. EtOH to (I)], hydrolysed by 1% H_2SO_4 at 100° (1 hr.) to *d*-xylomethylose, $[\alpha]_D^{25} +13.26^\circ$ in H_2O (cf. this vol., 609) [*p*-bromophenyl-osazone, cryst., $[\alpha]_D^{25} +64.7^\circ \rightarrow +29.4^\circ$ in 24 hr. in $\text{C}_5\text{H}_5\text{N}$ -EtOH (3 : 2); Ac_3 derivative, b.p. 105 — $106^\circ/0.3$ mm., $[\alpha]_D^{25} +60.87^\circ$ in CHCl_3 ; phenyl-osazone, m.p. 179 — 180° , $[\alpha]_D^{25} +66.6^\circ \rightarrow 0^\circ$ in 18 hr. in $\text{C}_5\text{H}_5\text{N}$ -EtOH (3 : 2)].

R. S. C.

Crystalline *d*-gulomethylose and [its] derivatives. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1935, 111, 335—346).—Partly a detailed account of work already reported (this vol., 734). *d*-Xylomethylose with aq. $\text{HCN}\cdot\text{NH}_3$ gives *d*-idomethylonolactone, a syrup, and *d*-gulomethylonolactone (I), $[\alpha]_D^{25} -68^\circ \rightarrow -63.8^\circ$ in H_2O . (I), MeI, and Ag_2O in COMe_2 give trimethylgulomethylono- γ -lactone, b.p. $96^\circ/0.3$ mm., oxidised by conc. HNO_3 at 95 — 100° to ι - $[\text{CH}(\text{OMe})\cdot\text{CO}_2\text{H}]_2$, and with 2% Na-Hg in 20% H_2SO_4 at 0° giving *d*-gulomethylose, m.p. 130 — 131° , $[\alpha]_D^{25} -42.3^\circ \rightarrow -38.03^\circ$ in 30 min. in H_2O [*p*-bromophenylhydrazones, m.p. 135 — 136° , $[\alpha]_D^{25} -16.1^\circ \rightarrow +9.8^\circ$ in 2 weeks in EtOH, $-49.12^\circ \rightarrow +34.7^\circ$ in 2 weeks in $\text{C}_5\text{H}_5\text{N}$; phenyl-osazone, m.p. 180 — 183° , $[\alpha]_D^{25} 0^\circ \rightarrow +17.7^\circ$ in 1 hr. in $\text{C}_5\text{H}_5\text{N}$ -EtOH (2 : 3)].

R. S. C.

Manufacture of anhydrous glucose.—See B., 1935, 1064.

Test of von Fellenberg's titrimetric method for determination of sugar. T. VON FELLEBERG and P. DEMONT (Mitt. Lebensm. Hyg., 1935, 26, 168—182; cf. A., 1921, ii, 136).—The tables previously given are incorrect for lactose and maltose, since the specimens used were mixtures of the anhyd. substances and their monohydrates. Correct data are now given for the monohydrates and complete data for the calculation of mg. of glucose, invert sugar, sucrose, lactose hydrate, or maltose hydrate from c.c. of 0.1N-I used are tabulated. E. C. S.

Determination of glucose in presence of disaccharides with Barfoed's reagent. T. VON FELLEBERG (Mitt. Lebensm. Hyg., 1935, 26, 182—192).—The Cu_2O formed by reduction of Barfoed's reagent with glucose (I) is determined by the author's titrimetric method (cf. preceding abstract). The reagent is only slightly reduced by sucrose, maltose, and lactose. A table is given for calculating mg. of (I) from c.c. of 0.1N-I used. The method is applied to the examination of malt extract, starch syrup, and malt bonbons. E. C. S.

2:3:6-Trimethylglucose anhydride. K. FREUDENBERG and E. BRAUN (Ber., 1935, 68, [B], 1988).—Contrary to Hess *et al.* (this vol., 1109), the conversion of methylcellulose into 2:3:6-trimethylglucose anhydride (I) is reproducible provided the initial material is insol. in H_2O . (I) cannot be a derivative of idose, since it is hydrolysed to homogeneous 2:3:6-trimethylglucose. H. W.

Methylation of glucosphenylosazone and its formulation as a derivative of fructopyranose. (Mrs.) E. E. PERCIVAL and E. G. V. PERCIVAL (J.C.S., 1935, 1398—1402).—Glucosazone with Me_2SO_4 in COMe_2 -EtOH at 50° containing the theoretical amount of 30% NaOH gives 5-methylglucosazone (I), m.p. 116—117°, $[\alpha]_D^{20}$ -49° to -12° in EtOH, which with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ affords 5-methylglucosone, reconverted into the osazone with $\text{NHPh}\cdot\text{NH}_2$, and reduced (Zn-AcOH) to 5-methylfructose. (I) with 0.5% HCl-MeOH gradually forms a pyranoside (which supports the 5-Me structure), together with about 15% of furanoside, which forms rapidly and then remains const. in amount and is probably a result of a side reaction; fructose yields a furanoside exclusively and rapidly. (I) when boiled with MeOH-3\%HCl gives 5-methylmethylfructopyranoside, which when methylated with $\text{Me}_2\text{SO}_4\text{-NaOH}$ and then twice with $\text{MeI-Ag}_2\text{O}$ gives a syrup, b.p. $110^\circ/0.03$ mm., hydrolysed (3% HCl) to 1:3:4:5-tetramethylfructose, and is converted through its osone (as above) into 3:4:5-trimethylfructose, $[\alpha]_D^{20}$ -43° in MeOH, which with MeOH-HCl slowly affords a fructopyranoside (II), indicating substitution in position 5. (II) is further methylated and then hydrolysed to tetramethylfructopyranose, which shows that (I) probably contains a pyranose ring. J. L. D.

Crystalline structure of the sugars. II. Methylated sugars and the conformation of the pyranose ring. E. G. COX, T. H. GOODWIN, and (Miss) A. I. WAGSTAFF (J.C.S., 1935, 1495—1504;

cf. this vol., 1195).—The supposition that the C_5O ring of simple pyranose sugars is in a Sachse strainless form is without foundation, for it takes no account of the different radius and valency angle of O and assumes that the C valencies are directed towards the angles of a tetrahedron (cf. A., 1929, 383; this vol., 810). X-Ray evidence suggests that the C are nearly, although not quite, co-planar, and O is displaced (1—0.5 Å.) out of their plane. Single crystals of many of these sugars have a shortest axis of about 4.5 Å., which is possible only in a direction almost perpendicular to the ring plane; the more highly methylated sugars have shorter axes (cf. A., 1931, 1219), and the fact that configuration does not alter this val. greatly for the pyranose sugars (the furanose sugars also have as short or shorter axes) is additional evidence in favour of the "flat" structure for the ring. The assumption of a "flat" ring permits the ready interpretation of the formation of benzylidene and similar derivatives as compared with analogous reactions in compounds generally agreed to possess a Sachse configuration, e.g., cyclohexane derivatives, and in which there is at least as much strain as in the sugars. These considerations are applied in throwing light on the spatial configurations of several sugars. α - and β -Glucose are found to have been assigned correct stereochemical structures. Data as to cell dimensions and space-groups are recorded for many sugars. J. L. D.

Ketone sugar series. V. Validity of Hudson's rules of isorotation in the ketose group. Preparation of the true α -fructose<2:7>pentaacetate. E. PACSU and F. B. CRAMER (J. Amer. Chem. Soc., 1935, 57, 1944—1946; cf. this vol., 735).— β -Acetochlorofructose<2:6> (β -fructopyranosidyl chloride acetate) and NaOAc in boiling Ac_2O give 71.2% of β - and 28.8% of α -fructopyranose penta-acetate, m.p. 122—123°, $[\alpha]_D^{20}$ $+47.4^\circ$ in CHCl_3 (hydrolysed by 0.1N-NaOH to fructose), the first pair of true $\alpha\beta$ -ketose isomerides of undoubted structure. The $[\alpha]$ lead to a_{alc} 32,850 and $b_{\text{fruct.ac.}}$ $-14,350$, and thence to $[\alpha]_D$ $+45.5^\circ$ for α -methylfructopyranose tetra-acetate [cf. 45.0° for Schlubach's product (A., 1928, 873)] and 51.3° for α -ethylfructopyranose tetra-acetate [cf. 51.6° for the author's product (*loc. cit.*)]. Hudson's rules, therefore, hold in this series. The following are calc.: a_{OMe} 30,850; a_{OEt} 33,650; a_{Cl} 44,750; $a_{\text{B-}}$ 63,350; a_{OH} 17,750; all except a_{OH} are much $>A_x$ in the aldose series. $[\alpha]_D$ are predicted thus: acetates of α -fructopyranosidyl chloride $+82.0^\circ$, fluoride $+8.0^\circ$, and bromide $+119.2^\circ$: α -fructopyranose tetra-acetate $+9.2^\circ$. R. S. C.

Colour reaction for fructose. S. SUGAHARA (J. Biochem. Japan, 1935, 22, 85—91).—Treatment of dil. aq. fructose (I) with $\text{H}_2\text{SO}_4\text{-Na}_2\text{WO}_4$ at slightly alkaline reactions produces a green ppt. At suitable concns. (e.g., 0.015%), (I) but not glucose (II) gives a positive reaction. Uric acid, $\text{CO}(\text{CH}_2\cdot\text{OH})_2$, and adrenaline react similarly to (I) even after addition of NaOH, when (I), (II), and arabinose give negative responses. The application of the reaction to deproteinised blood, uric acid-free urine, etc. is described. F. O. H.

Inversion of solutions of sucrose.—See this vol., 1468.

Test of Wein's gravimetric method for determination of maltose. C. ZACH (Mitt. Lebensm. Hyg., 1935, 26, 192—195; cf. Z. Anal. Chem., 1887, 26, 255).—The method is slightly modified to bring it into line with the invert-sugar determination. The mg. of Cu_2O corresponding with known wts. of maltose monohydrate are tabulated. E. C. S.

Comparative investigations on caramel and molasses colloids. A. JOSZT and S. MOLINSKI (Kolloid-Beih., 1935, 42, 367—383).—Three products of caramelisation of sucrose have been isolated by dialysis and their properties (solubility, composition, pentosan content, p_H , electrotitration behaviour, surface tension, viscosity, extinction coeff., colour, and ease of coagulation) determined. Points of similarity of these products with the colloids present in molasses are discussed. E. S. H.

Structure of heterosides based on their ultra-violet absorption spectra. (MME.) RAMART-LUCAS and J. RABATE (Bull. Soc. chim., 1935, [v], 2, 1596—1625).—Acetobromoglucose and phenols in quinoline with freshly prepared Ag_2O give the following: *phenol*, m.p. 132—134°, $[\alpha]_D^{20}$ —60.8°, o-, m.p. 166°, $[\alpha]_D^{20}$ —68.3°, m-, m.p. 178°, $[\alpha]_D^{20}$ —67.9°, and *p-cresol*, m.p. 177°, $[\alpha]_D^{20}$ —68.6°, *guaiacol*, m.p. 152.5°, $[\alpha]_D^{20}$ —70.5°, and *resorcinol-glucoside*, m.p. 210°. Piceoside and Cl_2 in 5% Na_2CO_3 yield *chloropiceoside*, m.p. 209.5°, which with emulsin gives glucose and *chloropiceol*, 107.5°. Curves are given for the absorption spectra of these glucosides, together with the curves for β -methyl-, benzyl-, amygdonitrile-, phenylethyl-, salicyl-, and cinnamyl-glucoside, methylmannoside, aucuboside, amygdalosite, benzylgalactoside, betuloside, arbutoside, methylarbutoside, salicoside, coniferoside, helicoid, monotropitoside, lusitanicoside, geoside, populoside, and the corresponding alcohols and phenols. The results are discussed. F. R. G.

Enzymic synthesis of α -glucosides. I. VINTILESCU, C. N. IONESCU, and A. KIZYK (Bull. Soc. Chim. Romania, 1935, 17, 131—136).—In the presence of brewers' yeast extract trimethylene glycol (I) and glucose afford *trimethylene glycol- α -monoglucoside* (II), m.p. 96°, $[\alpha]_D^{20}$ +137.48° (? in H_2O), obtained pure by $\text{Ba}(\text{OH})_2$ -hydrolysis of its Ac_5 derivative, m.p. 84°, $[\alpha]_D^{20}$ +112.62° in 95% EtOH, the isolation of which from the substrate is described. The amount of (II) formed increases with increase in (I) concn. *Mannitol- α -monoglucoside*, m.p. 140°, $[\alpha]_D^{20}$ +88.44°, is similarly prepared. J. W. B.

Application of the law of mass action to the synthesis of β -glucosides. I. VINTILESCU, C. N. IONESCU, and A. KIZYK (Bull. Soc. Chim. Romania, 1935, 17, 136—150).—The supposed deviation of the emulsin (I)-catalysed synthesis of β -methylglucoside (II) from the mass action law is only apparent. It is not due to the deactivation of (I) by high $[\text{MeOH}]$, since the activity of (I) is unaltered by long contact with CHO-free MeOH at p_H 4.7. Moreover, after formation of (II) from glucose and (I) in 10—90%

MeOH solutions (Bourquelot *et al.*, A., 1913, i, 542, 781) has ceased, further addition of glucose affords more (II), showing that a true equilibrium has been reached. The real cause is the sp. action of (I) on β -glucose (III) and the decrease in the ratio (C_1) β -total glucose as the $[\text{MeOH}]$ increases (A., 1934, 927). The val. of $K_\beta = \frac{[(\text{III})][\text{MeOH}]}{[(\text{II})][\text{H}_2\text{O}]}$ is independent of $[\text{MeOH}]$ and is 0.149, the proportion of (III) being determined polarimetrically. The increase in $K_t = \frac{[\text{total glucose}][\text{MeOH}]}{[(\text{II})][\text{H}_2\text{O}]} = K_\beta/C_1$, observed with increasing $[\text{MeOH}]$ (Euler *et al.*, A., 1924, i, 1266) is due to diminution of C_1 consequent on the displacement of the equilibrium (III) α -glucose towards the right. The strict application of the mass-action law is confirmed by the const. vals. of K_β for the β -glucosides of $\text{OEt-CH}_2\text{-CH}_2\text{-OH}$ (0.380) and of mannitol (0.051). J. W. B.

Structure of cymarose. R. C. ELDERFIELD (J. Biol. Chem., 1935, 111, 527—535).—Partly a detailed account of work previously reported (this vol., 848). Cymarose (I) is proved to be 3-methyl-digitoxose. (I), Br, and $\text{Ba}(\text{OBz})_2$ in H_2O give *cymarolactone*, b.p. 110—111°/0.2 mm., $[\alpha]_D^{25}$ —25° in H_2O (stable), leading to *cymaronic acid phenylhydrazide*, m.p. 154°, $[\alpha]_D^{25}$ +2° in MeOH, and, by $\text{Ag}_2\text{O-MeI}$, 5-methylcymar-1 : 4-lactone (II), b.p. 78—80°/0.2 mm., $[\alpha]_D^{25}$ —36° in CHCl_3 , which affords 5-methylcymaronic acid phenylhydrazide, m.p. 139°, $[\alpha]_D^{25}$ —6° in MeOH. *Methylcymaropyranoside* (mixture; prep. by 0.25% HCl-MeOH), b.p. 54—64°/0.2 mm., with MeI- Ag_2O gives *Me methylcymaropyranoside*, b.p. 45—48°/0.2 mm., which with 0.1N-HCl at 100° (10 min.) affords 4-methylcymar-1 : 5-lactone (III), b.p. 88—90°/0.2 mm., $[\alpha]_D^{27}$ +30° in CHCl_3 (*Ba* salt), giving 4-methylcymaronic acid phenylhydrazide, m.p. 115—116°, $[\alpha]_D^{27}$ +17.5° in CHCl_3 . (II) and conc. HNO_3 at 90—94° lead to $\alpha\beta$ -dimethoxyglutardimethylamide, m.p. 173—174°, $[\alpha]_D^{25}$ —56° in H_2O . The known position of the Me in (III) proves that of the Me in (II). *Me dimethyl-digitoxoside*, b.p. 43—46°/0.2 mm., from digitoxose by 0.1N-HCl-EtOH at room temp. (1 hr.) and subsequent methylation (Purdie), is shown by changes of α during glucoside formation to be a mixture of furanose and pyranose forms. When hydrolysed and oxidised, it yields (II). R. S. C.

Hemicellulose from oat hulls. E. ANDERSON and P. W. KRZMARICH (J. Biol. Chem., 1935, 111, 549—552).—A mixture of hemicelluloses is obtained from oat husks by extraction with aq. NaOH after removal of starch with hot H_2O . Hydrolysis with dil. H_2SO_4 gives *d*-xylose, *l*-arabinose, and a compound of *d*-glycuronic acid containing 2 mols. of *d*-galactose. The unsaponifiable residue contains 47% of SiO_2 . H. D.

Behaviour of cellulose towards liquid chlorine, iodine, and iodine monochloride. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1935, 66, 249—254; cf. this vol., 478).—Cellulose (I) is not dissolved by liquid Cl_2 at up to 149°, nor by liquid I at 150°; each has, however, apparently a chemical action on (I). ICl at 90° dissolves (I), forming a *product* sol. in EtOH. E. W. W.

X-Ray examination of the transformation of sodium cellulose by the action of carbon disulphide. W. SCHRAMEK and F. KUTTNER (Kolloid-Beih., 1935, 42, 331—366).—The action of CS_2 gives a sol. product only when the cryst. component of the fibre is Na-cellulose I; other Na-celluloses give insol. or partly sol. products. The CS_2 , after adsorption by the fibre, reacts to form $\text{SNa}\cdot\text{CS}\cdot\text{O}(\text{C}_6\text{H}_9\text{O}_4)(\text{C}_6\text{H}_{10}\text{O}_5)_n$. E. S. H.

Ammonia-cellulose. K. HESS and C. TROGUS (Ber., 1935, 68, [B], 1986—1988).—Condensation of dry NH_3 on cellulose at -77° to -80° and its subsequent removal by evaporation causes a profound alteration in the X-ray diagram of the material. The product is regarded as NH_3 -cellulose poor in NH_3 or as a third modification of cellulose provisionally named cellulose III. If it is treated with H_2O , MeOH , or aq. NH_3 , the original X-ray diagram is not restored. It does not appear to be the primary product of the reaction, since the diagram depends on the rate of evaporation of the NH_3 . H. W.

Mono- and tri-choline orthophosphates. E. L. JACKSON (J. Amer. Chem. Soc., 1935, 57, 1903—1905).—Choline chloride, H_3PO_4 , and P_2O_5 lead to *Ca choline diphosphate* (I), $\text{NMe}_3\text{CH}_2\text{CH}_2\text{O}\cdot\text{P}(\text{O})(\text{H})_2\text{O}\cdot\text{Ca}$, free from choline, but containing 3—4% of dicholine phosphate, which was isolated therefrom as *aurichloride*, m.p. $271.5\text{--}272^\circ$ (corr.; decomp.). (I) is stable to $N\text{-HCl}$ at 100° during 50 min. and leads to (impure) *choline phosphate aurichloride*, m.p. $174\text{--}176^\circ$ (corr.), and *platinichloride*, $+2\text{H}_2\text{O}$, m.p. $207\text{--}208^\circ$ (corr.; decomp.), hygroscopic. POCl_3 and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ in CCl_4 give a 60% yield of $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_3\text{PO}_4$, b.p. $180\text{--}182^\circ/2\text{--}3$ mm. (lit. $140^\circ/40$ mm), which under certain conditions with NMe_3 in EtOH gives *tri(choline chloride) phosphate*, $(\text{Cl}\{\text{NMe}_3\cdot[\text{CH}_2]_2\text{O}\})_3\text{PO}_4$, decomp. about 245° (*tri-aurichloride*, m.p. $216\text{--}230^\circ$), which at 90° (2 hr.) gives a substance (possibly a neurine derivative by intramol. change) with increased pharmacological activity without change of appearance or composition. R. S. C.

Interaction of amino-acids and salts.—See this vol., 1460.

Action of aromatic sulphonic and hydroxy-sulphonic acids on α - and β -amino-acids. II. G. MACHEK (Monatsh., 1935, 66, 345—356; cf. this vol., 970).—Hippuric acid (I) is largely unchanged when heated in boiling xylene with C_6H_6 and conc. H_2SO_4 , apparently owing to the sluggish interaction of the latter compounds with one another, since (I) and PhSO_3H readily give BzOH and *glycine benzenesulphonate*, m.p. $153\text{--}159^\circ$ (corr.). PhMe , *m*-xylene, H_2SO_4 , and (I) analogously give *glycine toluenesulphonate*, m.p. $200\text{--}201^\circ$ (corr.), and *m*-xylenesulphonate, m.p. $171.5\text{--}172.5^\circ$. *Glycine naphthalene-2-sulphonate*, m.p. $195\text{--}196^\circ$, is purified with difficulty when obtained from C_{10}H_8 and H_2SO_4 , but is readily isolated when $2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ is used. *Glycine naphthalene-1-sulphonate* has m.p. $170\text{--}171^\circ$ (corr.) after softening at about 140° . PhOH and H_2SO_4 , $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, and $2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, respectively, transform alanine into the corresponding

phenolsulphonate, m.p. $179.5\text{--}180.5^\circ$ (corr.), *toluenesulphonate*, m.p. $193.5\text{--}195^\circ$ (corr.), and *2-naphthalenesulphonate*, m.p. 227° after softening at 224° . Leucine yields a *toluenesulphonate*, m.p. $153\text{--}153.5^\circ$ (corr.), and *2-naphthalenesulphonate*, m.p. $202\text{--}203^\circ$ (corr.). The *phenolsulphonate*, m.p. $182\text{--}183^\circ$ (corr.), and *2-naphthalenesulphonate*, m.p. $157\text{--}158^\circ$ (corr.), of β -aminobutyric acid are described. H. W.

Creatinephosphoric acid. K. ZEILE (Z. physiol. Chem., 1935, 236, 263—272; cf. Fiske *et al.*, A., 1929, 590).—When creatine is boiled with POCl_3 a cryst. Ca salt very similar to but isomeric with Ca salt of the natural acid is obtained. The synthetic acid is more slowly hydrolysed than is the natural, and its hydrolysis is not accelerated by molybdate. The titration curves of the acids are similar. Diphenoxyphosphoryl chloride (I) with $\text{CS}(\text{NH}_2)_2$ yields *diphenoxyphosphorylthiocarbamide*, m.p. 149° , which, when warmed with HgO , gives the Hg^{II} salt, m.p. 135° , of diphenoxyphosphorylcyanamide. Methylisothiocarbamide (II) with (I) gives the corresponding salt, m.p. 170° , of (II). W. McC.

Synthesis of alkylamino-acids corresponding with chitosamic acid. E. VOTOČEK and R. LUKBŠ (Coll. Czech. Chem. Comm., 1935, 7, 424—429).—*d*-Glucosemethylamic acid, m.p. 230° (decomp.), $[\alpha]_D^{+4.0}$ to $+7.5^\circ$ in 2.5% HCl , is obtained by treatment of *d*-arabinose with aq. NH_2Me , HCN , and hydrolysis. Similarly, glucose affords *d*-glucoheptosemethylamic acid, m.p. $228\text{--}230^\circ$, $[\alpha]_D^{+18.2}$ to -35.9° in 2.5% HCl , converted by PhNCO into the carbamide derivative, $\text{C}_{15}\text{H}_{22}\text{O}_8\text{N}_2$, m.p. 210° . P. G. C.

Synthesis of homocystine. W. I. PATTERSON and V. DU VIGNEAUD (J. Biol. Chem., 1935, 111, 393—398).—A facile synthesis of homocystine is reported. $\text{CH}_2\text{Ph}\cdot\text{SNa}$ and $(\text{CH}_2\text{Cl})_2$ in MeOH give $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ (71—75% yield), which with $\text{CH}_3\text{Na}(\text{CO}_2\text{Et})_2$ and subsequent hydrolysis by KOH affords β -benzylthioethylmalonic acid (75%), m.p. $114\text{--}117^\circ$. This acid, when brominated, allowed to react with conc. aq. NH_3 at room temp., and then boiled with HCl , yields *S*-benzylhomocysteine, reduced by Na-liquid NH_3 to homocystine (I) (75% yield) with some $(\text{CH}_2\text{Ph})_2$ and PhMe , and by Na- EtOH to (I) (78%). $(\text{CH}_2\text{Ph})_2$ and PhMe are also produced in the reduction of $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{NR}_2$ by Na-liquid NH_3 or $\text{H}_2\text{-Pt}$. R. S. C.

Synthesis of crystalline cystinyldiglycine and benzylcystinyldiglycine and their isolation from glutathione. H. S. LORING and V. DU VIGNEAUD (J. Biol. Chem., 1935, 111, 385—392).—Dicarbobenzylloxycystinyldiglycine (I) (from dicarbobenzylloxycystine chloride and glycine), m.p. $182\text{--}183^\circ$ (corr.) (lit. $162\text{--}163^\circ$) [Et ester, m.p. 166° (corr.)], with Na in liquid NH_3 gives cryst. cystinyldiglycine (II), m.p. 210° (block), $[\alpha]_D^{27} -67.5^\circ$ in H_2O , which can be reconverted into (I) and leads to *S*-benzylcystinyldiglycine (III), m.p. $166\text{--}167^\circ$, also obtained from (I). Cryst. (II) and (III) were obtained by partial hydrolysis of glutathione. R. S. C.

Rotatory power of ricinoleamide. E. ANDRE and C. VERNIER (Ann. Off. nat. Combust. liq.,

1934, 9, 663—672; Chem. Zentr., 1935, i, 1532).—Ricinoleamides of varying properties are obtained by successive treatments of castor oil with EtOH-NH₃; the first reacting fraction yields an amide of m.p. 66.5—67°, $[\alpha]_D^{20} +2.35'$ to $+3.1'$ in CHCl₃, and the last reacting one of m.p. 63.5—64°, $[\alpha]_D^{20} +3.6'$ in CHCl₃. The oil thus contains two ricinoleic acids which may either be *d*- and *dl*-, or differ in the position of the double linking or OH. H. N. R.

Normal fatty acid amides of ethylenediamine. N. B. TUCKER (J. Amer. Chem. Soc., 1935, 57, 1989—1990).—Di-acet-, m.p. 173—173.5°, -propion-, m.p. 189°, -butyr-, m.p. 191—191.3°, *di-valer*-, m.p. 183°, -*hexo*-, m.p. 177—177.3°, -*hepto*-, m.p. 171.5°, -*octo*-, m.p. 169—169.5°, -*deco*-, m.p. 164°, -*undeco*-, m.p. 160.5°, -*dodeco*-, m.p. 159°, -*trideco*-, m.p. 156—156.4°, -*tetradeco*-, m.p. 154.5°, -*pentadeco*-, m.p. 153°, -*hexadeco*-, m.p. 148.5°, and -*heptadeco-ethylene-diamide*, m.p. 149.5—150°, are prepared by boiling (CH₂NH₂)₂ and the Et ester of the acid for 48 hr. Crystallographic data and solubilities are recorded for the first six compounds. R. S. C.

Chromium diguanide complexes. P. R. RAY and H. SAHA (J. Indian Chem. Soc., 1935, 12, 621).—Diguanide affords the triacidic, red base, [Cr(C₂H₆N₃)₃]H·OH, cryst., which gives cryst. salts. R. S. C.

Fulminic acid polymerisation.—See this vol., 1464.

Preparation of β-chlorovinylarsine sulphide. S. L. WARSCHAWSKI (J. Amer. Chem. Soc., 1935, 57, 2012—2013).—CHCl:CH·AsCl₂, b.p. 78°/12 mm., and excess of H₂S in EtOH give β-chlorovinylarsine sulphide, m.p. 114°, unstable to light, with only a faint odour (cf. A., 1925, i, 1470). R. S. C.

Wolfram's red salt and the possibility of tervalent platinum. H. D. K. DREW and H. J. TRESS (J.C.S., 1935, 1244—1251; cf. Reihlen *et al.*, this vol., 182).—Pt etn₂Cl₂ (etn=NH₂Et) and NH₂Pr⁺·H₂O yield the compound [Pt etn₂pn₂]Cl₂·2H₂O (pn=NH₂Pr⁺), which with H₂O₂—HCl gives a reddish-brown compound, m.p. 187° (impure), considered to be an analogue of Wolfram's salt, [Pt etnCl]Cl₂·2H₂O (I). A similar red compound is obtained from the compound [Pt pn₄]Cl₂·2H₂O (II), derived from K₂PtCl₆ and NH₂Pr⁺. [Pt etn₄]Cl₂·2H₂O (III), H₂O₂, and HCl yield according to conditions (I) and [Pt etn₄Cl₂]Cl₂ (IV), respectively. This is cream-white, readily reduced to (I), and with K[Pt(NH₃)Cl₃] gives yellow crystals, and with HAuCl₄ gives the salt [Pt etn₄Cl₂]AuCl₄, also obtained by treatment of (I) or (III) with HAuCl₄. The white compound [Pt pn₄Cl₂]Cl₂ (V) was similarly prepared, and became red when moistened and rubbed with steel. (I) is dehydrated to a yellow compound [rehydrated to the scarlet salt (I)] and reduced by NH₃Et, but not by C₂H₅N, to (III). With KBr and warm H₂O (I) yields the green compound [Pt etn₄Br]Br₂·2H₂O (VI), m.p. 182° (decomp.), which remained green on dehydration at 100° to the anhyd. salt. This turned reddish-chocolate when disturbed and then scarlet when moistened. With KNCS (I) gives the thiocyanate [Pt etn₄Cl](NCS)₂, which is unstable to boiling H₂O. (I) when boiled for a few

sec. with H₂O₂ yields [Pt etn₄OH]Cl₂·2H₂O (VII) (yellow), dehydrated to a yellow anhyd. salt, reconverted into (VII) in moist air. (VII) with HCl yields (I), and with HBr green needles, presumably (VI). (I) when boiled for a longer time with H₂O₂ gives [Pt etn₄(OH)₂]Cl₂, which with HCl yields (IV). A red colour was obtained when (III) and (V) or (II) and (V) were ground together between glass surfaces. H₂PtCl₆, HCl, and (I) yield [Pt etn₄Cl₂]PtCl₆·2H₂O and [Pt etn₂]PtCl₆. This when crystallised from HCl—H₂O yields the salt [Pt etn₄]PtCl₄ (VIII) and [Pt etn₄Cl₂]PtCl₆·2H₂O, and differs from the salt [Pt etn₄Cl₂]PtCl₄ (IX) prepared from (IV) and K₂PtCl₄. (I) and K₂PtCl₄ yield quantitatively the compound [Pt etn₄Cl]PtCl₄, but (I) when pptd. successively with 2 half-mol. proportions of K₂PtCl₄ yields (VIII) and (IX). Similarly (I) and 2 successive half-mol. proportions of K₂PdCl₄ give the salts [Pt etn₄]PdCl₄ (X) and [Pt etn₄Cl₂]PdCl₄ (XI), also prepared from (IV) and K₂PdCl₄. (I) and 1 mol. K₂PdCl₄ yields the salt [Pt etn₄Cl]PdCl₄, which can be separated by washing into (X) and (XI). The formulation of (I) as a double salt (Reihlen *et al.*, *loc. cit.*) does not accommodate all the above results, which support the view that (I) is a derivative of Pt^{III}. H. G. M.

Curves for use in colorimetric determination of carotene. W. S. FERGUSON (Analyst, 1935, 60, 680—683).—Curves are given connecting % carotene with Lovibond tintometer readings and with colorimeter readings using 1% aq. K₂Cr₂O₇ as standard. E. C. S.

Velocity of oxidation of sulphides and sulphoxides by peracetic acid.—See this vol., 1464.

Nitration. V. Nitration of monohalogenated derivatives of xylenes. P. S. VARMA and K. S. V. RAMAN (J. Indian Chem. Soc., 1935, 12, 540—541).—The following have been obtained by direct nitration of the appropriate monohalogenoxylene in Ac₂O with fuming HNO₃—nitrosulphonic acid mixture: 4-chloro-6-nitro-*m*-, 2-chloro-5-nitro-*p*-, (I), 4-bromo-6-nitro-*m*-, 2-bromo-5-nitro-*p*-, 4-iodo-6-nitro-*m*-, and 2-iodo-5-nitro-*p*-xylene (II). The reaction mixtures were refluxed on the water-bath for 4 hr. except that for (II), which was refluxed for about 2 hr. A little 3-chloro-*p*-toluic acid was isolated in the prep. of (I). H. G. M.

Hexabromomethylbenzene and hexamethylbenzenehexasulphonic acid. H. S. BACKER (Rec. trav. chim., 1935, 54, 745—749).—C₆Me₆ (improved prep.), Br, and ethylene bromide at the b.p. (20 hr.) give pure C₆(CH₂Br)₆ (I), m.p. 297°, which when heated with K₂SO₃·H₂O in an autoclave (210°, 14 hr.) gives hexamethylbenzene- ω -hexasulphonic acid, C₆(CH₂·SO₃H)₆·9H₂O [normal strychnine (+9H₂O), Th^I (+3H₂O), Ba (+9H₂O), brucine, and K salt (+3H₂O) (II)]. The crystal structure of (I) and (II) and the X-ray structure of (I) have been determined. H. G. M.

Uranium in organic synthesis. II. J. B. LAL (J. Indian Chem. Soc., 1935, 12, 616—621; cf. this vol., 1357).—CH₂PhCl and U with the ether, phenol, or hydrocarbon at 70—95° afford mixtures as follows: *o*- and *p*-OH·C₆H₄·CH₂Ph and the CH₂Ph ether, m.p. 365—367°, of the latter; *p*-C₆H₄Me·CH₂Ph,

dibenzyltoluene, b.p. 392—396°/760 mm., 280—285°/30 mm., and a substance, b.p. 280—300°; 1- and 2-C₁₀H₇·CH₂Ph; 5-, m.p. 110—111°, and β (3- or 4-)benzylacenaphthene, m.p. 47—49° (picrate, m.p. 100—101°); "α" m.p. 44—45°, and "β" benzylidiphenyl, m.p. 51—56°. U cannot be used for condensation of CH₂PhCl with CH₂Ph·CN, the Ullmann reaction with picryl chloride or *p*-C₆H₄Cl·NO₂, or for reduction of CPh₃, PhNO₂, *p*-C₆H₄Me·NO₂, or picric acid in H₂O or aq. EtOH. R. S. C.

2-Nitrofluorene. C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1935, [v], 2, 1703—1709).—2-Nitrofluorene (I) heated with PhCHO and piperidine at 160° yields 2-nitro-9-benzylidenefluorene (II), m.p. 155—156° [dibromide, m.p. 151—152° (decomp.)]. (I) with vanillin similarly gives 2-nitro-9-vanillylidene-fluorene, m.p. 173—175° (III) [Bz derivative (IV), m.p. 257—258°]. (I) and (III) in COMe, with 0.1*N* NaOH give intense red colours, whilst (II) and (IV) give feeble red colours. F. R. G.

Dissociable organic oxides and the anthracene structure. Existence of a photo-oxide of anthracene: its thermal decomposition. C. DUFRAISSE and M. GERARD (Compt. rend., 1935, 201, 428—430; cf. this vol., 969).—Insolation of anthracene affords an oxide which decomposes explosively at about 120° without liberation of O₂ (cf. this vol., 1233). J. L. D.

Compound of phenol and aniline. P. LAURENT (Compt. rend., 1935, 201, 554—556).—Curves constructed to determine the relationship between the sp. inductive capacity and composition of solutions of varying proportions of PhOH and NH₂Ph in CCl₄, cyclohexane, and Et₂O indicate the formation of a substance, 2PhOH·NH₂Ph, which has m.p. 29.2°, and is decomposed rapidly in air. J. L. D.

Synthesis of thiocyno-carbamide derivatives. Z. HORII (J. Pharm. Soc. Japan, 1935, 55, 14—21).—*p*-NH₂·C₆H₄·CNS (I) reacts with HCl and KCNO, yielding *p*-thiocyanophenylcarbamide, m.p. 205°, which is also formed by the interaction of phenylcarbamide and KCNS in AcOH in the presence of Br. With COCl₂, (I) affords *s*-bis-*p*-thiocyanophenylcarbamide, m.p. 218°. (I) and PhNCO in C₆H₆ yield phenyl-*p*-thiocyanophenylcarbamide, m.p. 193°; (I) and *o*-C₆H₄Me·NCO similarly afford *p*-thiocyanophenyl-*o*-tolylcarbamide, m.p. 208—209°. *o*-Toluidine reacts with NaCNS in presence of Br, yielding *p*-thiocyano-*o*-toluidine (II), m.p. 69—79°. (II), with KCNO, yields *p*-thiocyano-*o*-tolylcarbamide, m.p. 176°, also formed from *o*-tolylcarbamide and NaCNS. (II) yields *s*-bis-*p*-thiocyano-*o*-tolylcarbamide, m.p. 208—209°, on treatment with COCl₂. (II) and *o*-C₆H₄Me·NCO afford *o*-tolyl-*p*-thiocyano-*o*-tolylcarbamide, m.p. 198°; phenyl-*p*-thiocyano-*o*-tolylcarbamide, m.p. 194—195°, is prepared similarly. CH. ABS. (r)

Influence of substituents on the solubility of salts (especially nitrates) of secondary aromatic bases. F. KONEK and H. RUPE (Math. nat. Anz. ung. Akad. Wiss., 1934, 51, 325—326; Chem. Zentr., 1935, i, 1535).—Of 9 substituted dibenzylamines, the -Br-compound was distinguished by possessing a H₂O-sol. nitrate. H. N. R.

Action of perthiocyanic acid on amines. H. G. UNDERWOOD and F. B. DAINS (J. Amer. Chem. Soc., 1935, 57, 1768—1769).—The reaction of perthiocyanic acid with amines (2 mols.) at the lowest possible temp. (<100°) varies with the amine. The appropriate bases give *m*-tolyl-, m.p. 159°, *m*-chlorophenyl-, m.p. 164°, *p*-bromophenyl-, m.p. 169°, αβ-*di*-*p*-bromophenyl-, m.p. 184°, *p*-iodophenyl-, m.p. 240°, α-*naphthyl*-, m.p. 235—236°, *m*-amino-phenyl-, m.p. 226°, and 1-*p*-tolyl-1-methyl-dithiobiuret, m.p. 236°, αβ-*di*-*p*-xenyl-, m.p. 228°, αβ-dibenzyl-, m.p. 147—148°, *o*-phenylene-, m.p. 298—299°, and benzoxazole-thiocarbamide, m.p. 205°, and (from *o*-NH₂·C₆H₄·CO₂H or its Me ester) 4-keto-2-thio-tetrahydroquinoline, m.p. 285°. *p*-NO₂·C₆H₄·NH₂, 2 : 6 : 3-C₆H₄Br₂Me·NH₂, 2 : 5-C₆H₃Cl₂·NH₂, glycine, NHPH·CH₂·CO₂H, NHPHbz, and glutamic acid do not react. R. S. C.

Asymmetrical arylalkylcarbamides. Preparation, physical properties, and hypnotic effects. A. M. HJORT, E. J. DEBEER, J. S. BUCK, and W. S. IDE (J. Pharm. Exp. Ther., 1935, 55, 152—172).—Derivatives of the type NH₂·CO·NRR' are synthesised through the *sec*-amines, prepared by treating the primary amine with alkyl iodide and separation, by way of the NO-compound, by the Davis-Blanchard method (A., 1929, 918). The following are new: *n*-propyl-, b.p. 126° (28 mm.), *n*-amyl-, b.p. 139° (11 mm.), *n*-amyl-*p*-toluidine, b.p. 144° (12 mm.); ethyl-, b.p. 133—134° (12 mm.), and *p*-anisidine, b.p. 130° (12 mm.); methyl-, b.p. 120° (14 mm.), and -*m*-, b.p. 139—143° (13 mm.), and ethyl-*m*-phenetidine, b.p. 142° (12 mm.); methyl-, m.p. 113°, and -*m*-, m.p. 76°, ethyl-, m.p. 66°, and -*m*-, m.p. 63—64°, *n*-propyl-, m.p. 80—81°, -*m*-, m.p. 61—62°, and -*p*-, m.p. 59—60°, *n*-butyl-, m.p. 71—72°, and -*p*-, m.p. 36—37°, *n*-amyl- and -*p*-tolyl-, methyl-, m.p. 107—108°, and -*m*-, m.p. 109—110°, ethyl-, m.p. 98°, and -*m*-anisyl-, m.p. 109—110°, methyl-, m.p. 104—105°, and -*m*-, m.p. 113°, ethyl-, m.p. 80°, and -*m*-phenethylcarbamide, m.p. 72°. The hypnotic potencies of the compounds, injected intraperitoneally into mice, increase with each addition of a CH₂ in the aliphatic portion; the heptane : H₂O distribution coeffs. run parallel with hypnotic potency and toxicity. H. D.

Reactions of unsaturated compounds. IV. Addition of aniline to olefines. W. J. HICKINBOTTOM (J.C.S., 1935, 1279—1282; cf. this vol., 205).—NH₂Ph (I), NH₂Ph·HBr, and CMe₂·CHMe when heated under seal at 230—250° (5.5—25 hr.) yield NHPH₂ (II), *p*-amino-*tert*-amylbenzene, *tert*-amylaniline, and β-anilino-γ-methylbutane (*p*-toluenesulphonyl derivative, m.p. 83—84°). By similar treatment (I), a NHPH₂ salt, and CHMe·CMeEt yield *p*-amino-*tert*-hexylbenzene, b.p. 135°/28 mm. (hydrochloride; sulphate; Ac, m.p. 102—103°, and *p*-toluenesulphonyl derivative, m.p. 119—120°), *tert*-hexylaniline (picrate, m.p. 132—133°), and some (II); (I), NH₂Ph·HCl (III), and CMe₂·CHMe yield (II), *p*-aminotriethylcarbinylbenzene, m.p. 56—58°, b.p. 144—145°/32 mm. (Ac derivative, m.p. 140—141°; hydrochloride), and γ-anilino-γ-ethyl-*n*-pentane, b.p. 131—132°/26 mm. (picrate, m.p. 129—130°; nitrosoamine, m.p. 49—

50°), also prepared from (I) and *tert*.-heptyl iodide, b.p. 64—66°/21 mm. (obtained from $\text{C}_6\text{H}_5\text{I}$ and dry HI). A trace of an unidentified amine was also formed. (I), (III), and octylene (obtained from *sec*.-octyl alcohol and H_2SO_4) when heated under seal at 210—240° (24 hr.) yield (II), an unidentified primary amine, and *sec*.-octylaniline, b.p. 288—289° (corr.)/751 mm., 150°/20 mm. (*p*-toluensulphonyl derivative, m.p. 59°), also prepared from (I) and *sec*.-octyl bromide. Similarly (I), (III), and CMe_2CMe_2 yield β -*p*-aminophenyl- β - γ -dimethylbutane, b.p. 138—139°/23 mm. (*Ac* derivative, m.p. 118°; *hydrochloride*), and an unidentified *sec*. amine. The relative yields of primary and *sec*. amines depend on the experimental conditions; excess of (I) and a small amount of (III) favour the formation of an alkylaniline.

H. G. M.

1-Chloro-3:4-dinitrobenzene series. III. A. MANGINI (Atti R. Accad. Lincei, 1935, [vi], 21, 759—763; cf. A., 1934, 177; this vol., 855).—Experiments on the reactivity of the 3- NO_2 -group of 1:3:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ with nitroanilines, toluidines, aminophenols, and aminobenzoic acids show: (1) that substitution takes place relatively easily with *m*- and *p*- $\text{C}_6\text{H}_4\text{MeNH}_2$, *m*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and *m*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, but does not occur with the corresponding *o*-compounds; (2) that no reaction occurs with the three nitroanilines, even in $\text{C}_5\text{H}_{11}\text{OH}$ after prolonged boiling. The following were obtained: 5-chloro-2-nitro-3'-methyl-, m.p. 192—193° (decomp.), 5-chloro-2-nitro-3'-hydroxy-, m.p. 143—144° (decomp.), and 5-chloro-2-nitro-4'-hydroxydiphenylamine, m.p. 141—142°; 5-chloro-2-nitrodiphenylamine-3', m.p. 240.5—241°, and -4'-carboxylic acid, m.p. 270—272° (decomp.). T. H. P.

New derivatives of 2:2'-dinitrobenzidine. III. D. PONTE (Giorn. Farm. Chim., 1934, 83, 847—850; Chem. Zentr., 1935, i, 1863; cf. this vol., 613).—Partial reduction of 4:4'-di-iodo-2:2'-dinitrodiphenyl yields 4:4'-di-iodo-2-nitro-2'-aminodiphenyl, m.p. 155—156°. 4:4'-[2:7-]Di-iodocarbazole, m.p. 265—266°, and a *di*-iododiphenyleneiodonium iodide are described.

H. N. R.

Diphenyl series. VI. Halogenation of 2:4'-diaminodiphenyl. V. BELLAVITA (Gazzetta, 1935, 65, 632—646).—2:4'-Diaminodiphenyl (I) (1 mol.) treated in AcOH with Cl_2 (1 mol.) yields the Ac_2 derivative, m.p. 200°, of 5-chloro-2:4'-diaminodiphenyl (*hydrochloride*, m.p. 255°), which is diazotised and converted through 3-chlorodiphenyl into *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$, and into 2:5:4'-trichlorodiphenyl, m.p. 67°. 4:2'-Dichloro-3-aminodiphenyl, m.p. 44°, obtained by reduction of the corresponding NO_2 -compound (A., 1933, 388), is similarly converted into 2:3':4'-trichlorodiphenyl, m.p. 54°. With Cl_2 (2 mols.) (I) gives the Ac_2 derivative, m.p. 224°, of 5:3'-dichloro-2:4'-diaminodiphenyl (II) [*hydrochloride*, m.p. 225° (decomp.)], which is converted into 3:3'-dichlorodiphenyl. 4:2'-Dichloro-3:5'-diaminodiphenyl (III), m.p. 105° (Ac_2 derivative, m.p. 124°), is obtained from the corresponding (NO_2)₂-compound. Either (II) or (III) can be converted into 2:5:3':4'-tetrachlorodiphenyl, m.p. 103°. 5:3'-Dichloro-2:4'-di-iododiphenyl, m.p. 104°, is obtained either from 4:2'-di-iodo-3:5'-di-

aminodiphenyl, or from (II) by diazotisation. With Br (1 mol.) in AcOH , (I) gives the Ac_2 derivative, m.p. 228°, of 5-bromo-2:4'-diaminodiphenyl [*hydrochloride*, m.p. 253—255° (decomp.)], which gives rise to 3-bromodiphenyl and to 2:5:4'-tribromodiphenyl, m.p. 76°. 4:2'-Dibromo-3-aminodiphenyl, m.p. 88° (Ac_2 derivative, m.p. 118°), obtained from the NO_2 -compound, yields 2:3':4'-tribromodiphenyl, m.p. 91°. With Br (2 mols.) (I) forms the Ac_2 derivative, m.p. 235°, of 5:3'-dibromo-2:4'-diaminodiphenyl (IV), m.p. 121°, which can be converted into 3:3'-dibromodiphenyl. 4:2'-Dichloro-3:5'-dibromodiphenyl, m.p. 100°, is obtained from either (III) or (IV). By diazotisation and treatment with KI , (IV) yields 5:3'-dibromo-2:4'-di-iododiphenyl, m.p. 113°.

E. W. W.

Condensations between maleic anhydride and phenylhydrazones. G. LA PAROLA (Gazzetta, 1935, 65, 624—627).—Maleic anhydride (I) condenses with phenylhydrazones in C_6H_6 at 70° to form *benzylidene*, m.p. 123—124°, *p*-toluylidene, m.p. 107°, *anisylidene*, m.p. 136°, and *salicylidene*, m.p. 126°, derivatives of maleic acid monophenylhydrazide, $\text{CHR}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$. (I) does not react with $\text{CHPh}\cdot\text{N}\cdot\text{NPhMe}$.

E. W. W.

Stereoisomerism of azoxybenzene [derivatives]. V. E. MÜLLER and R. ILLGEN (Annalen, 1935, 521, 72—80; cf. A., 1933, 388).— $\text{CHPhMe}\cdot\text{CO}_2\text{H}$ and fuming HNO_3 under defined conditions give *o*- and *p*-nitrohydratropic acid (I), m.p. 87°. (I) is reduced by Zn dust in aq. $\text{NaHCO}_3\text{--NH}_4\text{Cl}$ to *p*-hydroxylaminoatropic acid (II), m.p. 155—158° after sintering at 95—96°, which with FeCl_3 yields the *p*-*NO*-acid (III), m.p. 93°. (II) and (III) in MeOH give *pp'*-di-(α -carboxyethyl)azoxybenzene (IV), m.p. 198°. Resolution of (I) by quinine gives the *d*- and *l*-forms, m.p. 88.5° and 86.5°, $[\alpha]_D^{25} +10.9^\circ$, -11.2° in MeOH , and thence the *d*- and *l*-forms of (II), m.p. 155—158°, $[\alpha]_D^{25} +9.6^\circ$ (V), -10.6° (VI) in MeOH , and of (III), m.p. 91°, and 92°, $[\alpha]_D^{25} +14.1^\circ$ (VII), -14° (VIII) in MeOH , respectively. (VI) and (VII) or (V) and (VIII) afford the *dl*-(+ -)-form of (IV), m.p. 198°. The *d*-(+)-form of (IV), m.p. 198°, $[\alpha]_D^{25} +14.3^\circ$ in MeOH , is obtained from (V) and (VII), in conformity with the *as*-structure of the N_2O group.

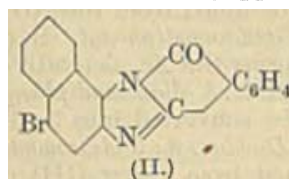
R. S. C.

New azo-derivatives of guaiacol. I. C. M. DANIEL and W. A. FLETCHER (Trans. Kansas Acad. Sci., 1934, 37, 119—122).—The following are described: 4-hydroxy-3:2'-dimethoxy-, m.p. 101.8°, 4-hydroxy-3-methoxy-2'-ethoxy-, m.p. 113.9°, 4-hydroxy-3-methoxy-4'-ethoxy-, m.p. 95.1°, and 4-hydroxy-3-methoxy-1':4'-dimethylazobenzene, m.p. 103.5°. *Na* salts of the above were prepared and also those of 4-hydroxy-3:3'-dimethoxy-, 4-hydroxy-3:4'-dimethoxy-, and 4-hydroxy-3-methoxy-3'-ethoxy-azobenzene, 4-hydroxy-3-methoxybenzeneazo- α -naphthylamine, 4-hydroxy-3-methoxybenzeneazo- β -naphthylamine, and 4-hydroxy-3-methoxybenzeneazo-4-naphthalenesulphonic acid.

CH. ABS. (p)

Chemistry of 2-arylaazo- α -naphthylamine compounds compared with their 1-arylaazo- β -naphthylamine isomerides. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1935, 65, 678—686).—

In 4-bromo-2-benzeneazo- α -naphthylamine (I) and its derivatives, the benzeneazo-grouping is unusually stable. The following are prepared: 4-bromo-2-p-toluene-, m.p. 170° (phthalimido-derivative, m.p. 220°), and -2-p-bromobenzene-, m.p. 149°, -azo- α -naphthylamine; diphenyl-pp'-bis-(4-bromo-2-azo- α -naphthylamine), m.p. 232°; 4-bromo-1-phthalimidonaphthalene, m.p. 220°. The phthalimido-derivative, m.p. 234°, from (I) is reduced (Zn in AcOH) to 1:2-o-benzoylene-5:4-($\alpha\beta$ -4'-bromonaphth)iminazole (II), m.p. 246°. (I) forms Ni, m.p. 280°, and Cu, m.p. > 300°, co-ordination compounds; with PhCHO and MeCHO it yields 1-anilino-2-phenyl-4:5-($\alpha\beta$ -4'-bromonaphth)iminazole (III), m.p. 195°, and the -2-methyl analogue, m.p. 202°.



E. W. W.

Preparation of some diazo-thioethers of thio- β -naphthol. J. T. DUNN, jun., and W. A. FLETCHER (Trans. Kansas Acad. Sci., 1934, 37, 123—126).—Diazonium chlorides and thiophenols afford sulphides of the type Ar·N:N·S·Ar. The following are described: diazobenzene, m.p. 59.5—60.5°, m-diazotoluene, m.p. 59—61° (decomp.), β -diazonaphthalene, m.p. 101—102°, sulphodiazobenzene (Na salt, m.p. > 275°), and 4-sulpho-1-diazonaphthalene (Na salt, m.p. > 240°), 2-naphthyl sulphides; Na salt of p-sulphodiazobenzene p-tolyl sulphide, decomp. on warming.

CH. ABS. (r)

Acyl derivatives of o-anisidine. L. H. AMUNDSEN and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 2005—2006).—The following N-derivatives of o-anisidine are prepared. EtCO, m.p. 33.5—34.5°; PrⁿCO, m.p. 24.5—25.5°; BuⁿCO, m.p. 25.5—26.5°; isovaleryl, m.p. 49—49.5°; n-hexoyl, m.p. 33—33.5°; n-heptyl, m.p. 42—43°; CH₂PhCO, m.p. 82.5—83°; Ph·[CH₂]₂CO, m.p. 59.5—60°; m-C₆H₄BrCO, m.p. 112.5—113°; p-OMe·C₆H₄CO, m.p. 96.5—97.5°; Bz, m.p. 66—67° (lit. 59.5°); Ac, m.p. 85—85.5°; Bz₂, m.p. 149.5—150°; and (EtCO)₂, m.p. 62.5—63.5°. o-Benzmethylamidophenyl benzoate has m.p. 114—115°.

R. S. C.

Amidines of the type of holocaine and derivatives. E. BUREŠ and M. KUNDERA (Časopis českoslov. Lek., 1934, 14, 272—285; Chem. Zentr., 1935, i, 1368).—3:5-Dibromo-4-acetamidophenetole condenses (POCl₃) with p-phenetidine to yield N:3:5-dibromo-p-phenetyl-NH-p-phenetylacetamidine (I), m.p. 131—132° (hydrochloride; sulphate; phosphate; tartrate; salicylate). (I) is also formed from acetyl- and 3:5-dibromo-p-phenetidine; with Ac₂O and EtOAc it yields 3:5-dibromoacetyl- and, with BzCl, 3:5-dibromobenzoyl-p-phenetidine. Di-p-phenetylacetamidine, m.p. 116—117° (acetate; tartrate; salicylate, m.p. 176—178°), is formed in an analogous manner.

H. N. R.

Rearrangement of o-hydroxysulphones. V. F. GALBRAITH and S. SMILES (J.C.S., 1935, 1234—1238; cf. A., 1934, 647).—The rates of change of a series of o-hydroxysulphones to ether-sulphinic acids and the behaviour of some anthraquinonyl sulphones in the presence of alkali are in agreement with previous conclusions. 1-Anthraquinonyl 4-hydroxy-m-tolyl sul-

phide, m.p. 228° [obtained when anthraquinone-1-bromothiol (I) is heated (150°; 5—6 hr.) with excess of p-cresol (II) in PhCl], is oxidised by H₂O₂-AcOH at 100° to the sulphone, m.p. 220° (Me ether, m.p. 225°), converted by 2N-NaOH at 130° into 1-anthraquinonyl 3-sulphino-p-tolyl ether, m.p. 174°. 1-Anthraquinonyl 2-acetoxy-1-naphthyl sulphide, m.p. 208°, is oxidised by H₂O₂-AcOH at 100° to the sulphone, m.p. 264—265°, hydrolysed by hot H₂SO₄-EtOH to 1'-anthraquinonyl-2-hydroxy-1-naphthylsulphone, m.p. 210°, which rearranges in the presence of 2N-NaOH at the b.p. to 1-anthraquinonyl 1-sulphino-2-naphthyl ether, m.p. 160° (decomp.). This is converted by the usual method into 2- α -anthraquinonyloxy-1-naphthyl disulphide, m.p. 238°, and on oxidation with KMnO₄ followed by treatment with 20% H₂SO₄ at 100° yields 1-anthraquinonyl 2-naphthyl ether, m.p. 170° (lit. 180°), also obtained from 1-chloroanthraquinone and β -C₁₀H₇OK when heated at 150° during 2 hr. 6-Bromo- β -naphthol and (I) when heated at 110° (4 hr.) yield 1-anthraquinonyl 6-bromo-2-hydroxy-1-naphthyl sulphide, m.p. 280—281°, the Ac derivative, m.p. 240°, of which is oxidised by H₂O₂-AcOH at 100° to 1'-anthraquinonyl-6-bromo-2-acetoxy-1-naphthyl sulphone, m.p. 223°. This is hydrolysed (H₂SO₄-EtOH) to the corresponding OH-sulphone, which on rearrangement yields 1-anthraquinonyl 1-sulphino-6-bromo-2-naphthyl ether, m.p. 170° (decomp.), reduced to 2- α -anthraquinonyloxy-6-bromo-1-naphthyl disulphide, m.p. 283—284°. Acid hydrolysis of 1-anthraquinonyl- β -acetoxyethylsulphone, m.p. 162—163° [obtained by oxidation of the corresponding sulphide (III) with H₂O₂-AcOH at 100°], yields 1-anthraquinonyl- β -hydroxyethylsulphone, m.p. 198°, which on rearrangement with NaOH-EtOH-H₂O at the b.p. yields a sulphinic acid (IV) which is methylated to methyl- β -1-anthraquinonyloxyethylsulphone, m.p. 145—146°. 1-Anthraquinonyl β -acetoxyethyl sulphoxide, m.p. 168° [also obtained by oxidation of (III)], is hydrolysed to 1-anthraquinonyl β -hydroxyethyl sulphoxide, m.p. 220°, which rearranges rapidly with NaOH-EtOH-H₂O at the b.p. yielding (IV) and di-(β -1-anthraquinonyloxyethyl) disulphide, m.p. 223°, also obtained by reduction of (IV). K 2-thiolbenzoate when heated with CH₂Cl·CH₂·OH at 100° (1 hr.) yields 2-carboxyphenyl β -hydroxyethyl sulphide, m.p. 127°, oxidised by H₂O₂-H₂O at 90° to the sulphoxide, m.p. 179°, further oxidised by H₂O₂-H₂O to the sulphone, m.p. 195°. The last two substances were recovered unchanged when heated (100°, 2 hr.) with N-NaOH. 2-Acetamido-2'-carboxydiphenylsulphone, m.p. 282°, and the corresponding amine were unaffected by 2N-NaOH at 100° during 3 hr. The following 4-hydroxy-m-tolyl sulphides were obtained by boiling the K salt of 4-hydroxy-m-tolylthiol with the appropriate bromo-compound in EtOH or EtOH-H₂O: 4-carboxy-2-nitrophenyl (V), m.p. 215° [Na salt; Ac derivative, m.p. 163°; the corresponding sulphone (VI), m.p. 265—266°]; 2-carboxy-4-nitrophenyl (VII), m.p. 237° [Ac derivative, m.p. 230—231°; gives the lactone, m.p. 178°, with hot Ac₂O; the corresponding sulphone (VIII), m.p. 245°]; 4-benzoyl-2-nitrophenyl, m.p. 165° [the corresponding sulphone (IX), m.p. 154°]; 2-benzoyl-4-nitrophenyl, m.p. 139° [prepared from 2-bromo-5-nitrobenzophenone, m.p. 122°; the corresponding

sulphone (X), m.p. 209°; 4-nitrophenyl [improved prep.; the corresponding sulphone, m.p. 162° (lit. 158°)]. Rearrangement of (VI) gives a *sulphinic acid*, converted without purification into 4-carboxy-2-nitrophenyl 3-methanesulphonyl-*p*-tolyl ether, m.p. 233°, and di-(*p*'-carboxy-*o*'-nitrophenoxy-*m*-tolyl) disulphide, m.p. 241°, by the usual methods, and degraded by successive treatment with HgCl₂ and HCl (cf. this vol., 485) to 4-carboxy-2-nitrophenyl *p*-tolyl ether, m.p. 212° (*Bt* ester, m.p. 78°), identical with the ether synthesised from (II) and 4-bromo-3-nitrobenzoic acid. Similarly (VIII) yields a *sulphinic acid*, characterised as di-(*o*'-carboxy-*p*'-nitrophenoxy-*m*-tolyl) disulphide, m.p. 257°. This and the preceding disulphide are converted by warm NaOH-EtOH into (VII) and (V), respectively (cf. A., 1932, 735). By similar methods the crude sulphinic acid obtained by rearrangement of (X) yields 4-nitro-2-benzoylphenyl *p*-tolyl ether, m.p. 129°, also prepared from (II) and 2-bromo-5-nitrobenzophenone, and (IX) yields 2-nitro-4-benzoylphenyl *p*-tolyl ether, m.p. 100°, identical with that synthesised from (II) and 4-bromo-5-nitrobenzophenone.

H. G. M.

Rearrangement of *o*-aminophenyl ethers. III. 2-Acylamidodiphenyl ethers. K. C. ROBERTS and C. G. M. DE WORMS. **IV. *N*-Alkylphenoxazines.** K. C. ROBERTS and (Miss) H. B. CLARK (J.C.S., 1935, 1309—1312, 1312—1313; cf. this vol., 484).—III. The rates of rearrangement of some acylamidodiphenyl ethers, 1 : 3 : 6-NHY·C₆H₃R·O·C₆H₃(NO₂)₂, to 2-acyloxydiphenylamines (NO₂)₂C₆H₃·NH·C₆H₃R·OY (I) (R=H, Me, I, Br, Cl; Y=Ac, Bz, *o*- and *m*-NO₂·C₆H₄·CO, picryl; not all combinations of R and Y have been studied) are in general agreement with the mechanism previously proposed. Those of the acetamido-ethers, however, appear to be anomalous. 2' : 4'-Dinitro-2-hydroxydiphenylamine (II) [*o*-nitrobenzoate (III), m.p. 151°], picryl chloride, and NaOAc or NaOEt yield an unstable picrate, decomp. 140—145°, converted by warm C₅H₅N-H₂O into 2 : 4-dinitro-*N*-(2' : 4'-dinitrophenyl)-phenoxazine, decomp. 305—310°. 2' : 4'-Dinitro-2-aminodiphenyl ether (IV) with cold AcOH-Ac₂O-H₂O gives an *Ac* derivative, m.p. 146°, which is rearranged to (I) (R=H, Y=Ac), and with *o*-NO₂·C₆H₄·COCl (V), COMe₂, and anhyd. Na₂CO₃ gives the *o*-nitrobenzoyl derivative, m.p. 232°, which is rearranged to (III) in C₅H₅N. (IV) with excess of (V) yields (III). A similar rearrangement also occurs during picrylation. The picryl derivative, decomp. 245—250°, of (IV) is obtained when 2-hydroxyphenylpicrylamine (VI) is treated with C₆H₃Cl(NO₂)₂ (VII), EtOH, and NaOAc, and is converted by C₅H₅N-H₂O (water-bath) into 1 : 3-dinitrophenoxazine. (VI), (VII), and NaOEt-EtOH yield 2-nitro-*N*-picrylphenoxazine, m.p. 225—230°. 4-Iodo-2' : 4'-dinitro-2-acetamidodiphenyl ether, m.p. 163°, is rearranged to 5-iodo-2' : 4'-dinitro-2-acetoxydiphenylamine, m.p. 200° [also obtained from the corresponding hydroxyamine (VIII)], and hydrolysed, with rearrangement, to (VIII). Similarly 4-iodo-2' : 4'-dinitro-2-(*o*-nitrobenzamido)diphenyl ether, m.p. 194° [also obtained from (VIII) and excess of (V)], is rearranged slowly to the *o*-nitrobenzoate, m.p. 174°, of (VIII). The *Ac*, m.p. 171°, and *Bz* derivatives, m.p. 176°, of 4-bromo-2' : 4'-dinitro-2-

aminodiphenyl ether (IX) are rearranged respectively to the *Ac*, m.p. 205°, and *Bz* derivatives, m.p. 172°, of 5-bromo-2' : 4'-dinitro-2-hydroxydiphenylamine (X) (*p*-toluenesulphonate, m.p. 211°), and are hydrolysed, with rearrangement, to (X). The *o*-, m.p. 178° [also obtained from (X) and excess of (V)], and *m*-nitrobenzoyl derivatives, m.p. 189°, of (IX) are rearranged respectively to the *o*- (XI), m.p. 202°, and *m*-nitrobenzoates, m.p. 183°, of (X). The foregoing derivatives of (X) were also obtained directly from (X). The *Ac*, m.p. 160°, *o*-, m.p. 200° [also obtained from 5-chloro-2' : 4'-dinitro-2-hydroxydiphenylamine (XII) and excess of (V)], and *m*-nitrobenzoyl derivatives, m.p. 197°, of 4-chloro-2' : 4'-dinitro-2-aminodiphenyl ether are rearranged respectively to the *Ac*, m.p. 207°, *o*- (XIII), m.p. 196°, and *m*-nitrobenzoyl derivatives, m.p. 184°, of (XII). (XI) and (XIII) were not rearranged under any conditions. Attempts to prepare *o*-nitrobenzoyl derivatives of 2' : 4'-dinitro-2-hydroxy-5-carboxydiphenylamine and the isomeric 2-amino-4-carboxydiphenyl ether or of their dinitrophenyl esters were unsuccessful.

IV. *N*-Methyl-*p*-toluenesulphon-*o*-anisidide. m.p. 100° (obtained from *p*-toluenesulphon-*o*-anisidide), is hydrolysed by heating under seal with fuming HCl at 170° (5 hr.) to *o*-methylaminophenol, which with (VII), NaOEt, and EtOH yields 2' : 4'-dinitro-2-hydroxy-*N*-methylidiphenylamine (XIV), m.p. 160°, and 2' : 4'-dinitro-2-methylaminodiphenyl ether, m.p. 182°, converted by C₅H₅N-H₂O-alkali, or by NaOH-EtOH-H₂O, at 100° into 3-nitro-6-methylphenoxazine, m.p. 182—183° [also obtained from warm alkaline solutions of (XIV)]. (II), (VII), and NaOEt in EtOH yield ON-*bis*-2 : 4-dinitrophenyl-*o*-aminophenol, m.p. 176°, converted by C₅H₅N-NaOH-H₂O into 3(?)-nitro-6-dinitrophenylphenoxazine, m.p. 230—233° (decomp.), unaffected by boiling alkali. (IV) would not condense with (VII) under conditions which precluded rearrangement of the ether.

H. G. M.

β-Substituted ethylamines. II. Catalytic hydrogenation of oximes. O. SCHALES (Ber., 1935, 68, [B], 1943—1945).—The production of *sec.* amines during the catalytic hydrogenation of oximes is ascribed to the intermediate formation of aldimine (I) which condenses with the primary amine. The occurrence of (I) in appreciable amount is avoided by slowly adding the oxime in AcOH to the Adams catalyst in AcOH-H₂SO₄. Under these conditions β-*p*-methoxyphenylethylamine and homopiperonylamine are obtained in 80% and 84% yield, respectively, from the appropriate oxime.

H. W.

Action of dicyanogen on phenols. G. HAHN and W. LEOPOLD (Ber., 1935, 68, [B], 1974—1986).—Contrary to Machek (A., 1932, 1245; 1933, 709), the action of C₂N₂ on phenols invariably involves addition of the phenolic OH to the triple linking of C₂N₂. Nuclear cyanisation is never observed. The primary products are so unstable that isomerisation cannot be attempted. Passage of C₂N₂ into aq. pyrocatechol (I) causes separation of an unstable oil almost instantaneously transformed by dil. HCl into di-*o*-hydroxyphenyl di-imino-oxalate (II) [C(C(NH)·O·C₆H₄·OH)]₂, decomp. 220°, which passes when heated into pyrocatechyl carbonate, m.p.

120°, thus excluding the possibility of the presence of Machek's "3-cyanopyrocatechol." The constitution of (II) follows from its hydrolysis by boiling HCl-EtOH to (I) and $(\text{CO}\cdot\text{NH}_2)_2$, its solubility in NaOH, and its ability to yield a Ac_2 and a Bz_2 , m.p. 129–130°, derivative. Treatment of (II) with CH_3N_2 in COMe_2 affords *di-o-anisyl di-imino-oxalate*, m.p. 164°, which is insol. in alkali and transformed by 4*N*-NaOH into guaiacol and $(\text{CO}\cdot\text{NH}_2)_2$. The constitution $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\text{C}(\text{CN})\cdot\text{NH}_2$ is assigned to the oil. If C_2N_2 is passed into (I) in H_2O containing H_3BO_3 (I) is pptd. without intermediate production of oil. In presence of NaH_2PO_4 the compound $[\text{C}(\text{NH}_2)(\text{OH})\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2$, m.p. 144° (decomp.), is produced, the constitution of which is established by the formation of a Me_2 ether, m.p. 129–130°, a Ac_4 derivative, m.p. 105°, and by its hydrolysis to (I), NH_4Cl , and $\text{H}_2\text{C}_2\text{O}_4$. The dependence of the course of the reaction on the p_{H} of the solution is

discussed. The constitution $[\text{C}_6\text{H}_4\langle\text{O}\rangle\text{C}(\text{NH}_2)]_2$ is assigned to the *product*, decomp. 139°, obtained when the reaction is conducted in MeOH. It is insol. in dil. NaOH and unaffected by CH_3N_2 . Warm AcCl causes resinification. It is hydrolysed to (I), $\text{H}_2\text{C}_2\text{O}_4$, $(\text{CO}\cdot\text{NH}_2)_2$, and occasionally *o*-hydroxyphenyl oxalate.

H. W.

New method for fission of methylenedioxy-groups. L. HELFER and M. MOTTIER (Rev. Marques Parfum. Savonn., 1934, 12, 362–364; Chem. Zentr., 1935, i, 1862).—Safrole gives a blue colour with NaNH_2 , which disappears on heating, with production of tar and evolution of NH_3 . The reaction is moderated by using an indifferent solvent, propenylpyrocatechol (methylated to *isoeugenol* and *isochavibetol*) being formed; *isosafole* is broken down similarly. Pyrocatechol methylene ether and dihydrosafrole similarly undergo fission to pyrocatechol and *n*-propylpyrocatechol, respectively.

H. N. R.

Synthesis of bis-2:2'-(1:3-diphenylinden-3-ol). Rubrene problem. J. C. ECK and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1898–1900).—*Bis-2:2'-(1:3-diphenylinden-3-ol)* (I) differs from dihydroxydihydorubrene. *Bis-2:2'-(1:3-indandione)* exists largely in the dienolic form, since with MgPhBr it gives 65% of *bis-2:2'-(1-phenylindan-3-on-1-ol)*, *forms*, m.p. 345° (block) and 358° (block), respectively, dehydrated by KHSO_4 at 250° to *bis-2:2'-(1-phenylinden-3-one)*, m.p. 213–214°. With LiPh this gives (I), *forms*, m.p. 273° (block), unstable, and m.p. 293° (block), stable, respectively, oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ to *o*- $\text{C}_6\text{H}_4\text{Bz}_2$ (88% yield). (I) and $\text{HCl}\cdot\text{Et}_2\text{O}$ give *bis-2:2'-(3-chloro-1:3-diphenylindenyl)*, m.p. 245–247° (block), which does not give rubrene with Ag. (I) sublimes at 280°/0.3 mm. and could not be converted into an oxide.

R. S. C.

Synthesis of bis-2:2'-(1:3-diphenylinden-3-ol). C. F. KOELSCH and H. J. RICHTER (J. Amer. Chem. Soc., 1935, 57, 2010).—Diphenylmethylenesuccinic acid [from $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, COPh_2 , and NaOEt] with H_2SO_4 gives 3-phenylindenone-2-acetic acid, m.p. 166–167°, which with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and NaOAc yields 2'-(3'-phenylindenone)methylenephthalide, m.p. 173.5–174°, converted by NaOMe into 2-3'-phenyl-

indenone-2'-hydrindane-1:3-dione, m.p. 190.5–191.5°. This with MgPhBr yields successively 1-hydroxy-1'-keto-1:3:3'-triphenyl-2:2'-di-indenyl, m.p. 244–245°, *bis-2:2'-(1:3-diphenylinden-3-ol)*, m.p. 292°, and *bis-2:2'-(1-chloro-1:3-diphenylindene)*, m.p. 237–242° (unreactive to Zn and Hg, but giving a Na derivative with 40% Na-Hg), identical with the products of Eck and Marvel (preceding abstract).

R. S. C.

Synthesis of pharmacologically important amines. X. Catalytic hydrogenation of ω -nitrostyrenes to β -arylethylamines. K. KINDLER and E. BRANDT (Arch. Pharm., 1935, 273, 478–483; cf. A., 1934, 669).—Owing to compound-formation with H_2SO_4 the appropriate ω -nitrostyrenes are readily hydrogenated in $\text{AcOH}\cdot\text{H}_2\text{SO}_4$ to good yields of tyramine, mescaline, homo-veratrylamine, -piperonylamine, and -myristicylamine.

R. S. C.

Synthesis of substances related to sterols. IV. Derivatives of chrysene (contd.). H. J. LEWIS, G. R. RAMAGE, and R. ROBINSON (J.C.S., 1935, 1412–1414).— $\beta\gamma$ -*Dianisyladipic acid-b*, m.p. 180° (*Me* ester, m.p. 67°, isolated from the Et_2O -sol. portion of the reduction products of *Me* 4-methoxycinnamate; A., 1933, 828), is cyclised by AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ to 2:11-diketo-5:14-dimethoxy-, m.p. 220°, reduced (Zn-Hg-conc. HCl) to 5:14-dimethoxy-1:2:9:10:11:18-hexahydrochrysene-b, m.p. 140–141°. Reduction (Al-Hg in Et_2O) of *Me* 3-methoxycinnamate affords mainly *Me* β -3-methoxyphenylpropionate, b.p. 146°/12 mm., and some *Me* $\beta\gamma$ -di-3-methoxyphenyladipate-a, m.p. 139.5°, hydrolysed to the acid, m.p. 247–248°, cyclised (90% H_2SO_4 at 100°) to 2:11-diketo-6:15-dimethoxy-, m.p. about 350°, reduced to 6:15-dimethoxy-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 159°. Condensation of piperonal with MeOAc and Na affords *Me* 3:4-methylenedioxy-cinnamate, m.p. 133–134° [probably not identical with the ester, m.p. 68–69°, of Feuerstein *et al.* (A., 1901, i, 465)], reduction of which gives only *Me* β -3:4-methylenedioxyphenylpropionate, b.p. 165–170°/13 mm., m.p. 34–35°. Similar reduction of *Me* 3:4-dimethoxycinnamate gives *Me* β -3:4-dimethoxyphenylpropionate, b.p. 175–180°/12 mm., m.p. 37°, and the *Me* ester, m.p. 184°, of $\beta\gamma$ -di-3:4-dimethoxyphenyladipic acid-a, m.p. 255°, cyclised to the 2:11-diketo-compound, m.p. 330° (decomp.), reduced to 5:6:13:14-tetramethoxy-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 204°. *cis*-Diketohexahydrochrysene with MgMeI in C_6H_6 and aerial oxidation of the product affords 2:11-dimethylchrysene, m.p. 237° [compound with 1:3:5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 222°; styphnate, m.p. 207° (decomp.)].

J. W. B.

cycloHexyl sulphite. W. VOSS and W. WACHS (Ber., 1935, 68, [B], 1939–1941).—Contrary to Carre *et al.* (this vol., 480) repetition of the action of SOCl_2 on cyclohexanol as described by Voss *et al.* (A., 1931, 462) affords cyclohexyl sulphite, b.p. 173–173.5°/14.5 mm., the identity of which is confirmed by analysis, determination of mol. wt., quant. hydrolysis, mol. refraction, and viscosity. Carre's results are unexplained.

H. W.

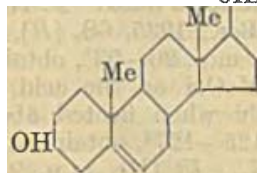
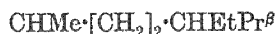
Synthesis of ephedrine derivatives. V. BRUCKNER and A. KRAMLÍ (Arch. Pharm., 1935, 273, 372—384).—Hydrochlorides of β -hydroxylamino- α -aryl-*n*-propyl acetates (I) with aldehydes and alkali give nitrones before migration of acyl occurs (method A). Sometimes the acyl is removed by hydrolysis, giving the OH-nitrone, which is also obtained by hydrolysis of the β -*N*-acylhydroxylamino- α -aryl-*n*-propyl alcohols with dil. H_2SO_4 and subsequent condensation with the aldehyde and Na_2CO_3 (method B). Nitrones are thus obtained by the methods given in parentheses from β -hydroxylamino- α -3:4-dimethoxyphenyl-*n*-propyl alcohol and PhCHO , m.p. 160° (A and B), *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 148—150° (A and B), *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 174° (B) [Ac derivative, m.p. 196° (A)], and 3:4- $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CHO}$, m.p. 148—150° (A), and from β -hydroxylamino- α -3:4-methylenedioxyphenyl-*n*-propyl alcohol and PhCHO , m.p. 149° (B) [Ac derivative, m.p. 158—159° (B)], *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 117—118° (B) [Ac derivative, m.p. 146° (decomp.) (A)], *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 171° (B) [Ac derivative, m.p. 196° (A)], and piperonal [Ac derivative, m.p. 158—160° (A)]. Reduction by Cu-Zn and AcOH affords 3:4-dimethoxy-*N*-benzyl-, m.p. 102—103.5°, and -homoveratryl-, m.p. 125—127°, and 3:4-methylenedioxy-*N*-benzyl-, m.p. 117.5—119.5°, and -homopiperonyl-norephedrine, m.p. 123.5—125°.

R. S. C.

Halogen derivatives of novocaine. II. 4-Bromo-2-aminobenzoylethylaminoethanol. J. FREJKA and F. VYMETAL (Coll. Czech. Chem. Comm., 1935, 7, 436—443).—2:4- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$, prepared from *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{COMe}$ or from *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ (the intermediate steps are described), is converted into β -chloroethyl 4-bromo-2-aminobenzoate, m.p. 80—81°, which, with NH_4Et , affords 4-bromo-2-aminobenzoylethylaminoethanol; the hydrochloride, m.p. 160°, has local anæsthetic action.

P. G. C.

Structure of sitosterol. M. VANGHELOVICI and B. N. ANGELESCU (Bull. Soc. Chim. Romania, 1935, 17, 177—190).—When heated with citraconic anhydride cholesterol (I) and sitosterol (II) (following formula suggested) afford, respectively, *cholesteryl*,



m.p. 195° (*Br*-derivative, m.p. 162°), and *sitosteryl*, m.p. 169°, *citraconate*. The following reactions, similar in both series, show the identity of the structures of ring II in (I) and (II). With conc. HNO_3 sitosteryl chloride affords *nitrodehydro-sitosteryl chloride*, m.p. 118°, reduced (Zn-AcOH) to *chlorositostan-6-one* (III), $\text{C}_{29}\text{H}_{49}\text{OCl}$ (*oxime*, m.p. 180°; *semicarbazone*, m.p. 207°; *p*-nitrophenylhydrazone, m.p. 188°), reduced by Na-Hg in boiling EtOH to *sitostan-6-one*, m.p. 77° (*oxime*, m.p. 173°). Oxidation of (III) with fuming $\text{HNO}_3\cdot\text{AcOH}$ affords a dibasic acid, $\text{C}_{24}\text{H}_{49}\text{O}_4\text{Cl}$, m.p. 277°. Reduction (Clemmensen) of (III) affords a *chlorositostane*, m.p.

108°. Reduction of chlorocholestan-6-one (*oxime*, m.p. 178°; *semicarbazone*, m.p. 155°; *p*-nitrophenylhydrazone, m.p. 207°) with Na-Hg-EtOH affords *ischolestan-6-one*, m.p. 97° (*oxime*, m.p. 157°), probably stereoisomeric with the known derivative, m.p. 98° (Windaus, A., 1920, i, 434), and by Clemmensen reduction gives an *ischolesteryl chloride*, m.p. 110°. The presence of the suggested side-chain in (II) is indicated by the production (in small yields) of COMe_2 and a solid ketone (menthol odour), which is not methylheptanone, by oxidation of sitosteryl acetate with $\text{CrO}_3\cdot\text{AcOH}$.

J. W. B.

Polyterpenoid nature of the sterols. F. S. SPRING (Chem. and Ind., 1935, 972—973).—A scheme is proposed whereby the cholestane skeleton is built up from six isoprene units by cyclisation and loss of three C. The ergosterol and stigmasterol structures are derived by use of one or two C, respectively, of another isoprene unit. Sterols with 30—32 C may thus be expected in nature.

R. S. C.

Relationship between cholesterol and carotene structures. W. H. D. BRYANT (Chem. and Ind., 1935, 907).—Formation of cholesterol by ring-closure is more probable from α - or β -carotene than from squalene (cf. Robinson, this vol., 209).

F. R. G.

Sterol group. XXI. Lumisterol. I. M. HELBRON, F. S. SPRING, and P. A. STEWART (J.C.S., 1935, 1221—1223).— BzO_2H titration and hydrogenation of lumisterol (I) confirm that it is tetracyclic with three ethylenic linkings. (I) with BzO_2H in CHCl_3 at 0° yields *lumistadienetriol monobenzoate* (II), m.p. 185—186°, $[\alpha]_D^{25} -68.0^\circ$ in CHCl_3 (gives carmine coloration, which changes to brown and then to green, with SbCl_3), hydrolysed by $\text{MeOH}\cdot\text{KOH}$ to *lumistadienetriol* (III), m.p. 180—181°, $[\alpha]_D^{25} -8.7^\circ$ in CHCl_3 (Ac_2 derivative, m.p. 128—130°, $[\alpha]_D^{25} -48.4^\circ$ in COMe_2 , extremely sol. in the common org. solvents). (I) is dehydrated by POCl_3 and $\text{C}_6\text{H}_5\text{N}$ giving *lumistatetraene*, m.p. 88—90°, $[\alpha]_D^{25} +298.9^\circ$ in CHCl_3 (coloration, changing from crimson, through purple, to green, with SbCl_3 in CHCl_3), which is not identical with Rygh's ergostatetraene (A., 1930, 203). This proves that other changes apart from possible epimerisation occur in the photochemical transformation of ergosterol (IV) into (I). Titration of (II) with BzO_2H and (III) with $\text{Pb}(\text{OAc})_4$ indicates that (II) is not and (III) is an α -glycol. By analogy with similar known reactions with (IV) it is concluded that (I) contains a $\Delta^{5,6}$ -ethenoid linking. Lumisteryl acetate is dehydrogenated by $\text{Hg}(\text{OAc})_2$ in AcOH to *dehydro-lumisteryl acetate*, m.p. 142—143°, $[\alpha]_D^{25} +126.4^\circ$ in CHCl_3 (cf. A., 1928, 424).

H. G. M.

Actiniasterol.—See this vol., 1398.

Colour standard for cholesterol determinations.—See this vol., 1552.

Physiologically active crystalline esters of vitamin-A.—See this vol., 1545.

Optically active diphenylhydroxyethylamines and isohydrobenzoin. VII. The 1:2-cyclohexanediols and related compounds. N. A. B. WILSON and J. READ (J.C.S., 1935, 1269—1273).—

Methods for the separation of *cis*- (I) and *dl-trans*-1:2-cyclohexanediol (II) are described. The following derivatives of (II) have been prepared by adding the appropriate acid chloride to (II) in C_5H_5N : *monobenzoate* (III), m.p. 92–93°, b.p. 200–205°/35 mm.; *dibenzoate*, m.p. 93°; *di-m*- m.p. 141–142°, and *di-p-nitrobenzoate*, m.p. 149–150°; *bis-3:5-dinitrobenzoate*, m.p. 179°. 1-(3':5'-*Dinitrobenzoate*)-2-benzoate prepared from (III) exists in two forms, m.p. 105° and 132.5°, respectively: 1-*p*-, m.p. 131°, and 1-*m-nitrobenzoate*-2-benzoate, m.p. 102°, were similarly prepared. The mono- and the di-*d*-camphor-10-sulphonate could not be recrystallised. The following derivatives of (I) were similarly prepared: *mono*-, b.p. 139–140°/0.5 mm. and *di-benzoate*, m.p. 63–64°, obtained as a mixture together with an unsaturated hydrocarbon; *di-p-nitrobenzoate*, m.p. 128–128.5°; *bis-3:5-dinitrobenzoate*, m.p. 169°; 1-(3':5'-*dinitrobenzoate*)-, m.p. 102°, 1-*p-nitrobenzoate*-, m.p. 82°, and 1-*m-nitrobenzoate*-2-benzoate, m.p. 96–97°. Both the *cis*- and the *dl-trans*-diols give an absorption edge in the ultra-violet region, the former being the less transparent. The *trans*-monobenzoate is more rapidly esterified than the *cis*-isomeride (cf. this vol., 88). (II) with *l*-menthoxyacetyl chloride and C_5H_5N yields *d*-, m.p. 126–127°, $[\alpha]_D -32.7^\circ$ in EtOH, and *l-trans*-1:2-cyclohexane mono-*l*-menthoxyacetate, m.p. 64°, $[\alpha]_D -91.7^\circ$ in EtOH, hydrolysed, respectively, to the *d*- and *l-trans*-diol, m.p. 113–114°, $[\alpha]_D +46.5^\circ$ (cf. A., 1922, i, 651). *l-trans*-1:2-cyclohexanediol *di-p-nitrobenzoate* has m.p. 126.5°, $[\alpha]_D -25.5^\circ$ in $CHCl_3$, and the corresponding *bis-3:5-dinitrobenzoate* has m.p. 160°, $[\alpha]_D -83.0^\circ$ in $CHCl_3$ (the corresponding *d-bis-ester* has m.p. 160°, $[\alpha]_D +83.9^\circ$ in $CHCl_3$). 1:2-cyclohexanedione (IV) shows an absorption band with head at about 2650 Å.; the mol. extinction coeff. is about 2700, corresponding with a marked proportion of the enol form (cf. A., 1934, 414). (IV) with $MgMeI$ in Et_2O yields *dl*-1-methylcyclohexane-1-ol-2-one, b.p. 91–95°/30 mm. (*semicarbazone*, m.p. 202°; *p-nitrobenzoate*, m.p. 125–126°; 3:5-dinitrobenzoate, m.p. 158°; the *l*-menthoxyacetate and *d*-camphor-10-sulphonate were syrups), reduced by Na-EtOH to *dl*-1-methylcyclohexane-1:2-diol, m.p. 84° (*bis-3:5-dinitrobenzoate*, m.p. 189°; acetone compound derived from the *cis*-diol had b.p. 72–73°/20 mm.).

2-Aminocyclohexanol (V) is most readily obtained by shaking 2-chlorocyclohexanol with conc. NH_3-H_2O , and with $MeI-NaOMe-MeOH$ yields *dl*-cyclohexane-1-ol-2-trimethylammonium iodide, m.p. 214°. The *d*-aminoalcohol (A., 1933, 156) when similarly treated yields the *d*-iodide, m.p. 217°, $[\alpha]_D +25.8^\circ$ in H_2O . Neither deamination nor exhaustive methylation indicated whether (V) has the *cis*- or the *trans*-configuration; when boiled with Ag_2O-H_2O both the *dl*- and the *l*-quaternary NH_4 iodide give a mixture of (II) (inactive) and 2-dimethylaminocyclohexanol which when heated yields cyclohexene oxide (VI) and $NHMe_2$. Deamination of (V) in the presence of H_2SO_4 gave some (VI) in addition to cyclopentyl-formaldehyde (cf. A., 1934, 892). Attempts to prepare a stereoisomeride of (V) were unsuccessful. cyclohexanone when treated below 5° with amyl nitrite and conc. HCl yields oximinocyclohexanone

nitrite, decomp. 190°, decomposed on attempted reduction (catalytic, or Na-EtOH). Crude 1:2-cyclohexanediol monobenzoate is oxidised by $K_2Cr_2O_7-H_2SO_4-H_2O$ to 1:2-cyclohexanolone benzoate, m.p. 85–86° (cf. A., 1913, i, 1201) (*oxime*, m.p. 120°). 1:2-cyclohexanoloneoxime, m.p. 109°, when reduced by Na-EtOH yields only the known form of (V).
H. G. M.

Nitrones. A new transposition reaction. I. V. BELLAVITA (Gazzetta, 1935, 65, 755–765).—N-Phenyl-*o*-, *m*-, and *p*- (II) -nitrobenzaloximes are converted by KCN in MeOH into *Me o*- (III), *m*-, and *p-nitrobenzoate-N-phenylimides*, m.p. 74.5°, 76.5°, and 47°, respectively, the transposition $CHR:NPh:O \rightarrow [OH:CR:NPh] \rightarrow OMe:CR:NPh$ having occurred. In the formation of (III) from (I), an intermediate substance, m.p. 103–105°, is isolated by adding H_2O ; with MeOH and KCN it gives (III). When (II) is treated with KCN in EtOH, *Et p-nitrobenzoate-N-phenylimide*, m.p. 46°, is formed. On hydrolysis, the imides give either the anilide of the acid, or aniline and the ester (or acid).

E. W. W.

β -Alkoxyethyl *p*-aminobenzoates. H. V. ASHBURN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1935, 57, 1862–1863).—The appropriate ethers, $OH-[CH_2]_xOR$, afford β -propoxy-, b.p. 181.6–182.6°, -isopropoxy-, b.p. 172–172.8°, -isobutoxy-, b.p. 184.8–185.6°, -sec-butoxy-, b.p. 183.5–184.5°, and tert-butoxy-ethyl *p-nitrobenzoate*, b.p. 174.8–175.8°, hydrogenated (PtO_2 ; 45 lb. per sq. in.) in EtOH in good yield to the corresponding *p-aminobenzoates*, m.p. 44.5° (138.4°), m.p. 95.4° (156°), an oil, b.p. 176.5–177.5°/0.7 mm. (150.3°), an oil, b.p. 177–178°/0.7 mm. (132.5°), and m.p. 77.4°, b.p. 173.5–174.5°/0.3 mm. (140°), respectively, figures in parentheses being the m.p. of the *picramides*. β -Methoxy-, -ethoxy-, and -n-butoxy-ethyl *p-aminobenzoate* have m.p. 75.9° (132°), 79.2° (136.7°), and 34° (123.1°), respectively.

R. S. C.

Resolution of *r*-mandelic acid with (–)-ephedrine. R. ROGER (J.C.S., 1935, 1544).—A method of resolution using only (–)-ephedrine is described.

J. W. B.

Nor- and bisnor-lithocholic acid. F. REINDEL and K. NIEDERLANDER (Ber., 1935, 68, [B], 1969–1973).—*Me lithocholate* (I), m.p. 90–93°, obtained by the action of HCl and MeOH on the acid, passes slowly when kept, rapidly when heated above its m.p., into the form, m.p. 125–127°, obtained directly from the acid and CH_2N_2 . *Et* (II), m.p. 92–93°, and CH_2Ph , m.p. 145–148°, *lithocholate* are obtained by means of HCl. *Et 3-acetyl-lithocholate*, m.p. 90–91°, is derived from (II) and boiling Ac_2O ; treatment of 3-acetyl-lithocholic acid with HCl and EtOH involves loss of Ac. (I) and $MgMeI$ in Et_2O afford *norepicopropane-3:24-diol*, $C_{26}H_{46}O_2$, m.p. 141–142° (also +1 H_2O). The corresponding *acetate*, m.p. 79–80°, is oxidised by CrO_3 (=6O) in AcOH at 100° to *acetylnorlithocholic acid*, m.p. 175–176° (also obtained in poorer yield by similar oxidation of *diphenylcholane-3:24-diol diacetate*), hydrolysed to *norlithocholic* [α -3-hydroxynorcholanic] acid, m.p. 170–171°, and, after re-solidification, m.p. 181–182°.

which is oxidised by CrO_3 in cold AcOH to *dehydronorlithocholic* [3-ketonorcholanic] acid, m.p. 179—180° [*Me* ester, m.p. 90°; semicarbazone, m.p. 208—210° (decomp.)]. *Me* norlithocholate, m.p. 99—100° (corresponding *Et* ester, m.p. 83—85°), is converted by MgMeI into *bisnorepicopropane-3:23-diol*, m.p. 196—197° (also $+0.5\text{H}_2\text{O}$) the acetate, m.p. 105—106°, of which is oxidised and then hydrolysed to *bisnorlithocholic* [α -3-hydroxybisorcholanic] acid, m.p. 210—212° (acetate, m.p. 200—202°; *Me* ester, m.p. 148—150°). H. W.

Synthesis of substances related to sterols. V. Condensation of phenylsuccinic anhydride with veratrole under the influence of aluminium chloride. R. ROBINSON and P. C. YOUNG (J.C.S., 1935, 1414—1416).—The above condensation in PhNO_2 affords β -veratroyl- α -phenylpropionic acid (I), m.p. 142—143° (NO_2 -derivative, m.p. 176—179°), the *Me* ester, m.p. 100—100.5°, of which is identical with the product obtained by condensation of β -carbomethoxy- β -phenylpropionyl chloride and veratrole with AlCl_3 in CS_2 . Reduction (Zn-Hg -conc. HCl) of (I) affords some 1-keto-6:7-dimethoxy-2-phenyl-1:2:3:4-tetrahydronaphthalene (II), m.p. 140—141°, and α -phenyl- γ -veratrylbutyric acid, m.p. 83°, cyclised by 80% H_2SO_4 to (II). With Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 (II) affords *Et* 6:7-dimethoxy-2-phenyl-3:4-dihydronaphthyl-1-acetate, m.p. 159—161.5°. J. W. B.

Synthesis of substances related to sterols. VI. R. ROBINSON and J. WALKER (J.C.S., 1935, 1530—1533).—Reduction of *Et* 3:4-dihydro-1-naphthylacetate (improved prep.) with Na in boiling EtOH gives β -1:2:3:4-tetrahydro-1-naphthylethyl alcohol, b.p. 158—160°/11 mm. (solidifies, but could not be crystallised). Condensation of the Grignard compound of β -1-naphthylethyl bromide (improved prep. of alcohol) and *Et* 2-methylcyclopentanone-2-carboxylate (improved prep.; with Me_2SO_4 *Et* cyclopentanonecarboxylate gives 27% of the *O-Me* ether) affords some α -di-1-naphthylbutane, and the crude OH -ester, which, after hydrolysis and re-esterification with CH_2N_2 , affords pure *Me* 2- β -1'-naphthylethyl-1-methylcyclopentan-2-ol-1-carboxylate, b.p. 206—214°/0.4 mm. (methylamide, m.p. 100°), dehydration-cyclisation of which could not be effected. Methylation of 2-hydroxymethylenecyclohexanone by the method of Bishop *et al.* (A., 1895, i, 62) effects *C*-methylation and hydrolysis to 2-methylcyclohexanone, but with Me_2SO_4 -aq. KOH is obtained the *O-Me* ether, b.p. 75—80°/13 mm., condensed with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ - NaOEt - EtOH to an intermediate, hydrolysed by boiling NaOEt - EtOH to 6-hydroxy-1:2:3:4-tetrahydronaphthalene-7-carboxylic acid, m.p. 178°. J. W. B.

8-Methylhydrindane derivatives and cis- and trans-2-methylcyclopentane-1-carboxylic-2-acetic acid. C. K. CHUANG, C. M. MA, and Y. L. TIEN (Ber., 1935, 68, [B], 1946—1952).—In connexion with a possible synthesis of sterol hydrocarbons, the following experiments are described. 2-Acetyl-1-methyl- Δ^1 -cyclopentene, b.p. 71°/11 mm., from 1-methyl- Δ^1 -cyclopentene and AcCl in presence of SnCl_4 , condenses readily with $\text{CHNa}(\text{CO}_2\text{Et})_2$ to *Et* 2:4-

diketo-8-methylhydrindane-1-carboxylate, b.p. 160—170°/3 mm., [monosemicarbazone, m.p. 208—209° (decomp.)], hydrolysed by boiling 5*N*- HCl to 2:4-diketo-8-methylhydrindane (I), m.p. 90—92° (dioxime, m.p. 137—138°), which is freely sol. in NaOH and Na_2CO_3 , and gives a brown colour with FeCl_3 and condenses with CH_2O to methylenedi-2:4-diketo-8-methylhydrindane, m.p. 123—124°. Reduction of (I) by Hg-Zn and conc. HCl at 170° affords 8-methylhydrindane, b.p. 80—82°/50 mm., which could not be dehydrogenated to C_{10}H_8 by Se at 280—300°. Oxidation of (I) with NaOBr smoothly yields cis-2-methylcyclopentane-1-carboxylic-2-acetic acid (II), m.p. 165—166° (*Ag* salt), transformed by the successive action of PCl_5 and NH_2Ph in Et_2O into the dianilide, m.p. 202—204°, and by boiling Ac_2O into the anhydride (III), m.p. 93—94°, reconverted by boiling H_2O or dil. acid into the *cis*-acid. Treatment of (II) with conc. HCl at 200° affords trans-2-methylcyclopentane-1-carboxylic-2-acetic acid, m.p. 101—102° (dianilide, m.p. 156—157°), which with boiling Ac_2O gives (III), which does not pass into an equilibrium mixture at 240° or 300°. H. W.

Multiplanar cyclohexane rings. R. D. DESAI and R. F. HUNTER (Nature, 1935, 136, 608—609).—Evidence that there are only two stereoisomerides of 4-methylcyclohexane-1-carboxylic-1-acetic acid is presented (cf. this vol., 1236). The carboxy-3:3-dimethylcyclohexane-1-acetic acid obtained from 3:3-dimethylcyclohexanone could not be isolated in more than one form. L. S. T.

Synthesis of phenanthrene and hydrophenanthrene derivatives. I. Bougault reaction. L. F. FIESER and E. B. HERSHBURG (J. Amer. Chem. Soc., 1935, 57, 1851—1854).— $\text{Ph}[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$ and $\text{Et}_2\text{C}_2\text{O}_4$ with KOEt or NaOEt give *Et* α -keto- β -carbomethoxy- δ -phenylvalerate, converted by H_2SO_4 at 25° into 3:4-dihydronaphthalene-1:2-dicarboxylic anhydride, b.p. 227—230°/23 mm., m.p. 126—127°, triboluminescent, which with S at 240—250° gives a 76% yield of 1:2- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$ (I), b.p. 211—214°/11 mm., m.p. 164—165° (cf. A., 1925, i, 402). β - $\text{C}_{10}\text{H}_7\cdot\text{OMe}$ (I), and AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ give a lactone, m.p. 238—239°, isomerised by AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ at 100° to a naphthaloylnaphthol, m.p. 264—265°. *Et* γ -1-naphthylbutyrate, b.p. 210—211°, treated as above affords a keto-ester, sulphonated by conc. H_2SO_4 , but with 80% H_2SO_4 at 100° cyclised to 3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride (II), m.p. 263.5—264.5°, which with S at 320—325° gives phenanthrene-1:2-dicarboxylic anhydride (III), m.p. 311—312°. *Et* γ -2-naphthylbutyrate, b.p. 227—228°/25 mm., affords similarly 1:2-dihydrophenanthrene-3:4-dicarboxylic anhydride, m.p. 151—152°. (II) and (III) are oestrogenic to mice. R. S. C.

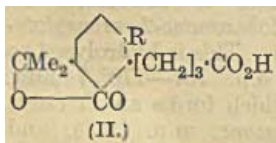
Intermediates for the synthesis of phenanthrene. R. GHOSE (Sci. and Cult., 1935, 1, 299).—*Et* cyclohexanone-2-carboxylate is converted by $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ into *Et*, cyclohexanone-2-carboxylate-2-acetate, b.p. 161—162°/5 mm. This is hydrolysed to cyclohexanone-2-acetic acid, b.p. 167—170°/7 mm. (semicarbazone, m.p. 200°), which forms an *Et* ester, b.p. 130°/10 mm. (semicarbazone, m.p. 196°), and when treated with Na-Hg and with dil. H_2SO_4 yields

hexahydro- α -coumaranone, b.p. 137°/15 mm. When either this or Δ^1 -cyclohexenyl-1-acetic acid is condensed with C_6H_6 ($AlCl_3$), 2-phenylcyclohexyl-1-acetic acid, m.p. 69–70°, b.p. 195–200°/8 mm. (chloride, b.p. 168–171°/7 mm.; amide, m.p. 196–197°), is formed. E. W. W.

Diphenyl series. III. [Synthesis of] phenanthrene [derivatives]. N. N. CHATTERJEE (J. Indian Chem. Soc., 1935, 12, 591–594; cf. this vol., 1361).—Et cyclohexanone-2-carboxylate, NaOEt, and CH_2Cl-CO_2Et give *Et*₂ cyclohexanone-2-carboxylate-2-acetate (I), b.p. 168–175°/11 mm., hydrolysed by conc. HCl to cyclohexanone-2-acetic acid, b.p. 163°/4 mm., the *Et* ester, b.p. 122°/5 mm., of which with MgPhBr affords *Et* 2-hydroxy-2-cyclohexylphenylacetate, b.p. 170–180°/8 mm. (corresponding acid, m.p. 129°). With S this yields *Et* diphenyl-2-acetate, b.p. 165–175°/8 mm., which, when hydrolysed by KOH and heated with conc. H_2SO_4 at 100°, gives 9-hydroxyphenanthrene, m.p. 153° (picrate, m.p. 185°). (I) and MgPhBr give *Et* 2-hydroxy-1-carbethoxy-2-cyclohexylphenylacetate (II), b.p. 180–190°/9 mm., and the lactone, m.p. 97°, of 2-hydroxy-1-carbethoxy-2-cyclohexylphenylacetic acid [also obtained by keeping (II) over H_2SO_4 ; with hot KOH–EtOH gives the 1-carboxy-lactone, m.p. 141°]. R. S. C.

Stereoisomerism of 2:2'-disubstituted derivatives of diphenyl. III. A. CORBELLINI and C. VIGANÒ (Gazzetta, 1935, 65, 735–743).—Et H diphenate, Mg, and EtBr give 2- α -hydroxy- α -ethyl-n-propyldiphenyl-2'-carboxylic acid (I), m.p. 92–93° (by pptn.) or 111° (from light petroleum) (Na salt), converted by Ac_2O into the corresponding lactone (II), m.p. 104°; 2:2'-di- α -hydroxy- α -ethyl-n-propyldiphenyl, m.p. 98–99°, is also formed. The substances previously regarded as (I) and (II) (A., 1933, 64) are a mixture of cis- and trans-, and either cis- or trans-2- α -ethylidene-n-propyldiphenyl-2'-carboxylic acid (III), respectively. (III) is obtained from (II) and HCl in EtOH; with I in $CHCl_3$ it gives 2- β -iodo- α -hydroxy- α -ethyl-n-propyldiphenyl-2'-carboxylic acid lactone, m.p. 111° (decomp.); a similar Br-compound is formed. Et H diphenate, Mg, and Pr^aBr yield 2- α -hydroxy- α -n-propyl-n-butylidiphenyl-2'-carboxylic acid, m.p. 149° (lactone, m.p. 92°, hydrolysed to the acid, m.p. 158°). CH_2PhCl yields 2-(α -hydroxy- β -phenyl- α -benzylethyl)diphenyl-2'-carboxylic acid, m.p. (from lactone, m.p. 146°) 172°. Pr^aBr , Bu^aBr , Bu^aBr , o- and p- C_6H_4MeI , 1- $C_{10}H_7Br$, and 2- $C_{10}H_7I$ give similar products, which are, however, not purified. E. W. W.

Picrotoxin. XII. Degradation of picrotic acid, $C_{15}H_{18}O_4$, to the dibasic acids, $C_{14}H_{14}O_6$ and $C_{12}H_{10}O_6$. P. HORRMANN [with K. THELO] (Arch. Pharm., 1935, 273, 433–446; cf. A., 1922, i, 161).—Previous evidence and the reactions described below indicate that picrotic acid (I) is (II; R=Me). Dry distillation of the base, $C_{14}H_{17}O_2 \cdot NMe_3 \cdot OH$, obtained by Hofmann degradation of (I), yields AcOH and an aldehyde, $C_{12}H_{12}O_3$, oxidised by aq. NH_3 – Ag_2O to an acid, $C_{12}H_{12}O_4$. Dry distillation of picrotin ketone (III) gives a residue, which on KOH-fusion affords



2:3- $C_6H_3Me_2 \cdot CO_2H$ and another acid. Picrotindicarboxylic acid with red P and I gives 64% of (I) and 30% of (II) (phenylhydrazones, m.p. 185°). (I) and 38% KOH at 280° give an acid, $C_{13}H_{14}(CO_2H)_2$, m.p. 138° (Ag_2 salt). (I) and $KMnO_4$ (30) give γ -4-carboxydimethylphthalide-3-n-butyric acid (II; R=CO₂H), m.p. 183°, affording at 300–330° H_2O , CO₂, and an α -tetralone derivative (IV), $C_{14}H_{14}O_3$, m.p. 147°, b.p. 228°/12 mm. [semicarbazone, m.p. 322° (decomp.); phenylhydrazones, m.p. 184°; oxime, m.p. 185° (decomp.)]. (IV) and hot HNO_3 (d 1.37) yield β -4-carboxydimethylphthalide-3-propionic acid (V), $+H_2O$, m.p. 235° (decomp.) (Ag_2 salt), and dimethylphthalide-3:4-dicarboxylic acid (VI), $+H_2O$, decomp. (slow heating) 293° or (rapid heating) 209–210° (with formation of the anhydride, m.p. 293°) (Ag_2 salt). (V) at 240–270°/12 mm. affords the 1-hydrindone derivative, $C_{13}H_{12}O_3$, m.p. 187° [phenylhydrazones, m.p. 210°; semicarbazones, m.p. 350° (decomp.)], oxidised by HNO_3 to (VI). R. S. C.

Synthesis of substances related to sterols. VII. W. S. RAPSON, R. ROBINSON, and (in part) R. HIRT (J.C.S., 1935, 1533–1543).—Four lines of synthesis are developed. (A) Reduction of Et 2-methylcyclopentanone-2-carboxylate with Na–Hg (CO₂ stream) is incomplete, but dehydration of the OH-ester with P_2O_5 in boiling C_6H_6 and fractionation affords *Et* 1-methyl- Δ^2 -cyclopentene-1-carboxylate (I), b.p. 70–71°/13 mm. (free acid, b.p. 110°/14 mm.), reduced (Bouveault) to 1-methyl- Δ^2 -cyclopentenylmethyl alcohol (II), b.p. 162–165°/760 mm. (p-nitrobenzoate, m.p. 67°), converted by PCl_5 in ligroin at –5° into the impure chloride, b.p. 40–56°/18 mm., which failed to give the required condensation product with $CHAcNa \cdot CO_2Et$. Dehydration of (II) with $KHSO_4$ affords a hydrocarbon (probably a dihydrotoluene), b.p. 112–113°/760 mm. m-OH- $C_6H_4 \cdot CHO$ is readily reduced electrolytically to the alcohol, converted by Me_2SO_4 (in situ) into 3:3'-dimethoxyhydrobenzoin $\alpha \alpha'$ - Me_2 ether, m.p. 112–113°, and m-OMe- $C_6H_4 \cdot CH_2 \cdot OH$ (III). (III) is converted through the chloride, nitrile, and ester into β -m-methoxyphenylethyl alcohol, the iodide of which condenses with $CHAcK \cdot CO_2Et$ in PhMe to give *Et* β -m-methoxyphenylethylacetate, b.p. 180°/2 mm., hydrolysed (cold aq. NaOH followed by hot 10% HCl) to γ -m-methoxyphenylpropyl Me ketone, b.p. 168°/19 mm. (semicarbazones, m.p. 109°), condensation of which with (I) was unsuccessful. (B) cyclopentanone cyanohydrin with $SOCl_2$ – C_5H_5N affords 1-cyano- Δ^1 -cyclopentene, b.p. 69°/15 mm. Et trans-cyclopentane-1-carboxylate-2-cyanoacetate (Cook et al., A., 1934, 1002) condenses with $CH_2Ph \cdot CH_2Br$ –K–PhMe to give *Et* α -cyano- α -(trans-2-carbethoxycyclopentyl)- γ -phenylbutyrate, b.p. 195–200°/1 mm., hydrolysed (conc. HCl, then 25% KOH–EtOH) to α -cyano- α -(trans-2-carboxycyclopentyl)- γ -phenylbutyric acid, m.p. 210° (decomp.), converted by boiling H_2SO_4 –AcOH into α -(trans-2-carboxycyclopentyl)- γ -phenylbutyric acid (IV), m.p. 160–161°, the trans-anhydride, m.p. 112°, of which is converted at 250° into the cis-anhydride, hydrolysed to the corresponding cis-acid, m.p. 133°. When heated with aq. H_2SO_4 at 100° (IV) gives 1-keto-2-(trans-2'-carboxycyclopentyl)-1:2:3:4-tetrahydronaphthalene, m.p. 164–165° (Me ester, m.p. 45°),

but with boiling $\text{Ac}_2\text{O}-\text{NaOAc}$, the corresponding *cis*-compound, m.p. 155—156°, is obtained. These with SOCl_2 afford, respectively, 1-hydroxy-2-(trans-2'-carboxycyclopentyl)- (V), m.p. 162°, and 1-hydroxy-2-(*cis*-2-carboxycyclopentyl)-3:4-dihydronaphthalene lactone, m.p. 66° (cryst. data by CROWFOOT). (V) is reduced by H_2 -1% Pd-SrCO₃ in EtOAc to 2-(2'-trans-carboxycyclopentyl)-1:2:3:4-tetrahydronaphthalene, m.p. 107°. Et cyclopentanone-2-carboxylate with PCl_5 in ligroin (b.p. 40—60°) affords Et 2-chloro- Δ^1 -cyclopentene-1-carboxylate, b.p. 95—98°/12 mm. (acid, m.p. 115—116°). (c) m-Benzoyloxybenzaldehyde, m.p. 54° ($\text{CH}_2\text{PhCl}-\text{NaOEt}$ on the OH-compound), with $\text{NHBz}-\text{CH}_2-\text{CO}_2\text{H}$ and Ac_2O at 100° affords m-methoxy-(?benzyloxy)benzylidenephénylisooxazolone, m.p. 129°, hydrolysed to the phenylpyruvic acid, converted by H_2O_2 -NaOH into m-benzoyloxyphenylacetic acid, m.p. 126°. The Na salt of this with 6-nitro-3-methoxybenzaldehyde and Ac_2O affords 2-nitro-5-methoxy- α -(m-benzoyloxyphenyl)cinnamic acid, m.p. 148°, reduced (FeSO_4 -aq. NH_3) to the 2-NH₂-acid, m.p. 137°. 2-Nitro-, m.p. 148°, and 2-amino-5-methoxy- α -(m-methoxyphenyl)cinnamic acid (VI), m.p. 185°, are similarly prepared. Diazotisation of (VI) effects cyclisation to a mixture of 2:5-, m.p. 191° (56%), and 2:7-dimethoxyphenanthrene-9-carboxylic acid, m.p. 265° (44%), decarboxylated, respectively, to 2:5-, m.p. 117° (picrate, m.p. 154—156°), and 2:7-dimethoxyphenanthrene (Fieser, A., 1929, 1171) (picrate, m.p. 144°). 2:5-Dihydroxyphenanthrene (Ac_2 derivative, m.p. 144°) has m.p. 180°. With dil. HCl the reaction product from the prep. of β -2-hydroxy-1-naphthylethyl Me ketone (A., 1934, 1356) affords 2-methyl-5:6-(1:2-naphtha)- γ -pyran, m.p. 44—45°. (d) Condensation of Et cyclopentanonecarboxylate with $n\text{-C}_8\text{H}_{17}\text{Br}$ and K in xylene affords Et 2-n-octylcyclopentanone-2-carboxylate, b.p. 157—165°/1 mm. (semicarbazone, m.p. 117°), hydrolysed by $\text{Ba}(\text{OH})_2$ to α -n-octyladipic acid, m.p. 74°, converted by distillation at 760 mm. into 2-n-octylcyclopentanone, b.p. 135—138°/11 mm. (semicarbazone, m.p. 183°), reduced (Na-EtOH) to 2-n-octylcyclopentanol, b.p. 140°/8 mm., the bromide, b.p. 135—140°/8 mm., of which loses HBr in attempted condensations to give n-octyl- Δ^1 -cyclopentene (VII), b.p. 125—128°/12 mm. (also obtained from $\text{C}_8\text{H}_{17}\text{-MgBr}$ and cyclopentanone). Condensation of (VII) with β -carbomethoxypropionyl chloride and AlCl_3 in CS_2 at <0° and heating the product with NPhMe_2 at 180° affords 2-(β -carbomethoxypropionyl)-1-n-octyl- Δ^1 -cyclopentene, b.p. 173—177°/1 mm. When refluxed with AcCl , cyclopentanone-2- β -propionic acid (VIII) gives the enolic lactone, b.p. 116—117°/17 mm., which could not be reduced, but cyclopentanol-2- β -propionic acid lactone, b.p. 138—139°/18 mm., is obtained by reduction (Na-EtOH) of (VIII) and distillation of the OH-acid. With PCl_5 at 130—140° it gives the 2-Cl-derivative, b.p. 126—127°/15 mm., converted by NPhEt_2 into Et Δ^1 -cyclopentene-1-propionate. γ -Phenylpropyl Me ketone (new prep.) is converted by 85% H_2SO_4 at 0° into 1-methyl-3:4-dihydronaphthalene, b.p. 107—108°/14 mm. J. W. B.

Action of trimethylene bromide on ethyl acetonedicarboxylate: new synthesis of ethyl

cyclohexane-2:6-dicarboxylate. P. C. GUHA and N. K. SESHADRIENGAR (Current Sci., 1935, 4, 158).— $[\text{CH}_2]_3\text{Br}_2$ (I) and the Na derivative of $\text{CO}(\text{CH}_2-\text{CO}_2\text{Et})_2$ (II) in C_6H_6 at 140—150° form Et₂ $\beta\zeta$ -dehydrohexan- ζ -ol- β -one- $\alpha\gamma$ -dicarboxylate (J.C.S., 1887, 51, 739) and a phloroglucinol lactone (J.C.S., 1897, 71, 1110), but (I) with the Mg derivative of (II) gives Et₂ cyclohexanone-2:6-dicarboxylate. E. W. W.

Mechanism of polymerisation reactions. IV. α -Phenylbutadiene. E. BERGMANN (J.C.S., 1935, 1359—1360).—Et sodiopropene- $\alpha\gamma$ -tricarboxylate in boiling C_6H_6 with $\text{CHBrPh}-\text{CO}_2\text{Et}$, followed by hydrolysis (18% MeOH-KOH) and decarboxylation at 130° gives δ -phenyl-n-butane- $\alpha\gamma\delta$ -tricarboxylic acid, m.p. 163—165° (decomp.), which is different from the acid (I) obtained by oxidising the dimeride of α -phenylbutadiene, as is the $\alpha\beta\delta$ -tricarboxylic acid (cf. this vol., 976). (I) is identical with δ -phenyl-n-butane- $\alpha\beta\gamma$ -tricarboxylic acid (this vol., 977), so that the dimeride is 2-benzoyl-1-styryl- Δ^3 -cyclopentene and implies that dimerisation is effected by 1:4-addition (cf. simple ethylenes) followed by cyclisation as a result of the activation of a further H atom by the newly formed conjugated system (cf. A., 1929, 674; 1931, 1031; 1932, 856). $\text{CHNa}(\text{CO}_2\text{Et})_2$ with Et₂ fumarate and subsequent treatment of the Na derivative with CH_2PhCl gives Et δ -phenyl-n-butane- $\alpha\beta\gamma$ -tricarboxylate, a mixture of diastereoisomerides, b.p. 220—230°/19 mm. and 230—240°/9 mm.; the former is hydrolysed to (I) and the latter to an acid, m.p. 168° (lit., 165°). J. L. D.

Substitution-syntheses of mellitic acid and replaceability of chlorine in the benzene nucleus. F. FEIST (Ber., 1935, 68, [B], 1941—1943).—Rosenmund's method (A., 1920, i, 44) for the replacement of Cl by CO_2H can be applied only with difficulty to PhCl and is inapplicable to polychlorobenzenes. The presence of negative substituents, however, enables it to proceed. Thus $\text{C}_6\text{Cl}_4(\text{CO}_2\text{K})_2$ is transformed by $\text{KCN}-\text{CuCN}-\text{H}_2\text{O}$ at 180—200° into mellitic acid in 60% yield. H. W.

Reduction reactions and oxidation reactions. [Aromatic aldehydes and Fehling's solution.] V. PAOLINI (Gazzetta, 1935, 65, 630—632).—PhCHO, anisaldehyde, and cuminaldehyde do not reduce Fehling's solution, but, by action of the alkali it contains, undergo the Cannizzaro reaction. Salicylaldehyde and vanillin are unaffected. E. W. W.

Perkin reaction. III. Condensation of acid chlorides with benzaldehyde. H. KATOH (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 2, A, 257—265).—In presence of NEt_3 , PhCHO reacts with the following acid chlorides (products and % yields of theory in parentheses): AcCl ($\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, 11.86), Pr^oCOCl ($\text{CHPh}\cdot\text{C}^o\text{Et}\cdot\text{CO}_2\text{H}$, 6.63), $\text{CH}_2\text{Ph}\cdot\text{COCl}$ ($\text{CHPh}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$, 43.78 of combined *cis*- and *trans*-forms), $\text{CMe}_2\text{CH}\cdot\text{COCl}$ (α -isopropenyleinnamic acid, 6.2). Lævulic acid gives α -benzylidenelævulic acid and $\text{CMePh}\cdot\text{CH}\cdot\text{COCl}$ does not react. Bases other than NEt_3 give lower yields. P. G. C.

New derivatives of dehydrodivanillin and the catalytic reduction of nitrostyrenes. K. MAURER and B. SCHIEDT (J. pr. Chem., 1935, [ii], 144, 41—

48).—Divanillin with Ac_2O and a little H_2SO_4 yields the *hexa-acetate*, m.p. 160° , and with Me_2SO_4 in NaOH gives *diveratraldehyde*, m.p. 138° , (*dioxime*, m.p. 184°), which with MeNO_2 and KOH in MeOH yields *bis-(3:4-dimethoxy- ω -nitrostyrene)*, m.p. 206° , hydrolysed $[\text{Pd}(\text{OAc})_2]$ to *dihomoveratrylamine*, an oil (*Ac*₂ derivative, m.p. 78°). 3:4-Methylenedioxy- ω -nitrostyrene, 3:4-dimethoxynitrostyrene, and β -nitro- α -methoxy- α -3:4-dimethoxyphenylethane similarly give homopiperonylamine ($\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ derivative, m.p. 131°), homoveratrylamine, and α -methoxyhomoveratrylamine (cf. Kindler *et al.*, this vol., 1362).

F. R. G.

Chemical reactivity and Raman spectra of the eugenols, vanillins, and safoles, and of piperonal, estragol, and anethole.—See this vol., 1446.

Isomerides and derivatives of hexetone. R. WEGLER and W. FRANK (Arch. Pharm., 1935, 273, 408—414).—The *d*- and *l*-forms of hexetone (3-methyl-5-isopropyl- Δ^2 -cyclohexenone) (I) have the same cardiac activity as *dl*-(I) (*phenylhydrazone-p-sulphonic acid*, m.p. 228° , gives only oily alkaloidal salts). $\text{CHPhMe}\cdot\text{NIL}$ is readily resolved by the *H* tartrate, the *l*-salt crystallising from MeOH and the *d*-salt being purified by crystallising the salt from the mother-liquors from H_2O . (I) is resolved by α -phenylethylsemicarbazide to give forms, $[\alpha]_D^{20} -37.8^\circ$ and $+37^\circ$, respectively. (I) and Grignard reagents give hydrocarbons. (I) and H_2 -Pd-black in MeOH give the saturated ketone, but with Pt-black the CO is also reduced to $\text{CH}\cdot\text{OH}$, or in AcOH slowly to CH_2 . (I) and $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ give a Schiff's base, b.p. $125^\circ/13$ — 14 mm., stable to H_2 -Pd-C, but reduced by H_2 -Pt-C to 3-methyl-5-isopropylcyclohexyl- β -hydroxyethylamine, b.p. $151^\circ/15$ — 16 mm. (I) and $\text{HCO}\cdot\text{NH}_2$ give a base, hydrolysed by conc. HCl to 3-methyl-5-isopropyl- Δ^2 -cyclohexenylamine, b.p. $90^\circ/12$ mm. [oxalate; resolved by $(\cdot\text{CHPh}\cdot\text{CO}_2\text{H})_2$], which with pyridine-3-carboxyl chloride gives the *amide*, b.p. $230^\circ/14$ mm.

R. S. C.

***p*-Bromophenacyl formate, a solid derivative of formic acid.** C. D. HURD and R. E. CHRIST (J. Amer. Chem. Soc., 1935, 57, 2007).—Contrary to Judefind *et al.* (A., 1920, i, 480) this compound, m.p. 140° , is readily prepared.

R. S. C.

Beckmann change. III. Rearrangement of ketoxime hydrochlorides. A. W. CHAPMAN (J.C.S., 1935, 1223—1229; cf. A., 1934, 1312).—The velocity of the rearrangement to NHPhBz (I) of $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ (II) in $(\cdot\text{CH}_2\text{Cl})_2$ in the presence of HCl at 100° is small at first, but increases with increasing time to a val. which is nearly const. for the last two thirds of the reaction. The time required for a given amount of change depends on the $[\text{HCl}]$. The initial slow period also occurs when the hydrochloride of (II) is used, but is reduced by the addition of (I) and completely abolished by addition of a small amount of $\text{CClPh}\cdot\text{NPh}$ (III) (A., 1931, 843). The change is inhibited by partial replacement of the $(\cdot\text{CH}_2\text{Cl})_2$ by EtOH , which prevents the formation of (III). The presence of HCl is essential to the progress of the change. The rearrangement does not take place

in Et_2O in presence of HCl , except when some (III) is also present.

(II) and (III) in Et_2O with $\text{NaOEt}\cdot\text{EtOH}$ yield *benzophenoneoxime O- α -phenyliminobenzyl ether* (IV), m.p. 72 — 76° , and 5—10% of *benzophenoneoxime N- α -phenyliminobenzyl ether*, m.p. 178 — 179° , which yields (I) with conc. HCl , and (I) and (III) with $\text{Et}_2\text{O}\cdot\text{HCl}$, but no benzoyl-*s*-diphenylbenzamidine (V) with $\text{Et}_2\text{O}\cdot\text{H}_2\text{SO}_4$. The constitution of (IV) is confirmed by the oxidation by $\text{KMnO}_4\cdot\text{AcOH}$ to $\text{CPh}_2\cdot\text{N}\cdot\text{OBz}$. (IV) yields (I) with conc. HCl , and (I) and (III) with $\text{Et}_2\text{O}\cdot\text{HCl}$, and (V) with $\text{Et}_2\text{O}\cdot\text{H}_2\text{SO}_4$. The dry hydrochloride of (II) when heated above 130° yields (I) and *s*-diphenylbenzamidine. (II) when heated at 100° with picric acid and MeNO_2 in a sealed tube gave some (I), but no benz-*N*-picrylanilide, which would have been expected had the change occurred through *N*-phenylbenzimidopicyrlyl ether.

The following mechanism of the Beckmann change accounts for the foregoing observations. (a) A primary slow rearrangement of (II) brought about by acids alone; (b) a much more rapid change beginning as soon as a trace of (I) is formed by (a) and proceeding as follows. (I) and HCl yield (III) which condenses with (II) giving (IV), which with HCl forms the salt $\text{CPh}_2\cdot\text{N}\cdot\text{O}\cdot\text{CPh}\cdot\text{NHPh}\cdot\text{Cl}$. This, by analogy with the picryl ethers, rearranges to $\text{NPh}\cdot\text{CPh}\cdot\text{O}\cdot\text{CPh}\cdot\text{NHPh}\cdot\text{Cl}$ which may rearrange further to (V) or be split by HCl to (I) and (III). The (III) thus formed can transform further quantities of (II). Attempts to prepare di-(α -phenyliminobenzyl) ether by interaction of (III) and dry Ag_2O failed, the only isolable products being (I) and (V).

H. G. M.

Preparation of *o*-nitrophenyl aryl ketones. M. BOËTIUS and H. ROMISCH (Ber., 1935, 68, [B], 1924—1932).—*o*-Nitrophenyl aryl ketones can be obtained by the Friedel-Crafts method if FeCl_3 in mol. proportion is substituted for AlCl_3 . $\text{C}_2\text{H}_5\text{Cl}_4$ at 30 — 40° is the most suitable solvent, but smaller yields can be obtained in PhNO_2 , CHCl_3 , and C_6H_6 ; CS_2 and CCl_4 are unsuitable. In addition to the ketones, larger amounts of black, amorphous products are obtained separable into portions sol. and insol. in Na_2CO_3 , but from which a homogeneous material could not be obtained by reduction, acetylation, or benzylation. Distillation of them with Zn dust affords acridine. $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ condenses with C_6H_6 in presence of $\text{C}_2\text{H}_5\text{Cl}_4$ and FeCl_3 to *o*-nitrobenzophenone (I), m.p. 105° (yield 20%). With mixtures of FeCl_3 and AlCl_3 containing 10% of the latter, (I) is not produced. The following *o*-nitrophenyl aryl ketones are described; *p*-tolyl, m.p. 155° (yield 17—14.6%); *m*-xylol, m.p. 81.5° (yield 19.7—22.6%); *p*-xylol (II), m.p. 94° (yield 41.6—47.4%); *mesityl*, m.p. 146° (yield 6.9%); *p*-methoxyphenyl, m.p. 105° (yield 1.4%). (II) is reduced by Sn and conc. HCl to *o*-aminophenyl *p*-xylol ketone, m.p. 88 — 90° after softening at 76 — 78° .

H. W.

Synthesis of substances related to the sterols. II. General method for the synthesis of substituted cyclohexenones. W. S. RAPSON and R. ROBINSON. III. Synthesis of certain ketohydro-

phenanthrene derivatives. R. ROBINSON and E. SCHLITTLER (J.C.S., 1935, 1285—1288, 1288—1291).—II. *cyclohexenones* are obtained by dehydration of diketones, e.g., $\text{CH}_3 \cdot \text{C}(\text{CO}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3 \rightarrow$

$\text{CH} \cdot \text{C}(\text{CO}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$. Sodiocyclohexanone (I) (from cyclohexanone, NaNH_2 , and Et_2O) and $\text{CHPh} \cdot \text{CH} \cdot \text{COMe}$ (II) in Et_2O yield 2-keto-4-phenyl- Δ^1 -octalin, m.p. 91—92°, b.p. 175—185°/1 mm., hydrogenated (Pd— SrCO_3) to 2-keto-4-phenyldecalin, m.p. 82—83° (2:4-dinitrophenylhydrazon, m.p. 180°). Similarly (I) and acetylcyclohexene (III) yield 9-keto- $\Delta^{10:11}$ -dodecahydrophenanthrene, m.p. 89°, b.p. 150—155°/1 mm. The Na derivative (IV) of 1-keto-2-methyl-1:2:3:4-tetrahydronaphthalene, (II), and C_6H_6 yield 3-keto-1-phenyl-11-methyl-2:3:4:9:10:11-hexahydrophenanthrene, m.p. 135°, b.p. 235—240°/1 mm. 1-Keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (V) (improved prep.) when refluxed with NaNH_2 and Et_2O in a current of H_2 and then treated with (III) yields 2-keto-10-methoxy-2:3:4:5:6:7:8:14:15:16-decahydrochrysene, m.p. 228—229°, hydrogenated (Pd— SrCO_3) to a saturated alcohol, $\text{C}_{19}\text{H}_{26}\text{O}_2$, m.p. 151°. 1-Acetylcyclopentene, b.p. 75—78°/22 mm. (semicarbazone, m.p. 210—211°; obtained not quite pure by heating the product obtained from the interaction at —10° of cyclopentene, anhyd. SnCl_4 , CS_2 , and AcCl , with NPhMe_2 at 180° during 3 hr), with the Na derivative of (V) and Et_2O yields 3-keto-7-methoxy-1:2:3:9:10:11-hexahydro-1:2-cyclopentenophenanthrene, m.p. 196—197°, hydrogenated (Pd— SrCO_3) in MeOH to a tetrahydro-derivative, $\text{C}_{18}\text{H}_{21}\text{O}_2$, m.p. 167—168°. An attempt to condense (IV) and (III) gave two forms (cis- and trans-), m.p. 205—206° and 126—127°, of a dimeride (VI).

$\text{CH}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{CHAc}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$ of (III). On oxidation by the Kuhn—Roth micro-method (VI) gave 1 mol. of AcOH .

III. 5-Keto-8-m-methoxyphenyloctoic acid, m.p. 69—70°, obtained by the method of G. M. Robinson (A., 1930, 742) from γ -m-methoxyphenylbutyryl chloride and Et sodio- α -acetylglutarate, is converted into the Me ester, which is cyclised by $\text{NaOEt-Et}_2\text{O}$ to β -m-methoxyphenylethylcyclohexane-2:6-dione, m.p. about 150° (has pseudo-acidic character, but gives negative Fe^{III} reaction in EtOH). This is dehydrated by P_2O_5 in C_6H_6 to 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene, m.p. 75—76°, b.p. 165—169°/0.23 mm. [2:4-dinitrophenylhydrazon, m.p. 256° (decomp.), sinters at 253—254°], which has no oestrogenic properties, and absorbs 6H_2 with an active Pt catalyst but only 2H_2 with a Pd-black— BaSO_4 catalyst. It is reduced by Na— EtOH to 1-hydroxy-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene (p-nitrobenzoate, m.p. 140°, sinters at 125°). An improved prep. of γ -m-methoxyphenylbutyric acid (VII) (A., 1932, 1122) is described. Et β -m-methoxyphenylpropionate, b.p. 145—146°/10.5 mm., is reduced by Na— EtOH to γ -m-methoxyphenylpropyl alcohol (cf. this vol., 752), converted through the corresponding chloride into the iodide, b.p. 152—162°/11 mm., which with $\text{KCN-H}_2\text{O-EtOH}$

gives some γ -m-methoxyphenylbutyramide, m.p. 96—97°, and the corresponding butyronitrile, b.p. 164—170°/11 mm., hydrolysed by $\text{KOH-MeOH-H}_2\text{O}$ to (VII), m.p. 49—50°. Dehydration of 1-allyl-2-methylcyclohexanol by P_2O_5 yields a dicyclic hydrocarbon, $\text{C}_{10}\text{H}_{16}$, b.p. 169—170°, which absorbs 1 mol. of Br in cold CHCl_3 . H. G. M.

Vat dyes of the benzanthrone series. XI. Formation and separation of isomeric dichlorobenzanthrones. XII. Constitution of the dichlorobenzanthrones. T. MAKI and Y. NAGAI (J. Soc. Chem. Ind. Japan, 1935, 38, 487—489B, 489—493B; cf. A., 1933, 611).—XI. Benzanthrone (I) when treated with AcOH , Cl_2 , and Fe at 100° (68 min.) gives a 94% yield of a mixture of two dichlorobenzanthrones, (II), m.p. 273.5—274.5° (corr.), and (III), m.p. 228° (corr.), separated by means of EtOH and AcOH . A eutectic, m.p. 203.5—204.5° (corr.), of (II) and (III) is also obtained.

XII. Oxidation of 13-chlorobenzanthrone (IV) with $\text{CrO}_3\text{-AcOH-H}_2\text{O}$ yields anthraquinone-1-carboxylic acid. Similarly, oxidation of (II) and (III) yields 6- and 8-chloroanthraquinone-1-carboxylic acid, respectively. The above eutectic gave only a mixture of these acids. Since dichlorination of (I) proceeds through (IV), (II) and (III) are 6:13- and 8:13-dichlorobenzanthrone, respectively. The fusion diagram of (II) and (III) is given. H. G. M.

Synthesis of benzoin. 2':4':6'-Trimethylbenzoin. R. C. FUSON, H. H. WEINSTOCK, jun., and G. E. ULLYOT (J. Amer. Chem. Soc., 1935, 57, 1803—1804).—Benzoin is obtained from α -ketoaldehydes, aromatic hydrocarbons, and AlCl_3 . 2':4':6'-Trimethylbenzoin [thus prepared from mesitylglyoxal (I) and C_6H_6 at 10°], m.p. 102° (urethane, m.p. 158.5—159°), is oxidised by air to $\text{PhCO} \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Me}_3$ (II), and with more (I) in C_6H_6 at 50° gives (II) and $[\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO} \cdot \text{CH}(\text{OH})]_2$ (cf. A., 1934, 525). $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO} \cdot \text{CH}_2\text{Bz}$ and SeO_2 in hot dioxan give mesityl Ph triketone (III), m.p. 90—91°, and other products including a substance, m.p. 169—170°. (III) gives 3-2':4':6'-trimethylbenzoyl-2-phenylquinazoline, m.p. 134—134.5°, and with 10% NaOH yields (II), $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO}_2\text{H}$, and CO_2 .

R. S. C.

(A) Structures of bimolecular reduction products of dibenzoyl ethylene. R. E. LUTZ and F. S. PALMER. (B) Reduction of unsaturated 1:4-diketones with zinc combinations. Formation of the cyclic bimolecular products. R. E. LUTZ, L. LOVE, jun., and F. S. PALMER. (C) Catalytic hydrogenation of unsaturated 1:4-diketones. R. E. LUTZ and F. S. PALMER (J. Amer. Chem. Soc., 1935, 57, 1947—1952, 1953—1957, 1957—1961).—(A) Reduction of $(\text{CHBz})_2$ with Zn— AcOH or other reducing agents gives bimol. products, including meso-“bisdibenzoyl ethane-A” (meso- γ - δ -dibenzoyl- α -diphenyl-n-hexa- α -dione) (I) and its less stable dl-B-isomeride (II), and three stereoisomeric 2:3:4-tribenzoyl-1-phenylcyclopentan-1-ols [-A (III), -B (IV), and -C (V)], termed “cyclobisdibenzoyl ethanes,” the structures of which are proved by the following reactions. (I), m.p. 202°, obtained from $(\text{CH}_2\text{Bz})_2$, $(\text{CHBz})_2$, and NaOEt (62% yield), from (III) and

cold NaOEt, or (IV) and 1 drop of C_5H_5N in hot EtOH, is stable in boiling PhCl or EtOH and distils unchanged at $240-250^\circ/\text{vac.}$ (II), m.p. 168° , best prepared from (III) and hot C_5H_5N -EtOH or by heating (III) at 200° [gives also $(CHBz)_2$ and $(CH_2Bz)_2$ in equal amount], is also obtained from (V) and C_5H_5N -EtOH, showing that (III) and (V) are stereoisomeric at C3 and 4. Since (I) is the *meso*-form, (IV) has the *cis*-configuration at C3 and 4, and (III) and (V) the *trans*. (II) at $230-240^\circ$ gives (I), $(CH_2Bz)_2$, and $(CHBz)_2$, and with cold NaOEt yields (I) only. (I) or (II) with H_2SO_4 - Ac_2O affords 3:3'-bis-(2:5-diphenylfuran) (VI), $\left[\begin{array}{c} \text{O} \begin{array}{c} \text{CPh:CH} \\ \text{CPh:C} \end{array} \end{array} \right]_2$, m.p. $195-196^\circ$

also obtained by AcCl with some 2:5-diphenyl-3:4-diphenacylfuran (VII), m.p. 165° . (VI) with HNO_3 -AcOH at $30-35^\circ$ gives "bis-1:2-dibenzoylethylene" ($\gamma\delta$ -dibenzoyl- $\alpha\alpha'$ -diphenylhexadiene- $\alpha\alpha'$ -dione), m.p. $214-218^\circ$, hydrogenated (Pt) in EtOAc to a little (I) and other products, and reduced by $Na_2S_2O_4$ to much (I) and by Zn-AcOH to substances, m.p. $160-165^\circ$ and $199-200^\circ$, respectively. (VII) and HNO_3 -AcOH give *cis*- $\gamma\delta$ -dibenzoyl- $\alpha\alpha'$ -diphenyl- Δ^1 -hexene- $\alpha\alpha'$ -dione, m.p. $183-184^\circ$, reduced by $Na_2S_2O_4$ in 70% EtOH to a mixture of (I) and (IV). (III), (IV), or (V) with Ac_2O - H_2SO_4 at 90° gives 2:3:4-tribenzoyl-1-phenyl- Δ^1 -cyclopentene (VIII), m.p. 182° , which with O_3 in $CHCl_3$ yields a 1:2-peroxide, m.p. $132-133^\circ$ (decomp.), which, when heated slowly to 140° , gives (VIII), or rapidly BzOH and a substance, m.p. $217-219^\circ$, and which regenerates (VIII) with KI-EtOH and is hydrolysed by 70% EtOH to 2:3:4-tribenzoyl-1-phenylcyclopentane 1:2-oxide, m.p. $117-119^\circ$. This oxide is unchanged by H_2SO_4 - Ac_2O , but with cold NaOMe gives slowly a little BzOH and much $\alpha\beta\gamma$ -tribenzoylpropane (β -phenacyl- $\alpha\delta$ -diphenyl-*n*-buta- $\alpha\delta$ -dione) (IX), m.p. 122° , which is obtained in 50-60% yield from $(CHBz)_2$ and $CHBz:CBz:ONa$ in cold EtOH or from $(CHBz)_2$ and $COPhMe$. (IX) is dehydrated by Ac_2O - H_2SO_4 to 3-phenacyl-2:5-diphenylfuran. The compound (A., 1891, 680), obtained from tricarballic chloride and previously called (IX), is α - or β -phenacyl- $\gamma\gamma$ -diphenylbutyro- γ -lactone, since it gives only a mono-phenylhydrazone and with $KMnO_4$ affords equal amounts of BzOH and $COPh_2$.

(b) Zn reduction of *trans*- $(CHBz)_2$ (X) gives large yields of bimol. products, that of *cis*- $(CHBz)_2$ (XI) only small yields thereof, whilst only unimol. products result by Zn-AcOH (room temp.) reduction of *cis*- and *trans*- $(CH:CO:C_6H_4Cl-p)_2$, *trans*- $(p-C_6H_4Me:CO:CH)_2$, *trans*- $(C_6H_5Me_3:CO:CH)_2$, *cis*- $(CBrBz)_2$, *cis*- $CHBz:CPhBz$ (XII), *cis*- $CBrBz:CPhBz$ (XIII), $CH_2Bz:CHXBz$ (XIV), or *dl*- or *meso*- $(CHXBz)_2$ (X=Cl or Br). Formation of the bimol. products probably involves conjugated reduction. $ZnBr_2$ often has a catalytic effect. (X) and hot Zn-AcOH or sol. reducing agents give $(CH_2Bz)_2$, but slower reduction or, best, Zn-AcOH- C_6H_6 at $30-35^\circ$ gives much (III), m.p. 161° , whereas under these conditions (XI) gives only $(CH_2Bz)_2$. (XIII) with Zn-AcOH gives mainly 2:3:5-triphenylfuran (XV). (XII) with Zn-AcOH gives a little (XIV) with much $CH_2Bz:CHPhBz$ (XVI). (XVI) is stable to Zn-AcOH, so that reduction of (XII) probably proceeds by way of

$OH:CPh:CH:CPh:CPh:OH$. If, however, $ZnBr_2$ is added, (XII) gives only (XV). Reduction of (XIII) thus undoubtedly proceeds by way of $OH:CPh:C:CPhBz$ and (XIII). *dl*- and *meso*- $(CHBrBz)_2$, but not $(CHClBz)_2$ or (XIV), with Zn-COMe₂ give much (III). (X) reacts with Zn-COMe₂ only if $ZnBr_2$ is added, but $CHBz:CBz$ and (XIV; X=Br) are not affected, so that reduction of $(CHBrBz)_2$ probably proceeds by way of (X). This is in harmony with the production of very little (III) if the concn. of (X) is kept low. (XI) with Zn- $ZnBr_2$ -COMe₂ gives mainly unimol. products. $Na_2S_2O_4$ in 60-65% EtOH with (X) gives mainly $(CH_2Bz)_2$, but deteriorated samples give bimol. products and the additive compound (XVI), $CH_2Bz:CHBz:SO_3Na$, m.p. $255-262^\circ$ (converted by hot conc. HCl into 2:5-diphenylfuran), whilst in one case mainly (II) was formed. $NaHSO_3$ in 90% EtOH converts (X) into much (III) and some (IV), (V), $(CH_2Bz)_2$, and (XVI). (IV), m.p. $202-203^\circ$, or (V), m.p. $204-205^\circ$, with NaOMe gives (I).

(c) Catalytic hydrogenation with PtO_2 of (X) in EtOAc or dioxan, or with Raney Ni in decahydronaphthalene or 95% EtOH, gives mostly $(CH_2Bz)_2$, but with PtO_2 in other solvents much (III) and sometimes (I) and (II) are formed. Acid increases the amount of $(CH_2Bz)_2$ formed in EtOH. Hydrogenation of (X) probably proceeds by a conjugate mechanism, but is unique in that (XI) gives 45-50% of $(CH_2Bz)_2$ and other similar ketones give mostly or only unimol. products. M.p. in (A), (B), and (C) are corr.

R. S. C.

Testicular hormone. L. RUZICKA (J. Amer. Chem. Soc., 1935, 57, 2011-2012).—Androstene-3:17-dione, androstane-3:17-dione and -diol are more active than androsterone. Androsten-3-ol-17-one with Na-EtOH gives *androstene-3:17-diol* (I), m.p. $175-178^\circ$ (corr.), the *dibromide* of which by partial oxidation and debromination gives *androstene-3-one-17-ol*, identical with testosterone, also obtained from (I) by partial hydrolysis of the diacetate and oxidation of the acetate dibromide.

R. S. C.

Constitution and preparation of the testicular hormone. E. S. WALLIS and E. FERNHOLZ (J. Amer. Chem. Soc., 1935, 57, 2012).—Concerning priority.

R. S. C.

Dideuteroandrostanone.—See this vol., 1408.

Two modifications of 4:2':3':4':6'-pentamethoxychalkone. G. MARTINEZ (Rend. Semin. Fac. Sci. Univ. Cagliari, 3, 147; Chem. Zentr., 1935, i, 1537).—Crystallographic examination shows the stable form, m.p. $111-112^\circ$, to be monoclinic ($a:b:c=1.267:1:0.83412$) and the labile form triclinic ($a:b:c=0.5660:1:0.7514$).

H. N. R.

Mechanism of additions to double linkings. II. **Steric course of two diene syntheses.** A. WASSERMANN (J.C.S., 1935, 1511-1514; cf. this vol., 938).—The additive products of cyclopentadiene with benzoquinone or maleic anhydride exist in geometrically isomeric forms ("endo-" and "exo-"), the rates of formation of which differ. The dipole induction energy is greater for orientations of the reacting mols. which might lead to the *endo*-additive

product than for orientations suitable for *exo*-addition. The activation energy of the latter process is greater.

H. J. E.

Reaction between 2 : 3-dimethyl-1 : 4-naphthaquinone and magnesium phenyl bromide. I. (MISS) H. M. CRAWFORD (J. Amer. Chem. Soc., 1935, 57, 2000—2004).—2 : 3-Dimethyl-1 : 4-naphthaquinone (I) reacts with MgPhBr by reduction and 1 : 2- and 1 : 4-addition to give mono- and di-additive products. (I) (348 g.; 1.87 mols.) and MgPhBr (3.5 mols.) give (I) + its *quinhydrone*, m.p. 136—140° (dissociated in C_6H_6), 65 g., 1 : 4-dihydroxy-1 : 2-diphenyl-2 : 3-dimethyl-1 : 2-dihydronaphthalene (II), m.p. 208—209° (2 active H) 40 g., 1-hydroxy-1-phenyl-4-keto-2 : 3-dimethyl-1 : 4-dihydronaphthalene (III), m.p. 197—197.5° (1 active H) 20 g., 2-phenyl-2 : 3-dimethyl-2 : 3-dihydro-1 : 4-naphthaquinone (IV), m.p. 123°, 2.4 g., and a compound (V), m.p. 137—138°, 14 g. When (I) (55.8 g., 0.3 mol.) and MgPhBr (0.55 mol.) react and the mixture is decomposed by AcCl, there are formed (I) 7.5 g., the *Ac* derivative, m.p. 153—157°, of (III) [also obtained from (III)] 0.22 g., 1 : 4-diacetoxy-2 : 3-dimethylnaphthalene, m.p. 189°, 7.9 g., and a substance (VI), $C_{24}H_{20}O$, m.p. 183°, b.p. 250—270°/15 mm., 1.1 g. With $K_2Cr_2O_7$ (IV) gives CPhMe, (III) gives o - C_6H_4 Bz-CO₂H, and (II) gives both products. (II) is stable to KMnO₄ in COMe₂ and to hot 20% H₂SO₄, but with PBr₃ in CHBr₃, ZnCl₂ and HCl in hot C_6H_6 , or I in AcOH yields (VI). (VI) is stable to hot HBr, $K_2Cr_2O_7$, and MgMeI. The Grignard reaction leads occasionally to small amounts of compounds, $C_{24}H_{22}O_2$, m.p. 203—204° [additive compound with 2 mols. of (I)=(V)], and $C_{24}H_{20}O$, m.p. 124° (no active H; with $K_2Cr_2O_7$ gives CPhMe and o - C_6H_4 Bz-CO₂H).

R. S. C.

Constitution of perezone. F. KOGL and A. G. BOER (Rec. trav. chim., 1935, 54, 779—794; cf. Fichter *et al.*, A., 1913, i, 279).—Perezone (I), m.p. 102—103° (cf. lit.), $[\alpha]_D^{20}$ —17.0° in Et₂O {m.p. and $[\alpha]$ are depressed when (I) is sublimed owing to facile racemisation; *Ag* salt; *Me* ether, b.p. 128—133°/0.002 mm.}, is shown, from the known results and those which follow, to be 2-hydroxy-3-methyl-6-(α , α -dimethyl- Δ^5 -hexenyl)benzoquinone. (I), has 1 active H (Zerevitinov) and when boiled with Ac₂O, NaOAc, and Zn yields triacetyl-leucoperezone (II), $C_{21}H_{18}O_6$, b.p. 176—178°/0.2 mm., $[\alpha]_D^{20}$ —30.7° in EtOH, whilst when treated successively with Na₂S₂O₄ and Me₂SO₄-KOH-MeOH it yields trimethyl-leucoperezone, b.p. 110°/0.01 mm. Hydroxyperezone (III) prepared by the method of Fichter (*loc. cit.*) is impure and contains some hydroxyperezone hydrate, m.p. 139° [contains 3 active H (Zerevitinov)], H₂O having been added across the ethylenic linking in the side-chain. An Et₂O solution of (I) when hydrogenated (Adams-Schriner) and then shaken with air yields dihydro-perezone (IV), m.p. 95°, but if treated with CH₂N₂ immediately after hydrogenation yields dihydro-perezone Me₁ ether, b.p. 150°/0.01 mm. (IV) when heated (water-bath) with NH₂Ph and EtOH affords anilino-dihydro-perezone, $C_{21}H_{27}O_3N$, m.p. 139°, which when heated (water-bath) with H₂SO₄-AcOH yields hydroxy-dihydro-perezone, m.p. 143—144°, $[\alpha]_D^{20}$ —30° in Et₂O. This when boiled with Ac₂O, NaOAc, and a little Zn

5 G

yields the *Ac*₄ derivative, m.p. 134°, $[\alpha]_D^{20}$ —46.6° in COMe₂, of hydroxydihydroleucoperezone (V), and when treated successively with Na₂S₂O₄ and Me₂SO₄-KOH-MeOH yields the *Me*₄ ether, b.p. 120°/0.01 mm., $[\alpha]_D^{20}$ —31.7° in EtOH, of (V). Perezinone (A., 1885, 777) prepared from (III) has 1 active H (Zerevitinov), and is considered to be 2-hydroxy-3 : 8-dimethyl-5-isopropenyl-5 : 6 : 7 : 8-tetrahydro-1 : 4-naphthaquinone. (I) and (IV) do not undergo a similar reaction, as they do not contain respectively the suitably situated OH or the ethylenic linking. Oxidation of (I) and (II) by H₂O₂ affords AcOH and an unsaturated C₉ carboxylic acid, hydrogenated to a nonoic acid, also obtained by oxidation of (IV) and shown, when completely racemised, to be α , ϵ -dimethyl-heptioic acid (VI) (A., 1929, 296). This acid was synthesised from isohexyl bromide and CHMeNa(CO₂Et)₂ through *Et*, methylisohexylmalonate, b.p. 145°/14 mm., hydrolysed to the acid, m.p. 114—115°, which by loss of CO₂ affords (VI). This is resolved by means of the cinchonidine salt, from which the *l*-acid, $[\alpha]_D^{20}$ —17.5° (*l*-amide, m.p. 75—77°, $[\alpha]_D^{20}$ —18.1° in EtOH), is obtained. (II) on ozonolysis gives COMe₂ but no other volatile aldehydes or ketones, showing the presence of :CMe₂ in (II). Distillation of (I) with Zn yields a hydrocarbon which is oxidised to p - C_6H_4 (CO₂H)₂ by H₂SO₄-CrO₃-H₂O, showing that the side-chains in (I) are in the *p*-positions.

H. G. M.

Lichen acids. VI. Constituents of *Ramalina scopulorum*. F. H. CURD and A. ROBERTSON (J.C.S., 1935, 1379—1381).—From *R. scopulorum*, *d*-usnic acid and Zopf's scopularic acid (I) have been isolated; the latter is identical with stictic acid (II) (Asahina *et al.*, A., 1933, 1050). The *dianil*, m.p. 234°, of (II) may be obtained from (II) and from (I), and differs from the monoanil and distictic acid anilide. (II) and KOH yield stictinic acid, m.p. 223—224°, by opening of the lactone ring, and (II) is methylated by MeI-Ag₂CO₃ to a *Me* ether, m.p. 174°, and by MeI-Ag₂O to an isomeric *Me* ether, m.p. 242—243°.

F. R. S.

Condensation of balata bromide with phenols and phenolic ethers. T. HARDIE and J. MAIR (J.C.S., 1935, 1242—1244).—Balata bromide when heated at 100—120° for 2.5 hr. with anhyd. FeCl₃ and PhOH affords *p*-dihydroxydiphenylhydrobalata, $[C_5H_8(C_6H_4\cdot OH)_2]_n$, m.p. 195—200° (shrinks at 130°; *di-p*-nitrobenzoate, m.p. 87—90°), oxidised by KMnO₄ in COMe₂ to complex resin acids and *p*-OH-C₆H₄-CO₂H. This shows that condensation has occurred in the *p*-position. Similar compounds are obtained from *o*-cresol (m.p. 193—195°; *di-p*-nitrobenzoate, m.p. 190—192°), *m*-cresol [m.p. 165—169° (shrinks at 140°); *di-p*-nitrobenzoate, m.p. 146—148°], *p*-cresol (m.p. 167—169°; shows a colour change when its acid suspension is made alkaline; *di-p*-nitrobenzoate, m.p. 143—145°), resorcinol [(I), m.p. 220°; *tetra-p*-nitrobenzoate, m.p. 195—200°], α -C₁₀H₇-OH (m.p. 190—195°; *di-p*-nitrobenzoate, m.p. 150—152°), anisole (m.p. 105—110°; gives fluorescent solution in EtOAc), phenetole (m.p. 125—130°; has fluorescent properties). *p*-Dimethoxy-, m.p. 195—197°, and *p*-diethoxy-diphenylhydrogutta-percha, m.p. 205—207°, are obtained from gutta-percha bromide by similar methods; both

give fluorescent solutions in EtOAc. (I) and the corresponding compounds of gutta-percha and caoutchouc show marked indicator properties, considered to be due to the presence of the compound obtained when resorcinol is heated at 110° with FeCl₃, although the indicator properties of this compound are less well-defined. None of the foregoing condensation products gives a depression of the f.p. of C₆H₆, and mol. wt. determinations (Rast) give variable results (cf. A., 1929, 321). H. G. M.

Jute lignin. VIII. Methylation of lignin.
IX. Acetylation of lignin. P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 542—546, 547—551).—VIII. Jute lignin (I) carefully isolated at a low temp. (cf. A., 1934, 1355) is insol. in alkali, gives 2.78% CH₃O, and has an OMe val. of 19.18% (cf. this vol., 978) [corresponding with 5 · OMe in (I) if its mol. wt. is 830], also obtained after (I) has been boiled with 28% H₂SO₄. These results show that the CH₂O₂ and ·OMe have not been affected during isolation of (I) and that the ·OMe is entirely present in ether form. After methylation of (I) an OMe val. of 34.51% is obtained corresponding with the presence of 5 free ·OH in (I) in addition to 5 ·OMe. In OMe determination (Zeisel) MeI first appears at the same temp. from (I) as from vanillin and vanillic acid, but at a lower temp. from methylated lignin. It is inferred that (I) contains OMe attached to the C₆H₆ nucleus and that the OH (subsequently methylated) are in the side-chain. Oxidation of methylated (I) by 5*N*-HNO₃ gave no anisic acid. (I) when boiled with 28% H₂SO₄ and subsequently methylated does not reduce Fehling's solution, although it will do so if the methylation is omitted. This confirms the view (cf. A., 1934, 1355) that the reducing action of ordinary lignin is due to 2 *o*-OH attached to the C₆ ring and formed by the hydrolysis of the CH₂O₂ when lignin is isolated in the ordinary way. It therefore contains no ·CHO.

IX. Two successive treatments with Ac₂O-C₅H₅N of (I) isolated as described above gave a product (II) the AcOH content (26.45%) of which is in good agreement with that (28.85%) required for 5 ·OH. Reducing lignin (III) [obtained when (I) is boiled with HCl or 28% H₂SO₄] when acetylated gives a product which has a higher AcOH content than (II) and does not reduce AgNO₃-NH₃-H₂O, in agreement with the view that the reducing action, when shown, is due to the presence of 2 *o*-OH (see above). Moreover (III), COMe₂, and P₂O₅ give a non-reducing compound insol. in alkalis (cf. Boeseken *et al.*, A., 1932, 860). The ·OMe and CH₂O₂ in (I) are unaffected by acetylation. (I) is not hydrogenated (Pd), and therefore contains no ethylenic linking (cf. this vol., 214). The amounts of ICl and IBr absorbed by (I) are comparable with those absorbed by many saturated C₆H₆ compounds, and are not evidence for an ethylenic linking. Raw jute and HCl-lignin give CHI₃ with NaOH-I. The foregoing quant. results are considered to support the val. of 830 for the mol. wt. of (I).

H. G. M.

Lignin. X. Lignin ethyl ether and thioglycollic acid. G. A. BERG and B. HOLMBERG (Svensk Kem. Tidskr., 1935, 47, 257—265).—When lignin from pinewood is extracted by means of EtOH-HCl,

lignin Et ether (I) is obtained, which is supposed to react as ROEt + SH·CH₂·CO₂H (II) = RS·CH₂·CO₂H + EtOH. By heating with (II) CH₂Ph·OEt yields CH₂Ph·S·CH₂·CO₂H, CHPhMe·OEt yields S-*α*-phenyl-ethylthioglycollic acid, m.p. 63—65°, CH₂Ph·CH₂·OEt does not react, CHPh₂·OEt yields S-benzhydrylthioglycollic acid, m.p. 129—130°, CPh₃·OEt yields S-triphenylmethylthioglycollic acid, m.p. 163—165° (Et ester, m.p. 94—95°), (I) yields a brown powder containing > 1 mol. of (II); also H₂O [not replaced by (II)] is eliminated. (I) with (II) in the presence of HCl yields an amorphous compound, C₄₀H_{41.5}O_{9.4}(S·CH₂·CO₂H)_{5.3}. E. P.

Cerin and friedelin. II. Functional derivatives. N. L. DRAKE and S. A. SHRADER (J. Amer. Chem. Soc., 1935, 57, 1854—1856; cf. this vol., 1373).—The following derivatives confirm identification of friedelin as a ketone and cerin (modified prep.), m.p. 250—256° (acetate, m.p. 259—261°) as a OH-ketone. *Friedelin oxime*, m.p. 290—294° (hydrolysed by H₃PO₄-C₅H₁₁·OH; *acetate*, m.p. 237—239°; rearranged by PCl₅ in CHCl₃ to an unreactive substance, m.p. 316—318°), 2:4-dinitro-, m.p. 297—299° (decomp.), and *p*-nitro-phenylhydrazone, m.p. 277—279° (decomp.). *Cerin Me ether*, m.p. 265—270°, [*α*]_D²⁵₄₉₁ —58.9° in CHCl₃ [*oxime*, m.p. 258—262°; 2:4-dinitro-phenylhydrazone, m.p. 284—285° (decomp.)], 2:4-dinitrophenylhydrazone, m.p. 253—255° (decomp.), *oxime*, m.p. 266—272°, H₂-derivative, *cerinol*, m.p. 293—295°, [*α*]_D²⁵₄₆₁ +9.4° (*Ac*₂ derivative, m.p. 267—269°).

R. S. C.

Determination of urushiol in lacquer. VII. Structure of the substance produced from urushiol by oxidation or polymerisation. S. HIRANO (J. Soc. Chem. Ind., Japan, 1935, 38, 445—447B).—A structure derived from 2:5:8:11-tetrahydroxy-3:4:9:10-perylenediquinone is proposed for the polymerisation and oxidation product of urushiol (cf. Majima, "Untersuchungen über den Japanlack," 1924, 108). H. G. M.

Toad poisons. VII. Bufo arenarum, Bufo regularis, and Xenopus laevis. H. JENSEN (J. Amer. Chem. Soc., 1935, 57, 1765—1768; cf. A., 1934, 412).—The secretion of *B. arenarum* yields arenobufagin (I), arenobufotoxin, bufothionine, and adrenaline (II); that of *B. regularis* yields regularobufagin (III), C₂₅H₃₄O₆, m.p. 235—236°, *regularobufotoxin*, C₃₉H₆₀O₁₁N₄, m.p. 205° after softening at 190°, (II), and regularobufotenine, C₁₁H₁₂O₂N₂ [flavinate, m.p. 264° (decomp.)]; picate, +H₂O, m.p. 203—204°; identical with that obtained from *B. valliceps* (A., 1934, 1232)]; that of *X. laevis* yields cholesterol, fatty acids, and bufotenidine, C₁₃H₁₈ON₂ (flavinate, +H₂O, m.p. 200°; picate, m.p. 197°; *hydriodide*, m.p. 208—209°). (I) with hot *N*-NaOH-EtOH gives AcOH and *arenobufaginic acid*, C₂₃H₃₄O₆, m.p. 220—235°, and with CrO₃ *arenobufagone*, C₂₅H₃₂O₆, m.p. 219—220°, but its *Ac* derivative (prep. by hot Ac₂O), m.p. 162—163°, is stable to CrO₃. (III) gives similarly *regularobufagone*, C₂₅H₃₂O₆, m.p. 210—211°, and with alkali *regularobufaginic acid*, C₂₃H₃₄O₆, decomp. from 125°, and AcOH, but with Ac₂O loses AcOH to give a substance, C₂₅H₃₂O₅, m.p. 224—225°, which does not give a ketone with CrO₃. (I) and (III) are thus *Ac* deriv-

atives of a doubly unsaturated lactone, $C_{23}H_{29}O_2(OH)_3$, of which one OH (that accessible to Ac_2O) is *sec.* and one is *tert.* and carries the Ac. Both probably have sterol structure. R. S. C.

Bongkreki acid.—See this vol., 1540.

Constitution of cuscutalein.—See this vol., 1550.

Bitter principle from *Andrographis paniculata*.—See this vol., 1549.

Isolation of pyrethrin.—See this vol., 1550.

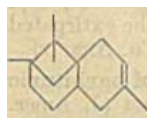
Derivatives of vitamin-E.—See this vol., 1546.

Volatile terpenes as acid hydrolysis products of saponins. K. LEUPIN (Schweiz. Apoth.-Ztg., 1934, 72, 755—756; Chem. Zentr., 1935, i, 2018—2019).—Steam-distillation of *Tilia* saponin and Merck's *Sapindus* saponin affords volatile terpenes as hydrolysis products; these were identified by their odour and by various colour reactions. A little $PrCO_2H$ (?) was present in the distillate. H. N. R.

Anomalous mutarotation of salts of Reyckler's acid. III. Reduction of ketimines of *d*-camphor-10-sulphonic acid. Formation of *sultams*. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1896—1898; cf. this vol., 1246).—*d*-Camphoranil-10-sulphonic acid with H_2 -PtO₂ in MeOH gives α - (I), m.p. 300—302° (block), $[\alpha] -88.5^\circ$, and β -2-anilino-camphor-10-sulphonic acid (II), m.p. 350—351°, $[\alpha] +8.5^\circ$ in $CHCl_3$ -MeOH. With $PhSO_2Cl$ or Ac_2O at 100° (I) gives the *sultam* (III), m.p. 172—173°, but the isomeric *sultam*, m.p. 137—138°, $[\alpha] +140.5^\circ$ in $CHCl_3$, is obtained from (II) only by $PhSO_2Cl$ - C_5H_5N at 100°. Both are hydrolysed by conc. HCl, the second more easily, to regenerate the parent acids. R. S. C.

Neutral salt action in non-aqueous solution.—See this vol., 1461.

Constitution of cedrene. R. ROBINSON and J. WALKER (Chem. and Ind., 1935, 906—907, 946—947).—Contrary to Treibs (this vol., 983) and Short (*ibid.*, 1376) the most probable structure of cedrene is as annexed. F. R. G.



Reactions of β -ketonic esters containing the furan nucleus. A. MIRONESCO and G. IOANID (Bull. Soc. Chim. Romania, 1935, 17, 107—129).—Condensation of the Mg compound of CH_2Cl - CO_2Et with furoyl chloride in Et_2O affords *Et* furoylacetate (I) [*amide* (II), m.p. 159°], also obtained (70% yield) by hydrolysis ($NaOEt$ - NH_4Cl -20% aq. NH_3 at 40°) of *Et* furoylacetylacetate, b.p. 167°/17 mm., obtained by condensation of CH_2Ac - CO_2Et and C_4H_3O - $COCl$ with Na in Et_2O . By the action of the appropriate alkyl halide on the Na derivative of (I) are obtained *Et* α -furoyl-propionate, b.p. 143°/11 mm. (*amide*, m.p. 183°), -isobutyrate, (III) b.p. 150°/20 mm. (*amide*, m.p. 164°), -butyrate, b.p. 148°/14 mm. (*amide*, m.p. 188°), - α -ethylbutyrate (IV), b.p. 177/25 mm. (*amide*, m.p. 164°), and - α -methylbutyrate (*amide*, m.p. 164°), and, with $(\cdot CH_2Br)_2$, *Et* 2-furoylcyclopropane-1-carboxylate (V), b.p. 148—149°/16 mm. [*amide*, m.p. 162°, prepared from (II)]. By hydrolysis

(HCl) of these esters or amides are obtained furoyl *Et* (VI) (*semicarbazone*, m.p. 189°), *Pr*^a, b.p. 96°/20 mm. (*semicarbazone*, m.p. 90°), *Pr*^b, b.p. 67°/33 mm., *Bu*^b, b.p. 96°/16 mm. (*semicarbazone*, m.p. 174°), α -ethyl-n-propyl, b.p. 97°/17 mm. (*semicarbazone*, m.p. 162°), and cyclopropyl, b.p. 75°/23 mm. (*semicarbazone*, m.p. 167°), *ketone*. With $MgRX$ compounds of the type C_4H_3O - CO - CHR - CO_2Et ($R=H$ or alkyl) regenerate the parent β -keto-ester when the product is hydrolysed, but (V) affords *Et* 1-(α -hydroxy- α -ethylfurfuryl)- (*Bz* derivative, b.p. 161°/12 mm.) and 1-(α -hydroxy- α -phenylfurfuryl)-, b.p. 180°/18 mm., -cyclopropane-1-carboxylate. With $MgEtBr$ (III) affords *Et* β -hydroxy- β -furyl- α -dimethyl-n-valerate, b.p. 160°/16 mm., together with unchanged (III), *Pr*^a CO_2Et , (VI), and the alcohol obtained from (VI) and $MgEtBr$. With $MgPhBr$ the ester group of (III) is attacked to give 2-furyl (β -hydroxy- β -diphenyl- α -dimethyl)ethyl *ketone*, b.p. 181°/12 mm. With $MgEtBr$ or $MgPhBr$ (IV) undergoes scission to give, respectively, 2-furyl-diethyl-, b.p. 84°/17 mm., and -diphenyl-, m.p. 90°, -carbinol. J. W. B.

Synthesis of hexahydro- α -coumaranone. R. GHOSH (J. Indian Chem. Soc., 1935, 12, 601—603).—*Et* cyclohexanone-2-carboxylate, Na, and CH_2Cl - CO_2Et in C_6H_6 give *Et*₂ cyclohexanone-2-carboxylate-2-acetate, b.p. 161—162°/5 mm., hydrolysed by hot 25% HCl to cyclohexanone-2-acetic acid, b.p. 169—170°/7 mm. [*semicarbazone*, m.p. 199—200°; *Et* ester, b.p. 130°/10 mm. (*semicarbazone*, m.p. 196°)], which is reduced by 30% Na-Hg to hexahydrocoumaranone, identical with that obtained from Δ^1 -cyclohexeneacetic acid. R. S. C.

Synthesis of coumarins from phenols and β -ketonic esters. III. Use of various condensing agents. D. CHAKRAVARTI (J. Indian Chem. Soc., 1935, 12, 536—539).—Except in the case of β - $C_{10}H_7$ -OH and CH_2Ac - CO_2Et (I) which give a coumarin and a chromone (A., 1932, 858), a phenol and a β -ketonic acid, when they condense, give a coumarin whatever the condensing agent used. Thus 7-hydroxy-4-methylcoumarin is formed from resorcinol and (I) when H_3PO_4 , $NaOAc$, $NaOEt$, or B_2O_3 is used, the best yield being with H_3PO_4 . Other examples are given. *Et* 5-hydroxy-4:7-dimethylcoumarin-3-acetate, m.p. 198—200°, is obtained from orcinol, CO_2Et - $CHAc$ - CH_2 - CO_2Et (II), and H_2SO_4 , P_2O_5 , or H_3PO_4 , and *Et* 7:8-dihydroxy-4-methylcoumarin-3-acetate, m.p. 186°, is obtained from pyrogallol, (II), and H_2SO_4 . H_3PO_4 is a better condensing agent for Pechmann's and for Bulow's reactions than is the usual agent. H. G. M.

Synthesis of coumarins from phenols and β -ketonic esters. IV. Coumarins from 4-chloro- and 2-nitro-resorcinol. D. CHAKRAVARTI and B. GHOSH (J. Indian Chem. Soc., 1935, 12, 622—626; cf. A., 1932, 1257).—4-Chlororesorcinol readily gives coumarins by H_2SO_4 or P_2O_5 . 2-Nitroresorcinol gives 60 and 15% yields of coumarins with CH_2Ac - CO_2Et and $CHMeAc$ - CO_2Et , respectively, with H_2SO_4 , but does not condense with the *Et*-, *Pr*^a-, or *Pr*^b-substituted esters; P_2O_5 gives intractable resins. The following coumarin derivatives are described: 6-Cl-7-OH-, m.p. 271° (*Ac* derivative,

m.p. 166°); 6-*Cl*-7-*OH*-4-*Me*-, m.p. 280° (*Ac* derivative, m.p. 168°); 8-*NO*₂-7-*OH*-4-*Me*-, m.p. 256° (decomp.) [*Ac* derivative, m.p. 198° (lit. 165°)]; 8-*NO*₂-7-*OH*-3:4-*Me*₂-, m.p. 260° (decomp.) (*Ac* derivative, m.p. 246°); 6-*Cl*-7-*OH*-3:4-*Me*₂-, m.p. 248° (*Ac* derivative, m.p. 170—171°); 6-*Cl*-7-*OH*-4-*Me*-3-*Et*-, m.p. 257—258° (*Ac* derivative, m.p. 145°); 6-*Cl*-7-*OH*-4-*Me*-3-*Pr*ⁿ-, m.p. 230° (*Ac* derivative, m.p. 135°); 6-*Cl*-7-*OH*-4-*Me*-3-*Bu*ⁿ-, m.p. 199°; 6-*Cl*-7-*OH*-3-*CH*₂*Ph*-4-*Me*-, m.p. 249°; 3:6-*Cl*₂-7-*OH*-4-*Me*-, m.p. 254° (*Ac* derivative, m.p. 192°); 6-*Cl*-7-*OH*-4-*Ph*-, m.p. 258—260°; 6-chloro-7-hydroxycoumarin-4-acetic acid, m.p. 210°, and *Et* 6-chloro-7-hydroxy-4-methylcoumarin-3-acetate, m.p. 174°

R. S. C.

Triarylpyrylium borofluorides. W. C. DOVEY and R. ROBINSON (J.C.S., 1935, 1389—1390).—COPhMe and BF₃ give 2:4:6-triphenylpyrylium borofluoride, m.p. 225—226°, also obtained in better yield from COPhMe and Ph styryl ketone; *p*-methoxyphenyl *p*-methoxystyryl ketone, *p*-methoxyacetophenone, and BF₃ afford 2:4:6-tri-*p*-methoxyphenylpyrylium borofluoride, m.p. 345—347°. F. R. S.

Constitution of the dihydroxy-derivative of diphenylene oxide obtained from resorcinol. K. HATA, K. TATEMATSU, and B. KUBOTA (Bull. Chem. Soc. Japan, 1935, 10, 425—432).—A substance (this vol., 220) obtained by passing resorcinol vapour over W₃O₈ at 500—550° is now proved to be 2:7-dihydroxydiphenylene oxide (I). *p*-Iodo-*m*-nitroanisole gives (Ullmann) 2:2'-dinitro-4:4'-dimethoxydiphenyl, m.p. 136—137°, reduced to 2:2'-diamino-4:4'-dimethoxydiphenyl, m.p. 110.5—111.0°; diazotisation and treatment with CuSO₄ solution affords 2:7-dimethoxydiphenylene oxide (II), m.p. 150°, together with 2:7-dimethoxyphenazone, m.p. 97°. Demethylation of (II) with HI gives (I), m.p. 241—241.5°. The absorption curves of diphenylene oxide, 2-hydroxydiphenylene oxide, and (I) are given.

P. G. C.

Bases prepared from pyrogallol ethers. (MME.) Y. DE LESTRANGE (Bull. Soc. chim., 1935, [v], 2, 1678—1684).—1:2:3-C₆H₃(OH)₃ heated with Et₂SO₄ and 10% Na₂CO₃ gives a mixture separated by fractionation into 1:2-dihydroxy-3- (I), m.p. 95.5° (*Ac* derivative, m.p. 75°), 1:3-dihydroxy-2- (II), m.p. 102° (*Ac* derivative, m.p. 77°), 2-hydroxy-1:3-di- (III), m.p. 90°, 3-hydroxy-1:2-di- (IV), b.p. 120°/11 mm., -ethoxybenzene. (I) and (II) with glyceryl α -dichlorohydrin give, respectively, a mixture of 8-ethoxy-2- or -3- and 8-ethoxy-3- or -2-hydroxymethylbenzdioxan (V), b.p. 190—193°/13 mm., and 2:6-bis- γ -chloro- β -hydroxypropoxyphenol. (V) with SOCl₂ in C₆H₅N yields a mixture of 8-ethoxy-2- or -3- and 8-ethoxy-3- or -2-chloromethylbenzdioxan, b.p. 173°/13 mm., which when heated in a sealed tube with NHEt₃ gives a mixture of 8-ethoxy-2- or -3- and 8-ethoxy-3- or -2-diethylaminomethylbenzdioxan, b.p. 188—190°/14 mm. (hydrochlorides, m.p. 228° and 140°). Similarly are prepared: mixtures of 8-methoxy-2- and -3-hydroxy-, b.p. 193°/12 mm., and -chloro-, b.p. 167°/10 mm., -diethylamino-methylbenzdioxan, b.p. 172—175°/10 mm. (hydrochlorides, m.p. 197° and ?). (III) and (IV) with epichlorohydrin give 2-epoxy-1:3-, b.p.

172°/12 mm., and 3-epoxy-1:2-diethoxybenzene, b.p. 172°/12 mm. These when heated (sealed) with NHEt₃ give 2- γ -diethylamino- β -hydroxypropoxy-1:3-, b.p. 198°/13 mm. (hydrochloride, m.p. 112—113°), and 3- γ -diethylamino- β -hydroxypropoxy-1:2-diethoxybenzene, b.p. 198°/13 mm. (hydrochloride, m.p. 78—80°). (III) and (IV) heated with NEt₂·CH₂·CH₂Cl and Na in EtOH yield, respectively, 2-diethylaminoethoxy-1:3-, m.p. 134—135°, and 3-diethylaminoethoxy-1:2-diethoxybenzene hydrochloride, m.p. 112—113° (free base, b.p. 180°/14 mm.). The colours given by (I), (II), (III), and (IV) with FeCl₃, NiSO₄, CoSO₄ and diazotised bases are described. F. R. G.

Pyrolysis. Elimination of two hydroxyl groups from a glycol. A. SCHOMBERG and R. MICHAELIS (J.C.S., 1935, 1403—1404).—1:4-Bisdiethylmethylene- $\Delta^{2:5}$ -cyclohexadiene with HNO₃ gives $\omega\omega'\omega'$ -tetraphenyl-*p*-xylylene glycol, a reaction analogous to the conversion of chromanorufen (I) into 5:12-dihydroxychromanorufan (II) (cf. Liebermann *et al.*, A., 1934, 531), which is easily reconverted by heat or AcOH into (I). (II) and NPhMe₂ give 5:12-bis-*p*-dimethylaminophenylchromanorufan, decomp. 340°, not obtained directly from (I).

F. R. S.

Bromonitrothiophen. V. S. BABASIAN (J. Amer. Chem. Soc., 1935, 57, 1763—1764).—2-Bromothiophen with HNO₃-AcOH in Ac₂O gives 2-bromo(?-5)-nitrothiophen, m.p. 45—46°, b.p. 235—237°/750 mm. Other nitrating agents cause oxidation; *e.g.*, pure HNO₃ gives H₂SO₄.

R. S. C.

[3-Aminopyridine.] A. BINZ and O. VON SCHICKH (Ber., 1935, 68, [B], 1989; cf. this vol., 498).—A correction.

H. W.

Synthesis of β -bromonicotdiethylamide. T. UGAI and S. IZUMI (J. Pharm. Soc. Japan, 1935, 55, 13—14).—3-Bromoquinoline (modified prep.) is oxidised (KMnO₄) to 5-bromopyridine-2:3-dicarboxylic acid, m.p. 165° [anhydride (I), m.p. 134—136°]. (I) and NHEt₃ yield β -bromonicotdiethylamide, b.p. 160°/4 mm., which is without action on the extirpated frog's heart.

CH. ABS. (r)

Synthesis of pyridine derivatives of barbituric acid. C. S. KUHN and G. H. RICHTER (J. Amer. Chem. Soc., 1935, 57, 1927—1929).— β -Picolyl bromide [from β -picoline and Br (2 mols.) in conc. HCl at 150°] with Et, alkylmalonates (I) give esters, which with CO(NH₂)₂ and NaOEt at 100° yield 5- β -picolyl-5-ethyl-, m.p. 213—214°, -*n*-propyl-, m.p. 250° (decomp.), -*n*-butyl-, m.p. 218—219°, and -isoamyl-barbituric acid, m.p. 229—230°. 2-Bromopyridine does not react with (I).

R. S. C.

2-Pyridylethylmalonic acid. L. A. WALTER and S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1891—1892).—CETNa(CO₂Et)₂ and 2-bromopyridine in EtOH give 2-ethoxypyridine (I), b.p. 66°/25 mm., 160—161°/760 mm. [HgCl₂-derivative, m.p. 152—153° (lit. 141°); hydrochloride, m.p. 90—91°]; without EtOH there are formed a little (I), CET₂(CO₂Et)₂, *Et* α -2-pyridylbutyrate, b.p. 97—98°/2 mm., and *Et*, 2-pyridylethylmalonate (19%), b.p. 136—137°/2 mm. The last ester does not give a barbituric acid derivative, as it is extremely easily cleaved. With

$\text{CO}(\text{NH}_2)_2$ it yields α -2-pyridylbutyramide, m.p. 125—126°.

R. S. C.

Arylated pyridines. IX. W. DILTHEY and H. DIERICH (J. pr. Chem., 1935, [ii], 144, 1—31; cf. A., 1926, 1254).—2:4:6-Triphenylpyrylium perchlorate (A., 1916, i, 829) heated with NH_2Ph or its appropriate derivative yields the following perchlorates; 1:2:4:6-tetraphenylpyridinium, m.p. 260°; 1-p-tolyl-, m.p. 243—244° [compound with $\text{NH}_2\text{OH}(\text{+H}_2\text{O})$, m.p. 163°]; 1-o-tolyl-, m.p. 254—255°; p-phenetyl-, m.p. 274°; o-anisyl-, m.p. 242—243°; p-anisyl-, m.p. 243° (iodide, m.p. 309—310°, compound with NH_2OH , m.p. 145—146°); 1-p-hydroxyphenyl-pyridinium (I), m.p. 245° [chloride, m.p. 380—381°; bromide, m.p. 382—383°; periodide, iodide, m.p. 340°; nitrate, m.p. 323—324° (decomp.); perhydroxide, m.p. 201° (decomp.); picrate, m.p. 214—215°; Ac derivative, m.p. 288° (periodide, m.p. 185°)]. (I) with KOH in MeOH yields a red base, m.p. 197—198°, $[\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{CPh}:\text{CH}:\text{CPh}:\text{CH}:\text{CPh}:\text{CPh}]$

$\begin{array}{c} \text{CH} \\ \text{---} \\ \text{N}(\text{C}_6\text{H}_4\text{OH})\text{CPh} \end{array} \text{CH} \text{OH}^-$ (anhydro-base; perchlorate, m.p. 225°, picrate, m.p. 240°; nitrate, m.p. 222—223°; chloride, m.p. 214—215°; bromide, m.p. 225—228°; iodide, m.p. 229°).

F. R. G.

Indoles and isatogens. XIX. Transformation of o-aminated tolans or stilbenes into derivatives of indole or indoline. P. RUGGLI and O. SCHMID (Helv. Chim. Acta, 1935, 18, 1215—1228).—A further example of the formation of an indoline under the action of picric acid is recorded. Acetylation of 4:6-diamino-1:3-distyrylbenzene (I) appears to yield an Ac_4 derivative, m.p. 198.5—199°, as well as the Ac_1 and Ac_2 [picrate, m.p. 232° (decomp.)] derivatives. Treatment of (I) with picric acid in boiling EtOH affords resinous matter and 6-amino-2-phenyl-5-styrylindoline (II), m.p. 210—211° [picrate; oxalate, m.p. 272°; yellow-orange monohydrochloride, and (?) higher hydrochlorides], in 23% yield. The presence of 1NH_2 in (II) is established by the isolation of 6-benzylideneamino-2-phenyl-5-styrylindoline (III), m.p. 143° (corresponding o-chlorobenzylidene compound m.p. 173°), from which (II) is regenerated by AcOH. Cautious treatment of (II) with warm Ac_2O gives the Ac_2 derivative (IV), m.p. 242° (picrate, decomp. 272°; hydrochloride, m.p. 232—242°), whereas more drastic treatment appears to yield a Ac_3 compound. With $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_6\text{H}_5\text{N}$ a di-p-toluenesulphonyl derivative, m.p. 250—251°, results. Attempts to prepare monoacyl compounds directly or by partial hydrolysis of diacyl compounds were unsuccessful. Cautious treatment of (II) with HNO_2 gives a compound, $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}_3$, the formation of which involves extensive decomp. Evidence against the possibility that (II) is an indole derivative is afforded by its strong basicity, the non-incidence of the pine-shaving reaction, and its inability to react with NaOEt and amyl nitrite. It is hydrogenated (Pd) to 6-amino-2-phenyl-5- β -phenylethylindoline, m.p. 163° (CHPh, m.p. 118°, and Ac, m.p. 220°, derivatives). [Under these conditions 2-phenylindole (V) is not hydrogenated to 2-phenylindoline (VI).] Stronger evidence is based on the production of (IV), since (V) is unchanged by boiling Ac_2O , whereas (VI) immediately affords

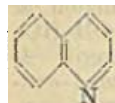
an Ac derivative, m.p. 129°. Further (V) does not react with EtI, whereas (VI) gives a cryst. ethiodide. (III) is converted into 6-benzylideneamino-2-phenyl-5-styryl-1-ethylindoline ethiodide, decomp. 251°, converted by dil. HCl into 6-amino-2-phenyl-5-styryl-1-ethylindoline ethiodide, m.p. 218°. Ring formation is not observed with the following substances: o-aminotolan, m.p. 89° (picrate, m.p. 85—90°, decomp. 95°), obtained by reduction of o-nitrotolan with SnCl_2 in HCl-AcOH at 40°; o-aminostilbene; cis- and trans-2:2'-diaminostilbene; Et o-aminocinnamate (picrate, decomp. 145°) obtained by reduction of $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ by SnCl_2 in AcOH-HCl, whereas H_2 and Ni afford dihydrocarbostyryl; 4-nitro-6-amino-1:3-distyrylbenzene; 6-amino-4-acetamido-1:3-distyrylbenzene, m.p. 218° [picrate, m.p. 225° (decomp.); corresponding Ac_2 derivative, m.p. 284°]; 2:4:6-triamino-1:3-distyrylbenzene; 4:6-diamino-3-styryl-1-o'-aminostyrylbenzene. Catalytic reduction of 2:4-dinitrostilbene leads to 2:4-diaminostilbene, m.p. 115°, which gives an orange monopicrate, decomp. 134°, and red dipicrate, decomp. 160°, which are interconvertible and from which the original material is regenerated. Isomerisation in PhNO_2 at 140° gives a picrate, decomp. 250°, from which (II) and a substance $\text{C}_{12}\text{H}_{12}\text{N}_2$, m.p. 152°, are isolated.

H. W.

Indoles and isatogens. XX. Aminated double stilbenes. P. RUGGLI and O. SCHMID (Helv. Chim. Acta, 1935, 18, 1229—1239).—The following observations were made during attempts to extend the indole synthesis of Thiele and Dimroth to benzodipyrroles. Brown resins are obtained when 4:6-diamino-1:3-distyrylbenzene is heated with its hydrochloride (I) or $\text{NH}_2\text{Ph}\cdot\text{HCl}$. When heated with anhyd. Na_2CO_3 (I) yields small amounts of a substance, $\text{C}_{10}\text{H}_{13}\text{N}$, m.p. 218° (Ac, m.p. 178°, and CHPh, m.p. 174°, derivatives). The poor yields of o-nitrostilbene (II) from $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III) and PhCHO are not due to lack of reactivity of CH_2 , but to concurrent decarboxylation of (III) to $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$. $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ afford (II) in 10% yield. Catalytic hydrogenation of (II) readily involves the ethylenic linking, and reduction is best effected by SnCl_2 . 4:6-Diamino-1:3-di-m'-aminostyrylbenzene, m.p. 190—191°, is obtained by hydrogenation (Ni) of the $(\text{NO}_2)_4$ -compound (improved prep.). $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (improved prep. by hydrogenation of $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$) is converted by Ac_2O into $\text{o-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 71°, which condenses with 4:6-dinitro-m-xylene in presence of piperidine at 130—120° to 4:6-dinitro-1-o'-acetamidostyryl-3-methylbenzene, m.p. 256°; the latter is hydrolysed by HCl in boiling AcOH to 4:6-dinitro-1-o'-aminostyryl-2-methylbenzene, m.p. 183°, catalytically reduced to 4:6:2'-triamino-3-methylstilbene, m.p. 152°, which gives a little indole when heated with its hydrochloride. 4:6-Dinitro-3-styryl-1-o'-acetamidostyrylbenzene, m.p. 267°, is hydrolysed to 4:6-dinitro-3-styryl-1-o'-aminostyrylbenzene, m.p. 193°, catalytically reduced to 4:6-diamino-3-styryl-1-o'-aminostyrylbenzene, m.p. 145°, which gives a little indole when heated with its hydrochloride. 4:6-Dinitro-3-m'-nitrostyryl-1-o'-acetamidostyrylbenzene, m.p. 270°, gives 4:6-dinitro-3-m'-

nitrostyryl-1-*o*'-aminostyrylbenzene, m.p. 249—250°, which could not be reduced satisfactorily to the tetra-amine. H. W.

Dipole moments and structures of some quinoline derivatives, and the orientation of Claus and Hofmann's α -nitroisoquinoline. (Mrs.) C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1935, 1470—1475).—Calculation of dipole moments from measurement of mol. polarisations and refractivities at infinite dilutions of quinoline, 2- and 6-methyl-, 2 : 4-dimethyl-, 5-, 6-, and 8-nitro-quinoline, and *p*-toluquinoline, indicates that in quinoline derivatives, except α -Me compounds, the mobilities of the linkages are so diminished by ring fusion that the skeleton is best formulated as (I). The nitration product, m.p. 110°, of solid isoquinolinium nitrate or sulphate (Claus and Hofmann, A., 1893, i, 366) is most probably the 5-compound. F. R. S.



(I)

4-Hydroxy-2-methylquinoline and its derivatives. M. MAURIN (Ann. Chim., 1935, [xi], 4, 301—363).—The following derivatives of 4-hydroxy-2-methylquinoline are described : *sulphate*; 3-*tolueneazo*-derivative, m.p. 210°; *methosulphate*, m.p. 126°; *ethosulphate*, m.p. 120°; *phthalidene* derivative, m.p. >300°; *Ac*, m.p. 134°, and *Bz* derivative; *methiodide cyanine*, m.p. about 230°; *ethiodide*, m.p. 205° (4-dimethylaminobenzylidene, m.p. 230°, *vanillylidene*, m.p. 205°, *anisylidene*, m.p. 218—222°, and *cinnamylidene* derivative, m.p. 215°); *methiodide* (4-dimethylaminobenzylidene, m.p. 230°, and *vanillylidene* derivative, m.p. 165°); 4-*ethoxy*-2-methylquinoline, m.p. 37—40° (*hydrochloride*, m.p. 170°; *ethiodide*, m.p. 205°); *ethylquinaldone*, m.p. 180—183°. 4-Methoxyquinaldone (*ethobromide*, m.p. 201°) heated with Me_2SO_4 gives a 4-methoxy-2-methylquinoline *methosulphate*, (I), m.p. 201° [*methochloride*, m.p. 200°; *cyanine*, m.p. 245° (*hydroxide*, m.p. 165°)], which gives a violet colour with alkalis. Prolonged heating of methylquinaldone with Me_2SO_4 in EtOH yields a second form of 4-methoxy-2-methylquinoline *methosulphate*, m.p. 201° (no colour with alkali). Two forms of the *methiodide* (II) (*cyanine*, m.p. about 235°) were also prepared and probable structures for these isomerides are given. (II) with the appropriate aldehydes or nitrosoamines yields the following derivatives : *anisylidene*, m.p. about 220°; *vanillylidene*, m.p. about 220°; *piperonylidene*, m.p. 220°; 4-dimethylaminophenylazomethine, m.p. 170°; 4-diethylaminophenylazomethine, m.p. 175°. (I) and HCl with the appropriate aldehyde yield the *vanillylidene*, m.p. 220°, and *piperonylidene*, m.p. 220°, *methochlorides*. F. R. G.

Attempts to find new antimalarials. XIV. Derivatives of 8-methylquinoline. W. O. KERMACK and T. W. WIGHT (J.C.S., 1935, 1421—1426).—6-Methoxy-8-methylquinoline (*hydrobromide*, m.p. 268°) is brominated to the 5-*Br*-compound (I), m.p. 116—117°. 4-Bromo-6-nitro-*m*-cresol, m.p. 146°, separated from a bromination mixture, is methylated to the -*m*-tolyl Me ether, m.p. 110—111°, reduced to 4-bromo-5-methoxy-*o*-toluidine, m.p. 79—80°. The base is converted (Skraup) into (I) and by diazotisation and CuBr into 4 : 6-dibromo-*m*-tolyl Me ether. A similar series of reactions on 6-bromo-4-nitro-*m*-cresol gives

6-bromo-4-nitro-*m*-tolyl Me ether, m.p. 113—115°, 2-bromo-5-methoxy-*p*-toluidine, m.p. 71—73°, and its *Ac* derivative, m.p. 130—133°. From a mixture of bromo-6-nitro-*m*-cresols, 7-bromo-6-methoxy-8-methylquinoline, m.p. 134—135°, is obtained. Bromination in $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ of 6-nitro-8-methylquinoline gives the 3-*Br*-compound, m.p. 188—189°. 8-Bromo-methylquinoline and H_2SO_4 yield 8-quinolylmethyl alcohol, m.p. 75—76°, and 5-nitro-8-quinolylmethyl alcohol, m.p. 148—149°, similarly obtained, with $\text{C}_5\text{H}_{11}\text{N}$ affords 5-nitro-8-piperidinomethylquinoline (*hydrobromide*, m.p. 248—249°).

o-Nitrobenzylethylamine and $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}\cdot\text{HCl}$ (II) condense to β -(*o*-nitrobenzylethylamino)triethyl amino (*picrate*, m.p. 167—168°), reduced to the -amino-compound (*picrate*, m.p. 134°). (II) and the appropriate amine yield β -(benzylethylamino)triethylamine (*picrate*, m.p. 150—152°) and the -*p*-nitrobenzyl compound (*picrate*, m.p. 195—197°), β -diethylamino-ethyl-propylamine (*monopicrate*, m.p. 133—135°), -*n*-butylamine (*dipicrate*, m.p. 234°), and -isobutylamine (*dipicrate*, m.p. 141°), which with $\text{C}_5\text{H}_{11}\text{N}$ give β -piperidino-ethylpropylamine (*dipicrate*, m.p. 169°), -*n*-butylamine (*dipicrate*, m.p. 191—192°), -isobutylamine (*dipicrate*, m.p. 167—168°), -ethylmethylamine (*dipicrate*, m.p. 174°), and -diethylamine (*dipicrate*, m.p. 154°). $\text{C}_6\text{H}_4\text{Br}_2$ and NH_2Me afford *s*-dimethylethylenediamine (*picrate*, m.p. 160°). Condensation of 8-bromomethylquinoline with the appropriate amine gives the following : 8-(β -diethylamino-ethylmethylaminomethyl)-quinoline (*trihydrobromide*, m.p. 215—216°), -diethylaminomethyl)-(*trihydrobromide*, m.p. 218—219°, *picrate*, m.p. 131—132°) -ethylpropylaminomethyl) (*monopicrate*, m.p. 113—115°, *dipicrate*, m.p. 163—164°), -ethyl-*n*-butylaminomethyl) (*dipicrate*, m.p. 178—180°), and -ethylisobutylaminomethyl) (*dipicrate*, m.p. 169—171°); 8-(β -piperidino-ethylpropyl-aminomethyl)quinoline (*trihydrobromide*, m.p. 210°), -ethyl-*n*-butylamino- (*trihydrobromide*, m.p. 211—212°), -ethylisobutylamino- (*dipicrate*, m.p. 210—211°), -ethylmethylamino- (*dipicrate*, m.p. 205—206°) and -diethylamino- (*trihydrobromide*, m.p. 222°), and *s*-bis-(8-quinolylmethyl)dimethylethylenediamine dihydrobromide, m.p. 232°. Bis-(8-quinolylmethyl)- β -diethylaminomethylamine, m.p. 97—98°, 8-(β -diethylaminomethylaminomethyl)quinoline trihydrobromide, m.p. 223—224°, 1- β -bis-(8'-quinolylmethyl)aminoethylpiperidine, m.p. 97—98°, and 1 : 4-bis-(8'-quinolylmethyl)piperazine (+0.5H₂O), m.p. 153—154°, are also described. F. R. S.

Dyes derived from acridic acid. M. P. GUPTA and S. DUTT (J. Indian Chem. Soc., 1935, 12, 581—584).—Acridic acid (quinoline-2 : 3-dicarboxylic acid) gives dyes of phthalein type with PhOH, m.p. 184°, resorcinol, m.p. 203° (*B*₁-derivative, m.p. >290°), phloroglucinol, quinol, and orcinol, m.p. >280°, *m*-NH₂·C₆H₄·OH, m.p. 280—285°, *m*-NMe₂·C₆H₄·OH, m.p. 168°, *m*-NEt₂·C₆H₄·OH, m.p. 120°, and *m*-C₆H₄(NH₂)₂, m.p. 295°. They are more absorptive than the corresponding dyes from quinoline-2 : 3 : 4-tricarboxylic acid. R. S. C.

Phenanthridine series. IV. Synthesis of plasmoguin-like derivatives. L. P. WALLS (J.C.S.,

1935, 1405—1410).—Phenanthridones have been prepared by oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7\text{--AcOH}$) of 9-methylphenanthridines and by the action of NaN_3 on a substituted fluorenone in H_2SO_4 , a method which gives a mixture of isomerides. The following have been obtained by the oxidation method: 9- and 9- ω -chloro-, 3-nitro-, m.p. $> 360^\circ$, and 3-bromo-phenanthridone, decomp. 302° (from 3-bromo-9-methylphenanthridine, m.p. $129.5\text{--}130^\circ$), which is converted by POBr_3 into 3:9-dibromophenanthridine, m.p. $170\text{--}171^\circ$. The following have been prepared from fluorenones: phenanthridone, 2(or 7)-nitro-, decomp. about 340° , 2(or 7)-chloro-7(or 2)-nitro-, m.p. 340° , 2:7-dinitro-, m.p. $> 340^\circ$, and 2(or 7)-amino-phenanthridone, m.p. about 285° (by reduction and also directly from the fluorenone). The mixture of OH-compounds, from the NH_2 -derivatives, may be separated by crystallisation to give 2-hydroxy-, m.p. $341\text{--}343^\circ$, -acetoxy-, m.p. $273\text{--}274^\circ$ (decomp.), and -methoxy-phenanthridone, m.p. 251° , and 9-chloro-2-methoxyphenanthridine, m.p. 137.5° , 7-hydroxy-, m.p. $320\text{--}322^\circ$ (decomp.), -acetoxy-, m.p. $261\text{--}264^\circ$ (decomp.), and -methoxy-phenanthridone, m.p. $271\text{--}272^\circ$, and 9-chloro-2-methoxyphenanthridine, m.p. 107° . $\text{NEt}_2\text{--CH}_2\text{--CH}_2\text{Cl}$ and $\text{CH}_3\text{Ac--CO}_2\text{Et}$ give δ -amino- α -diethylaminopentane (I) (dipicrate, m.p. $134\text{--}135^\circ$), which with 9-chlorophenanthridine condenses to α -diethylamino- α -methylbutylamino-9-phenanthridine, isolated as the dipicrate, m.p. $196\text{--}197^\circ$, and converted into the sulphate. 3:9-Dibromophenanthridine with $\text{NEt}_2\text{--CH}_2\text{--CH}_2\text{--NH}_2$ followed by HCl yield 3-bromo-9- β -diethylaminoethylaminophenanthridine dihydrochloride (dipicrate, decomp. about 156°) and with (I) affords 3-bromo-9- δ -diethylamino- α -methylbutylaminophenanthridine dihydrochloride (dipicrate, decomp. $217\text{--}218^\circ$). 9-Chloro-2-methoxyphenanthridine with $\text{N}(\text{CH}_2\text{--CH}_2\text{--NH}_2)_3$ gives 9- β -diethylaminoethylamino-2-methoxyphenanthridine dihydrochloride [dipicrate, m.p. 207° (decomp.)], and with (I) the 9- δ -diethylamino- α -methylbutylamino-dihydrochloride (dipicrate, decomp. $192\text{--}193^\circ$). Although these nuclear-substituted meso-aminophenanthridines resemble quinoline and acridine antimalarials in type they possess no therapeutic val. F. R. S.

Manufacture of acridinium compounds.—See B., 1935, 1069.

Synthesis of glyoxaline derivatives. R. WEIDENHAGEN and R. HERRMANN (Ber., 1935, 68, [B], 1953—1961).—The synthesis of glyoxalines is more readily effected from $\alpha\beta$ -hydroxyketones or $\alpha\beta$ -hydroxyaldehydes than from $\alpha\beta$ -diketones. Treatment of these with Cu--NH_3 solution readily yields the ketones which in presence of an aldehyde are immediately condensed to the glyoxaline, usually pptd. at the Cu salt. The carbinols may be replaced by their acetates and sometimes by the corresponding Cl-compounds. The yields may attain 90%. Thus are obtained: 4(5)-phenylglyoxaline, m.p. $129\text{--}130^\circ$, from $\text{CH}_2\text{Bz--OH}$, CH_2O , $\text{Cu}(\text{OAc})_2$, and NH_3 ; 4(5)-phenyl-2-methylglyoxaline, m.p. $161\text{--}162^\circ$; 4(5)-phenyl-2-ethylglyoxaline, m.p. 133° (Cu salt); 4(5)-phenyl-2-isopropylglyoxaline, m.p. 180° (Cu salt); 2:4(5)-diphenylglyoxaline, m.p. 193° (Cu salt; hydrochloride monohydrate, m.p. 273°); 4(5)-2'-hydroxy-

phenylglyoxaline, m.p. 181° (Cu salt), from 2: ω -dihydroxyacetophenone, m.p. 65° ; 4(5)-2'-hydroxy-5'-methylphenylglyoxaline, m.p. $136\text{--}137^\circ$ (Cu salt), from 2-hydroxy-5-methylbenzoylcarbinol, m.p. $76\text{--}77^\circ$; 4(5)-p-methoxyphenylglyoxaline, m.p. 137° ; 4(5)-p-acetamidophenylglyoxaline, m.p. $250\text{--}251^\circ$ (Cu salt); 4(5)-p-aminophenylglyoxaline ($+0.5\text{H}_2\text{O}$), m.p. 97° (Cu salt); 4(5)-p-carboxyphenylglyoxaline, m.p. 308° [Cu salt; hydrochloride ($+1\text{H}_2\text{O}$), m.p. 338°]; 4(5)-methylglyoxaline from acetol acetate or $\text{COMe--CH}_2\text{Cl}$; 2:4(5)-dimethylglyoxaline; 4(5)-hydroxymethylglyoxaline from $\text{CO}(\text{CH}_2\text{--OH})_2$; glyoxaline. H. W.

Acetanilidoalkylbarbituric acids [alkyl-5-barbiturylacetanilides]. J. A. TIMM (J. Amer. Chem. Soc., 1935, 57, 1943—1944).— $\text{NHPh--CO--CH}_2\text{Cl}$ (I) and 5-alkylbarbituric acids with NaOAc and KI (not NaOAc alone) in aq. EtOH give 5-ethyl-, m.p. $243\text{--}247^\circ$ (decomp.), -n-butyl-, m.p. $250\text{--}256^\circ$ (decomp.), -isobutyl-, m.p. $250\text{--}255^\circ$ (decomp.), -isoamyl-, m.p. $245\text{--}250^\circ$ (decomp.), and -allyl-5-barbiturylacetanilide, $\text{CO} < \begin{smallmatrix} \text{NH--CO} \\ \text{NH--CO} \end{smallmatrix} > \text{CR--CH}_2\text{--CO--NHPh}$, m.p. $237\text{--}242^\circ$ (decomp.). (I) and $\text{CNaEt}(\text{CO}_2\text{Et})_2$ in EtOH at 100° give only N,N' -diphenyldiketopiperazine and (?) $\text{OEt--CH}_2\text{--CO--NHPh}$. R. S. C.

Sulphur-containing barbiturate hypnotics. D. L. TABERN and E. H. VOLWILER (J. Amer. Chem. Soc., 1935, 57, 1961—1963).—Contrary to Johnson *et al.* (A., 1911, i, 502) Et_2 alkylmalonates, $\text{CS}(\text{NH}_2)_2$, and NaOEt--EtOH at $100\text{--}120^\circ$ give 5-ethyl-5-isopropyl-, m.p. 192° , -n-butyl-, m.p. $144\text{--}145^\circ$, -sec-butyl-, m.p. $163\text{--}165^\circ$, -allyl-, m.p. $172\text{--}173^\circ$, - β -methylallyl-, m.p. $160\text{--}161^\circ$, -isoamyl-, m.p. $167\text{--}169^\circ$, - α -methylbutyl-, m.p. $158\text{--}159^\circ$, -n-hexyl-, m.p. $136\text{--}137^\circ$, - β -ethylbutyl-, m.p. $137\text{--}138^\circ$, and - γ -chloro- Δ^8 -butenyl-, m.p. $128\text{--}130^\circ$, 5-cyclohexyl-5-ethyl-, m.p. $205\text{--}207^\circ$, 5-phenyl-5-ethyl-, m.p. $215\text{--}217^\circ$, 5-methyl-5- β -methylallyl-, m.p. $128\text{--}130^\circ$, 5:5-diallyl-, m.p. 134° , 5-allyl-5- β -methylallyl-, m.p. $180\text{--}182^\circ$, 5-sec-butyl-5-allyl-, m.p. $142\text{--}143^\circ$, 5- α -methylbutyl-5-allyl-, m.p. $127\text{--}129^\circ$, and ω -benzyl- ω -allyl-2-thiobarbituric acid, m.p. $140\text{--}150^\circ$. When injected intravenously into rabbits, many of these are powerful hypnotics of very brief action with low toxicity. R. S. C.

5:5-Diphenylbarbituric acid, 5-phenyl-5-cyclohexylbarbituric acid, and 5-phenyl-5-cyclohexenylbarbituric acid. H. J. MORSMAN (Helv. Chim. Acta, 1935, 18, 1254—1264).— $\text{CPh}_2(\text{COCl})_2$ (I) in Et_2O is transformed by NH_3 into diphenylmalon-diamide, m.p. $243\text{--}244^\circ$ (corr.), which with COCl_2 in PhMe at 150° or with $(\text{COCl})_2$ in boiling C_6H_6 affords 5:5-diphenylbarbituric acid (II), m.p. $298\text{--}299^\circ$, also obtained from (I) and $\text{CO}(\text{NH}_2)_2$ at 100° or in boiling xylene. (II) is best prepared by the addition of 20% oleum to alloxan monohydrate in C_6H_6 at 20° , heating the mixture at $70\text{--}75^\circ$, and removing by-products by the successive action of dil. NaOH and KMnO_4 in alkaline solution. Treatment of (II) with excess of CH_2N_2 in Et_2O gives 5:5-diphenyl-1:3-dimethylbarbituric acid, m.p. $206\text{--}207^\circ$ (corr.), also obtained from (I) and $\text{CO}(\text{NHMe})_2$ in boiling xylene. 5-Phenylbarbituric acid is obtained from $\text{CHPh}(\text{CO--NH}_2)_2$ and $(\text{COCl})_2$ in C_6H_6 at 80° .

CHPh(CO₂Me)₂, cyclohexenyl bromide, and KOMe in C₆H₆ afford *Me₂ phenylcyclohexenylmalonate* (III), m.p. 79—80° (*by-product*, m.p. 204—205°), transformed by boiling KOH—MeOH into *phenylcyclohexenylacetic acid*, m.p. 123—123.5° (corresponding *amide*, m.p. 167—168°). (III) and CO(NH₂)₂ in MeOH containing NaOMe at 105—108° give *5-phenyl-5-cyclohexenylbarbituric acid* (IV), m.p. 209—210°, also obtained from K 5-phenylbarbiturate and cyclohexenyl bromide in dioxan. Hydrogenation of (III) by PtO₂ in MeOH affords *Me₂ phenylcyclohexylmalonate*, m.p. 89—90°, whereas interaction of CHPh(CO₂Et)₂ and cyclohexyl bromide yields unchanged material, CH₂Ph·CO₂Et, and (IV). Similar hydrogenation of (IV) gives *phenylcyclohexylbarbituric acid*, m.p. 256° (corr.). (II) is only a feeble narcotic. H. W.

Formation of "triacylacetic ester." II. F. SEIDEL, W. THIER, A. UBER, and J. DITTMER (Ber., 1935, 68, [B], 1913—1924; cf. A., 1932, 931).—Evidence of the formation of CAc₂·CO₂Et by the action of AcCl on Et sodioacetate has been based on the formation of "Et 4-acetyl-3:5-dimethylpyrazole-4-carboxylate" (I) when the product is treated with N₂H₄. Since the substance when heated above its m.p. passes into β-5-hydroxy-3-methyl-4-pyrazolylcrotonolactone, m.p. 246°, and is hydrolysed by alkali to β-5-hydroxy-3-methyl-4-pyrazolylcrotonic acid, m.p. 154° (decomp.), it is now recognised as Et β-5-hydroxy-3-methyl-4-pyrazolylcrotonate (II). It arises from CHAc₂·CO₂Et, which loses Ac under the influence of N₂H₄; excess of N₂H₄ reacts with CH₂Ac·CO₂Et thus produced, yielding 3-methylpyrazol-5-one, which condenses with residual CH₂Ac·CO₂Et to (II). During unsuccessful attempts to prepare (I) synthetically, the following observations have been made. Et 3:5-dimethylpyrazole-4-carboxylate is converted by AcCl in C₅H₅N into *Et 1-acetyl-3:5-dimethylpyrazole-4-carboxylate*, m.p. 69°, in which the position of Ac is established by decarboxylation of the corresponding *acid*, m.p. 164°, to *1-acetyl-3:5-dimethylpyrazole*, b.p. 70°/12 mm., also obtained from 3:5-dimethylpyrrole (III) and AcCl in C₅H₅N or from NH₂·NHAc and CH₂Ac₂ in boiling EtOH. *1-Benzoyl-3:5-dimethylpyrazole*, b.p. 158°/12 mm., is derived from (III) and BzCl in C₅H₅N or from CH₂Ac₂ and NH₂·NHBz in boiling EtOH. N₂H₄·H₂O and CHAc₃ in H₂O afford *4-acetyl-3:5-dimethylpyrazole*, m.p. 128° [*monohydrate*, m.p. 121° (decomp.)], which with AcCl in C₅H₅N at 0° gives *1:4-diacetyl-3:5-dimethylpyrazole*, m.p. 50°. 3-Methylpyrazol-5-one, m.p. 270°, is obtained from N₂H₄·H₂O and Et isodehydracetate in boiling MeOH. *1-Phenyl-3-methylpyrazol-5-one*, CH₂Ac·CO₂Et, and NaOH in H₂O at 15—20° yield *Et β-5-hydroxy-1-phenyl-3-methyl-4-pyrazolylcrotonate*, m.p. 88°, which loses EtOH at 70° and forms *β-5-hydroxy-1-phenyl-3-methyl-4-pyrazolylcrotonolactone*, m.p. 132°. *β-5-Hydroxy-1-benzoyl-3-methyl-4-pyrazolylcrotonolactone* has m.p. 181°. H. W.

Piperazine. VI. Alkylation by means of aldehydes. W. T. FORSEE, jun., and C. B. POLLARD. VII. Procaine analogues. I. D. E. ADELSON, L. G. MACDOWELL, and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1788—1789, 1988—1989; cf. this

vol., 1253).—VI. Piperazine (I) and its *N*-Ph derivative are alkylated by CH₂O or MeCHO in Zn—HCl. H₂O-insol. aliphatic aldehydes rapidly effect alkylation in hot HCO₂H, but aromatic aldehydes require several days. The following derivatives of (I) are thus obtained: *N-Ph-N'-Me*, b.p. 109—100°/5 mm., *N-Ph-N'-Et*, b.p. 144—145°/10 mm., *NN'-Me₂*, b.p. 130—135° [*dihydrochloride*, m.p. 263° (decomp.)], *NN'-Et₂*, b.p. 174—177°, *NN'-Bu₂*, b.p. 195—195.5°/12 mm., *NN'-(CH₂Ph)₂*, m.p. 92—93° (also obtained from CH₂PhCl), and *NN'-di-p-methylbenzyl*, m.p. 101—102°.

VII. Anhyd. (I) and (CH₂)₂O in hot MeOH give a 98% yield of *NN'-di-β-hydroxyethylpiperazine*, m.p. 135—135.5°, the *di-p-nitrobenzoate*, m.p. 158—158.5°, of which is reduced (Fe) to the *di-p-amino-benzoate*, m.p. 203—204° (*tetrahydrochloride*, cryst., hygroscopic). R. S. C.

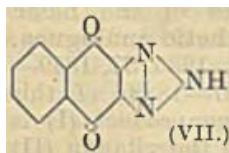
Naphthopyrazoles (benzindazoles). V. VESELY, A. MEDVEDEVA, and E. MULLER (Chem. Listy, 1935, 29, 259—263).—2:1-C₁₀H₆Me·NO₂ in C₂H₅Cl₄ and Cl₂ in presence of FeCl₃ at 40—50° yield *8-chloro-1-nitro-2-methylnaphthalene*, m.p. 114°, reduced by Fe in AcOH to *8-chloro-1-amino-2-methylnaphthalene*, m.p. 89° [*N-Ac derivative* (I), m.p. 214—215°], which, when diazotised and treated with NaOH, affords *8'-chloronaphtho-1':2':3:4-pyrazole*, m.p. 159° (*1-Ac derivative*, m.p. 196°), also obtained by treating (I) with HNO₂ in AcOH, and boiling a C₆H₆ solution of the *N*-NO-derivative so obtained. *4'-Nitro-*, m.p. 304—305° (*1-Ac derivative*, m.p. 196—197°), and *5'-bromo-naphtho-1':2':3:4-pyrazole*, m.p. 249—250° (*1-Ac derivative*, m.p. 168°), were prepared analogously. *1-Nitrosoacetamido-2-methylnaphthalene*, m.p. 82° (decomp.), affords *naphtho-1':2':3:4-pyrazole*, m.p. 158° (*picrate*, m.p. 193°; *1-Ac derivative*, m.p. 108—109°), when boiled in C₆H₆ for 4 hr., whilst *2-nitrosoacetamido-1-methylnaphthalene*, m.p. 91°, yields *naphtho-1':2':4:3-pyrazole*, m.p. 231° (*picrate*, m.p. 217—218°; *1-Ac derivative*, m.p. 116.5°), when similarly treated. R. T.

Comparison of heterocyclic ring systems with benzene. V. Benzotriazole (azimidobenzene) series. VI. Quinones of the quinoline and isoquinoline series. VII. Isologues of anthraquinone containing one and two triazole rings. L. F. FIESER and E. L. MARTIN (J. Amer. Chem. Soc., 1935, 57, 1835—1839, 1840—1844, 1844—1849; cf. this vol., 1377).—V. *E₀*, 0.672 volt, for K benzotriazole-4:5-quinone-7-sulphonate indicates that the aromaticity of the triazole ring is intermediate between that of thiophen and C₆H₆. Benzotriazole-quinones are difficult to prepare. *p*-NHAc·C₆H₄·OAc and HNO₃ (*d* 1.5) at 0—5° give *3-nitro-4-acetamidophenyl acetate*, m.p. 144—145°, hydrogenated (PtO₂) in hot EtOH to a little *2:2'-diacetamido-5:5'-acetoxyhydrazobenzene* (corresponding azo-compound, decomp. 280—285°) and 75% of *2-acetamido-5-acetoxyaniline* (I), m.p. 178—179°, which yields *3:4-diacetamidophenol*, m.p. 214—215° (lit. 205—207°), and its acetate, m.p. 187—188° (lit. 184—185°). (I) and HNO₂ give *5-acetoxy-1-acetylbenzotriazole*, m.p. 125—126°, hydrolysed by HCl to *5-hydroxybenzotriazole*, m.p. 234—235° (decomp.) [lit. 228° (decomp.)];

53% over-all yield from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$; hydrochloride, decomp. about 225° ; 4-p-, m.p. $224\text{--}225^\circ$, and 4-o-toluenazo-, m.p. $243\text{--}244^\circ$ (decomp.), NO_2 -, m.p. $262\text{--}263^\circ$ (lit. 236°), and NO - (II) -derivatives]. 4-Amino-5-hydroxybenztriazole, m.p. $216\text{--}217^\circ$ (decomp.), best (83%) obtained from (II) and aq. $\text{Na}_2\text{S}_2\text{O}_4$ (dihydrochloride, decomp. 225°), in dil. solution gives a quinone, which, however, cannot be isolated. (II) and NaHSO_3 , followed by H_2SO_4 at 40° , gives 4-amino-5-hydroxybenztriazole-7-sulphonic acid, cryst., which with $\text{Br}\cdot\text{H}_2\text{O}$ readily gives a quinone, which could not be isolated; the resultant solution, however, with SO_2 yields *K* 4:5-dihydroxybenztriazole-7-sulphonate, cryst. $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, with $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ in C_6H_6 yields $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, m.p. $92\text{--}93^\circ$, hydrogenated (PtO_2) in hot EtOH to $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ (III), m.p. $132\text{--}133^\circ$, a little 2:2'-diacetamidazo benzene, m.p. $270\text{--}271^\circ$, and 2-methylbenzimidazole. (III) leads to benztriazole, m.p. $98\text{--}99^\circ$ ($>90\%$ yield in each step; *Ac* derivative, m.p. $50\text{--}51^\circ$). Electrolytic reduction in conc. H_2SO_4 of 4-nitrobenztriazole and its 1-Me derivative, m.p. $181\text{--}182^\circ$ (lit. 173°), gives 4-amino-7-hydroxybenztriazole, decomp. about $225\text{--}230^\circ$, and -1-methyltriazole (sulphate; *Bz*₂ derivative, m.p. $262\text{--}263^\circ$), which do not give quinones, but similar reduction of 7-nitro-1-methylbenztriazole was unsuccessful.

VI. The aromaticity of the quinoline and isoquinoline rings, as indicated by the E_0 of quinones, is about equal, but $<$ that of triazole or thiophen rings. The general validity of connecting E_0 and aromaticity of fused rings is discussed. Caution is necessary in interpreting the results. 5(?8)-Hydroxyisoquinoline (IV) (from the $\alpha\text{-SO}_3\text{H}$) gives a PhN_2 -compound, reduced by SnCl_2 to 8(?5)-amino-5(?8)-hydroxyisoquinoline dihydrochloride (V), cryst. Electrolytic reduction in H_2SO_4 of 5(?8)-nitroisoquinoline, m.p. $104\text{--}108^\circ$, gives 5(?8)-amino-8(?5)-hydroxyisoquinoline (VI) (sulphate; dihydrochloride; *Bz*₂ derivative, m.p. $223\text{--}224^\circ$), which with FeCl_3 gives 5:8-dihydroxyisoquinoline hydrochloride, darkens at about 260° , also obtained similarly from (V) and from (IV) by Fe-reduction of the NO -derivative. The Ac_2 derivative, m.p. $208\text{--}209^\circ$, of (VI) is partly hydrolysed by cold 0.4% NaOH and then couples affording 5(?8)-acetamido-8(?5)-hydroxy-7(?6)-p-sulphobenzeneazoisquinoline, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to 7(?6)-amino-5(?8)-acetamido-8(?5)-hydroxyisoquinoline dihydrochloride, which with FeCl_3 affords 5(?8)-acetamidoisoquinoline-7:8(?5:6)-quinone hydrochloride.

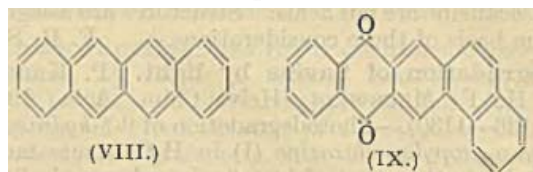
VII. lin-Naphthatriazole-8:9-quinone (VII) is strongly acidic; its E_0 differs from that of its 1-Me derivative and (VII) may thus be as shown.



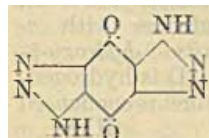
Naphthacene and "2:3-phthaloylphenanthrene" are probably (VIII) and (IX), respectively, on the theory that max. aromaticity must be achieved. Inability to give the

vat test is connected with low E_0 rather than with absence of a true quinone ring, as in (IX). 3-Chloro-2-acetamidonaphthaquinone and NH_3 in boiling PhNO_2 give 3-amino-2-acetamido-1:4-naphthaquinone, m.p. $233\text{--}234^\circ$, which does not give a triazole owing to its sparing solubility. Reduction by

$\text{Na}_2\text{S}_2\text{O}_4$ to the corresponding $(\text{OH})_2$ -compound [*Ac*₂ derivative, m.p. 255° (decomp.)] allows reaction to form



(VII), decomp. $240\text{--}245^\circ$ (*N*-Me derivative, m.p. $248\text{--}250^\circ$). The Ac_2 derivative, m.p. $253\text{--}254^\circ$, of 3:6-dichloro-2:5-diaminoquinone (improved prep.; 75% yield) with $\text{NH}_3\text{--EtOH}$ gives 3:6-diamino-2:5-diacetamidobenzoquinone, converted (only in hot AcOH) into



colourless bistriazolo-p-benzoquinone (X) (*Na* salt, $+\text{H}_2\text{O}$). The prep. of *K* 2:3-dihydroxynaphthalene-6-sulphonate, 2:3- $\text{C}_{10}\text{H}_6(\text{OH})_2$, and $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ is improved. Hydrogenation (PtO_2) of 2:5- $\text{C}_6\text{H}_3(\text{NHAc})_2\cdot\text{NO}_2$ in hot EtOH affords 2:5-diacetamidylaniline, m.p. $236\text{--}237^\circ$ (lit. $231\text{--}232^\circ$), converted into 5-aminobenztriazole and thence by way of the PhN_2 -compound into 4:5-diaminobenztriazole, the *Ac* derivative of which with HNO_3 gives 1:2:3:4-bistriazolobenzene, which did not yield a quinone.

R. S. C.

Condensation of 4-aminotetrazole with carbonyl compounds. E. BURES and F. BARSI (Časopis českoslov. Lck., 1934, 14, 345–352; Chem. Zentr., 1935, i, 1867).—4-Aminotetrazole (I) and MeCHO yield 4-amino-1-methylmethenyltetrazole, $\text{C}(\text{NH}_2)\cdot\text{N}=\text{N}>\text{N:CMe}$,

m.p. $164\text{--}165^\circ$. (I), with PhCHO and with cinnamaldehyde, similarly affords 4-amino-1-benzenyl-, m.p. 120° (decomp.) and -1-styrylcarbylamino-, m.p. $162\text{--}163^\circ$, -tetrazole, respectively; the last-named, with Br in CHCl_3 , yields 4-amino-1-dibromostyrylcarbylamino-tetrazole, m.p. $174\text{--}175^\circ$. (I) condenses with COMe_2 to yield 4-dimethylmethenyltetrazole, m.p. $187\text{--}188^\circ$. Aminoguanidine carbonate has m.p. 173° . H. N. R.

Rearrangement of allyl ethers in the purine series, with some remarks on the hydrogenation of allyl ethers. E. BERGMANN and H. HEIMHOLD (J.C.S., 1935, 1365–1367).—2:6-Dichloro-7-methylpurine (I) and Na allyloxide yield 2:6-diallyloxy-7-methylpurine, m.p. $111\text{--}112^\circ$, which on hydrogenation gives heteroxanthine, and on heating is isomerised to 1:3-diallyl-7-methylxanthine, m.p. $277\text{--}278^\circ$. (I) and Na in Δ^8 -hexen-8-ol, after heating, form 1:3-di-(α -methyl- Δ^8 -pentenyl)-7-methylxanthine, b.p. $215\text{--}225^\circ/12\text{ mm.}$, from which the products of ozonolysis are EtCO_2H and EtCHO . Ph allyl ether gives on hydrogenation PhOPr but 2:6-dipropoxy-7-methylpurine, m.p. 92° , is not affected by $\text{Pd}\text{--H}_2$. The isomerisation is due to migration of the allyl group from O to N.

F. R. S.

Constitution of the purine nucleosides. III. Potentiometric determination of the dissociation constants of methylated xanthines. A. G. OGSTON (J.C.S., 1935, 1376–1379).—Measurements of dissociation consts. indicate that 3-, 7-, 9-methyl-, 1:3-, 1:7-, and 1:9-dimethyl-xanthines, and xanthosine

are "zwitterions," xanthine, 1-methyl- and 3:7-dimethylxanthines are normal acids, whilst caffeine and isocaffeine are not acids. Structures are assigned on the basis of these considerations. F. R. S.

Degradation of flavins by light. P. KARRER and H. F. MEERWEIN (Helv. Chim. Acta, 1935, **18**, 1126—1130).—Photodegradation of 9- β -hydroxy- β -methyl-n-propylisoalloxazine (I) in H₂O occurs much more slowly than that of lactoflavin, whereas in 75% MeOH the difference in the rates is less marked. Preliminary dehydrogenation of β -OH is not therefore essential to degradation, which can be initiated in some other unknown manner. NH₂·CH₂·CO₂Et is converted by MgMeI into aminotrimethylcarbinol, b.p. 53—57°/15 mm., which condenses with o-C₆H₄Cl·NO₂ in boiling C₅H₅N to o-nitro- β -hydroxy- β -methyl-n-propylaniline (I), m.p. 83°. (I) is hydrogenated (Pd-C in abs. EtOH) and the product is condensed with alloxan to (I), decomp. 285°. H. W.

Modified flavin synthesis. P. KARRER and H. F. MEERWEIN (Helv. Chim. Acta, 1935, **18**, 1130—1134).—3:4-C₆H₃Me₂NH₂ and l-arabinose in boiling MeOH-H₂O give 3:4-dimethylphenyl-l-arabamine, C₆H₃Me₂NH·CH₂·[CH·OH]₃·CH₂·OH, m.p. 123°, which couples with p-NO₂·C₆H₄·N₂Cl in aq. acid solution to 6(?)-p-nitrobenzeneazo-3:4-dimethylphenyl-l-arabamine, reduced (Zn dust and AcOH or H₂-Ni-MeOH) to 9-l-1'-arabityl-6:7-dimethylisoalloxazine, m.p. 299°. Similarly, 3:4-dimethylphenyl-d-ribamine, m.p. 143°, is converted into 9-d-1'-ribityl-6:7-dimethylisoalloxazine, m.p. 280°. H. W.

Methylalloxazines. P. KARRER and C. MUSANTE (Helv. Chim. Acta, 1935, **18**, 1134—1140).—The fluorescence colours of solutions of alloxazines in MeOH induced by ultra-violet light depend greatly on substituents in the mol. Introduction of Me progressively displaces the fluorescence from violet through blue, greenish-blue, and yellow to yellow-violet, whereby Me *ortho* to the azine ring has greater displacing influence than at 6 or 7. Ph behaves similarly. 6-Nitro-2:4:5-trimethylaniline is reduced (Pt in EtOH) to the corresponding diamine, which condenses with alloxan (I) to 5:7:8(? 5:6:8)-trimethylalloxazine, decomp. >290°. 2-Nitro-3:4:5-trimethylaniline similarly affords 6:7:8(? 5:6:7)-trimethylalloxazine, whilst 5:6-dinitro-1:2:3:4-tetramethylbenzene, m.p. 171°, is transformed into 5:6:7:8-tetramethylalloxazine, 2-Chloro-3-nitro-toluene and NH₂·CH₂·CH₂·OH in boiling C₅H₅N afford non-cryst. 3-nitro-2- β -hydroxyethylaminotoluene, reduced and then condensed with (I) to 8-methyl-9- β -hydroxyethylisoalloxazine, m.p. 294°, degraded by sunlight to 8-methylalloxazine, 2:3-Diaminotoluene and (I) give 8(?5)-methylalloxazine. H. W.

Synthetic flavins. P. KARRER, H. SALOMON, K. SCHOPP, and F. BENZ (Helv. Chim. Acta, 1935, **18**, 1143—1146).—Condensation of d-deoxyribose with 4-amino-5-carbethoxyamino-o-xylene in MeOH at 100° in presence of H₂/25 atm. and Ni affords 2-carbethoxyamino-4:5-dimethylphenyl-d-deoxyribamine, CO₂Et·NH·C₆H₃Me₂·NH·[CH₂]₂·[CH·OH]₂·CH₂·OH, m.p. 115°, [α]_D +21°+2° in H₂O, which is transformed by alloxan into 6:7-dimethyl-9-d-1'-deoxyribityliso-

alloxazine, m.p. 283°, [α]_D²⁰ -78°±8° in 0.05N-NaOH. Similarly, d-ribose and o-NH₂·C₆H₄·NH·CO₂Et yield 2-carbethoxyaminophenyl-d-ribamine, m.p. 158°, [α]_D²⁰ ±0° in H₂O, hydrolysed and condensed to 9-d-1'-ribitylisoalloxazine, m.p. 283° (tetra-acetate, m.p. 237°). 2-Carbethoxyamino-5-methylphenyl-d-ribamine, m.p. 150°, [α]_D²⁰ -14.2°±2°, affords 7-methyl-9-d-1'-ribitylisoalloxazine, m.p. 285—286° (tetra-acetate, m.p. 215°).

H. W.

Optical activity of lactoflavin.—See this vol., 1521.

Formation of porphyrins from pyrrole and aldehydes. P. ROTHMUND (J. Amer. Chem. Soc., 1935, **57**, 2010—2011).—Pyrrole and dry CH₂O or MeCHO in MeOH-Et₂O with or without catalysts give cryst. porphyrins. R. S. C.

Optical absorption of porphyrins.—See this vol., 1444.

Photochemical reaction of chlorophyll. E. BAUR (Helv. Chim. Acta, 1935, **18**, 1157—1160).—A film of chlorophyll (I) in collodion when exposed to sunlight under air-free H₂O through which CO₂ is passed rapidly becomes yellow without apparent production of CH₂O. Similar films containing also methylene-blue (II) when exposed under H₂O through which O₂-free N₂ and CO₂, respectively, are passing slowly exhibit incomplete bleaching of (I) with pronounced formation of CH₂O, which is therefore produced from (I) and not from CO₂; the change cannot be accomplished from (I) without aid. (II) does not function as photosensitiser, but as redox agent, since it can be qualitatively replaced by Fe²⁺, Fe³⁺, or O. The course of the change is discussed. H. W.

Magnetic behaviour of porphyrin and porphyrindin.—See this vol., 1453.

Thiocarbonylsalicylamide (4-keto-2-thioketo-3:4-dihydro-1:3-benzoxazine). I. T. UGAI and M. HAYASHI (J. Pharm. Soc. Japan, 1935, **55**, 8—12).—Salicylic acid and allylthiocarbimide yield thiocarbonylsalicylamide (I), C₈H₅O₂NS, m.p. 253°. Methylation of (I) with CH₃N₃ affords a substance, C₉H₇O₂NS, m.p. 163°, whilst with alkaline H₂O₂ (I) yields a substance, C₈H₅ON, m.p. 227°. Methylation of carbonylsalicylamide yields a substance, C₈H₇O₂N, m.p. 149°. CH. ABS. (r)

Crystalline vitamin-B₁. X. Sulphite cleavage. III. Basic product. E. R. BUCHMAN, R. R. WILLIAMS, and J. C. KERESZTESY. XI. Presence of quaternary nitrogen. R. R. WILLIAMS and A. E. RUEHLE. XII. Sulphur-containing moiety. H. T. CLARKE and S. GURIN. XIII. Ultra-violet absorption of some derivatives of the basic cleavage product and their synthetic analogues. A. E. RUEHLE (J. Amer. Chem. Soc., 1935, **57**, 1849—1851, 1856—1860, 1876—1881, 1887—1888; cf. this vol., 1385).—X. The basic cleavage product (I) is probably C₄H₄NS·CH₂·CH₂·OH and the vitamin (II) a quaternary salt thereof. (I) [picrolonate, m.p. 184° (decomp.); platinichloride, m.p. 181° (decomp.); picrate, m.p. 162—163°; aurichloride, an oil; p-nitrobenzoate, m.p. 131°; methiodide (IV), cryst., very sensitive to alkalis (gives S'')] does not give the pine-

splinter reaction nor a colour with $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$, is stable to hot 20% NaOH, and does not give CHI_3 with NaOH-I. With HCl at 145° it affords the substance (III), $\text{C}_6\text{H}_5\text{NSCl}$ (hydrochloride), closely resembling it in ultra-violet absorption. With HNO_3 at 40° it gives Windaus' acid (V), $\text{C}_5\text{H}_5\text{O}_2\text{NS}$, decomp. $200\text{--}250^\circ$ (Me ester, m.p. 74°).

XI. Electrometric titration shows that (II) and (IV) have two basic centres, one very weak, the other not quite as strong as a true quaternary salt; two equivs. of alkali are required for complete liberation of these bases; after liberation of the strong basic centre slow rearrangement occurs to a much weaker base. (I) behaves as an ordinary weak base. 4-Methylthiazole ethiodide (VI) exactly resembles (II) and (IV), but 2:4-dimethylthiazole ethiodide behaves as a true quaternary salt. Previous speculation as to the nature of (II) is thus confirmed.

XII. (I), (III), and (V) are synthesised. The neutralisation of an extra mol. of alkali by (II) and (IV) is due to reversible opening of the thiazole ring; (VI) is similarly cleaved by alkali and its alkaline solution with air or I gives $\beta\text{-N-formethylaminoallyl disulphide}$, $[\text{HCO}\cdot\text{NET}\cdot\text{CMe}\cdot\text{CHS}]_2$, m.p. $101\text{--}102^\circ$. The sulphite cleavage of (II) is a peculiarity due to the pyrimidine portion, since synthetic thiazolium salts are not thus cleaved. (I) is readily oxidised by $\text{Br}\cdot\text{H}_2\text{O}$ and reacts relatively slowly with $\text{Pb}(\text{ONa})_2$; with (II) the relative rates of reaction are reversed. Synthetic thiazoles and thiazolium salts show similar behaviour. The hydrochloride of (II) gives a resinous additive product with KI , whence it is recovered by $\text{H}_2\text{O}\text{--}\text{Et}_2\text{O}$ with unimpaired activity. 4-Methylthiazole (VII) [modified prep. from $\text{HCS}\cdot\text{NH}_2$ and $\text{CH}_2\text{Cl}\cdot\text{COMe}$ (VIII)] [platnichloride, $\text{B}_3\text{H}_2\text{PtCl}_4$, m.p. 198°] gives (VI), m.p. $144\text{--}5^\circ$. 2:4-Dimethylthiazole (IX) (modified prep.) gives the ethiodide, m.p. 212° (decomp.). $\text{CHClAc}\cdot\text{CO}_2\text{Et}$ and $\text{HCS}\cdot\text{NH}_2$ in Et_2O at $0\text{--}5^\circ$ give *Et* 4-methylthiazole-5-carboxylate, m.p. 28° , b.p. $140^\circ/12\text{ mm.}$, which with $\text{NaOH}\cdot\text{EtOH}$ yields the corresponding acid, sublimes at 255° (Me ester, m.p. 75°), identical with (V). $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ and $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{Br}$ in EtOH give *Et* α -(β -ethoxyethyl)acetoacetate, b.p. $85\text{--}90^\circ/10\text{ mm.}$, which with SOCl_2 affords the α -Cl-ester, b.p. $115\text{--}118^\circ/12\text{ mm.}$ This with hot 15% H_2SO_4 and AcOH (1:1) gives *Me* α -chloro- γ -ethoxypropyl ketone, b.p. $72\text{--}73^\circ/12\text{ mm.}$, converted by $\text{HCS}\cdot\text{NH}_2$ into 4-methyl-5- β -ethoxyethylthiazole, b.p. 235° (decomp.) [platnichlorides, $\text{B}_3\text{H}_2\text{PtCl}_4$, m.p. $154\text{--}155^\circ$ (decomp.), and $\text{B}_3\text{H}_2\text{PtCl}_4$, m.p. $144\text{--}145^\circ$; picrate, m.p. 112°]. Conc HCl at 150° thence affords 4-methyl-5- β -chloroethylthiazole hydrochloride, m.p. $127\text{--}128^\circ$ (corresponding picrate, m.p. 139°), identical with (III), hydrolysed by H_2O at 150° to 4-methyl-5- β -hydroxyethylthiazole (hydrochloride; picrate, m.p. $162\text{--}163^\circ$), identical with (I). $\text{NPh}\cdot\text{CSMe}$ and (VIII) in EtOH give 3-phenyl-2:4-dimethylthiazolium platnichloride, m.p. 245° (decomp. from 240°), iodide, m.p. 210° , and chloride, an oil. (VIII) and $\text{HCS}\cdot\text{NPh}$ at 50° give 3-phenyl-4-methylthiazolium iodide, m.p. 241° .

XIII. The absorption spectra of (I), (VII), (IX), and 2-hydroxy-4-methylthiazole are very similar, as are those of (IV) and (VI). The identities of synthetic

and natural (I), (III), and (V) are confirmed by absorption spectra. (V) closely resembles (I), showing the small effect of replacement of OH by Cl. R. S. C.

Thiazole derivatives from ω -chloroacetylpyrocatechol. Z. HORII (J. Pharm. Soc. Japan, 1935, 55, 21—32).— ω -Chloroacetylpyrocatechol (I) and $\text{CS}(\text{NH}_2)_2$ (II) give 2-amino-4-(3':4'-dihydroxyphenyl)-thiazole hydrochloride, m.p. $235\text{--}236^\circ$. 2-Acetamido-, m.p. 268° , and 2-allylamino-, m.p. $208\text{--}209^\circ$, 4-(3':4'-dihydroxyphenyl)thiazole are similarly prepared from appropriately substituted (II). (I) and diphenylthiocarbamide afford 2-anilo-3-phenyl-4-(3':4'-dihydroxyphenyl)-2:3-thiazoline, m.p. $252\text{--}253^\circ$. The following are obtained from the appropriate disubstituted (II) and (I): 2-o-tolylimino-3-o-tolyl-, m.p. 130° ; 2-m-tolylimino-3-m-tolyl-, m.p. $226\text{--}227^\circ$; 2-p-tolylimino-3-p-tolyl-, m.p. 280° ; and 2-p-hydroxyanilo-3-p-hydroxyphenyl- (hydrochloride, m.p. $198\text{--}200^\circ$), 4-(3':4'-dihydroxyphenyl)-2:3-thiazoline. CH. ABS. (r)

Derivatives of o-thioldiphenylamine. W. J. EVANS and S. SMILES (J.C.S., 1935, 1263—1265).—2-o-Nitrophenyl-1-methylbenzthiazolium iodide (I) (this vol., 485) when boiled with $\text{CH}(\text{OEt})_3$, Ac_2O , and $\text{C}_5\text{H}_5\text{N}$ yields 2-2'-di-o-nitrophenylthiocarbonyne iodide, m.p. 269° (decomp.), whereby its structure as the salt of a pseudo-base is confirmed. 2-Nitro-2'-benzamidodiphenyl sulphide when boiled with COMe , and $\text{NaOH}\cdot\text{EtOH}$ is rearranged to a thiol, which with HI affords 1-phenyl-2-o-nitrophenylthiazolinium iodide, m.p. 195° . The thiol is regenerated by $\text{NaOH}\cdot\text{H}_2\text{O}$ and is methylated in alkaline solution (cf. *ibid.*, 615). Similarly 2-nitro-2'-cinnamidodiphenyl sulphide, m.p. 132° , is rearranged to a thiol, which on methylation yields 2-cinnamo-o-nitrophenylamidodiphenyl Me sulphide, m.p. $170\text{--}171^\circ$ (decomp. by warm HI into MeSH), and with HI yields 2-o-nitrophenyl-1-styrylthiazolinium iodide, m.p. 225° (decomp.). Rearrangement of 4-chloro-2-nitro-2'-acetamidodiphenyl sulphide (II) yields a thiol, which is rapidly converted into bis-2-aceto-p-chloro-o-nitrophenylamidodiphenyl disulphide, m.p. $187\text{--}188^\circ$, and when boiled with COMe_2 , EtOH , and NaOH yields 3-chlorothioldiphenylamine, m.p. 199° (also formed during the original rearrangement). 2:4-Dinitro-2'-acetamidodiphenyl sulphide (III) when boiled with COMe_2 and $\text{EtOH}\cdot\text{NaOH}$ yields 3-nitro-N-acetylthiodiphenylamine (IV), m.p. 146° , hydrolysed by $\text{EtOH}\cdot\text{NaOH}$ to 3-nitrothiodiphenylamine, which is also obtained when 4-nitrodiphenylamine-2-sulphinic acid (V) (corresponding methylsulphone, m.p. $170\text{--}171^\circ$) is reduced by HI in warm H_2O containing H_2SO_3 . This proves that (IV) is formed from the corresponding thiol and not from (III) before rearrangement. No stable thiazolinium salts analogous to (I) were obtained from the thiols derived from (II) and (III). The following substances are obtained when (V) is warmed with the appropriate aldehyde or ketone: 5-nitro-2-phenylbenzthiazoline S-dioxide, m.p. 147° , and its 1-methyl (VI), m.p. 150° , 1:1-dimethyl, m.p. 200° , and 1-p-hydroxyphenyl, m.p. 220° (decomp.), derivatives. Attempts to convert (VI) by oxidation in acid media into salts analogous to (I) failed. H. G. M.

Dithiazine rings. H. G. UNDERWOOD and F. B. DAINS (J. Amer. Chem. Soc., 1935, 57, 1769—1771).—Methylene halides and thiocarbamides give occasionally methylene ethers, $S\langle\begin{smallmatrix} \text{H}_2 \\ \text{C}(\text{NR}) \end{smallmatrix}\rangle\text{NPh}$, but usually

1:3:5-dithiazans, $S\langle\begin{smallmatrix} \text{CHR}'-\text{S} \\ \text{C}(\text{NR})-\text{NH} \end{smallmatrix}\rangle$, the stability of which is greatly increased if R is aromatic. CH_2I_2 and $\text{CS}(\text{NH}_2)_2$ (I) in hot EtOH give 4:6-di-imino-1:3:5-dithiazan, m.p. 202—209°, unstable (hydriodide, cryst., stable), hitherto (J.C.S., 1916, 109, 1255) assumed to be $\text{CH}_2[\text{S}\cdot\text{C}(\text{NH})\cdot\text{NH}_2]_2$. (I) and CHPhCl_2 (II) at 150° give 4:6-di-imino-2-phenyl-1:3:5-dithiazan, unstable to 0.1N-alkali (hydrochloride, m.p. 236°). $\text{NH}_2\cdot\text{CS}\cdot\text{NHPh}$ (III) and CH_2Br_2 at 120—130° give 4:6-dianilo-1:3:5-dithiazan, m.p. 107° (hydrobromide, m.p. 268°; with 15% KOH gives H_2S , PhNCS , and NH_2Ph ; 5- or 6-Bz derivative, m.p. 120—121°), the hydriodide, m.p. 263°, being similarly obtained with CH_2I_2 ; the structure of this base is proved by its prep. also from CH_2Br_2 and s-diphenyldithiobiuret (IV). $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ (V) at 130° gives 4:6-di-p-, m.p. 175° (hydrobromide, m.p. 283°), and -o-tolylimino-1:3:5-dithiazan, m.p. 174° (hydrobromide, m.p. 236°). (III) with CHMeBr_2 at 160° gives 4:6-dianilo-2-methyl-1:3:5-dithiazan, m.p. 181° (hydrobromide, m.p. 248°), and with (II) at 110—150° gives 4:6-dianilo-2-phenyl-1:3:5-dithiazan, m.p. 145° (hydrochloride, m.p. 232°), also obtained from (IV) at 150°. (V) yields similarly 4:6-di-p-tolylimino-2-phenyl-1:3:5-dithiazan hydrochloride, m.p. 222°. $\text{CS}(\text{NHPh})_2$ and CH_2I_2 in EtOH give an impure base and $\text{NHPh}\cdot\text{CS}\cdot\text{OEt}$ (cf. lit.). $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot p)_2$ and CH_2I_2 in hot COMe_2 give $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NCS}$, and the ether, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}$, m.p. 151°. $\text{NPh}\cdot\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ (VI) gives similarly the 4-thiolmethylene ether, $\text{C}_{16}\text{H}_{15}\text{N}_2\text{S}_2$, m.p. 125° (hydriodide, m.p. 275°), and PhNCS , but (II) gives triphenyl- and tritolyl-guanidine. (IV) with CH_2I_2 gives a dithiazan, but with CH_2Br_2 and $\text{NH}_3\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ it gives 2-anilotetrahydrothiazole-3-thioformanil, m.p. 165°, hydrolysed by KOH-EtOH to 2-anilinothiazolidine. (VI) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ in EtOH give 3-phenyl-4-thiazolidone-2-thiolmethyl- ψ -thiocarbamide, m.p. 127°, the :CHPh derivative, m.p. 157°, of which is hydrolysed to 5-benzylidene-3-phenylthiazolidone. Phenylmethylthiobiuret and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ or $\text{CH}_2\text{Cl}\cdot\text{COCl}\cdot\text{C}_6\text{H}_5\text{N}$ in COMe_2 afford phenylmethylthiazolidone-2-thiocarbamide, m.p. 222° (:CHPh derivative, m.p. 274°, hydrolysed as above).

R. S. C.

Thiohydrazides as reagents for aldehydes. H. WUYTS and H. WACHSMUTH (J. Pharm. Chim., 1935, [vin], 22, 289—305; cf. A., 1934, 537).—The appropriate aldehyde and thioacylhydrazine in EtOH with a little HCl give the following substituted 2:3-dihydro-1:3:4-thiadiazoles (thiadiazolines): 3:5-diphenyl-2-styryl-, m.p. 127.5—128°; 3:5-diphenyl-2-p-anisyl-, m.p. 130.5—131°; 3:5-diphenyl-2-piperonyl-, m.p. 154—154.5°; 3:5-diphenyl-2-(1-furyl)-, m.p. 111—111.5°; 5-phenyl-3-p-bromophenyl-, m.p. 112.5—113.5°; 5-phenyl-3-p-bromophenyl-2-methyl-, m.p. 93.5—94°; 2:5-diphenyl-3-p-bromophenyl-, m.p. 142.5—143.5°; 5-phenyl-3-p-bromophenyl-2-styryl-,

m.p. 114—114.5°; 5-phenyl-3-p-bromophenyl-2-p-anisyl-, m.p. 132.5—133°; 5-phenyl-3-p-bromophenyl-2-piperonyl-, m.p. 138—139°; 3-phenyl-5- α -naphthyl-, m.p. 71—71.5°; 3-phenyl-2-styryl-5- α -naphthyl-, m.p. 52—53.5°; 3:5-diphenyl-2-(2-hydroxyphenyl)-, m.p. 51—52.5°; 3:5-diphenyl-2-(4-hydroxy-3-methoxyphenyl)-, m.p. 132.5—133°; 5-phenyl-3-p-bromophenyl-2-(2-hydroxyphenyl)-, m.p. 159.5—161°; 5-phenyl-3-p-bromophenyl-2-(4-hydroxy-3-methoxyphenyl)-, m.p. 152.5—153°; 3-phenyl-2-(2-hydroxyphenyl)-5- α -naphthyl-, m.p. 72—73.5°; 3-phenyl-2-(4-hydroxy-3-methoxyphenyl)-5- α -naphthyl-, m.p. 156.5—157°.

F. R. G.

Fluorescent dehydrogenation product from vitamin-B₁.—See this vol., 1286.

Ergometrine. H. W. DUDLEY (Proc. Roy. Soc., 1935, B, 118, 478—484, and J. Amer. Chem. Soc., 1935, 57, 2009—2010).—Ergometrine, $\text{C}_{19}\text{H}_{23}\text{O}_2\text{N}_3$, m.p. 160—161°, $[\alpha]_D^{25} +40.25^\circ$ in EtOH, is identical with “ergotocine” of Kharasch and Legault (this vol., 872, 995) and with “ergobasine” of Stoll and Burekhardt (*ibid.*, 995). The hydrochloride, m.p. 245—246° (decomp.), $[\alpha]_D +63^\circ$ in H_2O , and hydrobromide, m.p. 236—237° (decomp.), oxalate, m.p. 193° (decomp.), $[\alpha]_D +55.4^\circ$ in H_2O , and interconvertible yellow, hydrated, m.p. 148° (decomp.), and red pierates, anhyd., m.p. 188—189° (decomp.), are described.

H. G. R.

Spectrographic absorption of ergometrine in relation to the B.P. colour test. N. L. ALLPORT and S. K. CREWS (Quart. J. Pharm., 1935, 8, 447—452).—Ergometrine (I), m.p. 164°, giving a colour test with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (II) (B., 1932, 1135) equiv. to that produced by 1.78 times its wt. of ergotocine (III) base, has an extinction coeff., $E_{1\%}^{1\text{cm.}}$ 1.85 at 316 m μ . In aq. tartaric acid solution, both (I) and (III) have a max. absorption band at 316 m μ , whilst the colours due to (II) are spectroscopically identical.

F. O. H.

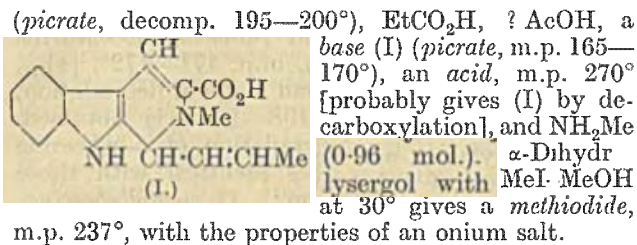
Ergostetrine. M. R. THOMPSON (J. Amer. Pharm. Assoc., 1935, 24, 748—753).—The prep. of the pure alkaloid, m.p. 160—162.5° (decomp.), $[\alpha]_D^{20} +50^\circ \pm 10^\circ$ in EtOH, colour reactions, and pharmacological properties are described. The identity of ergostetrine with ergometrine, ergotocine, and ergobasine is suggested.

H. G. R.

Optical rotation study of the new orally effective principle of ergot. E. C. KLEIDERER (J. Amer. Chem. Soc., 1935, 57, 2007—2008).—The $[\alpha]_D$ of ergotocine in H_2O remains const. ($+76.1^\circ$), but in MeOH changes gradually (from $+40.2^\circ$ to 61.8° in 95.5 hr.); that of its maleate changes both in H_2O ($+46.2^\circ$ to $+53.7^\circ$ in 48 hr.) and MeOH ($+37.9^\circ$ to $+24.6^\circ$ in 48 hr.). Only slight decrease in pharmacological activity accompanies this change in $[\alpha]$.

R. S. C.

Ergot alkaloids. VI. Lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1935, 111, 455—465; cf. this vol., 1137).—Formula (I) for lysergic acid is discussed. Dihydrolysergic acid and KOH in H_2 at 295—300° give 2-methyl-3-ethylindole (picrate, m.p. 148—150°), a base (? a methyl-ethyleneindole), b.p. 145—150°/0.2 mm., m.p. 68°



R. S. C.

Dehydrogenation of nicotine in toluene as a solvent. A. A. MORTON and D. HORVITZ (J. Amer. Chem. Soc., 1935, 57, 1860—1861).—Nicotine and S, best in PhMe , give H_2S (69%), thiodinicotyrine (18%), and nicotyrine (2.5%).

R. S. C.

Oxidation products of vasicine with hydrogen peroxide. T. P. GHOSE, S. KRISHNA, K. S. NARANG, and J. N. RAY (Current Sci., 1935, 4, 158—159).—Contrary to the view of Morris, Hanford, and Adams (this vol., 873) that the product, m.p. 168°, obtained by the authors (A., 1933, 77) from H_2O_2 and vasicine, is a mixture, it gives const. analytical vals., and has a homogeneous appearance under the microscope. It is now regarded as 4-hydroxy-2:3:2':3'-bis- α -hydroxytrimethylene-4:4'-bisdihydroquinazoly.

E. W. W.

Cotarnine series. IV. 5-Bromonarcotine, 5-bromocotarnine, 5-bromohydrocotarnine, and 5-bromonarceine and their derivatives. B. B. DEY and T. K. SRINIVASAN (J. Indian Chem. Soc., 1935, 12, 526—536).—Narcotine when treated with HBr , H_2O , Br, and subsequently with H_2S yields 5-bromonarcotine (I), m.p. 176°, $[\alpha]_D^{20}$ -95° in CHCl_3 (hydrochloride + H_2O , m.p. 120°; hydrobromide + H_2O , m.p. 168°; platinichloride; picrate, m.p. 197°, and methiodide, m.p. 220°), which with HBr -Br- H_2O yields a perbromide hydrobromide, m.p. 220° (decomp.), from which (I) is regenerated by H_2S . (I) is oxidised by HNO_3 - H_2O to 5-bromocotarnine (II), m.p. 135° (hydrochloride, m.p. 170° (decomp.); picrate, m.p. 171°; platinichloride; Bz derivative, m.p. 103°; oxime, m.p. 138°; oxime hydrochloride, m.p. 169°, and perbromide hydrobromide, m.p. 200° (decomp.)) (cf. Wright, J.C.S., 1877, 32, 525; Small, "Chemistry of the Opium Alkaloids," 1932, pp. 68, 70, and 98), also obtained, but less conveniently, by bromination of cotarnine. (II) with PhNCO and C_6H_6 yields phenyl-5-bromocotarnomethylcarbamide, m.p. 160° (oxime, m.p. 168—169°), and when heated with MeNO_2 at the b.p. yields anhydrobromocotarninonitromethane, m.p. 148° (hydrochloride, m.p. 166°). (II) when heated with excess of Ac_2O at the b.p. yields N-acetyl-5-bromocotarnidineacetic acid, m.p. 211° (Ag salt). (II) and MeI when heated under pressure yield 5-bromocotarnomethine methiodide, m.p. 179°, which when steam-distilled with NaOH yields 5-bromocotarnone, m.p. 104°, oxidised by KMnO_4 , K_2CO_3 , COMe_2 , and H_2O to 5-bromocotarnolactone, m.p. 172°, further oxidised to 5-bromocotarnic acid [2-methoxy-3:4-methylenedioxy-5-bromophthalic acid], m.p. 185° (anhydride, m.p. 225°). This establishes the constitution of (II). (II) is reduced by Na-Hg-N-HCl to 5-bromohydrocotarnine, m.p. 80° (hydrobromide, m.p. 242°), the perbromide hydrobromide, m.p. 166° (decomp.), of

which does not yield any (II) (contrast Wright, loc. cit.). (I) and $\text{Me p-toluenesulphonate}$ when heated at 100° (45 min.), then at 110—120° (30 min.), and subsequently treated with NaOH and steam yields 5-bromonarceine, m.p. 193° [hydrochloride, m.p. 241°; hydrobromide, m.p. 225°; picrate, m.p. 153°; platinichloride, m.p. 198° (decomp.); Me ester, m.p. 114°]. H. G. M.

Cotarnine series. V. Condensation of cotarnine with aromatic nitroaldehydes. B. B. DEY and (Miss) P. L. KANTAM (J. Indian Chem. Soc., 1935, 12, 604—607).—Cotarnine and $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ in EtOH give 1- o -nitrobenzoyl-5- α -hydroxy- o -nitrobenzylhydrocotarnine (I), m.p. 153° [hydrochloride, m.p. 172° (decomp.); hydrobromide + H_2O , m.p. 177° (decomp.); nitrate, m.p. 181° (decomp.); sulphate, m.p. 191—192° (decomp.); picrate, m.p. 175—176°], reduced by SnCl_2 to the corresponding $(\text{NH}_2)_2$ -base m.p. 122° (Ac_2 derivative, m.p. 126°). 1-m-Nitrobenzoyl- o - α -hydroxy-m-nitrobenzyl-, m.p. 146° [hydrochloride, m.p. 188° (decomp.); corresponding $(\text{NH}_2)_2$ -compound, m.p. 113°], 1-2'-nitro-4':5'-dimethoxybenzoyl-5- α -hydroxy-2'-nitro-4':5'-dimethoxybenzyl-, m.p. 168° [hydrochloride, m.p. 193° (decomp.)], and 1-6'-nitropiperonyl-5- α -hydroxy-6'-nitro-3':4'-methylenedioxybenzyl-hydrocotarnine, m.p. 168° [hydrobromide, m.p. 180° (decomp.)], are similarly obtained. 5-Bromocotarnine, however, condenses with only 1 mol. of aldehyde to give o -bromo-1- o -nitrobenzoyl-, m.p. 120° after sintering [hydrobromide, m.p. 162° (decomp.)], and 6-nitropiperonyl-hydrocotarnine, m.p. 125° (hydrobromide, m.p. 172°), thus confirming Robinson's formulation (A., 1924, i, 666) of (I) etc. The "1-cotarnino- o -nitrophenyl ketone" of Ahluwalia *et al.* (A., 1933, 960) was (I).

R. S. C.

Condensation of cotarnine and o -nitrobenzaldehyde. K. N. KAUL and G. S. AHLUWALIA (J. Indian Chem. Soc., 1935, 12, 610).—The compound formulated as "1-cotarnino- o -nitrophenyl ketone" (A., 1933, 960) is 5- o -nitrobenzoyl-1- α -hydroxy- o -nitrobenzylhydrocotarnine.

R. S. C.

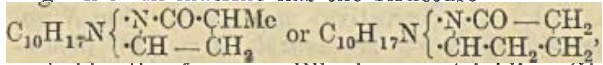
Corynantheine. RAYMOND-HAMET (J. Pharm. Chim., 1935, [viii], 22, 306—325; cf. this vol., 894).—Corynantheine hydrochloride hydrolysed with KOH in EtOH gives corynantheic acid, $\text{C}_{19}\text{H}_{22}\text{N}_2(\text{OMe})\text{-CO}_2\text{H}$, $[\alpha]_D^{20}$ $+7.53^\circ$ in $\text{C}_5\text{H}_5\text{N}$.

F. R. G.

Quinoidine. Occurrence of epiquinine and epiquinidine in cinchona bark. W. DIRSCHERL and H. THRON (Annalen, 1935, 521, 48—71).—A C_6H_6 extract of quinoidine (I), the svrupy residue of cinchona bark alkaloids after removal of the quinine (II) etc., deposits 4—5% of (II), and then yields with KMnO_4 - CrO_3 44% of quinic acid, absorbs 0.66 mol. of H_2 when hydrogenated, and by the $\text{Hg}(\text{OAc})_2$ method yields 65% of vinyl bases. With H_2SO_4 these last give amorphous quinoidotoxin, $[\alpha]_D^{25}$ $+16.6^\circ$ in $N\text{-HCl}$ [yielding quinotoxin oxalate, m.p. 166—167°, $[\alpha]_D^{20}$ (anhyd.) $+25^\circ$ in EtOH-CHCl_3 (1:2)], and thence its Bz and oximinobenzoyl derivatives, benzoylquinoidinonitrile, meroquinoidine, acetylmeroquinine, meroquinine Et ester, and β -collidine. The presence of epiquinine and epiquinidine in the bark, thus indicated, is confirmed by their direct isolation as benzoyl-d-tartrates, m.p. 160°, $[\alpha]_D^{25}$ -26.3° in EtOH ,

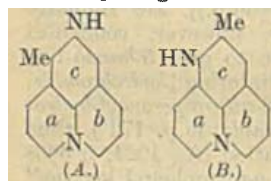
and m.p. 166—167°, $[\alpha]_D^{25} +1.9^\circ$, respectively, and by partial benzoylation of (I). *Benzoylquinotoxin* has m.p. 113—114°, $[\alpha]_D^{25} +36^\circ$ in EtOH. Toxins, if present at all, constitute < 10% of (I). R. S. C.

Constitution of matrine. XVII. H. KONDO, E. OCHIAI, and K. TSUDA (Ber., 1935, 68, [B], 1899—1904; cf. this vol., 766).—Catalytic dehydrogenation (Pd-asbestos at 270—280°) of the base, $C_{14}H_{26}N_2$, obtained by reduction of decarbonylmethylmatrinane affords the base, $C_{14}H_{20}N_2$, identical with that obtained by catalytic dehydrogenation of matrine. Oxidation with $KMnO_4$ of the methohydroxide of this base affords Pr^aCO_2H , showing the presence of a Pr^a side-chain. Control experiments with matrine methohydroxide do not give Pr^aCO_2H , so that the Pr^a chain is obtained by degradation of the lactam ring which in matrine has the structure



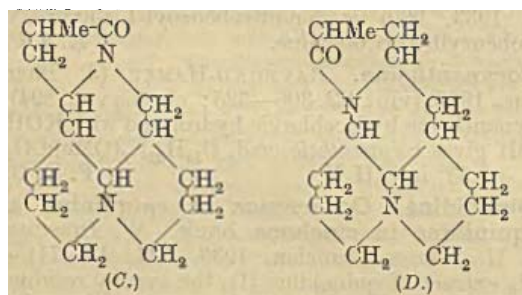
probably the former. Dihydro- α -matrinidine (I) is therefore $C_{10}H_{17}N \left\{ \begin{array}{l} -NH \\ -CHMe \end{array} \right.$; considered in conjunction

with the production of pyridine-2:3-dicarboxylic acid by oxidation of the compound, $C_{12}H_{14}N_2$, obtained by degradation of (I) with $CNBr$ and sub-



sequent oxidation, the structure A or B can be assigned to (I). Dehydro- α -matrinidine therefore has a 2-methylpyridine nucleus; in confirmation, it condenses with $PhCHO$ in presence of $ZnCl_2$ at 230—250° to benzylidene-

dehydro- α -matrinidine, m.p. 106—107°, hydrogenated (PtO_2) to the benzyl compound (platinichloride, decomp. 190°). If it be assumed that displacement of a ring does not take place during the formation of α -matrinidine the constitution of matrine (II) may be represented by C or D.



(II) and lupanine are not stereoisomerides. On oxidation lupanine methohydroxide gives glutaric acid, which is formed with certainty from its α -piperidone ring since it could not be obtained from sparteine but is derived from tetrahydrocytisine. H. W.

Curare alkaloids. I. Tubocurarine. H. KING (J.C.S., 1935, 1381—1389; cf. this vol., 655, 1138).—*d*-Tubocurarine chloride ($+5H_2O$), m.p. 274—275°, $[\alpha]_D^{25} +235^\circ$ in H_2O , is methylated to *O*-methyltubocurarine iodide ($+3H_2O$), m.p. 267°, $[\alpha]_D^{25} +178.2^\circ$ in H_2O . Hofmann degradation of the iodide yields *O*-methyltubocurarinemethine methiodide A ($+2.5H_2O$), m.p. 234°, and B ($+2.5H_2O$), m.p. 230° (A and B are

optically inactive), and *d*- ($+5H_2O$), m.p. 190°, $[\alpha]_D^{25} +105^\circ$ in MeOH, and *l*-*O*-methyltubocurarinemethine methiodide ($+5H_2O$), m.p. 171—172°, $[\alpha]_D^{25} -57^\circ$ in MeOH; at the second stage of degradation, a N-free substance, m.p. 198—199°, is obtained. Similar methylation and degradation of *d*-bebeerine yields a series of substances identical with those obtained from tubocurarine: *O*-methylbebeerinemethine methiodide A and B, and *d*-*O*-methylbebeerinemethine methiodide (a monomethiodide, $C_{41}H_{49}O_6N_2I \cdot H_2O$, has also been separated, m.p. 261°, $[\alpha]_D^{25} +63^\circ$ in *N*-HCl), and at the second stage, *O*-methylbebeerilene, m.p. 198—199°. Probable structures are given and discussed for tubocurarine and its derivatives. F. R. S.

Alkaloids of *Cutisus caucasicus*.—See this vol., 1549.

Preparation of asymmetric secondary arylarsinic acids. G. K. KAMAI (Trans. Kirov. Inst. Chem. Tech. Kazan, 1935, No. 3, 49—53).—Bart's method (A., 1922, i, 1201) is superior to that of Blicke and Smith (A., 1930, 99), whose phenyl-*p*-tolylarsinic acid (I) probably contained unoxidised tetra-arylsarsine oxide. Pure (I) has m.p. 159—160°; its prep. from $PhAsO$ and *p*- $C_6H_4Me \cdot N \cdot Cl$, from *p*- $C_6H_4Me \cdot AsO$ and PhN_2Cl , and from $MgPhBr$ and *p*- $C_6H_4Me \cdot AsO$ is described. Diazotised *p*-nitroaniline and $PhAsO$ yield phenyl-*p*-nitrophenylarsinic acid, m.p. 181° (NH_4 , Ba, Na, NH_4Ph , m.p. 162—166°, and *p*- $C_6H_4Me \cdot NH_2$, m.p. 78—79°, salts). CH. ABS. (r)

Preparation of 3-nitro-4-hydroxyphenylarsinic acid from *p*-chloroaniline. V. A. ISMAILSKI and A. M. SIMONOV (J. Pharm. Chim., 1935, 22, [viii], 337—357).—*p*-Chlorophenylarsinic acid with KNO_3 -conc. H_2SO_4 at 100° (cf. A., 1929, 584) gives 4-chloro-3-nitrophenylarsinic acid (I), which is converted by 40% alkali at 85° into 3-nitro-4-hydroxyphenylarsinic acid, also obtained by hydrolysis (25% NaOH at 100°) of 2-nitrodiphenylamine-4-arsinic acid, prepared by boiling the Na salt of (I) in H_2O with NH_4Ph . J. L. D.

Stereochemistry of tervalent arsenic. II. Preparation of *o*-, *m*-, and *p*-phenylmethylarsinobenzoic acids and their attempted resolution into optically active components. G. KAMAI (Ber., 1935, 68, [B], 1893—1898; cf. this vol., 875).—Attempts to resolve the acids into their optically active components were unsuccessful. $AsPhMeI$ is converted by Mg and *p*- C_6H_4MeBr into phenyl-*p*-tolylmethylarsine, b.p. 166—167°/8 mm. (compound, m.p. 59—60°, with $CuBr$), oxidised by $KMnO_4$ in H_2O to phenyl-*p*-carboxyphenylmethylarsine oxide hydrochloride (I), m.p. 150—152° (decomp.), which with H_2S affords phenyl-*p*-carboxyphenylmethylarsine sulphide, m.p. 159—160°. (I) is transformed by SO_2 in presence of I into *p*-phenylmethylarsinobenzoic acid, $AsPhMe \cdot C_6H_4 \cdot CO_2H$, m.p. 149—151° (NH_4 , Ba, strychnine, m.p. 183—185°, $[\alpha]_D^{25} -16.05^\circ$ in $CHCl_3$, quinine, m.p. 210—211°, $[\alpha]_D^{25} -56.91^\circ$ in $CHCl_3$, and non-cryst. brucine and cinchonine salts). The following compounds are obtained similarly: phenyl-*m*-tolylmethylarsine, b.p. 165—166°/9 mm., (non-

cryst. compound with CuBr), *phenyl-m-carboxyphenylmethylarsine oxide hydrochloride*, m.p. 148—150° (decomp.) (compound with HgCl₂), *phenyl-m-carboxyphenylmethylarsine sulphide*, m.p. 134—135°, and *m-phenylmethylarsinobenzoic acid*, m.p. 92—93° (quinine, m.p. 169—170°, $[\alpha]_D^{25}$ —83.01°, and strychnine, m.p. 138—139°, $[\alpha]_D^{25}$ —19.8°, salts): *phenyl-o-tolylmethylarsine*, b.p. 162—163°/? pressure, *phenyl-o-carboxyphenylmethylarsine oxide*, m.p. 226—227°, *phenyl-o-carboxyphenylmethylarsine sulphide*, m.p. 164—165°, and *o-phenylmethylarsinobenzoic acid*, m.p. 232—233°. H. W.

Heterocyclic compounds containing arsenic in the ring. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1935, 12, 627—628).—C₆H₆, CHCl:CH·AsCl₂, and AlCl₃ give 1-chloroarsindole (I). PhAsCl₂, C₂H₂, and AlCl₃ give β-chlorovinylphenylchloroarsine and di-(β-chlorovinyl)phenylarsine, the former with AlCl₃ yielding (I). Et o-aminocinnamate gives (Bart) cinnamic acid-o-arsinic acid, converted by HBr into o-α-bromo-β-carboxyethylphenylarsinic acid, which with alkali yields o-vinylphenylarsinic acid. With SO₂-HCl this gives o-vinylphenyldichloroarsine, whence (I) is obtained. Compounds of the types (CHPh:CH)₂Hg, CHPh:CH·HgCl, and (CHPh:CH)₃As, have been obtained. R. S. C.

Reactions of bismuthiol. J. V. DUBSKÝ and A. OKAČ (Chem. Obzor, 1934, 9, 171—173; Chem. Zentr., 1935, i, 1707; cf. A., 1934, 1193).—Dithiolthiodiazole (bismuthiol) (I) yields red needles with Bi salts. Analogues of (I) which cannot undergo tautomeric change do not give the colour reaction. H. N. R.

Reactions of bismuth with organic hydrosulphides. I. J. V. DUBSKÝ, A. OKAČ, and J. TRTILEK (Chem. Obzor, 1934, 9, 173—174; Chem. Zentr., 1935, i, 1707—1708; cf. preceding abstract).—Compounds of the type Bi(Bis)₃ and Bi(Bis)X [(Bis) = bismuthiol residue] can be isolated from the intensely coloured Bi salts of bismuthiol (I). The importance of the secondary valencies of the S atoms is shown by replacement of SH by OH, when the reaction no longer takes place. The colour reactions of many analogues of (I) with metallic salts are described. H. N. R.

Mercuration of ethylenes and reaction of methoxy-mercurials. G. F. WRIGHT (J. Amer. Chem. Soc., 1935, 57, 1993—2000).—The reaction of Hg(OAc)₂, MeOH, and ethylenes is in the main bimol. It is accelerated by NO₃⁺ or NaOMe, is slow in H₂O, faster in higher alcohols, and fastest in MeOH. These and other considerations indicate reaction thus: Hg(OAc)₂ + R''OH ⇌ AcOH + OR''·Hg·OAc (I); (I) + CHR:CHR' → OR''·CHR·CHR'·Hg·OAc (II). The facile decomp. of (II) by various reagents and the determination of Hg⁺⁺ in presence of org. mercurials by KCNS are described. *trans*-CHPh:CH·CO₂Me (III) gives 88% of Me α-chloromercuri-β-methoxy-β-phenylpropionate, m.p. 134°. The *cis*-cinnamate gives the *isomeride*, m.p. 141°, but both, when distilled at 25 mm., give (III), decomp. temp. being *trans*-170° and *cis*-157°, and both with Na₂S₂O₃ yield OMe·CHPh·CH₂·CO₂H (also obtained similarly from anhydro-α-hydroxymercuri-β-methoxy-β-phenyl-

propionic acid). *iso*Stilbene gives α-chloromercuri-β-methoxy-α-β-diphenylethane, m.p. 143°, but *trans*-stilbene does not react; this mercurial with a variety of reagents gives a mixture of isomeric stilbenes. Styrene affords α-acetozymmercuri-β-methoxy-β-phenylethane, m.p. 64—65°, stable to Ac₂O at 25° and boiling C₅H₁₁·OH, but reconverted into styrene by boiling Ac₂O and other reagents. α-Benzoyloxy-, m.p. 80° (stable in hot PhMe), and α-bromo-mercuri-β-methoxy-β-phenylethane (IV), m.p. 63°, are prepared; the latter affords OMe·CHPh·CH₂Br and thence CH₂:CPh·OMe. Styrene and Hg(OAc)₂ in dioxan give a gummy intermediate product, which with MeOH in ligroin gives (IV). CH₂Ph·CH:CH₂ gives β-chloromercuri-α-methoxy-α-phenylpropane, m.p. 95—95.5° (with products which, when brominated and hydrolysed, give CPhEt), converted by Br and hydrolysis into CHMeBr·CHPh·OMe, b.p. 122—125°, and CHMe:CPh·OMe, b.p. 96—97°/19 mm. cycloHexene yields a labile form, m.p. 114—115°, of 1-chloromercuri-α-methoxycyclohexane, converted slowly in hot EtOH into a stable form, m.p. 86°; evidence of the formation of an intermediate compound is given. 1-Lactomercuri-2-methoxycyclohexane, m.p. 144° (decomp.), is described. Phenylbutadiene affords diacetylmercuridimethoxyphenylbutane, m.p. 142—145°, and chloromercurimethoxyphenylbutene, m.p. 89° (corresponding Br-compound, m.p. 76°), which with O₃ in CHCl₃ gives PhCHO and, when further mercurated, forms dichloromercuridimethoxyphenylbutane, m.p. 180°, obtained more readily from the (HgOAc)₂-compound. R. S. C.

Decomposition voltage of Grignard reagents in dry ether. E. Q. ADAMS (J. Amer. Chem. Soc., 1935, 57, 2005).—Differences in the decomp. voltage produced by substitution show an alternating effect, diminishing in intensity as the substituent becomes more remote from the Mg. R. S. C.

Reaction between mercury diaryls and diaryl-selenium dihalides. H. M. LEICESTER (J. Amer. Chem. Soc., 1935, 57, 1901—1902).—In CS₂ or cold COMe₂ reaction occurs thus: HgAr₂ + SeAr₂X₂ → HgArX + RX + SeR₂. In hot COMe₂ or at 140—150° without a solvent, a second reaction follows, thus: HgArCl + SeAr₂Cl₂ → SeAr₂Cl·HgCl₂. SeAr₂Br₂ in COMe₂ leads also to CH₂Br·COMe. R. S. C.

Denaturation and structure of seed-globulins.—See this vol., 1433.

Combination of bivalent manganese with certain proteins, amino-acids, etc.—See this vol., 1460.

New absorption apparatus for micro-carbon-hydrogen determination. A. FRIEDRICH (Mikrochem., 1935, 19, 23—37). J. S. A.

Volumetric modification of the Pregl halogen micro-combustion method for organic iodine. P. L. KIRK and K. DOD (Mikrochem., 1935, 18, 179—181).—I obtained by the Pregl halogen combustion method is oxidised to IO₃⁺ by Br. When the colour is uniformly brown, the excess of Br is removed by boiling and KI added to the acidified solution. The I liberated is equiv. to 6 times that originally present. R. S.

Methods of chemical analysis by hydrogenation. H. TER MEULEN (Bull. Soc. chim., 1935, [v], 2, 1692—1694).—Methods are described for overcoming the difficulties observed by Gauthier (this vol., 506) in the determination of org. S, O, and N by hydrogenation in presence of a catalyst. J. W. S.

Determination of deuterium in organic compounds.—See this vol., 1408.

Micro-volumetric determination of methoxyl. D. T. GIBSON and T. H. CAULFIELD (J.C.S., 1935, 1419—1420).—Contrary to Viebock and Brecher (A., 1931, 246), the determination cannot be satisfactorily carried out on 1—5 mg. of material because the "blank" correction is significant and is increased by time, temp., and dilution. Improvements in technique are described. J. L. D.

Biochemical detection of organic compounds.—See this vol., 1416.

Structure and oxidation of nitrogenous substances. C. N. ACHARYA (Nature, 1935, 136, 644).—When N compounds are oxidised by a mixture of $\text{CrO}_3 + \text{H}_2\text{SO}_4$, full recovery of N is obtained in the form of NH_3 and NO_3^- when the N are attached to different C. When two or more N are attached to the same C, however, a definite amount is lost either as N_2 or N_2O . The proportions of NH_3 recovered from typical groups are: $\text{NH}\cdot\text{CO}\cdot\text{NH}$, 2/3 of total N; $\text{N}\cdot\text{CH}\cdot\text{N}$, 4/5; guanidine group, 4/11, and creatine group, 2/3. NH_2OH derivatives are almost quantitatively oxidised to NO_3^- , whilst in N_2H_4 derivatives the N is almost completely lost as gas. Cl⁻ present as impurity and as hydrochlorides of bases tends to increase the ratio $\text{NO}_3^- : \text{NH}_3$ and should be removed by Ag_2SO_4 . L. S. T.

Colour reactions for tartaric, citric, and aconitic acids. O. FURTH and H. HERMANN (Biochem. Z., 1935, 280, 448—457).—With Ac_2O and $\text{C}_5\text{H}_5\text{N}$ tartaric acid gives an emerald-green, citric acid a carmine-red, and aconitic acid a violet colour whereas many of the aliphatic dibasic acids give no or only a brown colour. The reaction is very sensitive and using the fluorescence in ultra-violet light can detect 10^{-6} g. of these acids.

P. W. C.

Determination of diacetyl and acetyl-methylcarbinol. C. R. BARNICOAT (Analyst, 1935, 60, 653—662).— Ac_2 is separated by distillation in CO_2 , and converted into Ni dimethylglyoxime, which is

dissolved in CHCl_3 and determined colorimetrically. $\text{CHMeAc}\cdot\text{OH}$ (I) is determined by oxidation to Ac_2 during distillation, the Ac_2 originally present being subtracted from the total determined. The results are slightly low owing to escape of Ac_2 in the CO_2 . The detection of added Ac_2 is difficult, but addition may be inferred from the ratio of Ac_2 to $\text{Ac}_2 + (\text{I})$. E. C. S.

Micro-detection of liquid amines, especially methylamine in presence of ammonia. A. VON WACEK and H. LOFFLER (Mikrochem., 1935, 18, 277—282; cf. A., 1934, 1278).—Methods of distinguishing between NH_3 and NH_2Me are discussed and photomicrographs are given of the products obtained with 1 : 2 : 4- and 1 : 4 : 8- $\text{C}_{10}\text{H}_5(\text{NO}_2)_3\cdot\text{OH}$, and 1 : 2 : 4 : 5- $\text{C}_{10}\text{H}_4(\text{NO}_2)_3\cdot\text{OH}$. R. S.

Microscopy of the amino-acids and their compounds. I. Phosphotungstates and phosphomolybdates. B. BULLOCK and P. L. KIRK. II. Picrates and flavianates. B. L. CROSBY and P. L. KIRK (Mikrochem., 1935, 18, 129—136, 137—143).—Photomicrographs of the above salts of a no. of NH_2 -acids are given, together with *n* vals. of the flavianates. R. S.

Determination of creatinephosphoric acid.—See this vol., 1521.

[Analytical reactions of vanillin, phenols, and "prontosil"].—See this vol., 1474.

Volumetric determination of camphor by the hydroxylamine method. R. VANDONI and G. DESSEIGNE (Bull. Soc. chim., 1935, [v], 2, 1685—1691).—Camphor, fenchone, menthone, carvone, and camphenilone are converted by $\text{NH}_2\text{OH}\cdot\text{HCl}$ into their oximes and the liberated HCl is titrated with $\text{N-Na}_2\text{CO}_3$ (bromophenol-blue indicator). Experimental error is <1%. F. R. G.

Determination of pyridine in presence of nicotine. R. L. FRATKIN, L. P. JURAVLEVA, and A. G. BLANKSCHTEIN (Sborn. Robot Chim. Otdela, 1935, 88—106).—The $\text{C}_5\text{H}_5\text{N}$ is distilled off in presence of excess of AcOH . The residue is made alkaline and the nicotine distilled in steam and determined as silicotungstate. The acid $\text{C}_5\text{H}_5\text{N}$ distillate is made alkaline, redistilled into dil. H_2SO_4 , pptd. with NH_4CNS and CuSO_4 , and the solution titrated with standard AgNO_3 . The method is more accurate than that of Mach and Sindlinger (A., 1924, ii, 357).

T. H. P.

Biochemistry.

Cerebral blood in conscious and narcotised men. D. LASZLO, H. URBAN, and E. WEISSENBERG (Arch. exp. Path. Pharm., 1935, 179, 266—272).—The difference in O_2 content of arterial and venous blood of the brain supply in man varies considerably, the average being 3.7 vol.-% (during Et_2O narcosis 2.23%). The difference in CO_2 content also diminishes (average vals. 4.6 and 3.9%, respectively), giving R.Q. of 1.3 before and 1.7 during narcosis. The effect is due to inhibition of metabolic oxidation and subsequent accumulation of acidic products. F. O. H.

Colloid osmotic pressure of the blood of sea-fish. P. MEYER (Compt. rend. Soc. Biol., 1935, 120, 303—305).—Vals. are given for the colloid osmotic pressure of the blood of a no. of fish. Those of teleosts are of the same order as for terrestrial mammals, whilst those of selachians are of the order of 3—6 cm. of H_2O . Results for teleosts do not support Krogh's hypothesis. R. N. C.

Study by micro-incineration of the red corpuscles of the teleostean fish, *Cichlasoma*

fascetum. A. POLIOARD and P. ROJAS (Compt. rend. Soc. Biol., 1935, 120, 366—367).—The nuclei on incineration yield a fine white ash. The peripheral zone of the cytoplasm yields a coarse yellow ash, less abundant than that from amphibia, which contains Fe, whilst the inner region yields no ash. The colour and character of the ash vary with the Fe content. R. N. C.

Thickness of the wall of the red blood-corpuscle. J. F. DANIELLI (J. Gen. Physiol., 1935, 19, 19—22).—Max. vals. for the dielectric consts. of lipid substances in unimol. films are calc. from surface potential measurements. These are in accordance with the val. 3 assumed by Fricke for the erythrocyte cell-wall. F. A. A.

Hæmatopoietic action of phosphoric acid compounds of creatine and creatinine. V. SUZUKI, W. NAKAHARA, and F. INUKAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 1—9).—The compound obtained by the interaction of creatine or creatinine with P_2O_5 and HPO_3 administered *per os* to normal rabbits in 30 mg. daily doses gave a marked increase in the erythrocyte count. A. L.

Hæmoglobin metabolism and its disorders. L. HEILMEYER (Zentr. inn. Med., 1934, 55, 818—828; Chem. Zentr., 1935, i, 1731—1732).—Porphyrin eliminated during hæmatoporphyrinuria is not a decomp. product of hæmoglobin (I), but results from defective synthesis. The decomp. of blood-pigment follows the stages, bilirubin urobilin and stereobilin. Urobilinogen is identical with mesobilirubinogen. A secondary decomp. of (I) leads to formation of uroerythrin and urochrome B. A. G. P.

Hæmoglobin studies. I. In rachitic chickens : effect of ultra-violet irradiation. G. H. MAUGHAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 389—390).—Hæmoglobin is low in the blood of rachitic chickens, but on ultra-violet irradiation increases to vals. > those of normal controls. R. N. C.

Escape of hæmoglobin from the red cell during hæmolysis. E. PONDER and D. MARSLAND (J. Gen. Physiol., 1935, 19, 35—44).—Cinematograph films of red blood-corpuscles losing hæmoglobin under the influence of saponin (I) show that the permeability is a function of the concn. of (I). In lysis by hypotonic solutions the permeability is nearly independent of the tonicity. F. A. A.

Volumetric determination of hæmoglobin. S. RUSZNYAK and E. B. HATZ (Biochem. Z., 1935, 280, 242—247).—Defibrinated blood (1—2 c.c.) is saturated with CO (excess removed in N_2) and the bound CO is liberated by the action of 32% aq. $K_4Fe(CN)_6$ containing lactic acid. The liberated CO is then determined by Winkler's method (B., 1934, 557). W. McC.

New hæmatological stain. I. Constituents and methods of use. D. M. KINGSLEY (Stain Tech., 1935, 10, 127—133).—A two-solution stain for general hæmatological use is described. When mixed it is stable for 8 months and may be used for blood-smears, fixed and frozen sections, and touch preps. H. G. R.

Absorption of carbon monoxide with reduced hæmatin and pyridine-hæmochromogen. L. E. CLIFCORN, V. W. MELOCHE, and C. A. ELVEHJEM (J. Biol. Chem., 1935, 111, 399—409).—The relative rates of absorption of CO by alkaline (I) and acid reduced hæmatin (II), and by pyridine-hæmochromogen (III) at 25° have been determined. (I) absorbs faster than (II). Excess of C_5H_5N expels CO from CO-(III). K for the system $CO-(III) \rightarrow CO+(III)$ in a solution containing no excess of C_5H_5N is 1.24×10^{-4} . J. N. A.

Effect of varying concentrations of oxyhæmoglobin on its light absorption. G. B. RAY and H. A. BLAIR (J. Biol. Chem., 1935, 111, 371—378).—Oxyhæmoglobin in all concns. at λ 540 and 560 m μ obeys Beer's and Lambert's laws, p_H and salts in solution having no effect. At λ 650 m μ Beer's law is not obeyed, the absorption diverging from the calc. val. at 4 g. per 100 c.c., indicating that mol. changes are taking place. J. N. A.

Modifications of blood composition under the influence of general application of short waves. A. COMPERE (Compt. rend. Soc. Biol., 1935, 120, 237—240).—Short-wave application in the dog causes diminution of the alkaline reserve and p_H of the blood, and increase of non-protein-N and total protein. Total fixed bases, mineral acids, and protein acidity are scarcely modified. Corpuscular vol. is generally diminished. R. N. C.

Regulation of protein disequilibrium of blood-serum under the influence of injections of serin : experiments on man. G. LEFROU and P. BONNET (Compt. rend. Soc. Biol., 1935, 120, 424—427).—Serin (I) injected into lepers exhibits feeble anaphylactic properties. Serum-globulin and total albumin are decreased, whilst (I) and the (I)-globulin ratio are increased. (I) injections hence exert a regulating effect on protein disequilibrium. R. N. C.

Application of the differential determination of albumoses, polypeptides, and amino-acids, using ninhydrin, to blood. E. CHERBULEZ and A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 150—152).—After pptn. with various reagents the various fractions are determined with ninhydrin (A., 1933, 1181). H. G. R.

Determination of the amino-acids of blood-serum with tyrosinase. A. MIRIMANOFF and E. PERROTTET (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 168—172).—The ninhydrin and tyrosinase methods are compared. The former is more rapid, but the latter can be carried out without clarification. H. G. R.

Modified Nessler's reagent for micro-determination of urea in tungstic acid blood-filtrate. J. F. BARRETT (Biochem. J., 1935, 29, 2442—2445).—Addition of NaOCl to Nessler's reagent prevents its reduction by glucose, creatinine, etc., and allows direct colorimetric determination of urea in blood-filtrates. F. A. A.

Effect of thyroidectomy on the lipin, fatty acid, cholesterol, and protein content of blood-serum. C. I. PARHON and I. ORNSTEIN (Bull. Soc. Chim. biol., 1935, 17, 1119—1123).—Thyroidectomy in

rabbits resulted in increases in total lipins, fatty acids, and cholesterol of the blood-serum. Little change was observed in the protein content. A. L.

Determination of blood-sugar. I. Deproteinisation with cadmium hydroxide. II. Iodometric micro-determination of blood-sugar. C. DUMAZERT (Bull. Soc. Chim. biol., 1935, 17, 1163—1170, 1171—1177; cf. this vol., 642).—I. A micro-method employing deproteinisation with $\text{Cd}(\text{OH})_2$, followed by oxidation (Hagedorn-Jensen), for the determination of blood-sugar is described. 0.1 c.c. of blood is used and the error is 1–2%. By this method, glucose in the blood-corpuscles of diabetics is $>$ that in the plasma.

II. Deproteinisation with $\text{Hg}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ followed by iodometric determination of the aldoses (A., 1934, 992) is employed. 1 c.c. of blood is used and the error is 3%. A. L.

Modifications of the glycerol content of the blood in glycolysis *in vitro*. M. POLONOVSKI, H. WAREMBOURG, and P. LAMOUR (Compt. rend. Soc. Biol., 1935, 120, 191—192).—Glycerol (I) and glycerophosphoric acid increase in blood during glycolysis *in vitro* at 37°. (I) falls after reaching 50% of the calc. val., so that a (I)-destroying reaction begins in the later stages of glycolysis. (I) variations are not \propto the hydrolysis of blood-lipins; they are almost wholly responsible for the increase of the residual chromic index, which is not affected by non-protein-N variations. R. N. C.

Significance of phosphoric esters in the course of blood-glycolysis. II. Degradation of hexose monophosphate in haemolysed blood. Z. DISCHE (Biochem. Z., 1935, 280, 248—264; cf. this vol., 104).—The degradation is preceded by a phosphorylation, \propto two thirds of the phosphoric acid which esterifies the monophosphate (I) being transferred from adenosinetriphosphoric acid. Decrease in the rate of trans-esterification \propto the decrease in the concn. of (I). The aldo-form of (I) is probably only indirectly involved, serving to provide nascent keto-form which is phosphorylated much more rapidly than is the ordinary keto-form. There is no evidence of direct conversion of (I) into 1 mol. of triose ester and 1 mol. of triose. W. McC.

Gravimetric determination of fat and cholesterol in blood. G. GORBACH and R. KADNER (Mikrochem., 1935, 18, 266—271).—The sample is extracted with ligroin in the micro-extractor (A., 1933, 139). Cholesterol in the extract is pptd. by digitonin and the fat obtained by difference. R. S.

Sulphur content of pancreatic blood and of thoracic lymph. VI. Glucose injection in vagotomised dogs. S. KUMAMI (J. Biochem. Japan, 1935, 22, 163—179).—The S content of the thoracic lymph of vagotomised dogs varies considerably from hr. to hr., the average tendency being a gradual diminution. That of blood from the pancreatic vein is not changed by injection of glucose, whereas that of thoracic lymph slowly falls and then returns to normal levels. The difference between these results and those in normal dogs is due to the influence

of vagotomy on insulin secretion (cf. A., 1934, 1379; this vol., 378). F. O. H.

Level of carbonyl compounds in human blood. R. E. JOHNSON, A. P. MEIKLEJOHN, R. PASSMORE, and R. H. S. THOMPSON (Biochem. J., 1935, 29, 2506—2509).—The amounts of total HSO_3^- -binding substances in human blood fall within the limits 1.96—4.00 with an average of 2.81, expressed as mg. of AcCO_2H per 100 g. of blood. The HSO_3^- -binding capacity of blood from various cases suffering from mental and physical diseases showed no appreciable difference from that of normal blood. The latter may contain some CO-compound other than AcCO_2H , COMe_2 , or $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$. J. N. A.

Blood-iodine values. H. DOERING (Biochem. Z., 1935, 280, 442—447).—The low blood-I vals. obtained by the Fellenberg method are correct, and there is no volatile I fraction which is lost on ashing in an open crucible. The high vals. obtained by ashing in a closed system are incorrect, and are due either to traces of Br and Cl being incompletely removed or to traces of oxidants which liberate I from KI in acid solution remaining after ashing. P. W. C.

Iodine in blood. A. STURM, K. PLOTNER, and K. MAASS (Biochem. Z., 1935, 280, 396—412).—A general discussion is given of the various methods for determination of I in blood, the objections raised to the author's modification of the Fellenberg method are refuted, and the interpretation of blood-I vals. particularly in hyperiodaemia is discussed. P. W. C.

Occurrence of bromine in the normal organism. T. LEIPERT (Biochem. Z., 1935, 280, 416—433).—The Br content of normal human blood is 0.160—0.4 mg. per 100 ml. and of plasma 0.18—0.45 mg. per 100 ml. Br, unlike Cl, is retained in the erythrocytes, and the distribution ratio is therefore very variable, and is controlled by the CO_2 tension of the blood. No evidence could be obtained of Br-protein complex formation, and no ultrafilterable org. Br could be detected, Br being present only in the ionised form. Br is excreted together with Cl, but the ratios of Cl to Br in plasma and urine are not identical. Br is constantly found together with Cl in intermediate metabolic processes, and administration of tissue diuretics leads to elimination of Br. Soon after birth, infants' urine has a high Cl : Br ratio (corresponding with the high blood ratio), and this diminishes during nutrition with milk. P. W. C.

Bromine content of the organism in mental patients. T. LEIPERT and O. WATZLAWEK (Biochem. Z., 1935, 280, 434—441).—Tables summarise the Br and Cl contents of the blood, the distribution of Br and Cl between erythrocytes and plasma, the dependence of the Br and Cl index on the CO_2 tension, the Br and Cl contents of the cerebrospinal fluid, and the Br and Cl urinary excretion of mental patients. The Br in these cases is always wholly present as Br^- , and is in no way either chemically or physically different from the normal condition. The preponderance of cases of low Br val. is probably due to deficient diet. No evidence was obtained for the existence of a Br-containing pituitary secretion, the gland exercis-

ing any effect on the Br content of the organism in a secondary way by regulation of the H_2O content.

Volumetric micro-determination of potassium in blood-serum. P. WENGER, C. CIMERMAN, and C. RZYMOWSKA (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 140—143).—The method of Shohl and Bennett (A., 1928, 1292) has been modified by incorporating a wet incineration ($HClO_4$ and HNO_3) and removal of NH_4 salts with $NaOH$. H. G. R.

Isoelectric point of the erythrocyte membrane and hæmalysis by ammonium chloride. M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1935, 120, 174—176).—Erythrocytes are not hæmolyzed by 4% NH_4Cl solution at p_H 8, the isoelectric point of the cell membrane. Hæmolysis occurs with an unneutralised solution of NH_4Cl at the same concn.

R. N. C.

Hæmolysis by glucosides (saponin and solanin) and production of cholesterol *in vivo*. V. DE LAVERGNE and P. KISSEL (Compt. rend. Soc. Biol., 1935, 120, 149—150).—Hæmolysis in guinea-pigs and rabbits by neutral or alkaline saponin (I) solutions cause an increase in plasma-cholesterol (II). Solanin and acid (I) solutions lower (II) by their pptg. action.

R. N. C.

Follicular hormone and coagulation of blood. M. SAVIANO (Mem. R. Accad. Lincei, 1935, 6, 165—183).—Subcutaneous injection of folliculin (I) in normal male dogs lowers the time of coagulation of the blood, and increases fibrinogen and blood-Ca, the Ca increase occurring almost completely in the diffusible fraction. These effects are not produced by (I) added to normal blood *in vitro*.

R. N. C.

Index of flocculability of sera in flocculation and gelification reactions. E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, 120, 430—432).—Serum flocculation by H_2O , melanin, Fe albuminate, urea-stibamine, and sulpharsenol, and CH_2O -leuco- and lacto-gelification, are explained in terms of the index of flocculability.

R. N. C.

Conditions of flocculation and gelification of pathological sera. E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, 120, 428—429).—Flocculation or gelification of pathological sera occurs if eglobulin rises or serin or cholesterol falls below certain limits. An "index of flocculability" is defined.

R. N. C.

Abscess of fixation and serum reaction to resorcinol. P. BORDET (Compt. rend. Soc. Biol., 1935, 120, 91—93).—The reaction of rabbit's serum to $m\text{-}C_6H_4(OH)_2$ is increased during formation of an abscess or injection of turpentine; it returns to normal when the abscess has been formed.

R. N. C.

Serum reaction to resorcinol, rate of corpuscular sedimentation, and time of serum lacto-gelification. P. BORDET (Compt. rend. Soc. Biol., 1935, 120, 93—95).—Turpentine or bacterial products that increase the reaction of rabbit's serum to $m\text{-}C_6H_4(OH)_2$ also increase the velocity of corpuscular sedimentation and reduce the time of seric lacto-gelification.

R. N. C.

Active group of heparin. S. BERGSTROM (Naturwiss., 1935, 23, 706).—By the action of $ClSO_3H$ in C_5H_5N on cellulose, chitin, starch, glycogen, gum arabic, yeast-nucleic acid, and chondroitin-sulphuric acid, acid esters were obtained which possessed anticoagulating action of which the strongest, that derived from cellulose, had an activity $< 1/10$ that of heparin. In contrast to natural heparin, the cellulose ester was markedly toxic to rabbits.

W. O. K.

Anticoagulant properties of the pyrogenic products of citric acid. A. LUMIERE and S. SONNERY (Compt. rend. Soc. Biol., 1935, 120, 213—214).—The anticoagulant power of citric acid increases as the successive CO_2H groups are neutralised; that of Na salts of acids produced by heating is $<$ that of citric acid and decreases in the order itaconic and aconitic $>$ citraconic $>$ mesaconic acid. Alkali citrates are more coagulant than heavy-metal citrates.

R. N. C.

Regulation of protein disequilibrium of blood-serum under the influence of injections of serin: animal experiments. G. LEFROU and P. BONNET (Compt. rend. Soc. Biol., 1935, 120, 342—343).—Rabbits injected weekly with serin show necrotic areas at the point of inoculation after 7—9 injections in females, and later in males. The Arthus anaphylactic reactions are probably due to serin in the injected serum.

R. N. C.

Immunology and its connecting links with chemistry. L. E. DEN DOOREN DE JONG (Chem. Weekblad, 1935, 32, 590—601).—A review. S. C.

Production of immune serum by injection of cholesterol adsorbed on kaolin. W. MUTSAARS (Compt. rend. Soc. Biol., 1935, 120, 263—266).—Injection of rabbits with a suspension of pure cholesterol (I) adsorbed on pure kaolin produces an immune serum the complement-fixing power of which with (I) is $>$ that of the serum obtained by injecting (I) in combination with swine serum. Hence foreign proteins are not necessary to give (I) antigenic properties, which are considerably influenced by its physical state.

R. N. C.

Characteristic chemical reaction of formalised toxic filtrates. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 120, 313—316).—Diphtheria and tetanus antitoxins (I) give a red colour, stable for some days, when heated to 100° with small quantities of Na 8-amino- α -naphthol-3:6-disulphonate (II). The toxins (III) give the same reaction if treated with small quantities of CH_2O , but not with excess. The reaction occurs in the cold with (I) from which the active principle has been pptd. with Na β -naphthylamine-3:6:8-trisulphonate and citric acid. (II) gives the same colour with H_2O_2 , peptone containing traces of CH_2O and NH_3 , or formalised broth, suggesting that the reaction with formalised (III) is due to oxidisers formed by the action of CH_2O on the NH_2 of (III). (I) hence contain oxidising substances that are non-sp. components of the formalised (III), which is active only after removal of the active principles by pptn. or destruction.

R. N. C.

Antigenic power of staphylococcal toxin and anatoxin: its resistance to heat. G. RAMON and

R. RICHOU (Compt. rend. Soc. Biol., 1935, 120, 291—293).—The antigenic power of the toxin is destroyed rapidly between 50° and 60°, whereas that of the anatoxin decreases slowly with rise of temp., only disappearing completely at 80°. R. N. C.

Agglutination of *Bacillus pullorum*. A. STAUB (Compt. rend. Soc. Biol., 1935, 120, 341—342).—Agglutination is most intense at p_H 7.5—8. Old sera are more sensitive to p_H than young sera. R. N. C.

Determination of ash content of the leg bones of chicks with slipped tendon. T. T. MILBY (Poultry Sci., 1935, 14, 247—251).—Bones were freed from flesh and stored in 95% EtOH. Samples were subsequently crushed, wrapped in filter-paper, extracted with hot 95% EtOH, dried at 105°, and ashed at dull red heat. The desirability of making determinations at intervals during the course of experiments on calcification is emphasised. Vals. for chicks having slipped tendon were not significantly different from those for control birds. The ash content of femurs from chicks receiving 3% of $MgCO_3$ in the ration was < that from chicks given a normal ration, but > that from rachitic chicks. A. G. P.

Chemical topography of the brain. Chemical composition of the brains of normal and fasting cats. H. GORODISSKI (Ber. Ukrain. Biochem. Inst., 1928, 3, 125—142).—In the brains of normal cats, the total P contents of the different parts are in the order: tract. optic. (I) > corp. genic. lat. (II) and corp. quad. post. (III) > nucl. caudat. (IV) > grey substance of the cortical centres (motor, auditory, visual). The distribution of P-containing lipins follows that of total P, and the richer the parts are in P-containing lipins, the greater is the proportion of saturated, and the less of unsaturated, phosphatides. The brains of fasting cats (5—24 days' hunger, 7—44% loss in wt.) show a diminution in total P of (I); the lipin-P (as % of total P) diminishes in all parts. The non-lipin-P increases in (II), (III), and the grey substance of the motor cortical centre. The content of saturated phosphatides diminishes in nearly all parts, but most in (I) and least in (IV). F. A. A.

Chemical composition of parts of the nervous system. I. Grey matter of parts of the central nervous system of dogs. II. Vegetative nervous system of cows. A. V. PALLADIN, E. J. RASCHBA, and R. M. HELMAN (Ukrain. Biochem. J., 1935, 8, No. 1, 5—26, 27—46).—I. As regards the amounts of cholesterol (I) and unsaturated phosphatides (II) the parts form the series: grey matter of the spinal cord > nucleus caudatus > cerebral cortex and cortex cerebelli. The amounts of saturated (II) and cerebroside in the spinal cord are < in the other parts. For total N, the order is cerebral cortex > cortex cerebelli and nucleus caudatus > spinal cord; as regards creatine, cortex cerebelli > nucleus caudatus > cerebral cortex > spinal cord. The quotients creatine-N:total N are: cortex cerebelli 4.20, nucleus caudatus 3.94, spinal cord 3.42, cerebral cortex 2.66. For amounts of dry residue, the order is: spinal cord > others. These results confirm the data of Abderhalden, Weil, *et al.* (I) is not a constituent of highly differentiated nerve-cells.

II. Ganglion nodosum n. vagi has a higher content of (I) than have ganglion coeliacus and the ganglion of the sympathetic trunk. For unsaturated (II) and acid-sol. P the order is: g. coeliacus > g. of sympathetic trunk, much > g. nodosum n. vagi; and for saturated (II): g. coeliacus (0.439) > g. nodosum n. vagi and g. of sympathetic trunk. The total P contents are: g. coeliacus 1.777, g. of sympathetic trunk 0.939, g. nodosum n. vagi 0.836. The total N is equally distributed. The val. of residual N exhibits considerable individual variations. The proportion of creatine-N is very low especially in g. nodosum n. vagi. The dry residue vals. are: g. coeliacus 24.4, g. of sympathetic trunk 21.1, g. nodosum n. vagi 20.5. The ganglia of the sympathetic and parasympathetic nervous systems differ in biological functions and in chemical composition. E. P.

Creatine content of various parts of the brains of vertebrate animals. A. V. PALLADIN and E. J. RASCHBA (Ukrain. Biochem. J., 1935, 7, No. 2, 51—71).—In the cow's brain, the cerebellum contains the largest amount of creatine, and then in decreasing amount the grey matter of the hemispheres, the white matter of the same, and the corpus callosum. The cerebella of rats, rabbits, and guinea-pigs contain most creatine, and the grey matter of the hemispheres of these animals, as well as that of the cow, contains the largest amount of total N and H_2O . J. N. A.

Creatine content of different parts of the brains of vertebrates. II. A. V. PALLADIN and E. J. RASCHBA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 85—116).—In the dog's brain the creatine contents are in the order: cerebellum > cerebral grey matter > white matter of hemispheres > medulla; in the cat: cerebral grey matter, cerebellum > white matter of hemispheres, medulla; in hens: cerebellum > lobi optici, hemispheres. In the pigeon large individual variations occur, vals. for all parts of the brain lying within the same limits. The creatine content of the total brains of lizards, frogs, and toads is > in the brains of mammals and birds. H. D.

Creatinephosphoric acid in the brains of various animals. H. GORODISSKI (Ber. Ukrain. Biochem. Inst., 1928, 3, 109—114).—The acid is present in the brain of various animals, the % being greater in mammals (dog, cat, guinea-pig, rat) than in birds (pigeon, drake, cock, siskin). F. A. A.

Lecithin in brain when the diet contains animal and plant lecithin. S. V. FOMIN (Ukrain. Biochem. J., 1935, 8, No. 1, 47—60).—Food containing lecithin (I) from soya bean or from egg-yolk, or brain (cow, rat) does not increase the (I) content in the brain of rats. E. P.

Studies on osmotic equilibrium and on the kinetics of osmosis in living cells by a diffraction method. B. LUCKE, M. G. LARRABEE, and H. K. HARTLINE (J. Gen. Physiol., 1935, 19, 1—17).—A diffraction method, permitting rapid measurement of the average vols. of large nos. of cells, is applied to the unfertilised eggs of *Arbacia punctulata*. Good agreement with previous measurements by other

methods is found for the permeability to H_2O and to $(CH_2OH)_2$, and the relationship $P(V-b)=\text{const.}$ is found to hold. F. A. A.

Increased permeability to water of ageing unfertilised eggs (*Arbacia punctulata*). A. J. GOLDFORB (J. Gen. Physiol., 1935, 19, 149—165).—The rates of swelling of the unfertilised eggs, kept in sea- H_2O for various times after shedding, and transferred to dil. sea- H_2O , are observed. These rates increase with age. This increase in permeability is not correlated with degree of injury. F. A. A.

Effect of temperature on the glutathione content of cold-blooded animals. L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1935, 120, 289—290).—Glutathione in frog's muscles is unchanged by temp.; in frog's liver and in *Carassius auratus* it falls with rise of temp. R. N. C.

Distribution of glutathione in the organs of some marine invertebrates. A. MONIER (Compt. rend. Soc. Biol., 1935, 120, 456—458).—The organs in descending order of glutathione (I) content are liver and hepato-pancreas, genital organs, muscles. In all cases reduced (I) is $>$ oxidised (I). R. N. C.

Chemical investigation of the liver oil of *Barbus brachicephalus*. S. EPELBAUM and D. ZUVERKALOV (Ber. Ukrain. Biochem. Inst., 1928, 3, 167—172).—The oil contains triglycerides of palmitic, oleic, and stearic acids. The acids present in the oil mostly have high mol. wt. and low I val. The oil gives a colour test for vitamin-A, approaching in intensity those of the usual liver oils. F. A. A.

Flavinphosphoric acid from liver. H. THEORELL, P. KARRER, K. SCHOPP, and P. FREI (Helv. Chim. Acta, 1935, 18, 1022—1026).—Partial separation of flavin (I) from flavinphosphoric acid (II) in liver extracts is effected by repeated treatment of the aq. solution with amyl alcohol. Further purification of (II) through the Ca and Hg salts leads to a product giving 42.8% of ash and, as judged by cataphoresis experiments and ability to give the yellow oxidation enzyme with proteins, containing about 25% of (II). The proportion of free (I) in liver is very small. H. W.

Optical activity of lactoflavin. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1935, 18, 1026—1027).—Lactoflavin has $[\alpha]_D^{25} -106^\circ \pm 4^\circ$, $-103^\circ \pm 3^\circ$, $-100^\circ \pm 4^\circ$, $-96.6^\circ \pm 4^\circ$, and $-90.0^\circ \pm 5^\circ$ in 0.05N-NaOH ($c=0.5$, 0.3, 0.25, 0.15, and 0.1, respectively). H. W.

Hepatic chlorine in hyperthyroidised animals. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1935, 120, 52—53).—Liver-Cl in guinea-pigs and rabbits is generally increased by treatment with thyroid powder or extract; occasionally it is diminished. R. N. C.

Comparative chemistry of muscle. I. TAKAHASHI (J. Biochem. Japan, 1935, 22, 1—4).—The H_2O , P_2O_5 , and SO_4 contents of various species of mammals, birds, reptiles, amphibia, fishes, molluscs, and arthropoda are tabulated and discussed. F. O. H.

Influence of extirpation of the motor region of the cerebral cortex on chemical changes in muscle. S. FOMIN and S. EPELBAUM (Ukrain. Biochem. J., 1935, 7, No. 2, 39—50).—Extirpation of the motor region increases the creatinephosphoric acid content of muscle, whilst the inorg. P is decreased, so that the total val. is unaltered. The proteolytic processes in the motor cerebral cortex region undergo no change. J. N. A.

Extractives of giant salamander muscle. F. YAMASAKI (J. Biochem. Japan, 1935, 22, 5—8).—Data are given for the contents of glutathione, creatine (I), creatinine (II), and total S in skeletal muscle and of (I) and (II) in involuntary muscle (heart, stomach, intestine). F. O. H.

Creatinephosphoric acid content of fish muscle. A. V. PALLADIN and R. R. SIGALOVA (Ukrain. Biochem. J., 1935, 7, No. 2, 29—37).—Muscle of *Cyprinus carpio* contained about 0.35% of creatine (I) and about 0.02% of creatinephosphoric acid (II) (expressed as P). With older fish, the (I) content rises to 0.46%. Addition of dried blood to the H_2O causes a very slight increase in (I). There is probably no fundamental difference between fish and mammals as regards the (II) content of their muscles. J. N. A.

Determination of creatinephosphoric acid. I. T. SORENI (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 217—239).—The Fiske-Subbarow (A., 1926, 443) and Lohmann (A., 1928, 665) methods gave similar results with cat, dog, and rabbit muscle, whilst large differences occurred with those from rats and pigeons. H. D.

Influence of various diets on the amino-acids in muscle. S. V. FOMIN and V. DEMIN (Ukrain. Biochem. J., 1935, 7, No. 2, 147—157).—The tyrosine content of rat muscle is fairly const. and is not decreased by continuous protein starvation. The metabolism in the tissues is disturbed by a gelatin and pea diet, and the amount of tyrosine is increased, whilst the proportion of tyrosine-N to total N remains normal. Complete starvation does not affect the tyrosine content of the muscle. J. N. A.

Influence of thyroidectomy on the amino-acid composition of muscle. S. V. FOMIN and I. E. POZNER (Ukrain. Biochem. J., 1935, 7, No. 2, 159—167).—Thyroidectomy increases the tyrosine (I) in muscle, whilst the amount of tryptophan is unchanged; after 40—51 days the (I) returns to normal. The thyroid gland regulates the distribution of (I) in the organism. J. N. A.

Effect of diet on nitrogen and phosphorus compounds of muscles during fatigue. I. Effect on muscle-creatine and -phosphagen of albino rats. M. S. MISCHKIS (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 74—83).—On a protein-free diet the phosphagen, creatine, and H_2O contents of rats' muscles increase. Total N is unaffected. H. D.

Influence of training on the change in the synthetic powers of muscle after work. B. M. KOLDAEV (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 63—73).—Training diminishes to some extent the

reduction in the power of the muscle to synthesise hexosephosphoric acid due to fatigue. H. D.

Influence of work and training on the oxidation-reduction potential of muscle-tissue. R. V. TSCHAGOVETZ (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 31—62).—Fatigue makes the redox potential in rabbit's and frog's muscle more positive; training the muscle makes it more negative. H. D.

Muscle activity and oxidation processes. II. Effect of training and fatigue on muscle-glutathione. A. V. PALLADIN, S. E. BORSHKOVSKI, and L. I. PALLADINA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 5—14).—Training a rabbit's muscle prevents the decrease in reduced glutathione consequent on fatigue. H. D.

Effect of training and fatigue on the power of muscle tissue to reduce methylene-blue by the Thunberg method. A. V. PALLADIN and A. M. KASHPUR (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 15—30).—The reduction of methylene-blue (I) by fatigued rabbit's muscle is slower than normal; a trained muscle reduces (I) more rapidly than normal. H. D.

Physico-chemical constants of muscle-tissue. III. Electrical conductivity and p_H in the autolysis of muscle-tissue of pigeons with avitaminosis-B. S. V. FOMIN and D. N. STRASHESKO. IV. S. V. FOMIN, Z. S. GERSCHENOVITSCH, and D. N. STRASHESKO (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 117—124, 125—133).—III. The *post-mortem* increase in κ of the muscles of pigeons in avitaminosis-B is $<$ normal.

IV. The κ of the muscular tissue of mammals was $7.3\text{--}7.9 \times 10^{-4}$ and that of amphibians and fishes $4.8\text{--}4.9 \times 10^{-4}$ mho. H. D.

Physico-chemical constants of muscle-tissue. I. Influence of various foods on the conductivity and p_H of rat muscle. S. V. FOMIN and Z. S. GERSCHENOVITSCH. II. Influence of training [by electrical stimulation] on the variation of the physical constants of muscle-tissue. S. V. FOMIN, Z. S. GERSCHENOVITSCH, and V. DEMIN (Ukrain. Biochem. J., 1935, 7, No. 2, 133—140, 141—145).—I. Various protein foods produce very little change in the physico-chemical consts. of rat-muscle tissue. A flesh diet causes a fall in $[H^+]$, a bean diet gives a decrease of 12.4% in κ , whilst a gelatin diet produces a rise of 7.13%.

II. Training of the muscle causes a rise of 15.6% in κ and an increase of 8.44% in NH_3 -acid-N. J. N. A.

Phosphorus and nitrogen compounds in fish muscle. E. V. LACHNO (Ukrain. Biochem. J., 1935, 8, No. 1, 61—71).—There are no characteristic differences between the creatinephosphoric acid (I), creatine (II), and total N contents of the muscles of certain vertebrate fishes (*e.g.*, carp, cod, perch, pike). They all contain (I) and their (II) content is slightly $<$ that of mammalian muscles. The total N is 2.79% (average), 5.77% of which is (II)-N. E. P.

Heat-coagulation and colloid structure of albumins.—See this vol., 1460.

Swelling of structured proteins. Influence of the reticular tissue on the swelling of collagen in water and hydrochloric acid. D. J. LLOYD and R. H. MARRIOTT (Proc. Roy. Soc., 1935, B, 118, 439—445).—Swelling of the collagen fibres from rats' tails is accompanied by rupture of the reticular sheath and rolling back to form rings. The reticular tissue of young rats is tougher and the swelling less. In HCl of $p_H < 2$ this tissue is weakened, and no differences were observed with age, but the swelling was $>$ would have been anticipated. H. G. R.

Mol. wt. and isoelectric point of thyroglobulin. M. HEIDELBERGER and K. O. PEDERSEN (J. Gen. Physiol., 1935, 19, 95—108; cf. this vol., 105).—Pig thyroglobulin (I) has a mol. wt. of 650,000 as determined from the sedimentation const. and diffusion data, 700,000 from sedimentation equilibrium measurements. Human (I) has a similar mol. wt. Native (I) has an isoelectric point at p_H 4.58, denatured (I) at p_H 5.0. The sp. vol. of (I) is 0.72. F. A. A.

Albumose and peptone content of the muscle of horned cattle. I. A. SMORODINCEV and N. N. KRILOVA (Bull. Soc. Chim. biol., 1935, 17, 1149—1156).—Failure of erepsin to produce any increase in the NH_2 -N of beef stored at $1\text{--}3^\circ$ for 15 days indicates that no albumoses or peptones are formed. A. L.

Acetylcholine in the tissues of invertebrates. Z. M. BACQ (Compt. rend. Soc. Biol., 1935, 120, 243—245).—Acetylcholine is found in large quantities in the tissues of the octopus, but only in traces or not at all in other invertebrates. Cholinergic nerves probably exist in molluscs, worms, and echinoderms. R. N. C.

Identification of acetylcholine extracted from the ganglionic cells of the octopus. Z. M. BACQ and F. MAZZA (Compt. rend. Soc. Biol., 1935, 120, 246—247).—Acetylcholine (I) is extracted from the ganglia of the central nervous system with $CCl_3 \cdot CO_2H$, and after removal of Cu with H_2S , pptd. with Reinecke's acid. The ppt. is dissolved in aq. $COMe_2$, SO_4 removed with $BaCl_2$, and H_2PtCl_6 and picric acid (II) are added to ppt. other impurities. After removal of excess of (II) with Et_2O and PhMe, (I) is pptd. by $HAuCl_4$ (III) and identified by its m.p. and analysis of the Au salt. A further impure fraction can be pptd. by (III) from the mother-liquor after evaporation. R. N. C.

Colloidal condition of cholesterol, cholesteryl ester, and lecithin. X. Reducing action of cholesterol sols. I. REMESOV and O. SEPALOVA (J. Biochem. Japan, 1935, 22, 71—83; cf. A., 1932, 632, 844).—Colloidal cholesterol (I) has a marked reducing action (5 and 10% sols correspond with 0.063 and 0.108% aq. glucose, respectively) which is dependent on concn. of (I), and is exerted in presence of serum or whole blood. Processes, *e.g.*, pptn., filtration, etc., which influence the colloidal condition influence the reducing activity. Direct injection of (I) sols into animals increases the reducing action of the blood; this is probably related to conversion of (I) into sugar by the liver. A correction for presence of (I) is necessary in glucose determinations in blood etc. containing (I). F. O. H.

Electrophoresis of sterols. III. Cholesterol surfaces. L. S. MOYER (J. Gen. Physiol., 1935, 19, 87—94).—Various cryst. forms of cholesterol (I) have the same electrophoretic mobility. The mobility of (I) ground with ice at -10° decreases to one half, reverting to the original val. on drying. The isoelectric point of (I), ground or unground, is near p_H 3.

F. A. A.

Biochemistry of the aphides of the terebinth. J. TIMON-DAVID and B. GOUZON (Compt. rend. Soc. Biol., 1935, 120, 164—166).—Analytical vals. are given for the common constituents. Lipins and glycogen are high, whilst H_2O and total N are low.

R. N. C.

Protective power of lipins.—See this vol., 1202.

Physical chemistry of lipins. III. Relations between the iodine value of monophosphatides and their relations to neutral salts. M. SPIEGEL-ADOLF (Biochem. J., 1935, 29, 2413—2415; cf. A., 1932, 1089).—Sols of egg and brain lecithin and kephalin variously treated show a parallelism between the decrease in I val. and the disappearance of the anomalous effect of Br^- on viscosity. F. A. A.

Pigments of human fat. L. ZECHMEISTER and P. TUZSON (Bull. Soc. Chim. biol., 1935, 17, 1110—1118).—The distribution of carotene, lycopene, xanthophylls, and capsanthin in the fat from several pathological human tissues is determined by chromatographic analysis. A. L.

Crystal forms produced by the solidification of fatty acids. M. OKRASINSKI (Wiad. farm., 1934, 61, 697—698; Chem. Zentr., 1935, i, 1952).—On cooling molten acids from cattle and horse fats, there are formed from numerous crystallisation centres groups of narrow polyhedra arranged similarly to tissue cells. Each polygon consists of many crystals in forms characteristic of the acids present.

A. G. P.

State of glycogen in the interior of the cell. I. Three-component system from clupein, nucleic acid, and glycogen or dextrin. S. J. VON PRZYŁECKI, W. GIEDROYC, and H. RAFAŁOWSKA (Biochem. Z., 1935, 280, 286—292).—If mixed in appropriate proportions [small amounts of nucleic acid (I) (from yeast or herring roe) or large excess of glycogen (II)] clupein (III) (as sulphate), (I), and (II) combine in solution (p_H 7.0—7.3) to produce three-component simplexes. Simplexes are also produced with dextrin (IV) instead of (II), (IV) being united to the arginine residue of (I). The affinity of (I) for (III) is much $>$ it is for (II).

W. McC.

Carbohydrates of the albuminous gland of *Rana esculenta*. F. N. SCHULZ and M. BECKER (Biochem. Z., 1935, 280, 217—226; cf. A., 1900, i, 478; 1934, 1251).—Dil. acid hydrolysis liberates from the dried gland 30—35% of reducing sugars (calc. as glucose) consisting of equimol. amounts of galactose (I) and glucosamine. In the gland (I) does not occur in the phosphorylated state. According to the season of the year, 1—1.5% of polysaccharide (almost entirely glycogen, only traces of galactogen) is present.

W. McC.

Determination of tissue-carbohydrates. N. R. BLATHERWICK, P. J. BRADSHAW, M. E. EWING, H. W. LARSON, and S. D. SAWYER (J. Biol. Chem., 1935, 111, 537—547).—Various modifications of other authors' methods of determining glycogen, lactic acid, and fermentable and non-fermentable reducing substances in muscle are described in detail and applied to the determination of carbohydrates in fasting rats. Immediate freezing of the muscle to be examined is necessary.

H. D.

Accumulation of electrolytes. VIII. Accumulation of potassium chloride in models. W. J. V. OSTERHOUT and S. E. KAMERLING (J. Gen. Physiol., 1935, 19, 167—178).—Models are described in which the accumulation of electrolytes, particularly K^+ , in living organisms is imitated.

F. A. A.

Histochemical determination of potassium during the evolution of the ovocytes of the hen. V. D. MARZA and L. T. CHIOSA (Compt. rend. Soc. Biol., 1935, 120, 345—347).— K is high in the large globules of the "primordial vitellus," the spherula of the globules of the white vitellus, and the granules within the globules of the yellow vitellus. It is low in all other tissues, but rises slightly in the ovular membranes during the third period of vitellogenesis. The diffused enzymes of the ciatrula in the parablasic region modify the vitellus globules considerably, and cause variations in their K content.

R. N. C.

Fixation of potassium by birds and fish. A. LEULIER and F. PAULANT (Bull. Soc. Chim. biol., 1935, 17, 1124—1136).—The K content of the embryo and the membrane of the eggs of the hen, duck, pigeon, and guinea-fowl is 0.15—0.167%, the corresponding val. for the turkey being somewhat smaller. The K content of hen-egg yolk (0.090%) is $<$ that of the others (0.110—0.156%). The increases in the wt. and K content of the chicken embryo run parallel during incubation, 85% of the available K being absorbed at the time of hatching. Growth and increase in K content of trout fry also follow the same course.

A. L.

Lactation. II. Technique for studying lactation in rats. R. G. DAGGS. **III. Effects of various dietary principles on lactation in rats.** R. G. DAGGS and R. L. TOMBOULIAN (J. Nutrition, 1935, 9, 575—580, 581—592).—A lactation-promoting factor occurs in a variety of natural products. Cystine or glutathione acts as a mammary stimulant.

A. G. P.

Dilatometric study of *in vitro* digestibility of milks. K. BHAGVAT and M. SREENIVASAYA (Proc. Indian Acad. Sci., 1935, 2, B, 316—321).—Digestion of milk preps. and of caseinogen (I) by trypsin is readily followed dilatometrically (A., 1934, 109, 450, 1137), the fall in the dilatometer being strictly \propto liberation of NH_2-N . The hydrolysis of (I) in milk does not differ from that of (I) in artificial media. F. O. H.

Heterogeneity of casein. C. GROH and E. FALTIN (Math. nat. Anz. ung. Akad. Wiss., 1934, 50, 457—466; Chem. Zentr., 1935, i, 1720—1721).—Casein obtained from colostrum milk is sol. in 70% aq. EtOH, particularly if this is slightly acidified.

It resembles the Osborne-Wakeman albumin in solubility, but its composition resembles that of ordinary casein. No essential and regular change in the composition of casein is observed in the first stage of lactation. R. N. C.

Reductase and coreductase of milk. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 166—167).—Dilution of milk inhibits the coreductase which may be added in the form of yeast or meat extract to restore the reducing action. H. G. R.

Standardisation of the methylene-blue reduction test by the use of methylene-blue thiocyanate. H. R. THORNTON and R. B. SANDIN (Amer. J. Publ. Health, 1935, 25, 1114—1117).—It is suggested that the thiocyanate be used, with 1 part of dye to 300,000 parts of milk as the standard concn. H. G. R.

Reductase-time of milk and the bacterial content. J. D. FILIPPO (Chem. Weekblad, 1935, 32, 601—602).—Examination of 426 samples shows that there is no abs. parallelism between the no. of bacteria present in milk and the time taken to decolorise methylene-blue solution. Milk which decolorises the reagent in < 2 hr. is unfit for human consumption, although 3.8% of such samples contained $0.5\text{--}1 \times 10^6$ and 1.3% $< 0.5 \times 10^6$ bacteria per c.c. S. C.

Ammonia content of human and cow's milk. M. POLONOVSKI and P. BOULANGER (Bull. Soc. Chim. biol., 1935, 17, 1178—1183).—The increase in the NH_3 content of human and cow's milk on keeping is mainly of bacterial origin, unlike that taking place in the blood. A. L.

Ammonia content of the liquids of the internal media of some invertebrates. J. SOUTERBICQ (Compt. rend. Soc. Biol., 1935, 120, 453—455).— NH_3 in the blood or secretions of invertebrates is > in vertebrates; max. NH_3 occurs in carnivorous species such as *Maja* and *Sepia*. R. N. C.

Colloid osmotic pressure of the nutrient liquids of the marine invertebrates. P. MEYER (Compt. rend. Soc. Biol., 1935, 120, 305—307).—Vals. are given for a no. of marine invertebrates. The colloid osmotic pressure of the internal medium increases with the species in genealogical order, suggesting a relation with the general organisation of the animal. The tunicates are an exception to this rule, the colloid-osmotic pressure being < that of crustacean internal media. R. N. C.

Application of the micro-quinhydrone electrode to the determination of the p_H of the aqueous humour of rachitic and normal rats. J. A. PIERCE (J. Biol. Chem., 1935, 111, 501—506; cf. this vol., 1218).—The p_H of the aq. humour is scarcely influenced by temp. The average val. for normal rats was 7.46 and for rachitic rats 7.38. H. D.

Secretory phenomena in the oviduct of the fowl including the process of shell formation examined by the microincineration technique. K. C. RICHARDSON (Phil. Trans., 1935, B, 225, 149—195).—The processes leading to the formation of the

chalaza, egg-white, shell-membranes, and shell have been studied by cytological methods. H. G. R.

Bile acids of *Mugil cephalus*, Linn. K. WATANABE (J. Biochem. Japan, 1935, 22, 119—121).—The principal acid is taurochenodeoxycholic acid (A., 1925, i, 405). F. O. H.

Effect of grape as compared with other fruit juices on urinary acidity and the excretion of organic acids. R. C. CLOUSE (J. Nutrition, 1935, 9, 593—610).—Bottled concord grape and orange juices tend, in general, to increase urinary p_H , whereas apple juice has the reverse effect. The CO_2 -combining power of blood is increased by feeding grape and orange juices and decreased by apple. The increased excretion of org. acids caused by grape and orange juices is not due entirely to unoxidised residues of fruit acids, but includes uric and citric acids. Org. acids are concerned in the maintenance of the acid : base ratio of the body. A. G. P.

Water exchange [in the organism]. IX. Variations in diuresis and urinary p_H in animals on acidogenic and alkalogenic diets. M. SAVIANO (Atti R. Accad. Lincei, 1935, [vi], 21, 715—720).—The greater is the diuresis produced in dogs or rabbits, the nearer approaches the urinary to the blood- p_H . With alkalogenic diets, diuresis produces a p_H < that of the blood; this is due to constancy of the CO_2 tension and diminution of HCO_3' in the urine. F. O. H.

Surface-active substances in urine. K. YUSAWA (J. Biochem. Japan, 1935, 22, 49—70).—Normal human urine has σ 78.0—90.0 (average 83.2) dynes per sq. cm.; it is lowest in summer, and higher at p_H 8—9 (NaOH) than at p_H 3—4 (HCl). Separation of the constituents affecting σ by dialysis, extraction with solvents, etc. indicate them to be fatty acid derivatives of indole, C_6H_6 , and pyrrole, conjugated glycuronates, and ethereal sulphates. The effect of substances of these types on σ and the influence of $[\text{H}']$ are tabulated and discussed. F. O. H.

Excretion of the so-called synergistic gonadotropic factor of the anterior pituitary in the urine of castrates. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1934, 13, 1471—1472; Chem. Zentr., 1934, ii, 3268).—The Evans synergistic gonadotropic factor is present in measurable quantities in the urine of castrates and women at the menopause, and in smaller quantities in ox and gelding urine. Methods of testing are described. R. N. C.

Uroerythrin. M. WEISS (Deut. Arch. klin. Med., 1934, 177, 97—106; Chem. Zentr., 1935, i, 2036).—Uroerythrin, an orange-red pigment occurring in urine, is a reducing substance and is decolorised by light. It resembles urobilin in pptn. reactions. It shows weak absorption bands at 525—540 and 490—500 $m\mu$, similar to those of cochineal (I); the bands are sharpened and shifted towards the red by 33% H_3PO_4 . Acids colour it red, alkalis green. It is determined spectroscopically in urine by extracting with $\text{C}_5\text{H}_{11}\cdot\text{OH}$, clearing the emulsion with EtOH , adding 33% H_3PO_4 , and comparing with a (I) standard. It is not an elimination product of the bile, its excretion under pathological conditions

depending on the liver. It is possibly identical with xanthorubin from the serum of hepatectomised dogs.

R. N. C.

Factors concerning the solubility of uric acid in urine. M. RANGIER (J. Pharm. Chim., 1935, [viii], 22, 357—364).—Mainly a discussion of the nature of the uric acid-urochrome complex (cf. this vol., 774).

J. L. D.

Origin of the histidine in the urine of pregnant women. R. KAPPELLER-ADLER and F. HAAS (Biochem. Z., 1935, 280, 232—241).—Added histidine (I) is readily destroyed by the healthy and diseased liver of men and women and by the liver of ovariectomised women, but is scarcely or not at all attacked by the liver of pregnant women, in whom the histidase of the liver appears to be inactivated so that (I) passes into the urine and even accumulates in the liver. The liver of gravid animals (cat, guinea-pig) destroys (I). Extracts of placenta contain no preformed (I), and there is no relation between (I) excretion in pregnant women and the function of the placenta. W. McC.

Excretion of cocaine. H. A. OELKERS and E. VINCKE (Arch. exp. Path. Pharm., 1935, 179, 341—348).—Urinary excretion of cocaine (I) (method of determination in urine is given) following subcutaneous injection into mice, rats, guinea-pigs, rabbits, cats, or dogs is slight, max. after 1 hr., and dependent on vol. and reaction of the urine. Thus with marked excretion of acidic urine, 16% of the injected wt. of (I) is excreted. Absorption of (I) occurs through the bladder. Determination of (I) by its mydriatic action in mice is not sufficiently accurate. F. O. H.

Volumetric determination of glucose in urine. E. MEES (Süddeut. Apoth.-Ztg., 1935, 75, 2—3; Chem. Zentr., 1935, i, 1425).—An iodometric method, employing Fehling's solution, is described.

H. N. R.

Micro-determination of urea in blood and urine. M. LEVINSON (Bull. Soc. Chim. biol., 1935, 17, 1157—1162).—The method is based on the oxidation of the urea with excess of NaOBr and determination of the excess iodometrically. A. L.

Determination of minute amounts of lead in urine. J. R. ROSS and C. C. LUCAS (J. Biol. Chem. 1935, 111, 285—297).—The urine is freed from PO_4^{3-} and metals other than Pb, and then treated with a soln. of diphenylthiocarbazone in CCl_4 in presence of $\text{NH}_3\text{-CN}'$; the red colour produced is compared colorimetrically with Pb standards. Only 100—200 c.c. of urine are required and the error is ± 0.004 mg. of Pb for amounts < 0.1 mg. of Pb. J. N. A.

Approximate determination of stercoporpyrins. I. BOAS (Biochem. Z., 1935, 280, 227—231).—An improvement of the method of Willstätter and Stoll ("Untersuchungen über Chlorophyll," 1913) is described. Account is taken of the amounts of porphyrin which pass into the solvents (COMe_2 , EtOH) used for purifying the faeces. W. McC.

Determination of phosphorus in faeces. C. MARIA (Arch. Farm. sperim., 1935, 60, 386—388).—2 g. of faeces are fused with $\text{Na}_2\text{CO}_3\text{-KNO}_3$ and the residue is extracted with H_2O , neutralised with AcOH, and treated with AcOH-NaOAc. Alternatively 0.2 g.

is ignited with glucose- Na_2O_2 (A., 1904, ii, 516), and the residue is treated with AcOH etc. In each case the liquid is titrated for PO₄''' by U acetate.

F. O. H.

Importance of ecology in relation to disease. R. P. STRONG (Science, 1935, 82, 307—317).—A lecture.

L. S. T.

Chemical decomposition and characteristics of the substances employed in the therapy of pernicious anaemia. J. SLADEK, S. SAWCZYCKA, and M. LIPSCHUTZ (Časopis českoslov. Lek., 1934, 14, 305—317; Chem. Zentr., 1935, i, 1406).—The tyrosine and tryptophan contents of the albumin fraction of fresh cow's liver are 1.24% and 1.56%, respectively, before and 4.68% and 5.58% after extraction with COMe_2 . The therapeutic activity for pernicious anaemia remains in the residue. The liver extract used for intramuscular injection contains free NH_2 -acids. The method of Duesberg and Koll is recommended for the evaluation of therapeutic liver preps., and gives best results if the preps. are suspended in a buffer solution and filtered after prolonged extraction. The results are more comparable if the absorption in the blue region of the spectrum resembles that of the blank test. There is no clear evidence of a relation between the concn. of the active principle in the prep. and the strength of the absorption bands in the blue region. COMe_2 completely, and aq. COMe_2 partly, extracts the active principle. More active material is extracted by 0.5% HCl in 20% EtOH than by NaOH at the same concn.

R. N. C.

Blindness in cattle associated with a constriction of the optic nerve and probably of nutritional origin. L. A. MOORE, C. F. HUFFMAN, and C. W. DUNCAN (J. Nutrition, 1935, 9, 533—551).—A form of blindness in calves and young growing dairy cattle (distinct from vitamin-A blindness) is associated with the feeding of poor-quality roughage. Deficiency of vitamin-D or of Ca is not the major factor. The latter occurs in maize silage, timothy hay, and cod-liver oil.

A. G. P.

Chemistry of carcinoma. I. A. VON CHRISTIANI (Z. Krebsforsch., 1935, 41, 445—447; Chem. Zentr., 1935, i, 2028).—The Et_2O -sol. substance protecting carcinomatous cells from cytolysis is identified as a cholesteryl ester.

A. G. P.

Effect of X-rays on the metabolism and growth of transplantable tumours. G. BANCROFT, L. V. BECK, and M. A. RUSSELL (Biochem. J., 1935, 29, 2416—2423).—X-Rays are allowed to fall on one of two duplicate tumours implanted in the same rat, and the histological changes and the effect on aerobic glycolysis, R.Q., and O_2 uptake of the excised tissue followed. Using the two tumours Philadelphia 1 sarcoma (I) and Walker 256 carcinoma (II), glycolysis remains unchanged until extensive degeneration has taken place; O_2 uptake is lowered. The R.Q. is always lowered with (I), less definitely with (II). (I) is less sensitive to X-rays than (II); sensitivity does not appear to be directly associated with blood-sugar level.

F. A. A.

Cancer and mineral metabolism. R. BERG (Chem.-Ztg., 1935, 59, 813—815, 834—836).—The

significance of the mineral balance of foodstuffs, notably the Ca/Mg ratio, is discussed. A. G. P.

Synthetic hydrocarbons with carcinogenic action. R. SIBONI (Boll. Chim. farm., 1935, 74, 709—720).—A review.

Action of the serum of mice with tar cancer on the fluorescent power of solutions of uranine. A. BOUTARIC and J. BOUCHARD (Compt. rend. Soc. Biol., 1935, 120, 293).—No inhibition of the fluorescent power is produced by the cancerous sera.

R. N. C.

Existence in the liver of substances inhibitory to benzopyrene cancer of the white mouse. J. MAISIN, H. VASSILIADIS, and A. GODENIR (Compt. rend. Soc. Biol., 1935, 120, 259—261).—The COMe_2 -insol. fraction of Et_2O extract of liver contains a substance that inhibits the growth of experimental (benzopyrene) tumours and cancers in mice. The inhibitory effect is increased by boiling, suggesting that thermolabile activating substances are also contained in the extract.

R. N. C.

Preparation of organic peroxides and peroxidogens. W. KOCH and J. MAISIN (Compt. rend. Soc. Biol., 1935, 120, 104—106).—Acid peroxides are prepared by a modification of the method of D'Ans and Kneip, and ether peroxides by oxidation of the ethers with O_2 in presence of Pt. The name "peroxidogen" is given to the unsaturated compounds prepared from fructose, paraldehyde, MeCHO , and Et_2O by slow dehydration over H_2SO_4 . Peroxides are decomposed by H_2O into H_2O_2 and acids. Their prophylactic effect in benzopyrene cancer in mice is not simply due to O_2 liberation; the most active contain sufficient O for complete combustion to CO_2 and H_2O , and in many cases can, in presence of the corresponding acid, undergo intramol. rearrangement, which liberates a considerable quantity of energy.

R. N. C.

Effect of organic peroxides on the prophylaxis of experimental cancer in mice. W. KOCH and J. MAISIN (Compt. rend. Soc. Biol., 1935, 120, 106—108).—Diformaldehyde diperoxide has a definite prophylactic action on benzopyrene cancer.

Modification of the Weltmann reaction in cancer: diminution of the coagulation band. G. CARRIERE, P. MARTIN, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 31—32).—The coagulation band is diminished in the sera of most cases of cancer.

R. N. C.

Production of lactic acid in irradiated and non-irradiated tumours. W. HAARMANN (Biochem. Z., 1935, 280, 173—183).—The capability of extirpated human tumours to produce lactic acid (I) from added carbohydrates (II) [glucose (III), fructose, glycogen, Na hexosediphosphate] and AcCO_2Na varies greatly with the kind of tumour, the (II) used and its concn., the nature and amount of other (II) present, and the capability of the tumours anaerobically to destroy (I). Almost always more (I) is produced from (III) than from other (II). Irradiated tumours behave similarly, but in some cases the production of (I) by them is reduced, although destruction of the

cells does not occur. Tumours are more sensitive to irradiation than is normal tissue. W. McC.

Histological modifications at the surface of the graft and the spleen in the course of regression of the Jensen sarcoma under the action of insulin. O. LAMBRET and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 188—190).—Insulin induces disappearance of hepatic and muscular glycogen, and hyperplasia of the spleen, in rats where the graft shows marked regression.

R. N. C.

Variations of the fibrinogen content of the blood in neoplastic affections. R. LOICQ (Compt. rend. Soc. Biol., 1935, 120, 253—255).—Blood-fibrinogen is increased in guinea-pigs with tumours resulting from inoculation with the Murray liposarcoma and in patients with neoplastic tumours.

R. N.

"Polypeptidaemia index" in experimental cancer in the guinea-pig, and in neoplastic tumours in man. R. LOICQ (Compt. rend. Soc. Biol., 1935, 120, 250—253).—The "polypeptidaemia index" represents the difference between the Kjeldahl N vals. of the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and phosphotungstic acid filtrates of the blood. It is increased in guinea-pigs with tumours resulting from inoculation with the Murray liposarcoma, but is scarcely affected in patients with neoplastic tumours in absence of cachexia or infection.

R. N. C.

Action on an experimental tumour of intravenous injections of ascorbic acid unassociated with iron, or associated with copper. F. ARLOING, A. MOREL, and A. JOSSEAND (Compt. rend. Soc. Biol., 1935, 120, 205—206).—Injection of L-ascorbic acid in NaHCO_3 solution in rabbits with experimental tumours causes hepatic, renal, and peritoneal lesions. The Cu-dehydroascorbic acid complex causes rapid development of neoplastic lesions and visceral metastases, in sharp contrast with the Fe complexes.

R. N. C.

Action on experimental and human cancer of injections of combinations of iron and vitamin-C (ascorbic acid). F. ARLOING, A. MOREL, and A. JOSSEAND (Compt. rend. Soc. Biol., 1935, 120, 201—204).—In the reaction between Fe salts and ascorbic acid, (I), Fe^{III} is partly reduced by (I) to Fe^{II} , which unites with (I) to form violet, strongly-reducing *ferroscorbon* (II), whilst the unreduced Fe^{III} forms yellow, stable, non-reducing *ferriscorbon* (III) with dehydroascorbic acid. Perifocal reactions appear rapidly on injection of (II) in cases of cancer, but scarcely ever on injection of (III). (III) lends itself more than (II) to use in prolonged stabilisation treatment. Both cause vaso-dilatation.

R. N. C.

Hepatic function. II. In portal cirrhosis and congestive heart failure. A. CANTAROW (Arch. Int. Med., 1935, 56, 521—529).—In cases of liver cirrhosis, the bromosulphonephthalein (I) test of liver function did not run parallel with the concn. of serum-bilirubin (II), the latter being more closely related to the degree of ascites. Similar observations were made in four cases of Banti's disease. In congestive heart failure the severity was more closely

related to the retention of (I) than to the concn. of (II).
W. O. K.

Importance of the "Takata reaction" for the diagnosis of liver disease in its relation to galactose and bilirubin overloading. L. SCHINDEL and E. BARTH (Klin. Woch., 1934, 13, 1329—1332; Chem. Zentr., 1934, ii, 3286).—The reaction is measured by the alterations in the flocculating effect of HgCl_2 on the serum. It is positive in liver disease, particularly cirrhosis.
R. N. C.

Pancreatic diabetes in the dog deprived of its sympathetic nervous system. J. T. LEWIS and E. S. TURCATTI (Compt. rend. Soc. Biol., 1935, 120, 274—276).—Pancreatectomy in dogs that have been sympathetomised or deprived of the nervous tissue encircling the large vessels from the coeliac trunk to below the superior mesenteric artery results in diabetic symptoms similar to those appearing in untreated animals. Blood-sugar rises similarly in both cases, but the final rise 24—48 hr. before death, as well as the glycosuria, in the sympathetomised animal is > in animals operated by the other method.
R. N. C.

Treatment of severe diabetic acidosis. Comparison of methods, with particular reference to the use of sodium *dl*-lactate. A. F. HARTMANN (Arch. Int. Med., 1935, 56, 413—434).—Parenteral administration of Na *dl*-lactate to combat diabetic acidosis is advocated.
W. O. K.

Experimental diphtheric intoxication and ascorbic acid of the adrenals. G. MOURIQUAND, P. SÉDALLIAN, and A. COEUR (Compt. rend. Soc. Biol., 1935, 120, 216—217).—The AgNO_3 reaction of the adrenals of guinea-pigs diminishes 18 hr. after the injection of diphtheria toxin.
R. N. C.

Disturbance of corpus luteum formation in avitaminosis-C and diphtheric intoxication. J. VON GAGYI (Virchow's Archiv, 1934, 293, 674—681; Chem. Zentr., 1935, i, 1580).—A physiological relationship is indicated between ovaries and adrenals in respect of vitamin-C economy.
A. G. P.

Experimental azotæmia by injection of diphtheria toxin in the guinea-pig. J. CHALIER, M. JEUNE, and R. J. FOURNIER (Compt. rend. Soc. Biol., 1935, 120, 206—207).—Blood-urea begins to rise 6—9 hr. after injection of diphtheria toxin, and continues to rise until death; adrenaline secretion begins to fall at the same time.
R. N. C.

Proteinases (cathepsin) in the tissues of the infantile organism with dysentery and toxic dyspepsia. B. GOLDSTEIN and M. GUINZBURG (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 147—159).—The cathepsin per g. of dry matter is < normal in glycerol extracts of liver, kidney, and spleen of children who have died of toxic dyspepsia.
H. D.

Composition of the ash of thyroid gland and goitre. J. STRAUB (Endokrinol., 1934, 15, 15—25; Chem. Zentr., 1935, i, 1577).—Glands from Hungarian lowlands have less Ca and more K than those of Switzerland. This is an effect rather than a cause of the goitrous condition.
A. G. P.

Chemotherapy of malaria. S. P. JAMES (Nature, 1935, 136, 743—745).
L. S. T.

Two cases of myxœdema treated with thyrotropic hormone. M. WACHSTEIN (Klin. Woch., 1934, 13, 1434—1436; Chem. Zentr., 1934, ii, 3269).—Basal exchange is scarcely or not at all affected even by large quantities.
R. N. C.

Liver-arginase in myasthenia gravis. Origin of creatine. A. T. MILHORAT (J. Biol. Chem., 1935, 111, 379—384).—The amount of arginase (I) in the liver of a boy with myasthenia gravis was normal, although large amounts of creatine had been excreted in the urine. There is no evidence that the creatinuria occurring in m. gravis is related to a lack of liver-(I), and that an insufficient amount of (I) might permit the preservation of the guanidine group in arginine, and the oxidation and conversion of the latter into creatine.
J. N. A.

Indicanæmia in nephritis. I. GAVRILA and MIHAILEANU (Compt. rend. Soc. Biol., 1935, 120, 358—360).—Indicanæmia in patients without renal lesions varies between 0.20 and 0.92 mg. per 1000. Indicanæmia generally \propto blood-N in acute nephritis following scarlatina. In chronic nephritis it is const. if blood-N is < 1 g. per 1000, but increases with N above this level. It bears no relation to blood-Cl, albuminuria, or arterial pressure.
R. N. C.

Role of cellular lysis (hæmolysis and leucolysis) in the cholesterol content of pleural effusions. V. DE LAVERGNE and P. KISSEL (Compt. rend. Soc. Biol., 1935, 120, 151—152).—Cholesterol (I) in pleural effusions is of local origin and is controlled by cellular lysis, depending on the no. and type of the destroyed cells. (I) is high in hæmorrhagic effusions, suggesting that hæmolysis takes place more readily than leucolysis. In putrid pleurisy, where leucocyte destruction is definite, (I) is > in hæmorrhagic pleurisy.
R. N. C.

Inorganic constituents of the central nervous system of rabbits with experimental rabies. N. W. ROMENSKI (Ann. Inst. Pasteur, 1935, Suppl., 181—190).—In experimental rabies, Na is decreased and Ca increased in the brain and marrow. Mg and K are increased in the latter.
H. G. R.

Silicosis and anthracotic lungs. F. V. TIDESWELL (Refract. J., 1934, 10, 185—186).—An attempt to separate the "active" SiO_2 producing silicosis from the inactive form by a 2% KOH solution is described.
CH. ABS. (e)

Impregnation of the organism by dust. III. Partition of silica dust in the lungs. G. ANTOINE (J. Pharm. Chim., 1935, [viii], 22, 412—430; cf. this vol., 1396).—Determinations on roughly chopped tissue are subject to wide variations (0.0099—0.033%), but results on finely minced material do not vary > 20%. There is a regular increase in the SiO_2 content of a lung with age, and the superior lobe has a larger content than the other parts. The SiO_2 content of silicates from different lungs is fairly const. (86—94%). The two lungs from the same individual give similar results.
P. G. M.

Intestinal stasis in low mineral diets. E. C. ROBERTSON and M. E. DOYLE (J. Nutrition, 1935, 9, 553—567).—Stasis induced by low-mineral feeding is relieved by supplements of CaCO_3 and K_2CO_3 , but not by vitamin-B. A. G. P.

Effect of traumatism on the distribution of chloride and sodium between the blood and tissues and the acid-base equilibrium. H. CHABANIER, C. LOBO-ONELL, A. DE GASTRO-GALHARDO, and E. LEHR (Bull. Soc. Chim. biol., 1935, 17, 1145—1148).—In the traumatised muscle the increase in Cl^- and Na^+ over the normal val. is maintained as long as 48 hr. In the blood, however, whilst the corresponding vals. increase up to 24 hr., there is a subsequent decrease to $<$ normal; at the same time, the alkaline reserve decreases for the first 24 hr. and then increases. A. L.

Chemotherapy of tuberculosis. V. Ethyl silicylricinoleate. E. HESSE, G. MEISSNER, M. SEBELIN, and H. MÜLLER (Arch. exp. Path. Pharm., 1935, 179, 296—309).—The ester (I) is absorbed to the extent of approx. 55% from the intestine (dog). Retention of SiO_3^{2-} does not occur in mice. (I) is excreted through the intestine after oral or subcutaneous, and through the kidneys after intramuscular administration. Favourable results (formation of new tissue and encapsulation) in tubercular rabbits follow continuous administration of (I). F. O. H.

Chemistry of tubercular sputum. S. NAKAYAMA (J. Biochem. Japan, 1935, 22, 35—40).—The sputum (H_2O , 96.59%; fat, 0.68%; fat-free residue, 2.72%) yields on fractionation (with EtOH , Et_2O , COMe_2 , etc.) cholesterol, phosphatide (?), a cryst. substance, m.p. 136° , Ca , Mg , P , S , Cl , and protein (the hydrolysate of which yields histidine, arginine, tyrosine, and, in relatively high proportion, lysine). The high P content is characteristic. F. O. H.

Spectrographic investigation of gold distribution following gold therapy in men and animals. W. GERLACH (Arch. exp. Path. Pharm., 1935, 179, 286—295).—Storage of Au occurs mainly in the liver, spleen, and, with greater variations, in the kidney of tubercular men and animals treated with solganal-B; the diseased tissue (e.g., lungs) contains relatively small amounts. Localisation of Au is, however, significantly influenced by calcification of the tissue. The histochemical method of Kurosu (A., 1928, 549) is considered worthless (cf. B., 1932, 266). F. O. H.

Action of magnesium in experimental uræmia. F. AMANTEA (Arch. Farm. sperim., 1935, 60, 353—364).—With rabbits in which uræmia has been produced by nephrectomy, ligature of the ureters, or injection of U salts, administration of Mg salts increases the blood-urea, the level returning to normal within a few hr. This is due to liberation of urea from the tissues. F. O. H.

Metabolism during pregnancy. C. N. COONS [with A. T. SCHIEFELBUSCH, G. B. MARSHALL, and R. R. COONS] (Oklahoma Agric. Exp. Sta. Bull., 1935, No. 223, 113 pp.).—In balance studies retention of Ca was high, that of P and Mg relatively lower, of N

low, of Fe definitely inadequate, and of S usually negative. High storage of Ca , N , and Fe in early pregnancy proceeded independently of, and far in excess of, foetal requirements when conditions were favourable for storage, and in such cases increased retention in late pregnancy was not observed. A. G. P.

Growth and development, with special reference to domestic animals. XXXV. Energetic efficiency of milk production and the influence of body-weight thereon. S. BRODY and R. C. PROCTER. XXXVI. Endogenous nitrogen and basal energy relationships during growth. U. S. ASHWORTH (Missouri Agric. Exp. Sta. Res. Bull., 1935, No. 222, 40 pp., No. 223, 20 pp.).—XXXV. The distribution of the total digestible nutrients in the diet between milk production, maintenance, and live-wt. increase is examined and a mathematical relationship established. Under customary conditions of observation the gross efficiency of milk production decreased with body-wt., but if other related factors were const. milk-production efficiency would probably be independent of body size.

XXXVI. The ratio of endogenous urinary N to the heat of basal metabolism increases with advancing age. Rats receiving a high- N diet excreted more N per unit body-wt. than did those having a low- N diet. Endogenous N approximates more closely to a logarithmic function of body-wt. than to a logarithmic function of basal heat production. More consistent results are obtained by relating min. endogenous N to the initial body-wt. than to body-wt. attained at the time of min. N excretion. A. G. P.

Determination of basal metabolism by interferometric gas analysis. M. BOURDEAU (J. Pharm. Chim., 1935, [viii], 22, 393—411).—The apparatus and method described can be applied to any mixture of three gases which have no action on the metal chamber employed, provided that one of them can be easily eliminated. The results compare favourably with those obtained using Plantefol's precision eudiometer and the time taken for a determination is 15 min. compared with 50 min. P. G. M.

"Water intoxication" and water diuresis in adrenal insufficiency; importance of the adrenals in osmo-regulation. R. RIGLER (Klin. Woch., 1935, 14, 227—228).— H_2O administered orally or 0.2% aq. NaCl injected intraperitoneally in adrenalectomised rabbits, rats, and mice is excreted less rapidly than in normal animals, even if good general health is maintained. The adrenals must therefore function as regulators of the osmotic condition of the body-fluids. R. N. C.

Influence of calcium ions on energy metabolism of the mammalian heart. H. C. PETERS, C. E. REA, and M. B. VISSCHER (Proc. Soc. Exp. Biol. Med., 1934, 32, 268—271).—The mechanical energy of contraction and total liberated energy of the mammalian heart are increased by Ca^{++} . R. N. C.

Depigmentation of the eggs of *Cyprinus carpio*. T. BUSNITA and N. GAVRILESCU (Compt. rend. Soc. Biol., 1935, 120, 224—225).—The deposition of yellow eggs instead of the normal green is associated with the

retention of the green pigment of the bile by the hepatic tissues; the pigmentation of the eggs is hence related to the biliary function. R. N. C.

Individuality in nutritive instincts and causes and effects of variations in the selection of food. W. F. DOVE (Amer. Naturalist, 1935, 69, 469—544).—The genetics and physiology of nutritive instincts are studied. E. A. H. R.

Influence of certain dietary constituents on the response of rats to gossypol ingestion. W. D. GALLUP and R. REDER (J. Agric. Res., 1935, 51, 259—266).—A high protein intake was favourable to the detoxication of gossypol (I). Diets rich in lactose (20%) or acid diets containing much Ca, which were detrimental to growth in normal rats, had relatively small effects on rats receiving (I). Alkaline diets high in Ca (1.2%) were the most satisfactory for nullifying the action of (I). A. G. P.

Effects of common food ingredients on the iodine content of hens' eggs. H. J. ALMQUIST and J. W. GIVENS (Poultry Sci., 1935, 14, 183—190).—Use of marine products (fish meal, oyster shell) in poultry rations provides > the I requirements of hens. The I content of eggs is not closely related to that of the ration. A. G. P.

Effect of mineral supplements on the length of the tail and wing feathers in white Leghorn hens. W. A. HENDRICKS (Poultry Sci., 1935, 14, 221—227).—No effects of practical significance were observed. A. G. P.

Synthetic diets for herbivora, with special reference to the toxicity of cod-liver oil. L. L. MADSEN, C. M. MCCAY, and L. A. MAYNARD [with G. K. DAVIS and J. C. WOODWARD] (Cornell Univ. Agric. Exp. Sta. Mem., 1935, No. 178, 52 pp.).—Prolonged feeding of cod-liver oil caused degeneration of skeletal and heart muscle, and fatty liver. Substitution of a vitamin-A and -D concentrate lessened but did not prevent the injury, which was not entirely prevented by exclusion of cod-liver oil from the diet. Other factors are probably involved. Vitamin-B (yeast) decreased the injury in goats. A. G. P.

Synthetic diet for rabbits. R. PASSMORE (Biochem. J., 1935, 29, 2469—2470).—A diet containing washed Diophane enabled two out of three rabbits to maintain wt. H. D.

Effects of glucose on the respiratory exchange of adrenalectomised dogs. A. MORALES (Compt. rend. Soc. Biol., 1935, 120, 272—274).—The blood-sugar curve falls a little after adrenalectomy and then begins to rise; glucose (I) accelerates the rise, and the curve returns to its initial level after 1 hr. The increase due to (I) is increased 48 hr. after adrenalectomy, and the normal level is not reached again until after 5 hr. Basal metabolism and the R.Q. fall progressively after adrenalectomy. (I) increases basal metabolism and R.Q. R. N. C.

Respiratory quotients of normal and tumour tissue. K. A. C. ELLIOTT and Z. BAKER (Biochem. J., 1935, 29, 2433—2441).—The results differ from those of Dickens and Šimer (A., 1930, 1468), no significant differences being found between the R.Q.

of different tissues or between normal and tumour tissue of well-fed adult animals. F. A. A.

Respiration of the brain. L. CRASNARU and N. GAVRILESCU (Compt. rend. Soc. Biol., 1935, 120, 226—228).—Novarsenobenzene decreases respiration of the brain, although it increases that of other tissues. It serves to distinguish in the brain between O₂ consumption in carbohydrate metabolism and in one or more other undefined oxidative systems co-existent with carbohydrate metabolism. R. N. C.

Oxygen consumption in muscle activity in relation to fibre length. P. W. SMITH (Proc. Soc. Exp. Biol. Med., 1934, 32, 257—260).—O₂ consumption in activity rises on extension to a max., afterwards falling; resting O₂ consumption rises with increasing rapidity, whilst the curve for total O₂ consumption is a straight line. R. N. C.

[Digestion of] bread. W. HEUPTKE (Deut. med. Woch., 1934, 60, 1823—1827; Chem. Zentr., 1935, i, 1464).—Aleurone-protein is digested by pepsin and trypsin in a few hr. without destruction of the cell-wall. The protein of bran is easily digested. High faecal N following the feeding of brown bread is not due to defective resorption, but is derived from the intestinal secretion. Of the dry matter of faeces 4—5% represents intestinal N. The val. of rye bread is discussed. A. G. P.

Protein metabolism of the armadillo, *Chaetophractus villosus*, Desmarest. B. BRAIER (Compt. rend. Soc. Biol., 1935, 120, 361—362).—Total protein catabolism in the fasting state is low compared with those of the dog and rat. After a diet of meat the azoturic coeff. of the urine is raised from 65% to 75%; allantoin, representing 95—96% of the purines, is unchanged. Creatinine is < in the fasting dog or rat. R. N. C.

Biological value of the protein of dry diffusion residues in the beet sugar industry. S. E. BORSHKOVSKI, I. S. ONOPRIENKO, and L. S. TSCHERKASOVA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 177—198).—The biological val. of dry press-cake from the beet industry is equal to that of clover hay and is < that of caseinogen; it is increased by mixing with these materials.

Effect of starvation on aminogenetic and proteolytic processes in the cerebrum. A. V. PALLADIN and M. F. GULI (Ukrain. Biochem. J., 1935, 7, No. 2, 73—89).—The cerebra of dogs, rats, and pigeons showed large variations in the H₂O content and in the coeffs. of aminogenesis and proteolysis, as did also those of the starving animals. There is a definite difference between the summer and winter cerebral metabolism of the pigeon. J. N. A.

Nuclein metabolism. VII. Polynucleotidase. VIII. Bound and free purines in ox organs. IX. Tissue-ammonia and nuclein metabolism. K. MAKINO (J. Biochem. Japan, 1935, 22, 93—96, 97—107, 109—118).—VII. Hydrolysis of yeast- or thymus-nucleic acid by commercial trypsin preps. produces depolymerisation but not fission of the nucleotides (I) or nucleosides (II).

VIII. Data are given for the content and nature

of purines, free and as (I), (II), or nucleoprotein-nucleic acid, in fresh and autolysed spleen, liver, and pancreas.

IX. Autolysis of liver, kidney, and spleen is accompanied by formation of NH_3 , two important sources of which are adenosine-mono- and -tri-phosphoric acids. Added thymus-nucleic or guanylic acid is deaminated to the same extent with each of the three tissues; yeast-nucleic acid differs to an extent dependent on the tissue. F. O. H.

Metabolism of the phospholipins. VIII. Passage of elaidic acid into tissue-phospholipins. Evidence of the intermediary role of liver-phospholipin in fat metabolism. R. G. SINCLAIR (J. Biol. Chem., 1935, 111, 515—526; cf. this vol., 1397).—Rats are fed with elaidic acid (I) and the % of (I) in the tissue-phospholipins is determined by pptn. as its Pb salt. The phospholipins of young rats on a diet rich in (I) contain up to 33% of (I) and of adult rats up to 30%; in the liver the entrance of (I) into the phospholipins is much > in the muscles. It is suggested that there are two classes of phospholipins, one functioning as the constituent of membranes containing a high % of unsaturated fatty acids and another functioning as intermediaries in fat metabolism and containing chiefly saturated fatty acids. H. D.

Creatine formation in the organism. I. TAKAHASHI and T. KUMON (J. Biochem. Japan, 1935, 22, 9—14).—Arginine, carnitine, or γ -amino- β -hydroxybutyric acid in presence of autolysing liver-tissue (dog) at 37° produces creatine; similar results are obtained by perfusion experiments on the isolated liver. A mechanism is advanced based on methylation or demethylation of these compounds and subsequent addition of guanidine. F. O. H.

Creatine : creatinine ratio in hibernating and spawning frogs. F. YAMASAKI (J. Biochem. Japan, 1935, 22, 15—34).—Creatine (I) formation in male frogs (whole body) is somewhat > that in females. In both sexes, the (I) content during April is only 50—80% of that during other months, whilst the creatinine (II) level during winter hibernation is < the summer level. In the female, (II) is also min. during April, and is therefore related to the spawning period. F. O. H.

Influence of acid diet on creatine excretion. L. PALLADINA (Ber. Ukrain. Biochem. Inst., 1928, 3, 23—28).—In opposition to the findings of Underhill (A., 1916, i, 865), feeding rabbits on acid diet does not produce creatinuria unless the food intake is lessened. F. A. A.

Synthesis of aspartic acid from fumaric acid in the liver. K. P. JACOBSON, J. TAPADINHAS, and F. B. PEREIRA (Compt. rend. Soc. Biol., 1935, 120, 33—36).—Aspartic acid (I) appears in dog's blood that has been mixed with NH_4 fumarate (II) and perfused through the isolated liver. < 10% of the (II) used is transformed into (I). Considerable quantities of (II) are converted by fumarase into malic acid. R. C.

Effect of injections of extract of spleen on metabolism of carbohydrates. M. POLONOVSKI,

H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 181—182).—Spleen extract does not affect blood-sugar or the residual chromic index in normal subjects, but in cancerous and diabetic subjects the residual chromic index is depressed, indicating that the breakdown of the intermediary products of carbohydrate metabolism is accelerated. R. N. C.

Relation of adrenal cortex to carbohydrate metabolism. T. KONOMI (J. Biochem. Japan, 1935, 22, 149—161).—Ligature of the pancreatic duct in rabbits produces a slight hyperglycaemia and an increase in the size of the adrenal cortex and in its content of co-enzyme (I) for anaerobic decomp. of hexose phosphate by striated muscle (A., 1934, 1400). Similar effects follow injection of lactic acid. The rate of blood-glycolysis is increased by (I), whilst the ability to decompose hexose diphosphate lost by blood on haemolysis is restored. F. O. H.

Effect of fatigue on the oxidation of phenol in various diets. A. V. PALLADIN and L. I. PALLADINA (Ukrain. Biochem. J., 1935, 7, No. 2, 19—27).—On a basic diet (mainly oats) fatigue caused rabbits to excrete nearly all the injected PhOH in the urine. With an acid diet (beet and hay) only 30—40% of the PhOH was oxidised in fatigue, whilst the normal animal oxidised 59—65%. Fatigue also decreases the synthesis of conjugated PhOH compounds, less being formed on a basic than on an acid diet. J. N. A.

Influence of hunger on administered phenol. A. PALLADIN, S. MALIAR, and A. ROZENBERG (Ber. Ukrain. Biochem. Inst., 1928, 3, 15—21).—During hunger, as on an acid diet, a smaller proportion of PhOH injected into rabbits is excreted in the urine as uncombined PhOH than on a normal diet. F. A. A.

Synthesis of conjugated glycuronic acids during fasting. L. M. MAKAREVITSCH-GALPERIN (Ber. Ukrain. Biochem. Inst., 1930, 4, 53—63).—During fasting the excretion of conjugated glycuronic acids in the urine of rabbits is decreased, as is also the excretion of mentholglycuronic acid (I) after the subcutaneous injection of menthol in oil. After prolonged fasting the excretion of (I) rises somewhat, but is still < normal. W. O. K.

Synthesis of thymolglycuronic acid on an acid and alkaline diet. M. G. KUSNETZOVA (Ber. Ukrain. Biochem. Inst., 1930, 4, 17—29).—Rabbits, subcutaneously injected with thymol in EtOH, excreted more thymolglycuronic acid on an alkaline than on an acid diet. W. O. K.

Influence of the character of the diet on the synthesis of mentholglycuronic acid. A. PALLADIN and E. PERSOVA (Ber. Ukrain. Biochem. Inst., 1928, 3, 7—14).—After the injection of menthol into rabbits, more mentholglycuronic acid is excreted on an acid than on a basic diet. F. A. A.

Influence of the character of the diet on the oxidation of benzaldehyde in the rabbit. D. A. ZUYERKALOV (Ber. Ukrain. Biochem. Inst., 1930, 4, 174—185).—The excretion of BzOH by rabbits ceases when they are on an acid but increases on an

alkaline diet. The oxidation of PhCHO to BzOH and the excretion of hippuric acid (I) are independent of the acid or basic character of the diet, except that acid diets somewhat decrease the synthesis of (I).

W. O. K.

Ketogenesis-antiketogenesis. II. **Ketogenesis from amino-acids.** N. L. EDSON (Biochem. J., 1935, 29, 2498—2505).—With rat-liver slices the most strongly ketogenic NH_2 -acids are leucine (I), tyrosine (II), and phenylalanine (III), whilst hydroxyproline (IV) has a considerable action. The other NH_2 -acids are either non-ketogenic, or show a slight ketone formation. With the fed rat only (I), (II), (III), and (IV) show ketogenesis, whilst with the starved animal only *dl*-(I) is ketogenic, many of the others being antiketogenic. Muconic acid is not ketogenic and arginine and ornithine are antiketogenic, possibly because they lower the effective concn. of NH_3 by promoting urea synthesis. It is suggested that the catabolism of (III) involves (a) conversion into (II) and breakdown through $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ and homogentisic acid, and (b) deamination and formation of $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$.

J. N. A.

Influence of various carbohydrates on formation of lactic acid and lactacidogen in aqueous brain extract. H. GORODISSKI and S. EPELBAUM (Ber. Ukrain. Biochem. Inst., 1930, 4, 115—121).—Lactic acid and lactacidogen are formed from mannose, glucose, galactose, maltose, dextrin, and starch in aq. extracts of cat's brain.

W. O. K.

Lactic acid and lactacidogen during short autolysis of aqueous extracts of cat's brain. H. GORODISSKI and S. EPELBAUM (Ber. Ukrain. Biochem. Inst., 1930, 4, 123—133).—During autolysis of aq. brain extracts, lactic acid (I) disappears and lactacidogen (II) is synthesised, (I) being utilised for the synthesis of (II). During the autolysis of the whole brain, (I) may either increase or decrease, but (II) always decreases.

W. O. K.

Formation of acetaldehyde from lactic acid. A. UTEVSKI (Ber. Ukrain. Biochem. Inst., 1930, 4, 89—97).—Addition of 0.05N-Na lactate to the minced pectoralis of the pigeon did not result in an increased formation of MeCHO, except in the presence of $\text{C}_2\text{O}_4^{''}$ or F^- .

W. O. K.

Velocity of resorption of alcohol in the "small stomach" (Pavlov). R. O. FAITELBERG and B. M. MEDVEDEV (Ukrain. Biochem. J., 1935, 8, No. 1, 169—190).—1 c.c. of 40% EtOH (I) per kg. body-wt. is introduced into the small stomach of a dog. After 20—30 min. (I) appears in the blood and in the breath, whilst the resorption of O_2 and the elimination of CO_2 increase, and the R.Q. decreases. (I) is completely eliminated after 5 hr. Catarrh of the mucous membrane retards resorption of (I).

E. P.

Coefficient of ethyl alcohol oxidation and basal metabolism in some homœothermic species. E. LE BRETON, M. NICLOUX, and G. SCHAEFFER (Compt. rend., 1935, 200, 1133—1135).—The velocity of EtOH oxidation in the mouse, rat, guinea-pig, rabbit, and pigeon \propto the intensity of basal exchange. The fowl gives anomalous results.

R. N. C.

Adjustment of the mineral nutrition of test animals during investigation of the biological value of proteins. S. E. BORSHKOVSKI and L. S. TSCHERKASOVA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 199—216).—Feeding of $\text{Ca}_3(\text{PO}_4)_2$ to rabbits on a diet of sedge hay increased assimilation of Ca, P, and N. The necessity for control of the mineral balance of the test animals during a determination of the biological val. of proteins is emphasised.

H. D.

Bile acids and calcium metabolism. XI. **Calcium excretion in thyroparathyroidectomised dogs.** S. TUZIOKA (J. Biochem. Japan, 1935, 22, 123—137).—Excretion of Ca in dog's bile is > that in the urine; thyroparathyroidectomy primarily (after 1 day) decreases the former and does not affect the latter, but 6—7 days later markedly diminishes both excretions. The diminished level of bile-Ca, but not that of urine-Ca, is increased (but not to normal levels) by administration of thyroparathyroid extracts and, to a greater extent, by that of cholic acid.

F. O. H.

Radioactive indicators in the study of phosphorus metabolism in rats. O. CHIEWITZ and G. HEVESY (Nature, 1935, 136, 754—755).—The distribution of P in the excreta and organs of rats fed daily with small amounts of Na phosphate containing $^{15}\text{P}^{22}$ as a radioactive indicator is recorded. The average time which a P atom spends in the organism of a normally fed rat is approx. 2 months. Bone formation appears to be a dynamic process involving continuous loss and replacement of P atoms.

L. S. T.

Resorption and excretion of calcium, magnesium, and phosphorus. Distribution of inorganic phosphate in the different sections of the digestive tract. J. MAREK, O. WELLMANN, and L. URBANYI (Math. nat. Anz. ung. Akad. Wiss., 1934, 51, 329—331; Chem. Zentr., 1935, i, 2039).—Analytical vals. are given for the contents of the various sections of the digestive tracts in young pigs after a long period of feeding with a basal diet supplemented by vitamin-D or different mineral substances. The solubility of the latter in dil. HCl and their elimination as $\text{PO}_4^{'''}$ are established.

R. N. C.

Comparative pharmacodynamic properties of some cardiotonic glucosides. A. BEAUNE (Bull. Sci. pharmacol., 1934, 41, 590—594; Chem. Zentr., 1935, i, 1413—1414).—The pharmacological actions on the heart of a no. of drugs of the digitalis, strophanthus, and intermediary groups are compared.

R. N. C.

Determination of cardio-active glucosides by the step-photometer. F. HAUSCHILD (Arch. exp. Path. Pharm., 1935, 179, 255—259).—The aq. glucoside (0.004—0.00025% of digitoxin, *g*- or *k*-strophanthin) is treated with alkali and picric acid (A., 1922, ii, 882) and the resulting colour is compared with suitable standards by means of the step-photometer. The average error is 1.3%.

F. O. H.

Ergot alkaloids.—See this vol., 1512.

Pharmacology of ergometrine. G. L. BROWN and H. H. DALE (Proc. Roy. Soc., 1935, B, 118,

446—477).—Ergometrine produced central excitation with general sympathetic stimulation, but with only a trace of the sp. paralysing action on motor sympathetic effects. It causes cyanosis of the cock's comb, but, unlike ergotoxine (I), does not lead to gangrene. It is less toxic than (I) and causes a rise in body-temp. in toxic doses. A pressor action is exhibited in the spinal cat, which is < that of the alkaloids of the (I) group.

H. G. R.

Comparative toxicity of aqueous extracts of *Ustilago maidis* and ergot preparations. B. DRAGIŠIĆ and B. VARIČAK (Arch. exp. Path. Pharm., 1935, 179, 319—326).—Aq. extracts of *U. maidis* (corn-ergot) produce similar but more marked symptoms of toxicity in mice than does ergotamine (I) or ergotine, indicating a high content of (I)-like substances.

F. O. H.

Toxicity of ripe poppy capsules. R. BUNGE (Arch. exp. Path. Pharm., 1935, 179, 465—474).—The pharmacological properties (mice, frogs) of the crude contents and alkaloid fractions of ripe and unripe poppy capsules indicate that, in addition to morphine (I), other alkaloids present include codeine (II) and thebaine (III), but not narcotine or papaverine. The toxicity of the crude alkaloid prep. is the same for ripe and unripe capsules, and is > that corresponding with the (I) content owing to the presence of (II) and (III).

F. O. H.

Increase in local anaesthesia by morphine. W. KEIL and G. HEPP (Arch. exp. Path. Pharm., 1935, 179, 420—424).—Min. effective concns. for complete anaesthesia of rabbits' cornea for 15—20 min. are novocaine (I) 2%, tutocaine (II) and cocaine (III) 0.5%, pantocaine (IV) 0.02%, percaine (V) 0.002%. At the conclusion of anaesthesia, intravenous injection of 5 mg. of morphine produces a second anaesthesia of duration 20—25 min. for (I), (II), and (IV), 40 min. for (III), and 70 min. for (V). The application of this phenomenon to the determination of analgesic activity is discussed.

F. O. H.

Increase and diminution of the convulsive action of local anaesthetics. W. KEIL and I. RUHLING (Arch. exp. Path. Pharm., 1935, 179, 415—419).—The toxicity of intravenously injected novocaine or percaine in rats is increased nearly 4 times by administration of adrenaline or "corbasil" (o-dihydroxyphenylpropanolamine hydrochloride). Similarly ephedrine (*d*, *l*, or *dl*) increases the convulsive action of cocaine by 200—250%. Slight novocaine convulsions are reduced by NaNO₂ (2 mg. per kg.) or glyceryl nitrate (5 mg. per kg.); adonine has a similar action.

F. O. H.

Anæsthetic properties of trichloroethylene. J. C. KRANTZ, jun., C. J. CARR, and R. MUSSER (J. Amer. Pharm. Assoc., 1935, 24, 754—756).—Anaesthesia by inhalation in the rat and rabbit is accompanied by stimulation of the skeletal muscles and a mild hyperglycæmia. No anaesthesia is obtained on rectal administration.

H. G. R.

Pharmacological differentiation of veramon and a mixture of its components. R. FISCHER and H. SALZER (Arch. exp. Path. Pharm., 1935, 179, 327—333).—Solutions of veramon cannot be

differentiated from those of the 1:1 mol. mixture of veronal and pyramidone by physico-chemical tests or by their pharmacological action in rabbits (cf. A., 1933, 74).

F. O. H.

Toxicity of pyramidone-veronal mixture. H. SALZER and R. FISCHER (Arch. exp. Path. Pharm., 1935, 179, 334—340).—The central action of pyramidone (I) following administration of (I)-veronal (II) mixtures to rabbits rapidly and proportionately disappears, so that finally a pure (II) action is shown. (I) also retards the excretion of (II) and hence prolongs the narcosis.

F. O. H.

Asymmetrical arylalkylcarbarnides.—See this vol., 1488.

Toad poisons. VII.—See this vol., 1502.

Mode of action of commercial preparations of histidine. A. SCHWARTZ, L. ISRAEL, and A. JACOBI (Compt. rend. Soc. Biol., 1935, 120, 124—126).—The production of urticaria on the skin by commercial preps. of histidine is due to traces of histamine.

R. N. C.

Hyperpolypeptidæmia induced by intraperitoneal injections of peptone in the rabbit. C. LAMBRET and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 184—186).—Injection of peptone induces const. hyperpolypeptidæmia, the intensity of which varies with the rabbit. Non-protein-nitrogen, whilst NH₂-acids vary. The increased polypeptide content disappears in 24 hr. At the same time corpuscular and plasma-Cl fall and blood-sugar rises.

R. N. C.

Liberation of histamine-like substances in the infarction of the intestine. G. UNGAR, X. J. CONTIADES, and R. G. PALMER (Compt. rend. Soc. Biol., 1935, 120, 326—328).—Embolisms provoked by lycopodium in the intestinal arteries of the dog cause an increase of gastric secretion both in the embolised animal and in another animal with which it is cross-circulated, suggesting that histamine-like substances are liberated; infarction appears in the intestine in 3—4 hr. The same effects occur with non-embolising irritants.

R. N. C.

Effect of glycerophosphate and lecithin-fatty acids on sensitivity of cats to adrenaline. A. VON JENEFY and J. VON MEHES (Arch. exp. Path. Pharm., 1935, 179, 403—414).—Aq. glycerophosphate (I) (0.001—1.0%) has a slight choline-like peripheral action, inhibited by atropine (II). Suspensions of fatty acids (III) from egg-lecithin have a slight depressor action, decreasing on continuous administration and inhibited by (II). The ester (IV) from (I) and (III) has a choline-like depressor action and is inhibited by (II). (IV) enhances the pressor action of adrenaline, especially in decapitated, (II)-treated cats even after adrenalectomy. (IV) probably combines with adrenaline-antagonistic choline in the blood.

F. O. H.

Effect of tetrahydro- β -naphthylamine on creatinephosphoric acid, creatine, and lactacidogen of white and red muscle. A. PALLADI and E. SAVRON (Ber. Ukrain. Biochem. Inst., 1932, 3, 65—70).—Tetrahydro- β -naphthylamine (I) leads

to a diminution in the lactacidogen content of the biceps muscle of rabbits, and to a smaller diminution in the semitendinosus. (I) increases the creatine (II) content of red and white muscle, and the increase in the red is > in the white. Rabbits poisoned with (I) show a greater % of (II) as creatinephosphoric acid than normal rabbits.

F. A. A.

Experimental intoxication by apiole : toxicity ; lesions of the liver and kidney. A. PATOR, G. PATOR, BEDRINES, and PAYEN (Compt. rend. Soc. Biol., 1935, 120, 192—194).—The lesions are described. The same alterations are produced by cryst. apiole, free from $(o\text{-C}_6\text{H}_4\text{Me})_3\text{PO}_4$, as by green apiole.

R. N. C.

Physiological inversion of the hypertensive effects of 3:4-dihydroxyphenylaminomethylcarbinol. RAYMOND-HAMET (Compt. rend. Soc. Biol., 1935, 120, 421—424).—The pressor effect in the dog is inverted by raising the arterial pressure by pinching the second carotid artery.

R. N. C.

Effects of dinitrocresol on oxidation and fermentation. M. E. KRAHL and G. H. A. CLOWES (J. Biol. Chem., 1935, 111, 355—369; cf. this vol., 1027).—The principal effect of 4:6-dinitro-*o*-cresol (I) on oxidation precedes and is not directly concerned with O activation and transfer. (I) does not increase the rate of O_2 consumption in dehydrogenase systems or in a tissue which has been frozen and thawed, and its effect on oxidations depends largely on the active functioning of a naturally occurring O transfer system. (I) markedly stimulates the anaerobic fermentation of yeast, the effect varying with the type of yeast.

J. N. A.

Action of *p*-phenylenediamine on the chemical processes in striped muscle. A. PARSCHEIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 113—116).—Injection of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ hydrochloride or sulphate into the dorsal sac of the frog produces rigidity of the muscles and an increased formation of lactic acid. The amount of creatinephosphoric acid is unchanged.

J. N. A.

Sodium salicylate poisoning ; favourable influence of glucose. H. MADISSON (Deut. Arch. klin. Med., 1934, 176, 612—625; Chem. Zentr., 1934, ii, 3277).—Fatty degeneration is attended by disappearance of glycogen, and is lessened by treatment with glucose.

R. N. C.

Effect of bromobenzene on the utilisation of cystine and methionine by the growing rat. A. WHITE and R. W. JACKSON (J. Biol. Chem., 1935, 111, 507—513).—The normal growth of rats fed on a diet containing caseinogen (I), starch, sugar, and lard is inhibited by feeding PhBr; the effect is counteracted by feeding cystine or methionine although taurine, Na_2SO_4 , or a digest of (I) is ineffective. Bromophenylmercapturic acid is isolated from the urine of rats fed with PhBr.

H. D.

Acute toxicity of ethyl chaulmoograte. G. A. EMERSON and H. H. ANDERSON (Proc. Soc. Exp. Biol. Med., 1934, 32, 289—291).

R. N. C.

Toxicity of carbon tetrachloride. E. CIARAVINO (Boll. Chim. farm., 1935, 74, 741—748).— CCl_4

or CHCl_3 (<0.55 mg.) is detected (*e.g.*, in cadavers) by vaporisation in a current of H_2 , which on ignition in contact with Cu produces a green flame (due to formation of HCl). Aspiration of the products of combustion and absorption in aq. NH_3 , the Cl' content of which is subsequently determined, affords a quant. method. CCl_4 and CHCl_3 are differentiated by suitable colour reactions.

F. O. H.

Relative toxicological effects of synthetic ethanol and grain fermentation ethanol in blended whiskies. C. W. MUEHLBERGER (Amer. J. Publ. Health, 1935, 25, 1132—1134).—The effects on man are identical.

H. G. R.

Aluminium as a factor contributing to the rise and progress of different pathological processes in the organism. A. L. TCHIJEVSKI and T. S. TCHIJEVSKAJA (Acta Med. Scand., 1934, 83, 501—504).—Food cooked in Al vessels increases the no. of cases of inflammation of the gastro-intestinal tract, colitis, and nephritic and hepatic diseases. Al salts and colloids react with biological membranes and may alter the charges they carry from negative to positive. Feeding white mice from Al vessels increases the no. of cases of spontaneous cancer.

G. H. F.

Therapeutic action of organic arsenic compounds. H. SCHLOSSBERGER (Ber., 1935, 68, [A], 149—163).—A review.

Synthesis of mentholglycuronic acid in arsenic poisoning. E. M. PERSOVA (Ber. Ukrain. Biochem. Inst., 1930, 4, 43—51).—After injection of a solution of menthol in oil into normal rabbits, up to 22% was excreted in the urine combined with glycuronic acid, whilst in the case of rabbits poisoned with As only 1—10% was so excreted.

W. O. K.

Antagonistic effect of potassium iodide in baldness due to thallium acetate. O. V. HYKES and F. A. DIAKOV (Nature, 1935, 136, 685).—KI reduces the toxicity of TlOAc to rats and prevents the loss of hair produced by Tl poisoning.

L. S. T.

Histo-spectrographic study of the fixation of manganese in experimental chronic intoxication by manganese dioxide. A. POLICARD (Compt. rend. Soc. Biol., 1935, 120, 364—366).—Rats on a diet containing MnO_2 excrete most of it in their faeces, but exhibit renal sensitivity after some weeks. Mn can be detected histo-spectrographically in the renal cortex and the liver, but in later stages tends to pass the cerebral cortex and base; if the MnO_2 is then discontinued Mn may also be carried to the lung and testicle.

R. N. C.

Influence of phosphorus poisoning on the synthesis of mentholglycuronic acid. B. NAZARJANZ (Ber. Ukrain. Biochem. Inst., 1928, 3, 159—165).—A diminution in the spontaneous excretion of glycuronic acid during P poisoning depends on the diminution in the food intake. P poisoning, if accompanied by pathological changes in the liver, is accompanied by a diminution in the synthesis of mentholglycuronic acid.

F. A. A.

Influence of phosphorus poisoning on the creatinephosphoric acid, lactacidogen, and creatine content of red and white muscle. A.

PALLADIN and A. KUDRJAVZEVA (Ber. Ukrain. Biochem. Inst., 1928, 3, 57—63; cf. A., 1924, i, 915).—Poisoning with large doses of P leads to an increase of creatinephosphoric acid (I) and creatine (II), and a decrease in lactacidogen in red and white muscle. The increase in (I) is much greater in red than in white muscle. The % of (II) combined with H_3PO_4 is increased, and the increase is greater in red than in white muscle. Poisoning with small doses of P leads to increase of (I) and of bound (II) in red muscle, but the (I) content of white muscle remains normal.

F. A. A.

Treatment of poisoning due to inhalation of hydrocyanic acid. W. WIRTH (Arch. exp. Path. Pharm., 1935, 179, 558—602).—S compounds (e.g., $Na_2S_2O_3$, $Na_2S_4O_6$), some heavy metals (Ni and Co and a few Fe salts), methæmoglobin-producing substances (e.g., $NaNO_2$), aldo- and keto-derivatives (e.g., glucose and dihydroxyacetone), and alkali carbonates are efficacious, the prophylactic activity being > the curative power. Characteristic changes in blood-[H⁺] occur in rabbits after inhalation of HCN.

F. O. H.

Effects of inhalation of hydrogen fluoride. II. Response following exposure to low concentration. W. MACHLE and K. KITZMILLER. III. Fluorine storage following exposure to sublethal concentrations. W. MACHLE and E. W. SCOTT (J. Ind. Hyg., 1935, 17, 223—229, 230—240).—II. A concn. of 0.0152 mg. per litre, although slightly irritating, was tolerated by guinea-pigs, but growth-rate was somewhat slower than usual. The erythrocyte count was decreased and lesions, similar to but less severe than those observed with higher concns., developed.

III. Normal rabbits contain 10 mg. of F per kg., but this may be increased as much as 10-fold by exposure to sublethal concns. of HF. The bulk of the F is stored in the bones, but it is found in all other tissues except the blood, fat, and liver.

H. G. R.

Action of nitrites on the intestine. F. BERNHEIM (Arch. int. Pharmacodyn. Therap., 1934, 48, 91—96; Chem. Zentr., 1934, ii, 3275).— $MeNO_2$ and $EtNO_2$ relax guinea-pigs' intestines, $MeNO_2$ being 5—10 times more active.

R. N. C.

Nitric oxide and toxicity of nitrous gases. G. PFLESSER (Arch. exp. Path. Pharm., 1935, 179, 545—557).—Exposure of mice to NO +air in an apparatus such that oxidation is retarded indicates that NO is more toxic than equiv. concns. of other N oxides. Thus max. concns. tolerated are 0.03% for NO and 0.12% for NO_2 , whilst the respective toxic symptoms are markedly different. The results are correlated with the toxicity of mixed nitrous gases.

F. O. H.

Toxicity of concentrated salt solutions. F. LASCH and D. ROLLER (Arch. exp. Path. Pharm., 1935, 179, 459—464).—Intravenous injection of hypertonic (20—30%) aq. Na or Li sulphate, tartrate, H phosphate, citrate, or chloride has a lethal action, producing tetanic convulsions, respiratory and circulatory failure, and finally pulmonary œdema, due to disturbances of ionic equilibrium of the blood. Follow-

ing such treatment, intravenous injection of org. Ca before the onset of œdema alleviates or inhibits the toxicity.

F. O. H.

Effect of sodium hydrogen carbonate on glycæmia from pilocarpine and from ligature of the portal vein. V. PAPILIAN and V. PREDA (Compt. rend. Soc. Biol., 1935, 120, 58—60).— $NaHCO_3$ inhibits the hyperglycæmia produced by ligature of the portal vein, by mobilising glycogen in the liver. It has no effect on hyperglycæmia produced by pilocarpine.

R. N. C.

Effect of radium rays on living cells. C. S. GAGER (Science, 1935, 82, 327).—A discussion.

L. S. T.

Action of radium on glycolytic activity of neoplastic tissues. C. GRANDCLAUDE, M. POLO-NOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 183—184).—Ra irradiation disturbs carbohydrate metabolism in tumours; glycolytic activity in the neoplastic tissues is depressed.

R. N. C.

Effects of rare earths on the polarisation capacity of frog's skin and their significance in relation to colloidal chemistry and permeability. K. YOMOGITA (Z. Biol., 1935, 96, 487—501).—The salts of certain tervalent rare earths in low concns. (0.001—0.0005M) irreversibly decrease the polarisation capacity of surviving frog-skin, but in higher concns. (0.0025—0.0015M) they produce only a reversible reduction, whilst in still higher concns. the effect is again irreversible. The results are considered in relation to the action of positively charged multivalent cations on the negatively charged cell colloids.

W. O. K.

Influence of functional changes in the auditory centres on proteolysis. S. FOMIN (Ber. Ukrain. Biochem. Inst., 1928, 3, 143—146).—A lessening of auditory stimulation is accompanied by a retardation of proteolysis in the auditory centres, and the ratio of residual N to total N is less in the experimental animals (young dogs) than in controls.

F. A. A.

Liberation of histamine-like substances by excitation of the peripheral end of the splanchnic nerve: hæmorrhagic lesions of the intestine by intra-arterial injections of histamine. G. UNGAR, X. J. CONTADES, and A. GROSSIORD (Compt. rend. Soc. Biol., 1935, 120, 328—330).—Splanchnic excitation in one dog causes increase of gastric secretion in another animal cross-circulated with it, hæmorrhagic lesions occurring in the intestine of the former animal. Injection of histamine in the afferent artery of an intestinal loop produces similar lesions.

R. N. C.

Delayed effects of denervation of the adrenal gland on adrenaline secretion. J. A. SGROSSO (Compt. rend. Soc. Biol., 1935, 120, 270—272).—Electric excitation of the recently denervated adrenal of the dog provokes a discharge of adrenaline (I), which does not occur 2—3 months after denervation. (I) discharge is also provoked from the recently denervated gland by nicotine, coniine, or candicine iodide (II), but the response decreases with the passage of time. The response to (II) is increased

by previous electric excitation, but is unaffected by yohimbine. R. N. C.

Displacement of ions in electrolytes during the very short discharges employed in electrophysiology. P. FABRE (Compt. rend. Soc. Biol., 1935, 120, 23—26).—The inertia factor involved in the displacement of ions by ordinary shocks of 10^{-4} sec. duration does not appear in shocks of 10^{-6} sec. duration. R. N. C.

Determination of [the concentration of] enzymes. B. RUBIN and L. NAUMOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 83—86).—An investigation of difficulties that arise in extracting completely and in determining the concns. of enzymes. J. L. D.

Spectroscopy of an enzyme reaction.—See this vol., 1189.

Embryo-chemistry of amphibia. VII. Enzymes in eggs of giant salamander. I. TAKAHASHI (J. Biochem. Japan, 1935, 22, 45—47).—After 2—3 weeks' development, the embryos contain amylase, nuclease, and glycerophosphatase, but not esterase, trypsin, arginase, or urease. F. O. H.

Action of hydrogen cyanide on the oxidase of *Althaea rosea*. V. ZANOTTI (Boll. Chim. farm., 1935, 74, 669—670).—Exposure to gaseous HCN temporarily inhibits the oxidase activity of *A. rosea* leaves. F. O. H.

Influence of reduced glutathione and ascorbic acid on the destruction of adrenaline by the oxidising enzymes of the potato. J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 45—48).—Asparagine, alanine, glycine, and leucine inhibit the spontaneous oxidation of adrenaline (I) in decreasing order of activity, but have no effect on the oxidation of (I) by potato juice. This oxidation is inhibited by ascorbic acid and by reduced, but not by oxidised, glutathione. R. N. C.

Spectroscopy of purified enzymes. I. Xanthine oxidase and catalase. R. ITOH (J. Biochem. Japan, 1935, 22, 139—148).—Purified xanthine oxidase (from milk) has an absorption max. at 279 $m\mu$ at p_H 7; with increased alkalinity the val. shifts to a longer λ . Liver- and blood-catalase have max. at 406 and 266 $m\mu$ and haemin one at 406 $m\mu$. The activity of these catalases is not related to flavins, traces of which occur even in highly purified preps. F. O. H.

Catalase in embryonic development. III. Catalase activity during growth period of *Salmo irideus* and *Esox lucius* embryos. U. SAMMARTINO (Arch. Farm. sperim., 1935, 60, 372—385).—Fertilised eggs of *S. irideus* exhibit a continuous increase in catalase activity after approx. 12 days' incubation; this increase is associated with the initiation of blood circulation and general growth of the embryo. Similar phenomena occur in *E. lucius*, in which catalase activity begins to increase on the 5th day. F. O. H.

Influence of training [by electrical stimulation] and fatigue on the catalase of muscle. A. V. PALLADIN and E. J. RASCHBA (Ukrain. Biochem. J., 1935, 7, No. 2, 5—18).—Training increased the cata-

lase content of rabbit muscle, whilst fatigue caused no essential change, but on the earlier trained muscle it increased the catalase activity. Experiments with glutathione showed that after training the conditions for oxidation-reduction processes in muscle were improved. J. N. A.

Ascorbic acid and blood-catalase. II. Demonstration of vitamin-C deficiency. G. TÖROK and L. NEUFELD (Klin. Woch., 1934, 13, 1816—1818).—Injection of ascorbic acid increases the catalase action of blood in cases of known vitamin-C deficiency; it has no similar effect on normal cases. By this method, latent -C deficiency, with no clinical symptoms, can be recognised. G. H. F.

Dilatometric studies in the enzymic hydrolysis of polysaccharides. III. Hydrolysis of starch, amylose, and amylopectin by taka-diastase. H. B. SREERANGACHAR (Proc. Indian Acad. Sci., 1935, 2, B, 333—341; cf. this vol., 250).—When sol. starch is hydrolysed by takadiastase, the dilatometric depression per millimol. of maltose liberated is 4.0, whilst the depression per 1° fall in α is 10.7. For potato starch and two amylopectin (I) preps., the respective vals. are 4.0, 3.6, and 3.7 per millimol. of maltose and 10.7 [for one of the (I) preps.] per 1° fall in α . F. O. H.

Taka-amylase. IV. Effect of alcohol and salts on amylase and maltase action. V. Changes in amylase and maltase activities of a taka-diastase solution on keeping. VI. Proportion of amylase and maltase in taka-diastase on purification. T. KITANO (J. Soc. Chem. Ind. Japan, 1935, 38, 447B, 447—449B, 449—450B).—IV. Maltase (I) activity of a taka-diastase (II) solution is largely inhibited by 40% EtOH, but amylase (III) inhibition is slight. No such preferential inhibition is obtained with 25% NaCl.

V. The (I) of a (II) solution is more thermolabile than the (III). Acid destroys both enzymes to about the same extent, but alkali destroys (III) more rapidly than (I).

VI. In the fractional pptn. of (II) with EtOH, the first fractions are richer in (III), and the later richer in (I). Dialysis, especially after keeping, causes a greater decrease in (I) than in (III).

E. A. H. R.

Salt activation. II. Influence of salts on the stability of amylase. K. V. GRI (J. Indian Chem. Soc., 1935, 12, 567—574; cf. this vol., 1162).—The alteration of the rate of hydrolysis of starch by the amylase of sweet potato is due to stabilisation or sensitisation of the enzyme by the added salt. At $p_H < 6$ (the optimum) 0.05N-NaCl increases the stability; at p_H 6 it is without effect. Higher salt concns. decrease the stability. The following orders of efficiency are found: $\text{NaF} > \text{NaCl} > \text{Na}_2\text{SO}_4 > \text{NaNO}_3$; $\text{CaCl}_2 > \text{NaCl} > \text{KCl} > \text{LiCl}$. R. S. C.

Action of different amylases on starch. E. OHLSSON and O. ROSEN (Svensk farm. Tidskr., 1934, 38, 497—552; Chem. Zentr., 1935, i, 1402).—The activities of taka-diastase, amylase from ungerminated barley, and amylase from green malt are compared. Differences in the activity curves

for the two malt amylases were apparent under all experimental conditions (A., 1932, 303). Ungerminated barley and saccharogen-amylase, as prepared by the authors, contain small proportions of dextrinogen-amylase. A. G. P.

Direct and quantitative study of amylolytic activity of amylases. M. L. CALDWELL and F. C. HILDEBRAND (J. Biol. Chem., 1935, 111, 411—420).—An accurate method for the measurement of amylase activity depends on the determination of residual starch or amylose (I) at any stage of its hydrolysis by various amylases through its quant. pptn. by EtOH. Under specified conditions the ppts. are not appreciably contaminated by dextrans or maltose, and the difference between the wts. of original (I) and pptd. (I) gives a measure of the amylolytic activity of the amylase. J. N. A.

Blood-amylase response to acetylcholine and its modification by eserine and atropine. W. ANTROPOL, A. SCHIFRIN, and L. TUCHMAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 383—385).—Blood-amylase is increased by intramuscular administration of acetylcholine. The response is increased by previous administration of eserine and inhibited by atropine. R. N. C.

Emulsin. XXIII. Influence of substitution in the benzene nucleus on the enzymic fission of phenol- β -*d*-glucosides. II. B. HELFERICH and C. P. BURT (Annalen, 1935, 520, 156—163; cf. this vol. 964).—Guaiacol with tetra-acetylglucosidyl bromide and NaOH-aq. COME₂ affords the Ac₄ derivative, m.p. 155—157°, [α]_D²⁰ —30.2° in CHCl₃, of *guaiacol- β -*d*-glucoside* (I), m.p. 155.5—157.5°, [α]_D²⁰ —66.8° in H₂O, obtained by deacetylation with NaOMe-MeOH. By similar methods are obtained *isoeugenol- β -*d*-glucoside* (II), m.p. 187.5—189.5°, [α]_D²⁰ —60.0° in EtOH (Ac₄ derivative, m.p. 140—143°, [α]_D²⁰ —24.8° in CHCl₃), and the 3-CH₂Ph ether, m.p. 165—168°, [α]_D²⁰ —60.20° in EtOH, of *protocatechualdehyde-4- β -*d*-glucoside* (III). The Ac₄ derivative of (III) with tetra-acetylgalactosidyl bromide-NaOH-aq. COME₂, and deacetylation of the Ac₄ derivative gives *protocatechualdehyde-4- β -*d*-glucoside-3- β -*d*-galactoside*+H₂O, [α]_D²⁰ —100.5° in H₂O, hydrolysed by emulsin, at p_H 5.0, more slowly than the corresponding β -*d*-diglucoside (*loc. cit.*). (I) (*p*-position free) and (II) (C:C in *p*-position) are both attacked more slowly by emulsin than is vanillin- β -*d*-glucoside (*p*-CHO). J. W. B.

Inactivation and regeneration of the glycolytic enzyme system of muscle extract. L. MICHAELIS and J. RUNNSTRÖM (Proc. Soc. Exp. Biol. Med., 1934, 32, 343—349).—The glycolytic enzyme (I) of muscle extract, after inactivation by exposure to O₂, can be reactivated to a degree > the original activity by thioglycollic acid, thus corroborating the oxidation-reduction reversible inactivation hypothesis. There is evidence that (I) contains ·SH. R. N. C.

Mechanism of glyoxalase activation by glutathione. J. GIRŠAVIČIUS and P. A. HEYFETZ (Nature, 1935, 136, 645—646; cf. this vol., 476).—The compound formed between glutathione (I) and

AcCHO (II) is regarded as the true substrate of glyoxalase action. From the rate at which lactic acid is produced and the changes in free ·SH which occur in the reaction between (I) and (II), it is concluded that (I) first combines by means of its ·SH with the substrate, (II), and then, as the enzyme-catalysed reaction develops, enters into further transformations in which its ·SH is again involved. L. S. T.

Inactivation of fumarase. K. P. JACOBSON and J. TAPADINHAS (Compt. rend. Soc. Biol., 1935, 120, 36—38).—The inactivation of fumarase (I) by Ag⁺ depends on the time of incubation; (I) is completely inactivated in 6 hr. but a reactivation occurs in 24 hr. (I) in fresh liver extract is more resistant to Ag⁺ than in old extracts. R. N. C.

Influence of different diets on the enzymes of the organism. IV. Fasting and the enzymes of the tissues. B. GOLDSTEIN and K. I. KATKOVA. **V. Protein-free food and the enzymes of blood and tissues.** B. GOLDSTEIN, R. R. SIGALOVA, and V. D. MELNISHENKO (Ukrain. Biochem. J., 1935, 7, No. 2, 91—101, 103—129).—IV. In starving rabbits there is no alteration in the lipase (I) of liver, kidney, and lung. The wt. of the liver decreases rapidly, due to a decrease in the total quantity of tissue, and this simultaneously produces a decrease in the blood-(I). The amylase of the liver is not affected.

V. Rabbits fed on a protein-free diet live 1.5—2 months. There is no alteration in the amylase of the blood and liver, or in the (I) of the lung. There is a very small increase of (I) in the liver, and a marked increase in the kidney. Sometimes there is an increase of (I) in the blood. J. N. A.

Thyroid gland, lipase, and catalase. E. KEESER (Arch. exp. Path. Pharm., 1935, 179, 310—318).—Liver-lipase is inhibited *in vitro* by thyroxine (I), thyroid extracts, thyronine (II), di-iodotyrosine (III), and extracts of blood, brain, liver, spleen, and anterior and posterior pituitary lobes. The inhibition by (I) is suppressed by the anti-thyroid factor from thyroidectomised animal's serum. Blood- and organ-catalase *in vitro* are activated by thyroid and anterior pituitary preps. and inhibited by (III), KI, and anti-thyroid factor, whilst (I), (II), iodo-dihydroxypropane (IV), and glutathione (V) are without action. The catalytic activity of thyroid gland sections is enhanced by (IV) and (V) and inhibited by (III), NH₄SCN, and quinol. The mechanism of these and allied phenomena is discussed. F. O. H.

Choline-esterase in invertebrates. Z. M. BACQ (Compt. rend. Soc. Biol., 1935, 120, 247—248).—Choline-esterase is present in the blood and tissues of molluscs, the blood of *Sipunculus*, and the muscles of *Spirographis*, *Holothuria*, and *Ascidia*. It is absent from crustacean blood and tissues, ascidian and insect blood, and beetle and sponge tissues. Crustacean muscles are insensible to acetylcholine, which disappears rapidly on injection without being fixed by the tissues. R. N. C.

Cholesterol esterase in blood. W. M. SPERRY (J. Biol. Chem., 1935, 111, 467—478).—When serum or heparinised human plasma is incubated at 37—40°,

the ratio of combined to total cholesterol (I) increases several fold. Heating to 55–60° destroys this effect, attributed to an enzyme having an optimum at p_H 8. The free (I) of red blood-cells is not esterified under these conditions, and the esterification is less in haemolysed whole blood. F. A. A.

Tyrosine-tyrosinase reaction in presence of *l*-ascorbic acid. F. SCHAFF (Helv. Chim. Acta, 1935, 18, 1017–1021).—In spite of the presence of *l*-ascorbic acid (I) the typical tyrosinase (II) reaction (introduction of a second OH in the mol.) can proceed unchecked under the influence of (II); the solution remains colourless, although frequently saturated with O_2 , but the presence of appreciable amounts of 3 : 4-dihydroxyphenylalanine (III) is soon detected by $FeCl_3$. Restriction of oxidation by (I) takes place only when the change does not require further aid from (II) and there is no evidence of direct influence of (I) on the actual (II) action. (III) is also produced from tyrosine in presence of (I), but in much smaller amount than when (II) is present. H. W.

Antityrosinase function of glutathione *in vitro*. F. CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 73–74).—0.5% of glutathione completely inhibits tyrosinase reactions *in vitro*. H. G. R.

Occurrence of arginase in the giant salamander. T. KUMON (J. Biochem. Japan, 1935, 22, 41–43).—*In-vitro* experiments in PO_4''' buffer at p_H 6.6 indicate a high arginase content in the liver, smaller amounts in the kidney, blood, and spleen, and its absence from the pancreas, heart, and skeletal muscle. F. O. H.

Affinity relations of animal and vegetable dipeptidases. W. GRASSMANN, L. KLENK, and T. PETERS-MAYR (Biochem. Z., 1935, 280, 307–324).—Animal (kidney) and vegetable (yeast) dipeptidases do not differ as regards their affinities for dipeptides. The affinity for leucylglycine is 10 times that for alanylglycine (I) and the affinity for (I) is 4–9 times that for glycylglycine (II), whilst the affinity for glycyl-leucine is > that for glycyl-alanine (III) and that for (III) is > that for (II), although, in the second series, the differences are less pronounced. Regularities are also observed in the variation of the degree of restriction of the dipeptidases by NH_2 -acids, which then form the series leucine > valine (IV) > alanine (V) > glycine. Glutamic acid has no restrictive power, but phenyl-alanine and tryptophan are powerful inhibitors, and proline, asparagine, and arginine have effects intermediate between those of (IV) and (V). Glycyl-aminobenzoic acids (VI) are slightly attacked by dipeptidases practically free from aminopolypeptidase (from yeast) and much more attacked by non-purified liver extracts of about the same dipeptidase content. The enzymic hydrolysis of (VI) is affected by H_2S much < is that of ordinary dipeptides. As regards enzymic hydrolysis (VI) do not differ qualitatively (cf. Balls *et al.*, A., 1931, 392).

W. McC.

Behaviour of pepsin in the ultracentrifuge after alkaline inactivation. J. ST. L. PHILPOT (Biochem. J., 1935, 29, 2458–2464).—The sediment-

ation const. (*s*) of pepsin (I) brought to p_H < 7 falls by about 1/3, although the (I) remains homogeneous. Reduction of the p_H of such a prep. to < 4.8 is accompanied by a large rise in *s*, and loss of homogeneity, three distinct components being present having *s* 10, 20, and 25 times that of normal (I). Thus alkali-inactivated (I) is unlike denatured proteins in being homogeneous, but has undergone some change which makes it more readily denatured by acid. F. A. A.

Cathepsin of tissues. B. GOLDSTEIN (Ukrain. Biochem. J., 1935, 8, No. 1, 87–104).— H_2S , used as activator for cathepsin (I), sometimes restricts its activity. A weak activation or inhibition but not a strong inhibition is converted into a strong activation by dilution. E. P.

Cathepsin in the embryo and in maternal tissues. I. B. GOLDSTEIN and E. J. MILGRAM (Ukrain. Biochem. J., 1935, 8, No. 1, 139–168).—The difference between the amounts of activated (I) and non-activated (II) cathepsin increases in the maternal organs during (and possibly parallel with) the growth of the embryo. In the placenta the val. of (II) is very low; the difference between the amount of (I) and (II) is very great in rat's, less in rabbit's and guinea-pig's, and very low in human placenta. The concn. of (I) and (II) in the embryo is low and increases with the growth. After birth the concn. increases, being > in the corresponding maternal organs. After reaching a max. it falls to the normal val. The difference between the amounts of (I) and (II) increases rapidly. Thus the protein metabolism of the embryo is controlled by the maternal organs and by the placenta. The difference between the amounts of (I) and (II) increases parallel with the synthetic action. E. P.

Proteinases and proteolytic processes of muscle tissues. I. Activity of muscle proteinases on qualitatively different protein diets. S. FOMIN and M. MISCHKIS (Ukrain. Biochem. J., 1935, 7, Nos. 3–4, 135–145).—The activity of the muscle proteinases of rats is increased by incomplete diets of beans or gelatin. H. D.

Proteinases and proteolytic processes in muscle. II. Activity of muscle proteinases of the dog's leg after training. S. V. FOMIN and V. I. DEMIN (Ukrain. Biochem. J., 1935, 8, No. 1, 73–85).—The activity of the muscle proteinases in the weighted hind leg of a dog was increased > in the other leg, due to increased oxidation. E. P.

Tissue proteinases in organs of animals in different stages of phylogenetic evolution. B. GOLDSTEIN and E. J. MILGRAM (Ukrain. Biochem. J., 1935, 8, No. 1, 105–138).—As regards concn. of cathepsin (I), the organs form the series: kidney > liver > spleen > muscle; and the animals the series: rat, frog, pigeon > dog, cat, hen, rabbit, guinea-pig > cow. The concn. of (I) is possibly related to the intensity of the metabolism, which decreases as body-wt. increases. With mammals kidney-(I) is strongly activated, but liver-(I) is slightly inhibited or slightly activated by H_2S . With amphibia, H_2S has no action or restricts slightly the activity of liver-(I), but activates kidney-(I) slightly. With

birds H_2S strongly restricts the activity of kidney-(I) and slightly that of liver-(I). The different actions of H_2S on kidney extracts are possibly due to the different end-products of protein metabolism with mammals and birds. With mammals H_2S activates spleen-(I); with frogs it greatly restricts its activity.

E. P.

Intracellular proteinases. XVI. Activation and inhibition of papain. E. MASCHMANN and E. HELMERT. **XVII. Effect of arsenic compounds on the activity of liver-cathepsin.** E. MASCHMANN (Biochem. Z., 1935, 280, 184—203, 204—212; cf. this vol., 1279).—XVI. Papain, if activated as much as possible by a $\cdot\text{SH}$ compound [cysteine (I), reduced glutathione (II)], is further activated by certain substances [e.g., citric acid, malic acid (III), AcCO_2H , $\text{K}_4\text{Fe}(\text{CN})_6$] which sometimes have sp. effects. O_2 and a heavy metal are also involved. Very small amounts of (I) [but not of reduced (II)] inhibit and even irreversibly inactivate papain with disappearance of (I). For activation (I), (II), or O_2 and heavy metal can be replaced or (when these are present in insufficient quantity) strengthened by Fe^{II} in complex combination [but not by $\text{K}_4\text{Fe}(\text{CN})_6$] if certain substances [e.g., ascorbic acid (IV), (III), tartaric acid, but not lactic or glycollic acid or AcCO_2H] which bind Fe are present. Fe^{II} in complex combination can be partly replaced by (IV). No part is played by any (I)—Fe compound. Results differ according to the type of buffer (acetate, citrate) used.

XVII. The degradation of gelatin (V) (at p_{H} 4) and clupein (VI) (p_{H} 5) by liver-cathepsin (pig) is usually inhibited by As compounds (15 tested), although occasionally slight activation or no action results. The degradation of (VI) is sometimes unaffected by compounds which check that of (V).

W. McC.

Activation of the proteolytic enzymogen system of the ventricle. R. EGE and J. OBEL (Biochem. Z., 1935, 280, 265—275; cf. A., 1934, 450).—Neutral or slightly acid extracts of the mucous membrane of the stomach (man, dog, pig, ox, cod) contain small amounts of preformed enzymes capable of coagulating milk. Activation of the enzymes sets in at $p_{\text{H}} < 5$ and the rate increases as $[\text{H}^+]$ increases, the degree of acceleration varying from species to species of animal. There is no relation between dependence of the rate on $[\text{H}^+]$ and the ratio pepsin:rennin. At alkaline reaction the stability of the enzymogen is in all cases $>$ that of the activated enzymes.

W. McC.

Initial phosphorylations of glycogen. J. K. PARNAS and T. BARANOWSKI (Compt. rend. Soc. Biol., 1935, 120, 307—310).—In the hydrolysis of adenosinetriphosphoric acid (I) by muscle pulp in presence of glycogen (II), the liberated $\text{PO}_4^{\text{'''}}$ preferably esterifies (II), but a certain quantity forms free H_3PO_4 . The amounts of hydrolysis and esterification increase with dilution and (II) concn. The enzymes of muscle extract transform (I) into inosinic acid, and rapidly hydrolyse (II) in presence of $\text{PO}_4^{\text{'''}}$, forming the Robison-Embsden hexose monophosphoric ester. (I) and (II) in absence of free $\text{PO}_4^{\text{'''}}$ are

transformed into the Harden-Young fructose di-phosphoric ester. $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ does not affect this reaction. Both reactions proceed independently if (I), (II), and $\text{PO}_4^{\text{'''}}$ are all added to the extract.

R. N. C.

Action of ultra-violet light on yeast-invertase. VI. The activating zone. G. GORBACH and H. RUESS (Biochem. Z., 1935, 280, 213—216; cf. A., 1934, 1033).—It is light of λ 365—366 $\text{m}\mu$ which directly activates the invertase (I) of yeast autolysates and dialysates on short irradiation. There is no connexion between the activation and the light blue fluorescence of the (I) solutions.

W. McC.

Preservation and the rate of respiration of yeasts. F. CHODAT and A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 74—76).—The ageing of yeast is much slower at 6° than at 25° . In 48 hr. at 25° the respiratory activity is reduced by 50%.

H. G. R.

Assimilation by yeast of high and low mol. wt. nitrogen compounds. N. NIELSEN (Compt. rend. Lab. Carlsberg, 1935, 21, No. 6, 139—150; cf. A., 1934, 1034).—The N compounds of wort can be separated by dialysis into fractions of low and high mol. wt., the former of which is much the more readily assimilated by yeast.

E. A. H. R.

Action of glutathione on cytochrome-C *in vitro*. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, 120, 69—72).—Glutathione (I) rapidly reduces cytochrome-C (II) *in vitro* in neutral solution. Reduced (I) is responsible for keeping (II) in its reduced form in boiled yeast, in plasmolysis of which it is released in large quantities.

R. N. C.

Reaction chain of alcoholic fermentation. O. MEYERHOF (Helv. Chim. Acta, 1935, 18, 1030—1052).—A lecture.

H. W.

Chemical actions taking place in the fermentation (organic) cell. M. C. POTTER (Zentr. Bakt. Par., 1935, II, 93, Reprint. 11 pp.).—During yeast fermentation of 1 mol. of sucrose, approx. 8 coulombs of energy are liberated. The e.m.f. of a fermenting cell depends on the chemical reactions involved, and is developed in open or closed circuit. The electricity liberated is independent of the p_{H} of the medium if this does not restrict the activity of the organism.

A. G. P.

Kinetics of alcoholic fermentation of sugars by brewer's yeast. III. Temperature coefficients of the rates of fermentation of glucose and fructose. R. H. HOPKINS and R. H. ROBERTS (Biochem. J., 1935, 29, 2486—2490).—The method of Hopkins (this vol., 661) was used. The temp. coeff. of fermentation of glucose by yeast is independent of concn. between 0.25 and 5.0%, varying between 2.0 and 1.24 between 15° and 35° . With fructose (I) the temp. coeff. decreases at concns. $< 1\%$. Below 0.25% concn. the temp. coeff. agrees with that for the mutarotation of β -(2:6)-fructose, and it is concluded that the enzyme attacks only one form of (I), and the rate of conversion into this form determines the rate of fermentation at low concns.

H. D.

Mechanism of oxidation processes. XLII. Decomposition of citric acid by yeast. H. WIE-

LAND and R. SONDERHOFF (Annalen, 1935, 520, 150—156).—Contrary to the earlier statement (A., 1933, 865) gaseous H_2 (3 mols.) is evolved in the anaerobic fermentation of citric acid (I) by "impoverished" yeast (II). Since no H_2 is obtained with (II) alone, whereas HCO_2Na and (II) give H_2 , it is assumed that the H_2 is produced from the HCO_2H first split off from (I). A little $MeCHO$ (but no $COMe_2$) was detected as its 2:4-dinitrophenylhydrazone; 70% decomp. in accordance with the equation given (*loc. cit.*) is thus observed. Since (II) is unable to decompose $CO(CH_2CO_2H)_2$ (III) into CO_2 and $2AcOH$, it is suggested that, in the anaerobic decomp. of (I), fission of HCO_2H affords the keto-form of (III) which decomposes $AcOH + CH_2(CO_2H)_2$, followed by $CH_2(CO_2H)_2 \rightarrow AcOH + CO_2$. In agreement, it is shown that $CH_2(CO_2H)_2$ is decarboxylated by (II) at p_H 7.0. The aerobic decomp. of (I) with (II) begins more rapidly than the anaerobic reaction, and the initial stage is probably the dehydrogenation $(CO_2H \cdot CH_2)_2C(OH) \cdot CO_2H - 2H + O \rightarrow CO(CH_2CO_2H)_2 + CO_2 + H_2O$. The velocity of dehydrogenation of (I) by methylene-blue in presence of (II) is reduced as (I) is replaced by HCO_2H .

Action of organic substances on alcoholic fermentation. V. FOLLICULIN. A. MOSSINI (L'Ind. Chimica, 1935, 17, 524—526; cf. A., 1934, 1261).—The evolution of CO_2 during alcoholic fermentation is increasingly accelerated in presence of amounts of folliculin rising from 0.00005 to 0.05 mg. %. When the fermentation slackens owing to decrease in the amount of sugar present, addition of fresh sugar is followed by increased gas evolution. Degenerated yeast also responds to the stimulating effect of folliculin. T. H. P.

Pseudo growth-factors of grape must. A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 172—178).—A feebly acidic substance which inhibits yeast growth is formed by sterilisation of must at 110° . H. G. R.

Effects of 2:4-dinitrophenol on respiration of commercial cake yeast. J. FIELD, jun., A. W. MARTIN, and S. M. FIELD (Proc. Soc. Exp. Biol. Med., 1935, 32, 1043—1046; cf. A., 1934, 1262).—The total concn. of 2:4- $C_6H_3(NO_2)_2 \cdot OH$ (I) causing optimal stimulation of yeast respiration $\propto p_H$, but the concn. of undissociated (I) is const. for a wide p_H range. Any fixed (I) concn. may stimulate respiration at one p_H and inhibit it at another. Reduction of p_H to a sufficient extent in a suspension of yeast cells in liquid containing (I) suspends respiration immediately. The results suggest that the active agent in stimulating respiration is undissociated (I). R. N. C.

Inhibitory action of the lower aliphatic acids and aldehydes on cytochrome reduction in yeast. L. V. BECK (Biochem. J., 1935, 29, 2424—2432).—Marked inhibition is shown by fatty acids (concn. 0.01M), less by the corresponding aldehydes, and none by the alcohols or urethanes. HCO_2H and CH_2O act differently from the other members of the series. Strong acids have a small action. The Na salts

diminish the inhibiting action of their acids. All inhibitions are reversible on addition of glucose.

F. A. A.

Effects of certain organic acids and protein derivatives on the growth of *Colpidium*. A. M. ELLIOTT (Arch. Protistenk., 1935, 84, 472—494).—Single NH_2 -acids were unsatisfactory N sources for *C. striatum* and *C. campylum*, but proteins and their products of partial hydrolysis were suitable. Among peptones examined those containing high proportions of NH_2 -acids and NH_2-N (Van Slyke) were the more effective. Relationships exist between p_H , growth, and the nature of the N source utilised. The Na salts of the 5 lower fatty acids and Na citrate were toxic at p_H 5.8, whereas glycollate, pyruvate, and tartrate were only moderately toxic. Growth of *C. striatum* was accelerated by $NaOAc$ at p_H 6.5—7.5 and that of *C. campylum* at p_H 7.0. $PrCO_2Na$ accelerated growth of both species at $p_H > 7.0$. A. G. P.

Effect of certain carbohydrates and organic acids on growth of *Chlorogonium* and *Chilomonas*. J. B. LOEFER (Arch. Protistenk., 1935, 84, 456—471).—Greatest acceleration of growth of *Chlorogonium euchlorum* was produced by fructose (I), galactose (II), maltose (III), and lactose (IV), less by glucose (V), arabinose (VI), xylose (VII), and rhamnose (VIII); negative effects were obtained with sucrose (IX), starch (X), and dextrin (XI). *C. elongatum* was similarly affected except that (IV) proved a poor source of C. The order of efficiency with *Chilomonas* was (XI) > (I), (IV), (II), (III) > (VI), (V), (IX), (VII), whereas (VIII) and (X) were inactive. The growth of *Chilomonas* was accelerated by fatty acid salts in the descending order $AcOH$, Pr^oCO_2H , $BuCO_2H$, $EtCO_2H$, Pr^sCO_2H . Negative results were obtained with hexoate. The two species of *Chlorogonium* were affected similarly, except that $EtCO_2H$ produced no effect. A. G. P.

Colloidal changes indicated by experiments on *Paramecia* as the basis of sympathetic nervous processes. T. WENSE (Arch. exp. Path. Pharm., 1935, 179, 475—482).—In their influence on vacuole pulsations, chemotaxis, protoplasmic viscosity, and rate of movement of *Paramecia*, choline (I) and pilocarpine show a marked antagonism to adrenaline (II). The action of (I) is inhibited by atropine and curare. K and Ca resemble (I) and (II), respectively. These phenomena indicate a colloid-chemical basis for the transmission of sympathetic nerve stimuli. F. O. H.

Biological action of rays from radioactive substances. I. Effect of small dose radiation on the reproductive activity of a unicellular organism. Y. KIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 27—47).—Irradiation of *Paramecium caudatum* with β - and γ -radiation from pitchblende, monazite, and a U-X prep. caused an increased rate of reproduction, the γ -rays being mainly responsible. No concomitant pathological effects on the organism were produced. A. L.

Mode of action of chemotherapeutically-used dyes. V. FISCHL and E. SINGER (Z. Hyg. Infektionskrankh., 1934, 116, 348—355; Chem. Zentr., 1934,

ii, 3276).—*T. nagana* absorbs both trypanflavin (I) and atebirin (II), but only (I) is trypanocidal. The fluorescence intensity produced by (II) is exceedingly small. Immobilisation by light is not obtained with fluorescent dyes other than (I). The therapeutic effect of (I) is not related to its photodynamic property. (II) has an affinity for malaria plasmodia, whilst (I) is absorbed by certain development forms of the parasite. R. N. C.

Superiority of silver nitrate over mercuric chloride for surface sterilisation in the isolation of *Ophiobolus graminis*, Sacc. F. R. DAVIES (Canad. J. Res., 1935, 13, C, 168—173).—The organism was isolated more readily from plant tissue treated with AgNO_3 than from that sterilised with HgCl_2 . A. G. P.

Reversible heat-activation inducing germination and increased respiration in the ascospores of *Neurospora tetrasperma*. D. R. GODDARD (J. Gen. Physiol., 1935, 19, 45—60).—Heat-activated *N. tetrasperma* ascospores may be rendered dormant again by preventing respiration; these dormant spores may be caused to germinate by reheating. Respiration increases after activation and again at the time of germination; these changes also occur in the reversible activation. The heat-activation takes place within the temp. limits 49—52°; heat-killing begins at about 62°. $\text{CH}_3\text{I}\cdot\text{CO}\cdot\text{NH}_2$ inhibits germination without greatly affecting respiration; respiration is diminished by CN' . F. A. A.

Role of vitamin- B_1 in nitrogenous metabolism of *Phycomyces*. W. H. SCHOFFER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 113—115).—The beneficial effect of vitamin- B_1 is limited by the amount of asparagine present in the medium. H. G. R.

Mould sterols. I. Formation of sterols by *Aspergillus niger*. K. BERNHAUER and G. PATZELT (Biochem. Z., 1935, 280, 388—393).—The formation of sterols on solutions of varying sugar content proceeds in general parallel with the formation of mycelium, and on the Ca salts of gluconic and quinic acids is only half that on glucose. The mechanism of sterol formation is discussed. P. W. C.

Optimal conditions for accumulation of citric acid and the mechanism of citric acid formation [by moulds]. T. CHRZASZCZ and E. PEYROS (Biochem. Z., 1935, 280, 325—336).—For optimal yields of citric acid (I), the choice of strain of organism is very important, the initial concn. of sugar should be 20%, the salts should include 0.3% NH_4NO_3 , 0.1% KH_2PO_4 , and 0.1% MgSO_4 and a trace of FeCl_3 , the temp. should be 28—30°, and the duration of fermentation 7—11 days. Zn salts inhibit formation of (I). It is advantageous partly to neutralise the (I) formed with CaCO_3 , but the reaction fluid must be always acidic. The view of Emde (this vol., 407) that (I) is formed from sugar by way of quinic acid cannot be correct since yields of (I) much > theoretically possible by this mechanism have frequently been obtained. P. W. C.

Utilisation of organic acids by *Aspergillus niger*. T. A. BENNET-CLARK and C. J. LA TOUCHE

(New Phytol., 1935, 34, 211—231).—Removal of external sugar supplies from *A. niger* causes a decline in the respiration rate to a low level (starvation rate). Prolonged starvation does not permanently injure the fungus, which recovers when sugar is again supplied. Addition of citric, malic, glycollic, or oxalic acid to starving cultures does not increase the CO_2 output, although the acid disappears rapidly, probably through reduction to OH-aldehyde. A. G. P.

Flavour of shoyu. I. K. SHOJI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 872—877).—The aromatic substances in shoyu, a seasoning material prepared by fermenting koji with *Aspergillus oryzae*, consist of AcOH , BuCO_2H , and hexoic acid, amyl, hexyl, and higher alcohols, aldehydes, ketones, and phenolic compounds, the last-named being the most important. A. L.

Reaction of the medium and the activity of ordinary and preformed felts of an *Aspergillus*. V. BOLCATO (Annali Chim. Appl., 1935, 25, 423—432).—When an *Aspergillus* capable of forming citric (I) and gluconic (II) acids is grown in sucrose solution containing mineral nutrients, (I) is formed when the p_{H} is <, and (II) when it is >, 3.4. Preformed felts, especially if they have had prolonged contact with the culture liquid, form (I) at p_{H} vals. much > 3.4. Formation of (II), however, requires limited conditions, outside of which (I) is formed. T. H. P.

Interconversion of aromatic and hydroaromatic compounds by micro-organisms. II. Quinic acid and inositol. K. BERNHAUER and B. GORLICH (Biochem. Z., 1935, 280, 394—395).—*B. gluconicum*, *B. xylinoides*, and *P. griseofulvum* convert quinic into protocatechuic acid. With these organisms and inositol the formation of aromatic substances could not be detected, the mol. being degraded to AcOH and lactic acid. P. W. C.

Effect of glucose and mineral elements on the growth of *B. pyocyaneus*. J. REGNIER, R. DAVID, and J. MORCHOISNE (Compt. rend. Soc. Biol., 1935, 120, 418—420).—Growth in peptone- H_2O is accelerated by glucose (I) or a mixture of NaCl , KCl , MgSO_4 , and Na nucleate, or by both together. (I) increases NH_3 production. R. N. C.

Effect of the constitution of peptones on the growth of *B. pyocyaneus*. J. RÉGNIER, R. DAVID, and J. MORCHOISNE (Compt. rend. Soc. Biol., 1935, 120, 415—418).—The nutrient vals. of different peptones are of the same order, and are unaffected by dialysis except for mucus peptone, where rate of growth is reduced considerably. Growth is also slow with gelatin peptone. The type of enzyme used for preparing the peptones appears to have no influence on the nutrient val. R. N. C.

Effect of bongkreik acid on carbohydrate metabolism. A. G. VAN VEEN and W. K. MERTENS (Rec. trav. chim., 1935, 54, 373—380, and Geneesk. Tijds. Ned.-Indie, 1935, 75, 1059—1071, 1116—1127).—Bongkreik acid, $\text{C}_{11-13}\text{H}_{16-20}\text{O}_3$, containing OH and three double linkings, is obtained together with toxoflavin (I) (cf. A., 1934, 454, 537) by the action of bongkreik bacteria on coconut. It is optically

active and stable in a fatty medium, but in a pure state is prone to oxidation and polymerisation. Alkaline solutions are more stable. It is extremely toxic to men and apes (lethal dose < 0.5 mg.), being much more virulent than (I), whilst the polymeride is non-toxic and optically inactive. It causes the glycogen content of the liver to disappear rapidly; the blood-sugar at first increases rapidly, but finally falls to the lethal limit. Administration of glucose alone or in conjunction with insulin, or of ergotamine, has no beneficial effect. The lactic acid, NH_2 -acid, inorg. P, and "guanidine" contents of the blood are increased, but the NaCl content is unchanged. Bongkreik poisoning is very similar to that caused by "synthalin" (decamethylenediguanidine), but is much more severe. S. C.

Dehydrogenase of *B. aertrycke* S. and R. E. SORU (Compt. rend. Soc. Biol., 1935, 120, 232—235).—The velocity of decolorisation of methylene-blue by *B. aertrycke* S and R varies with the H donator, and decreases in the order glucose, Na lactate, asparagine, Na succinate, glycerol; glycine does not cause decolorisation. In all cases decolorisation by the S bacillus is more rapid than by the R bacillus. R. N. C.

Respiration of acetone bacteria and bacterial autolysates. O. EHRLSMANN (Z. Hyg., 1934, 116, 490—494; Chem. Zentr., 1935, i, 1887).—The effect of redox indicators on respiratory activity in lactate-oxidising cultures of COMe_2 bacteria is a function of its redox potential. The solubility of the dye, its composition (no. of SO_3H groups), and the electrolyte content of the medium are important factors. The enzyme system indicated by Barron and Hastings (A., 1933, 533) for *Gonococcus* can be demonstrated in other species. A. G. P.

Respiratory system of bacteria. W. FREI (Zentr. Bakt. Par., 1935, I, 134, 26—35).—Bacteria are classified according to the presence of cytochrome, indophenol oxidase, peroxidases, catalases, and sp. respiratory pigments. The chemical mechanism of respiration in the various classes of organisms is discussed. A. G. P.

Formation and structure of cellulose membranes. W. K. FARR (Paper Trade J., 1935, 101; T.A.P.P.I. Sect., 183—186).—The cellulose (I) membrane present in cultures of *Acetobacter xylinus* is a part of the organism itself, and has not been synthesised from the culture medium by enzymes of bacterial origin. Each bacterium also possesses a coating of non-(I) material which serves as its contact surface with the nutrient solution. The presence of this material, largely pectic in nature, may be detected by solubility tests, and located by staining with Ru-red. It constitutes only about 2% of the membrane. In the filamentous alga *Spirogyra*, the (I) units are definitely oriented with respect to the surface of the protoplasm. H. A. H.

Fate of vitamin-C in the digestive tract. I. ACTION OF INTESTINAL BACTERIA ON VITAMIN-C. W. STEPP and H. SCHRODER (Klin. Woch., 1935, 14, 147—148).—The effect of common *B. coli* and intestinal bacteria on ascorbic acid varies. It is destroyed

in 24 hr. by some strains of *B. coli* and by *B. paratyphosus* B, possibly having some influence.

R. N. C.

Oxidations by means of acetic acid bacteria. III. Formation of a reducing saccharic acid (aldehydogluconic acid) and 5-ketogluconic acid. K. BERNHAUER and K. IRRGANG. IV. Formation of 2-ketogluconic acid by *Bact. gluconicum*. V. Comparative experiments on the preparation of l-sorbose by different bacteria. K. BERNHAUER and B. GORLICH (Biochem. Z., 1935, 280, 360—366, 367—374, 375—378).—III. In the action of *B. gluconicum* on Ca gluconate (I) small amounts of Ca 5-ketogluconate are formed together with a large amount (50% of the gluconate) of a reducing very sol. Ca salt which gives an intense naphthoresorcinol-HCl test and the same osazone as 5-ketogluconic acid (II) and is probably an aldehydogluconic acid (III) (l-guluronic acid). The same substance is obtained in small amounts when *B. xylinum* ferments a solution of glucose in presence of CaCO_3 or containing (I).

IV. *B. gluconicum* produces, in addition to (II) and (III), also 2-ketogluconic acid, isolated as the K salt and identified by comparison of its Me ester and quinoxaline derivative with authentic specimens.

V. The yields of l-sorbose isolated from glucose with *B. xylinum*, *B. xylinoides*, and *B. gluconicum* were 48, 53, and 64%, respectively, the material with the latter organism being almost pure. P. W. C.

Butyl- and acetone-fermentations. I. Intermediate products of the butyl alcohol-acetone fermentation. K. BERNHAUER and K. KURSCHNER (Biochem. Z., 1935, 280, 379—387).—Using fresh active cultures of *Clostridium butyricum*, AcOH is converted almost exclusively into COMe_2 (yield 97%). The organism during fermentation loses its physiological character and then converts AcOH chiefly into EtOH (yields COMe_2 30%, EtOH 70%). The organism after transfers in a cereal mash with and without CaCO_3 recovered its power to give large yields of COMe_2 . In fermentation of starch, PrCO_2H is the precursor of BuOH. Added acetaldol and β -hydroxybutyric acid are not converted into PrCO_2H , but added crotonic acid is converted partly into BuOH and partly into AcOH and COMe_2 . P. W. C.

Formation of hydrogen from glucose and formic acid by so-called "resting" *B. coli*. II. A. TASMAN (Biochem. J., 1935, 29, 2446—2457; cf. this vol., 1028).—The fermentation of glucose by both growing and resting *B. coli* takes place mainly by way of HCO_2H , but partly by way of AcCO_2H : in only a few cases (different bacterial strains) is the latter the chief reaction. F. A. A.

Determination of volatile acids in bacterial cultures. L. A. ALLEN and J. HARRISON (Biochem. J., 1935, 29, 2471—2476).—Volatile acids are determined in bacterial cultures in the presence of lactic acid and CO_2 by acidification and steam-distillation at const. vol. and each 100-ml. fraction is titrated with aq. Ba(OH)_2 until a const. titre is obtained. The neutralised acids are acidified and the process is repeated, the total titre in the latter case representing volatile acids. H. D.

Soluble dry filter for bacterial count in air. P. OESTERLE (Arch. Hyg. Bakt., 1934, 113, 137—142; Chem. Zentr., 1935, i, 2052).—A 2 : 1 : 1 mixture of NaCl, cryst. MgSO_4 , and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is dried at 100—150° and sterilised at 180°. J. S. A.

Antigenic fixatives of tubercle bacilli. II. Purification of the lipin fraction with hapten activity extracted from heat-killed bacilli. M. A. MACHEBŒUF and A. BONNEFOI. **III. Separation of the hapten-active phosphatides from the nitrogenous impurities.** M. A. MACHEBŒUF, G. LÉVY, and M. FAURE (Bull. Soc. Chim. biol., 1935, 17, 1201—1209, 1210—1234; cf. this vol., 256).—II. Fractional pptn. with COMe_2 of a CHCl_3 solution of the COMe_2 -insol. fraction of the lipins of the tubercle bacillus does not lead to any concn. of the hapten activity. Fractional pptn. with MeOH, although somewhat more effective, shows that the difference in solubility between active and inactive substances is very small and yields in the least sol. fraction a product of increased activity.

III. Repeated fractional pptn. of the COMe_2 -insol. lipins with MeOH yields a product (I) of high hapten activity sparingly sol. in MeOH and containing P 3.36%, N 0.13%, 3.3% of reducing sugars after hydrolysis, and no unsaponifiable matter. (I), although very active in the fixation of complement, has no pptn. activity. It is very sol. in H_2O , to which it passes from Et_2O solutions, the rate being dependent on the p_{H} of the aq. layer. A. L.

Relationship between electrophoretic migration velocities, virulence, and types of diphtheria and diphtheria-like bacilli. K. P. DOZORS and K. F. RAUSS (Amer. J. Publ. Health, 1935, 25, 1099—1102).—The diphtheroid strains show the max., avirulent strains the min., and virulent strains an intermediate velocity. The demarcation between the zones is not sharp and determinations show an error of 14% compared with virulence tests on guinea-pigs. H. G. R.

Variation in the buffering power of the culture fluid during bacteriolysis. F. CHODAT and M. RAAD (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 109—112).—During the true period of lysis there is a diminution in buffering power. H. G. R.

Action of respiratory and cellular fermentation inhibitors on transmissible bacterial lysis. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 156—160).—Lysis is inhibited by concns. of CH_3I - CO_2H which do not affect bacterial growth. KCN, CO, or phenylurethane has no effect on lysis. H. G.

Peroxidase and transmissible bacterial lysis. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, 164—166).—Thermolabile peroxidase of the culture is not removed by ultra-filtration (cf. following abstract), but is rendered thermostable. H. G. R.

Size of phage particles. Preparation of a purified lytic principle. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, 161—164).—Using a Seitz filter No. 6, the lytic activity can be filtered out and eluted with physiological saline. It is not affected by washing with C_6H_6 or Et_2O on the filter. H. G. R.

Accelerating effect of manganous ions on phage action. A. P. KRUEGER and N. S. WEST (J. Gen. Physiol., 1935, 19, 75—86).—Phage action on *Staphylococcus aureus* is accelerated by the presence of Mn^{++} . Phage formation is not increased or bacterial growth affected, but the Mn^{++} lowers the lytic threshold; lysis occurs when the phage/bacterium ratio is about 12 instead of 54. The phage distribution is altered in growing phage-bacterium mixtures, the extra-cellular phage concn. being 4 times that in the absence of Mn^{++} . F. A. A.

Action of mercury-lamp radiations on various bacteriophages. C. LEVADITI and J. VOET (Compt. rend. Soc. Biol., 1935, 120, 385—387).—The bacteriophages for *B. coli*, *Staph. K*, and the C_{16} bacteriophage are equally sensitive to Hg-lamp radiations, all being destroyed by exposure for 1 hr. R. N. C.

Cultivation of human influenza virus in an artificial medium. T. FRANCOIS, jun., and T. P. MAGILL (Science, 1935, 82, 353—354).—The culture virus has been readily transmitted to mice and ferrets. Its capacity to infect experimental animals is inhibited by sp. anti-influenza immune serum. After repeated cultivation *in vitro*, certain alterations in the immunological characteristics of the virus occur. L. S. T.

Sensitivity of the influenza bacillus against vitamin-C and quinol. O. GROOTEN and N. BEZSSONOFF (Compt. rend. Soc. Biol., 1935, 120, 121—123).—The development of the Bordet-Gengou bacillus (*B. pertussis*) is arrested and the bacillus itself killed by reductone, ascorbic acid (I), and hydroxybenzenes. Generally, the bactericidal power \propto the reducing power, except in the case of quinol (II), which is a more effective bactericide than pyrogallol. E_h of the cultures falls approx. 170 mv. on addition of (I), but only 5 mv. on addition of (II). R. N. C.

Action of medicaments *in vitro*. E. SINGER and V. FISCHL (Z. Hyg. Infektionskrankh., 1934, 116, 356—360; Chem. Zentr., 1934, ii, 3276).—Atoxyl (I) associated with liver-pulp is adsorbed more readily by *Spirochaetus recurrentis*, *B. proteus*, red corpuscles, collodion, and animal C than when untreated with liver. Addition of glutathione (II) and lentils increase As absorption *in vitro* by trypanosomes and spirochaetes. Liver or lentil pulp also increases Au absorption by spirochaetes. Glycogen, cystine, $\text{SH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, and Na thioglucose are inactive. Ascorbic acid destroys trypanosomes *in vitro*, the effect being increased by (I), but it attacks spirochaetes only in combination with the Au-CS(NH_2)₂ compound. (I) solution becomes trypanocidal on addition of (II). R. N. C.

Chemotherapy of bacterial infections. G. DOMAGK (Angew. Chem., 1935, 48, 657—667).—The application of chemotherapeutic substances in infections due to various types of pathogenic bacteria is discussed. F. O. H.

Effect of adrenaline on the utilisation of fructose introduced at constant velocity into the circulation at the three levels of assimilation. M. WIERZUCHOWSKI and H. FISZEL (Compt. rend. Soc. Biol., 1935, 120, 377—380; cf. this vol., 1017).—The blood-fructose (I) level reached on continuous

injection of (I) into normal dogs on a protein diet is > the carbohydrate diet level, but < the fasting level; adrenaline (II) raises the three levels. Urinary (I) at the three levels increases in the same order as above, and is also further increased by (II); 1 mg. of (II) lowers (I) assimilation by 6.03 mg. at the carbohydrate, 10.5 mg. at the protein, and 23.18 mg. at the fasting level. Hence (II) determines the glycogenolysis of glycogen (III) formed from injected sugars such as (I), as well as that of the body-(III).

R. N. C.

Inactivation of adrenaline by extracts of organs. J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 42—45).—Adrenaline is inactivated *in vivo* by extracts of animal organs to varying extents according to the organ concerned and the species. The max. effects are obtained with extracts of guinea-pig liver and kidney and dog spleen, whilst extracts of muscular tissue are always inactive.

R. N. C.

Effect of cortin on adrenaline secretion. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1935, 120, 248—250).—Injection of cortin in the dog induces hyperglycemia by augmenting adrenaline secretion, the increased secretion appearing 20—40 min. after injection and persisting for 60—90 min.

R. N. C.

Chemical basis of the panoptic reaction applied to the detection of adrenaline in the tissues. T. PAWLIKOWSKI and T. SLEBODZINSKI (Compt. rend. Soc. Biol., 1935, 120, 465—466).—Adrenaline (I) reduces $K_2Cr_2O_7$ *in vitro*, forming CrO_2 , which oxidises methylene-blue to a green compound. These reactions are responsible for the metachromatic green coloration of the cells of the medulla in the panoptic reaction.

R. N. C.

Absorption and fate of insulin following percutaneous application. I. S. HERMANN and H. KASSOWITZ. II. S. HERMANN (Arch. exp. Path. Pharm., 1935, 179, 524—528, 529—536).—I. Application of paste containing insulin (I) (5 units) to the washed (light petroleum) skin of rabbits reduces the blood-sugar from approx. 90 to 14—30 mg. per 100 c.c., producing convulsions in 30% of the animals. The effect is partly or wholly inhibited by addition of cholesterol to the paste and is dependent on the site of application, being greatest above compact red muscle. The hypoglycemic activity of extracts from dog's skin treated with (I) paste indicates that (I) permeates both horizontally and vertically.

II. Presence of lipin-sol. acids (*e.g.*, AcOH) inhibits the action of (I) paste. For max. absorption of (I), the skin must be freed as far as possible from lipins and an alkalisalation of the skin induced (*e.g.*, by meat diets). The results are discussed with reference to lymph transport and cell permeability.

F. O. H.

Action of insulin in fasting pigeons. D. GIGANTE (Atti R. Accad. Lincei, 1935, [vi], 21, 763—768).—The resistance of the pigeon to insulin (a single dose) shows not so much gradual diminution as fasting is prolonged, as a sudden fall when the critical stage of inanition is reached.

T. H. P.

Influence of insulin on the phosphorus exchange in muscle. S. F. EPSTEIN (Ber. Ukrain.

Biochem. Inst., 1930, 4, 107—114).—Administration of 5—20 clinical units of insulin (I) to rabbits results after 15 min. in a rise in the hexosemonophosphoric acid (II) and a fall in the creatinephosphoric acid (III) and $H_4P_2O_7$ (IV) in muscle. In pigeons, muscle-(II) is unaltered but -(III) and -(IV) are decreased after administration of (I).

W. O. K.

Influence of insulin on the production of optically active substances in muscle-glucose-salt mixtures. P. NORMARK and E. SAVRON (Ber. Ukrain. Biochem. Inst., 1930, 4, 31—42).—Mixtures of minced muscle, glucose, and NaCl in phosphate buffer (p_H 7.3) with and without insulin (I) were incubated and then dialysed through a collodion membrane against isotonic aq. NaCl. The α and reducing power of the dialysate were the same whether (I) was present or absent.

W. O. K.

Inactivation of insulin. Effects of certain metal derivatives and of thiol compounds. E. D. SCHOCK, H. JENSEN, and L. HELLERMAN (J. Biol. Chem., 1935, 111, 553—559).—Insulin (I) is inactivated by benzoquinone (II) in 0.067*M*- Na_2HPO_4 (but not in 0.01*N*-HCl) and by thiolsalicylate, Cu_2O , phenylmercuric oxide, thioglyoxaline, thiolhistidine, ergothionine, and ascorbic acid do not inactivate (I). (I), inactivated by (II), suffers a decrease in NH_2 -groups.

H. D.

Parathyroid hormone and vitamin-A. F. HOFF and B. ZU JEDDELOH (Z. ges. exp. Med., 1934, 95, 67—75; Chem. Zentr., 1935, i, 2036).—Parathyroid hormone injected into rats in large doses produces Ca deposition in the heart muscles and subcutaneous connective tissue as occurs in human osteitis fibrosa generalisata. Excess of vitamin-A (I) ("Vogan") in growing rats induces skeletal decalcification and spontaneous fracture, but no Ca metastasis or hypercalcaemia. Symptoms follow resembling those in (I) deficiency. The observed fat deposition in the organs is considered to be due to the fat present in the "Vogan" preps. rather than to (I).

R. N. C.

Relation of the thyrotropic hormone to the sugar and ketone content of the blood. F. SILBERSTEIN and F. GOTTDENKER (Klin. Woch., 1934, 13, 1434; Chem. Zentr., 1934, ii, 3269).—Injection of large quantities of thyrotropic hormone (I) in normal cats causes a considerable increase in blood-ketones and -sugar (II). In thyroidectomised animals (II) only is raised. Repeated injections of (I) in both normal and thyroidectomised animals cause a weaker (II) reaction.

R. N. C.

Basic amino-acids yielded by thyroglobulin. A. WHITE and W. G. GORDON (Proc. Soc. Exp. Biol. Med., 1934, 32, 354—357).—Thyroglobulin contains 0.62% of histidine, 8.22% of arginine, and 1.93% of lysine.

R. N. C.

Significance of thyroid gland in antithyrotropic-protective action of the blood. H. EITEL and A. LOESER (Arch. exp. Path. Pharm., 1935, 179, 440—447).—Stimulation of the thyroid gland by thyrotropic hormone from anterior pituitary gland increases the protective action of the blood for antithyrotropic activity (this vol., 1171). Hence the thyroid is related to the formation of the protective

principle, a relation confirmed by diminution in protective action on thyroidectomy and return to normal levels on subsequent administration of thyroid hormone. Thus the increase in protective action is not a sp. result of anterior pituitary secretion, but follows increased thyroid activity. F. O. H.

Thyroid and ovary. Experimental basis for the di-iodotyrosine treatment of climacteric disturbance. A. LOESER (Klin. Woch., 1935, 14, 4—6).—Removal of the ovaries in female guinea-pigs causes a hyperactivity of the thyroid, due to increased secretion of the thyrotropic hormone of the anterior pituitary. The enhanced secretion is suppressed by oral administration of di-iodotyrosine. R. N. C.

Strengthening of the anti-thyroid protective power of blood by the thyrotropic hormone of the pituitary. H. EITEL and A. LOESER (Klin. Woch., 1934, 13, 1677—1678).—If guinea-pigs are injected with sheep serum and thyrotropic substance (I) simultaneously, the two counterbalance each other; this is a method of assay of the anti-thyrotropic substance (II) of serum. If serum donors are previously treated with (I), the anti-thyroid potency of their blood is increased; it is not increased by previous treatment with thyroxine, and it is not high in serum from cases of Graves' disease. (II) is present in serum, and to a smaller extent in corpuscles.

G. H. F.

Action of anterior pituitary fractions on the blood-sugar. K. J. ANSELMINO and F. HOFFMANN (Arch. exp. Path. Pharm., 1935, 179, 273—285).—Single injections of total extracts of anterior pituitary lobe induce an increase in blood-sugar in dogs. Repeated administration, however, produces a refractory period during which the level may even diminish. Anti-insulin preps. of Lucke (A., 1933, 643) have an indefinite hyperglycaemic action which is probably due to traces of posterior lobe hormone. Extracts of the anterior lobe contain a hypoglycaemic (pancreatropic) factor which markedly stimulates the islets of Langerhans. Ultrafiltrates of the total extract at 5.4 have a hypoglycaemic action; heating at 100° for 15 min. to destroy the pancreatic hormone reveals, however, the presence of the hyperglycaemic factor. F. O. H.

Antuitrin-S and blood-elements. S. H. GEIST and F. SPIELMAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 353—354).—Injections of antuitrin-S do not affect the formed blood-elements. R. N. C.

Experimental dissociation of the effects of anterior pituitary glands of various species on thyroid and ovary. L. LOEB, W. C. ANDERSON, J. SAXTON, S. J. HAYWARD, and A. A. KIPPEN (Science, 1935, 82, 331—333).—The changes induced in the ovary and the thyroid gland of the immature guinea-pig by substances present in the anterior pituitary glands of various species are described. Experimental changes in the preponderance of these various effects have been produced and the action of the gland of one species has been made like that of another in its effect on the guinea-pig. This has been accomplished by the use of H₂O, aq. NaCl, EtOH, Et₂O, glycerol, and dil. aq. CH₂O. The data

obtained suggest that the effect of the various hormones may depend on the presence of certain NH₂-acids, which form part of one or more polypeptide or protein mols. L. S. T.

Thyrotropic activity of pituitary gland in man. R. MULLER, H. EITEL, and A. LOESER (Arch. exp. Path. Pharm., 1935, 179, 427—439).—The thyrotropic hormone content (A., 1934, 1410) of pituitary gland in men (74 *post-mortem* cases) approximates to that of animals. The level, which is independent of age and sex, varies considerably, but the high content in sufferers from tuberculosis and other infectious diseases is noteworthy. F. O. H.

Testis-stimulating potency of frozen turkey pituitaries injected subcutaneously into young male chicks. T. C. BYERLY, W. H. BURROWS, and H. W. TITUS (Poultry Sci., 1935, 14, 189—190).—Cockerel pituitaries had higher gonad-stimulating potency than did those of turkeys. A. G. P.

Gonad-stimulating potency of individual pituitaries. R. H. JAAP (Poultry Sci., 1935, 14, 237—246).—The stimulatory effect of pituitary was increased by injection of blood-sera in ducks but not in chickens. A. G. P.

Hormone content of the pituitary of the blue whale (*Balaenoptera sibbaldi*). J. VALSO (Klin. Woch., 1934, 13, 1819—1820).—Neither prolactin nor intermedin is found in the posterior lobe. R. N. C.

Corpus luteum hormone.—See this vol., 1195.

Dependence of the function of the corpus luteum on the ovarian follicles and the place of origin of the hormone in the ovary. A. WESTMANN (Arch. Gynakol., 1934, 158, 476—504; Chem. Zentr., 1935, i, 1726).—The lutein cell formed in the rabbit's ovary from the granulosa of a ripe follicle by cauterisation of the ovum and of the follicle is abnormal in that it secretes no corpus luteum hormone (I). Destruction of the follicle also hinders the growth of an already existing corpus luteum, but growth is normal if some follicles are left or follicular hormone (II) is administered. Hence (II) is necessary for the function of the corpus luteum to be fulfilled, and is possibly used by the granulosa cell for the formation of (I). R. N. C.

Extraction of folliculin and an associated pharmacological problem. K. GAD-ANDERSEN and E. JARLØV (Acta med. Scand., 1934, 84, 233—240; Chem. Zentr., 1935, i, 1889).—The activities of commercial folliculin preps. when given subcutaneously and orally are compared. Preps. obtained without the use of Et₂O show good activity orally. R. N. C.

Doses of folliculin necessary to produce intersexuals and the limiting stage of intervention. E. WOLFF and A. GINGLINGER (Compt. rend. Soc. Biol., 1935, 120, 114—116).—The limiting stage of incubation of the hen's egg, beyond which it is no longer possible to transform male embryos into intersexuals by injections of folliculin, is approx. the 8th day. The threshold dose for feminisation is approx. 25 units. R. N. C.

Gonadotropic substances in mare's serum. H. H. COLE and G. H. HART (Proc. Soc. Exp. Biol.

Med., 1934, 32, 370—373).—Pregnant and non-pregnant mare's serum contains a prol-an-like substance that stimulates the gonads when combined with the pituitary synergist. Pregnancy serum contains a second substance that is active *per se*. R. N. C.

Disappearance of prol-an from the blood of the nephrectomised female rabbit. A. LIPSCHUTZ, A. FUENTE-ALBA, and T. VIVALDI (Compt. rend. Soc. Biol., 1935, 120, 323—326).—Prol-an injected intravenously is removed from the blood less rapidly in the nephrectomised than in the normal rabbit, suggesting that under normal conditions it is not all excreted in the urine, but partly destroyed in the organs. R. N. C.

Assay of the gonadotropic hormone of pregnancy urine on male rats. V. KORENCHESKY, M. DENNISON, and S. L. SIMPSON (Biochem. J., 1935, 29, 2522—2533).—The method is described. There is a regular relation between the dose of gonadotropic hormone (I) and the effect on the prostate (II), seminal vesicles (III), and penis. It is suggested that one male rat unit (Ml. R.U.) be the min. total dose, injected in 6 equal portions on 3 days, which on the 5th day produces an increase of 40% in the actual wt. of (II) and about 70% in the wt. of (III). 1 Ml. R.U. was equal to about 5 F.R.U. The qual. effect of (I) on the sexual organs is very similar to that of androsteronediol, but different from that of androsterone. J. N. A.

Testicular hormone.—See this vol., 1500.

Synthetic preparation of testosterone.—See this vol., 1371.

Influencing of the secondary sex characteristics of the carp (*Rhodeus amarus*) by hormones and other means. W. WUNDER (Med. Klin., 1934, 30, 874—876; Chem. Zentr., 1934, ii, 3267).—Subcutaneous injection of testicle extract in normal male carp produces mating colours, which persist for a period dependent on the amount of hormone and the time of the year. Adrenaline and yohimbine (I) also exhibit this activity, and prol-an at spawning time, whilst folliculin (II), 0.9% NaCl, trichlorobutyl alcohol, and acetylcholine are inactive. The action of (II) on the oviduct of the female carp is sp., 0.9% NaCl, thyroid, and anterior pituitary hormones being inactive. R. N. C.

Prolonged treatment of male and female rats with androsterone and its derivatives, alone or together with oestrone. V. KORENCHESKY, M. DENNISON, and S. L. SIMPSON (Biochem. J., 1935, 29, 2534—2552).—Prolonged treatment of castrated rats with androsterone (I), androsteronediol (II), and their H₂O-sol. esters not only restored the sexual organs to or towards the normal condition, but also increased the wts. of adrenals, thymus, liver, kidneys, and heart. (II) had all the properties of a true male hormone, but very large doses of (I) and H₂O-sol. (II) had a depressing effect on the gain in body-wt., deposition of fat, and stimulation of the liver. (I) and oestrone (III) had a co-operative effect on the prostate and seminal vesicles, but an antagonistic action on the adrenals. (I) and (II) have no rejuvenating effect. With ovariectomised rats large doses of

(II) caused a partial recovery of the atrophied uterus and vagina, the effect being less with (I). (III) caused a return towards the normal wt. of these organs and (III) together with (I) or (II) showed a co-operative recovery effect. It is suggested that the male hormones, being natural stimulants, may be used for treating suitable human diseases. J. N. A.

Vitamin-A content of eggs as related to rate of production. M. C. KOENIG, M. M. KRAMER, and L. F. PAYNE (Poultry Sci., 1935, 14, 178—182).—Eggs from low-producing pullets had higher vitamin-A contents than those from high-producing pullets when nearing the end of the first year of production. After only 4 months' production no difference was apparent, the -A val. being intermediate between those of the two groups after 1 year. A. G. P.

Growth-promoting effect of flavin on the chick. S. LEFKOVSKY and T. H. JUKES (Science, 1935, 82, 326).—Liver extract contains two H₂O-sol. factors which promote growth in chicks. The first promotes growth when added to a heated diet of yellow maize meal, wheat middlings, and commercial casein, supplemented with salts and cod-liver oil, and is the factor of Elvehjem and Koehn (this vol., 669). The second factor is flavin, which has no effect when added to this diet, but promotes growth when added to the unheated diet. Both factors are distinct from vitamin-B₁. L. S. T.

Effect of heavy administration of viosterol on the metabolism of the rat. C. I. REED (Proc. Soc. Exp. Biol. Med., 1934, 32, 274—277).—Small quantities of viosterol increase the metabolic rate; larger (toxic) doses produce a transient elevation of the metabolic rate followed by a decline below the original level. R. N. C.

Carotene and vitamin-A metabolism. H. WENDT (Klin. Woch., 1935, 14, 9—14; Chem. Zentr., 1935, i, 1730).—Prolonged feeding of carotene and vitamin-A increased the proportion of these in the serum to a max. of 58 Lovibond yellow units and 4.5 blue units, respectively. Large dosages of -A caused hyperlipaemia and hyperlipinaemia in rabbits but not in dogs. Diseases affecting fat resorption caused low vals. for carotene and -A. Neither was present in cases of goitre, but administration of I effected a return toward normal levels. Highest vals. occurred in diabetes. A. G. P.

Carotenoids and vitamin-A in cow's blood-serum. A. E. GILLAM and M. S. E. RIDI (Biochem. J., 1935, 29, 2465—2468).—The average contents of carotene, determined spectrophotometrically, in cow's and bull's blood sera were, respectively, 0.40 and 0.08 mg. per 100 ml. in summer and 1.11 and 0.42 in winter. The presence of vitamin-A, lutein, and occasionally cryptoxanthine in the serum was established. H. D.

Physiologically active crystalline esters of vitamin-A. S. HAMANO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 69—73).—Vitamin-A concentrate (Biosterin) with β -C₁₀H₇·COCl in C₅H₅N gave the physiologically active cryst. β -naphthoate, C₃₁H₃₆O₂, m.p. 76°, which readily promoted the growth of albino rats and cured xerophthalmia. On hydro-

lysis, vitamin-A, $C_{20}H_{30}O$, was obtained. Similarly an active ester, $C_{35}H_{56}O_2$, m.p. 124° , was obtained from anthraquinone-2-carboxylic acid. J. N. A.

Preparation of a potent vitamin-A concentrate. H. N. HOLMES, H. CASSIDY, R. S. MANLY, and E. R. HARTZLER (J. Amer. Chem. Soc., 1935, 57, 1990—1993).—Saponified halibut-liver oil (freed from unsaponifiable matter and most of the cholesterol) in C_5H_{12} , when cooled in EtOH-solid CO_2 and filtered through solid CO_2 on sintered glass, gives a concentrate with a blue val. 45,000—60,000. Filtration through C and MgO gives a concentrate with a blue val. 90,000—140,000. The blue val. is decreased by about 10% if the humidity of the air around the tintometer rises from 35 to 60%. R. S. C.

Crystalline vitamin- B_1 .—See this vol., 1510.

Relative vitamin- B_2 contents of dried whey and dried skim-milk. V. HEIMAN (Poultry Sci., 1935, 14, 137—146).—A relationship between the vitamin- B_2 content of the diet and the growth rate of chicken is established. The $-B_2$ ratio of dried skim-milk : dried whey is 1 : 1.5. Egg production is not appreciably affected by the amount of $-B_2$ supplied. The hatchability of eggs from pullets receiving suboptimal amounts of dried whey or skim-milk is slightly higher in the case of the former feed. The $-B_2$ content of eggs and the greenish-yellow pigment of the whites are directly related to the $-B_{2c}$ content of the diet. Dried egg whites are richer in $-B_2$ than are dried yolks. The lactochrome content of dried whey is $>$ that of dried skim-milk and the quantity present is correlated with growth response and hatchability. A. G. P.

Suggested relation between cystine and vitamin- B_2 . F. T. G. PRUNTY and M. H. ROSCOE (Biochem. J., 1935, 29, 2491—2497).—There is no relation between cystine (I) and the vitamin- B_2 complex in the nutrition of the rat, and a deficiency of vitamin- B_2 together with a deficiency of (I) such that growth was affected had no effect on the incidence of dermatitis. The (I) intake of rats had no effect on the glutathione content of the tissues. Some of the purified caseinogen used in basal diets for vitamin work is deficient in (I). J. N. A.

Vitamin-B and -C in preserved spinach and acid preserved foods. S. V. FOMIN and P. T. MAKAROVA (Ukrain. Biochem. J., 1935, 8, No. 1, 191—202).—Vitamin-B is destroyed; -C is almost intact. E. P.

Determination of ascorbic acid.—See this vol., 1483.

Electrometric determination of vitamin-C (ascorbic acid). J. DIGLERIA (Mezög.-Kutat., 1934, 7, 226—235; Chem. Zentr., 1935, i, 1409).—Pure ascorbic acid (I) gives identical results when determined by I or 2 : 6-dichlorophenol-indophenol (II). (I) is decomposed in feebly acid or neutral solution, even during the short time lag, but the decomp. is negligible at $p_H \geq 4$. E_h of (I) is strictly dependent on p_H , the change for 1 p_H unit being 58 mv.; E_{HCl} at p_H 0 is $+0.3295$ volt. The I titration vals. in fruits and vegetables are $>$ the (II) titration vals., the deviations occasionally being $>$ 100%. R. N. C.

Vitamin-C in the medlar and alkekengi. E. CASERIO (Ind. ital. conserve aliment., 1934, 9, 190—192; Chem. Zentr., 1934, ii, 3272).—The juice of the ripe alkekengi contains twice as much vitamin-C as lemon-juice. The ripe medlar contains relatively no vitamin. R. N. C.

Relation between the vitamin-C contents of various vegetable tissues and the presence or absence of chlorophyll. L. RANDOIN, A. GIROUD, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 120, 297—300).—The chemical and biological vitamin-C vals. of the green and white parts of the leaf tissue show a clear relation to their chlorophyll contents. R. N. C.

Normal content of ascorbic acid in the organism. A. GIROUD, C. P. LEBLOND, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1935, 120, 414—415).—The mean normal ascorbic acid contents of the adrenals, liver, and muscles of animals are given. In animals in which scurvy cannot be produced, the vals. on a vitamin-C-deficient diet are slightly less. R. N. C.

Fixation and elimination of ascorbic acid. A. GIROUD, R. CHUC, R. RATSIMAMANGA, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 120, 330—333).—Ascorbic acid (I) injected intravenously in guinea-pigs is rapidly oxidised to dehydroascorbic acid and is stored in the adrenals, liver, and kidney (greatest accumulation). In all organs (I) reaches a max. and then falls. Kidney-(I) is excreted in the urine, excretion beginning immediately (I) rises. Some (I) is fixed by the liver. R. N. C.

Ascorbic acid (vitamin-C) and the blood-aqueous humour barrier. H. GOLDMANN and W. BUSCHKE (Klin. Woch., 1935, 14, 239).—Increase of the permeability of the blood-aq. humour barrier by subconjunctival injection of NaCl lowers the ascorbic acid (I) content of the aq. humour; it becomes normal again with the permeability. Adrenaline, which prevents the increase of permeability, also brings the (I) of the aq. humour to normal if injected after NaCl; it has no effect when injected alone. Injection of (I) into the blood-stream to one eye increases (I) in the anterior chamber of that eye only. (I) probably diffuses from the blood into the aq. humour in the reversibly-oxidised form, and is then reduced by the cryst. lens. R. C. N.

Comparison of the antirachitic potency of cod-liver oil and irradiated ergosterol on a curative and preventive basis. W. C. RUSSELL, M. W. TAYLOR, and D. E. WILCOX (J. Nutrition, 1935, 9, 569—574).—The two sources of vitamin-D produced similar curative responses when fed to white rats on an equiv. preventive basis. With chickens, cod-liver oil was superior. A. G. P.

Antirachitic effect of ultra-violet radiation transmitted by a smoky atmosphere. H. M. BARRETT (J. Ind. Hyg., 1935, 17, 199—216).—Development of rickets in rats on a rachitic diet is not prevented by irradiation through smoke similar to that of an average urban atm. H. G. R.

Crystalline derivatives of vitamin-E. R. KIMM (Sci. Papers Inst. Phys. Chem. Res. Tokyo,

1935, 28, 74—76).—Vitamin-*E* concentrate from rice embryo oil when treated with β -C₁₀H₇·COCl in C₅H₅N gave a cryst. β -naphthoate, C₄₀H₅₄O₂, m.p. 156°, from which the free vitamin-*E* is calc. to be C₂₀H₄₈O. On regeneration it had a high activity. Three other cryst. substances, C₄₃H₆₀O₂, m.p. 158°, C₄₀H₅₄O₂, m.p. 134°, and an uninvestigated fraction, m.p. 168°, were obtained. An amorphous ester of anthraquinone-2-carboxylic acid was prepared.

J. N. A.

Vitamin-*E* content of eggs as related to the diet of the hen and to hatchability. G. L. BARNUM (J. Nutrition, 1935, 9, 621—635).—Vitamin-*E* may be a limiting factor in the hatchability of eggs from hens on certain diets. Deficiency of -*E* is associated with first-week embryonic mortality, and may be reduced by supplying -*E* in poultry diet.

Pituitary. IV. Effect of vitamin-*E* deficiency on the female albino rat. S. I. STEIN (J. Nutrition, 1935, 9, 611—619).—No difference in the wt. of the pituitary, differential counts of cells in the anterior lobe, or histology was observed between sterile (vitamin-*E*-deficient) and pregnant rats cured of the deficiency.

A. G. P.

Salt-tolerance of *Ruppia maritima* in lakes of high magnesium sulphate content. E. MCKAY (Plant Physiol., 1935, 10, 425—446).—Periodic examinations are recorded of the p_H , d , and osmotic pressure of the lake-H₂O, and the sap composition of the plants growing thereon. *Ruppia* tolerates high [Mg⁺⁺] and [SO₄⁼⁼], its distribution being limited by the Na₂SO₄ concn. of the H₂O. The time of flowering and seed development is influenced by the salt concn. of the lake. The p_H of the lake-H₂O is not a factor governing plant distribution.

A. G. P.

Physiological role of asparagine and related substances in nitrogen metabolism of plants. A. E. MURNEEK (Plant Physiol., 1935, 10, 447—464).—A discussion of current views.

A. G. P.

Stock-scion chemistry and the fruiting relationships in apple trees. H. L. COLBY (Plant Physiol., 1935, 10, 483—498).—The translocation of nutrients and the distribution of reserves between stock and scion are examined in relation to root and shoot development.

A. G. P.

Factors rendering the plasmolytic method inapplicable in determining the osmotic values of plant cells. E. C. M. ERNEST (Plant Physiol., 1935, 10, 553—558).—When the osmotic pressure of the external liquid surrounding the cell is only slightly different from that of the cell fluid, plasmolysis becomes so slow that secondary changes may occur within the cell, which invalidate the customary interpretation of the data.

A. G. P.

Growth and composition of Deglet Noor dates in relation to water injury. A. R. C. HAAS and D. E. BLISS (Hilgardia, 1935, 9, No. 6, 295—344).—Changes in the mineral and org. constituents and in the H₂O content of dates with advancing growth are recorded. The nature of "H₂O injury" and factors affecting it are examined.

A. G. P.

Physiological gradients in citrus fruits. A. R. C. HAAS and L. J. KLOTZ (Hilgardia, 1935, 9, No. 3, 181—217).—Variations in the end-to-end distribution of N, sugar, oil, mineral matter, and carotenoid substances of lemon, orange, and grapefruit are recorded. K manuring increased the K content of Valencia oranges. Deficiency of K is associated with breakdown of the peel. Fumigation with HCN increased the permeability of the peel, notably at the calyx end.

A. G. P.

Inhibition of photosynthesis in *Chlorella pyrenoidosa* by the iodoacetyl radical. H. L. KOHN (J. Gen. Physiol., 1935, 19, 23—34).—CH₂I·CO·NH₂ (I) inhibits photosynthesis in *C. pyrenoidosa*, interfering with the dark (Blackman) reaction. This action, which is slow owing to the slow penetration of the radical, is also shown by CH₂I·CO₂H, but not by NH₂Ac. Concns. of (I) which inhibit photosynthesis (about 10⁻⁴M) increase respiration; smaller concns. (> 10⁻⁵M) may increase the rate of photosynthesis by reacting with the photochemical complex, and higher concns. (< 10⁻³M) inhibit respiration.

F. A. A.

Effect of blue-violet rays on photosynthesis [in plants]. R. H. DASTUR and R. J. MEHTA (Ann. Bot., 1935, 49, 809—821).—Rates of photosynthesis increase with the intensity of blue-violet rays from various sources. Photosynthetic activity is greatest in white light, intermediate in red, and feeble in the blue-violet region. In white light, assimilation is related not only to the total intensity, but also to the distribution of radiations of different

A. G. P.

Wound healing in *Tradescantia fluminensis*, Vell. R. BLOCH (Ann. Bot., 1935, 49, 651—670).—Healing processes in wounded stems involve cell division and elongation, thickening of walls, formation of suberin lamellae, and the impregnation of walls with lignin and fatty matter. Disturbed metabolism leads to increased protein and decreased carbohydrate contents of adjacent areas of stems, and the deposition of tetragonal CaC₂O₄·3H₂O (distinct from the normal raphides) in pith parenchyma.

A. G. P.

Non-dependence of carbon dioxide assimilation of green plants on the presence of small amounts of oxygen. Reversible inhibition of assimilation by carbon monoxide. H. GAFFRON (Biochem. Z., 1935, 280, 337—359).—Mol. O₂ is not necessary either in the free or bound condition for CO₂ assimilation in green plants (*Chlorella* etc.) and the hypothesis that the mechanism involves a reaction between irradiated chlorophyll and O₂ is discounted (A., 1935, 1288). A reversible inhibition of assimilation occurs when the plants are exposed to the action of CO in the dark, and suggests that the enzyme responsible for the Blackman reaction is closely related to catalase.

P. W. C.

Seasonal changes in the acidity of the rhubarb (*Rheum hybridum*). T. A. BENNET-CLARK and W. M. WOODRUFF (New Phytol., 1935, 34, 77—91).—Sprouting of rhizomes is associated with an increase in NH₄ compounds or in "malate" (I) [acids of the malic group and including citric acid]. Translocation of (I) from rhizome to young leaves takes place,

but deamination of NH_2 -acids to form NH_4 malate is probably not an intermediate stage. Formation of *l*-malic acid occurs principally at the height of summer and not during sprouting. The acid is associated with carbohydrate rather than protein metabolism. The mol. ratio of NH_4^+ : malic acid in the plant is at all times small (0.1). A. G. P.

Testing plant tissue for emanations causing leaf epinasty. F. E. DENNY (Contr. Boyce Thompson Inst., 1935, 7, 341—347).—Apparatus and technique are described. Epinasty was produced by volatile products from a no. of plants. Positive responses were given by petals, anthers, pistils, immature fruits, leaves, and tubers. Potato tubers, germinating maize, wheat, and oats, mycelium of *Rhizopus nigricans*, and mature sporophores of two species of mushrooms failed to produce epinasty. A. G. P.

Effects of zinc and iron salts on the cell structure of mottled orange leaves. H. S. REED and J. DUFRENOY (Hilgardia, 1935, 9, No. 2, 113—141).—Mottle-leaf of citrus is associated with a change in the oxidation-reduction equilibrium of the leaf cells. Nitrites occur in the sap of mottled but not of normal leaves. Cytological changes in mottled trees during recovery following application of Zn are described. In the new shoots thus formed neither Ca deficiency nor phloem necrosis is apparent, whilst chloroplasts develop and form starch. Beneficial effects of Fe on hypoplastic cells of mottled leaves are negligible. Zn is intimately concerned with the oxidation-reduction potential of the cell. A. G. P.

Several chemical growth-substances which cause initiation of roots and other responses in plants. P. W. ZIMMERMANN and F. WILCOXON (Contr. Boyce Thompson Inst., 1935, 7, 209—229; cf. A., 1933, 437; B., 1933, 1027).—Plant responses to a no. of growth-stimulating substances are examined. α -Naphthylacetic and indolylbutyric acids were the most active root-forming substances. Both caused less epinastic response than indolylacetic acid. Local application of C_2H_4 or C_3H_6 in lanoline paste stimulated root initiation. Evidence is obtained of the utilisation of $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$ by plants for the production of growth substance. Emanations from plants (probably C_2H_4) causing epinasty were increased by treatment with growth-substance. Positive growth-responses were also obtained with β -naphthylacetic, acenaphthyl-5-acetic, phenylacetic, fluoreneacetic, and anthraceneacetic acids (see also Hitchcock, this vol., 795). A. G. P.

Tobacco as a test plant for comparing the effectiveness of preparations containing growth-substances. A. E. HITCHCOCK (Contr. Boyce Thompson Inst., 1935, 7, 349—364).—The relative efficiency of growth-substances in causing epinasty in tobacco leaves was, naphthylacetic (I) and indolylacetic (II) > indolylbutyric (III) and indolylpropionic (IV) > phenylacetic (V) > phenylpropionic (VI) > phenylacrylic (VII) acids. The rooting response of tobacco was in the order (III) > (II) > (VII) > (V) > (I) > (VI) > (IV). Application of lanoline preps. of the substances to decapitated tobacco stems retarded the growth of upper buds but stimulated

that of middle and lower buds. Lanoline preps. of C_2H_4 and C_3H_6 caused similar effects. The epinastic was more suitable than the rooting response of tobacco for comparative tests. A. G. P.

Presence of ozone in air and its effect on the growth of plants. E. BRINER, F. CHODAT, and H. PAILLARD (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 128—132).—Samples of the plants *Zea mays* and *Avena sativa* exposed for 8—25 days to air containing 0.01—10 p.p.m. of O_3 showed a higher rate of growth than samples exposed to de-oxygenated air. O_3 favoured production of pigments of the xanthophyll group. S. J. G.

Similarities in the effects of ethylene and the plant auxins. W. CROCKER, A. E. HITCHCOCK, and P. W. ZIMMERMANN (Contr. Boyce Thompson Inst., 1935, 7, 231—248).—The action of C_2H_4 , C_3H_6 , C_2H_2 , and CO on plants is principally that of anaesthetics and stimulants, and resembles in many respects that of a no. of growth-promoting substances. A. G. P.

Effect of auxins on *Phytophthora cactorum*. L. H. LEONIAN (J. Agric. Res., 1935, 51, 277—286).—The presence of substances promoting growth and reproduction of *P. cactorum*, in canned peas and in sprouting maize roots, is demonstrated. The last named are active after crushing or autoclaving. Norit adsorbs growth-promoting but not sexuality-promoting substances. A. G. P.

Pantothenic acid as a nutrilit for green plants. R. J. WILLIAMS and E. ROHRMAN (Plant Physiol., 1935, 10, 559—563).—The growth of *Ricciocarpus natans* is stimulated by pantothenic acid (A., 1933, 982). A. G. P.

Do sexual hormones influence the germination and growth of plants? K. GAD-ANDERSEN and E. JARLOV (Acta med. scand., 1934, 84, 241—252; Chem. Zentr., 1935, i, 1889).—The favourable action of follicular hormone (I) preps. on the growth of hyacinths is not due to (I), but to an associated plant-growth hormone. R. N. C.

Effects of animal hormones on plants. L. HAVAS and J. CALDWELL (Ann. Bot., 1935, 49, 729—747).—A prep. of the oestrogenic hormone was toxic to tomato plants when administered by the root or through cut petioles. Extracts of testis, ovary, pituitary, adrenal, thyroid, and thymus produced no marked stimulatory or toxic effects. A. G. P.

Changes in the chemical composition of developing apples. H. O. ASKEW (J. Pomology, 1935, 13, 232—246).—Starch formation begins in apple tissue near the periphery and extends towards the core area. During maturation hydrolysis of starch proceeds from the core outwards. The decline in % of N and ash with advancing growth follows the relationship $\log_{10} C = a + bt$ (C = concn. of constituent concerned, t = time from first sample, and a and b are consts.). The rate of increase of dry matter declined slightly and that of N and ash intake considerably, approx. 95 days from full bloom. After a further 25 days the intake of N and ash ceased. A. G. P.

Accumulation of boron by reciprocally grafted plants. F. M. EATON and G. Y. BLAIR (Plant Physiol., 1935, 10, 411—424).—The distribution of

B in plant organs is effected by the transpiration stream and is irregular. B combines with org. matter in the tissues, the compounds having low mobility. Accumulation of B in leaves of grafted scions is partly controlled by that of the stock. The intake of B is controlled by the characteristics of the root cells, by the nature of the B compounds in the plant, and by the form of the equilibrium between mobile and immobile B compounds. A. G. P.

Solubility of potassium in maize tissues. V. H. MORRIS and J. D. SAYRE (Plant Physiol., 1935, 10, 565—568).—In maize tissue K exists entirely in solution in the cell sap. There is no evidence of fixed or non-ionisable K in any tissue except, possibly, in cob tissue. A. G. P.

Changes in nitrogen compounds in the wheat grain at different stages of development. G. L. TELLER (Plant Physiol., 1935, 10, 499—509).—Changes in the N distribution of developing grain are examined. The early stages, marked by high proportions of non-protein N, are associated with increasing gliadin and decreasing glutenin contents, and a slight decline in albumins and globulins. These changes are partly due to the filling of the grain with endosperm, which contains more gliadin and less glutenin than the bran. The total N of the grain is influenced by seasonal conditions. A. G. P.

Distribution of nitrogen in the seed of *Zea mays* at different stages of maturity. L. ZELNY (Cereal Chem., 1935, 12, 536—542).—Globulin and glutelin are synthesised at a relatively uniform rate throughout the growth period of the maize grain, whilst zein is present only in very small quantities in the early stages and is rapidly synthesised as the grain approaches maturity. This rapid increase in the ratio of zein-N to total N is closely paralleled by the decrease in H₂O-sol. non-protein-N, indicating that the H₂O-sol. N compounds are largely utilised in the synthesis of the zein. The asparagine, glutamine, or other content of the non-protein-N fraction remains relatively const. throughout the growth period of the kernel. The simpler NH₂-compounds undergo rapid condensation (probably chiefly the condensation of NH₂-acids into polypeptides) as the grain approaches maturity. The basic N of the H₂O-sol. non-protein-N increases as the grain approaches maturity, simultaneously with a considerable decrease in the basic NH₂-N, which indicates that the H₂O-sol. basic N compounds in mature maize mainly consist of org. N bases which do not yield primary alkylamines on hydrolysis. Proteose or peptone is present in maize. E. A. F.

Biochemical phases of oleoresin production. E. GERRY and J. A. HALL (Plant Physiol., 1935, 10, 537—543).—The nature and formation of oleoresins and their precursors are discussed. A. G. P.

Insulin-like materials from plant tissues. C. E. BRAUN and F. M. REES (J. Chem. Educ., 1935, 12, 453—458).—A review and discussion. The presence of an insulin-like substance in plant tissues is still a matter of doubt. L. S. T.

Proteins of tobacco seed. II. G. S. ILJIN (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 163—

168).—The solubility of the proteins of tobacco seed is increased by phosphates but not by acids.

E. P.

Alkaloids of hanfangchi.—See this vol., 1257.

Tubocurarine.—See this vol., 1514.

Composition of purple-flowered i-mao-tsao [*Leonurus sibiricus*, L.]. T. H. TANG and C. W. HSU (Nat. Shangtung Univ. Chem. Lab. Repts., 1934, Nos. 3—4, 93—104).—No evidence of the presence of alkaloids was found. CH. ABS. (p)

Alkaloids of *Cytisus caucasicus*. A. OREKHOV and S. NORKINA (Arch. Pharm., 1935, 273, 369—372).—The leaves of this plant contain *d*- α -lupanine, pachycarpine, and a little of a base, m.p. 120—122°, insol. in Et₂O, but sol. in CHCl₃. R. S. C.

Characteristics of *Nicotiana* species. M. I. CHMURA (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 107—116).—*Nicotiana* species contain alkaloids volatile and non-volatile with steam. The m.p. of their picrates are different from those of *N. tabacum*. Some species contain much citric and maleic acids and ash. In *N. glauca* after topping, the amount of alkaloids, N, proteins, and citric acid is increased, that of carbohydrates is decreased. E. P.

Electrolysis in the isolation of plant products. A. A. SCHMUK (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 47—54).—Acids and bases (e.g., citric acid and nicotine) may be separated by electro-dialysis, which reduces the nicotine content of tobacco, but has no influence on its quality. E. P.

Crystalline bitter principle from *Andrographis paniculata*. S. S. G. SIRCAR and A. MOKTADAR (Sci. and Cult., 1935, 1, 300).—A bitter principle of this plant (cf. A., 1914, i, 1118, 1204) is isolated as a substance (I), C₂₀H₃₀O₅, m.p. 220° (decomp.), [α]_D —123.5° in AcOH, which contains OH (not acetylated under ordinary conditions) and CH₂O₂ groups, and one double linking (which is hydrogenated, and combines quantitatively with HCl and ICl). The presence of a lactone group is shown by hydrolysis to two isomeric *OH*-acids, m.p. 156° and 180°, respectively, both reconverted into (I). (I) is readily dehydrated above its m.p., and combines with POCl₃ and with PhNCO. E. W. W.

Concentration of heavy isotopes in cellulose.—See this vol., 1469.

Cress-seed mucilage. K. BAILEY (Biochem. J., 1935, 29, 2477—2485).—The dispersible cellulose component of cress-seed mucilage gave *l*-arabinose, *d*-galactose, *l*-rhamnose, *d*-glucose, and *d*-galacturonic acid on acid hydrolysis. The mucilages of cress seed, mustard seed, and linseed are systems of polyuronides and may be fractionated by their solubilities in dil. aq. Ba(OH)₂, 1% NaOH, and in aq. EtOH. H. D.

Phosphorus of starches. T. POSTERNAK (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 182—183).—Starches can be divided into two groups: (1) those of rhizomes, where P is combined as an ester-salt with a glucose residue; (2) those of cereals where P is in the form of lecithins and not directly linked to the polysaccharide. H. G. R.

Isolation and determination of starch in plant tissue. C. NIEMANN, R. H. ROBERTS, and K. P. LINK (Plant Physiol., 1935, 10, 579—580).—Plant material is extracted with C_6H_6 -EtOH (2:1) and the residue boiled with 1% HNO_3 in 85% EtOH (reflux). The filtered residue is washed free from acid with 95% EtOH, and after partial drying is extracted with 20% EtOH. The extract is evaporated to small vol. and the starch polysaccharides are pptd. by pouring into $COMe_2$ -EtOH (1:1), separated by centrifuge, dried, and weighed. For determining starch in the 20% EtOH extract, the latter is evaporated to small bulk, boiled with HCl, and examined by customary methods for glucose. A. G. P.

Constituents of lesser centaury (*Erythraea centaurium*). T. KARIYONE and K. KASHIWAGI (J. Pharm. Soc. Japan, 1934, 54, 1077—1090).—"Erytaurin" (I) (A., 1908, i, 903) on hydrolysis by emulsin yielded erythrocentaurin, which is assumed to be an aglucone of (I). CH. ABS. (p)

Tobacco glucoside. M. E. KURILO (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 117—131).—A glucoside, $C_{21}H_{20}O_{12}$, 2 or $4H_2O$, m.p. 220—232°, isolated from tobacco, is possibly composed of *d*-glucose and quercetin. The sugar residue is in the 3, 3', or 4' position. E. P.

Isolation of stachyose from the pea (*Pisum sativum*). G. TANRET (Bull. Soc. Chim. biol., 1935, 17, 1235—1236).—The method is described. A. L.

Carbohydrates of tobacco. J. M. SCHABANOV (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 133—135).—The medulla of the "Camel" tobacco plant stem contains 2.5% of carbohydrates, chiefly fructose. E. P.

Electrometric determination of carbohydrates and reducing substances in makhorka tobacco. N. P. GOVOROV (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 181—197).— Fe^{III} salts are added to an aq. extract of makhorka and the solution is electrometrically titrated with $K_2Cr_2O_7$. E. P.

Extraction of inositol from tobacco. A. P. SMIRNOV (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 75—86).—Aq. extract of tobacco is pptd. with $Pb(OAc)_2$, Pb is removed with H_2S , the filtrate heated with NaOH, cooled, exposed to the atm., treated with conc. aq. Na plumbite, and the pptd. Pb-inositol compound is decomposed with H_2S . E. P.

Supposed occurrence of acids with uneven number of carbon atoms in vegetable oils and fats. II. Acid fraction of mean mol. wt. 354 from the seeds of *Butea frondosa*, Roxb. U. S. K. RAO and B. L. MANJUNATH (J. Indian Chem. Soc., 1935, 12, 611—615; cf. this vol., 1435).—The acid A, m.p. 74.5—75.5°, of Katti *et al.* (B., 1930, 292) is an inseparable, eutectic mixture of behenic (I) and lignoceric (II) acid. Fractionation/1 mm. of the Me ester gives a little pure (II). (II) gives eutectics, m.p. 62° and 56.5°, with stearic and palmitic acid, respectively. The following are described: *p*- $C_6H_4Ph\cdot CO\cdot CH_2$ behenate, m.p. 101—102°, and erucate, m.p. 72.5—73.5°; *p*- $C_6H_4Br\cdot CO\cdot CH_2$ palmitate, m.p. 83—84° (lit. 81.5°), stearate, m.p. 87.5—88.5° (lit.

78.5°), behenate, m.p. 93—94°, and erucate, m.p. 60—60.5°. These and similar esters give only slight depressions of the m.p. when mixed and cannot be separated by crystallisation. R. S. C.

Resin of *Nicotiana rustica*. V. N. SCHIROKALA (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 151—162).—The acids obtained from the resin were esterified with MeOH. Palmitic and linolenic acids were identified. E. P.

Point fern (*Engelsiuss*) and some of its relatives as medicinal plants. F. W. FREISE (Sci. pharmaceutica, 1934, 5, 129—131; Chem. Zentr., 1935, i, 1585—1586).—The rhizomes, roots, and fronds of *Polypodium vulgare*, L., *P. lepidopteris*, Kunze, *P. incanum*, Schw., *P. squaridum*, Vel., and *P. perispermum*, Cav., yield a volatile oil (rhizomes and roots), d_4^{20} 0.8385—0.8412, n_D^{20} 1.4855, $[\alpha]_D^{20}$ -8° 45' to -2° 50', containing butyric, hexoic, lauric, and succinic acids, Me salicylate, butyric, isovaleric and α -methylbutyric esters; a fatty oil d_4^{20} 0.9355—0.9385, f.p. -7°, b.p. 245—248° (decomp.), containing 1.10—1.37% of unsaponifiable matter and no filicic acid and acting as an energetic purgative, but not as an anthelmintic; a resin, m.p. 74—86°, acid val. 22—26, sap. val. 55—65; another resin, acid val. 110—145, sap. val. 155—210, containing BzOH and its esters, which is strongly anthelmintic. A glucoside, samambain, and saponins (stem, rind, and rhizome scales) are also present. H. N. R.

Citric acid content of *Nicotiana rustica*. M. L. KOLESNIK (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 41—46).—*N. rustica* from different districts of U.S.S.R. contains 3.6—11.8% of citric acid (I). Plants grown in some districts have high (I) and nicotine contents. E. P.

(A) Citrates occurring in some species of *Kleinia*. A new succulent type. (B) Citrates in succulent plants. G. A. BORGSTROM (Kung. fysiogr. Sällsk. Lund. Forhandl., 1934, 4, No. 16, 8 pp., No. 25, 8 pp.; Chem. Zentr., 1935, i, 2034).—(A) Citric acid (I) was detected in leaves of a no. of species of *Kleinia*, but not in stems of others. The amount of acid present declined during the day.

(B) No (I) was found in *Crassulaceae*. A. G. P.

Constituents of *Ramalina scopularum*.—See this vol., 1501.

Constituents of pyrethrum flowers. II. Isolation of pyrethrin-II. F. B. LAForge and H. L. HALLER (J. Amer. Chem. Soc., 1935, 57, 1893—1896; cf. B., 1935, 1068).—Pure pyrethrin-II is isolated for the first time. Purification is effected without heat or chemical reaction until the essential final stage, distillation at 10^{-6} mm. The substance obtained from semicarbazones is impure. Purity is checked by OMe content. Seil's method shows an apparent pyrethrin-I content in the pure material and slightly too low a purity for the nearly pure. R. S. C.

***Cuscuta reflexa*, Roxb. II. Constitution of cuscutalin.** R. R. AGARWAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 586—590; cf. this vol., 1432).—Cuscutalin (I), m.p. 68° (*Ac*, m.p. 74°, and CO_2Et -derivative, m.p. 105°), a OH-lactone, contains two ethylenic linkings, of which one is α to the lactone

grouping. With $\text{Me}_2\text{SO}_4\text{-KOH}$ it gives *dimethoxycuscutalin Me ester*, m.p. 78°, by opening of the lactone ring, and with hot conc. HCl *anhydrocuscutalin* (II), $\text{C}_{18}\text{H}_{20}\text{O}_3$, m.p. 71–72°. With Br-CHCl_3 , (I) gives “*dibromocuscutalin bromide*” (*bromocuscutalin dibromide*), $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Br}_2$, m.p. 63°, reduced (Zn dust-AcOH) to *dihydrocuscutalin*, m.p. 91°. (I) is monobasic, with slow neutralisation, when titrated with alcoholic alkali. With hot 0.1N-KOH-EtOH it gives a yellow solution, whence AcOH ppts. an *isomeride*, m.p. 102°. With KOH at 140–180° (I) gives $\text{CHPh:CH:CO}_2\text{H}$, HCO_2H , and an unsaturated, aromatic *hydrocarbon*, m.p. 80–82°. With 3% KMnO_4 it gives $\text{H}_2\text{C}_2\text{O}_4$ and PhCHO . When (I) is dry distilled, some sublimes and some carbonises, whilst a little (II) is also formed. R. S. C.

Absorption spectra of α - and β -carotenes and lycopene.—See this vol., 1189.

Reaction of trichloroacetic acid and of chloral hydrate with carotene. V. E. LEVINE and G. E. BIEN (Proc. Soc. Exp. Biol. Med., 1934, 32, 335–337).— $\text{CCl}_3\text{-CO}_2\text{H}$ and $\text{CCl}_3\text{-CHO}$, H_2O give an intense blue colour with carotene in CHCl_3 solution, the absorption spectrum showing a band between 640 $\text{m}\mu$ and the end of the visible spectrum. The colour is thermostable, but is discharged by H_2O or EtOH. Ergosterol with both reagents gives an initial red which changes through green to blue. R. N. C.

Constituents of the unsaponifiable fraction of wheat-germ oil with particular reference to vitamin-E. J. C. DRUMMOND, E. SINGER, and R. J. MACWALTER (Biochem. J., 1935, 29, 2510–2521).—The unsaponifiable fraction contains approx. 3% of a *hydrocarbon*, $\text{C}_{18}\text{H}_{38}$, n_D^{40} 1.4722, and 7% of a *hydrocarbon*, $\text{C}_{25}\text{H}_{52}$ [*hydrochloride* (8HCl), m.p. 116–120°; *bromide* (16Br), decomp. 160–180°]. The vitamin-E (I) fraction contains a sterol-like substance, $\text{C}_{29}\text{H}_{48}\text{O}_2$ (?), m.p. 105–106°, $[\alpha]_D^{20} +58.5^\circ$ in C_6H_6 (*acetate*, m.p. 98–100°, $[\alpha]_D^{20} +65.7^\circ$ in C_6H_6 ; *dinitrobenzoate*, m.p. 156–158°, $[\alpha]_D^{20} +56.9^\circ$ in C_6H_6). It is of no val. in counteracting (I) deficiency in female rats. Hot alkalis seem to inactivate (I), and there is considerable loss of activity on distillation in high vac. The most active fractions of (I) show the characteristic absorption band at 294 $\text{m}\mu$, but this probably is due to another substance, and not to (I). The unsaponifiable fraction from cotton-seed oil contains (I), but it is absent in the fractions from linseed and sunflower-seed oils. J. N. A.

Phytosterol of wheat-germ oil. A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 112–123; cf. Anderson *et al.*, B., 1927, 49).—The mixture obtained from the oil by saponification and extraction of the residue with Et_2O yielded dihydro-sitosterol, m.p. 142–143, $[\alpha]_D^{20} +24.04^\circ$, α -sitosterol (I), m.p. 134–135°, $[\alpha]_D^{20} -22.71^\circ$ (*acetate*, m.p. 116–117°, $[\alpha]_D^{20} -23.55^\circ$), β -sitosterol (II), m.p. 136–137, $[\alpha]_D^{20} -31.53^\circ$ (*acetate*, m.p. 122–123°, $[\alpha]_D^{20} -36.7^\circ$; *benzoate*, m.p. 146–147°, $[\alpha]_D^{20} -12.3^\circ$), γ -sitosterol, m.p. 147°, $[\alpha]_D^{20} -43.13^\circ$ (*acetate*, m.p. 143–143.5°, $[\alpha]_D^{20} -47.7^\circ$; *acetobromide*, m.p. 140–141°, $[\alpha]_D^{20} -46.23^\circ$; *benzoate*, m.p. 152°, $[\alpha]_D^{20} -19.63^\circ$), a δ -sterol (III) m.p. 146–147°, $[\alpha]_D^{20} -23.9^\circ$ [*acetate*,

m.p. 113.5–114.5°, $[\alpha]_D^{20} -24.35^\circ$; *benzoate*, m.p. 157–158°, $[\alpha]_D^{20} -15.98^\circ$; *acetobromide* (IV), m.p. 118–120°], and a *hydrocarbon*, m.p. 66°. (I) and (II) were not completely purified and (III) may have been contaminated with ergosterol. Debromination of (IV) with Zn and AcOH yields a *cryst. substance*, m.p. 115°, and a resin containing Br. W. McC.

Phytosterolin of wheat-germ. II. A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 124–127).—The substance is a mixture chiefly composed of the glucosides of β - and γ -sitosterol. A substance not pptd. by digitonin and exhibiting absorption bands at 328 and 280 $\text{m}\mu$ is also present. W. McC.

Chemical nature of the amino-acids excreted by leguminous root nodules. A. I. VIRTANEN and T. LAINE (Nature, 1935, 136, 756–757).—About one half of the mixture of NH_2 -acids excreted by the nodules of leguminous plants consists of aspartic acid (I) (cf. A., 1933, 437). Cystine, arginine, histidine, and aromatic NH_2 -acids are absent, and the remaining N, precipitable by phosphotungstic acid, probably comes from lysine (II). (I) and (II) probably represent the primary NH_2 -acids formed in the fixation of N by leguminous plants. L. S. T.

Simplified determination of the Schmulke and polyphenol coefficients [of tobacco]. E. I. KOVALENKO (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 147–150). E. P.

Determination of small amounts of chloride in plant tissue. M. CATTLE (New Phytol., 1935, 34, 151–154).—The material is ground to a paste with H_2O and the mixture heated with a few drops of octyl alcohol (to prevent frothing). AgNO_3 , HNO_3 , and H_2O_2 are added in the order named and the mixture is boiled. After a second treatment with H_2O_2 the solution is conc. and excess of Ag determined by Volhard's method. “Wet ashing” with acid is preferable to that with alkali. A. G. P.

Analysis of chloride in *Cladophora*. E. W. JONES (New Phytol., 1935, 34, 155).—The alkaline “wet ashing” method (cf. preceding abstract) is modified for very small amounts of Cl. The determinations are made nephelometrically. A. G. P.

Sulphur content of plants. J. FRAZER (Plant Physiol., 1935, 10, 529–535).—The S content of coniferous and other plants in localities in which the atm. is contaminated by factory chimneys etc. is notably > that in unpolluted areas. A. G. P.

Action of sulphurous acid on leaf cells. A. ANDRE (Angew. Bot., 1935, 17, 207–221).—A discussion of smoke injury problems. A. G. P.

Problem of a plant virus infection. K. M. SMITH (Nature, 1935, 136, 395–396).—The occurrence of a virus in the roots of a high proportion of normal tobacco plants under conditions usually regarded as virus-proof is described and possible explanations are advanced. L. S. T.

Heavy hydrogen in biology. G. VON HEVESY (Naturwiss., 1935, 23, 775–780).—A review.

Apparatus for heavy water studies in small animals. H. G. BARBOUR and F. J. COCHRAN

(Science, 1935, 82, 179—180).—A modified Haldane metabolism train is described. L. S. T.

Analysis of small volumes of gas.—See this vol., 1476.

Micro-method of gas analysis. J. A. CAMPBELL and H. J. TAYLOR (J. Physiol., 1935, 84, 219—222).—Modifications introduced into Krogh's method render it easier, more rapid, and of wider application.

R. N. C.

Determination of intracellular p_H by the method of vital stains. L. LISON (Compt. rend. Soc. Biol., 1935, 120, 102—104).—The presence of chromotropes in cells introduces errors into the determination of intracellular p_H by vital stains, since all the basic p_H indicators are metachromatic. The metachromatic error may reach 6 p_H units. R. N. C.

Electrodes for parallel determination of the oxido-reduction potential and p_H in biological media. R. TSCHAGOVETZ and Z. S. GERSCHENOVITSCH (Ukrain. Biochem. J., 1935, 8, No. 1, 203—209).—The apparatus is described. E. P.

Unpolarisable electrodes to carry action currents. E. SCHUTZ (Z. Biol., 1935, 96, 510—512).—The connexion is made through Ringer's solution to a Pt electrode covered with Pt-black to prevent polarisation. W. O. K.

Apparatus for physiological experiments. F. F. ANDERSON (Chinese J. Physiol., 1935, 9, 209—212).—The following are described: Et₂O bottle for mammalian experiments, pressure bottle for anticoagulant, contact breaker for use with a sensitive thermo-regulator, and apparatus for isolated smooth muscle prep. E. P.

Colour reaction of fructose.—See this vol., 1484.

Colour standard for cholesterol determinations. A. SHAPIRO, H. LERNER, and E. POSEN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1300—1301).—A colour standard for use in Schoenheimer and Sperry's micro-method for determination of serum-cholesterol is prepared by diluting 1 c.c. of Carter's Midnight Black Ink to 1 litre with 10% AcOH. The method is simplified by using a mixture of H₂SO₄ and Ac₂O. R. N. C.

Determination of urea. N. N. DASTUR, R. KARNAD, B. N. SASTRI, and A. VENKATASUBBAN (Proc. Indian Acad. Sci., 1935, 1, B, 817—822).—(NH₄)₂CO₃ produced by enzymic decomp. of urea may be titrated directly with HCl in EtOH after adding COMe₂ to the solution, using naphthyl-red. The method is applicable to urine analysis.

A. G. P.

Removal and determination of small amounts of benzene in biological material. W. P. YANT, H. H. SCHRENK, and P. H. MAUTZ (U.S. Bur. Mines, Rept. Invest., 1935, No. 3282, 7 pp.).—The material in a macerated, finely-ground, or fluid condition is mixed with H₂O and acidified. The C₆H₆ is removed from the refluxing mixture by bubbling through a current of N₂, and absorbed in nitrating acid. The

C₆H₄(NO₂)₂ formed is determined by the Smyth modification of the Elliott and Dalton method.

W. O. K.

Spectrophotometric methods for determining porphyrins. E. VIGLIANI (Diagnostica tec. lab. [Napoli], Riv. mensile, 1934, 5, 625—654).—Copro-porphyrin and protoporphyrin are very unstable in HCl. A spectrophotometric method for urinary porphyrins is described and is compared with the fluorometric method.

CH. ABS. (p)

Isolation and determination of volatile substances from biological fluids and other mixtures. F. LAUERSEN (Biochem. Z., 1935, 280, 38—40).—An apparatus is described and its use illustrated by determinations of COMe₂ and β -hydroxybutyric acid in deproteinised blood filtrates.

P. W. C.

Titration of fluorine in biological materials. E. W. SCOTT and A. L. HENNE (Ind. Eng. Chem. [Anal.], 1935, 7, 299—300).—A suitable technique for ashing, volatilisation of F as SiF₄ by distillation with HClO₄, and titration with Ce(NO₃)₃ or Th(NO₃)₄ is described (cf. A., 1933, 242).

F. O. H.

Micro-determination of total sulphur in biological substances. H. TOYODA and S. KISHI (Gann, 1934, 28, 458—461).—Org. matter is destroyed by fusion with KClO₃-Na₂O₂. The residue is dissolved in hot H₂O, treated with 50% HCl and Br, and S is pptd. as BaSO₄.

CH. ABS. (p)

Micro-determination of calcium in small quantities of biological liquids. M. SAVIANO (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 460—463).—Norbo's method (A., 1932, 531) is modified by substitution of an iodometric for the acidimetric titration.

CH. ABS. (p)

Spectrographic determination of lead in biological material. J. CHOLAK (Ind. Eng. Chem. [Anal.], 1935, 7, 287—290).—The material (blood, liver, spleen, muscle, foods) is digested with H₂SO₄-HNO₃, ashed at 500°, and the solution of the ash in dil. HCl is examined spectrographically, using a microphotometer and comparing with known standards of Pb and Bi in suitable media (cf. this vol., 399). The accuracy is ± 0.01 mg. for 0.01—0.20 mg. Pb per 100 c.c.

F. O. H.

Determination and recognition of lead in biological tissues and fluids. C. N. MYERS, F. GUSTAFSON, and B. THORNE (J. Lab. Clin. Med., 1935, 20, 648—657).—Fairhall's method gives satisfactory results in the micro-determination of Pb (0.02—> 0.50 mg.) in biological specimens if a micro-burette is used in the final titration. Certain elements (e.g., Cu, Bi) interfere.

NUTR. ABS. (m)

Histochemical demonstration of gold. F. GUERCIO and U. CIULLA (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 456—459).—Tissue is treated with 2% H₂C₂O₄ for 24—48 hr., washed, fixed in CH₂O, and paraffined in the usual way. The prep. is dipped in H₂O₂ for 24 hr. A red coloration due to an oxide of Au develops.

CH. ABS. (p)